STUDIES OF SOME β-PROPANOLAMINES, IMIDAZO [2,1-b] THIAZOLES AND YLIDES, BY X-RAY ANALYSIS

A THESIS

SUBMITTED TO THE UNIVERSITY OF GLASGOW

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN THE FACULTY OF SCIENCE

BY

IAN R. CAMERON

CHEMISTRY DEPARTMENT

NOVEMBER 1975

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A C K N O W L E D G E M E N T S

I wish to express my gratitude to my supervisors, Professor G. A. Sim and Dr. A. F. Cameron for their interest during this research, and in particular to Dr. Cameron for his guidance and encouragement throughout. I would also like to thank Dr. C. J. Gilmore for his advice on the use of existing crystallographic computer programs. In addition, my thanks extend to the Science Research Council for their maintenance grant, and to Imperial Chemical Industries Limited (Pharmaceuticals Division) for supplying many of the compounds investigated. Finally, thanks are due to my fiancée for her patience whilst typing this thesis.

SUMMARY

In this thesis, single crystal X-ray diffraction techniques have been used to determine the crystal and molecular structures of ten compounds. The contents are presented in four Parts, the first of which is a brief discussion on some theoretical aspects of these techniques, with special emphasis being placed on the Direct Methods of structure determination used predominantly in this research.

In Part 2, X-ray analysis has been used to study the molecular structures and conformations of five similar compounds of interest in the treatment of certain heart disorders. In particular, the compound Inderal (1-(2-Hydroxy-3-isopropylamino-propoxy)-naphthalene) is used extensively as a β-adrenergic receptor blocking agent, and in order to investigate possible characteristic conformational differences and/or similarities between active and inactive β-blocking agents and their relationship to the conformationally-restricted anti-depressant Vivalan (2-(2-Ethoxy-phenoxymethyl)morpholine), the crystal-structures of the five compounds, (+) 1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene hydrochloride, (±) 1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene hydrochloride, (±) 1-(4-Acetamidophenoxy)-3-isopropylaminopropan-2-ol perchlorate, (±) 2-(2-Ethoxyphenoxy-methyl)morpholine oxalate and (±) 1-(2,6-Dichlorophenoxy)-3-isopropylaminopropan-2-ol hydrochloride have been determined and appropriate comparisons have been made. In addition, since the conformations of flexible molecules in the solid state need not

necessarily correspond with the conformations which pertain in solution, the solid-state study has been matched by spectroscopic studies and by theoretical predictions of the free molecule conformation (both undertaken elsewhere). To date, neither of these latter projects have been completed, but where possible the solid state conformations have been compared with the conformations indicated by the other techniques.

Part 3 is concerned with the elucidation of the molecular structures of the similar compounds, 6 β-(1-Ethyl-1-hydroxypropyl)-5α-phenyl-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole and 5,5-Diphenyl-6-oxo-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole. In the former case, the method of synthesis may feasibly result in either of the two isomers, 6 β-(1-Ethyl-1-hydroxypropyl)-5α-phenyl-2,3,4,5-tetrahydroimidazo [2,1-b] thiazole or 5 β-(1-Ethyl-1-hydroxypropyl)-6α-phenyl-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole and since conventional spectroscopic techniques were unable to differentiate between these possibilities an X-ray analysis has been carried out. Spectroscopic studies of the minor product of the reaction of ethylene dibromide with 5,5-diphenyl-2-thiohydantoin showed apparent anomalies from expected results and in order to confirm the detailed molecular structure of 5,5-Diphenyl-6-oxo-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole, an X-ray analysis has been carried out.

The contents of Part 4 include a brief discussion of the various modes of π bonding postulated for second-row ylides and since N-dichlorophosphinoyl-1-triphenylphosphazene and N-diphenylphos-

phazene may both be regarded as belonging to this class of compound, the crystal-structure analyses of both these ylides have been carried out in order to obtain further information regarding the bonding systems and conformations exhibited by second-row ylides. These results have also been compared with the known dimensions of similar bonding systems and appropriate comparisons have been made. Also included in Part 4 is the X-ray analysis of the final product obtained from reacting a methanolic solution of methyl 6 β-phenyl-acetamido-penicillanate with chloramine T, at room temperature. The spectroscopic analysis of this product revealed three possible structures and since one possibility was an unusual ylide, and since comparison of this compound with other ylide systems was thought to afford the opportunity for detailed investigations of bonding and conformational patterns within second-row ylide systems, the crystal structure analysis has been carried out and the compound characterised.

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Section 2.1.

THE CRYSTAL AND MOLECULAR STRUCTURES OF (+) AND (±) INDERAL HYDROCHLORIDE

Section 2.2.

THE CRYSTAL AND MOLECULAR STRUCTURE OF (±) ERALDIN PERCHLORATE

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PART I

SOME THEORETICAL ASPECTS OF X-RAY CRYSTALLOGRAPHY

1.1. X-RAY DIFFRACTION

The wave-nature of X-rays and the triperiodicity of the internal structures of crystals were first demonstrated in 1912 by the researches of W. Friedrich and P. Knipping[1] arising from a suggestion by Max von Laue, that a crystal might act as a three-dimensional diffraction-grating for X-rays. Von Laue's interpretation of the observed diffraction pattern indicated that the conditions for diffraction maxima may be expressed in terms of a set of mathematical equations,[2]

$$\begin{aligned} (a.2\ \mathrm{Sin}\,\theta)/\lambda &= h \\ (b.2\ \mathrm{Sin}\,\theta)/\lambda &= k \\ (c.2\ \mathrm{Sin}\,\theta)/\lambda &= l \end{aligned} \qquad (1)$$

where a, b, c are the unit cell dimensions

θ is the diffraction angle of the X-ray beam,

λ is the X-ray wavelength,

h, k, l are integers.

These equations (1) are known as the Laue equations and when they are simultaneously satisfied a diffracted beam of maximum intensity is produced. W. L. Bragg[3] identified the arbitrary integers h, k and l with the Miller indices of the crystal lattice planes responsible for diffraction of the X-ray beam and by treating diffraction as reflection from planes in the lattice he deduced that the conditions for diffraction maxima may be represented by the simple equation,

$$n\lambda = 2d(hkl)\mathrm{Sin}\,\theta\ , \qquad (2)$$

where θ is the angle of incident and reflected rays from a crystal plane, d is the interplanar spacing for the set of planes (hkl)

and n is an integer.

That reflection in the above sense is not analogous to true reflection from a mirror plane is seen from the restrictions set by the integer values for n.

From a consideration of Bragg's law (equation (2)) in the form,

$$\text{Sin}\,\theta = \frac{n\lambda}{2}\left(\frac{1}{d}\right)$$

it is seen that Sin θ is inversely proportional to the interplanar spacing d. The interpretation of X-ray diffraction patterns may thus be facilitated by construction of a 'reciprocal lattice' based on 1/d, a quantity which varies directly as Sin θ . This construction is obtained by considering normals to all possible direct lattice planes (hkl) to radiate from some lattice point taken as the origin and to terminate at a point a distance $1/d_{(hkl)}$ from this origin. The set of points thus determined constitutes the reciprocal lattice which provides a convenient method in crystallography for discussing X-ray diffraction patterns.

1.2. DIFFRACTION DATA COLLECTION

The main problem of crystallographic diffraction data collection may be best considered in two parts: (1) Geometry of diffraction; which includes the calculation of the size, shape and symmetry of the reciprocal and direct lattices, usually by utilisation of photographic methods involving oscillation, Weissenberg and Precession photographs. (2) Assignment of an observed intensity to every point in the reciprocal lattice so that the diffraction pattern may ultimately be related to the distribution of diffracting electrons in the unit cell. In Parts 2, 3 and 4 of this thesis, the intensity data have been collected by counter

measurement on a computer-controlled four-circle diffractometer, the quantity measured by this instrument being the 'integrated intensity' which may adequately be defined as 'a measure of the total number of photons of the characteristic wavelength being used which are diffracted in the proper direction by a reciprocal lattice point passing from the outside to the inside of the sphere of reflection or vice versa'. (The sphere of reflection defines that region of space where Bragg's Law is satisfied). An adequate discussion on the use of four-circle diffractometers in intensity data collection is given in standard text-books such as those written by G. H. Stout and L. H. Jensen[4], and U. W. Arndt and B. T. M. Willis[5].

1.3. DATA REDUCTION

The intensity data thus represent all the information available from physical measurements and in order that a complete crystal-structure solution might be carried out, this information must be reduced to a more usable form involving the quantity $F_{(hkl)}$, which is the amplitude of the wave diffracted from the set of planes (hkl) within the crystal. This structure amplitude, $F_{(hkl)}$, can be related to the experimentally observed intensity, $I_{(hkl)}$, by the expression,

$$F_{(hkl)} = \left(\frac{K\, I_{(hkl)}}{L\, p}\right)^{\frac{1}{2}} \qquad (3)$$

where

(i) p is the polarisation factor which compensates for partial polarisation of the diffracted beam. When the radiation used has been monochromatised by prereflection from a crystal, and the original, prereflected and scattered beams are coplanar, the

polarisation factor is expressed as,

$$p = \frac{1 + \mathrm{Cos}^2 2\theta_m \, \mathrm{Cos}^2 2\theta}{1 + \mathrm{Cos}^2 2\theta_m} \qquad (4a)$$

where θ_m is the Bragg angle of the monochromator crystal. However, in the absence of a monochromator crystal, this expression reduces to the more commonly expressed form,

$$p = \frac{1 + \mathrm{Cos}^2 2\theta}{2} \qquad (4b)$$

(ii) L is the Lorentz factor which allows for the varying times required for reciprocal lattice points to pass through the sphere of reflection, depending on their position in reciprocal space and their direction of approach to the sphere. The expression for this factor is dependent on the method of data collection, but for four-circle diffractometer data, it may be written as,

$$L = \frac{1}{\mathrm{Sin}\ 2\theta} \qquad (5)$$

(iii) K is a scale factor required to place the set of observed structure amplitudes on a correct absolute scale but since it is of importance only when the absolute magnitudes of the $|F_{(hkl)}|$s are required, it is frequently given the value of unity and the set of structure amplitudes thus obtained are known as relative structure amplitudes, $|F_{rel}|$, and are on an arbitrary scale. These $|F_{rel}|$s may be defined by,

$$|F_{rel}| = k' \, |Fo| = \left(I_{(hkl)}/L\ p\right)^{\frac{1}{2}} \qquad (6)$$

The scaling between $|F_{rel}|$ and $|Fo|$ is usually obtained at a later stage by comparison of the $|F_{rel}|$s with the $|Fc|$ values obtained on the basis of the structure found.

In recent years, the increased use of Direct Methods (see 1.6.b)

in structure solution has necessitated the placing of intensity data on an absolute scale, and one method commonly used to obtain the necessary scale factor employs the application of a Wilson-plot as described by Wilson (1942)[6]. This plot derives from the expression,

$$\ln\left(\frac{I_{rel}}{\sum_{i=1}^{N} fo_i^2}\right) = \ln C - 2B\left(\frac{\sin^2\theta}{\lambda^2}\right) \qquad (7)$$

where I_{rel} is the observed intensity on an arbitrary scale,

N is the number of atoms in the unit cell,

fo_i is the scattering factor for each atom,

B is related to the mean square amplitude (U) of atomic vibration by the expression, $B = 8\pi^2 U$,

C is related to the scale constant k, needed to convert $|F_{rel}|$ to $|F_{abs}|$ by $k = C^{-\frac{1}{2}}$ where $|F_{abs}| = k|F_{rel}|$.

In addition to Lorentz and polarisation factors, the observed intensities and hence structure amplitudes are affected by the physical phenomena of extinction and absorption. Extinction, which is dependent on the physical perfection and size of the crystal, results in attenuation of the incident beam especially when the crystal is in a diffracting position, and thus reduces the intensity of the diffracted beam. Since many crystals used in X-ray diffraction studies are small and imperfect, this effect is often ignored.

The intensity of radiation passing through a crystal is also reduced by absorption, which is a function of the material constitution of the crystal and of the path-length of the X-ray

beam through the crystal. Absorption is therefore dependent upon the sizes and shapes of crystals, and correction hence becomes difficult for all but spherical and cylindrical crystals. However, if crystals are small and the linear absorption coefficient (μ) is not high, the error due to absorption becomes small and is often ignored.

SCATTERING FACTORS

The X-ray scattering factor fo is defined as the ratio of the amplitude of the radiation scattered by the atom at rest, to the amplitude scattered under the same conditions by an electron. Since the electrons in an atom occupy a finite volume whose linear dimensions are comparable with the wavelength of X-ray radiation, phase differences between waves scattered by different parts of the atom must be considered in the evaluation of fo. At low angles of diffraction, such differences are small and fo assumes a value equal to the total number of electrons in the atom or ion (Z), whilst at higher values of these angles (θ) the scattering amplitude is reduced by interference effects. The value of fo is thus a function of $\sin\theta/\lambda$ and results obtained from the calculation of X-ray scattering factors of different atoms or ions are usually presented in the form of tables giving fo at fixed intervals of $\sin\theta/\lambda$, e.g. [7]. However the reliability of calculated scattering factors is dependent on the accuracy of the total wave function used to represent the electron density and only in the case of the hydrogen atom is the exact form of such wave functions known. In addition, fo's are usually calculated on the basis of a stationary atom and since atoms in crystals vibrate about their lattice position, this motion must affect the

atomic scattering factor. Since the magnitude of vibration generally increases with temperature, it is often referred to as thermal motion and has the effect of smearing the electron cloud, thus decreasing the scattering power of the real atom. The scattering factor corrected for isotropic thermal motion can be expressed as

$$f = fo \exp \left[-B \left(\frac{\sin^2 \theta}{\lambda^2} \right) \right] \qquad (8)$$

where the Debye factor B can be related to the mean square amplitude (U) of atomic vibration by the expression,

$$B = 8\pi^2 U \qquad (9)$$

However, in many cases thermal motion occurs via anisotropic modes of vibration and Cruickshank has expressed the scattering factor in such situations as :- [8]

$$f = fo \exp \left[-2\pi^2 \left(U_{11}h^2a^{*2} + U_{22}l^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}lha^*c^* + 2U_{23}klb^*c^* \right) \right] \qquad (10)$$

where a^*, b^* and c^* are the reciprocal cell translations and U_{ij} are thermal parameters expressed in terms of mean-square amplitudes of vibration, i and j being with reference to the reciprocal axes a^*, b^* and c^*.

1.4. THE STRUCTURE FACTOR

The structure factor $F_{(hkl)}$ may be considered as the resultant of j waves scattered in the direction of the reflection hkl by the j atoms in the unit cell. Each of these waves has an amplitude proportional to f_j (the scattering factor of atom j) and a phase, α with respect to a wave scattered by hypothetical electrons at the origin of the cell. For the general plane (hkl) the phase change from the origin to the point $x_j\ y_j\ z_j$ is

$2\pi(hx_j/a + ky_j/b + lz_j/c)$ and the resultant vector is given by the expression,

$$F_{(hkl)} = \sum_{j=1}^{N} f_j \exp\left[2\pi i\,(hx_j + ky_j + lz_j)\right] \qquad (11)$$

where the summation is taken over all the atoms in the unit cell and $x_j y_j z_j$ are the fractional coordinates of these atoms referred to the direct cell axes a, b and c.

The structure factor is thus a complex quantity characterised by an amplitude $|F|$ and a phase constant α which can be evaluated by means of the equations,

$$|F_{(hkl)}| = \sqrt{A_{hkl}^2 + B_{hkl}^2} \qquad (12)$$

$$\alpha(hkl) = \tan^{-1}\frac{B_{hkl}}{A_{hkl}} \qquad (13)$$

where

$$A_{hkl} = \sum_{j=1}^{N} f_j \operatorname{Cos} 2\pi(hx_j + ky_j + lz_j) \qquad (14)$$

$$B_{hkl} = \sum_{j=1}^{N} f_j \operatorname{Sin} 2\pi(hx_j + ky_j + lz_j) \qquad (15)$$

These equations can be further simplified by the presence of symmetry e.g. when the cell origin is chosen as a centre of symmetry, the resultant vector can be obtained by summing the cosine terms alone since B_{hkl} becomes zero.

Derivation of equation (11) assumes that all the scattering matter in the unit cell is concentrated into a number of spherically symmetrical atoms situated at known points $(x_j y_j z_j)$. In the actual crystal it is unlikely that this will be the case and a more general definition is required in order to dispense with the idea of separate atoms and electrons at individual sites in the crystal. If $\rho(xyz)$ is assumed to be the electron density at a point (xyz), the amount of scattering matter in the volume element Vdxdydz is ρVdxdydz,

where V is the volume of the unit cell. The structure factor equation for each volume element may thus be written as,

$$F_{(hkl)} = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\, \exp 2\pi i(hx + ky + lz)\, dxdydz \quad , \qquad (15)$$

an expression which more closely represents the situation within the crystal.

1.5. ELECTRON DENSITY

Since the internal structure of a crystal is triperiodic, the electron density, ρ at a point (x, y, z), can be represented by a three-dimensional Fourier series such as

$$\rho(xyz) = \sum_{h'}\sum_{k'}\sum_{l'} C_{(h'k'l')} \exp 2\pi i(h'x + k'y + l'z) \qquad (16)$$

where h', k', l' are integers between $-\infty$ and $+\infty$

It can be shown that, when equation (16) is substituted in equation (15), the integral over one period is zero for all terms except that one for which h = -h', k = -k', l = -l' i.e. when,

$$C_{(\bar{h}\bar{k}\bar{l})} = \frac{1}{V} F_{(hkl)} \qquad (17)$$

Hence the Fourier coefficients, $C_{(h'k'l')}$ are directly related to the corresponding structure factors and the electron density may be represented as a Fourier transform of the structure factors, expressed by,

$$\rho(xyz) = \frac{1}{V} \sum_{h}\sum_{k}\sum_{l}^{-\infty\ +\infty} F_{(hkl)} \exp\left[-2\pi i(hx + ky + lz)\right] \qquad (18)$$

Equation (18) thus gives the basic form of Fourier summation as used in crystal-structure analysis. As previously mentioned (1.4.) the structure factor $F_{(hkl)}$ is a complex quantity of which only the structure amplitude may be derived from experimental data (1.3.). From equation (18) it is seen that for elucidation of electron density within a crystal structure, a knowledge of the phase angle

$\alpha_{(hkl)}$ is required. The fundamental problem in X-ray crystallography is thus to determine the phase angles appropriate to the observed structure amplitudes and two methods of overcoming this phase problem are described in the following section.

1.6. PHASE DETERMINATION

(a) The Patterson Method.

Whereas a triple Fourier series using $F_{(hkl)}$ as coefficients yields a map of atomic positions, Patterson demonstrated that a function of the form,[9]

$$P_{(uvw)} = \frac{1}{V} \sum_{-\infty}^{\infty} \sum \sum |F_{(hkl)}|^2 \exp\left[2\pi i (hu + kv + lv)\right] \quad , \qquad (19)$$

employing $|F_{(hkl)}|^2$ as coefficients, would give an interatomic vector representation of the crystal structure. A peak in this function $P_{(uvw)}$ at the point in space $(u_1\ v_1\ w_1)$ corresponds to an interatomic distance in the crystal, defined by a vector whose components are u_1 v_1 and w_1, the value of the function being proportional to the product of the scattering factors of the two atoms involved. The structure amplitudes are derived directly from the observed intensity data and the Patterson synthesis (19) may thus be calculated directly.

For a molecule containing N atoms in a unit cell, there are N(N-1) discrete interatomic vectors in the cell, resulting in poor resolution due to the more densely packed arrangement and the greater intrinsic breadth of Patterson peaks as compared to Fourier peaks. The latter problem may be greatly reduced by a process known as sharpening, in which the scattering power of all atoms is considered as being concentrated at the nucleus, i.e. point atoms,

but, for even a moderately complicated structure it is very difficult to obtain the atomic coordinates of all atoms by inspection of the Patterson synthesis alone. However, the presence of an atom of high scattering power in the structure, i.e., a heavy atom, alleviates this problem since vector peaks involving such atoms will have considerably greater peak heights than those involving only lighter atoms.

An additional tool in the solution of the Patterson function was introduced by Harker in 1936,[10] when he indicated that in cases where certain symmetry elements are present in the crystal many of the useful heavy-atom peaks are concentrated in particular lines and sections of the $P_{(uvw)}$ function. Thus the position of a heavy atom can be obtained from a Patterson function and the appropriate phases calculated. If the scattering power of this atom dominates the structure factor, then a first approximation to the phasing has been obtained and an electron-density distribution can be computed which may reveal the positions of some of the light atoms. Including these atoms in a subsequent structure-factor calculation will yield improved phase angles and a closer representation of the true electron density results. Through several cycles of such calculations, it is normally possible to elucidate a complete structure. The main disadvantage of this heavy atom method is that, for a very heavy atom the dominance in the structure factor becomes too great, and uncertainty in light-atom coordinates increases until, in extreme cases the light atoms may not be located. This method is most successful when the sum of the squares of the atomic numbers of the heavy atoms is equal to that of the lighter atoms[4]:-

i.e. $$\frac{\sum Z^2_h}{\sum Z^2_l} \approx 1 \qquad (20)$$

Difficulties also arise in structure elucidation when the heavy atoms are situated in or close to a special position in the unit cell so that their symmetry is higher than that of whole molecules. This may lead to heavy atom contribution to only a certain class of reflection while for the other reflections its contributions are reduced. A fourier map computed on the heavy atom alone therefore displays additional false symmetry (pseudosymmetry). because the systematic omission of a class of reflection imposes a higher symmetry on the entire structure. Where possible this problem is solved by selecting a chemically reasonable part of the molecular framework from the pseudosymmetrically related peaks. Inclusion of these atoms along with the heavy-atom position in subsequent structure-factor and electron-density calculations is often sufficient to remove the pseudosymmetry.

(b) Direct Methods

The term 'direct' is usually reserved for those methods which attempt to derive the phases of the structure factors directly by mathematical means from the measured X-ray intensities. Ideally, direct methods reduce the phase problem to an objective procedure in which any decisions are of a purely mathematical nature, the physical basis of these methods being the assumptions that,

(a) electron-density is everywhere positive

(b) electron density consists of discrete spherically-symmetric atoms.

In order to make use of assumption (b), in direct methods, it is advantageous to convert the observed structure factors to either unitary or normalised structure factors.

The unitary structure factor is defined by,

$$U_{(hkl)} = \frac{F_{(hkl)}}{\sum_{j=1}^{N} f_j} \qquad (21)$$

and represents the structure factor expressed as a fraction of its maximum possible value, whilst the normalised structure factor is defined by,

$$\left|E_{(hkl)}\right|^2 = \frac{\left|F_{(hkl)}\right|^2}{\epsilon \sum_{j=1}^{N} f_j^{\,2}} \qquad (22)$$

where ϵ is a number which corrects for space group extinctions. Most formulae in direct methods are now expressed in terms of the normalised structure-factor.

Early attempts by Harker and Kasper (1948)[11] and subsequently Karle and Hauptman (1950)[12] showed that application of classical inequalities to the formulae for $F_{(hkl)}$ lead to relationships between the magnitudes of some $F_{(hkl)}$s and the signs and phases of some others. These relationships are in the form of inequalities which vary with the symmetry of the crystal under consideration and are dependent on the positivity of electron density. Phase information however, is restricted to those reflections with large intensities and as the complexity of the crystal increases, other relationships between structure factors must be utilised. The next stage in the development of direct methods was initiated by Sayre (1952)[13] who showed that for a structure containing

equal and resolved atoms, the structure factors are inter-related by precise equations of the form,

$$F_{(h)} = \phi_h \sum_k F_{(k)} \cdot F_{(h-k)} \qquad (23)$$

where ϕ_h is a calculable scale term, and $F_h = F_{(hkl)}$, $F_k = F_{(h'k'l')}$.

Further extension of Sayre's work by Cochran (1952)[14] and Zachariasen (1952)[15] indicated that for centrosymmetric crystals the sign relationship,

$$S(h).S(k).S(h+k) \approx 1 \qquad (24)$$

(where S means sign of)

is probably true, especially when the structure factors are large. A qualitative estimate of the associated probability has been attempted by several authors e.g.[16-20]

In 1953, Karle and Hauptman[16] suggested a similar formula (utilising the normalised structure factor) might be of use in obtaining phase information and expressed the relationship,

$$S\, E_{(h)} \approx S \sum_k E_{(k)} \cdot E_{(h-k)} \qquad (25)$$

which they termed the $\sum_2$ relationship relating to centrosymmetric crystals. Although these authors also derived a probability function, $P_+(h)$ which determined the probability that the sign of E_h be positive, subsequent work[21] has shown that this quantity might be better applied in the form given by Woolfson (1954)[17] and Cochran and Woolfson (1955)[18],

$$P_+(h) \approx \tfrac{1}{2} + \tfrac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} |E_{(h)}| \sum_k E_{(k)} \cdot E_{(h-k)} \qquad (26)$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$

In the case of non-centrosymmetric crystals, J. Karle and I. L. Karle[22] (1956) have shown that an analogous $\sum_2$ relationship between phases

of the structure factors might be represented by the expression

$$\phi_h \approx \langle \phi_k + \phi_{h-k} \rangle_k \qquad (27)$$

and in addition they derived the relationship,

$$\tan \phi_h = \frac{\sum_k |E_{(k)} \cdot E_{(h-k)}| \text{ Sin } (\phi_k + \phi_{h-k})}{\sum_k |E_{(k)} \cdot E_{(h-k)}| \text{ Cos } (\phi_k + \phi_{h-k})}$$

by which the probable phase ϕ_h may be obtained from a knowledge of those phases ϕ_k and ϕ_{h-k}. The reliability with which this phase ϕ_h may be determined using the tangent formula (28) and the variance of ϕ_h for a given set of (ϕ_k and ϕ_{h-k}) have been related to the quantity α_h defined by Karle and Karle [21] as

$$\alpha_h^2 = \left[\sum_k K_{hk} \cos (\phi_k + \phi_{h-k})\right]^2 + \left[\sum_k K_{hk} \text{Sin } (\phi_k + \phi_{h-k})\right]^2$$

$$\text{where } K_{hk} = 2\sigma_3\sigma_2^{-3/2} \left|E_{(h)}E_{(k)}E_{(h-k)}\right| . \qquad (29)$$

Equation (28) is based on the premise that all phases inserted in the equation are correct. However, in structure determination, these phases are themselves uncertain and have an associated variance. More recent work (1971)[23] has suggested that the use of a weighted tangent formula for phase determination might be more useful, in which each phase is accompanied by an associated weight. Such an expression has been derived and is of the form,

$$\tan \phi_h = \frac{\sum_k W_h W_{h-k} \left|E_{(k)} \cdot E_{(h-k)}\right| \text{ Sin } (\phi_k + \phi_{h-k}) = T_h}{\sum_k W_h W_{h-k} \left|E_{(k)} \cdot E_{(h-k)}\right| \text{ Cos } (\phi_k + \phi_{h-k}) = B_h}$$

where,

$$W_h = \tanh\left\{\sigma_3 \sigma_2^{-3/2} \left|E_{(h)}\right| \left(T_h^2 + B_h^2\right)^{\frac{1}{2}}\right\} \qquad (30)$$

Phase determination procedures utilising equations such as (25) - (30) have been described by Karle and Karle (1966)[21] for

both centrosymmetric and non-centrosymmetric crystals. Both procedures require respective $\sum_2$ listings involving all reflections with $|E|$ values greater than a fixed limit (this limit is arbitrary and is frequently chosen as $E \geqslant 1.4$). In this way relationships between the phases of the structure-factors are set up, and by obtaining a knowledge of a small set of phases, further phase determination may be possible via these relationships.

A structure invariant is a single structure factor or linear combination of structure factors whose phase is independent of unit-cell origin position in any space group, whilst a structure seminvariant may be described as a single structure factor or linear combination of structure factors whose phase is invariant with the shift of origin, provided the origin is restricted to points in the unit cell with identical point group symmetry. As the observed structure amplitudes are independent of origin position and choice of enantiomorph (in the non-centrosymmetric case) they can only define the absolute value of the phases of structure invariants and seminvariants, hence in order to obtain explicit values for individual phases, both the enantiomorph (non-centrosymmetric case) and origin position must be defined. In order to fix an origin, certain linearly independent reflections whose phases are dependent on the choice of origin, (i.e. non-seminvariants) must be chosen, the required number of these reflections being dependent on the space group, e.g. three linearly independent, non-seminvariant reflections are required for origin definition in space group $P\bar{1}$, whilst only one is required in the case of space group $R\bar{3}$. A complete description of the theory of

structure-invariants and origin definition is given in a series of papers by Hauptman and Karle (1953, 1956, 1959)[16,22,24] and Karle and Hauptman (1961)[25].

In choosing reflections required for origin definition, preference is given to those reflections with the largest $E_{(hkl)}$ values which can enter into large numbers of combinations required by formulae (25) or (27). The unit cell origin is thus uniquely defined by assigning phases arbitrarily (within the limits set by phase restrictions imposed by space group symmetry) to a properly chosen set of reflections. These phase assignments hence constitute a starting set of phases from which further phase information may be derived.

In the case of centrosymmetric structures, phase determination may proceed by means of the 'Symbolic Addition' method in which some additional symbols are assigned, as required, to other large $E_{(hkl)}$ reflections which appear to enter into many combinations consistent with formula (25). By accepting new phase values thus determined with a probability greater than a specified value (e.g. Karle and Karle (1966)[21] suggest a probability value greater than 0.97), it is possible to obtain the phases of many of the remaining large $E_{(hkl)}$ reflections in terms of phase specifications and the unknown symbols. Phase determination is also enhanced by the fact that when the sign of a reflection is known, the signs of all the symmetry-related reflections are also known. If p unknown symbols are assigned, then by giving these symbols all possible combinations of the signs + and -, 2^p Fourier maps, with the determined $E_{(hkl)}$'s as coefficients, can be

calculated and the structure may be obtained from the correct map (termed E-map).

A non-centrosymmetric space group may exist as one of two enantiomorphs and hence in order to determine explicit phases for reflections, both the origin defining reflections and an enantiomorph defining reflection must be determined. The enantiomorph may be defined by specifying that the sign of the phase of a particular structure invariant should lie between 0 and π rather than between π and 2π.

After the phase values of the origin and enantiomorph defining reflections have been specified, some additional symbols may be assigned (as needed) to other reflections with large values of $|E_{(hkl)}|$ which enter into many combinations as required by formula (27). By assigning p unknown symbols every possible combination of the values $\pm \pi/4$ and $\pm 3\pi/4$, starting sets of phases can be utilised in formula (28) or (30) and 4^p Fourier-maps with the determined $E_{(hkl)}$'s as coefficients can be calculated.

It is advantageous to have some figure of merit to associate with each set of phases in order to judge their relative plausibilities. One such figure which could be used is the 'R index' figure of merit described by Karle and Karle (1966) [21],

$$R = \frac{\sum_h \left| |E_h|_{obs} - |E_h|_{calc.} \right|}{\sum_h |E_h|_{obs.}} \qquad (31)$$

where $|E_h|^2_{calc}$ is computed from the sum of the squares of $|E_h|\cos \phi_h$ and $|E_h|\sin \phi_h$ and subsequently scaled by equating

$\sum |E_h|^2_{obs}$ and $\sum |E_h|^2_{calc}$. This indicator is not absolute and will vary from structure to structure but however, solution sets of highest R-value have much less probability of being correct.

Ideally, a ratio of approximately 10 $E_{(hkl)}$ values per atom in the asymmetric unit should be used in the calculation of an E-map. On those occasions in which only partial determination of the correct structure is obtained, those phases appropriate to the observed fragment may be further utilised in the tangent formula (28) or (30) to generate the remaining phases necessary for complete structure determination.

In cases where an incorrect solution has been obtained, the peaks in the E-map generally do not make good chemical sense, although sometimes partial structures can be found which are incorrectly orientated in the unit cell. Under such circumstances it is usually best to choose a different basic set of phases.

Several completely automatic computer programs have been developed which will carry out the E-generation, $\sum_2$ listing, symbolic addition and solution procedures. In the X-ray '72 suite of programs [26], used extensively in the structure determinations reported in parts 2, 3 and 4, some relevant programs are;

(i) NORMSF - calculates normalised structure factors.

(ii) SINGEN - develops $\sum_2$ structure invariant relationships, i.e. finds reflections which have indices satisfying the conditions,

$$h_1 + h_2 + h_3 = 0$$
$$k_1 + k_2 + k_3 = 0$$
$$l_1 + l_2 + l_3 = 0$$

(iii) PHASE - is designed to obtain a set of phases for the solution of centrosymmetric structures and treats the output of the Singen program by a direct solution of product equations using a symbolic addition technique. Two kinds of product equations are used.

(a) $\sum_2$ equations e.g. $S(h_1).S(h_2).S(h_3) = +$

(b) Equations which are produced by elimination of a single phase between two different $\sum_2$ relationships e.g. $S(h_1).S(h_2).S(h_3) = +$ and $S(h_4).S(h_5).S(h_3) = -$ hence $S(h_1).S(h_2).S(h_4).S(h_5) = -$.

These relationships practically always make it possible to produce a sufficient number of product equations to reduce a chosen number of 'generator' reflections to be expressed in terms of those reflections with highest $|E_{(hkl)}|$ values which are suitable for origin definition. Origin definition is automatically carried out, in this program, by arbitrary assignment of signs to these origin-defining reflections, thus enabling phase determination of all 'generator' reflections which are then substituted into all $\sum_2$ relationships involving those reflections with $E_{(hkl)}$ values greater than a specified limit. In this way phase determination is obtained for the required number of reflections and an E-map can be computed. Details of the actual procedure are given in reference (27).

(iv) TANGEN - applies a weighted tangent formula (30) to a small set of starting phases to produce a sufficient number of phases to permit structure solution. In this program, phase refinement is also carried out by repeated tangent iteration.

Outwith the X-ray '72 suite of programs, the computer program MULTAN (multiple-tangent-formula method) [28] has been used for structure determination in Parts 2, 3 and 4. This program utilises a multisolution method, first described by Germain and Woolfson (1968) [28] and differs from pure symbolic addition methods since, instead of representing unknown phases by symbols, it assigns them explicit values. Whenever possible, the program defines the origin, using reflections with restricted phases but when this is not feasible general reflections are used. The considerations relating to using general reflections are as follows - initially a phase may be in any of the quadrants 1, 2, 3 or 4 (where quadrant 1 is the range of values between 0 and $\pi/2$, quadrant 2 is the range between $\pi/2$ and π, quadrant 3 is between π and $-\pi/2$, and quadrant 4 is between 0 and $-\pi/2$). By shifting an origin, a phase in quadrant 1 may be changed to quadrant 2 while a phase in quadrant 4 may be changed to quadrant 2. Hence restricting the phase to quadrants 1 and 4, fixes the origin. However, a phase in quadrant 4 may be changed to quadrant 1 by change of enantiomorph (in non-centrosymmetric cases) and thus restricting a phase to quadrant 1 fixes the origin and enantiomorph simultaneously. In MULTAN this corresponds to fixing the phase as $\pi/4$. If general reflections are to be used in origin definition, then the first may be made equal to $\pi/4$ to fix the origin and enantiomorph whilst each of the remaining general reflections must be allowed two possible values $\pm \pi/4$ in order to complete the origin fixing.

Since a knowledge of the phases of just one or two reflections at an early stage of phase determination is very valuable, the program includes a formula which determines phases from the values of

$|E|^2$ alone. This $\sum_1$ formula is taken as a special case of a $\sum_2$ relationship in which two reflections are the same i.e.

$$\phi_i \pm \phi_j \pm \phi_j + \sigma \approx 0 \qquad (32)$$

where σ is a resultant phase shift due to translational symmetry and ϕ_i must belong to a structure seminvariant with a restricted phase. The program thus recognises which reflections are centric structure invariants and deduces phase relationships of the type (32). Phase determinations with a probability greater than a specified value are hence included in the starting sets of phases. To increase the efficiency of phase-determining procedures, a specified number of general reflections can be assigned all possible combinations of the phase values $\pm \pi/4$ and $\pm 3\pi/4$ (thus giving a maximum error of 45° and a mean error of 22.5° for any reflection) and the starting sets of phases thus obtained are subjected to the tangent formula. Multan is thus a multisolution method of phase determination since each set of starting phases will generate a full set of phases, the correct solution being obtained from examination of the 'figure of merit' and/or by trial and error.

1.7. ACCURACY AND LEAST-SQUARES REFINEMENT

When a model of the structure has been found, its accuracy may be estimated by comparison between observed and calculated structure factors. This estimation is usually expressed in terms of the R-factor or 'residual index' defined as

$$R = \frac{\sum (k\,|Fo| - |Fc|)}{\sum (k|Fo|)} \qquad (33)$$

where k is a scaling constant.

Least-squares is applied to crystal structure refinement by

minimising some function of the differences between observed and calculated structure amplitudes with respect to the atomic parameters. The function most commonly minimised is

$$D = \sum_{hkl} w(|Fo| - |Fc|)^2 = \sum_{hkl} w \Delta F^2 \qquad (34)$$

where the summation is taken over all independent structure amplitudes and w is the weight associated with each term. Ideally each w should equal the inverse square of the standard deviation of the corresponding observation, but, in practice it is usually necessary to apply a more flexible weighting scheme in which several parameters can be varied to give approximately the same average $w\Delta F^2$ for systematic groups of the data, obtained by batching them according to $|Fo|$ and $\mathrm{Sin}\,\theta/\lambda$.

If the atomic parameters which determine $|Fc|$ are, $p_1 p_2 \text{--------} p_n$, then the condition that the function (34) approaches a minimum is,

$$\frac{\partial D}{\partial p_s} = \sum_{hkl} w(|Fo| - |Fc|) \cdot \frac{\partial |Fc|}{\partial |p_s|} = 0 \qquad (35)$$

for s = 1 to n.

When the set of parameters, p_s, used in this refinement procedure approximates reasonably to the true values, ΔF i.e. $(|Fo| - |Fc|)$ may be expanded as a first order Taylor Series involving the set of parameters, p, and parameter changes, Δp, i.e.

$$\Delta F(p + \Delta p) = \Delta F(p) - \Delta p_1 \cdot \frac{\partial |Fc|}{\partial p_1} - \text{-------} - \Delta p_n \cdot \frac{\partial |Fc|}{\partial p_n} \qquad (36)$$

Substituting equation (36) into equation (23) yields the set of n normal equations of least-squares for s = 1 to n, i.e.

$$\sum_{r=1}^{n} \left[\sum_{hkl} w \frac{\partial |Fc|}{\partial p_r} \cdot \frac{\partial |Fc|}{\partial p_s} \right] \Delta p_r = \sum_{hkl} w \Delta F \frac{\partial |Fc|}{\partial p_s} \qquad (37)$$

These equations can be solved to give the set of parameters shifts to be applied to the initial parameters. In matrix notation, the n normal equations can be expressed as,

$$M \Delta p = N \qquad (38)$$

and the set of parameter sets may thus be written as

$$\Delta p = M^{-1} N \qquad (39)$$

where M^{-1} is the inverse matrix of M, such that $M^{-1}M = 1$. Since the least-squares normal-equation matrix is symmetrical, $\frac{1}{2}n(n+1)$ elements on and above the leading diagonal must be stored by the appropriate computer program and as the complexity of the structure increases it is frequently necessary to make approximations because of limited computer storage. (In Parts 2, 3 and 4 all least-squares refinement was carried out via the CRYLSQ program of the X-ray '72 suite of programs).

Because of the omission of higher terms in the Taylor Series, it is usually necessary to compute several cycles of least-squares refinement before a minimum is obtained and the course of such refinement may be followed by examination of the values

$$R = \frac{\sum (k|Fo| - |Fc|)}{\sum (k|Fo|)} \qquad (33)$$

$$R' = \frac{\sum w(k|Fo| - |Fc|)^2}{\sum wk^2 |Fo|^2} \qquad (40)$$

calculated after each cycle of refinement. The refinement process

may be assumed complete when the calculated shifts (Δp) are considerably less than the estimated standard deviations for the corresponding parameters.

It is customary to test the refined model, obtained by least-squares methods, by calculating a Difference Fourier summation with ($|Fo| - |Fc|$) as coefficients. This 'Difference Map' thus indicates any significant departure of the calculated model from the true crystal structure.

1.8. ESTIMATED STANDARD DEVIATIONS

The least-squares method of refinement allows the calculation of new parameters but, to assess their precision, it is necessary to have knowledge of the corresponding estimated standard deviations.

The estimated standard deviation in a parameter p_i may be expressed as,

$$\sigma(p_i) = \sqrt{M_{ij}^{-1} \left(\sum_{hkl} w \Delta F^2 \right) / m-n} \qquad (41)$$

where M_{ij}^{-1} is the i^{th} diagonal element of the inverse matrix M^{-1},

m is the number of observations,

n is the number of parameters,

w is the weight of the appropriate ΔF.

Of special importance are the estimated standard deviations of atomic positional parameters which can be used in the calculation of bond-length and bond-angle standard deviations, necessary for assessment of the reliability of determined molecular dimensions.

Bond-length standard deviations for example may be used to assess whether a particular bond length in a molecule is significantly

different from a similar bond or a theoretical value. If two bonds l_1 and l_2, with estimated standard deviations $\sigma(l_1)$ and $\sigma(l_2)$ respectively, are found to differ experimentally by δl, the possible significance of this difference can be estimated by using a set of numerical significance levels suggested by Cruickshank (1953)[29]. He expressed the standard deviation of δl as,

$$\sigma = \sqrt{\sigma(l_1)^2 + \sigma(l_2)^2} \qquad (42)$$

and defined P as the probability that the two bonds could differ by δ_1 by chance. Hence it is possible to assess the significance level of differences in bond lengths as follows:-

If $\delta_1 \leqslant 1.645\sigma$, then $P \geqslant 5\%$ i.e. insignificant difference.

If $2.327\sigma > \delta_1 > 1.645\sigma$, then $5\% > P > 1\%$ i.e. possibly significant difference.

If $3.090\sigma > \delta_1 > 2.327\sigma$, then $1\% > P > 0.1\%$ i.e. significant difference.

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PART 2

X-RAY STUDIES OF SOME β-PROPANOLAMINES

INTRODUCTION

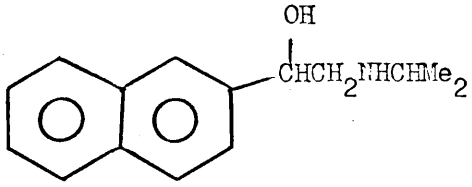
In 1962, the compound Alderlin (I) was found to block specifically cardiac and other β-adrenergic receptors in laboratory animals but was also found to be carcinogenic.[1] Subsequent investigations[2] of non-carcinogenic compounds with β-blocking activities revealed that racemic Inderal (IV) is about ten times more potent than racemic Alderlin and also that the (-) isomer of Inderal is 60-100 times more active than the (+) isomer whose efficiency as a β-blocker is similar to that of compound II which has neither hydroxyl group nor chiral centre. Easson and Stedman (1933)[3] had previously suggested that efficient attachment to a specific receptor site requires the presence of amino, phenyl and β-hydroxyl groups, and the above results indicate that the stereospecificity of the receptor site is such that the hydroxyl group of the (+) isomer is unable to bind efficiently to it. The absolute configuration of the chiral centre in (-) Inderal has been characterised as S by synthetic methods[4] and experiments[5] have shown that of the compounds listed in Table 2(a), only the 2,6-dichloro-derivative (VII) is totally inactive as a β-blocking agent. This inactivity of the 2,6-dichloro compound is common to all 2,6-disubstituted derivatives with the exception of the 2,6-difluoro compound, which suggests that the steric influence of large substituents at these positions prevents efficient attachment to the receptor sites.

Vivalan (VI), a well-known anti-depressant, is also totally inactive as a β-blocking agent but in view of the previously mentioned activity of compound II, it is unlikely that this inactivity can be attributed

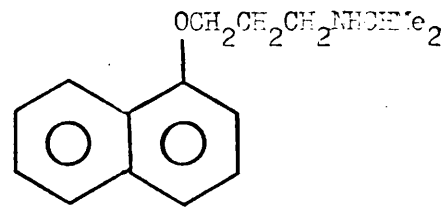
solely to the lack of a hydroxyl group and it is plausible that the conformational differences caused by the restrictions of the morpholine ring may also contribute to the absence of β-blocking effects. However, some side-effects of Inderal are similar to the effects of Vivalan on the central nervous system, thus suggesting that Inderal may be able to adopt not only the conformation required for activity at a β-adrenergic receptor site, but may also be able to adopt that conformation pertinent to Vivalan-like central-nervous-system effects.

In order to investigate the possible characteristic conformational differences and/or similarities between active and inactive β-blocking agents, and their relationship to the conformationally-restricted anti-depressant Vivalan, X-ray analyses of the series of compounds (+) Inderal hydrochloride (III), (±) Inderal hydrochloride (IV), (±) Eraldin perchlorate (V), (±) Vivalan oxalate (VI) and (±) 2,6-dichloro derivative (VII) have been carried out. All the compounds have been studied as salts (the exact nature of each salt being determined largely by the availability of suitable crystals for X-ray work) because biogenic monamines are thought to exist in the cationic (quaternery ammonium) form under physiological conditions. Separate analyses of (+) Inderal hydrochloride and of (±) Inderal hydrochloride were undertaken to investigate the possible effects of different crystal environments on the same molecule. Moreover, since the conformations of flexible molecules in the solid state need not necessarily correspond with the conformation which pertain in solution, the solid-state study was matched by spectroscopic studies[6] aimed at determining the solution conformations and also by

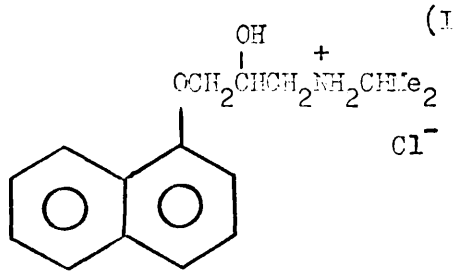
theoretical predictions of the free molecule conformation.[7] To date, neither of these latter projects have been completed, but where possible the solid state conformations have been compared with the conformations indicated by the other techniques.



(I)

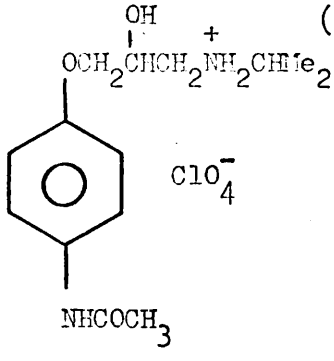


(II)



(III) = (+) Inderal Hydrochloride

(IV) = (±) Inderal Hydrochloride



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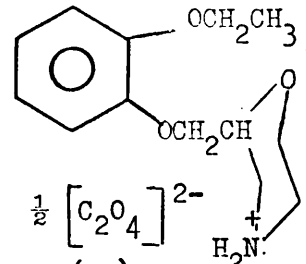

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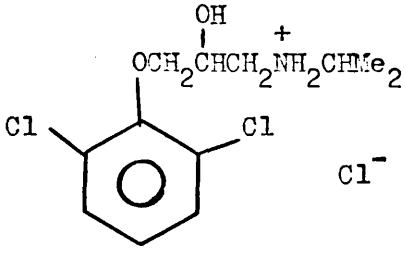
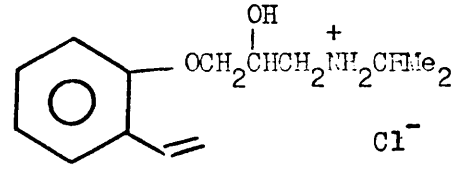
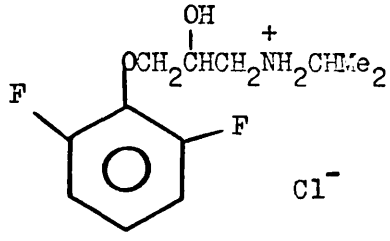


(VII)



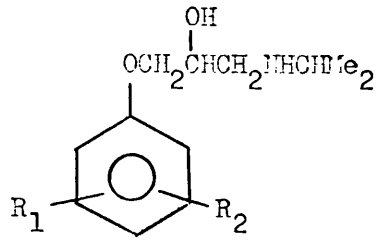
(VIII)



(IX)

Table 2(a)

Compounds Tested for β-blocking Activity



R_1	R_2	
2-Cl	H	Active
3-Cl	H	Active
4-Cl	H	Active
2-Cl	3-Cl	Active
3-Cl	4-Cl	Active
2-Cl	5-Cl	Active
3-Cl	5-Cl	Active
2-Cl	6-Cl	Inactive
(±) Inderal		Active
(±) Eraldin		Active

S E C T I O N 2.1.

THE CRYSTAL AND MOLECULAR STRUCTURES OF

(+) INDERAL HYDROCHLORIDE [(+)1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene Hydrochloride]

and

(±) INDERAL HYDROCHLORIDE [(±)1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene Hydrochloride]

EXPERIMENTAL

(+) INDERAL HYDROCHLORIDE

(+) 1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene Hydrochloride

CRYSTAL DATA

$C_{16}H_{22}NO_2Cl$; M=295.8; Monoclinic, a=12.431Å, b=9.728Å, c=6.884Å, β=93.99°; U=830.53Å^3; D_c=1.19 g.cm.$^{-3}$; D_m=1.21 g.cm.$^{-3}$; Z=2; F_{000}=316; Space group $P2_1$; μ=2.46 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs, taken with Cu-Kα (λ=1.5418Å) radiation, and from precession photographs, taken with Mo-Kα (λ=0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_1$ was indicated both by systematic absences and by optical activity.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.1 x 0.4 x 0.2 mm.) rotating about b, to graphite-monochromated Mo radiation (Mo-Kα_1) and by using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 54°$) to collect 1183 independent reflections with $I \geqslant 2\sigma_I$ ($\sigma_I = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The position of the chlorine atom was determined from the Patterson

function, the y-coordinate being arbitrarily assigned the value, 0.2500, to define the origin in space group $P2_1$. This value was held constant throughout subsequent refinement.

Initial attempts at structure determination were hindered by the inevitable presence of pseudo-symmetry resulting from the arbitrary choice of the chlorine y-coordinate. An electron-density calculation, based on those phases appropriate to the chlorine atom, revealed several plausible atomic sites. Careful choice of atomic positions from the range of pseudo-symmetrically related peaks, and their inclusion in a subsequent round of structure-factor and electron-density calculations, reduced the extent of the pseudo-symmetry. It hence proved possible to determine all non-hydrogen atomic positions after several rounds of structure-factor and electron-density calculations in which all non-hydrogen atoms had been assigned an arbitrary isotropic temperature factor $U_{iso}=0.05\text{Å}^2$. After each calculation the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational and scale parameters by full-matrix least-squares calculations converged after 9 cycles when R was 0.054 and R' was 0.007. Details of the refinement are given in Table 2.1.1.

Positions of the carbon and nitrogen-bonded hydrogen atoms were obtained by calculation, staggered conformations being assumed for all methyl groups, while the hydroxyl hydrogen-atom position was

obtained from a difference synthesis. Contributions from the hydrogen atoms, with arbitrary temperature factors $U_{iso}=0.03\text{Å}^2$, were included in all structure-factor calculations, but their positions were not refined.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure factors. The scheme is of the form;

If $A|Fo| > |Fc|$, $W=10^{-9}$,

otherwise $W=X.Y$,

with $X=1$ if $\sin\theta > B$, else $X=\frac{\sin\theta}{B}$

and $Y=1$ if $|Fo| < C$, else $Y=\frac{C}{|Fc|}$

The most suitable values for A, B and C were found to be 0.5, 0.5 and 7.0 respectively.

At the conclusion of refinement, difference syntheses and electron-density calculations revealed no errors in the structure. In all structure factor calculations, the atomic scattering factors used were those given in reference (35). Observed and calculated structure-factors are listed in Appendix 1. Positional and vibrational parameters with estimated standard deviations are given in Table 2.1.2. The values of e.s.d.s are derived from the inverse of the least-squares normal equation matrix and should be regarded as minimum values.

EXPERIMENTAL

(±) INDERAL HYDROCHLORIDE

(±) 1-(2-Hydroxy-3-isopropylaminopropoxy)-naphthalene Hydrochloride

CRYSTAL DATA

$C_{16}H_{22}NO_2Cl$; M=295.8; Monoclinic, a=13.984Å, b=8.289Å, c=13.974Å, β=98.49°; U=1602.03Å^3; D_c=1.23 g.cm.$^{-3}$; D_m=1.24 g.cm.$^{-3}$, Z=4; F_{ooo}=632; Space group $P2_1/n$; μ =2.46 cm.$^{-1}$; Mo-Kα X-rays; λ =0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs, taken with Cu-Kα (λ =1.5418Å) radiation, and from precession photographs, taken with Mo-Kα (λ =0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_1/n$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer. Data were collected by exposing a small crystal (0.2 x 0.3 x 0.2 mm.), rotating about b, to graphite-monochromated Mo radiation (Mo-Kα_1) and by using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 50^\circ$) to collect 1535 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The structure was determined by centro-symmetric Direct Methods using the computer programs, DATRDN, NORMSF, PHASE, FOURR, Fc and CRYLSQ, contained in the X-ray '72 suite of programs.

Phase determination was initiated by assigning phases to those 80 reflections with highest $|E|$ values. Each phase was either assigned directly or was expressed, via $\sum_2$ relationships, in terms of the three linearly independent non-structure-seminvariant reflections given in Table 2.1.3.

The unit-cell origin was defined by assigning each of these reflections an arbitrary phase value of 360°, and the phases of the above 80 reflections were then used in a series of sigma-2 relationships from which phase values for all 204 reflections with $E \geqslant 1.4$ were assigned.

An E-map based on these 204 reflections revealed 19 possible atomic sites. Subsequent structure-factor and electron-density calculations revealed plausible positions for all non-hydrogen atoms. Each atom was assigned an arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ and least-squares refinement was initiated.

After one cycle of full-matrix calculations, the isotropic temperature factor of the hydroxyl-oxygen atom increased to a value $U_{iso}=0.11\text{Å}^2$. To investigate this phenomenon, contributions from this atom were omitted and an electron-density difference synthesis was calculated, which indicated that two sites with approximate equal electron densities were stereochemically acceptable for the hydroxyl group.

However, since each molecule contains only one hydroxyl group, it was concluded that each crystallographic molecular site is statistically occupied by molecules of (+) and (-) absolute stereochemistry.

Each of the two disordered atomic sites was initially assigned a population parameter of 0.5 with respect to the electron density of one oxygen atom. Refinement of these population parameters in subsequent least-squares calculations indicated that this assignment had been correct. After each of the above calculations, the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational, electron-density population and scale parameters converged after 12 cycles of full-matrix least-squares calculations when R was 0.060 and R' was 0.005. Details of the refinement are given in Table 2.1.4.

Vibrational parameters of the disordered oxygen atoms were not refined until after the population parameters had been satisfactorily refined. 15 hydrogen-atom positions were selected from a difference synthesis and their positional parameters were refined in cycles 9-10. The remaining hydrogen-atom positions were calculated and included in subsequent calculations but were not refined. A fixed isotropic temperature factor $U_{iso}=0.03\text{Å}^2$ was arbitrarily assigned to all hydrogen atoms.

An appropriate weighting scheme was chosen by examination of a series of bivariate (Fo and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated

structure-factors. The scheme was of the form;

If A $|Fo| > |Fc|$, $W=10^{-9}$

otherwise W=X.Y,

with X=1 if $\sin\theta > B$, else $X=\frac{\sin\theta}{B}$

and Y=1 if $|Fo| < C$, else $Y=\frac{C}{|Fc|}$

The most suitable values for A, B and C were found to be 0.75, 0.4 and 9.0 respectively. At the conclusion of refinement, a difference synthesis and electron-density distribution revealed no errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (35). Observed and calculated structure-factors are listed in Appendix 2. Positional and vibrational parameters with estimated standard deviations, are given in Table 2.1.5. Values of e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

(+) INDERAL AND (±) INDERAL HYDROCHLORIDES

D I S C U S S I O N

Diagrammatic representations of the (+) and (±) compounds are shown in Figures 2.1.1. and 2.1.2. respectively. In both diagrams, the hydrogen atoms are omitted, for clarity, but for the purposes of discussion are numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, least-squares planes, intra-ionic non-bonding distances and inter-ionic distances are given in Tables 2.1.6. to 2.1.10.

Both compounds exist as hydrochloride salts in which the protonated-nitrogen atom bears the cationic charge and, as would be expected, there are no statistically-significant differences between the corresponding bond lengths and endo-cyclic valency angles of these compounds.

The naphthalene-ring system in both compounds is close to planar, with the maximum deviation from the least-squares plane through the rings being 0.027Å in the (+) compound and 0.020Å in the (±) compounds, and in addition, atoms O(1) and C(6) lie close to the aforementioned planes, their respective distances being -0.020 and 0.192Å in the (+) compounds and -0.043 and 0.239Å in the (±) compound. These approximately coplanar arrangements of atoms result in steric crowding. In particular, deformation of the bond angles O(1)C(7)C(8) [124.5(7)° and 124.6(6)° for the (+) and (±) compounds respectively] and O(1)C(7)C(15) [113.8(6)° and 114.8(4)°] may be a result of possible steric interactions e.g.

C(8)···C(6) [2.82 and 2.83Å], H(8)···H(6) [2.32 and 2.20Å] and H(8)···H(6') [2.22 and 2.20Å]. The non-bonded distances C(14)···O(1) [2.75Å in both compounds] and H(14)···O(1) [2.40 and 2.45Å] also suggest some steric interactions between these atoms but, within the limits of experimental error, no corresponding distortions are obvious. The remaining dimensions of the naphthalene rings are, within experiemental error, similar to those reported for other naphthalene systems[8-12], including Naphthalene itself[12].

In both compounds, the values observed for bond angle C(3)N(1)C(4) [116.4(6) and 117.6(4)] are larger than might otherwise be expected for a tetrahedral valency angle and similar values for the corresponding angle in compounds such as Isoprenaline[13] [114.7(5) and 115.5(6)°] suggest that this may be a genuine effect. Bond lengths C(5) - C(6) [1.489(10) and 1.485(7)Å], C(2) - C(3) [1.502(15) and 1.485(9)Å] and C(1) - C(3) [1.477(15) and 1.523(9)Å] appear shorter than might be expected for $C(sp^3)$ - $C(sp^3)$ bonds but are similar to values reported for many compounds[13-21] containing an alkyl chain bonded to an aromatic system e.g. a $C(sp^3)$ - $C(sp^3)$ bond length of 1.493(8)Å has been reported by E. M. Gopalakrishna and L. Cartz (1972)[19]. It is possible that such apparent shortening may be due largely to the effects of thermal librational motions of the molecules[22].

Those dimensions not previously discussed are typical of accepted literature values, with the exception of those concerning atom positions O(20) and O(21) of the (±) Inderal Hydrochloride, whose apparently anomalous values e.g. O(21) - C(5) [1.375(9)Å] and

O(20) - C(5) [1.332(8)Å] , are probably the result of the disordering effect peculiar to this compound.

(+) INDERAL HYDROCHLORIDE

The alkoxy chain is in a fully-extended conformation [torsion angles C(5)C(6)O(1)C(7)175.4(6)°, C(4)C(5)C(6)O(1)173.8(6)°, N(1)C(4) C(5)C(6) -163.7(6)° and C(3)N(1)C(4)C(5) -170.2(6)°] in which the hydroxyl group is gauche with respect to atoms N(1) and O(1) [N(1) C(4) C(5) O(21) 77.4(7)° and O(21) C(5) C(6) O(1) -65.0(7)°]. Newman Projections illustrating the appropriate conformations about bonds C(4) - C(5) and C(5) - C(6) are given in Figure 2.1.3.

Atoms N(1) and O(21) are almost equidistant from the chloride ion, the dimensions, N(1)··· Cl [3.14Å] , H(2N)··· Cl [2.18Å], angle N(1) H(2N) Cl [166.1°] , O(21)··· Cl [3.13Å] , H(021)··· Cl [2.15Å] and angle O(21) H(021) Cl [166.1°] , suggesting hydrogen bonding of the types, $\geq N^+$ - H···Cl^- and -O-H···Cl^- (it is noted however, that atom position H(2N) is calculated, assuming tetrahedral geometry at atom N(1)). The distortion of torsion angle N(2) C(4) C(5) O(21) [77.4(7)°] from the ideal staggered conformation value, may be interpreted as an effect of the hydrogen-bonding arrangements, since the corresponding value in several similar compounds, e.g. Thl165(a)[14] [-47.8(4)°] , is less than 60°, possibly due to electrostatic interactions between atoms N(1) and -O(H).

A diagram representing the crystal-packing arrangements is given in Figure 2.1.4.

(±) INDERAL HYDROCHLORIDE

As previously noted, (see Experimental) both (+) and (-) cations equally occupy equivalent crystallographic sites and as a result, the conformations of both enantiomers, at equivalent sites, are identical except for those changes induced by the differing configurations at the chiral centre. Figure 2.1.5. illustrates the alternative configurations and conformations about bonds C(4) - C(5) and C(5) - C(6), demonstrating that atom N(1) is gauche with respect to both alternative hydroxyl positions [torsion angles N(1)C(4) C(5)O(21)49.4(6)°, and N(1)C(4)C(5)O(20) -50.4(6)°], while the inter-atomic non-bonded distances N(1)···O(21) [2.89Å] and N(1) ···O(20) [2.82Å] suggest possible electrostatic interactions between these pairs of atoms (hydrogen bonds of the type $\rangle N^{+} - H \cdots O\text{-}R$, are unlikely, relevant dimensions being H(1N)···O(21) 2.95Å, H(1N)···O(20) 2.41Å, H(2N)···O(21) 3.94Å and H(2N)···O(20) 3.67Å).

Space-group symmetry requires that both the (+) and (-) enantiomers, occupying equivalent crystallographic sites (a), have centrosymmetrically-related enantiomers occupying equivalent sites (b), and it follows that the (+) enantiomer at a site (a) has a different conformation from the (+) enantiomer at a site (b), a similar phenomenon occurring in the case of the (-) enantiomer. The crystal hence contains two closely-related conformations of the Inderal cation and also the inverse images of these conformations, all of which are apparently present to the same extent. Although uncommon, this type of packing disorder is not unique, a similar phenomenon having been reported in the X-ray analysis of 1-p-Bromobenzenesulphonyloxymethyl-5-methylbicyclo [3,3,1] nonan-9-ol[23].

No hydroxyl-hydrogen atoms could be located from difference syntheses and hence no accurate assessment of possible hydrogen-bond geometries of the type, -O-H···Cl^-, can be made, although inter-ionic distances, O(21)···Cl^- [3.12Å] and O(20)···Cl^- [2.99Å], suggest possible hydrogen bonding involving these pairs of atoms, while dimensions N(1)···Cl^- [3.12 and 3.27Å], H(2N)···Cl^- [2.08Å], H(1N)···Cl^- [2.21Å], angle N(1) H(2N) Cl^- [161.8°] and N(1) H(1N) Cl^- [166.5°] suggest strong hydrogen-bonds, of the form $\rangle N^+$ - H···Cl^-, between the ammonium group and two chloride ions. A diagram illustrating the crystal-packing arrangements is given in Figure 2.1.6. and demonstrates that, in the present compound, atom N(1) can hydrogen bond to two chloride ions, whilst atoms O(21) or O(20) can equally hydrogen bond to one anion which is however, at a different equivalent position from that chloride ion hydrogen-bonded to the aforementioned atom, N(1).

In contrast to the (+) Inderal Hydrochloride, the alkoxy chain of the (±) compound does not adopt a fully-extended conformation [torsion angles C(3)N(1)C(4)C(5) -81.6(5)° and C(4)C(5)C(6)O(1) -59.[illegible]° -59.3(5)°] and a possible rationalisation of these observed deviations from the sterically more-favoured fully-extended conformation may be obtained by consideration of the geometries required for efficient hydrogen bonding. Figure 2.1.7. illustrates the differing conformations about both bonds C(6) - C(5) and C(4) - N(1) in the (+) and (±) compounds. It is thus plausible that the respective positions of the cations relative to the anions may be a factor in the determination of these adopted conformations.

It is noted that the crystal structure of (±) Inderal Hydrochloride has been reported,[24] but although corresponding dimensions of both determinations are similar within experimental error, no packing disorder was reported despite anomalies in the published atomic parameters and in particular, in the values of B_{ij} observed for the hydroxyl-oxygen atom. These anomalies are similar to those which led to the suspicion of disorder in the present crystal, and which have been successfully accounted for, via a disordered model.

In addition, a recent publication (1975)[36] has confirmed the crystal and molecular structure of (+) Inderal Hydrochloride to be experimentally identical with the analysis described in this thesis.

TABLE 2.1.1.

COURSE OF REFINEMENT

Parameters Refined	Cycles	Final R	Final R'
x, y, z, U_{iso} for all non-hydrogen atoms; overall scale factor; unit weights.	1 - 3	0.120	0.014
As above except H-positions in calculation but not refined and weighting scheme applied.	4 - 5	0.103	0.021
x, y, z, U_{ij}(i, j = 1, 2, 3) for all non-hydrogen atoms; overall scale factor; H atoms included but not refined; weighting scheme applied.	6 - 9	0.054	0.007

TABLE 2.1.2.

(a) Atomic Fractional Coordinates and E.S.Ds of (+) Inderal Hydrochloride

ATOM	x/a	y/b	z/c
C(1)	1.2924(7)	0.4566(15)	-0.2132(17)
C(2)	1.2444(7)	0.5903(12)	-0.5150(17)
C(3)	1.2200(6)	0.5605(10)	-0.3086(14)
C(4)	1.0590(6)	0.5076(8)	-0.1140(10)
C(5)	0.9478(6)	0.4404(8)	-0.1309(9)
C(6)	0.8916(6)	0.4670(8)	0.0495(10)
C(7)	0.7200(6)	0.4202(8)	0.1722(9)
C(8)	0.7461(6)	0.4885(9)	0.3451(10)
C(9)	0.6724(7)	0.4852(11)	0.4899(10)
C(10)	0.5772(7)	0.4216(11)	0.4652(10)
C(11)	0.4510(7)	0.2750(10)	0.2567(12)
C(12)	0.4258(7)	0.2046(9)	0.0891(12)
C(13)	0.4982(7)	0.2051(10)	-0.0595(11)
C(14)	0.5930(6)	0.2744(9)	-0.0353(9)
C(15)	0.6214(5)	0.3498(7)	0.1383(9)
C(16)	0.5477(6)	0.3485(8)	0.2894(10)
O(1)	0.7842(4)	0.4155(7)	0.0190(6)
O(21)	0.9558(5)	0.2959(6)	-0.1529(7)
N(1)	1.1031(4)	0.5178(6)	-0.3065(8)
Cl(1)	1.0555(2)	0.2500(-)	-0.5534(3)

TABLE 2.1.2. (Cont.)

(b) Hydrogen-atom Fractional Coordinates for (+) Inderal Hydrochloride

ATOM	x/a	y/b	z/c
H(1)	1.2815	0.3647	-0.2818
H(1')	1.3673	0.4760	-0.2052
H(1'')	1.2714	0.4354	-0.0765
H(2)	1.3184	0.6173	-0.5289
H(2')	1.1959	0.6565	-0.5794
H(2'')	1.2337	0.5014	-0.5963
H(3)	1.2357	0.6506	-0.2383
H(1N)	1.0571	0.5827	-0.3844
H(2N)	1.0958	0.4276	-0.3706
H(4)	1.1080	0.4486	-0.0266
H(4')	1.0565	0.5971	-0.0511
H(5)	0.9051	0.4752	-0.2471
H(6)	0.9314	0.4246	0.1633
H(6')	0.8907	0.5685	0.0792
H(8)	0.8162	0.5386	0.3608
H(9)	0.6934	0.5323	0.6181
H(10)	0.5282	0.4249	0.5703
H(11)	0.3988	0.2780	0.3642
H(12)	0.3573	0.1550	0.0725
H(13)	0.4797	0.1541	-0.1823
H(14)	0.6456	0.2759	-0.1408
H(021)	1.0000	0.2781	-0.2675

TABLE 2.1.2. (Cont.)

(c) Anisotropic Temperature Factors and E.S.Ds of (+) Inderal Hydrochloride ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.051	0.136	0.116	0.017	-0.001	0.002
C(2)	0.064	0.098	0.115	-0.007	0.019	0.019
C(3)	0.047	0.068	0.099	-0.010	0.001	-0.009
C(4)	0.055	0.054	0.057	0.001	-0.002	-0.011
C(5)	0.064	0.052	0.049	-0.009	-0.002	0.006
C(6)	0.061	0.062	0.053	-0.008	-0.002	-0.001
C(7)	0.066	0.049	0.047	0.001	0.003	0.005
C(8)	0.071	0.064	0.056	0.012	-0.001	-0.010
C(9)	0.080	0.094	0.053	0.006	-0.002	-0.016
C(10)	0.083	0.084	0.048	0.018	0.016	0.003
C(11)	0.072	0.078	0.073	0.002	0.018	0.010
C(12)	0.073	0.064	0.083	-0.012	0.005	0.009
C(13)	0.081	0.073	0.067	-0.013	-0.006	-0.002
C(14)	0.070	0.063	0.049	0.003	0.004	0.002
C(15)	0.061	0.048	0.047	0.004	0.002	0.006
C(16)	0.068	0.058	0.054	0.006	0.005	0.010
O(1)	0.063	0.085	0.048	-0.016	0.007	-0.005
O(21)	0.107	0.056	0.063	-0.014	0.021	0.000
N(1)	0.044	0.040	0.066	-0.003	0.001	-0.004
Cl(1)	0.081	0.052	0.068	-0.009	-0.001	-0.018
Average Estimated Standard Deviations						
Cl	0.001	0.001	0.001	0.001	0.001	0.001
N	0.003	0.003	0.003	0.002	0.002	0.003
O	0.004	0.004	0.003	0.003	0.002	0.002
C	0.005	0.005	0.004	0.004	0.003	0.004

TABLE 2.1.3.

h	k	l	E
0	-5	-5	3.22
-1	-4	-3	3.00
-1	-3	-1	2.98

TABLE 2.1.4.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, for all non-hydrogen atoms; U_{iso} of all non-hydrogen atoms except O(20) and O(21); P.P. of O(20) and O(21); H-atoms in calculation but not refined; scale factor; unit weights.	1 - 4	0.145	0.018
x, y, z, of all non-hydrogen atoms; U_{ij} of non-hydrogen atoms except O(20) and O(21); P.P. of O(20) and O(21), scale factor; unit weights; H-atoms in calc. but not refined.	5 - 6	0.080	0.007
x, y, z, U_{ij} of all non-hydrogen atoms; P.P. of O(20) and O(21) constant; H-atoms in calc. but not refined.	7 - 8	0.07	0.006
x, y, z, of all atoms except calculated positions; P.P. of O(20) and O(21) constant; scale factor; unit weights.	9 - 10	0.066	0.005

Table 2.1.4. (Cont.)

Parameters Refined	Cycles	Final R	Final R'
x, y, z, U_{ij} of all non-hydrogen atoms; P.P. of O(20) and O(21) constant; scale factor; weighting scheme adjusted.	11 - 12	0.060	0.005

TABLE 2.1.5.

(a) Atomic Fractional Coordinates and E.S.Ds of (±) Inderal Hydrochloride (with Population Parameters)

ATOM	x/a	y/b	z/c	P.P.
C(1)	-0.1067(6)	0.1539(9)	0.5199(5)	1.0
C(2)	-0.2769(5)	0.2427(8)	0.4654(4)	1.0
C(3)	-0.1735(4)	0.2691(5)	0.4562(4)	1.0
C(4)	-0.0638(4)	0.2960(5)	0.3270(4)	1.0
C(5)	-0.0520(3)	0.4764(5)	0.3142(3)	1.0
C(6)	0.0418(3)	0.5152(5)	0.2818(4)	1.0
C(7)	0.2113(3)	0.4704(5)	0.3331(3)	1.0
C(8)	0.2374(4)	0.5520(5)	0.2565(4)	1.0
C(9)	0.3337(4)	0.5579(6)	0.2430(4)	1.0
C(10)	0.4042(4)	0.4831(6)	0.3037(4)	1.0
C(11)	0.4501(4)	0.3135(8)	0.4496(5)	1.0
C(12)	0.4239(5)	0.2319(8)	0.5263(5)	1.0
C(13)	0.3289(5)	0.2277(7)	0.5430(4)	1.0
C(14)	0.2577(4)	0.3063(5)	0.4820(3)	1.0
C(15)	0.2820(3)	0.3912(5)	0.4002(3)	1.0
C(16)	0.3789(3)	0.3976(5)	0.3849(3)	1.0
O(1)	0.1183(2)	0.4567(3)	0.3525(2)	1.0
O(21)	-0.0768(6)	0.5704(9)	0.3878(6)	0.5
O(20)	-0.1256(4)	0.5409(7)	0.2552(5)	0.5
N(1)	-0.1594(3)	0.2529(4)	0.3523(3)	1.0
Cl(1)	-0.1512(1)	-0.1065(1)	0.2882(1)	1.0

TABLE 2.1.5. (Cont.)

(b) Hydrogen-atom Fractional Coordinates and E.S.Ds of (±) Inderal Hydrochloride (with Population Parameters)

ATOM	x/a	y/b	z/c	P.P.
H(1)	-0.1294(-)	0.0374(-)	0.5204(-)	1.0
H(1')	-0.0810(-)	0.1876(-)	0.5861(-)	1.0
H(1'')	-0.0539(-)	0.1769(-)	0.5000(-)	1.0
H(2)	-0.2912(35)	0.2581(63)	0.5347(34)	1.0
H(2')	-0.3179(35)	0.2986(64)	0.4165(35)	1.0
H(2'')	-0.2930(35)	0.1547(63)	0.4466(35)	1.0
H(3)	-0.1534(34)	0.3870(61)	0.4735(33)	1.0
H(1N)	-0.2162(35)	0.3200(62)	0.3085(33)	1.0
H(2N)	-0.1731(35)	0.1285(62)	0.3317(34)	1.0
H(4)	-0.0113(35)	0.2636(60)	0.3804(33)	1.0
H(4')	-0.0553(35)	0.2592(61)	0.2604(33)	1.0
H(5)	-0.1040(-)	0.4918(-)	0.2577(-)	0.5
H(5')	-0.0517(-)	0.5246(-)	0.3794(-)	0.5
H(6)	0.0450(-)	0.4592(-)	0.2167(-)	1.0
H(6')	0.0476(-)	0.6337(-)	0.2712(-)	1.0
H(8)	0.1843(34)	0.5829(60)	0.2169(33)	1.0
H(9)	0.3547(35)	0.6026(61)	0.1844(34)	1.0
H(10)	0.4791(35)	0.4862(60)	0.2959(34)	1.0
H(11)	0.5210(35)	0.3183(60)	0.4245(34)	1.0
H(12)	0.4836(35)	0.1798(59)	0.5709(34)	1.0
H(13)	0.3028(35)	0.1662(59)	0.6045(33)	1.0
H(14)	0.1879(35)	0.3006(61)	0.4943(33)	1.0

TABLE 2.1.5. (Cont.)

(c) Anisotropic Temperature Factors and E.S.Ds of (±) Inderal Hydrochloride ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.104	0.098	0.078	-0.006	-0.015	0.002
C(2)	0.092	0.077	0.088	-0.017	0.026	-0.015
C(3)	0.078	0.042	0.073	-0.003	0.012	-0.017
C(4)	0.053	0.039	0.081	0.005	0.011	0.001
C(5)	0.055	0.038	0.070	0.001	0.004	-0.006
C(6)	0.061	0.041	0.071	0.003	-0.000	-0.000
C(7)	0.053	0.033	0.058	-0.004	0.007	-0.005
C(8)	0.058	0.050	0.073	-0.002	0.009	0.010
C(9)	0.083	0.057	0.075	-0.006	0.020	0.011
C(10)	0.062	0.056	0.091	-0.005	0.019	0.002
C(11)	0.061	0.087	0.093	0.006	-0.002	0.003
C(12)	0.089	0.096	0.085	0.011	-0.018	0.022
C(13)	0.090	0.077	0.066	0.002	-0.004	0.009
C(14)	0.071	0.048	0.055	-0.004	0.002	-0.003
C(15)	0.058	0.035	0.052	-0.005	0.003	-0.004
C(16)	0.054	0.046	0.071	-0.003	0.003	-0.006
O(1)	0.052	0.052	0.058	-0.001	0.005	0.006
O(21)	0.094	0.050	0.089	0.002	0.018	-0.005
O(20)	0.044	0.033	0.092	0.002	-0.020	-0.000
N(1)	0.058	0.030	0.070	0.000	0.004	-0.007
Cl(1)	0.0864	0.0369	0.0952	-0.0002	0.0085	-0.0150
Average Estimated Standard Deviations						
Cl	0.0009	0.0005	0.0008	0.0005	0.0006	0.0005
N	0.002	0.001	0.002	0.001	0.002	0.001
O	0.003	0.002	0.003	0.002	0.003	0.002
C	0.003	0.003	0.003	0.002	0.002	0.002

TABLE 2.1.6.

Intramolecular Bonded Distances and E.S.Ds (Å)

ATOM A	ATOM B	(+) Inderal HCl	(±) Inderal HCl
C(1)	C(3)	1.477(15)	1.523(9)
C(2)	C(3)	1.502(15)	1.485(9)
C(3)	N(1)	1.512(9)	1.508(6)
N(1)	C(4)	1.472(9)	1.476(6)
C(4)	C(5)	1.526(11)	1.518(6)
C(5)	C(6)	1.489(10)	1.485(7)
C(5)	O(21)	1.418(10)	1.375(9)
C(5)	O(20)	-	1.332(8)
C(6)	O(1)	1.428(9)	1.429(6)
O(1)	C(7)	1.367(8)	1.371(5)
C(7)	C(8)	1.382(10)	1.361(6)
C(7)	C(15)	1.409(10)	1.419(6)
C(8)	C(9)	1.400(11)	1.388(8)
C(9)	C(10)	1.336(13)	1.352(8)
C(10)	C(16)	1.429(11)	1.426(7)
C(11)	C(12)	1.359(12)	1.362(9)
C(11)	C(16)	1.403(12)	1.425(8)
C(12)	C(13)	1.409(12)	1.383(10)
C(13)	C(14)	1.358(12)	1.375(8)
C(14)	C(15)	1.426(9)	1.425(6)
C(15)	C(16)	1.433(9)	1.403(6)

TABLE 2.1.7.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	(+)Inderal HCl	(±) Inderal HCl
C(1)	C(3)	C(2)	113.3(8)	112.5(5)
C(1)	C(3)	N(1)	111.4(8)	110.4(4)
C(2)	C(3)	N(1)	108.6(7)	109.5(4)
C(3)	N(1)	C(4)	116.4(6)	117.6(4)
N(1)	C(4)	C(5)	110.6(5)	112.6(4)
C(4)	C(5)	C(6)	109.7(6)	111.4(4)
C(4)	C(5)	O(21)	111.3(6)	115.3(5)
C(4)	C(5)	O(20)	-	112.4(4)
O(21)	C(5)	C(6)	107.6(6)	115.9(5)
O(20)	C(5)	C(6)	-	111.2(4)
C(5)	C(6)	O(1)	107.7(6)	108.8(4)
C(6)	O(1)	C(7)	117.7(5)	118.1(3)
C(15)	C(7)	C(8)	121.1(6)	120.6(4)
O(1)	C(7)	C(8)	124.5(7)	124.6(4)
O(1)	C(7)	C(15)	113.8(6)	114.8(4)
C(7)	C(8)	C(9)	118.4(7)	120.1(5)
C(8)	C(9)	C(10)	122.5(7)	122.1(5)
C(9)	C(10)	C(16)	120.7(7)	118.9(5)
C(10)	C(16)	C(15)	118.1(7)	119.9(4)
C(10)	C(16)	C(11)	123.8(7)	121.0(5)
C(15)	C(16)	C(11)	118.2(7)	119.0(4)
C(16)	C(11)	C(12)	122.5(8)	119.9(5)
C(11)	C(12)	C(13)	119.6(8)	121.5(6)
C(12)	C(13)	C(14)	120.4(7)	120.6(5)
C(13)	C(14)	C(15)	121.4(6)	119.6(5)
C(14)	C(15)	C(7)	123.4(6)	122.2(4)
C(14)	C(15)	C(16)	118.1(6)	119.4(4)
C(7)	C(15)	C(16)	118.5(6)	118.4(4)

TABLE 2.1.8.

Selected Torsion Angles and E.S.Ds (°)

				(+) Inderal HCl	(±) Inderal HCl
C(1)	C(3)	N(1)	C(4)	64.8(9)	-63.5(5)
C(2)	C(3)	N(1)	C(4)	-169.7(7)	172.2(4)
N(1)	C(4)	C(5)	C(6)	-163.7(6)	-175.9(4)
N(1)	C(4)	C(5)	O(21)	77.4(7)	49.4(6)
N(1)	C(4)	C(5)	O(20)	—	-50.4(6)
C(5)	C(4)	N(1)	C(3)	-170.2(6)	-81.6(5)
C(4)	C(5)	C(6)	O(1)	173.8(6)	-59.3(5)
O(21)	C(5)	C(6)	O(1)	-65.0(7)	75.1(6)
O(20)	C(5)	C(6)	O(1)	—	174.5(4)
C(5)	C(6)	O(1)	C(7)	175.4(6)	175.6(4)
O(1)	C(7)	C(8)	C(9)	179.8(7)	-179.7(4)
O(1)	C(7)	C(15)	C(14)	3.1(10)	-0.9(6)
O(1)	C(7)	C(15)	C(16)	-179.8(6)	179.2(4)
C(8)	C(7)	O(1)	C(6)	9.6(10)	7.8(6)
C(15)	C(7)	O(1)	C(6)	-171.4(6)	-172.1(4)

TABLE 2.1.9.

Selected least-squares planes in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

A. (+) Inderal Hydrochloride.

(a) Plane Equation:=

$0.41048X' - 0.82375Y' + 0.39107Z' = 0.73888$

(b) Deviations (Å) of atoms from plane (starred atoms define the plane)

C(1)	1.666(13)	C(7)*	-0.004(8)
C(2)	-0.401(11)	C(8)*	0.013(8)
C(3)	0.227(9)	C(9)*	0.023(10)
N(1)	-0.022(6)	C(10)*	-0.014(10)
C(4)	0.313(8)	C(11)*	-0.002(9)
C(5)	0.243(8)	C(12)*	0.016(9)
O(21)	1.387(6)	C(13)*	0.012(9)
C(6)	0.192(8)	C(14)*	0.000(8)
O(1)	-0.020(6)	C(15)*	-0.027(7)
Cl(1)	1.266(1)	C(16)	-0.017(8)

TABLE 2.1.9. (Cont.)

B. (±) Inderal Hydrochloride.

(a) Plane Equation:-

$0.06022X' + 0.82900Y' + 0.55599Z' = 5.94548$

(b) Deviations (Å) of atoms from the plane (starred atoms define the plane)

C(1)	-1.047(7)	C(7)*	-0.017(4)
C(2)	-0.993(6)	C(8)*	-0.014(5)
C(3)	-0.789(5)	C(9)*	0.006(5)
N(1)	-1.679(3)	C(10)*	0.010(5)
C(4)	-1.493(4)	C(11)*	-0.013(7)
C(5)	-0.340(4)	C(12)*	-0.016(7)
O(21)	0.841(8)	C(13)*	0.001(6)
O(20)	-0.405(6)	C(14)*	0.020(5)
C(6)	-0.239(4)	C(15)*	0.006(4)
O(1)	-0.043(3)	C(16)*	0.016(4)
Cl(1)	-4.626(1)		

TABLE 2.1.10.

(a) (+) Inderal Hydrochloride.

Intra ionic non-bonding distances < 3.6Å

Atom A	Atom B		Å
C(1)	C(4)		3.07
C(6)	C(8)		2.82
C(14)	O(1)		2.75
O(1)	O(21)		2.77
O(21)	N(1)		3.07
Interionic distances < 3.8Å			
C(5)	Cl		3.77
O(21)	Cl		3.13
N(1)	Cl		3.14
C(10)	C(14)	I	3.72
C(1)	C(12)	II	3.55
C(1)	C(13)	II	3.64
C(7)	C(12)	III	3.34
C(8)	C(11)	III	3.73
C(8)	C(12)	III	3.40
C(9)	C(11)	III	3.54
C(9)	C(12)	III	3.63
C(10)	C(11)	III	3.73
C(10)	C(12)	III	3.78
C(15)	C(12)	III	3.51
C(16)	C(12)	III	3.75
H(2N)	Cl		2.18
H(021)	Cl		2.15

where the position of atom B is given by,

I = x, y, 1+z
II = 1+x, y, z
III = 1-x, $\frac{1}{2}$+y, z

TABLE 2.1.10. (Cont.)

(b) (±) Inderal Hydrochloride

Intra-ionic non-bonding distances < 3.6Å

Atom A	Atom B		Å
C(1)	C(4)		3.08
C(3)	C(5)		3.29
C(3)	O(21)		3.06
C(4)	O(1)		2.85
C(6)	C(8)		2.83
O(1)	C(14)		2.75
O(1)	O(20)		3.55
O(1)	O(21)		3.00
O(20)	N(1)		2.82
O(21)	N(1)		2.89
O(20)	H(1N)		2.41
O(20)	H(2N)		3.67
O(21)	H(1N)		2.95
O(21)	H(2N)		3.94

Inter-ionic distances < 3.80Å

C(4)	Cl		3.57
N(1)	Cl		3.12
H(2N)	Cl_I		2.08
C(5)	Cl_I	I	3.72
O(20)	Cl_I	I	2.99
O(21)	Cl_I	I	3.12
C(1)	O(1)	II	3.70
C(1)	O(21)	II	3.53
C(2)	C(7)	II	3.70
C(2)	C(15)	II	3.58
C(3)	C(7)	II	3.74
C(3)	O(1)	II	3.50
C(14)	O(21)	II	3.48
O(1)	O(21)	II	3.77
O(21)	O(21)	II	3.72
C(11)	C(11)	III	3.59
C(13)	O(20)	IV	3.69
C(9)	C(1)	V	3.78
C(8)	C(7)	VI	3.79
C(8)	C(15)	VI	3.55
C(8)	C(16)	VI	3.72
C(9)	C(7)	VI	3.61
C(9)	C(15)	VI	3.65
C(9)	O(1)	VI	3.66
C(2)	Cl	VII	3.75

TABLE 2.1.10.

Inter-ionic distances Cont.

Atom A	Atom B		Å
O(20)	C(2)	VII	3.59
O(20)	N(1)	VII	3.61
O(20)	Cl	VII	3.32
N(1)	Cl	VII	3.27
H(IN)	Cl	VII	2.21

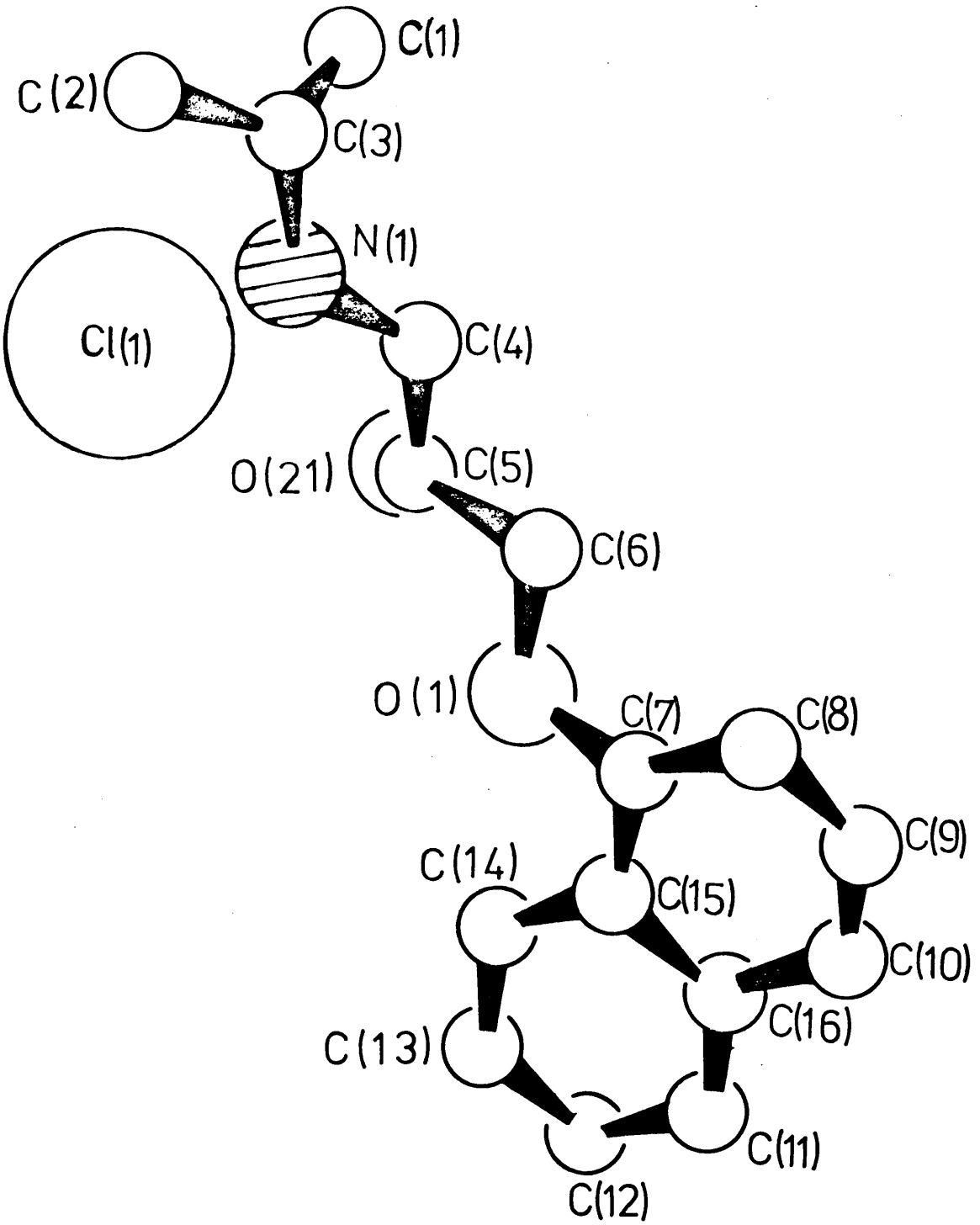
where the position of atom B is given by,

I	=	$x, 1+y, z$
II	=	$-x, 1-y, 1-z$
III	=	$1-x, 1-y, 1-z$
IV	=	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
V	=	$\frac{1}{2}+x, \frac{1}{2}-y, (\frac{1}{2}+z)-1$
VI	=	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
VII	=	$(\frac{1}{2}-x)-1, \frac{1}{2}+y, \frac{1}{2}-z$

FIGURE 2.1.1.

Diagrammatic representation of

(+) INDERAL HYDROCHLORIDE


C(1)
C(2)
C(3)
N(1)
Cl(1)
C(4)
O(21)
C(5)
C(6)
O(1)
C(7)
C(8)
C(9)
C(14)
C(15)
C(10)
C(16)
C(13)
C(11)
C(12)

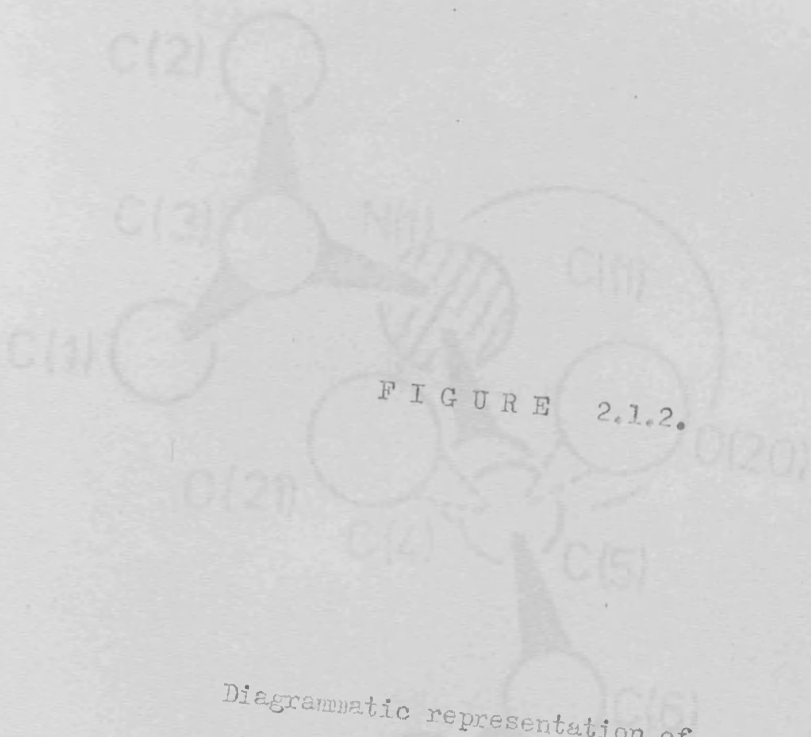
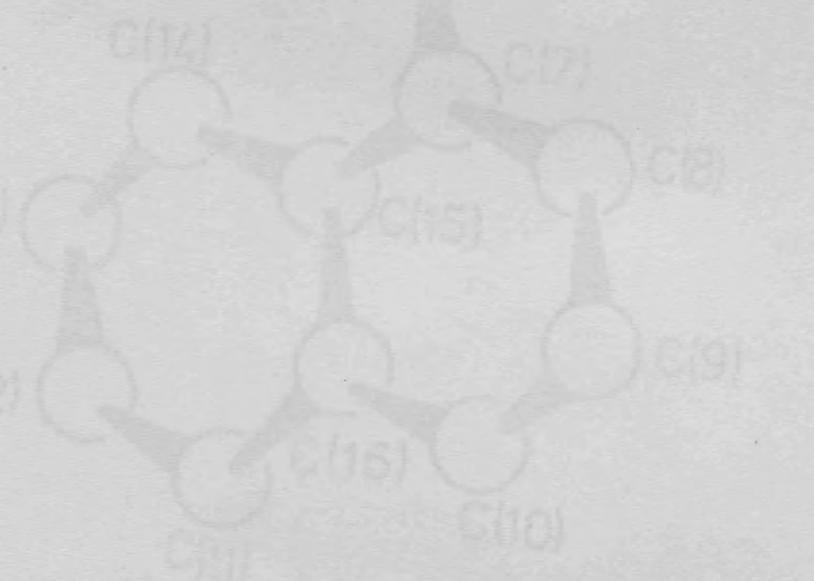
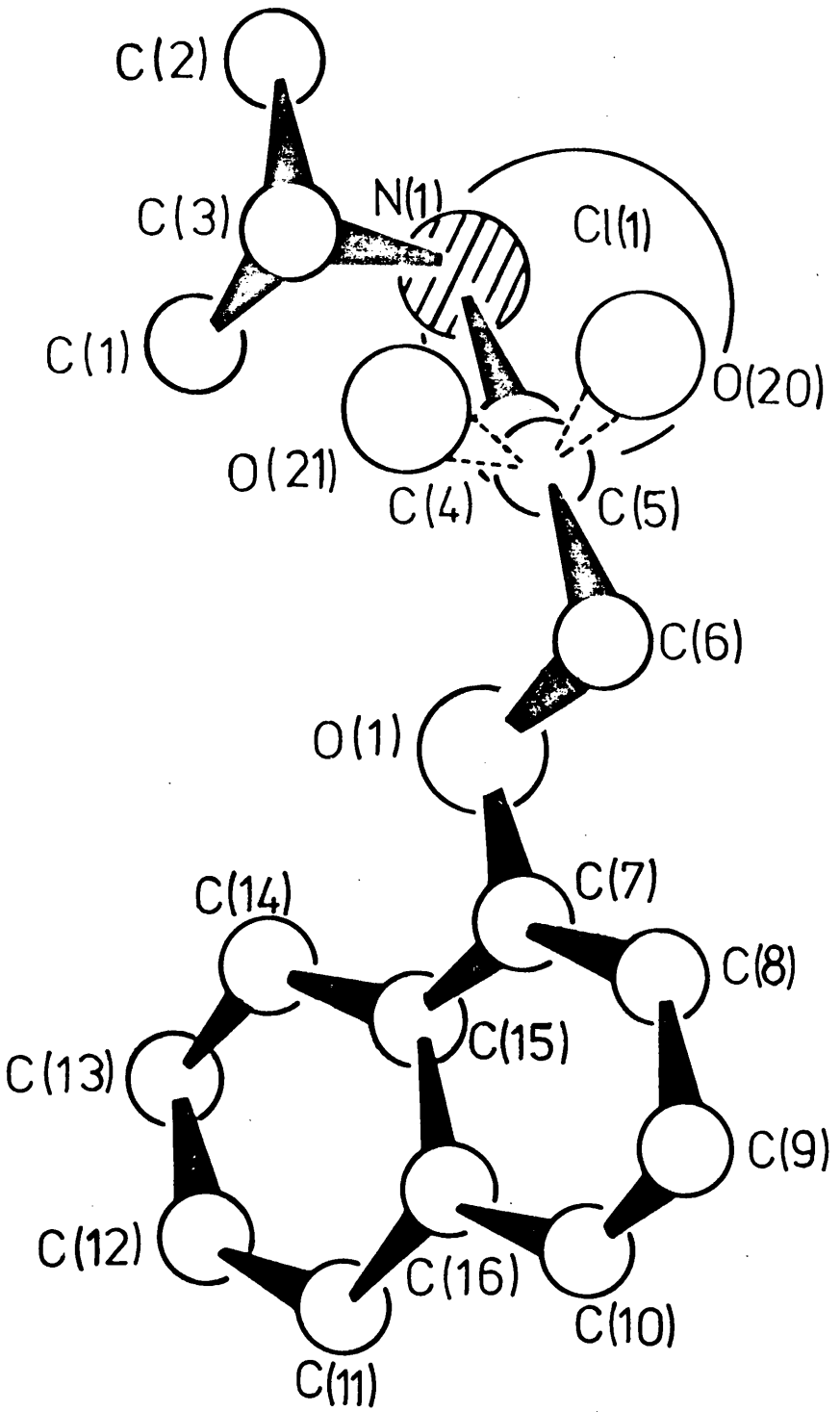


FIGURE 2.1.2.

Diagrammatic representation of

(±) INDERAL HYDROCHLORIDE




C(2)
C(3)
N(1)
Cl(1)
C(1)
O(20)
O(21)
C(4)
C(5)
C(6)
O(1)
C(14)
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C(13)
C(9)
C(12)
C(16)
C(10)
C(11)

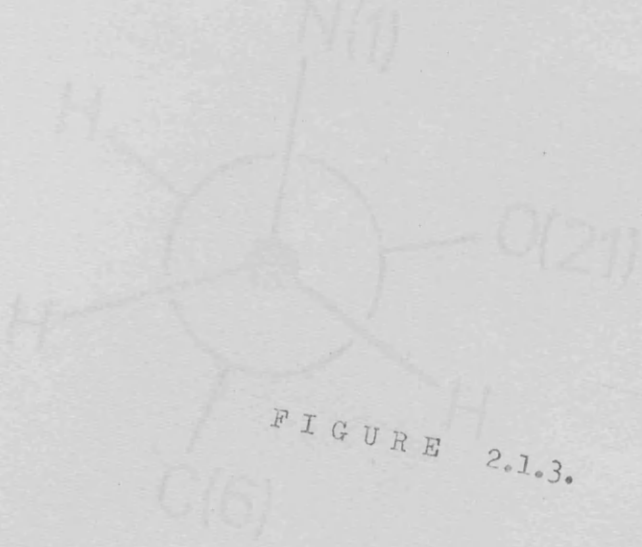
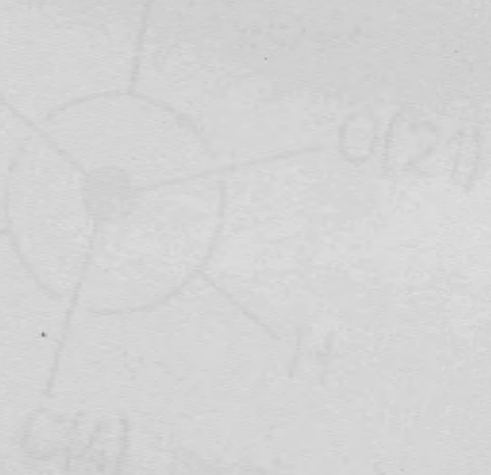


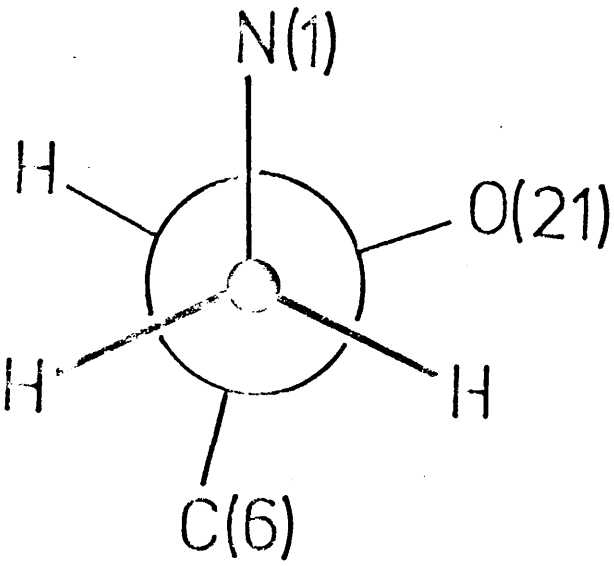
FIGURE 2.1.3.

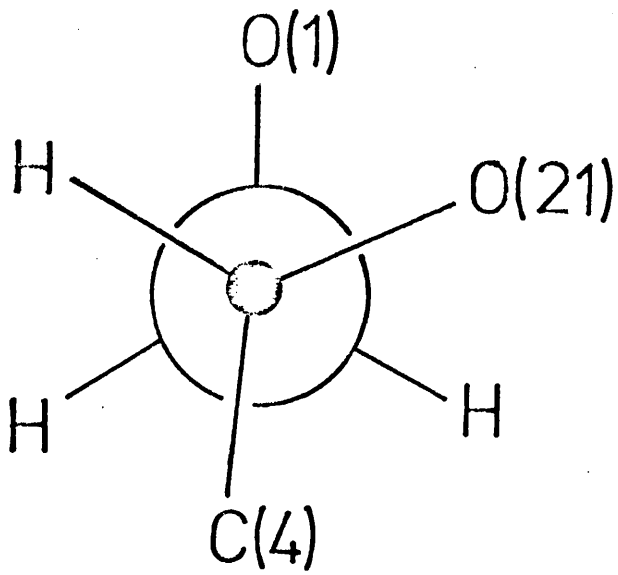
(+) INDERAL HYDROCHLORIDE

Conformations about bonds

C(4) - C(5) and C(5) - C(6)




N(1)
H
O(21)
H
H
C(6)


O(1)
H
O(21)
H
H
C(4)

F I G U R E 2.1.4.

Crystal-packing arrangements for

(+) INDERAL HYDROCHLORIDE

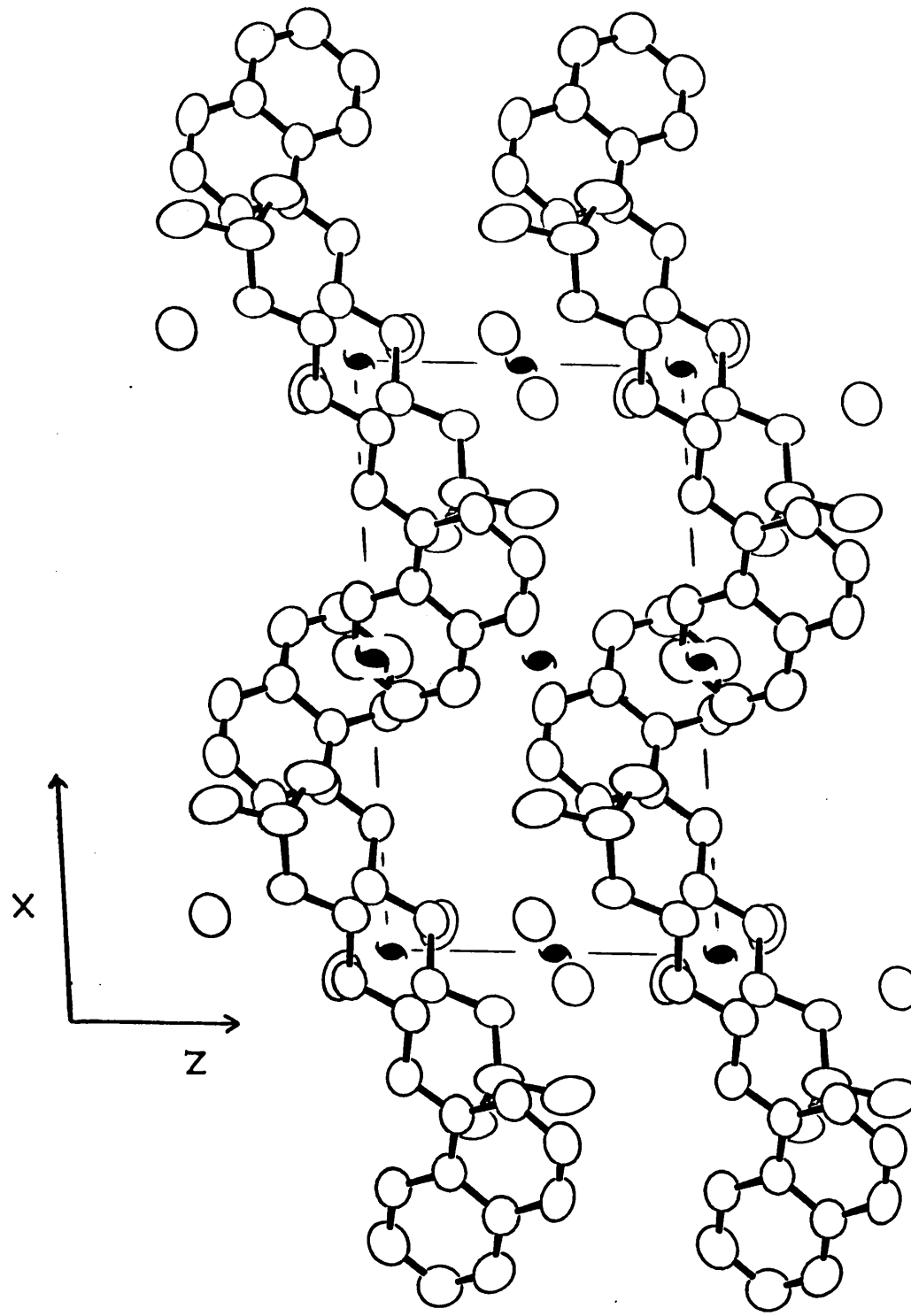
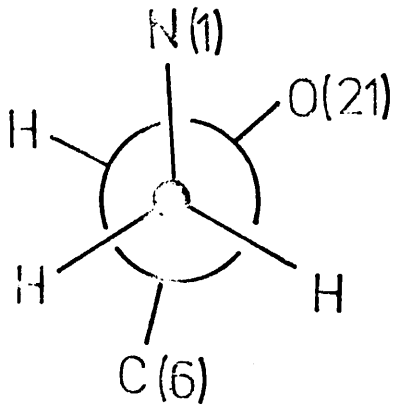
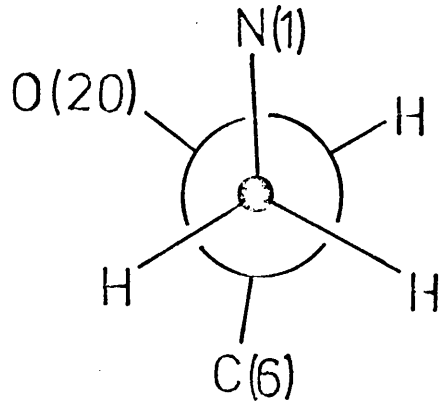
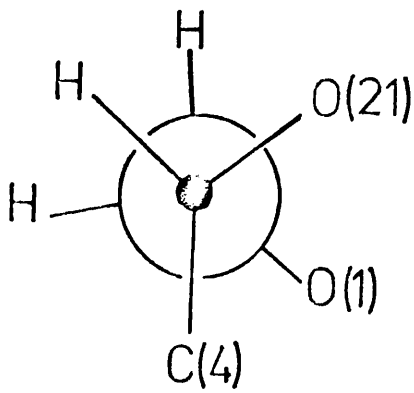

X
Z

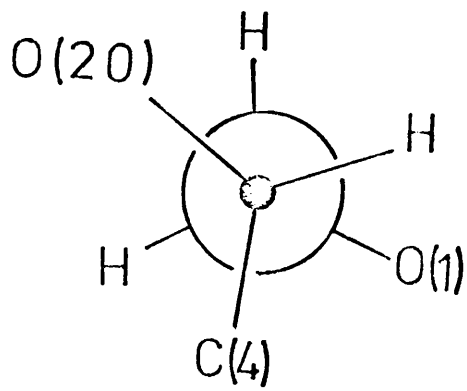
FIGURE 2.1.5.

Alternative configurations and conformations about bonds C(4) - C(5) and C(5) - C(6) in (±) INDERAL HYDROCHLORIDE

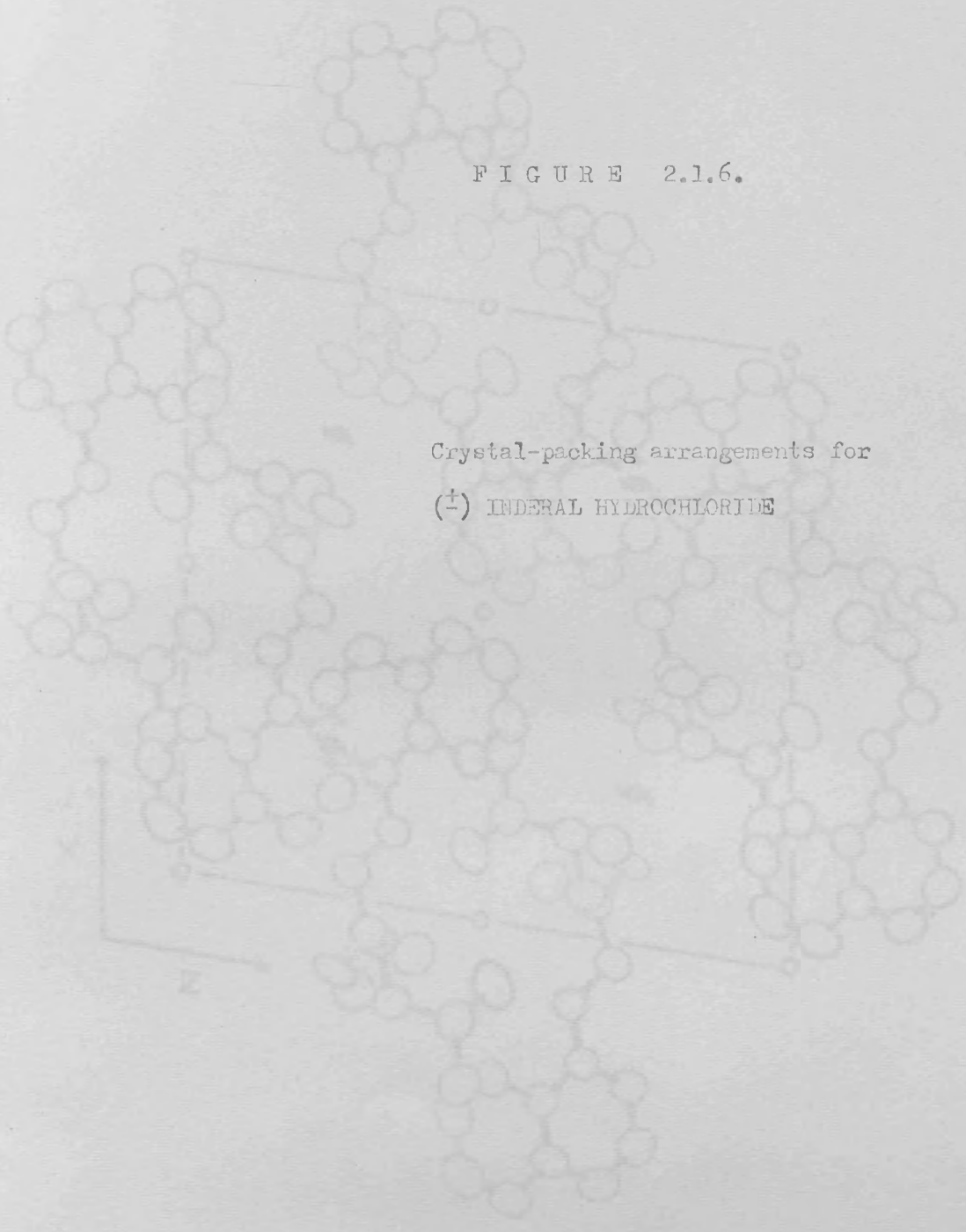

N(1)
O(21)
H
H
H
C(6)


N(1)
O(20)
H
H
H
C(6)


H
H
O(21)
H
O(1)
C(4)

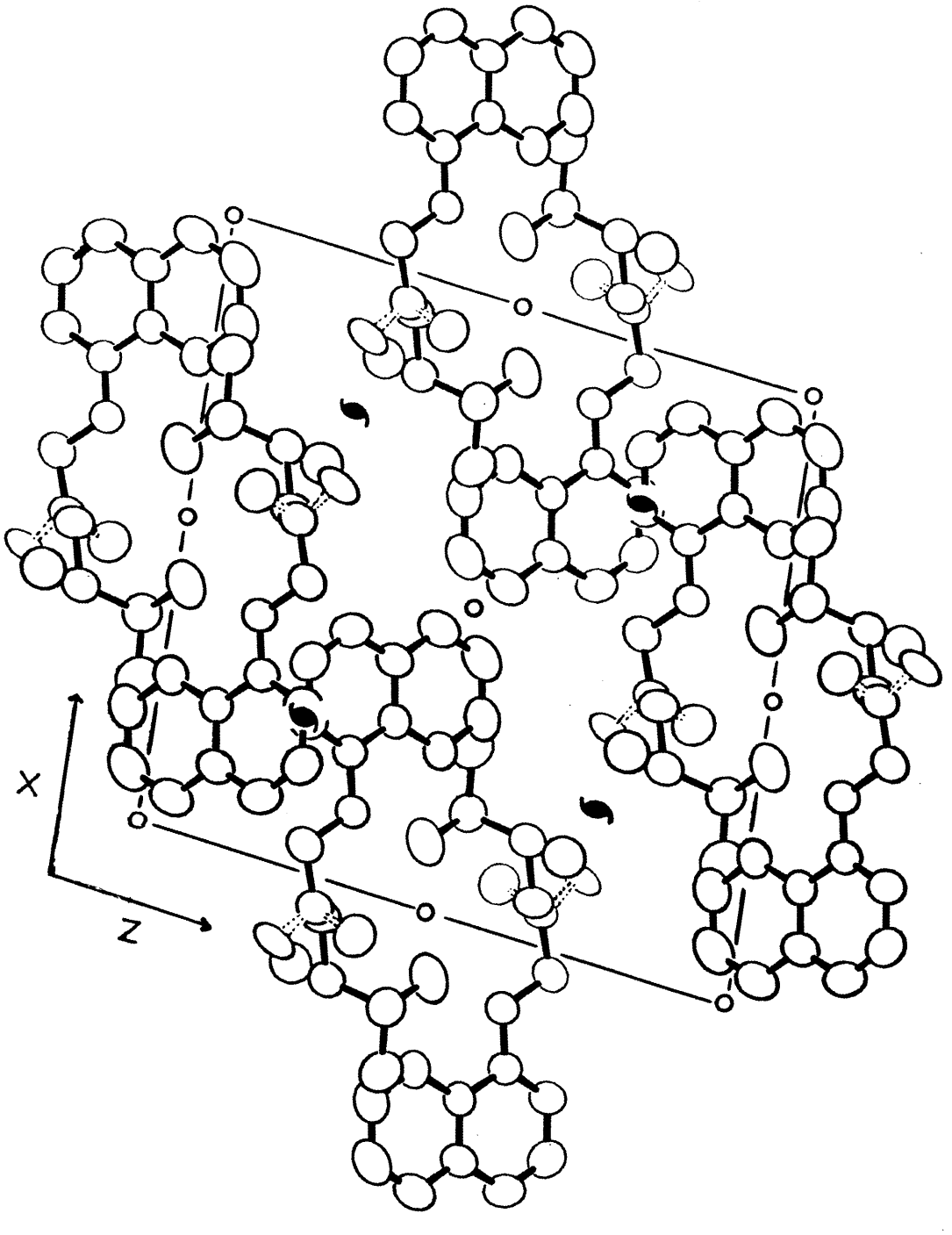

O(20)
H
H
H
O(1)
C(4)

F I G U R E 2.1.6.



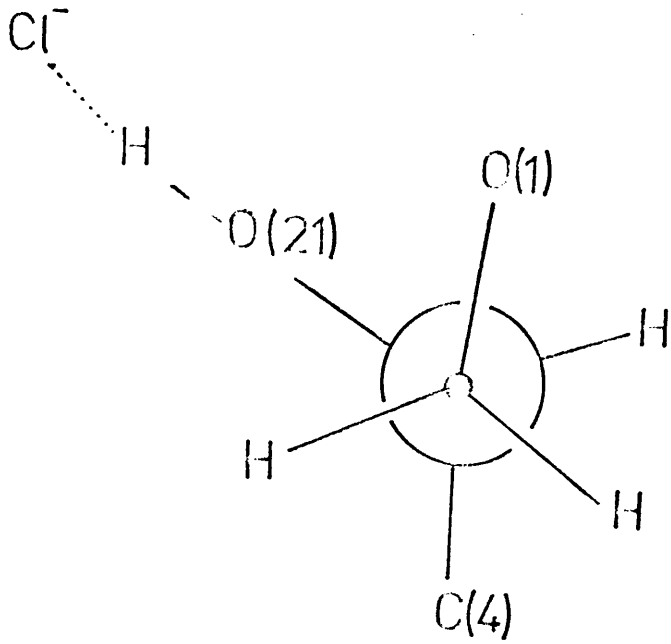
Crystal-packing arrangements for

(±) INDERAL HYDROCHLORIDE

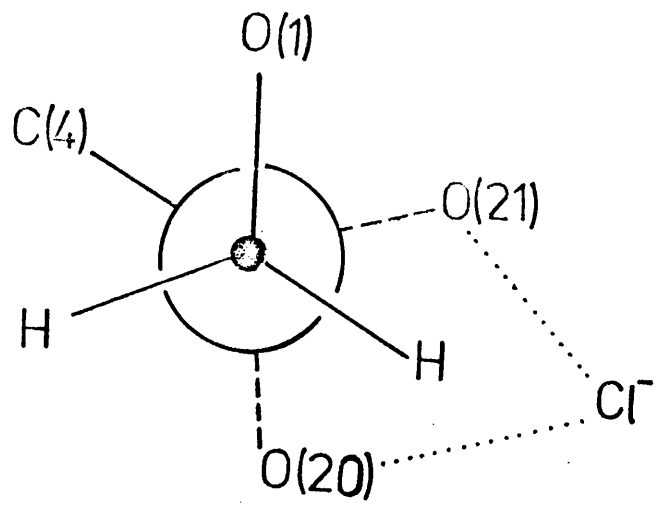

X
Z

F I G U R E 2.1.7.

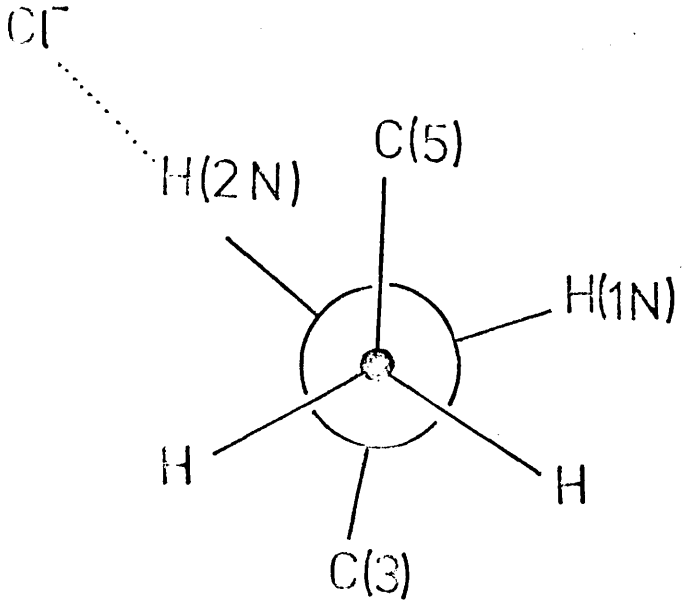
Relative conformations about bonds
C(6) - C(5) and C(4) - N(1) in
(+) and (±) INDERAL HYDROCHLORIDE



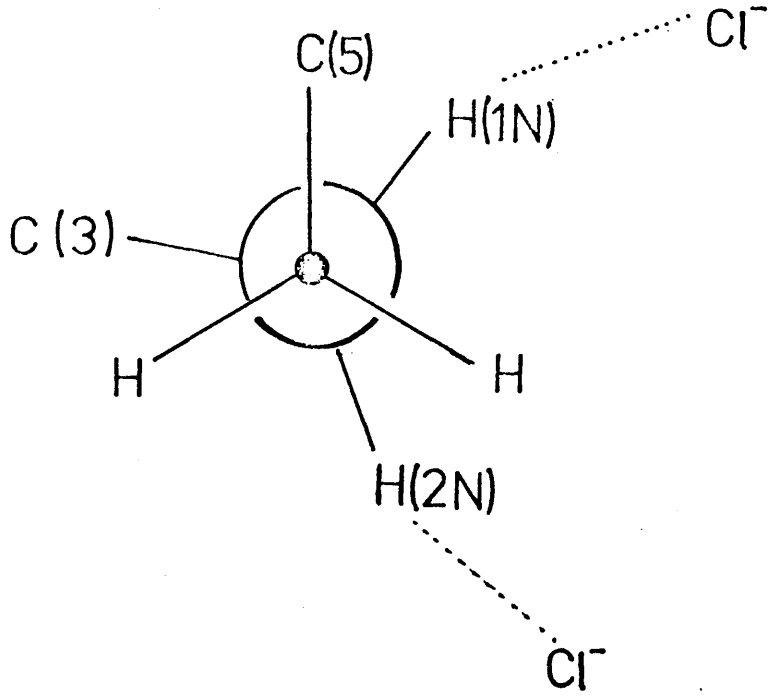
(+) INDERAL HYDROCHLORIDE



(±) INDERAL HYDROCHLORIDE



(+) INDERAL HYDROCHLORIDE



(±) INDERAL HYDROCHLORIDE

SECTION 2.2.

THE CRYSTAL AND MOLECULAR STRUCTURE OF (±) ERALDIN PERCHLORATE [(±)1-(4-Acetamidophenoxy)-3-isopropylaminopropan-2-ol]

EXPERIMENTAL

(±) BRAIDIN PERCHLORATE

(±) 1-(4-Acetamidophenoxy)-3-isopropylaminopropan-2-ol Perchlorate

CRYSTAL DATA

$C_{14}H_{22}N_2O_7Cl$; $\frac{1}{2}$MeOH; M=381.9; Triclinic, a=10.686Å, b=10.913Å, c=8.936Å, α=100.15°, β=84.96°, γ=77.70°; U=993.58Å; D_c=1.28 g.cm.$^{-3}$; D_m=1.30 g.cm.$^{-3}$; Z=2; F000=404; Space group $P\bar{1}$; μ=2.36 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs, taken with Cu-Kα (λ=1.5418Å) radiation and from precession photographs, taken with Mo-Kα (λ=0.7107Å) radiation and were subsequently refined by least-squares calculations before data collection. The space group $P\bar{1}$ was suggested by photographic evidence, density measurements (by flotation with ethyl benzoate/carbon tetrachloride) and the racemic nature of the compound, and was subsequently confirmed by structure refinement.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer by exposing a small crystal (0.2 x 0.4 x 0.2mm.), rotating about b, to graphite-monochromated Mo radiation (Mo-Kα_1) and by using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 50°$) to collect 1306 independent reflections with $I \geqslant 2\sigma_I$ ($\sigma_I = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The structure was determined by centro-symmetric Direct Methods using the computer program MULTAN and appropriate programs contained in the X-ray '72 suite of computer programs.

Phase determination was initiated by choosing six reflections, three of which defined the unit-cell origin and were given phase values of 360°, and three of which were selected because of their ability to form a large number of sigma-2 phase relationships. Since the phases of the three non-origin-defining reflections were unknown, they were given all possible combinations of the values 360° and 180° to initiate a series of calculations utilising the weighted tangent formula of Direct Methods (the correct starting set being given in Table 2.2.1.), from which the phases of 154 reflections with $E \geq 1.4$ were assigned.

An E-map based on these 154 reflections, revealed 22 plausible atomic positions and subsequent structure-factor and electron-density calculations confirmed all non-hydrogen atomic positions, with the exception of those positions associated with possible perchlorate-oxygen atoms. The electron-density distribution attributed to such atoms indicated a high degree of disorder which was subsequently investigated by a series of electron-density calculations and difference syntheses. Six stereochemically-acceptable atomic sites were finally selected as possible perchlorate-oxygen atomic positions and each was assigned a population parameter related by ratio to its observed electron density, the total population parameter over all six positions being equivalent to the electron-density population of four oxygen atoms.

The foregoing series of calculations also revealed the presence of a third moiety in the unit cell but accurate assignment of individual atomic positions was hindered by disorder. Stereochemical and space-group symmetry considerations indicated that the moiety was not a molecule of the solvent of crystallisation (ethanol) and attempts to characterise it by i.r. spectroscopy proved unsuccessful. Careful selection of possible atomic sites, during initial structure refinement, showed that the observed electron density could best be attributed to a molecule of methanol, statistically distributed between two centrosymmetrically-related crystallographic-molecular sites, and in all subsequent calculations the carbon and oxygen atoms of the methanol molecule were assigned population parameters of 0.50.

An arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ was assigned to each non-hydrogen atom and after each calculation, the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Computing limitations forced the use of an arbitrary blocking strategy in which the parameters of groups of atoms were refined simultaneously (considering all off-diagonal elements within the group), while the remaining parameters were held constant. Details of the refinement are given in Table 2.2.2. and show convergence of positional, vibrational and scale parameters after 20 cycles of least-squares calculations, when R was 0.073 and R' was 0.007. No refinement of population parameters was carried out.

Where possible, hydrogen-atom positions were selected from difference

syntheses or were calculated (staggered conformations being assumed for all methyl groups) and were assigned arbitrary temperature factors, $U_{iso}=0.03\text{Å}^2$ in subsequent calculations, no refinement of positional or vibrational parameters being carried out.

An appropriate weighting scheme was chosen by examination of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure-factors. The scheme was of the form;

If A $|Fo| > |Fc|$, $W=10^{-9}$

otherwise $W=X.Y$,

with $X=1$ if $\sin\theta > B$, else $X=\frac{\sin\theta}{B}$

and $Y=1$ if $|Fo| < C$, else $Y=\frac{C}{|Fo|}$

The most suitable values for A, B and C were found to be 0.75, 0.45 and 9.00 respectively. At the conclusion of refinement difference syntheses and electron-density calculations revealed no gross errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (35). Observed and calculated structure-factors are given in Appendix 3, while positional and vibration parameters, with estimated standard deviations are shown in Table 2.2.3. The values of e.s.d.s. are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

(±) ERALDIN PERCHLORATE

DISCUSSION

A diagrammatic representation of this compound is given in Figure 2.2.1., hydrogen atoms being omitted for clarity but, for the purposes of discussion, numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, least-squares planes, intra-ionic non-bonding distances and inter-ionic distances are listed in Tables 2.2.4. to 2.2.8.

The high degree of disorder in the perchlorate anion prevents accurate assessment of its dimensions, and those positions quoted as oxygen-atom positions may best be regarded as having an increased probability of occupation by an oxygen atom. Similarly, the dimensions of the methanol molecule are influenced by the partial occupancy of its atomic sites and by possible disorder, and the apparently long C(15)-O(15) [1.64(4)Å] bond is probably a result of these effects.

The Eraldin cation shows no evidence of disorder, with the largest observed vibrational parameter being U_{33}=0.123, in the case of atom C(2). Those hydrogen atom positions (H(1N) and H(2N)) bonded to atom N(1) were calculated, assuming tetrahedral nitrogen-atom geometry, while H(N2) was selected from a difference synthesis.

The phenyl ring is planar, within experimental error, with atoms O(1) and N(2) respectively, 0.012 and -0.016Å distant from the least-squares plane through the ring atoms. The least-squares plane through atoms O(3), N(2), C(13) and C(14) confirms the planarity

of the acetamide group, the dihedral angle [20.4°] between the foregoing planes, being similar to the corresponding value [17.6°] observed in Acetanilide[25]. This value, which is less than the angle of 90° required for minimum steric interactions [C(11)··· C(13)3.04Å and O(3)··· C(11)2.86Å], suggests possible π-electron communication between the acetamide and aromatic system. The remaining dimensions of the acetanilide portion of the present compound are similar to those reported for Acetanilide[25] and other similar systems[26].

The alkoxy chain has a fully-extended conformation [torsion angles C(7)O(1)C(6)C(5) - 176.7(5)°, O(1)C(6)C(5)C(4)166.5(5)°, C(6)C(5) C(4)N(1)177.4(5)° and C(5)C(4)N(1)C(3)174.1(5)°], in which the hydroxyl group is gauche with respect to atoms N(1) and O(1) [torsion angles N(1)C(4)C(5)O(2) 54.7(7)° and O(2)C(5)C(6)O(1) -71.9(6)°]. Figure 2.2.2. illustrates the conformations about bonds C(4) - C(5) and C(5) - C(6). The interatomic distance N(1) ···O(2) [2.82Å] suggests possible electrostatic interactions between these atoms although hydrogen bonding of the form $\geq N^{+}-H\cdots \overset{H}{O}-R$, seems unlikely [H(1N)···O(2) 3.02Å and H(2N)···O(2) 2.53Å].

The distortions of torsion angles C(1)C(3)N(1)C(4) [-75.5(7)°] and C(2)C(3)N(1)C(4) [161.9(6)°] from the ideal staggered-conformation values may be largely due to intra-ionic [C(1)··· C(4) 3.13Å] and inter-ionic [C(1)···O(22) 3.28Å and C(4)···O(11) 3.32Å] steric interactions, while interionic distances such as C(9)···O(17) [3.45Å] and C(11)···N(2) [3.53Å] suggest that possible steric interactions between these pairs of atoms may contribute to

the deviation of torsion angle C(6)O(1)C(7)C(8) [-22.2(10)°] from the approximately-eclipsed conformations found in similar systems e.g. the corresponding torsion-angle values for (+) Inderal Hydrochloride and (±) Inderal Hydrochloride are respectively, 9.6(10)° and 7.8(6)°.

A diagram representing the crystal-packing arrangements of this compound is given in Figure 2.2.3. and shows that each cation may be associated with two perchlorate anions and, where possible, with a molecule of methanol. The disorder in the perchlorate anion and the partial occupancy of the methanol molecule, prevent accurate assessment of the dimensions of possible hydrogen bonds, but inter-ionic distances, N(2)···O(17) [2.96Å], N(1)···O(13) [2.94Å], O(15)···O(23) [2.82Å] and O(2)···O(15) [2.61Å], suggest interactions between these pairs of atoms.

Bond lengths C(5) - C(6) [1.504(10)Å], C(1) - C(3) [1.493(12)Å] and C(2) - C(3) [1.523(13)Å] appear shorter than might be expected for $C(sp^3)$ - $C(sp^3)$ bonds but, as previously noted, in the cases of (+) Inderal hydrochloride and (±) Inderal hydrochloride, these apparently anomalous values may be a result of thermal librational motion of the cations[22]. The remaining dimensions of the present compound agree with those of accepted literature values for similar bonding systems.

TABLE 2.2.1.

h	k	l	E	Phi	
2	-1	-1	3.22	360°	Origin Defining Reflections
1	1	-2	3.23	360°	
6	7	2	2.54	360°	
6	-3	6	2.11	360°	
2	1	-2	2.69	180°	
4	1	3	2.87	360°	

TABLE 2.2.2.

COURSE OF REFINEMENT

Parameters Refined	Cycles	Final R	Final R'
x, y, z, and U_{iso} of all non-hydrogen atoms, except Methanol atoms; scale factor,; unit weights.	1 - 4	0.170	0.036
As in cycles 1 - 4 plus hydrogen-atom contributions but with no refinement of hydrogen atoms; scale factor; unit weights.	5 - 6	0.152	0.024
x, y, z, U_{ij} (i,j = 1, 2, 3) of perchlorate atom positions; x, y, z, U_{iso} of Methanol C and O atoms; structure-factor contributions from all other atoms but with no refinement of these atoms; scale factor; unit weights.	7 - 11	0.112	0.013
x, y, z, U_{ij} of non-hydrogen atoms of cation; structure-factor contributions from all other atoms but with no refinement of these atoms; scale factor, unit weights.	12 - 14	0.079	0.008
x, y, z, U_{ij} of perchlorate atoms and of Methanol C and O atoms; structure-factor contributions from all other			

TABLE 2.2.2. (Cont.)

Parameters Refined	Cycles	Final R	Final R'
atoms but with no refinement of these atoms; scale factor; weighting scheme adjusted.	15 - 17	0.075	0.008
x, y, z, U_{ij} of non-hydrogen cation atoms; structure-factor contributions from all other atoms but with no further refinement of these atoms; scale factor; weighting scheme adjusted.	18 - 20	0.073	0.007

TABLE 2.2.3.

(a) Atomic Fractional Coordinates and E.S.Ds for Compound V (with Population Parameters)

ATOM	x/a	y/b	z/c	P.P.
C(1)	1.3839(10)	0.4735(8)	0.6714(12)	1.0
C(2)	1.3399(10)	0.5876(11)	0.9453(13)	1.0
C(3)	1.2819(7)	0.5389(6)	0.8031(9)	1.0
C(4)	1.1079(7)	0.4247(7)	0.7369(8)	1.0
C(5)	1.0407(6)	0.3223(6)	0.7761(8)	1.0
C(6)	0.9422(7)	0.3064(6)	0.6682(8)	1.0
C(7)	0.8193(6)	0.1541(6)	0.5895(8)	1.0
C(8)	0.7384(8)	0.2316(7)	0.5197(11)	1.0
C(9)	0.5433(8)	0.1845(6)	0.4265(10)	1.0
C(10)	0.6530(6)	0.0556(6)	0.4060(7)	1.0
C(11)	0.7326(6)	-0.0228(6)	0.4793(7)	1.0
C(12)	0.8175(7)	0.0238(6)	0.5712(8)	1.0
C(13)	0.5698(6)	-0.1065(7)	0.2350(7)	1.0
C(14)	0.4649(7)	-0.1212(7)	0.1407(8)	1.0
O(1)	0.9048(5)	0.1907(4)	0.6850(6)	1.0
O(2)	0.9832(4)	0.3569(4)	0.9322(5)	1.0
O(3)	0.6540(5)	-0.1977(4)	0.2488(6)	1.0
N(1)	1.2013(5)	0.4481(5)	0.8440(6)	1.0
N(2)	0.5651(5)	0.0146(5)	0.3094(7)	1.0
C(15)	0.9459(34)	0.0463(32)	1.0688(50)	0.45
O(15)	0.9808(14)	0.1873(12)	1.1043(10)	0.45
O(11)	1.1632(23)	0.3572(30)	1.3568(17)	0.56
O(13)	1.2516(13)	0.3742(12)	1.1375(11)	1.00
O(16)	1.1667(34)	0.2952(57)	1.3253(53)	0.76
O(17)	1.3702(11)	0.2394(14)	1.2671(16)	1.00
O(22)	1.3181(59)	0.4063(46)	1.3186(76)	0.25
O(23)	1.2397(25)	0.1915(21)	1.1370(29)	0.43
Cl(1)	1.2586(2)	0.3028(2)	1.2397(3)	1.00

TABLE 2.2.3.

(b) Hydrogen-atom Fractional Coordinates

ATOM	x/a	y/b	z/c
H(1)	1.4347	0.3903	0.6892
H(1')	1.3391	0.4492	0.5735
H(1'')	1.4276	0.5179	0.6518
H(2)	1.3971	0.5089	0.9779
H(2')	1.3959	0.6476	0.9226
H(2'')	1.2720	0.6308	1.0311
H(3)	1.2263	0.6129	0.7730
H(1N)	1.2613	0.3641	0.8510
H(2N)	1.1527	0.4867	0.9508
H(4)	1.1599	0.3915	0.6279
H(4')	1.0486	0.5000	0.7118
H(5)	1.1073	0.2377	0.7645
H(6)	0.9827	0.2977	0.5560
H(6')	0.8662	0.3820	0.6885
H(8)	0.7170	0.3408	0.5399
H(9)	0.5976	0.2457	0.3650
H(11)	0.7298	-0.1153	0.4667
H(12)	0.9051	-0.0415	0.6088
H(14)	0.3809	-0.0894	0.2097
H(14')	0.4680	-0.0668	0.0619
H(14'')	0.4684	-0.2103	0.0860
H(02)	1.0486	0.3907	0.9286
H(N2)	0.5203	0.0697	0.2873

TABLE 2.2.3. (Cont.)

(c) Anisotropic Temperature Factors and E.S.Ds for Compound V ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.110	0.062	0.112	-0.037	0.044	-0.003
C(2)	0.093	0.117	0.123	-0.069	-0.011	0.005
C(3)	0.055	0.039	0.076	-0.016	-0.003	0.006
C(4)	0.057	0.059	0.050	-0.013	-0.016	0.012
C(5)	0.051	0.042	0.056	-0.013	-0.005	-0.002
C(6)	0.065	0.048	0.072	-0.022	-0.017	0.014
C(7)	0.051	0.051	0.060	-0.015	-0.016	0.004
C(8)	0.081	0.044	0.114	-0.019	-0.047	0.011
C(9)	0.080	0.040	0.112	-0.019	-0.045	0.022
C(10)	0.043	0.036	0.059	-0.007	-0.011	0.003
C(11)	0.063	0.036	0.054	-0.012	-0.010	0.004
C(12)	0.062	0.040	0.060	-0.008	-0.012	0.008
C(13)	0.050	0.047	0.057	-0.014	-0.008	0.005
C(14)	0.057	0.060	0.061	-0.014	-0.016	0.005
O(1)	0.067	0.052	0.055	-0.027	0.003	-0.004
O(2)	0.073	0.049	0.080	-0.025	-0.027	0.013
O(3)	0.073	0.037	0.092	-0.002	-0.027	-0.000
N(1)	0.045	0.044	0.053	-0.014	-0.011	0.005
N(2)	0.048	0.033	0.089	-0.005	-0.026	0.007
C(15)	0.15(4)	0.13(3)	0.30(5)	-0.06(2)	-0.07(3)	0.132(3)
O(15)	0.12(1)	0.06(1)	0.13(1)	-0.05(1)	-0.05(1)	0.06(1)
O(11)	0.18(2)	0.34(3)	0.04(1)	0.14(2)	0.05(1)	0.05
O(13)	0.24(1)	0.18(1)	0.13(1)	0.06(1)	0.02(1)	0.10(1)
O(16)	0.21(3)	0.56(9)	0.40(5)	-0.18(5)	-0.04(3)	0.26(6)
O(17)	0.16(1)	0.22(1)	0.25(1)	0.07(1)	-0.05(1)	0.11(1)
O(22)	0.29(6)	0.15(4)	0.42(7)	-0.18(5)	-0.28(6)	0.17(5)
O(23)	0.19(2)	0.12(2)	0.18(2)	-0.10(2)	0.05(2)	-0.08(2)
Cl(1)	0.077(1)	0.063(1)	0.071(1)	0.004(1)	-0.002(1)	0.024(1)
Average E.S.Ds for the Eraldin Cation						
O	0.003	0.003	0.003	0.002	0.003	0.002
N	0.003	0.003	0.004	0.002	0.003	0.003
C	0.005	0.004	0.005	0.004	0.004	0.004

TABLE 2.2.4.

Intramolecular Bonded Distances and E.S.Ds (in Å)

ATOM A	ATOM B	Å
C(1)	C(3)	1.493(12)
C(2)	C(3)	1.523(13)
C(3)	N(1)	1.515(8)
N(1)	C(4)	1.472(8)
C(4)	C(5)	1.525(9)
C(5)	C(6)	1.504(10)
C(5)	O(2)	1.425(8)
C(6)	O(1)	1.432(8)
O(1)	C(7)	1.376(8)
C(7)	C(8)	1.349(10)
C(7)	C(12)	1.407(9)
C(8)	C(9)	1.393(12)
C(9)	C(10)	1.390(9)
C(10)	C(11)	1.368(9)
C(11)	C(12)	1.392(9)
C(10)	N(2)	1.419(8)
N(2)	C(13)	1.359(9)
C(13)	O(3)	1.223(8)
C(13)	C(14)	1.479(10)
C(15)	O(15)	1.643(37)
Cl	O(11)	1.35(2)
Cl	O(13)	1.30(1)
Cl	O(16)	1.22(4)
Cl	O(17)	1.31(1)
Cl	O(22)	1.51(6)
Cl	O(23)	1.45(2)

TABLE 2.2.5.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	
C(1)	C(3)	C(2)	111.8(7)
C(1)	C(3)	N(1)	110.7(6)
C(2)	C(3)	N(1)	108.0(6)
C(3)	N(1)	C(4)	114.1(5)
N(1)	C(4)	C(5)	110.9(5)
C(4)	C(5)	C(6)	108.8(5)
O(2)	C(5)	C(4)	109.9(5)
O(2)	C(5)	C(6)	111.8(5)
C(5)	C(6)	O(1)	106.3(5)
C(6)	O(1)	C(7)	115.9(5)
O(1)	C(7)	C(8)	126.0(6)
O(1)	C(7)	C(12)	114.1(6)
C(12)	C(7)	C(8)	119.9(7)
C(7)	C(8)	C(9)	121.2(7)
C(8)	C(9)	C(10)	119.4(7)
C(9)	C(10)	C(11)	119.6(6)
C(10)	C(11)	C(12)	121.0(6)
C(11)	C(12)	C(7)	118.9(6)
C(9)	C(10)	N(2)	116.3(6)
C(11)	C(10)	N(2)	124.1(5)
C(10)	N(2)	C(13)	127.5(5)
O(3)	C(13)	C(14)	122.4(6)
N(2)	C(13)	C(14)	115.8(6)
N(2)	C(13)	O(3)	121.9(6)

TABLE 2.2.6.

Selected Torsion Angles (°) and E.S.Ds for Compound V

C(1)	C(3)	N(1)	C(4)	-75.5(7)
C(2)	C(3)	N(1)	C(4)	161.9(6)
C(3)	N(1)	C(4)	C(5)	174.1(5)
N(1)	C(4)	C(5)	C(6)	177.4(5)
N(1)	C(4)	C(5)	O(2)	54.7(7)
C(4)	C(5)	C(6)	O(1)	166.5(5)
O(2)	C(5)	C(6)	O(1)	-71.9(6)
C(5)	C(6)	O(1)	C(7)	-176.7(5)
O(1)	C(7)	C(8)	C(9)	-179.2(7)
O(1)	C(7)	C(12)	C(11)	178.8(6)
C(6)	O(1)	C(7)	C(8)	-22.2(10)
C(6)	O(1)	C(7)	C(12)	159.9(6)
N(2)	C(10)	C(11)	C(12)	179.3(6)
C(9)	C(10)	N(2)	C(13)	158.9(7)
C(11)	C(10)	N(2)	C(13)	-22.0(10)
C(14)	C(13)	N(2)	C(10)	-179.7(6)
O(3)	C(13)	N(2)	C(10)	2.1(10)

TABLE 2.2.7.

Selected least-squares planes in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations:-

Plane 1 $-0.5396X' - 0.2959Y' + 0.7882Z' = -1.1671$

Plane 2 $-0.6071X' + 0.0513Y' + 0.7930Z' = -1.6990$

(b) Deviations (Å) of atoms from the planes (starred atoms define the plane)

Plane 1: N(2)* 003(6), O(3)* 0.003(5), C(13)* -0.009(7), C(14)* 0.003(7), C(10) -0.011(6), C(7) -0.124(7), O(1) -0.112(5)

Plane 2:

C(1)	-3.428(10)	C(11)*	0.008(7)
C(2)	-1.502(11)	C(12)*	0.000(7)
C(3)	-1.986(7)	C(13)	-0.414(7)
C(4)	-1.179(7)	C(14)	-0.319(7)
C(5)	-0.405(7)	O(1)	0.012(5)
C(6)*	-0.438(7)	O(2)	0.928(4)
C(7)*	-0.008(7)	O(3)	-0.794(5)
C(8)*	0.007(9)	N(1)	-1.125(5)
C(9)*	0.001(9)	N(2)	-0.016(6)
C(10)*	-0.009(6)		

(c) Dihedral angle between planes 1 and 2 is 20.4°

TABLE 2.2.8.

(a) Intramolecular Non-bonding Distances < 3.6

ATOM A	ATOM B		Å
C(1)	C(4)		3.13
C(6)	C(8)		2.84
C(10)	O(3)		2.87
C(11)	C(13)		3.04
C(11)	O(3)		2.86
O(1)	O(2)		2.90
N(1)	O(2)		2.82

(b) Interionic non-bonding distances < 3.8Å

C(5)	O(15)		3.57
O(2)	O(15)		2.61
O(15)	O(23)		2.82
O(2)	O(23)		3.75
C(2)	O(13)		3.37
C(3)	O(13)		3.77
O(2)	O(13)		3.56
N(1)	O(13)		2.94
C(1)	O(22)	I	3.28
C(4)	O(16)	I	3.65
C(4)	O(11)	I	3.32
C(6)	O(16)	I	3.69
C(6)	O(11)	I	3.68
C(9)	O(17)	II	3.45
C(10)	O(17)	II	3.69
C(14)	O(23)	II	3.74
C(14)	O(17)	II	3.78
N(2)	O(17)	II	2.96
C(10)	C(13)	III	3.71
C(10)	N(2)	III	3.59
C(11)	C(13)	III	3.78
C(11)	C(14)	III	3.73
C(11)	N(2)	III	3.53
C(12)	C(14)	III	3.63
N(2)	N(2)	III	3.66

where the position of atom B is given by,

I = x, y, z-1
II = x-1, y, z-1
III = 1-x, -y, 1-z

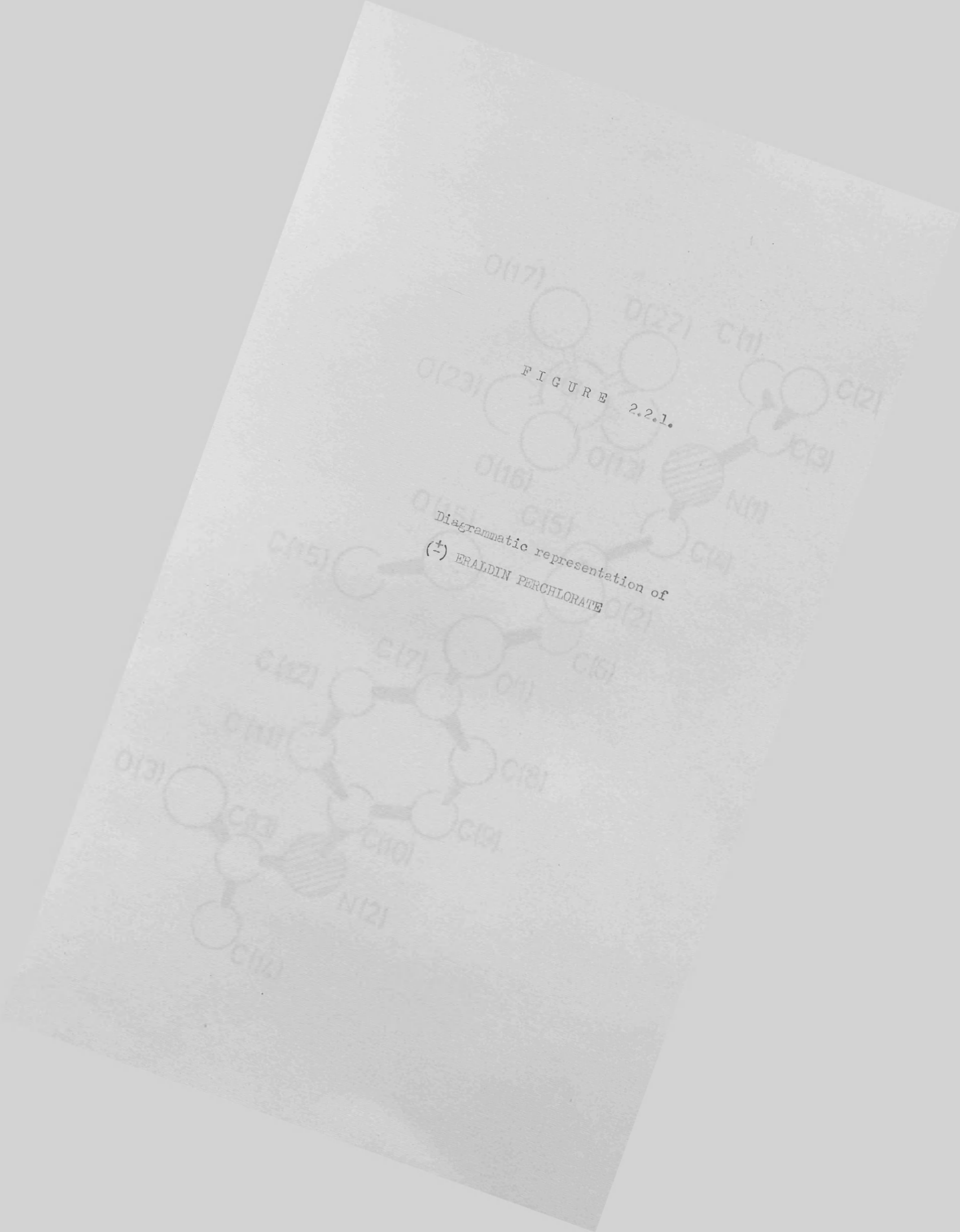
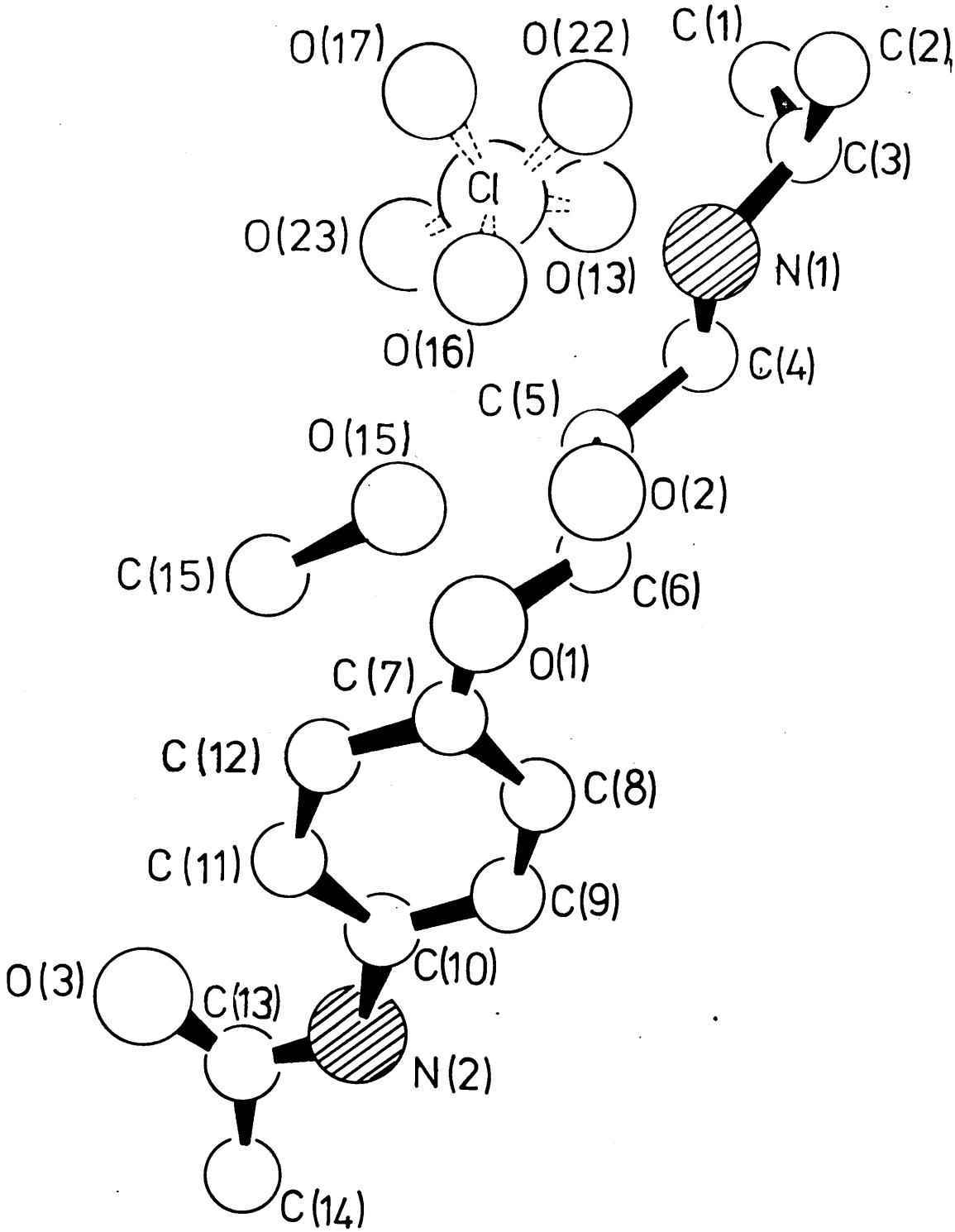


FIGURE 2.2.1.

Diagrammatic representation of
(±) ERALDIN PERCHLORATE


O(17)
O(22)
C(1)
C(2)
Cl
C(3)
O(23)
O(13)
N(1)
O(16)
C(4)
C(5)
O(15)
O(2)
C(15)
C(6)
O(1)
C(7)
C(12)
C(8)
C(11)
C(9)
C(10)
O(3)
C(13)
N(2)
C(14)

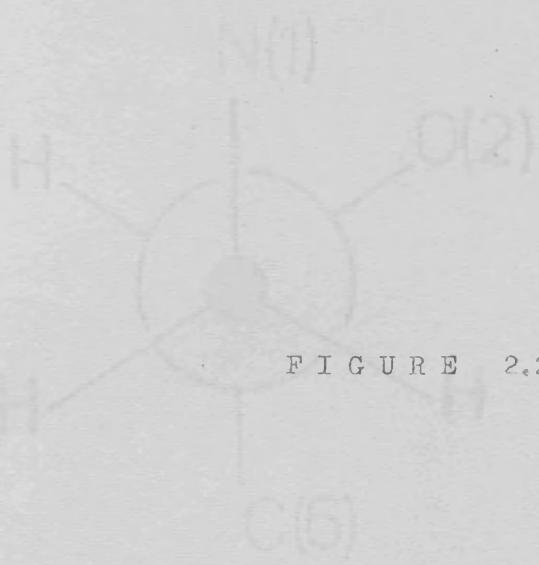
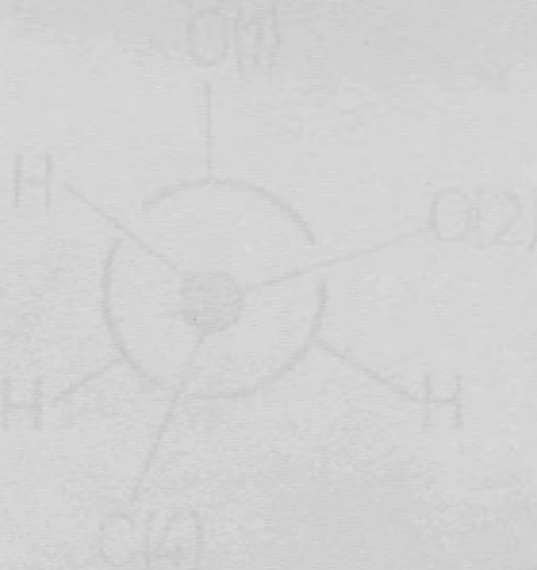


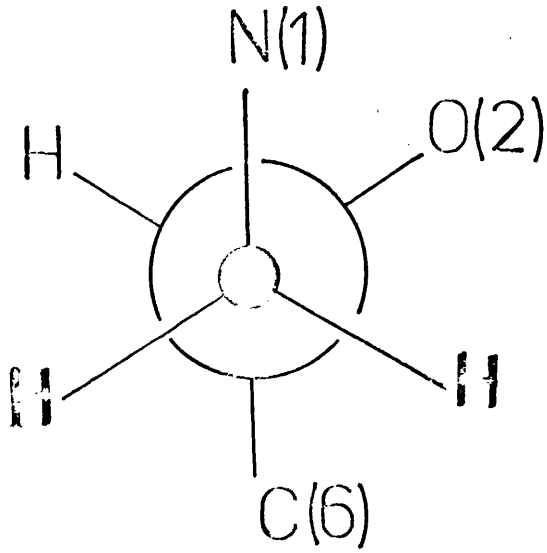
FIGURE 2.2.2.

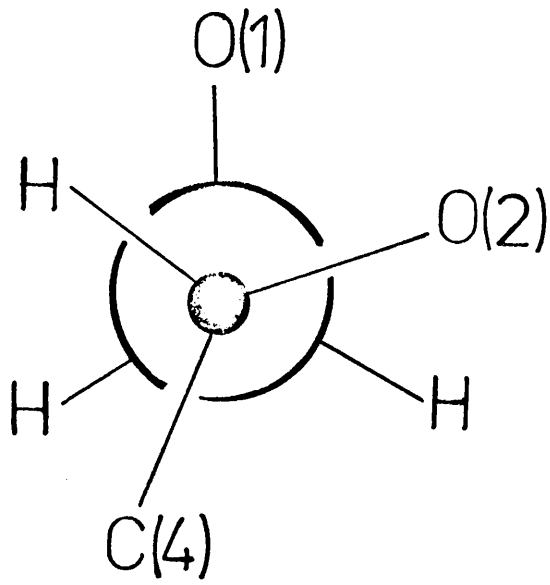
(±) ERALDIN PERCHLORATE

Conformations about bonds

C(4) - C(5) and C(5) - C(6)



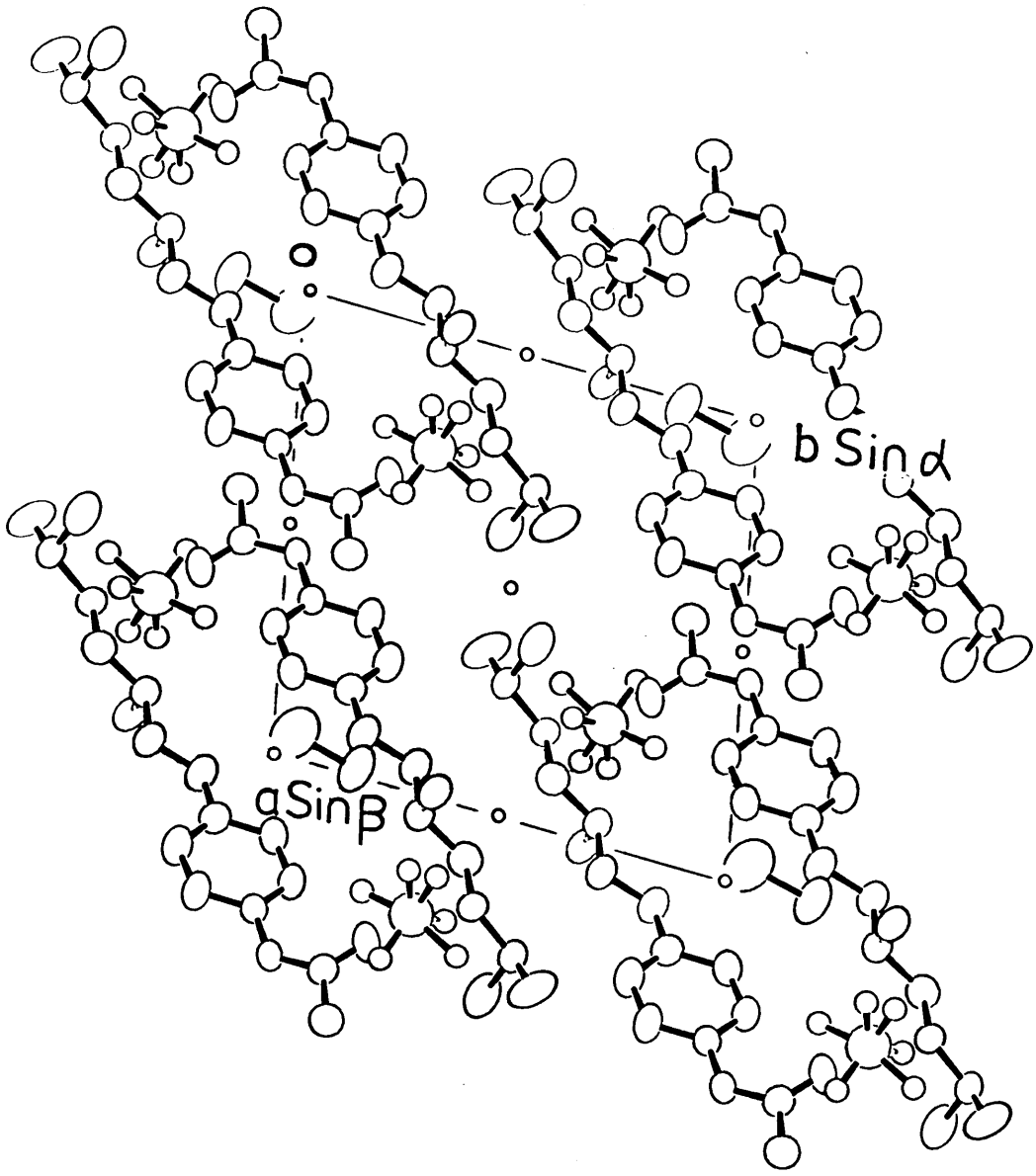

N(1)
O(2)
H
H
H
C(6)


O(1)
H
O(2)
H
H
C(4)

F I G U R E 2.2.3.

Crystal-packing arrangements for

(±) ERALDIN PERCHLORATE


b Sin α
a Sin β

S E C T I O N 2.3.

THE CRYSTAL AND MOLECULAR STRUCTURE OF

(±) VIVALAN OXALATE [(±)2-(2-Ethoxyphenoxymethyl) morpholine Oxalate]

EXPERIMENTAL

(±) VIVALAN OXALATE

(±) 2-(2-Ethoxyphenoxymethyl)morpholine Oxalate

CRYSTAL DATA

$C_{15}H_{20}NO_7$; M=326.3; Monoclinic, a=11.583Å, b=5.896Å, c=22.447Å, β=112.497°; U=1416.32Å^3; D_c=1.54 g.cm.$^{-3}$; D_m=1.55 g.cm.$^{-1}$; Z=4; F_{000}=600; Space group $P2_1/c$; μ=1.31 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs taken with Cu-Kα (λ=1.5418Å) radiation, and from precession photographs taken with Mo-Kα (λ=0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_1/c$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, exposing a small crystal (0.3 x 0.4 x 0.2 mm.) rotating about b, to graphite-monochromated Mo radiation (Mo-Kα_1) and by using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 54°$) to collect 1363 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The structure was determined by centrosymmetric Direct-Methods

using computer programs, DATRDN, NORMSF, SINGEN, TANGEN, Fc and FOURR, from the X-ray '72 suite of programs.

Phase determination was initiated by assigning phases to five reflections, three of which adequately defined the unit-cell origin and were given phases of 360^{o}, and two of which were chosen on the basis of their ability to form a large number of $\sum_2$ phase relationships. Since the phases of the latter two reflections were unknown, they were given all possible combinations of the phases ± 60 and 180^{o} to initiate a series of calculations utilising the Tangent formula of Direct Methods, the correct starting set proving to be that shown in Table 2.3.1., from which the phases of 165 reflections with $E \geq 1.4$ were assigned.

An E-map based on these 165 reflections revealed the positions of all non-hydrogen atoms in the cationic moiety, subsequent structure-factor and electron-density calculations revealing the complete structure. Each non-hydrogen atom was assigned an arbitrary temperature factor, $U_{iso} = 0.05 \text{Å}^2$ and after each round of calculations the data were placed on an approximate absolute scale by equating $k \sum |Fo|$ and $\sum |Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational and scale parameters by full-matrix least-squares calculations converged after 10 cycles, when R was 0.046 and R' was 0.003. Details of the refinement are given in Table 2.3.2.

Hydrogen-atom positions were selected from an electron-density difference synthesis and were included in all subsequent structure-

factor calculations, a temperature factor U_{iso}=0.03Å^2 having been arbitrarily assigned. No refinement of hydrogen-atom positional or vibrational parameters was carried out.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure-factors. The scheme was of the form;

If A $|Fo| > |Fc|$, W=10^{-9},

otherwise W=X.Y,

with X=1 if $\sin\theta > B$, else X= $\frac{\sin\theta}{B}$

and Y=1 if $|Fo| < C$, else Y= $\frac{C}{|F_o|}$

The most suitable values for A, B and C were found to be 0.75, 0.50 and 20.0 respectively.

At the conclusion of refinement, a difference synthesis and electron-density distribution revealed no errors in the structure. In all structure-factor calculations, the atomic scattering factors used were those given in reference (35). Observed and calculated structure-factors are listed in Appendix 4, and positional and vibrational parameters, with estimated standard deviations are given in Table 2.3.3. Values of e.s.d.s. are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

(±) VIVALAN OXALATE

DISCUSSION

A diagrammatic representation of this compound is given in Figure 2.3.1., hydrogen atoms being omitted, for clarity, but for the purposes of discussion, numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, least-squares planes, intra-ionic non-bonding distances and inter-ionic distances are given in Tables 2.3.4. to 2.3.8.

In the Vivalan moiety, the quaternary nitrogen atom N(1) bears the cationic charge, while delocalisation of the anionic charge on the oxalate ion is demonstrated by bond lengths O(4) - C(15) [1.248(4) Å] and O(5) - C(15) [1.237(4)Å].

The morpholine ring adopts a chair conformation in which atoms C(2), C(3), C(4) and C(5) are coplanar, within experimental error, with atoms O(2) and N(1) respectively -0.655 and 0.662Å distant from this plane. In the present compound, torsion angle N(1)C(4)C(5)O(2) [-57.6(4)°] is determined by the chair conformation of the morpholine ring, in contrast to the corresponding angles in compounds III, IV and V, which may be influenced by possible electrostatic interactions and hydrogen-bond effects.

The equatorial orientation of the 2-ethoxy phenoxy substituent is demonstrated by torsion angles N(1)C(4)C(5)C(6) [-176.6(3)°] and C(2)O(2)C(5)C(6) [178.8(3)°], while the staggered conformation of the substituents about bond C(5) - C(6) is shown by torsion angles C(4)C(5)C(6)O(1) [166.4(3)°] and O(2)C(5)C(6)O(1) [73.9(3)°] (see Figure 2.3.2.), whose deviations from ideal values may arise from

steric interactions, e.g. O(2)···O(1) [2.90Å].

The approximate planarity of the 2-ethoxyphenoxymethyl substituent is shown by the perpendicular distances of atoms O(1) [-0.057Å], C(6) [-0.213Å], O(3) [-0.020Å], C(13) [-0.005Å] and C(14) [-0.012Å from the least-squares plane through the phenyl ring atoms, the maximum deviation of a ring atom from this plane being 0.015Å. This arrangement of atoms results in several interatomic non-bonded distances shorter than the sum of the appropriate Van der Waal's radii e.g. C(8)···C(6) [2.79Å], C(11)···C(13) [2.82Å] and O(3)···O(1) [2.61Å] and possible steric interactions between such pairs of atoms may contribute to deformations of the external bond angles of the phenyl ring e.g. O(1)C(7)C(12) [115.6(3)°] O(1)C(7)C(8) [124.6(4)°], C(7)C(12)O(3) [116.7(3)°] and C(11) C(12)O(3) [124.8(4)°] and may also contribute to the slight deviations of the phenyl-ring atoms from planarity.

The oxalate ion is sited on a crystallographic centre of inversion and has dimensions typical of reported literature values[24-30].

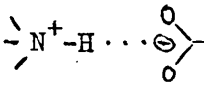
The crystal packing is dominated by hydrogen bonding of the type  , with each Vivalan cation capable of associating with two oxalate anions, and each anion capable of accepting a hydrogen bond from four cations. The direction of the possible hydrogen bonding is along the crystallographic b axis, the possible dimensions being; N(1)···O(4) [2.72Å], H(1N)···O(4) [1.74Å], angle N(1) H(1N) O(4) [162.2°], N(1)···O(5) [2.70Å], H(2N)···O(5) [1.65Å] and angle N(1)H(2N)O(5) [157.7°]. Figures 2.3.3. and 2.3.4. illustrate these crystal packing arrangements.

TABLE 2.3.1.

h	k	l	E	Phi	
6	3	-17	3.40	360°	Origin Defining Reflections
-5	3	-7	3.30	360°	
1	1	-4	3.16	360°	
4	2	-9	2.47	180°	Variable Reflections
1	1	-2	2.22	180°	

TABLE 2.3.2.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} of C N O atoms; scale factor; unit weights.	1 - 3	0.126	0.015
x, y, z, U_{iso} of C N O atoms; H-atoms in calculation but not refined; scale factor; unit weights.	4 - 5	0.111	0.011
x, y, z, U_{ij}(i, j = 1, 2, 3) of C N O atoms; H-atoms in calculation but not refined; scale factor, unit weights.	6 - 8	0.046	0.002
x, y, z, U_{ij}(i, j = 1, 2, 3) of C N O atoms; H-atoms in calculation but not refined; scale factor; weighting scheme adjusted.	9 - 10	0.046	0.003

TABLE 2.3.3.

(a) Atomic Fractional Coordinates and E.S.Ds of Compound VI

ATOM	x/a	y/b	z/c
C(2)	0.4564(3)	0.3477(7)	0.7006(2)
C(3)	0.4151(3)	0.5026(6)	0.6424(2)
C(4)	0.6238(3)	0.4625(6)	0.6411(2)
C(5)	0.6589(3)	0.3079(6)	0.7001(1)
C(6)	0.7946(4)	0.3375(8)	0.7405(2)
C(7)	0.9525(3)	0.1690(8)	0.8318(2)
C(8)	1.0398(4)	0.3316(8)	0.8320(2)
C(9)	1.1583(4)	0.3398(10)	0.8819(2)
C(10)	1.1892(4)	0.1795(10)	0.9300(2)
C(11)	1.1047(4)	0.0117(9)	0.9292(2)
C(12)	0.9851(4)	0.0043(8)	0.8808(2)
C(13)	0.9275(4)	-0.3214(9)	0.9271(2)
C(14)	0.8178(4)	-0.4727(9)	0.9137(2)
O(1)	0.8327(2)	0.1554(5)	0.7866(1)
O(2)	0.5879(2)	0.3683(4)	0.7375(1)
O(3)	0.8947(2)	-0.1518(6)	0.8773(1)
N(1)	0.4880(3)	0.4467(5)	0.6023(1)
C(15)	0.4775(3)	0.9207(5)	0.5211(1)
O(1)	0.4775(3)	0.9971(4)	0.5729(1)
O(5)	0.4454(3)	0.7260(4)	0.5010(1)

TABLE 2.3.3. (Cont.)

(b) Hydrogen-atom Fractional Coordinates

ATOM	x/a	y/b	z/c
H(2)	0.4445	0.1771	0.6911
H(2')	0.4088	0.4042	0.7275
H(3)	0.4427	0.6763	0.6614
H(3')	0.3175	0.5000	0.6121
H(4)	0.6527	0.6344	0 6598
H(4')	0.6638	0.3969	0.6171
H(5)	0.6416	0.1310	0.6805
H(6)	0.8395	0.3230	0.7100
H(6')	0.8051	0.5000	0.7567
H(8)	1.0000	0.4539	0.7928
H(9)	1.2490	0.3889	0.8862
H(10)	1.2853	0.1374	0.9689
H(11)	1.1303	-0.1243	0.9571
H(13)	1.0000	-0.4439	0.9286
H(13')	0.9353	-0.2333	0.9701
H(14)	0.7526	-0.4367	0.9230
H(14')	0.7875	-0.5556	0.8729
H(14'')	0.8215	-0.6136	0.9346
H(1N)	0.4494	0.5647	0.5619
H(2N)	0.4676	0.2871	0.5846

TABLE 2.3.3. (Cont.)

(c) Anisotropic Temperature Factors ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	0.050	0.046	0.038	0.001	0.021	0.006
C(3)	0.053	0.042	0.036	0.005	0.021	0.002
C(4)	0.052	0.047	0.035	-0.003	0.019	0.000
C(5)	0.048	0.046	0.032	0.001	0.014	0.001
C(6)	0.051	0.058	0.049	-0.001	0.014	0.007
C(7)	0.044	0.066	0.047	0.009	0.013	-0.004
C(8)	0.053	0.068	0.063	0.004	0.019	-0.000
C(9)	0.043	0.091	0.075	0.007	0.021	-0.011
C(10)	0.043	0.098	0.063	-.010	0.019	-0.015
C(11)	0.053	0.085	0.049	0.020	0.018	0.004
C(12)	0.048	0.068	0.044	0.012	0.017	0.000
C(13)	0.057	0.075	0.046	0.021	0.016	0.012
C(14)	0.067	0.075	0.062	0.010	0.025	0.018
O(1)	0.051	0.066	0.052	0.002	0.007	0.010
O(2)	0.050	0.052	0.027	-0.002	0.014	0.001
O(3)	0.053	0.076	0.049	0.010	0.012	0.015
N(1)	0.050	0.032	0.028	-0.003	0.014	0.002
C(15)	0.046	0.030	0.029	0.007	0.013	0.002
O(4)	0.099	0.037	0.046	-0.012	0.044	-0.007
O(5)	0.103	0.031	0.040	0.008	0.034	0.001
Average E.S.Ds						
O	0.002	0.002	0.001	0.001	0.001	0.001
N	0.002	0.001	0.001	0.001	0.001	0.001
C	0.002	0.003	0.002	0.002	0.002	0.002

TABLE 2.3.4.

Intramolecular Bonded Distances and E.S.Ds (in Å)

ATOM A	Atom B	Å
C(2)	C(3)	1.514(5)
C(2)	O(2)	1.429(4)
C(3)	N(1)	1.485(5)
C(4)	C(5)	1.529(5)
C(4)	N(1)	1.476(5)
C(5)	C(6)	1.489(5)
C(5)	O(2)	1.424(4)
C(6)	O(1)	1.438(5)
C(7)	C(8)	1.389(6)
C(7)	C(12)	1.406(6)
C(7)	O(1)	1.369(4)
C(8)	C(9)	1.398(6)
C(9)	C(10)	1.375(7)
C(10)	C(11)	1.384(7)
C(11)	C(12)	1.392(5)
C(12)	O(3)	1.371(5)
C(13)	C(14)	1.482(6)
C(13)	O(3)	1.438(5)
C(15)	C(15)	1.556(5)
C(15)	O(4)	1.248(4)
C(15)	O(5)	1.237(4)

TABLE 2.3.5.

Valency Angles and E.S.Ds (in °)

ATOM A	ATOM B	ATOM C	
O(2)	C(2)	C(3)	111.3(3)
N(1)	C(3)	C(2)	109.0(3)
C(5)	O(2)	C(2)	111.1(2)
C(4)	N(1)	C(3)	110.4(3)
N(1)	C(4)	C(5)	110.1(3)
C(6)	C(5)	C(4)	109.0(3)
O(2)	C(5)	C(4)	109.9(3)
O(2)	C(5)	C(6)	108.6(3)
O(1)	C(6)	C(5)	108.1(3)
C(7)	O(1)	C(6)	115.7(3)
C(12)	C(7)	C(8)	119.8(3)
O(1)	C(7)	C(8)	124.6(4)
C(9)	C(8)	C(7)	120.8(4)
O(1)	C(7)	C(12)	115.6(3)
C(11)	C(12)	C(7)	118.5(4)
O(3)	C(12)	C(7)	116.7(3)
C(10)	C(9)	C(8)	119.0(4)
C(11)	C(10)	C(9)	120.8(4)
C(12)	C(11)	C(10)	121.0(4)
O(3)	C(12)	C(11)	124.8(4)
C(13)	O(3)	C(12)	117.0(3)
O(3)	C(13)	C(14)	108.1(3)
O(5)	C(15)	O(4)	124.6(3)

TABLE 2.3.6.

Selected Torsion Angles and E.S.Ds (in °)

O(2)	C(2)	C(3)	N(1)	57.8(4)
C(3)	C(2)	O(2)	C(5)	-60.7(3)
C(2)	C(3)	N(1)	C(4)	-55.9(4)
N(1)	C(4)	C(5)	C(6)	-176.6(3)
N(1)	C(4)	C(5)	O(2)	-57.6(4)
C(5)	C(4)	N(1)	C(3)	56.3(4)
C(4)	C(5)	C(6)	O(1)	-166.4(3)
O(2)	C(5)	C(6)	O(1)	73.9(3)
C(4)	C(5)	O(2)	C(2)	59.6(3)
C(6)	C(5)	O(2)	C(2)	178.8(3)
C(5)	C(6)	O(1)	C(7)	-174.0(3)
O(1)	C(7)	C(8)	C(9)	176.8(4)
C(8)	C(7)	C(12)	O(3)	-179.5(4)
O(1)	C(7)	C(12)	C(11)	-178.5(4)
O(1)	C(7)	C(12)	O(3)	0.9(5)
C(8)	C(7)	O(1)	C(6)	-6.0(5)
C(12)	C(7)	O(1)	C(6)	173.5(3)
C(10)	C(11)	C(12)	O(3)	-178.2(4)
C(7)	C(12)	O(3)	C(13)	179.7(3)
C(11)	C(12)	O(3)	C(13)	-0.9(6)
C(14)	C(13)	O(3)	C(12)	-179.4(3)

TABLE 2.3.7.

Selected least-squares planes, in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations:-

Plane 1 $0.59816X' - 0.59695Y' - 0.53465Z' = -7.5-624$

Plane 2 $-0.08340X' - 0.79485Y' - 0.60105Z' = -10.30079$

Plane 3 $0.59169X' - 0.59311Y' - 0.54600Z' = -7.75395$

(b) Deviations (Å) of atoms from the plane (starred atoms define the plane)

Plane 1

C(2)	-1.936(4)	C(10)*	-0.008(5)
C(3)	-1.822(3)	C(11)*	0.012(4)
C(4)	-0.219(4)	C(12)	-0.002(4)
C(5)	-0.390(3)	C(13)	-0.005(4)
C(6)*	-0.213(4)	C(14)	-0.012(5)
C(7)*	-0.012(4)	O(1)	-0.057(3)
C(8)*	0.015(4)	O(2)	-1.699(2)
C(9)*	-0.005(5)	O(3)	-0.020(3)
		N(1)	-0.471(3)

Plane 2: C(2)* 0.001(4), C(3)* -0.001(4), C(4)* 0.001(4), C(5)* -0.001(3), C(6) -0.745(4), N(1) 0.662(3), O(2) -0.655(2)

Plane 3: O(3)* -0.000(3), C(13)* 0.000(4), C(14)* 0.000(5) C(12) 0.014(4), O(1) -0.010(3)

(c) Dihedral angles between planes:-

(1) - (2) 41.8°, (1) - (3) 0.8°, (2) - (3) 41.4°

TABLE 2.3.8.

Intramolecular Non-bonding distances < 3.6Å

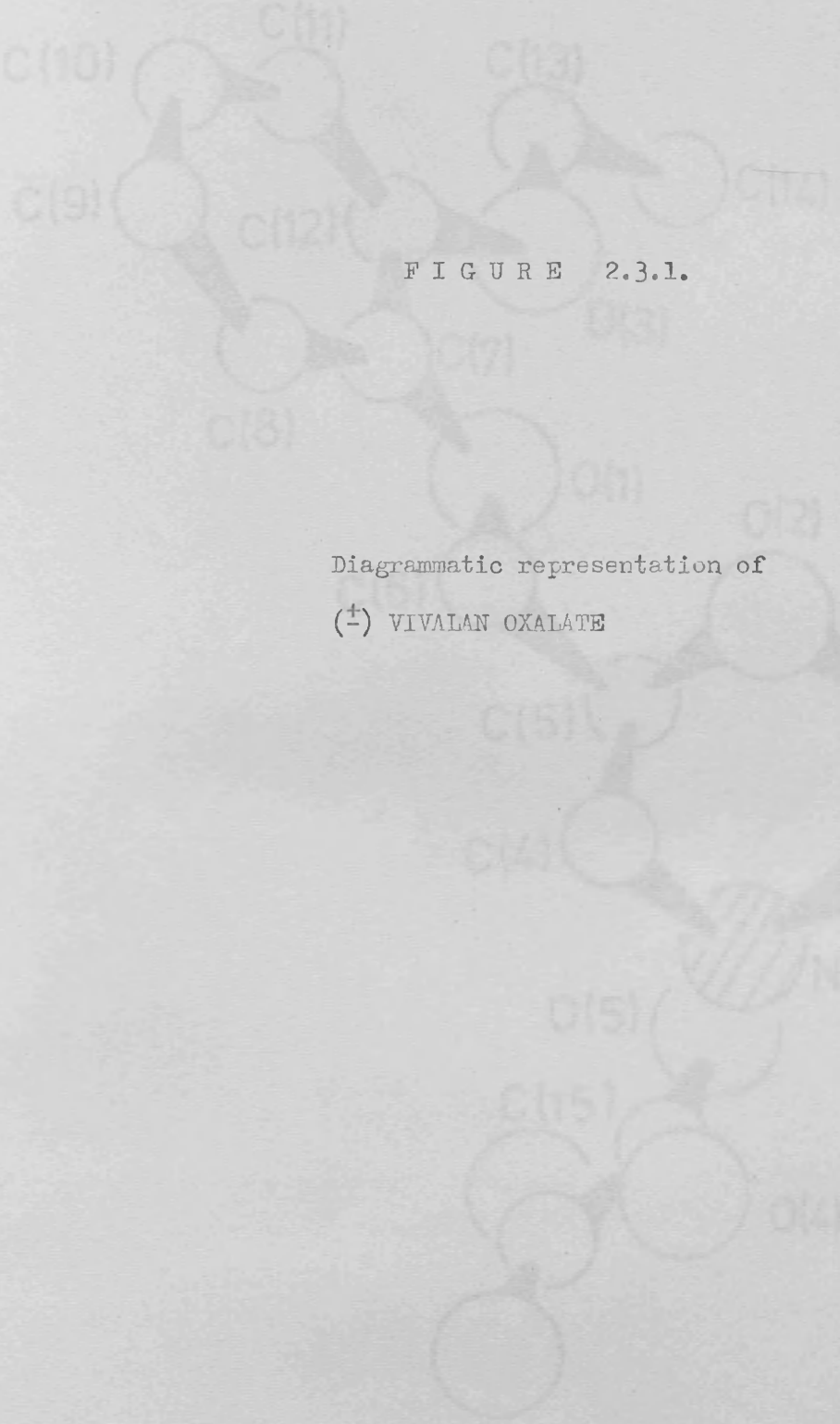
ATOM A	ATOM B		Å
C(8)	C(6)		2.79
C(11)	C(13)		2.82
O(1)	O(2)		2.90
O(1)	O(3)		2.61
O(2)	N(1)		2.84

Interionic Distances < 3.8Å

C(4)	C(15)		3.73
N(1)	C(15)		3.31
C(3)	O(4)		3.51
C(4)	O(4)		3.63
N(1)	O(4)		3.30
C(3)	O(5)		3.58
C(4)	O(5)		3.40
N(1)	O(5)		2.70
C(7)	C(13)	I	3.76
C(7)	C(14)	I	3.53
C(8)	C(13)	I	3.54
C(8)	O(3)	I	3.80
C(9)	C(13)	I	3.77
O(1)	C(14)	I	3.65
N(1)	C(15)	II	3.58
N(1)	O(4)	II	2.72
C(4)	O(5)	III	3.18
N(1)	C(15)	III	3.66
N(1)	O(5)	III	2.89
O(5)	O(5)	III	2.96
C(2)	C(2)	IV	3.59
C(2)	C(14)	IV	3.73
C(2)	O(2)	IV	3.49
C(2)	O(3)	IV	3.75
C(3)	C(14)	IV	3.75
C(3)	O(2)	IV	3.46
C(3)	O(3)	IV	3.55
O(4)	C(14)	V	3.54
C(10)	O(5)	VI	3.66

where the position of atom B is given by,

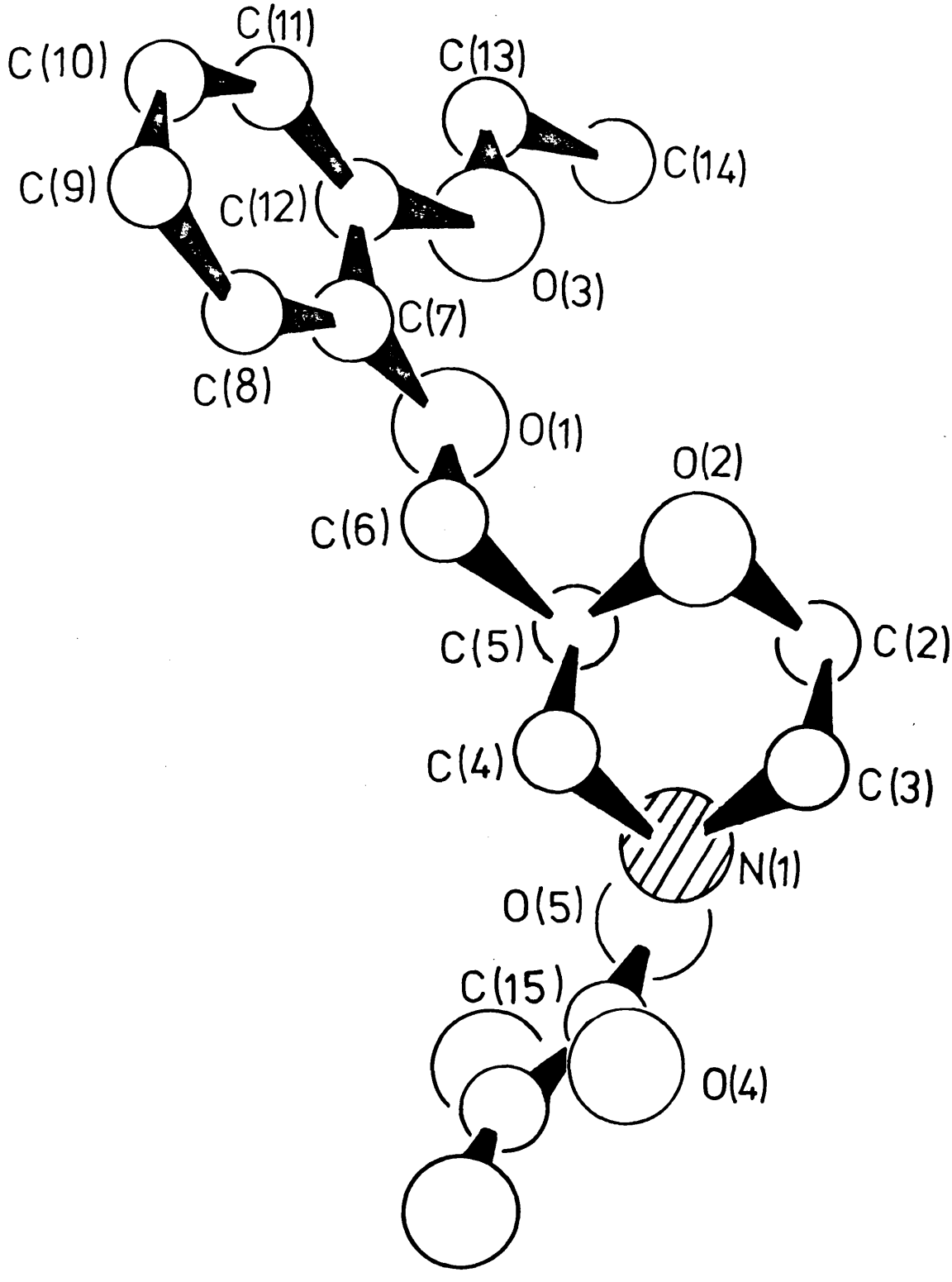
I	= x, 1+y, z	IV	= 1-x, $\frac{1}{2}$+y, ($\frac{1}{2}$-z)+1
II	= x, y-1, z	V	= 1-x, ($\frac{1}{2}$+y)+1, ($\frac{1}{2}$-z)+1
III	= 1-x, 1-y, 1-z	VI	= 1+x, $\frac{1}{2}$-y, $\frac{1}{2}$+z

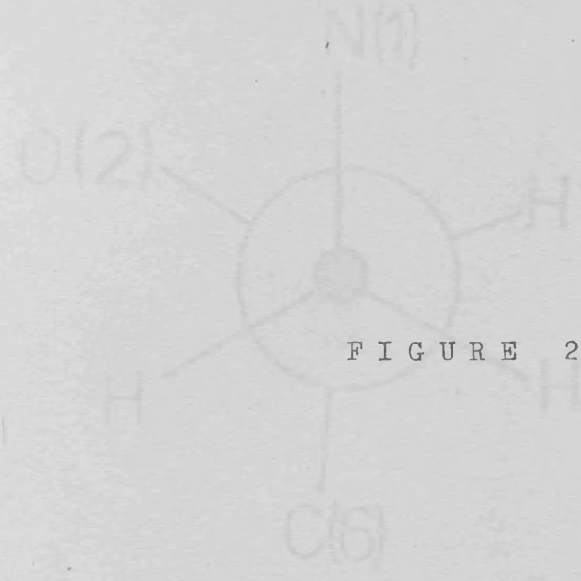


F I G U R E 2.3.1.

Diagrammatic representation of

(±) VIVALAN OXALATE


C(10)
C(11)
C(13)
C(14)
C(9)
C(12)
O(3)
C(7)
C(8)
O(1)
O(2)
C(6)
C(5)
C(2)
C(4)
C(3)
N(1)
O(5)
C(15)
O(4)

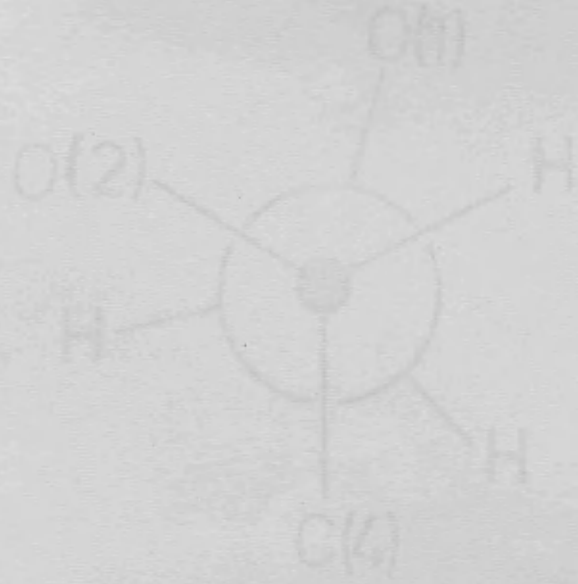


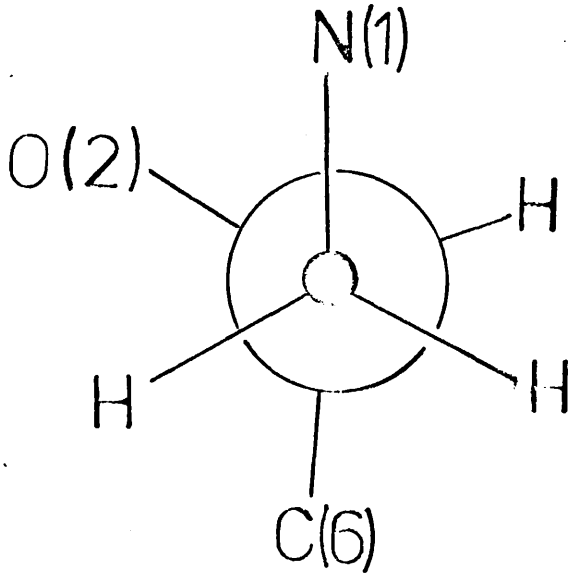
F I G U R E 2.3.2.

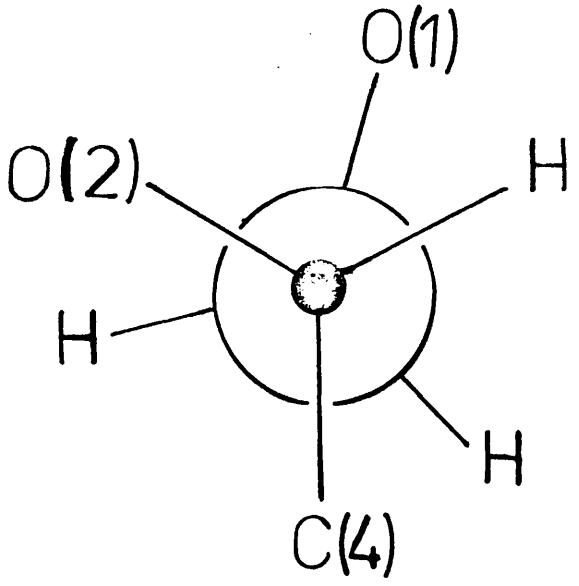
(±) VIVALAN OXALATE

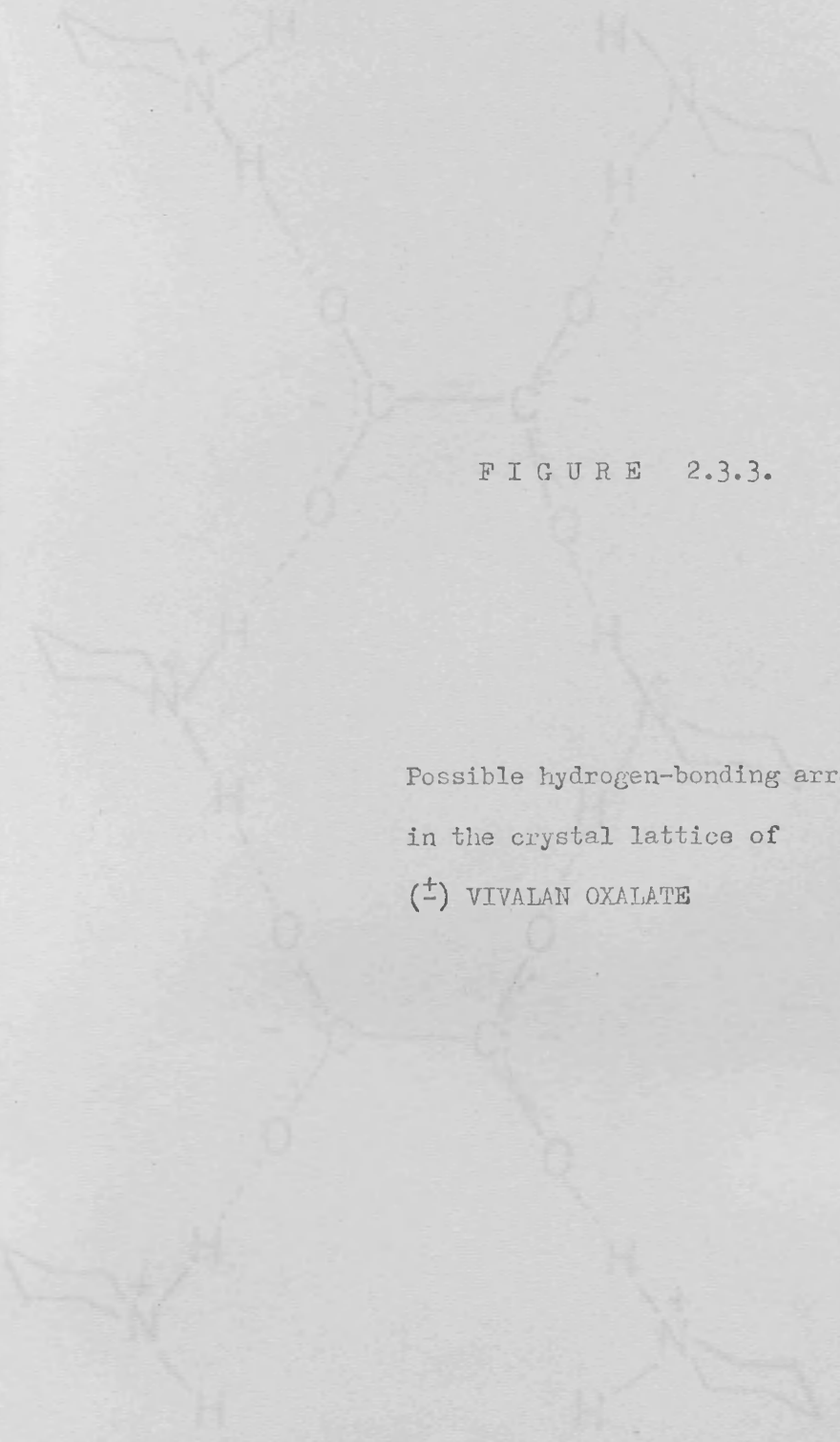
Conformations about bonds

C(4) - C(5) and C(5) - C(6)



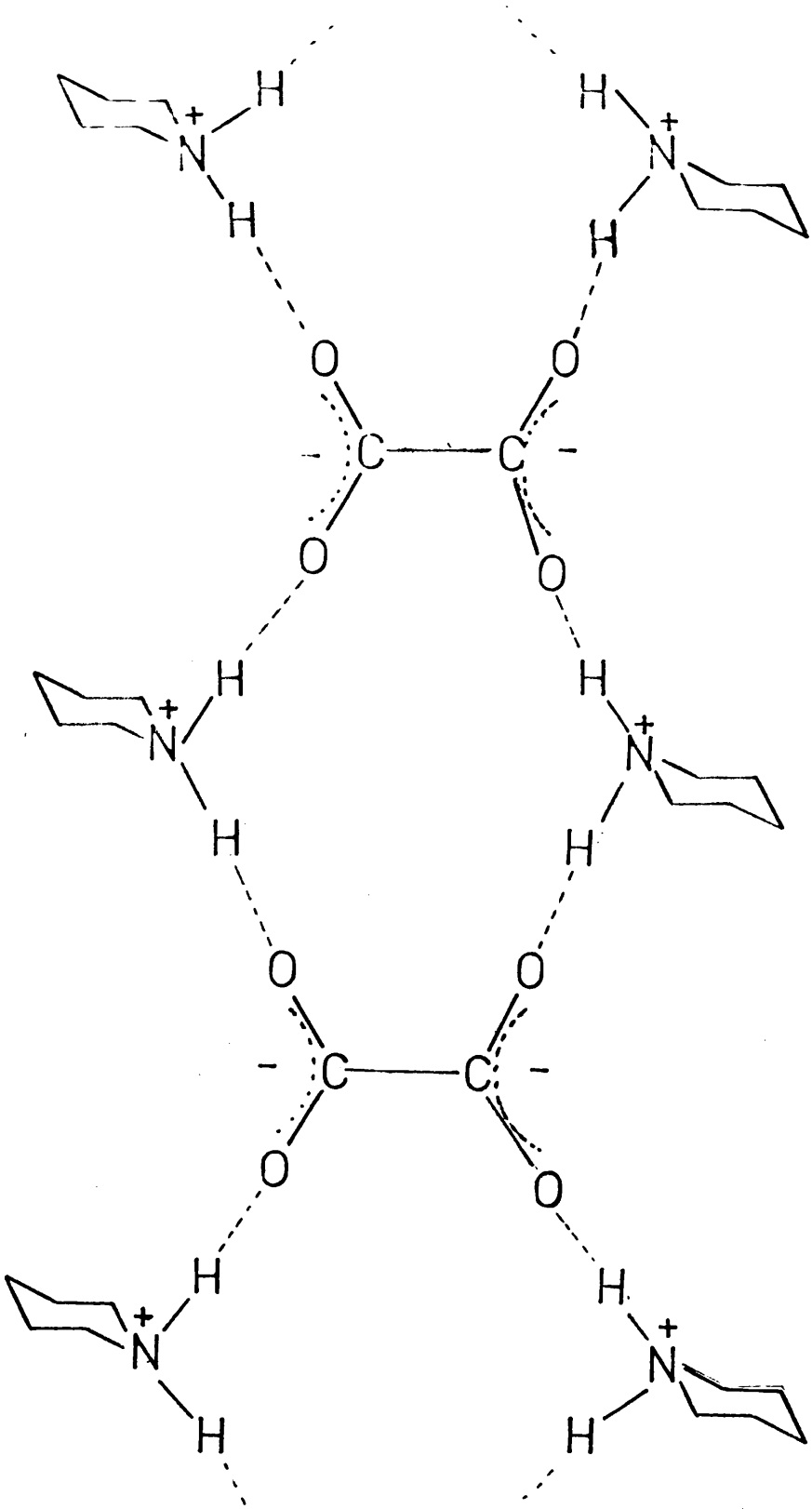

N(1)
O(2)
H
H
H
C(6)


O(1)
O(2)
H
H
H
C(4)



F I G U R E 2.3.3.

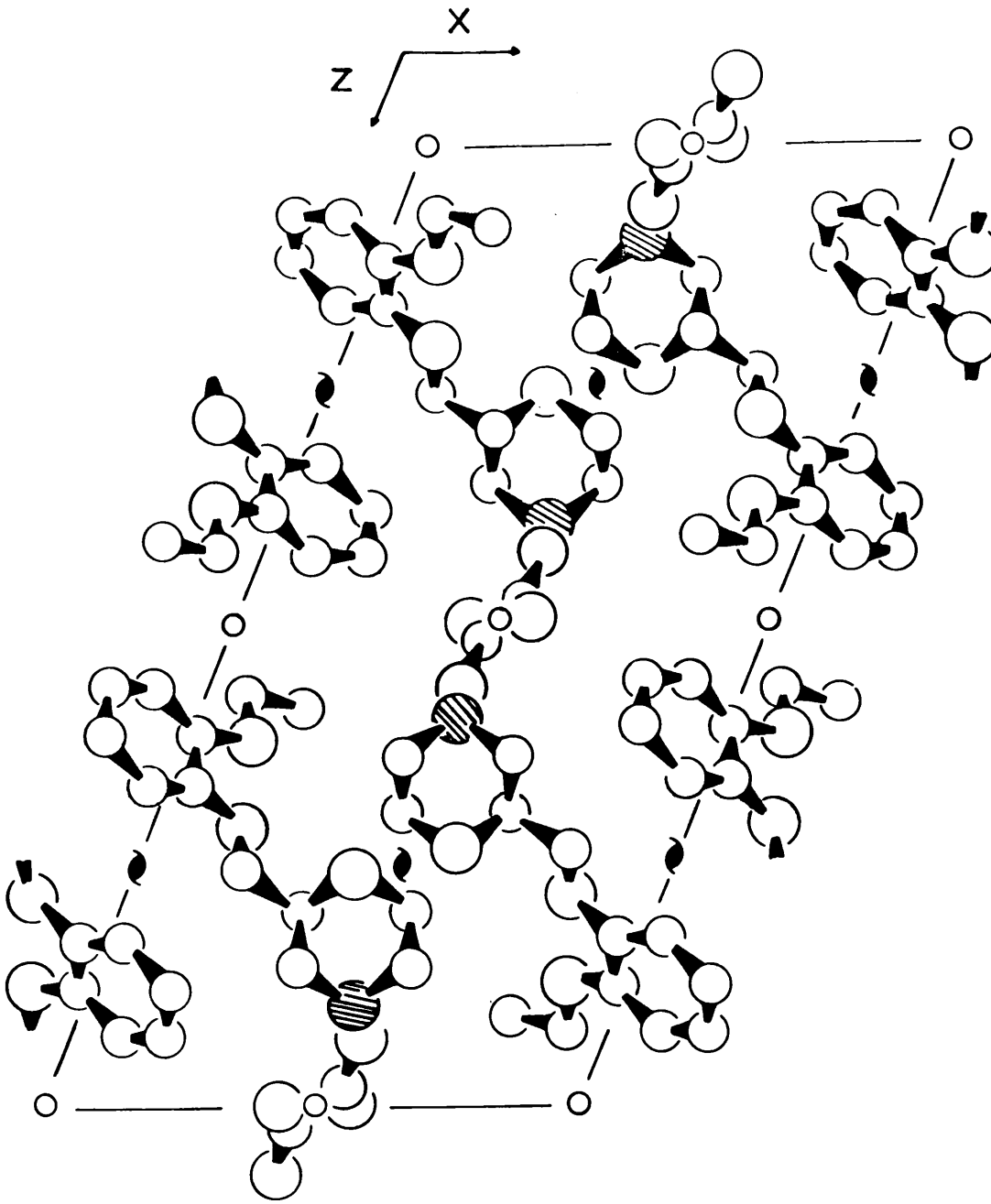
Possible hydrogen-bonding arrangements
in the crystal lattice of
(±) VIVALAN OXALATE



F I G U R E 2.3.4.

Crystal-packing arrangements for

(±) VIVALAN OXALATE


X
Z

S E C T I O N 2.4.

THE CRYSTAL AND MOLECULAR STRUCTURE OF (±) 2,6-DICHLORO DERIVATIVE [(±)1-(2,6-Dichlorophenoxy)-3-isopropylaminopropan-2-ol Hydrochloride]

EXPERIMENTAL

(±) 2,6-DICHLORO DERIVATIVE

(±) 1-(2,6-Dichlorophenoxy)-3-isopropylaminopropan-2-ol Hydrochloride

CRYSTAL DATA

$C_{12}H_{18}NO_2Cl_3$; M=314.6; Orthorhombic, a=10.288Å; b=5.141Å, c=28.421Å; U=1503.13Å^3; D_c=1.40 g.cm^{-3}, D_m=1.41 g.cm.$^{-3}$; Z=4; F_{000}=656; Space group $P2_12_12_1$; μ=6.04 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs, taken with Cu-Kα (λ=1.5418Å) radiation, and from precession photographs, taken with Mo-Kα (λ=0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_12_12_1$ was indicated by systematic absences, despite the racemic nature of the sample.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.2 x 0.4 x 3 mm.) rotating about b, to graphite-monochromated Mo-radiation (Mo-K) and using the θ,ω scan technique (in the range $0 < 2 \leqslant 60^\circ$) to collect 949 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made.

STRUCTURE DETERMINATION

The structure was determined by non-centrosymmetric Direct Methods

using the computer program, MULTAN, and appropriate programs contained in the X-ray '72 suite of programs.

Phase determination was initiated by assigning phases to those reflections shown in Table 2.4.1. and utilising them in a series of calculations, based on the weighted tangent formula of Direct Methods, from which phases were assigned to those 200 reflections with $E \geqslant 1.18$.

An E-map based on these 200 reflections revealed the positions of the three chlorine atoms and subsequent structure-factor and electron-density calculations revealed plausible atomic sites for all non-hydrogen atoms. An arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ was given to each atom and least-squares refinement was initiated.

After one cycle of full-matrix calculations, the isotropic temperature factor of the hydroxyl-oxygen atom increased to a value $U_{iso}=0.10\text{Å}^2$. To investigate this phenomenon contributions from this atom were omitted and an electron-density difference synthesis was calculated, which indicated that two sites with approximate equal electron-densities were stereochemically acceptable as the hydroxyl group. However, since each molecule contains only one hydroxyl group, it was concluded that each crystallographic-molecular site is statistically occupied by molecules of (+) and (-) absolute stereo-chemistry.

Since the sample is racemic, the (+) and (-) molecules were assumed to be equally numerous in the crystal and each site was correspondingly given a fixed population parameter (P.P.) of 0.50 with respect to the electron density of one oxygen atom. After each calculation, the

data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational and scale parameters converged after 10 cycles of full-matrix least-squares calculations, when R was 0.051 and R' was 0.003. Details of the refinement are given in Table 2.4.2.

Positions of the carbon and nitrogen-bonded hydrogen atoms were obtained by calculation, staggered conformations being assumed for all methyl groups, but the positions of the alternative hydroxyl-hydrogen atoms could not be calculated and were omitted. Contributions from the hydrogen atoms, with arbitrary temperature factors $U_{iso}=0.03\text{Å}^2$, were included in all structure-factor calculations but the values were not refined.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure factors. The scheme is of the form;

If A $|Fo| > |Fc|$, $W=10^{-9}$,

otherwise W=X.Y,

with X=1 if $\sin\theta > B$, else $X=\frac{\sin\theta}{B}$

and Y=1 if $|Fo| < C$, else $Y=\frac{C}{|Fo|}$

The most suitable values for A, B and C were found to be 0.75, 0.30 and 20.0 respectively.

At the conclusion of refinement, a difference synthesis and electron-density distribution revealed no errors in the structure. In all structure-factor calculations, the atomic scattering factors used

were those given in reference (35). Observed and calculated structure-factors are listed in Appendix 5. Positional and vibrational parameters with estimated standard deviations are given in Table 2.4.3. The values of the e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

2,6-DICHLORO DERIVATIVE

D I S C U S S I O N

A diagrammatic representation of this compound is given in Figure 2.4.1., hydrogen atoms being omitted, for clarity, but for the purposes of discussion, numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, intra-ionic non-bonding distances and inter-ionic distances are given in Tables 2.4.4. to 2.4.8.

The present compound exists as the hydrochloride salt in which the quaternary nitrogen atom bears the cationic charge. The phenyl ring is planar, within experimental error, with atoms Cl(2), Cl(3) and O(1) respectively 0.022, -0.012 and 0.034Å distant from the least-squares plane through the ring atoms. In the similar compounds, III - VI, atom C(6) is approximately coplanar with the aromatic system but in the present compound, steric interactions between atoms Cl(2), Cl(3) and C(6) [Cl(2)···C(6) 3.40Å and Cl(3)···C(6) 3.62Å] result in displacement of atom C(6) so that it is positioned -1.246Å distant from the least-squares plane through the phenyl-ring atoms.

The alkoxy chain is in a fully-extended conformation [torsion angles C(3)N(1)C(4)C(5) - 163.2(6)°, N(1)C(4)C(5)C(6) - 172.2(6), C(4) C(5)C(6)O(1) - 171.2(6)° and C(5)C(6)O(1)C(7) - 171.3(6)°] and since both (+) and (-) enantiomers occupy equivalent crystallographic sites, their respective conformations are identical except for those changes induced by differing configurations at the chiral centre. The atom positions O(21) and O(20) hence represent the hydroxyl-oxygen atoms

of the (+) and (-) isomers respectively and Figure 2.4.2. illustrates the alternative configurations and conformations about bonds C(4)-C(5) and C(5) - C(6). In both enantiomers, the quaternary nitrogen atom is gauche with respect to the hydroxyl group [torsion angles O(21)C(5)C(4)N(1) 84.9(8) and O(20)C(5)C(4)N(1) - 61.7(8)°] and, as in similar compounds (e.g. III, IV and V), interatomic non-bonding distances N(1)···O(21) [3.01Å] and N(1)···O(20)[2.85Å] suggest possible weak electrostatic interactions between these pairs of atoms, although hydrogen bonding of the type, $\geq N^{+}-H\cdots \overset{H}{O}-R$, is unlikely [H(1N)··· O(21) 2.64Å, H(1N)···O(20) 2.96Å, H(2N)···O(21) 3.68Å and H(2N)··· O(20) 2.55Å, where atom positions H(1N) and H(2N) were calculated, assuming tetrahedral geometry at atom N(1) .

Because of the aforementioned (see Experimental) packing disorder, no hydroxyl-hydrogen atoms could be located and hence no assessment of possible hydrogen-bond dimensions of the type, R-O-H···Cl^{-}, can be made. Inter-ionic distances, O(21)···Cl(1) [3.24 and 3.14Å] and O(20)···Cl(1) [3.18Å] however, suggest interactions between these pairs of atoms, while the dimensions N(1)H(1N)Cl(1) [172.2°], H(2N)···Cl(1) [2.14Å] and angle N(1)H(2N)Cl(1) [180.0°] indicate possible hydrogen bonding of the type $\geq N^{+}-H\cdots Cl^{-}$, between the cation and two chloride ions. This arrangement of crystal packing, in which both the (+) and (-) enantiomers equally occupy equivalent sites in a crystal of acentric space group, is uncommon and in the present compound, restricted rotation about bond O(1) - C(7) may be a factor contributing towards this phenomenon. Figure 2.4.3. illustrates the crystal-packing arrangements of this compound.

Distortions of torsion angles C(3)N(1)C(4)C(5) [-163.2(6)°] and

O(21)C(5)C(4)N(1) [84.9(8)°] from their respective ideal values, may be influenced by the aforementioned hydrogen-bonding arrangements, while the deviations of torsion angles O(21)C(5)C(6)O(1) [-70.0(8)°] and O(20)C(5)C(6)O(1) [77.2(8)°] from ideal staggered-conformation values, may be a result of steric interactions (e.g. O(21)···O(1) 2.79Å and O(20)···O(1) 2.92Å) and possible hydrogen-bond effects.

The apparently anomalous geometries of the bonds involving O(21) and O(20) e.g. C(5) - O(21) 1.633(14)Å and C(5) - O(20) 1.583(14)Å are probably a result of the disordering effects, peculiar to this compound, while the apparently short $C(sp^3)$ - $C(sp^3)$ bonds, C(5) - C(6) [1.488(11)Å], C(4) - C(5) [1.475(11)Å], C(1) - C(3) [1.512(12)Å] and C(2) - C(3) [1.496(11)Å], may be an effect of thermal librational motion of the cation[22], similar to that postulated in compounds III, IV and V. The remaining dimensions of the alkoxy chain are similar to those observed in compounds III, IV and V, while those dimensions of the phenyl ring which have not been discussed are typical of accepted literature values.

TABLE 2.4.1.

The phase values of the three origin-defining reflections were arbitrarily assigned within the limits of space-group-symmetry restrictions, but the phase of the 0 2 2 reflection was determined by application of the appropriate $\sum_1$ formula to all reflection data with $E \geqslant 1.18$. The criteria for using reflections 2 1 1 and 6 2 12 in the starting set of phases were their ability to form large numbers of $\sum_2$ phase relationships and their ability to satisfy the requirements of enantiomorph definition (the enantiomorph was defined by reflection 2 1 1). Since the values of phases a, and b were unknown they were given all possible combinations of the values $\pm \pi/4$ and $\pm 3\pi/4$, the correct values proving to be 315° and 45° respectively.

h	k	l	E	Phi	
2	0	13	1.95	90°	Origin Defining Reflections
5	0	5	1.94	90°	
2	1	0	1.67	360°	
0	2	2	2.21	180°	
2	1	1	2.96	(a)	
6	2	12	2.81	(b)	

TABLE 2.4.2.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} of all non-hydrogen atoms; scale factor; unit weights.	1 - 2	0.116	0.013
As in cycles 1 - 2 with contributions from calculated hydrogen-atom positions; no refinement of hydrogen-atom positions.	3 - 4	0.108	0.012
x, y, z, U_{ij} (i, j = 1, 2, 3) of all non-hydrogen atoms; contributions from hydrogen atoms but with no refinement; scale factor; unit weights.	5 - 6	0.052	0.003
As in cycles 5 - 6 with the weighting scheme adjusted.	7 - 8	0.051	0.003

TABLE 2.4.3.

(a) Atomic Fractional Coordinates and E.S.Ds of Compound VII (with Population Parameters)

ATOM	x/a	y/b	z/c	P.P.
C(1)	0.1647(8)	-0.0129(17)	-0.0889(3)	1.0
C(2)	0.3221(9)	0.2992(18)	-0.1238(3)	1.0
C(3)	0.2333(7)	0.2455(16)	-0.0832(2)	1.0
C(4)	0.2413(7)	0.2277(19)	0.0060(3)	1.0
C(5)	0.3197(8)	0.3071(16)	0.0471(3)	1.0
C(6)	0.2533(7)	0.2537(19)	0.0926(3)	1.0
C(7)	0.2902(8)	0.3126(17)	0.1743(3)	1.0
C(8)	0.3553(8)	0.1245(18)	0.2003(3)	1.0
C(9)	0.3197(10)	0.0668(20)	0.2456(3)	1.0
C(10)	0.2197(11)	0.1932(23)	0.2663(3)	1.0
C(11)	0.1526(10)	0.3838(20)	0.2422(3)	1.0
C(12)	0.1881(7)	0.4422(17)	0.1966(2)	1.0
O(1)	0.3285(5)	0.3744(11)	0.1296(2)	1.0
O(21)	0.2910(12)	0.6187(21)	0.0429(4)	0.5
O(20)	0.4369(10)	0.1076(24)	0.0478(3)	0.5
N(1)	0.3142(5)	0.2477(12)	-0.0385(2)	1.0
Cl(1)	0.0069(2)	0.2507(4)	0.4590(1)	1.0
Cl(2)	0.1052(2)	0.6824(5)	0.1663(1)	1.0
Cl(3)	0.4827(2)	-0.0405(6)	0.1732(1)	1.0

TABLE 2.4.3. (Cont.)

(b) Hydrogen-atom Fractional Coordinates and Population Parameters

ATOM	x/a	y/b	z/c	P.P.
H(1)	0.2330	-0.1579	-0.0924	1.0
H(1')	0.1069	-0.0525	-0.0631	1.0
H(1'')	0.1134	-0.0177	-0.1201	1.0
H(2)	0.3720	0.4681	-0.1209	1.0
H(2')	0.3948	0.1552	-0.1262	1.0
H(2'')	0.2755	0.2963	-0.1545	1.0
H(3)	0.1653	0.3871	-0.0810	1.0
H(1N)	0.3682	0.4106	-0.0372	1.0
H(2N)	0.3769	0.0937	-0.0394	1.0
H(4)	0.2055	0.0448	0.0113	1.0
H(4')	0.1597	0.3467	0.0046	1.0
H(5)	0.3543	0.4899	0.0462	0.5
H(5')	0.4171	0.2722	0.0499	0.5
H(6)	0.2455	0.0608	0.0997	1.0
H(6')	0.1622	0.3289	0.0935	1.0
H(9)	0.3667	-0.0640	0.2652	1.0
H(10)	0.1934	0.1404	0.3002	1.0
H(11)	0.0801	0.4852	0.2588	1.0

TABLE 2.4.3. (Cont.)

(c) Anisotropic Temperature Factors of Compound VII ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.058	0.047	0.086	0.001	-0.003	0.001
C(2)	0.073	0.058	0.050	-0.001	0.002	-0.012
C(3)	0.051	0.035	0.043	0.008	-0.006	-0.001
C(4)	0.043	0.053	0.041	-0.001	0.004	0.007
C(5)	0.062	0.053	0.052	-0.023	0.003	-0.010
C(6)	0.047	0.063	0.045	-0.012	0.008	0.003
C(7)	0.049	0.058	0.044	-0.016	-0.003	-0.000
C(8)	0.059	0.062	0.049	-0.007	-0.009	0.000
C(9)	0.074	0.075	0.061	-0.006	-0.025	0.010
C(10)	0.095	0.083	0.045	-0.008	0.003	0.011
C(11)	0.074	0.076	0.050	-0.011	0.015	-0.005
C(12)	0.049	0.060	0.049	-0.013	-0.005	0.003
O(1)	0.053	0.070	0.038	-0.019	0.001	-0.004
O(21)	0.085	0.044	0.068	0.007	0.017	0.001
O(20)	0.047	0.072	0.048	0.012	0.001	-0.007
N(1)	0.040	0.034	0.042	-0.005	0.008	-0.001
Cl(1)	0.047	0.041	0.117	-0.003	0.012	-0.021
Cl(2)	0.068	0.063	0.067	0.004	0.003	0.007
Cl(3)	0.073	0.096	0.109	0.024	0.008	0.007
Average E.S.ds						
Cl	0.001	0.001	0.002	0.001	0.001	0.001
O	0.006	0.006	0.005	0.005	0.005	0.005
N	0.003	0.003	0.003	0.003	0.003	0.003
C	0.005	0.005	0.005	0.005	0.004	0.004

TABLE 2.4.4.

Intramolecular Bonded Distances and E.S.Ds (in Å)

ATOM A	ATOM B	Å
C(1)	C(3)	1.512(12)
C(2)	C(3)	1.496(11)
C(3)	N(1)	1.520(9)
N(1)	C(4)	1.475(9)
C(4)	C(5)	1.475(11)
C(5)	C(6)	1.488(11)
C(5)	O(21)	1.633(14)
C(5)	O(20)	1.583(14)
C(6)	O(1)	1.446(9)
O(1)	C(7)	1.369(9)
C(7)	C(8)	1.389(12)
C(7)	C(12)	1.396(11)
C(8)	C(9)	1.368(12)
C(8)	Cl(3)	1.742(9)
C(9)	C(10)	1.352(15)
C(10)	C(11)	1.381(15)
C(11)	C(12)	1.377(11)
C(12)	Cl(2)	1.732(8)

TABLE 2.4.5.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	
C(1)	C(3)	C(2)	114(7)
C(1)	C(3)	N(1)	110.5(6)
C(2)	C(3)	N(1)	108.0(6)
C(3)	N(1)	C(4)	116.0(5)
N(1)	C(4)	C(5)	112.4(6)
C(4)	C(5)	C(6)	112.6(7)
C(4)	C(5)	O(21)	96.6(7)
C(4)	C(5)	O(20)	104.3(7)
O(21)	C(5)	C(6)	99.2(7)
O(20)	C(5)	C(6)	102.6(7)
C(5)	C(6)	O(1)	107.9(6)
C(6)	O(1)	C(7)	115.0(6)
O(1)	C(7)	C(8)	121.1(7)
O(1)	C(7)	C(12)	121.9(7)
C(8)	C(7)	C(12)	117.0(7)
C(7)	C(8)	C(9)	121.4(8)
C(7)	C(8)	Cl(3)	117.8(6)
Cl(3)	C(8)	C(9)	120.8(7)
C(8)	C(9)	C(10)	120.6(9)
C(9)	C(10)	C(11)	120.3(8)
C(10)	C(11)	C(12)	119.3(9)
C(11)	C(12)	Cl(2)	119.6(7)
Cl(2)	C(12)	C(7)	119.0(5)
C(11)	C(12)	C(7)	121.5(8)

TABLE 2.4.6.

Selected Torsion Angles and E.S.Ds for Compound VII

C(1)	C(3)	N(1)	C(4)	-64.6(8)
C(2)	C(3)	N(1)	C(4)	173.3(6)
N(1)	C(4)	C(5)	C(6)	-172.2(6)
N(1)	C(4)	C(5)	O(21)	84.9(8)
N(1)	C(4)	C(5)	O(20)	-61.7(8)
C(5)	C(4)	N(1)	C(3)	-163.2(6)
C(4)	C(5)	C(6)	O(1)	-171.2(6)
O(21)	C(5)	C(6)	O(1)	-70.0(8)
O(20)	C(5)	C(6)	O(1)	77.2(8)
C(5)	C(6)	O(1)	C(7)	-171.3(6)
O(1)	C(7)	C(8)	C(9)	178.2(8)
O(1)	C(7)	C(8)	Cl(3)	-2.8(11)
O(1)	C(7)	C(12)	C(11)	-178.1(8)
O(1)	C(7)	C(12)	Cl(2)	1.6(10)
C(8)	C(7)	O(1)	C(6)	99.5(9)
C(12)	C(7)	O(1)	C(6)	-83.3(9)

TABLE 2.4.7.

Least-squares plane for the phenyl ring, in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equation:-

$0.63677X' + 0.69222Y' + 0.33963Z' = 4.70104$

(b) Deviations (Å) of atom from the plane (starred atoms define the plane)

C(1)	-4.525(9)	C(11)*	0.002(10)
C(2)	-2.721(9)	C(12)*	0.003(8)
C(3)	-3.103(8)	O(1)	0.034(5)
C(4)	-2.252(8)	O(21)	-0.995(11)
C(5)	-1.060(8)	O(20)	-0.179(12)
C(6)*	-1.246(8)	N(1)	-2.133(6)
C(7)*	-0.005(8)	Cl(1)	0.667(2)
C(8)*	0.003(9)	Cl(2)	0.002(2)
C(9)*	0.002(10)	Cl(3)	-0.012(3)
C(10)*	-0.004(11)		

TABLE 2.4.8.

Intramolecular Non-bonding Distances < 3.6Å

ATOM A	ATOM B		Å
C(1)	C(4)		3.07
C(6)	C(8)		3.31
C(6)	Cl(2)		3.40
C(6)	Cl(3)		3.62
C(6)	C(12)		3.18
O(1)	O(20)		2.92
O(1)	O(21)		2.79
O(1)	Cl(2)		2.98
O(1)	Cl(3)		2.93
O(20)	N(1)		2.85
O(21)	N(1)		3.01

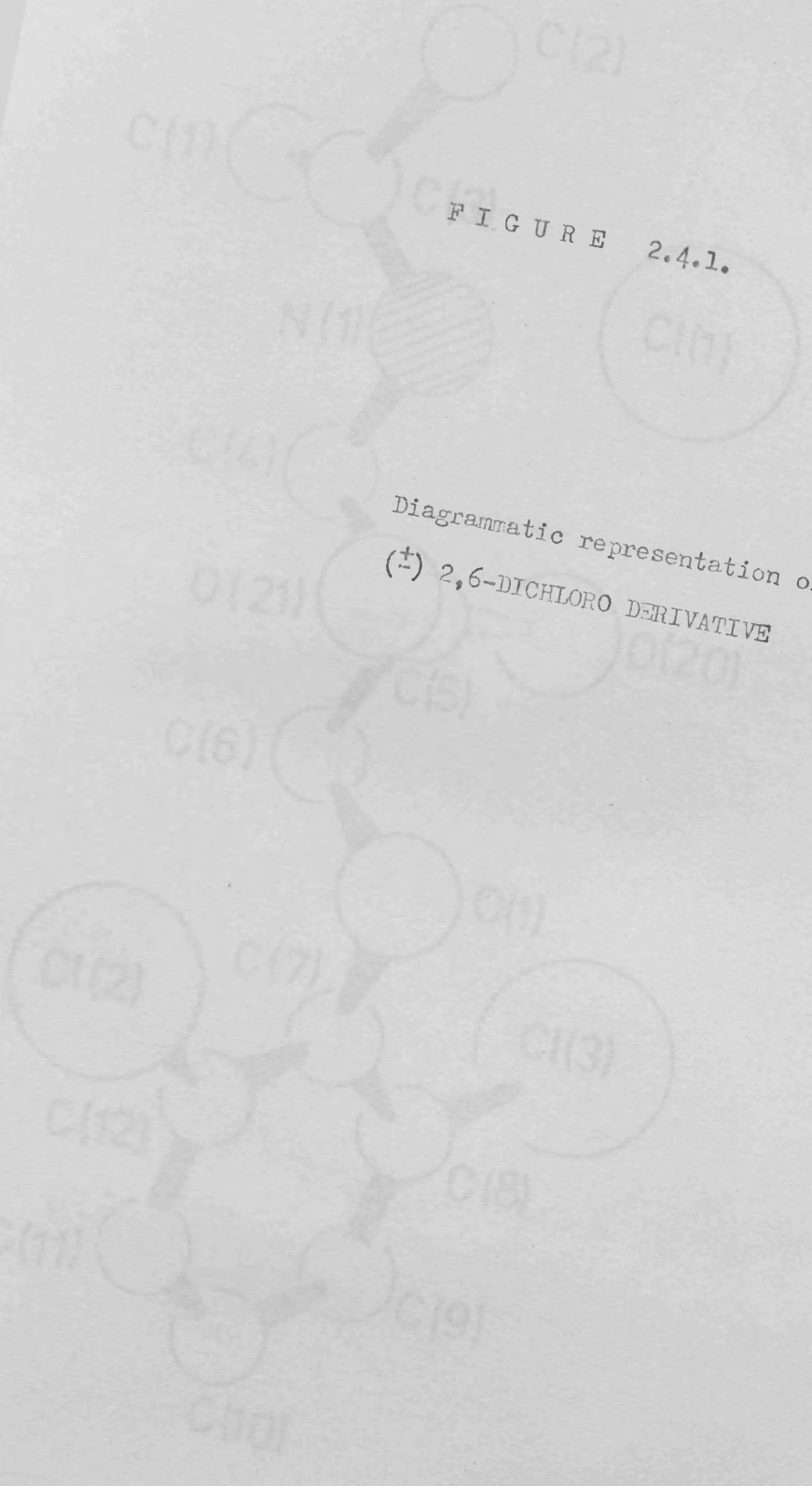
Interionic Distances < 3.8

N(1)	Cl(1)	I	3.16
O(20)	Cl(1)	I	3.18
O(21)	Cl(1)	II	3.24
N(1)	Cl(1)	II	3.17
C(12)	C(9)	III	3.75
O(1)	Cl(3)	III	3.62
O(21)	C(4)	III	3.34
O(21)	C(5)	III	3.55
O(21)	C(6)	III	3.58
O(21)	O(20)	III	2.93
Cl(2)	C(7)	III	3.76
Cl(2)	C(8)	III	3.57
Cl(2)	C(9)	III	3.72
O(1)	C(1)	IV	3.72
O(20)	C(1)	IV	3.35
O(20)	C(3)	IV	3.30
O(20)	C(4)	IV	3.59
O(21)	Cl(1)	V	3.14
Cl(2)	Cl(1)	V	3.76
C(4)	Cl(1)	VI	3.68
C(9)	Cl(3)	VII	3.68
C(10)	Cl(3)	VII	3.77

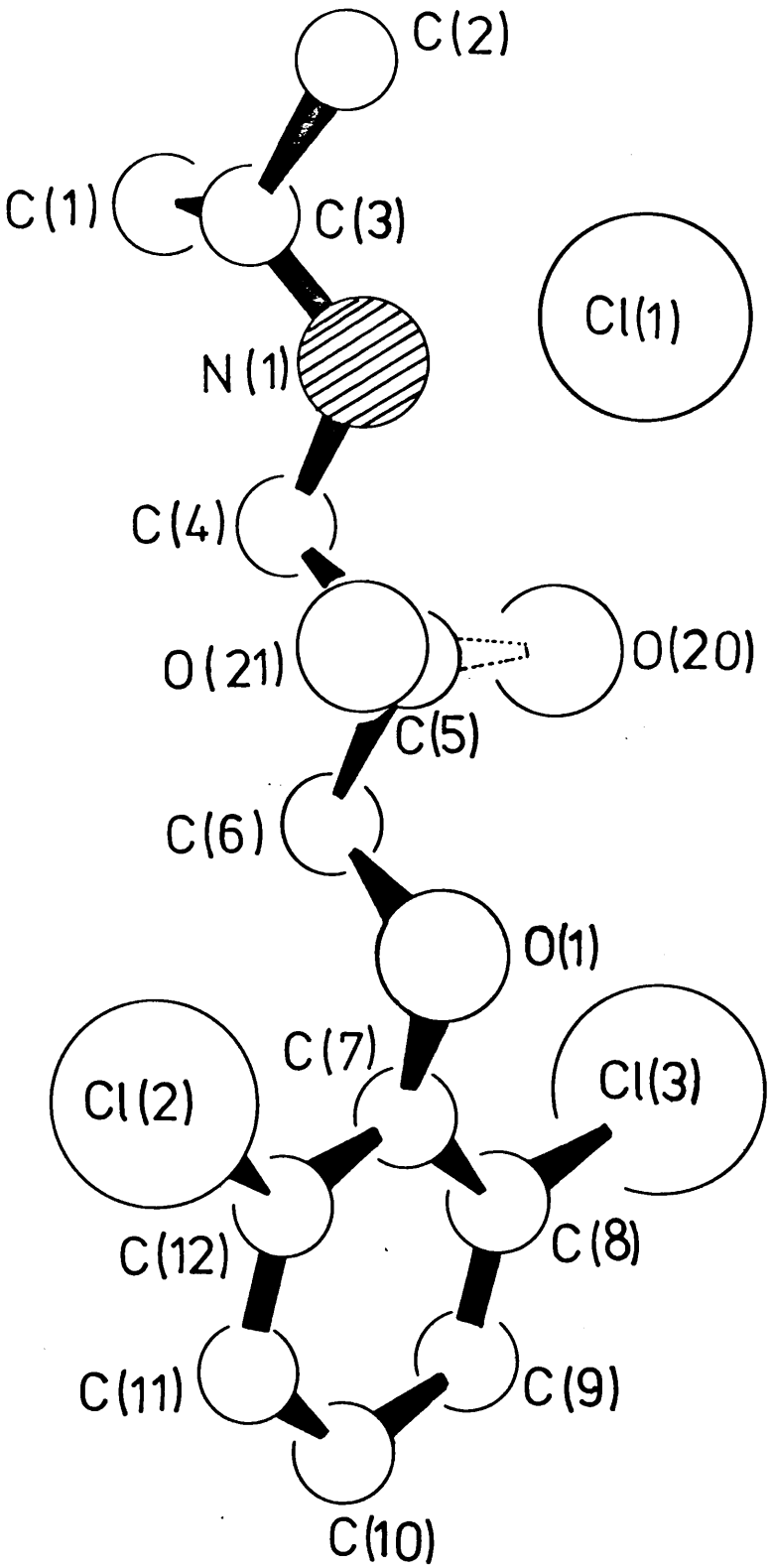
where the position of atom B is given by,

I	= $\frac{1}{2}$-x, -y, ($\frac{1}{2}$+z)-1	V	= -x, $\frac{1}{2}$+y, $\frac{1}{2}$-z
II	= $\frac{1}{2}$-x, 1-y, ($\frac{1}{2}$+z)-1	VI	= -x, ($\frac{1}{2}$+y)-1, $\frac{1}{2}$-z
III	= x, 1+y, z	VII	= 1-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z
IV	= $\frac{1}{2}$+x, $\frac{1}{2}$-y, -z		

FIGURE 2.4.1.



Diagrammatic representation of
(±) 2,6-DICHLORO DERIVATIVE


C(2)
C(1)
C(3)
Cl(1)
N(1)
C(4)
O(21)
O(20)
C(5)
C(6)
O(1)
C(7)
Cl(2)
Cl(3)
C(12)
C(8)
C(11)
C(9)
C(10)

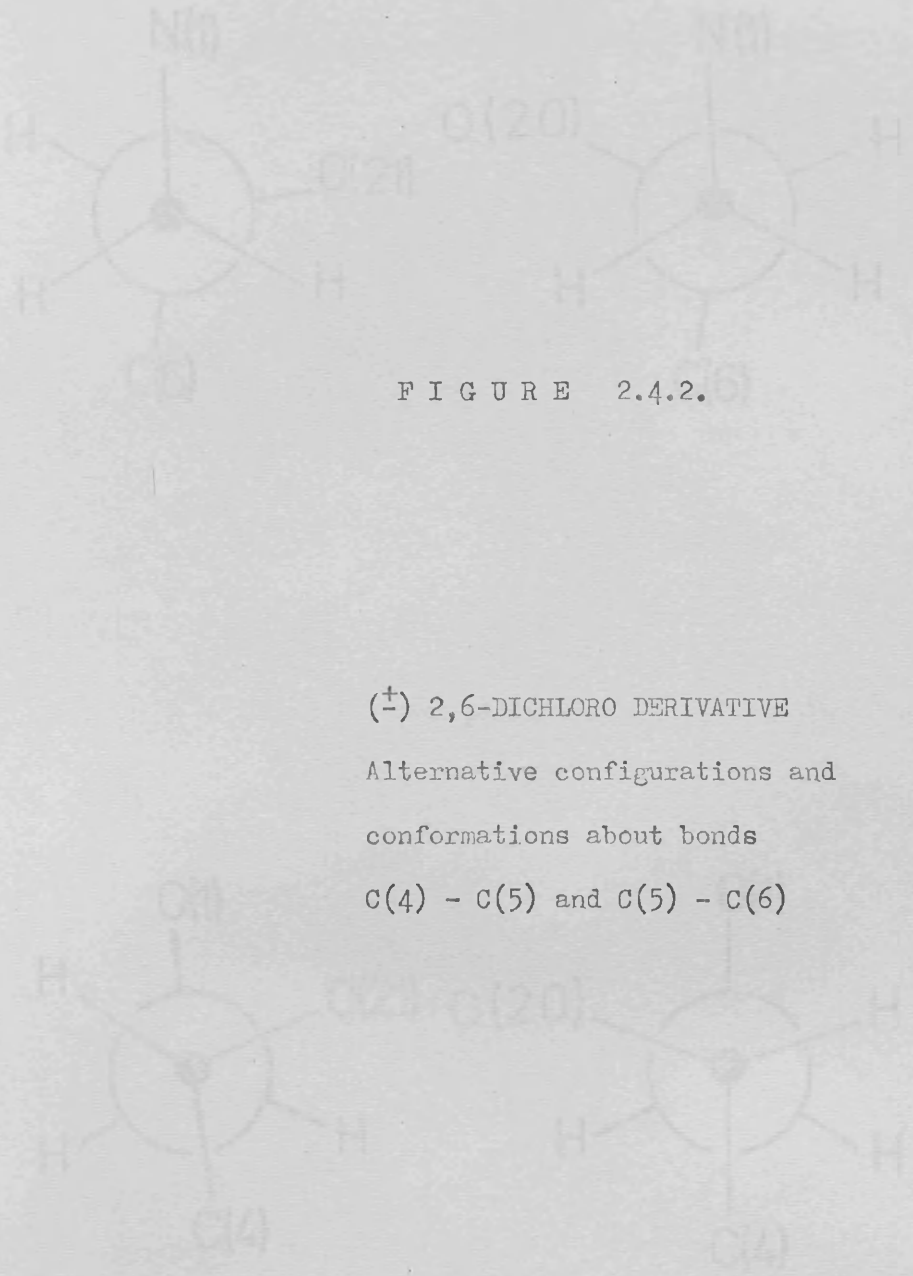
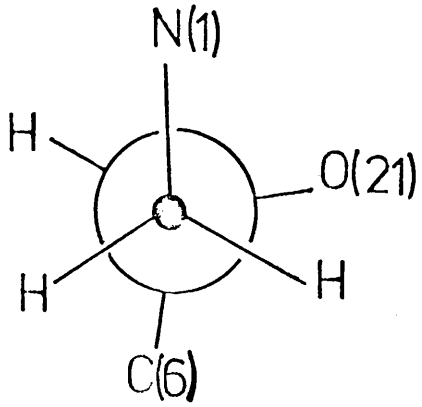
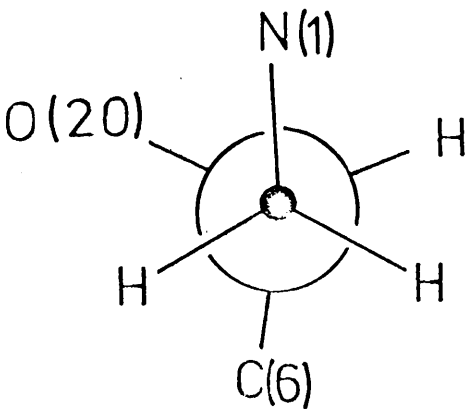


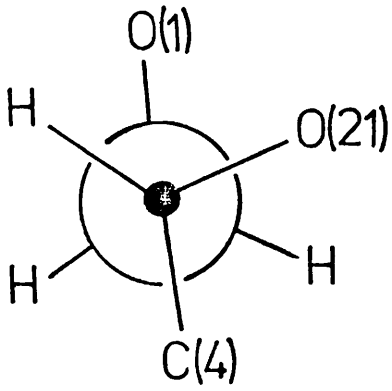
FIGURE 2.4.2.

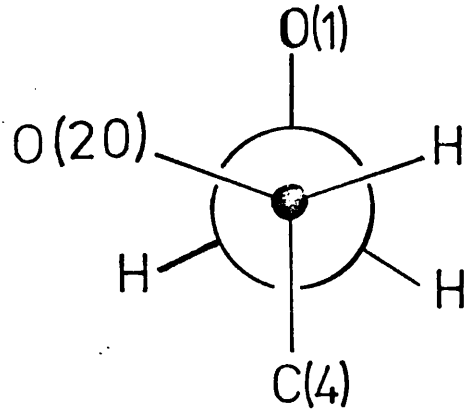
(±) 2,6-DICHLORO DERIVATIVE

Alternative configurations and conformations about bonds C(4) - C(5) and C(5) - C(6)


N(1)
H
O(21)
H
H
C(6)


N(1)
O(20)
H
H
H
C(6)

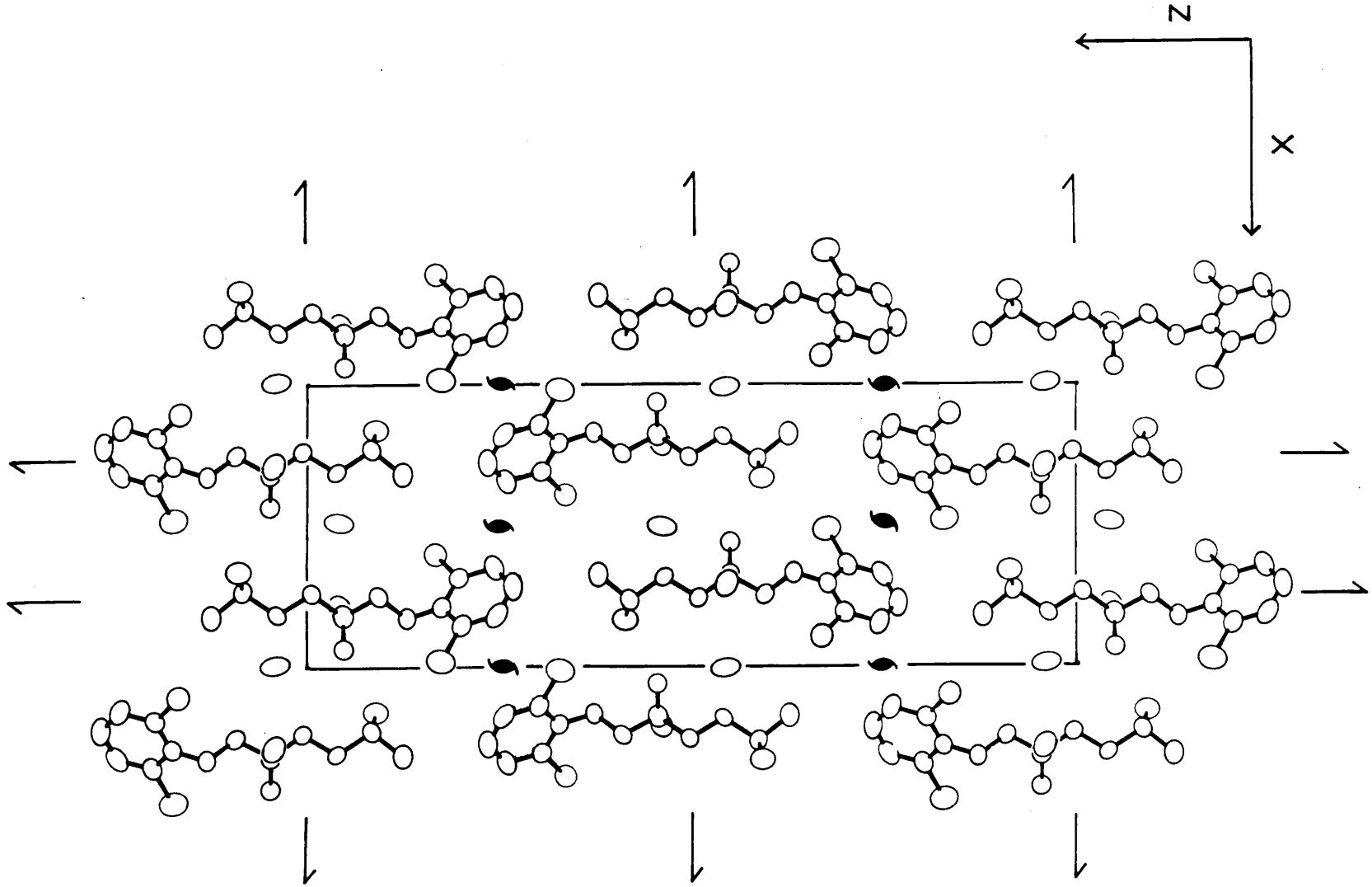

O(1)
H
O(21)
H
H
C(4)


O(1)
O(20)
H
H
H
C(4)

F I G U R E 2.4.3.

Crystal-packing arrangements for

(±) 2,6-DICHLORO DERIVATIVE


Z
X
1
1
1

SECTION 2.5.

RELATIVE CONFORMATIONS OF SOME BIOGENIC MONAMINES

OVERALL DISCUSSION

The crystal structure of the compound Alprenalol (VIII) has been reported[24] and in view of its partial-agonistic effects on the β-adrenergic nerves, a comparison between the conformations of this compound and of compounds III-VII is of interest. From examination of the torsion angles listed in Table 2.5.1., it is seen that, in all compounds (III-VIII), the methyl groups are staggered with respect to atom C(4) but that the conformations of the respective side chains differ considerably, with the sterically-favoured fully-extended conformation (torsion angles (f), (c), (g), and (j) close to 180°) being observed in only three compounds (III, V and VII). In compound VI, the deviation from a fully-extended conformation is determined by the conformation of the morpholine ring, but in compounds IV and VIII no such restriction exists and the conformations could be interpreted as possibly resulting from the crystal-packing arrangements.

A numbering scheme for each possible staggered conformation about bonds C(4) - C(5) and C(5) - C(6) is given in Figure 2.5.1. and the relative conformations about these bonds may be described by a two-numbered system e.g. the conformation of the (+) Inderal cation may be described as, $[3,6]$, with the conformation about bond C(4) - C(5) = 3 and the conformation about bond C(5) - C(6) = 6. Table 2.5.2. lists the appropriate conformations for compounds III - VIII and shows that, in the crystal structure, conformation $[3,6]$ is the most common, while conformations $[3,4]$ and $[3,5]$ are also observed.

As yet, little information about the conformations of compounds III - VIII, in solution, has become available but n.m.r. studies of several similar compounds have been carried out and the percentage population of each of the conformers 1 - 6 has been calculated[6]. Table 2.5.3. summarises the available information and shows that those compounds containing a quaternary nitrogen atom have a major conformation of [3,4] in solution, while the [3,6] conformation is also a significant contributor. Theoretical calculations have also been carried out[7] which suggest that for the β-propanolamine system, in isolated space, the major conformation is [3,6], with [3,5] as a minor contributor.

Although conformer [3] is the sterically most-favoured conformation, its dominance in both solid state and solution suggests that electrostatic interactions between the hydroxyl group and the quaternary nitrogen atom may also be important factors in maintaining this conformation. Further evidence supporting this suggestion derives from the predominance of this conformation in similar systems. Table 2.5.4. lists the relevant torsion-angle values and N(1)···O(H) interatomic distances for several of these compounds, showing that, in most cases, the atomic separation distance is less than the sum of the Van der Waal's covalent radii (2.90Å). The variations in the values of torsion angle N(1) C(4) C(5) O(H) [-47.8(4) to 84.9(8)°] and in the non-bonding interatomic distances N(1)···O(H) [2.64 to 3.07Å] however, suggest that strong interactions e.g. hydrogen bonding at a receptor site, might be sufficient to overcome these electrostatic influences and that the conformation required for activity could well differ from [3].

The presence of the [4], [5] and [6] conformers in the solid state, suggests that the energy barriers between these conformations are small enough to be overcome by the crystal-packing arrangements and similarly, the large contributions from both [4] and [5] conformers, in solution, suggest relatively free rotation about the C(5) - C(6) bond.

Diagrams illustrating the orientation of the aromatic system with respect to atoms O(1), C(5) and C(6) are given in Figure 2.5.2. and it is noted that in all compounds, with the exception of the biologically inactive compound VII, the aromatic system is approximately orientated along the direction of the O(1) - C(6) bond, while the aryloxy group is trans with respect to atom C(5) (the apparent deviation observed in the case of Eraldin (V) has previously been noted as a possible result of inter-ionic interactions). This approximately coplanar arrangement of the aromatic ring atoms O(1), C(5) and C(6) is best demonstrated by Figure 2.5.3. which shows the orientations of the 2-hydroxy 3-isopropylaminopropoxy chain relative to the aromatic systems and permits comparisons of compound VII with compounds III - VI. In compounds III - VI, atoms O(1), C(5) and C(6) lie close to the plane of the aromatic system but in compound VII, the steric influences of the chlorine substituents prevent this arrangement of atoms. As previously noted (see Introduction), the 2,6-difluoro derivative (IX) is an active β-blocker and it is feasible that the steric influences of the fluorine atoms are smaller than those of the chlorine atoms and could permit a greater degree of rotation about bond O(1) - C(7). This being the case, it is possible that at least one requirement of the receptor site may be

the ability of the compound to adopt an arrangement of atoms in which atoms O(1), C(5) and C(6) lie close to the plane of the aromatic system.

Compound VI (Vivalan) is able to adopt this near-planar arrangement of atoms and although it contains no hydroxyl group, by analogy with compound II some β-blocking activity might therefore be expected. The lack of any such activity for Vivalan, hence suggests that the conformation of the morpholine ring hinders attachment to the β-adrenergic receptor site. Moreover, the apparent flexibility of the Inderal cation is demonstrated by the presence of the three conformations [3,4] , [3,5] and [3,6] in the solid state, and in this case, effects on the central nervous sytem in addition to β-blocking activity, may derive from an ability to mimic the conformations of Vivalan, associated with central-nervous-system activity.

From these studies it would appear that the geometry of the β-adrenergic receptor site is such that, approximate coplanarity of the aromatic ring atoms with atoms O(1), C(5) and C(6) is required for β-blocking activity, along with conformations about bonds, C(4) - C(5) and C(5) - C(6), which differ from those permitted by the constraints of a morpholine ring (as in Vivalan) and which are consistent with having an absolute configuration (S) at the chiral centre.

A recent review entitled 'Molecular Characteristics of Biogenic Monamines and their Analogs' (1973)[34] summarises the results of crystal-structure analyses, solution n.m.r. studies and theoretical studies of a number of amines, known to stimulate the sympathetic

nervous system (sympathomimetic amines). The actions of several of these compounds e.g. Isoprenaline are blocked by the actions of the β-blockers and since both classes of compound are active at a β-adrenergic receptor site, comparisons between their respective conformations may be of interest.

In general, it has been found that compounds such as Isoprenaline, which exhibit strong direct sympathomimetic activities, have the following structural features:-

a) An aromatic six-membered ring system.
b) An extended ethylamine side chain approximately perpendicular to the ring system.
c) A positively charged tetravalent nitrogen atom.
d) A hydrophilic and hydrophobic side i.e. the hydroxyl group on the β-carbon atom is cis with respect to the meta-phenolic hydroxyl group.
e) An R configuration at the β-carbon atom.

Comparison of the R configuration of e.g. (-) Isoprenaline with the S configuration of (-) Inderal (Figure 2.5.4.) shows that both stereochemistries are identical at the chiral centre, as might be expected from their respective attachment to the same receptor sites. The main differences between the conformations of the sympathomimetic compounds and the β-blocking compounds appear to be the relative orientations of the aromatic systems with respect to the appropriate side chains, with the aforementioned near-planar arrangement of the aromatic ring atoms with atoms O(1), C(5) and C(6) being dominant in the β-blocking compounds, and the perpendicular arrangement of side

chain and aromatic system being observed predominantly in the sympathomimetic amines. Although it has been suggested[34] that in the case of the (-) Isoprenaline and analogous systems, the barrier to rotation about the bond linking the ethanolamine chain to the aromatic system, is quite large, there is as yet, little unambiguous information as to the magnitude of this barrier and hence it is difficult to assess the significance of the aforementioned differences in terms of possible hydrogen bonding at a receptor site.

In conclusion, it is becoming apparent that for the most part, conformational studies of biologically-active flexible molecules using solid-state or solution data, are unlikely to yield unambiguous information regarding the geometries of biological receptor sites. The present analyses and resulting comparisons suggest a range of conformational possibilities which are probably influenced by specific hydrogen-bonding arrangements. Hence it seems likely that the energy involved in binding (possibly via hydrogen bonds) to a receptor site, will be sufficient to allow adoption of what might otherwise be considered a sterically unfavourable conformation by the active molecule.

It is probable that further studies of the conformations of β-blocking agents in relation to their detailed biological activities, should be carried out on more rigid molecules. In such cases the solid-state conformations will be more pertinent to the conformation adopted by the molecule at a receptor site.

TABLE 2.5.1.

TORSION ANGLES AND E.S.Ds (°) of COMPOUNDS III - VIII

Torsion Angle					III	IV	V	VI	VII	VIII
(a)	C(1)	C(3)	N(1)	C(4)	64.8(9)	-63.5(5)	-75.5(7)		-64.6(8)	-46
(b)	C(2)	C(3)	N(1)	C(4)	-169.7(7)	172.2(4)	161.9(6)	-55.9(4)	173.3(6)	-168
(c)	N(1)	C(4)	C(5)	C(6)	-163.7(6)	-175.9(4)	177.4(5)	-176.6(3)	-172.2(6)	170
(d)	N(1)	C(4)	C(5)	O(21)	77.4(7)	49.4(6)	54.7(7)	-	84.9(8)	-
(e)	N(1)	C(4)	C(5)	O(20)	-	-50.4(6)	-	-57.6(4)	-61.7(8)	-75
(f)	C(3)	N(1)	C(4)	C(5)	-170.2(6)	-81.6(5)	174.1(5)	56.3(4)	-163.2(6)	-60
(g)	C(4)	C(5)	C(6)	O(1)	173.8(6)	-59.3(5)	166.5(5)	-166.4(3)	-171.2(6)	-76
(h)	O(21)	C(5)	C(6)	O(1)	-65.0(7)	75.1(6)	-71.9(6)	-	-70.0(8)	-
(i)	O(20)	C(3)	C(6)	O(1)	-	174.5(4)	-	73.9(3)	77.2(8)	169
(j)	C(5)	C(6)	O(1)	C(7)	175.4(6)	175.6(4)	-176.7(5)	-174.0(3)	-171.3(6)	-174
(k)	C(6)	O(1)	C(7)	C(8)	9.6(10)	7.8(6)	-22.2(10)	-6.0(5)	99.5(9)	-3

TABLE 2.5.1.

TABLE 2.5.2.

Compound	Conformation in the Crystal	
III	[3,6]	
IV	[3,5]	[3,4]
V	[3,6]	
VI	[3,6]	
VII	[3,6]	[3,6]
VIII	[3,5]	

TABLE 2.5.3.

% Population of Rotamers in Aqueous Solution

	1	2	3	4	5	6
± Inderal	12.7	15.4	71.9	30.9	32.6	36.5
± Inderal HCl	2.5	3.8	93.7	50.4	9.1	40.5
± Eraldin HCl	3.3	6.6	90.1	47.4	12.2	40.4
Noradrenaline HCl	10	14	76	-	-	-
Adrenaline HCl	6	17	77	-	-	-
Isoprenaline HCl	6	11	83	-	-	-

TABLE 2.5.4.

Compound	Reference	τ_1°	N(1)···O(H)
Salbutamol	15	-59.9	2.82
Alupent (A)	17	55.5	2.78
Alupent (B)	17	68.0	2.86
Thl165(a)	14	-47.8	2.77
Thl179	16	52.1	2.74
Noradrenaline	31	-64	2.85
Ephedrine	32	-70	2.88
Isoprenaline (A)	13	-62	2.82
Isoprenaline (B)	13	-50	2.64
Alprenolol	24	-75	2.95
III	-	77.4	3.07
IV	-	49.4	2.89
IV	-	-50.4	2.82
V	-	54.7	2.82
VI	-	-57.5	2.84
VII	-	84.9	3.01
VII	-	-61.7	2.85

where,

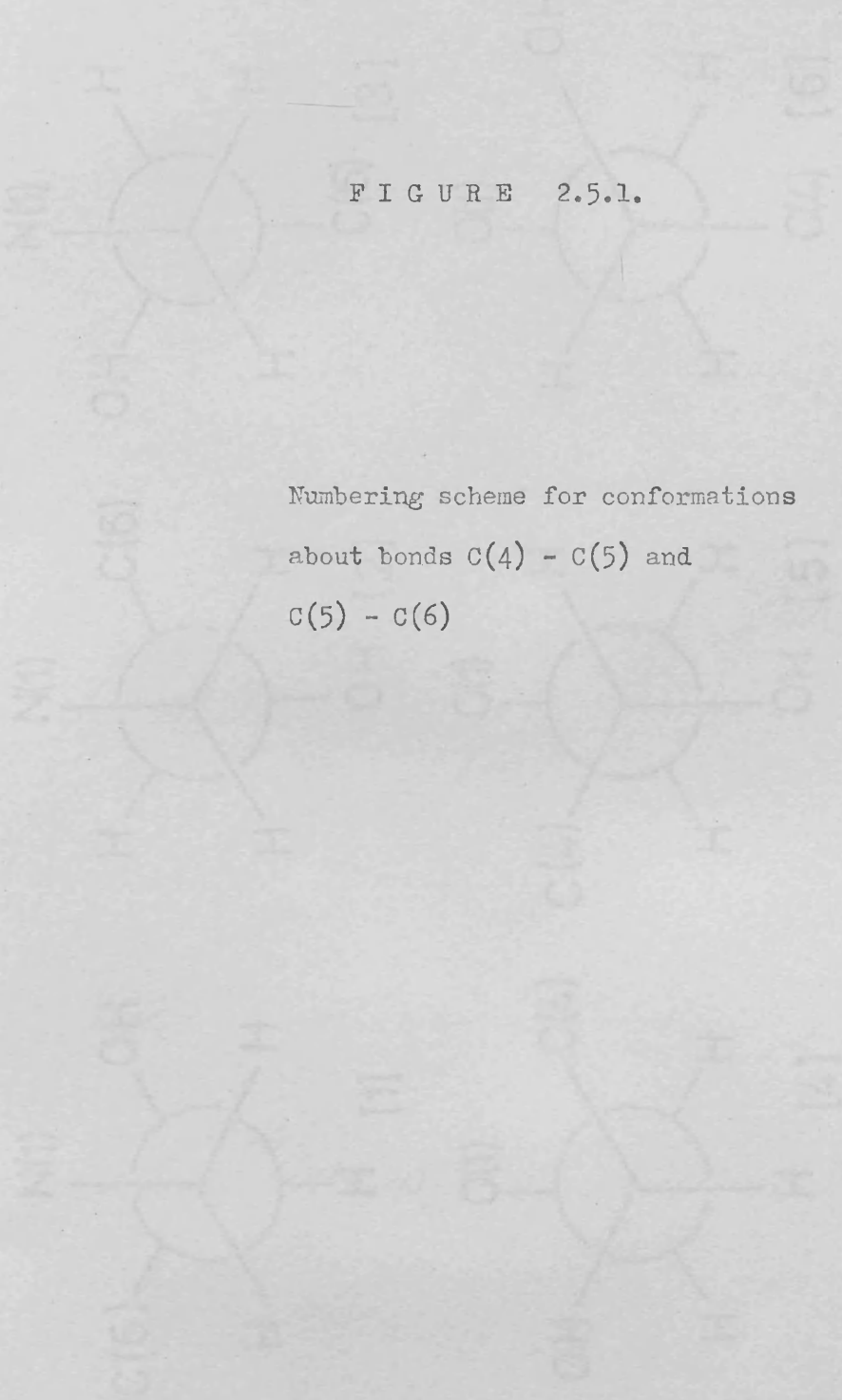
τ_1° = Torsion Angle N(1) C(4) C(5) O(H)

and, N(1)···O(H) is the interatomic distance in Å

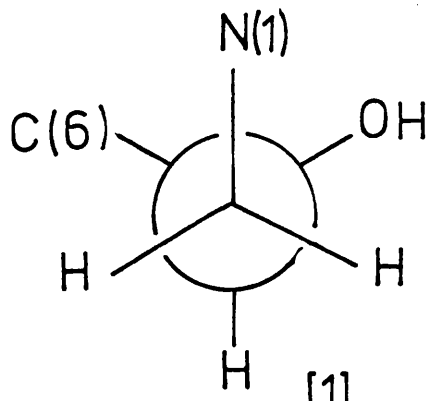
NOTE

Thl165(a) and Thl179 are diastereomers of the compound dl-N-[2(4-Hydroxyphenyl)] 1-methylethyl-2(3,5-dihydroxyphenyl)-2-hydroxyethylamine Hydrobromide.

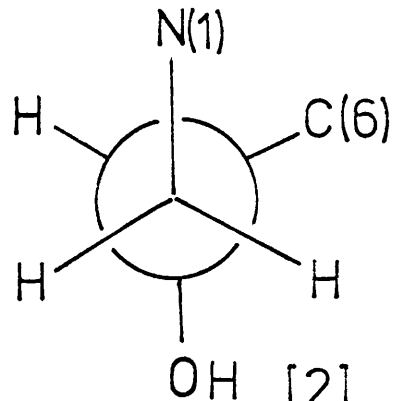
F I G U R E 2.5.1.



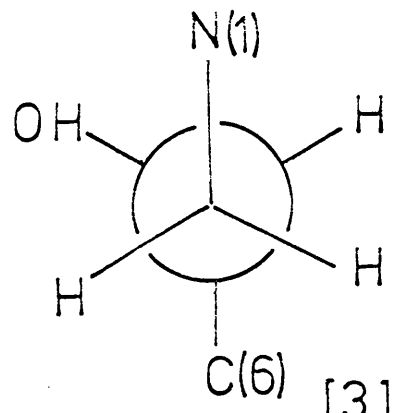
Numbering scheme for conformations about bonds C(4) - C(5) and C(5) - C(6)


N(1)
C(6)
OH
H
H
H

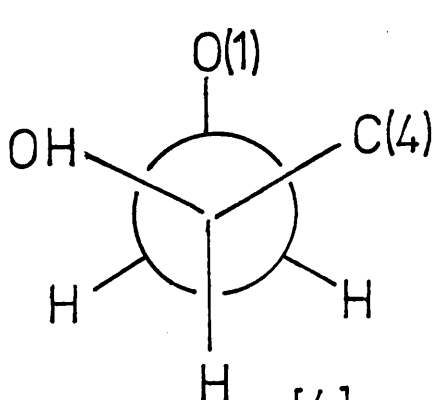
[1]


N(1)
H
C(6)
H
H
OH

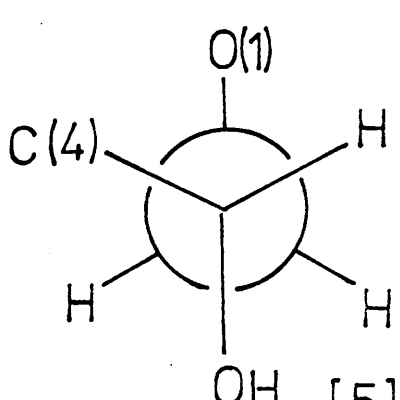
[2]


N(1)
OH
H
H
H
C(6)

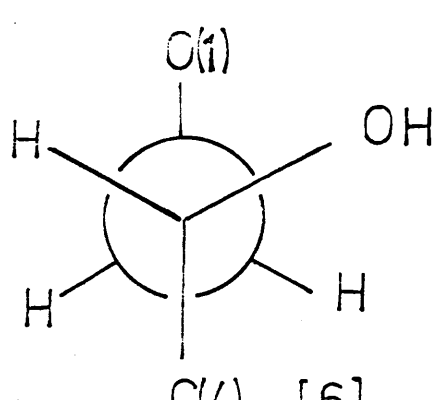
[3]


O(1)
OH
C(4)
H
H
H

[4]


O(1)
C(4)
H
H
H
OH

[5]


O(1)
H
OH
H
H
C(4)

[6]

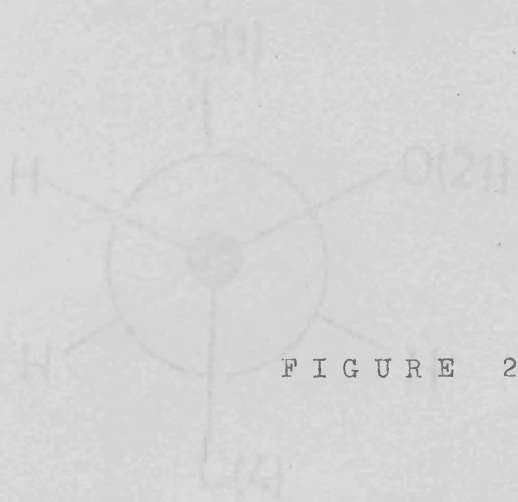
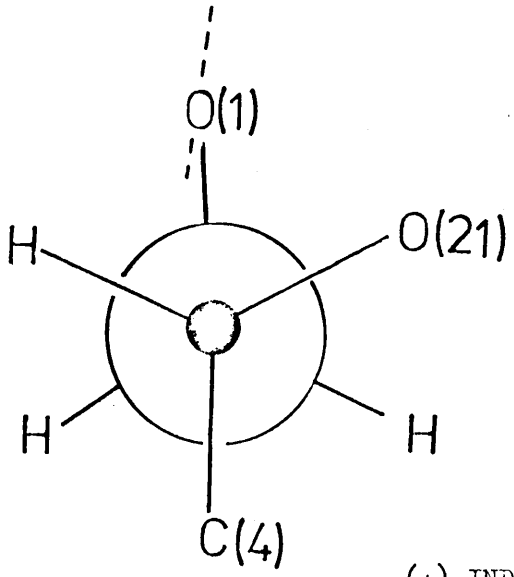
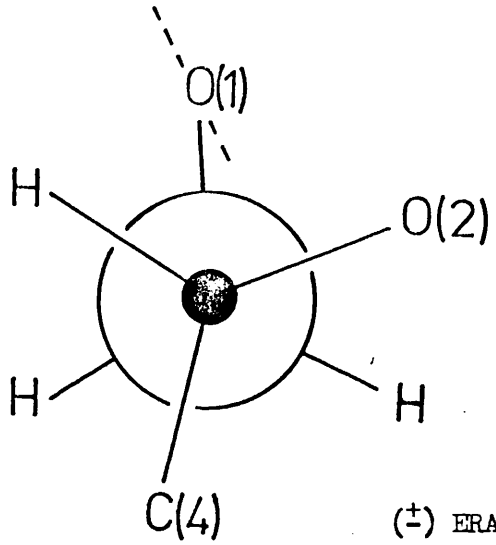


FIGURE 2.5.2.

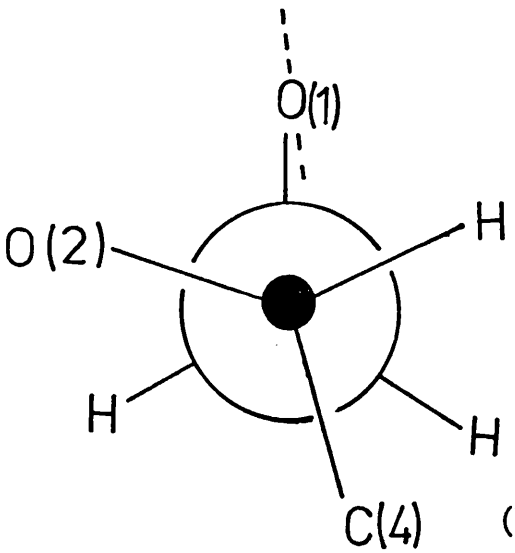
Orientation of the aromatic system with respect to atoms O(1), C(5) and C(6)



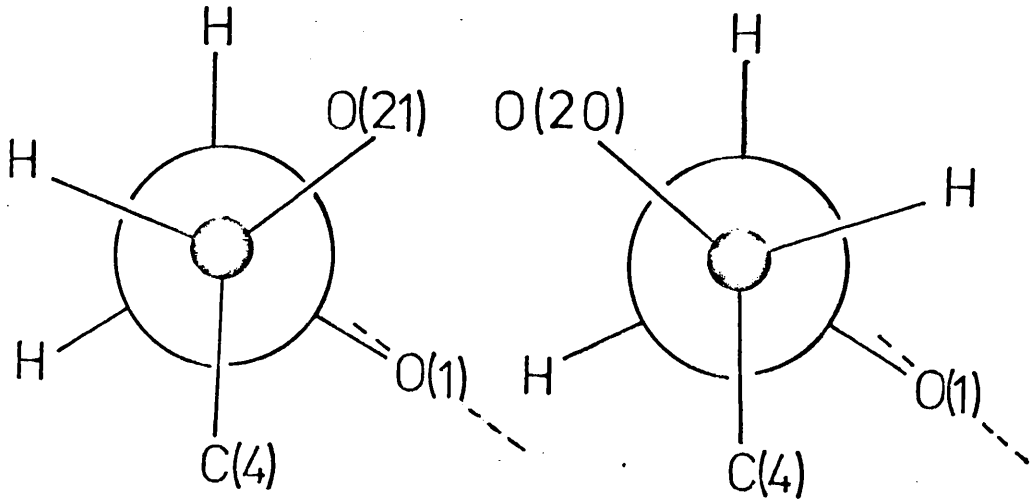
(+) INDERAL HCl.



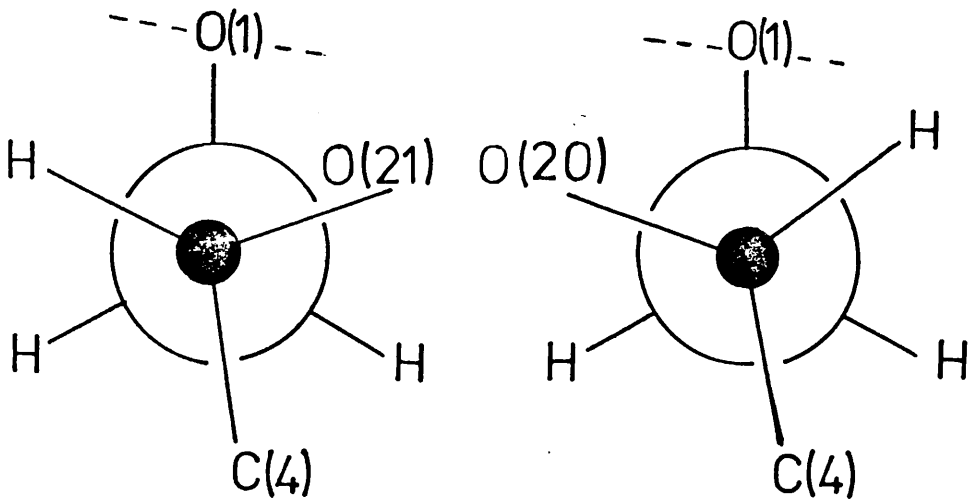
(±) ERALDIN Per.



(±) VIVALAN Ox.



(±) INDERAL HCl.

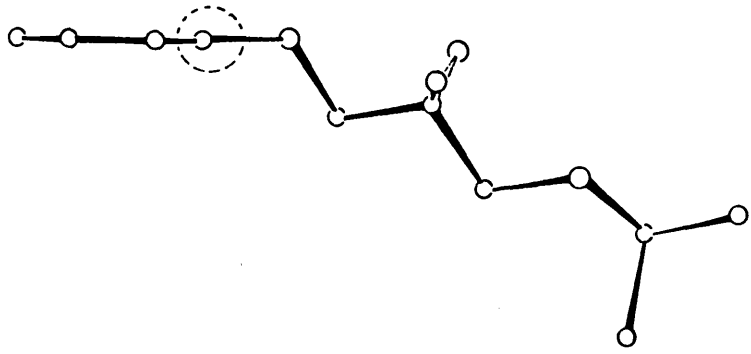


(±) 2,6-DICHLORO DERIVATIVE

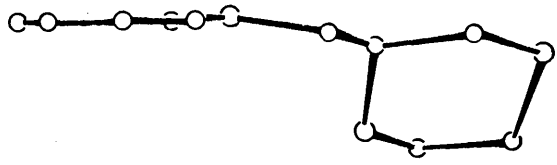
F I G U R E 2.5.3.

Orientation of the 2-hydroxy 3-isopropylaminopropoxy chain relative to the aromatic system

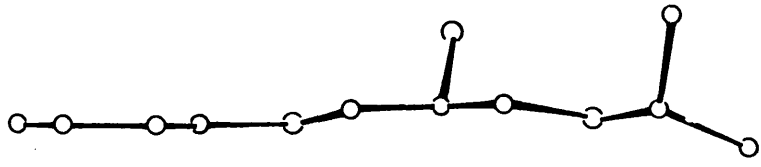
(±) 2,6 Dichloro



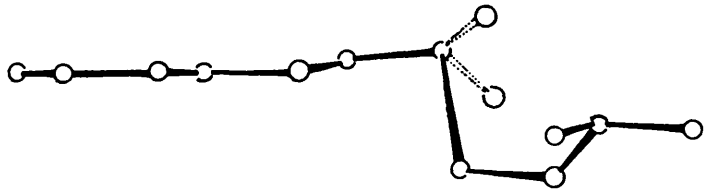
(±) Vivalan



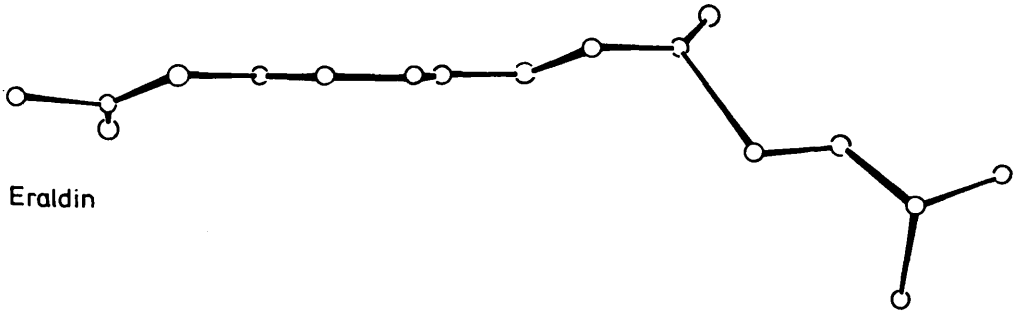
(+) Inderal



(±) Inderal

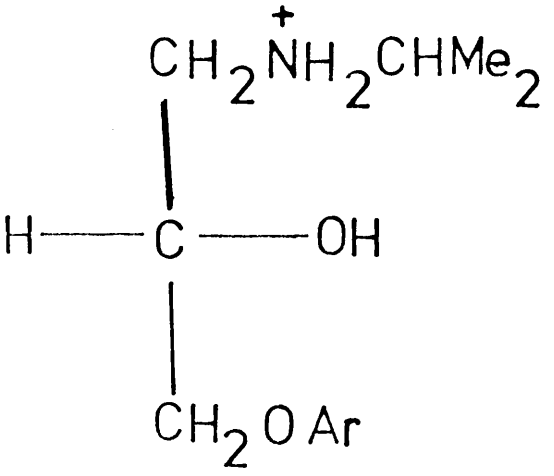


(±) Eraldin

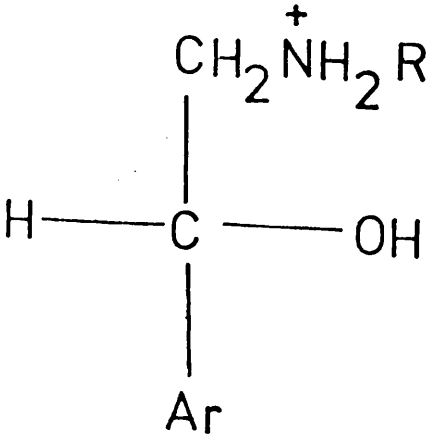


F I G U R E 2.5.4.

Comparison of R and S absolute stereochemistries in (-) Isoprenaline and (-) Inderal



S



R

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* **Present address - Imperial Chemical Industries Ltd., Pharmaceuticals Division, Mereside, Alderley Park, MACCLESFIELD, Cheshire SK10 4TG.**

PART 3

THE X-RAY INVESTIGATION OF TWO IMIDAZO [2,1-b] THIAZOLE DERIVATIVES

INTRODUCTION

The synthetic route illustrated in Scheme 1 has been used in the preparation of a compound which is known to have an imidazo [2, 1-b] thiazoline nucleus, but whose detailed molecular structure could not be unambiguously determined by spectroscopic methods[1].

Since the direction of the condensation reaction (i) could not be predicted with absolute certainty, the products of this reaction may be represented by either structure (1) or structure (2). In addition, the non-hydrogen ring substituents may be either cis or trans with respect to each other and because of the non-specificity of reaction (i) both isomers were formed. Reaction of this mixture with NaH (ii) results in the thermodynamically more stable trans isomer (1' or 2') being formed exclusively, with the final compound 3 or 4 being produced after alkylation (iii) by EtMgBr. The trans stereochemistry of the ring substituents was confirmed by n.m.r. evidence but the individual assignment of the imidazoline ring protons was not made with complete certainty and it was not possible to determine which of the structures (3) or (4) represented the true reaction product.

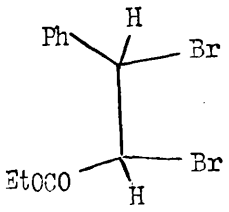
In order to resolve this ambiguity an X-ray analysis of the final product (3 or 4) has been carried out and has shown the compound to have the structure (3).

In addition to the analysis of (3), an X-ray analysis of the analogous compound (6) has also been carried out. This compound is the minor product of the reaction of ethylene dibromide with

5,5-diphenyl-2-thiohydantoin[2] which, in a manner analogous to Scheme 1, produces the isomers (5) or (6). Whilst the major product (5) has been fully characterised by conventional spectroscopic methods[3] and the minor product is expected to have the molecular structure (6), certain spectroscopic features of compound (6) have proven inconsistent with the spectra observed for similar conjugated systems[3]. Details of the infra-red vibrational frequencies $\nu_{C=O}$ and $\nu_{C=N}$ of six similar compounds (5) - (10) are given in Table 3.0.1., which suggest that the conjugative system in (6) is not analogous to those in compounds (8), (9) and (10). The value, $\nu_{C=O}$, observed for compound (6) is comparable to the value observed for compound (5) and is consequently higher than is common in conjugated systems. In contrast, the value of $\nu_{C=N}$ is lower in compound (6) than in the other five compounds, which suggests a greater decrease in bond order than is usual in a conjugated system. Furthermore, the C^{13} n.m.r. spectrum suggests deshielding effects on the carbon atom of the $\diagdown\!\!\diagup C=N$ and $\diagdown\!\!\diagup C=O$ bonds of compound (6) relative to compound (5).

In an attempt to rationalise the apparently anomalous spectroscopic results, the compound has been studied by X-ray analysis and the molecular structure (6) has been established.

SCHEME I



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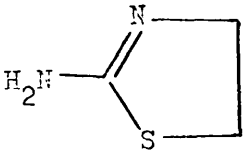
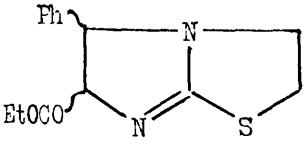


(i) Base



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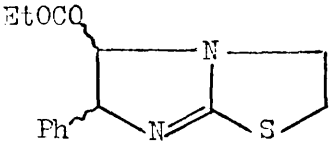


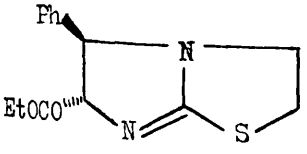
cis + trans

(1)

cis + trans

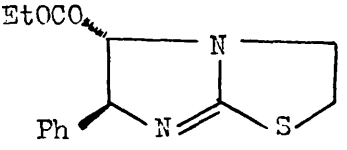
(2)

(ii) NaH



trans

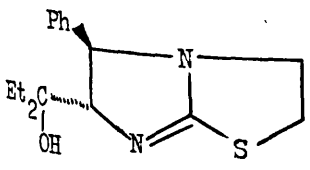
(1')



trans

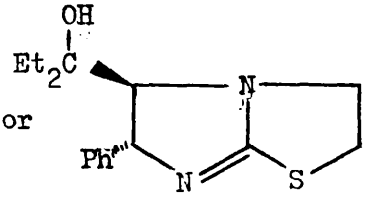
(2')

(iii) EtMgBr

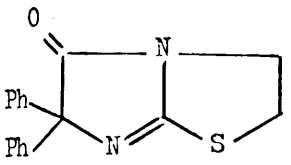


(3)

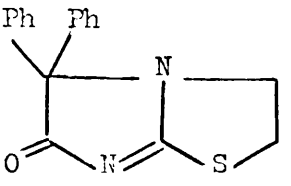
or



(4)



(5)



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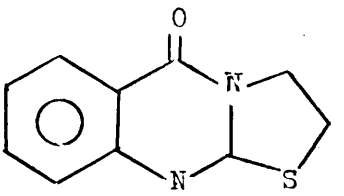

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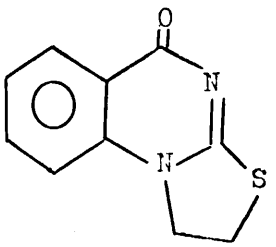

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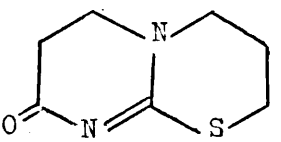

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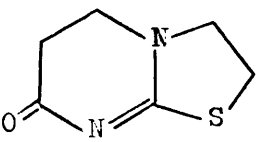

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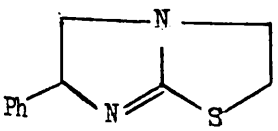

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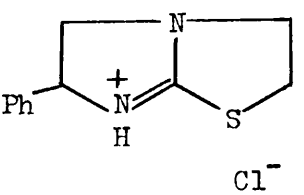

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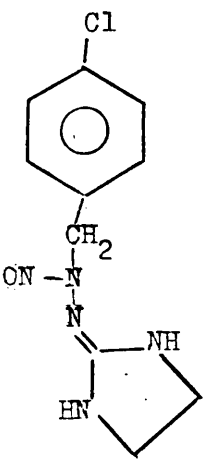

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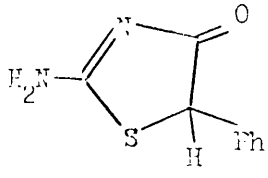

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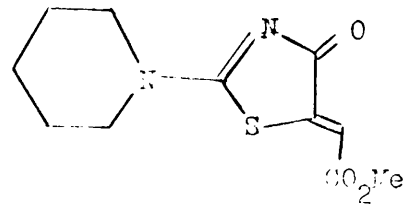


(15)

TABLE 3.0.1.

Compound	$\nu_{C=O}(cm.^{-1})$	$\nu_{C=N}(cm.^{-1})$	$\delta_{C=O}(C^{13})$	$\delta_{C=N}(C13)$
(5)	1728	1608	166.5	176.8
(6)	1725	1495	190.6	190.1
(7)	1684	1554	-	-
(8)	1644	1525	-	-
(9)	1658	1536	-	-
(10)	1676	1542	-	-

S E C T I O N 3.1.

THE CRYSTAL AND MOLECULAR STRUCTURE OF 6β-(1-ETHYL-1-HYDROXYPROPYL)-5α-PHENYL-2,3,5,6-TETRAHYDROIMIDAZO [2,1-b] THIAZOLE

EXPERIMENTAL

6β-(1-Ethyl-1-hydroxypropyl)-5α-phenyl-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole

CRYSTAL DATA

$C_{16}H_{22}N_2SO$; M=290.42; Orthorhombic, a=13.695Å, b=10.581Å, c=11.261Å, U=1631.79Å^3; D_c=1.19 g.cm.$^{-3}$; D_m=1.20 g. cm.$^{-3}$; Z=4; F_{ooo}=624; Space Group $P2_12_12_1$; μ =1.99 cm.$^{-1}$; Mo-Kα X-rays; λ =0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs taken with Cu-Kα (λ =1.5418Å) radiation and from precession photographs taken with Mo-Kα (λ =0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_12_12_1$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.2 x 0.4 x 0.3mm.) rotating about a, to graphite-monochromated Mo-radiation (Mo-$K\alpha_1$), and using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 60^\circ$) to collect 1563 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made.

STRUCTURE DETERMINATION

The structure was determined by non-centrosymmetric Direct Methods using the computer program MULTAN and appropriate programs contained

in the X-ray '72 suite of computer programs.

Phase determination was initiated by assigning phases to those reflections shown in Table 2.1.1. and utilising them in a series of calculations based on the weighted tangent formula of Direct Methods from which phases were assigned to those 200 reflections with $|E| \geqslant 1.35$. An E-map based on these 200 reflections revealed plausible atomic sites for 15 non-hydrogen atoms and subsequent structure-factor and electron-density calculations indicated the positions of all non-hydrogen atoms. Each atom was assigned an arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ and after each round of calculations the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational and scale parameters converged after 14 cycles of full-matrix least-squares calculations when R was 0.058 and R' was 0.005. Details of the refinement are given in Table 3.1.2.

16 Hydrogen-atom positions were located from difference-syntheses and their positional parameters were refined in cycles 11-12. The remaining hydrogen-atom positions were calculated and included in subsequent calculations but were not refined. A fixed temperature factor $U_{iso}=0.03\text{Å}^2$ was arbitrarily assigned to all hydrogen atoms.

An appropriate weighting shceme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure-factors. The scheme was of the form:

If A $|Fo| > |Fc|$, $W=10^{-9}$,

otherwise $W=X.Y$,

with $X=1$ if $\sin\theta > B$, else $X = \frac{\sin\theta}{B}$

and $Y=1$ if $|Fo| < C$, else $Y = \frac{C}{|Fc|}$

The most suitable values for A, B and C were found to be 0.75, 0.50 and 10.00 respectively. At the conclusion of refinement, a difference synthesis and electron-density distribution revealed no errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (11). Observed and calculated structure-factors are given in Appendix 6. Positional and vibrational parameters with estimated standard deviations are given in Table 3.1.3. Values of e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

DISCUSSION ON THE MOLECULAR AND CRYSTAL STRUCTURE OF COMPOUND (3)

Crystal structure analysis has shown the final reaction product to be compound (3) and a diagrammatic representation of this molecule is shown in Figure 3.1.1., giving the numbering scheme for all non-hydrogen atoms. To avoid extensive atomic overlap, all hydrogen atoms are omitted from Figure 3.1.1., but, for the purposes of discussion, are numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, least-squares planes, intramolecular non-bonding distances and intermolecular distances are given in Tables 3.1.4. - 3.1.8.

Atoms N(1), N(2), S(1), C(5) and C(3) are coplanar, within experimental error, with atoms C(1), C(2) and C(4) respectively -0.146, -0.355 and -0.143Å distant from this plane. The dihedral angle between the foregoing plane and the least-squares plane through the phenyl ring is 96.7°, while the orientation of the phenyl ring, with respect to its immediate neighbours, is given by appropriate torsion angles (e.g. C(12)C(11)C(1)C(4)-132.2(5)° and C(12)C(11)C(1)N(1)114.4(5)°).

The relevant torsion angles about the C(1) - C(4) bond H(1)C(1)C(4)C(6)-3.6(25), C(11)C(1)C(4)H(4)4.5(26)° and N(1)C(1)C(4)N(2)-0.3(4)° indicate an eclipsed conformation for the substituents on atoms C(1) and C(4), with the phenyl and 1-ethyl, 1-hydroxypropyl substituents trans with respect to each other. In contrast, the substituents about bonds C(4) - C(6), C(6) - C(7) and C(6) -C(9) adopt the sterically more-favoured staggered conformations, as shown in Figure 3.1.2. Several of these interatomic distances, such as C(8)···O(1) [3.20Å] C(8)···C(9) [3.07Å], C(10)···O(1)

[2.94Å] and C(4)··· C(10) [3.07Å] are shorter than the sum of the appropriate Van der Waal's covalent radii and the values observed in valency angles, O(1)C(6)C(7) [113.3(4)°] , O(1)C(6)C(4) [102.9(4)°] , C(10)C(9)C(6) [117.0(5)°] and C(8)C(7)C(6) [117.7(5)°] , may be rationalised by consideration of possible steric interactions between these pairs of atoms.

The endocyclic valency angles of the imidazo [2, 1-b] thiazoline system are typical of those reported for the similar compounds (11)[4] and (12)[5].

Of the C(sp^3) - C(sp^3) bonds in the present molecule, the shortest values are observed for C(2) - C(3) [1.490(9)Å] and C(9) - C(10) [1.493(11)Å] . In the case of bond C(2) - C(3), similar values [1.502(11) and 1.491(16)Å] have been reported for corresponding bonds in the heterocyclic systems (12)[5] and (13)[6] respectively, whilst the effects of possible thermal librational motion have been noted in Part 2 (compounds III, IV, V and VII) and may account for the apparently short C(9) - C(10) bond length. The longest C(sp^3) - C(sp^3) bond in the present molecule (C(1) - C(4) 1.570(6)Å) may perhaps be correlated with the eclipsing of substituents on atoms C(1) and C(4), bond extension having been previously noted under similar conditions, e.g. in some bicyclo [2.2.1.] heptyl derivatives[7]. Whilst bond lengths C(1) - N(1) [1.460(7)Å] , N(1) - C(2) [1.434(7)Å] and C(4) - N(2) [1.483(6)Å] are within a range of values acceptable for C - N single bonds, bond lengths, C(5) - N(2) [1.283(6)Å] and C(5) - N(1) [1.358(6)Å] are both significantly shorter, the value of C(5) - N(2) being comparable to that of a formal C=N bond[8]. Delocalisation of the electron lone pair on N(1)

is suggested by the value of bond length C(5) - N(1) and by the sum of the valency angles around this atom [355.2(6)°] . Bond lengths C(5) - S(1) [1.744(4)Å] and C(3) - S(1) [1.834(6)Å] are unequal and agree with reported values for similar compounds, (e.g. compound (11)[4] has corresponding values of 1.752(4) and 1.834(6)Å) suggesting delocalisation of an electron lone pair, on S(1), into the bonding system of the molecule. These results hence suggest some delocalisation of electron lone pairs over atoms N(2), C(5), N(1) and S(1).

The dimensions of the phenyl-ring substituent do not differ, by more than the experimental error, from accepted literature values for this system and similarly, other molecular dimensions which have not been previously discussed are not significantly different from expected values.

Examination of the crystal-packing arrangements reveals the possibility of hydrogen bonding of the form [R-O-H··· N(2)] and the crystal structure consists of two independent and unlinked helices extending in the direction of the crystallographic c axis. The possible hydrogen-bond dimensions are; O(1)··· N(2) [2.80Å] , N(2)··· H(01) [1.94Å] and angle O - H···N(2) [162.0°] . A diagram representing the crystal packing is given in Figure 3.1.3.

TABLE 3.1.1.

h	k	l	E	Phi	
6	5	6	2.62	45°	Origin Defining Reflections
3	3	7	2.46	a	
3	4	2	2.36	b	
0	8	4	2.35	180°	
6	7	5	2.41	c	
5	5	7	2.05	d	

The phase value of 0 8 4 was determined by application of the $\sum_1$ formula to all 200 reflections with $E \geqslant 1.35$, while the inclusion of the remaining five reflections, in the starting set, was based on their high $|E|$ values, ability to form large numbers of phase relationships and their ability to adequately define a unit cell origin and enantiomorph. The enantiomorph was defined by assigning the phase value 45° to reflection 6 5 6, while unknown phases a, b, c and d were systematically given all possible combinations of the values $\pm \pi/4$ and $\pm 3\pi/4$, the correct values proving to be 225°, 315°, 315° and 315° respectively.

TABLE 3.1.2.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} for all non-hydrogen atoms; scale factor, unit weights.	1 - 3	0.116	0.014
x, y, z, U_{iso} for all non-hydrogen atoms; contributions from hydrogen atoms but with no refinement; scale factor; unit weights.	4 - 5	0.103	0.010
x, y, z, U_{ij} (i, j = 1, 2, 3) of all non-hydrogen atoms. H-atoms in calculation but not refined; scale factor; unit weights.	6 - 10	0.065	0.005
x, y, z of hydrogen atoms; all other atoms in calculation but not refined; scale factor unit weights.	11 - 12	0.062	0.004

TABLE 3.1.2. (Cont.)

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{ij} (i, j = 1, 2, 3) of non-hydrogen atoms; hydrogen atoms in calculation but not refined; scale factor; weighting scheme adjusted.	13 - 14	0.058	0.005

TABLE 3.1.3.

(a) Atomic Fractional Coordinates and E.S.Ds for Compound (3)

ATOM	x/a	y/b	z/c
S(1)	0.00790(9)	0.31120(12)	0.79885(11)
N(1)	0.1118(3)	0.2476(4)	0.6179(4)
N(2)	0.1824(3)	0.4083(3)	0.7194(3)
O(1)	0.3143(3)	0.4763(4)	0.4431(3)
C(1)	0.1941(4)	0.2779(4)	0.5406(4)
C(2)	0.0207(4)	0.1867(6)	0.5919(5)
C(3)	-0.0367(4)	0.1826(6)	0.7042(6)
C(4)	0.2428(3)	0.3889(4)	0.6116(4)
C(5)	0.1113(3)	0.3300(4)	0.7103(6)
C(6)	0.2537(4)	0.5131(5)	0.5400(4)
C(7)	0.1526(4)	0.5622(5)	0.5008(5)
C(8)	0.1485(6)	0.6891(8)	0.4373(7)
C(9)	0.3069(5)	0.6125(5)	0.6158(6)
C(10)	0.4075(6)	0.5804(7)	0.6571(8)
C(11)	0.2593(4)	0.1638(4)	0.5228(4)
C(12)	0.2683(5)	0.1082(6)	0.4104(6)
C(13)	0.3271(5)	0.0030(7)	0.3965(7)
C(14)	0.3767(5)	-0.0475(6)	0.4916(9)
C(15)	0.3679(5)	0.0050(6)	0.6018(7)
C(16)	0.3095(5)	0.1109(5)	0.6178(5)

TABLE 3.1.3.

(b) Hydrogen-atom Fractional Coordinates and E.S.Ds for Compound (3)

ATOM	x/a	y/b	z/c
H(1)	0.1746(29)	0.3063(39)	0.4639(37)
H(20)	0.0309(29)	0.1236(39)	0.5304(36)
H(21)	-0.0078(32)	0.2425(38)	0.5251(34)
H(30)	-0.1091(-)	0.1985(-)	0.6838(-)
H(31)	-0.0024(39)	0.0944(35)	0.7441(36)
H(4)	0.3122(30)	0.3678(38)	0.6282(37)
H(70)	0.1230(29)	0.4964(41)	0.4526(36)
H(71)	0.1012(30)	0.5524(39)	0.5701(37)
H(80)	0.0762(30)	0.7097(40)	0.4069(40)
H(81)	0.1698(-)	0.7570(-)	0.4934(-)
H(82)	0.1936(-)	0.6869(-)	0.3675(-)
H(90)	0.3128(-)	0.6932(-)	0.5643(-)
H(91)	0.2722(29)	0.6337(37)	0.7001(38)
H(101)	0.4369(28)	0.6590(38)	0.6990(38)
H(102)	0.4081(28)	0.5111(40)	0.7147(37)
H(103)	0.4481(28)	0.5372(39)	0.6053(37)
H(01)	0.3048(29)	0.5000(38)	0.3682(37)
H(12)	0.2346(29)	0.1518(39)	0.3386(35)
H(13)	0.3361(-)	-0.0394(-)	0.3155(-)
H(14)	0.4223(-)	-0.1247(-)	0.4806(-)
H(15)	0.4059(-)	-0.0341(-)	0.6728(-)
H(16)	0.3225(28)	0.1646(38)	0.6888(37)

TABLE 3.1.3.

(c) Anisotropic Temperature Factors ($\AA^2$) for Compound (3)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0569	0.0593	0.0555	-0.0091	0.0089	0.0090
N(1)	0.0457	0.0629	0.0654	-0.0090	0.0016	-0.0254
N(2)	0.0562	0.0485	0.0321	-0.0103	0.0015	0.0004
O(1)	0.0732	0.0867	0.0546	0.0195	0.0224	0.0129
C(1)	0.0638	0.0496	0.0392	0.0029	-0.0035	-0.0066
C(2)	0.0696	0.0752	0.0646	-0.0198	-0.0081	-0.0124
C(3)	0.0489	0.0660	0.0951	-0.0127	-0.0018	-0.0002
C(4)	0.0467	0.0442	0.0404	-0.0029	0.0055	0.0013
C(5)	0.0430	0.0405	0.0419	0.0005	0.0004	0.0064
C(6)	0.0556	0.0472	0.0494	0.0068	0.0174	0.0077
C(7)	0.0624	0.0573	0.0613	0.0137	0.0105	0.0131
C(8)	0.0884	0.1068	0.0945	0.0369	0.0227	0.0526
C(9)	0.0731	0.0512	0.0866	-0.0165	0.0173	0.0084
C(10)	0.0943	0.0801	0.1039	-0.0259	-0.0087	0.0042
C(11)	0.0581	0.0427	0.0528	-0.0029	0.0153	-0.0095
C(12)	0.0753	0.0672	0.0680	-0.0132	0.0139	-0.0168
C(13)	0.0850	0.0933	0.1057	-0.0094	0.0297	-0.0467
C(14)	0.0691	0.0562	0.1474	-0.0016	0.0280	-0.0222
C(15)	0.0804	0.0633	0.1027	0.0163	0.0038	0.0016
C(16)	0.0894	0.0545	0.0641	0.0117	0.0012	0.0004
Average Estimated Standard Deviations ($\AA^2$)						
S	0.0007	0.0006	0.0006	0.0006	0.0006	0.0006
N	0.0020	0.0020	0.0020	0.0018	0.0017	0.0018
O	0.0025	0.0026	0.0019	0.0022	0.0018	0.0020
C	0.0032	0.0030	0.0032	0.0028	0.0030	0.0030

TABLE 3.1.4.

Intramolecular Bonded Distances and E.S.Ds (in Å) for Compound (3)

ATOM A	ATOM B	Å
C(1)	N(1)	1.460(7)
C(1)	C(4)	1.570(6)
C(1)	C(11)	1.515(7)
N(1)	C(5)	1.358(6)
N(1)	C(2)	1.434(7)
C(2)	C(3)	1.490(9)
C(3)	S(1)	1.834(6)
S(1)	C(5)	1.744(4)
C(5)	N(2)	1.283(6)
N(2)	C(4)	1.483(6)
C(4)	C(6)	1.549(7)
C(6)	C(7)	1.543(8)
C(7)	C(8)	1.522(10)
C(6)	C(9)	1.538(8)
C(9)	C(10)	1.493(11)
C(6)	O(1)	1.425(6)
C(11)	C(12)	1.401(8)
C(12)	C(13)	1.383(10)
C(13)	C(14)	1.376(12)
C(14)	C(15)	1.365(12)
C(15)	C(16)	1.388(9)
C(11)	C(16)	1.389(8)

TABLE 3.1.5.

Valency Angles (°) and E.S.Ds for Compound (3)

ATOM A	ATOM B	ATOM C	
C(5)	S(1)	C(3)	91.3(2)
C(2)	C(3)	S(1)	107.2(4)
N(1)	C(5)	S(1)	111.7(3)
N(2)	C(5)	S(1)	130.1(3)
C(2)	N(1)	C(1)	130.4(4)
C(5)	N(1)	C(1)	108.7(4)
C(4)	C(1)	N(1)	100.9(4)
C(11)	C(1)	N(1)	111.0(4)
C(5)	N(1)	C(2)	116.1(4)
C(3)	C(2)	N(1)	107.4(5)
N(2)	C(5)	N(1)	118.2(4)
C(5)	N(2)	C(4)	105.6(3)
C(1)	C(4)	N(2)	106.5(3)
C(6)	C(4)	N(2)	111.2(3)
C(4)	C(6)	O(1)	102.9(4)
C(7)	C(6)	O(1)	113.3(4)
C(9)	C(6)	O(1)	109.6(5)
C(11)	C(1)	C(4)	114.4(4)
C(6)	C(4)	C(1)	114.3(4)
C(12)	C(11)	C(1)	120.4(5)
C(16)	C(11)	C(1)	120.7(4)
C(7)	C(6)	C(4)	110.4(4)
C(9)	C(6)	C(4)	109.7(4)
C(9)	C(6)	C(7)	110.7(4)
C(8)	C(7)	C(6)	117.7(5)
C(10)	C(9)	C(6)	117.0(5)
C(16)	C(11)	C(12)	118.9(5)
C(13)	C(12)	C(11)	119.4(6)
C(15)	C(16)	C(11)	120.7(5)
C(14)	C(13)	C(12)	120.8(7)
C(15)	C(14)	C(13)	120.4(6)
C(16)	C(15)	C(14)	119.8(7)

TABLE 3.1.6.

Selected Torsion Angles (°) and E.S.Ds for Compound (3)

C(5)	S(1)	C(3)	C(2)	-14.5(4)
C(3)	S(1)	C(5)	N(1)	0.3(4)
C(3)	S(1)	C(5)	N(2)	179.2(5)
C(2)	N(1)	C(1)	C(4)	156.9(5)
C(2)	N(1)	C(1)	C(11)	-81.5(6)
C(5)	N(1)	C(1)	C(4)	2.9(5)
C(5)	N(1)	C(1)	C(11)	124.5(4)
C(1)	N(1)	C(2)	C(3)	-179.0(5)
C(5)	N(1)	C(2)	C(3)	-26.6(6)
C(1)	N(1)	C(5)	S(1)	173.7(3)
C(1)	N(1)	C(5)	N(2)	-5.4(6)
C(2)	N(1)	C(5)	S(1)	15.6(5)
C(2)	N(1)	C(5)	N(2)	-163.5(4)
C(5)	N(2)	C(4)	C(1)	-2.6(5)
C(5)	N(2)	C(4)	C(6)	122.5(4)
C(4)	N(2)	C(5)	S(1)	-173.9(4)
C(4)	N(2)	C(5)	N(1)	5.0(5)
N(1)	C(1)	C(4)	N(2)	-0.3(4)
N(1)	C(1)	C(4)	C(6)	-123.5(4)
C(11)	C(1)	C(4)	N(2)	-119.5(4)
C(11)	C(1)	C(4)	C(6)	117.3(4)
N(1)	C(1)	C(11)	C(12)	114.4(5)
N(1)	C(1)	C(11)	C(16)	-64.2(6)
C(4)	C(1)	C(11)	C(12)	-132.2(5)
C(4)	C(1)	C(11)	C(16)	49.1(6)
N(1)	C(2)	C(3)	S(1)	24.4(6)
N(2)	C(4)	C(6)	O(1)	179.0(4)
N(2)	C(4)	C(6)	C(7)	-59.9(5)
N(2)	C(4)	C(6)	C(9)	62.4(5)
C(1)	C(4)	C(6)	O(1)	-60.4(5)
C(1)	C(4)	C(6)	C(7)	60.7(5)
C(1)	C(4)	C(6)	C(9)	-177.0(4)
O(1)	C(6)	C(7)	C(8)	-69.8(7)
C(4)	C(6)	C(7)	C(8)	175.5(5)
C(9)	C(6)	C(7)	C(8)	53.8(7)
O(1)	C(6)	C(9)	C(10)	-52.3(7)
C(4)	C(6)	C(9)	C(10)	60.0(7)
C(7)	C(6)	C(9)	C(10)	-178.0(6)
C(1)	C(11)	C(12)	C(13)	-179.1(6)
C(1)	C(11)	C(16)	C(15)	178.9(5)

TABLE 3.1.7.

Least-squares planes for various portions of the molecular framework in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations

Plane (1) = $0.78173X' + 0.59226Y' - 0.19525Z' = 2.65023$

Plane (2) = $0.49408X' - 0.66198Y' + 0.56362Z' = 2.94412$

(b) Deviations (A°) of Atoms from Planes (Starred Atoms Define Plane)

Plane (1) = C(11)* 0.003(5), C(12)* -0.002(7), C(13)* -0.001(7), C(14)* 0.004(7), C(15)* -0.003(7), C(16)* -0.000(6), C(1) -0.019

Plane (2) = C(3)* -0.002(6), C(5)* 0.006(4), N(1)* -0.000(4) N(2)* -0.004(4), S(1)* 0.000(1), C(1) -0.146(5), C(2) -0.355(6) C(4) -0.143

(c) Dihedral Angles ($^{\circ}$) between Planes

(1) - (2) 96.7°

TABLE 3.1.8.

Intramolecular Non-bonding Distances < 3.6Å

ATOM A	ATOM B	Å
C(2)	C(11)	3.37
N(2)	C(7)	2.98
N(2)	C(9)	2.99
N(2)	C(11)	3.56
C(5)	C(6)	3.35
C(5)	C(7)	3.45
C(5)	C(11)	3.41
N(1)	C(6)	3.53
O(1)	C(10)	2.94
N(1)	C(12)	3.50
N(1)	C(16)	3.07
C(1)	C(7)	3.09
C(1)	O(1)	2.89
C(4)	C(10)	3.07
C(4)	C(16)	3.08
C(8)	C(9)	3.07
C(8)	O(1)	3.20
O(1)	C(11)	3.51

Intermolecular Distances < 3.8Å

S(1)	O(1)	I	3.69
N(2)	C(8)	I	3.53
N(2)	O(1)	I	2.80
C(5)	O(1)	I	3.48
C(14)	C(7)	II	3.78
O(1)	C(3)	II	3.12
O(1)	C(2)	II	3.33
C(12)	C(3)	II	3.70
N(2)	C(3)	III	3.63

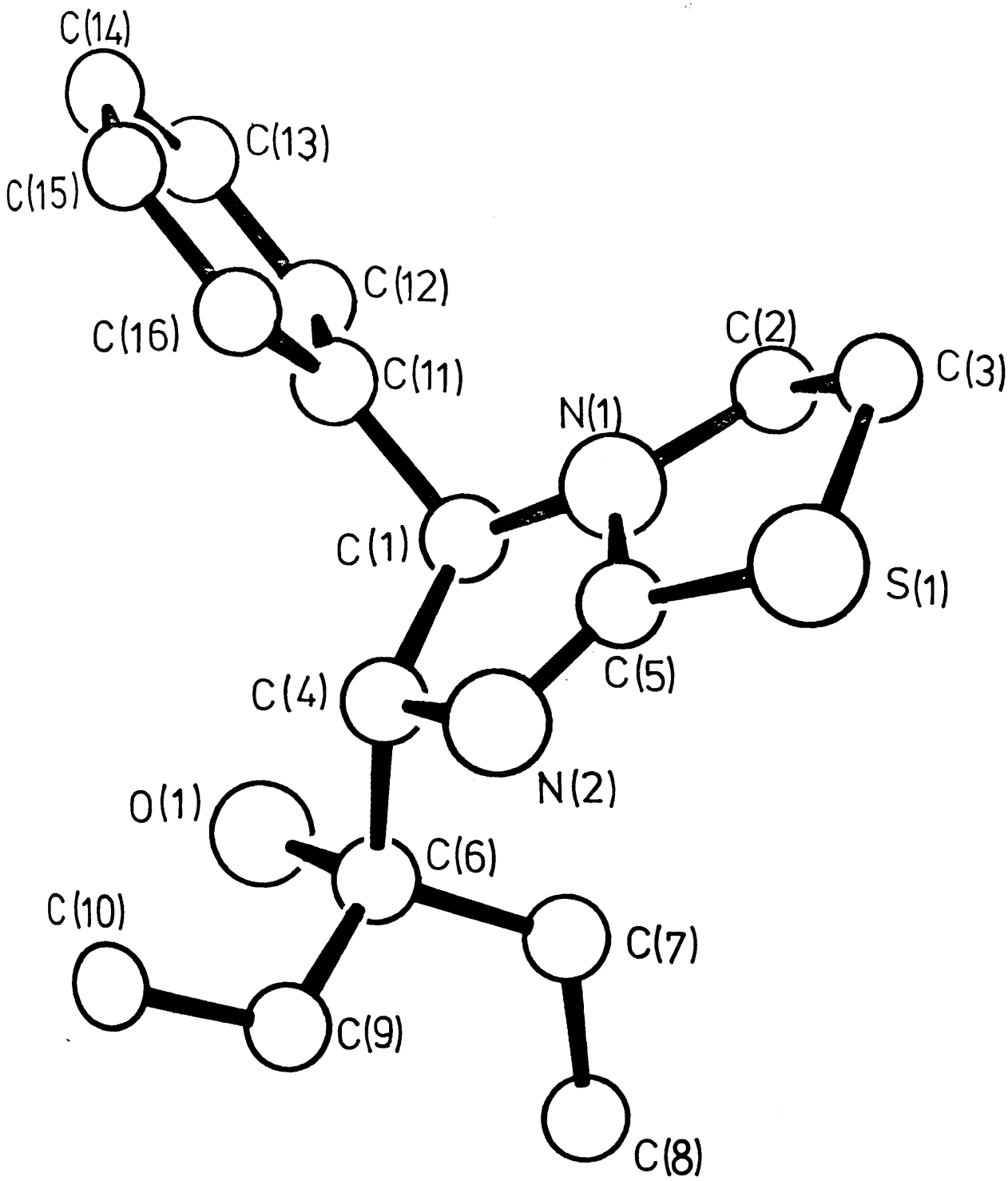
where the position of atom B is given by,

I = $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
II = $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
III = $-x, \frac{1}{2}+y, (\frac{1}{2}-z)+1$

FIGURE 3.1.1.

Diagrammatic representation of

Compound (3)


C(14)
C(13)
C(15)
C(12)
C(16)
C(11)
C(2)
C(3)
N(1)
C(1)
S(1)
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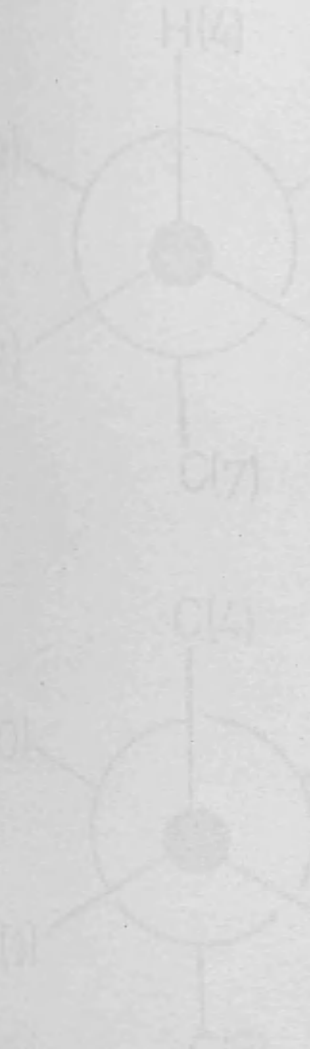
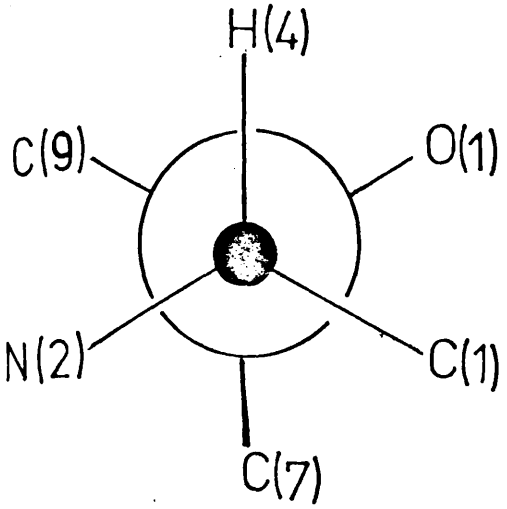
O(1)
C(6)
C(10)
C(7)
C(9)
C(8)



F I G U R E 3.1.2.

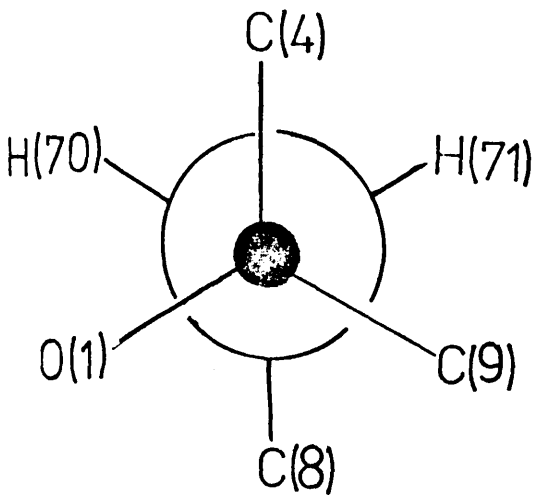
Conformations about bonds C(4) - C(6),

C(6) - C(7) and C(6) - C(9)

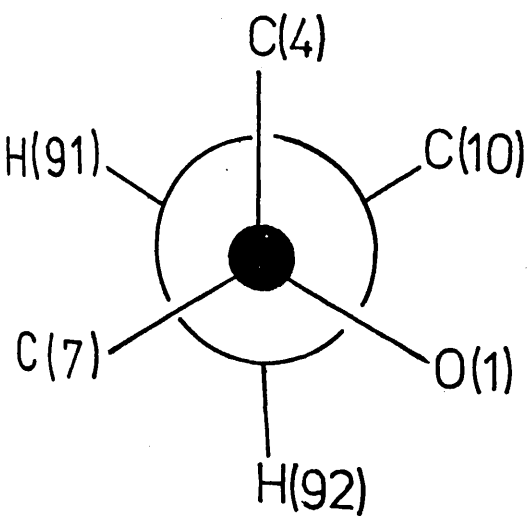


TORSION ANGLES

C(1)	C(4)	C(6)	C(7)	60.7(5)
C(1)	C(4)	C(6)	C(9)	-179.0(4)
C(1)	C(4)	C(6)	O(1)	-60.5(5)
N(2)	C(4)	C(6)	C(7)	-59.8(5)
N(2)	C(4)	C(6)	C(9)	62.5(5)
N(2)	C(4)	C(6)	O(1)	179.0(4)
H(4)	C(4)	C(6)	C(7)	178.3(24)
H(4)	C(4)	C(6)	C(9)	-59.4(25)
H(4)	C(4)	C(6)	O(1)	57.1(25)



C(4)	C(6)	C(7)	C(8)	175.4(5)
C(9)	C(6)	C(7)	C(8)	53.7(7)
O(1)	C(6)	C(7)	C(8)	-69.8(6)
C(4)	C(6)	C(7)	H(71)	41.7(24)
C(4)	C(6)	C(7)	H(70)	-59.2(26)
C(9)	C(6)	C(7)	H(71)	-79.9(24)
C(9)	C(6)	C(7)	H(70)	179.2(26)
O(1)	C(6)	C(7)	H(71)	156.5(24)
O(1)	C(6)	C(7)	H(70)	55.6(26)

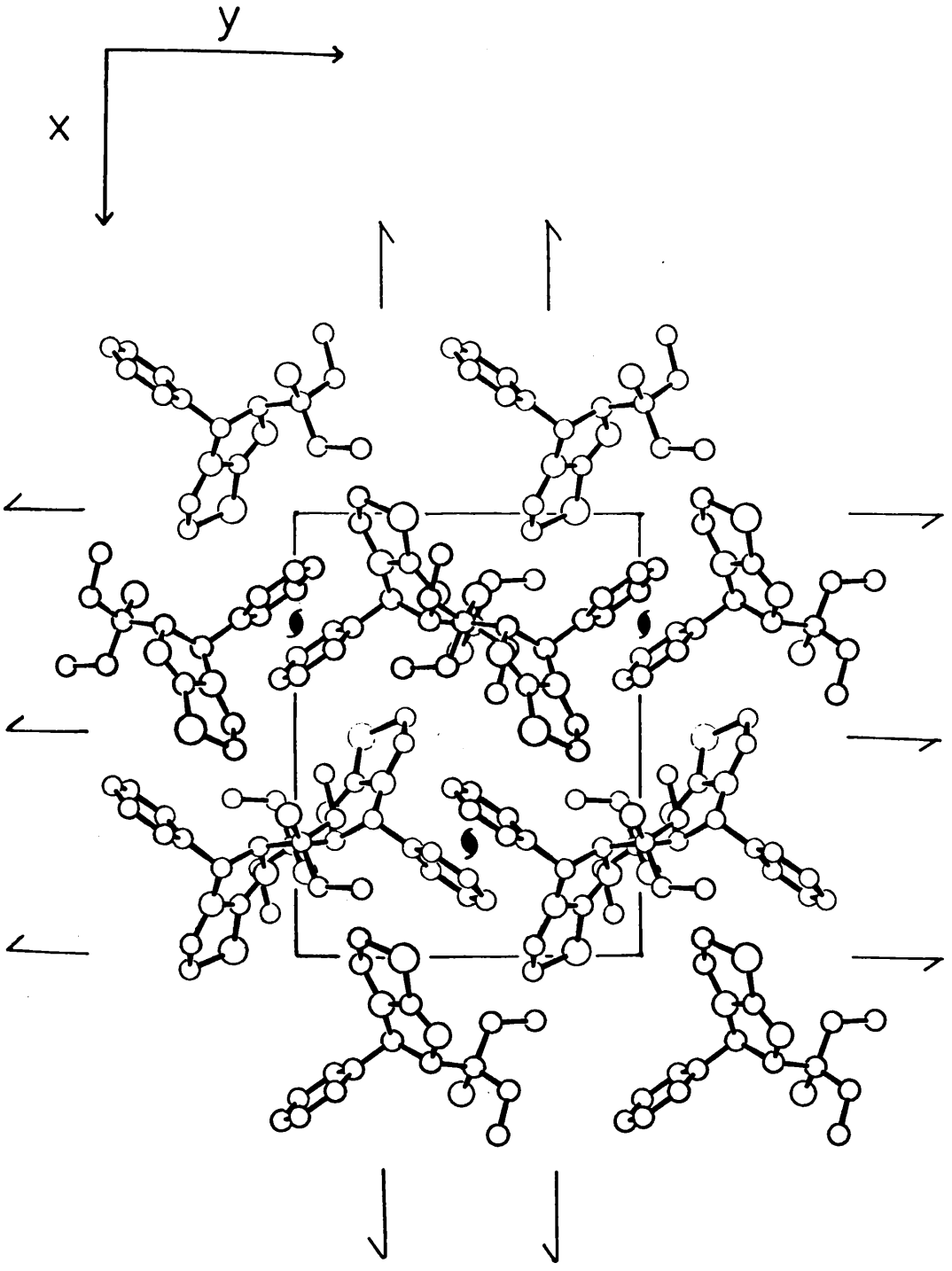


C(4)	C(6)	C(9)	C(10)	59.9(7)
O(1)	C(6)	C(9)	C(10)	-52.3(7)
C(7)	C(6)	C(9)	C(10)	-178.0(5)
C(4)	C(6)	C(9)	H(92)	179.6(4)
C(4)	C(6)	C(9)	H(91)	-57.2(24)
O(1)	C(6)	C(9)	H(92)	67.4(6)
O(1)	C(6)	C(9)	H(91)	-169.4(24)
C(7)	C(6)	C(9)	H(92)	-58.3(6)
C(7)	C(6)	C(9)	H(91)	64.9(24)

F I G U R E 3.1.3.

Crystal-packing arrangements for

Compound (3)


y
x

S E C T I O N 3.2.

THE CRYSTAL AND MOLECULAR STRUCTURE OF 5,5-DIPHENYL-6-OXO-2,3,5,6-TETRAHYDROIMIDAZO [2,1-b] THIAZOLE

EXPERIMENTAL

5,5-Diphenyl-6-oxo-2,3,5,6-tetrahydroimidazo [2,1-b] thiazole

CRYSTAL DATA

$C_{17}H_{14}N_2SO$; M=294.26; Monoclinic, a=9.289Å, b=14.754Å, c=10.945Å, β=103.48°; U=1452.59Å^3; D_c=1.34 g.cm.$^{-3}$; D_m=1.35 g.cm.$^{-3}$; Z=4; F_{000}=616; Space group $P2_1/c$; μ=2.23 cm.$^{-1}$; Mo-Kα X-rays; λ = 0.7107Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs taken with Cu-Kα (λ =1.5418Å) radiation and from precession photographs taken with Mo-Kα (λ =0.7107Å) radiation and were subsequently refined by least squares calculations before data collection. The space group $P2_1/c$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.3 x 0.4 x 0.2 mm.) rotating about c, to graphite-monochromated Mo-radiation (Mo-Kα_1) and using the θ, ω scan technique (in the range $0 < 2\theta \leqslant 60°$) to collect 2579 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made.

STRUCTURE DETERMINATION

The structure was determined by centrosymmetric Direct Methods using the computer programs DATRDN, NORMSF, SINGEN, PHASE, Fc, FOURR and CRYLSQ, contained in the X-ray '72 suite of programs.

Phase determination was initiated by assigning phases to those 100 reflections with highest $|E|$ values. Each phase was either assigned directly or was expressed, via $\sum_2$ phase relationships, in terms of the three linearly independent non-structure seminvariant reflections given in Table 3.2.1.

The unit-cell origin was defined by assigning each of the reflections shown in Table 3.2.1., an arbitrary phase value of 360^{o} and the phases of the above 100 reflections were then included in a series of $\sum_2$ phase relationships from which phase values of 315 reflections with $E \geqslant 1.4$ were assigned.

An E-map based on these 315 reflections revealed plausible atomic positions for all non-hydrogen atoms. Subsequent structure factor and electron-density calculations verified these positions. Each non-hydrogen atom was assigned an arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ and after each of the above calculations, the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Refinement of positional, vibrational and scale parameters converged after 13 cycles of full-matrix least-squares calculations when R was 0.045 and R' was 0.003. Details of the refinement are given in Table 3.2.2.

All hydrogen-atom positions were selected from difference syntheses and each atom was assigned an arbitrary temperature factor $U_{iso}=0.03\text{Å}^2$ in all subsequent calculations. Positional parameters of these hydrogen atoms were refined in cycles 10-11, but no refinement of vibrational parameters was carried out.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure-factors. The scheme was of the form:-

If $A|Fo| > |Fc|$, $W=10^{-9}$,

otherwise $W=X.Y$,

with $X=1$ if $\sin\theta > B$, else $X = \frac{\sin\theta}{B}$

and $Y=1$ if $|Fo| < C$, else $Y = \frac{C}{|Fo|}$

The most suitable values for A, B and C were found to be 0.75, 0.45, and 10.00 respectively. At the conclusion of refinement, difference synthesis and electron-density revealed no errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (11). Observed and calculated structure-factors are listed in Appendix 7. Positional and vibrational parameters with standard deviations are given in Table 3.2.3. Values of estimated standard deviations are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

DISCUSSION ON THE MOLECULAR AND CRYSTAL STRUCTURE OF COMPOUND (6)

A diagrammatic representation of this molecule is shown in Figure 3.2.1. and gives the numbering scheme for all non-hydrogen atoms, hydrogen atoms being omitted to avoid extensive atomic overlap, but, for the purposes of discussion, numbered as the atoms to which they are bonded. Details of bond lengths, bond angles, torsion angles, least-squares planes, intra-molecular non-bonding distances and intermolecular distances are given in Tables 3.2.4. to 3.2.8.

Atoms N(1), N(2), C(5) and S(1) are coplanar, within experimental error, with atoms C(4) and O(1) respectively 0.084 and 0.046Å distant from this plane. The resulting deviations (torsion angle O(1)C(4)N(2) C(5) - 175.8(2)°) from the planar geometry, ideal for conjugation, are small and would not be expected to have a gross effect on possible conjugation. The endocyclic bond angles of the imidazo [2, 1-b] thiazoline system of the present molecule are similar to the corresponding angles of compound (3), although bond angles N(1)C(1) C(4) [98.1(1)°] and C(4)N(2)C(5) [104.4(2)°] are significantly smaller than in compound (3), the corresponding values being 100.9(4)° and 105.6(3)° respectively. In addition, atom C(4) of compound (6) is sp^2 hybridised and it is plausible that the bond angle C(1)C(4)N(2) is relatively more strained than in compound (3), and hence that the degree of bond angle strain is greater in the imidazoline system of, compound (6), than of compound (3).

Possible steric interactions between atoms of the phenyl rings and atom O(1) are suggested by interatomic distances such as C(12)··· O(1) [3.18Å], C(13)··· O(1) [3.18Å] and C(6)··· O(1) [2.99Å] and may

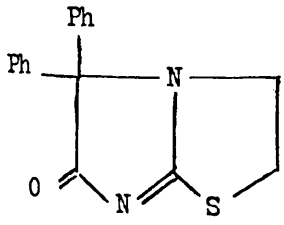
perhaps contribute towards the observed deviations from planarity of the proposed conjugated system. Further possible steric interactions between the pairs of atoms C(13)··· N(1) [3.42Å] , C(7)··· C(17) [3.21Å] , C(7)··· C(12) [2.93Å] , C(11)··· C(4) [3.26Å] , C(4) ···C(13) [2.98Å] and C(2)··· C(17) [3.24Å] are also noted and may largely determine the orientations of the phenyl rings with respect to the imidazo-[2,1-b] thiazoline system and with respect to each other, the dihedral angle between the planes of the phenyl rings being 72.5°.

Bond length C(1) - C(4) [1.577(3)Å] is longer than might otherwise be expected for a $C(sp^3)$ - $C(sp^2)$ bond (e.g. a corresponding bond length in the similar heterocyclic compound (14)[9] is 1.542(8)Å), and this may be a genuine effect since the corresponding bond in compound (3) also appears to be slightly extended, and in addition, the apparent increase of endocyclic bond-angle strain in the imidazoline system of the present molecule has already been noted. It is also noted that bond length C(2) - C(3) [1.525(3)Å] is significantly longer than the corresponding bond in compound (3) [1.490(9)Å].

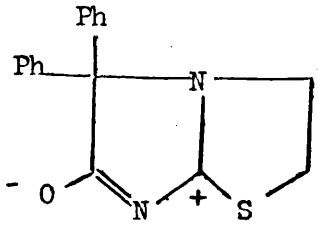
The presence of conjugation within this molecule is indicated by the shortening of bond N(2) - C(4) and by the lengthening of bond C(5) - N(2) with respect to the corresponding values in compounds (3) and (11)[4], while increased delocalisation of the N(1) and S(1) electron lone pairs is suggested by the shortening of bonds C(5) - N(1) and C(5) - S(1), relative to those values observed in compounds (3) and (11), relevant values being given in Table 3.2.9. These results thus demonstrate the expected delocalisation of electrons over atoms

O(1), C(4), N(2), C(5), N(1) and S(1). It is noted however, that in the present molecule, bond length N(2) - C(4) [1.383(3)Å] is significantly longer than the corresponding bonds in similar conjugated systems such as compounds (14)[9] [1.353(6)Å] and (15)[10] [1.340(9)Å], whilst bond length C(4) - O(1) is, within experimental error, identical in all three compounds (respective values for the present molecule and compounds (14) and (15) being 1.213(3), 1.225(4) and 1.223(8)Å.

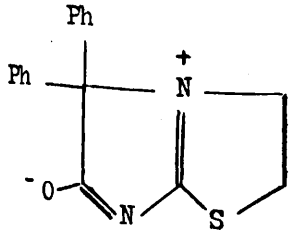
A possible rationalisation of these results and of the spectroscopic data may be made by consideration of canonical structures (a) - (g).



(a)



(b)



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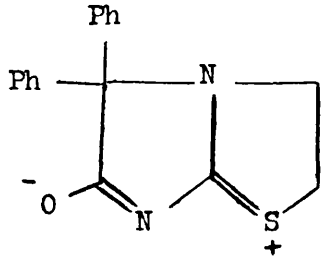
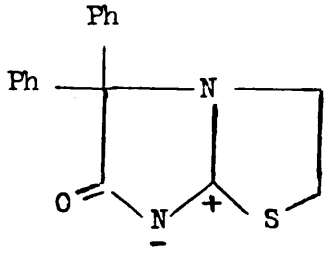
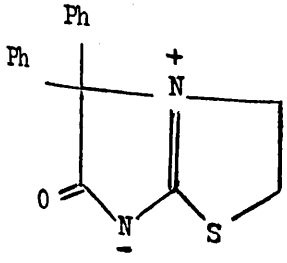


(d)



(e)



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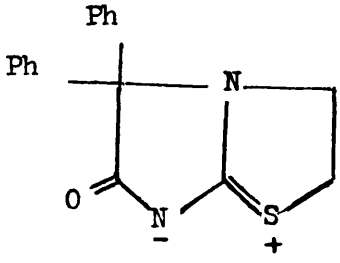
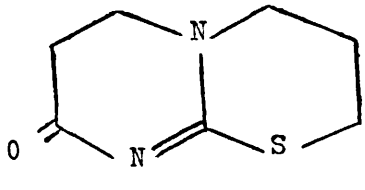
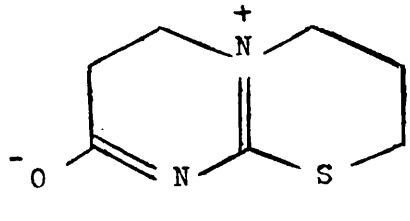


(g)

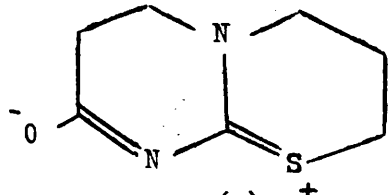
Bond-angle strain, in the imidazoline ring of (6), has already been noted, particularly in the case of bond angle C(4)N(2)C(5) [104.4(2)°] whose value is grossly distorted from the ideal value associated with an sp^2 hybridised atom. Canonical structures (a) - (d) require sp^2 hybridisation of atom N(2) and are consequently subject to considerable bond-angle strain with respect to the value of 104.4(2)° observed for angle C(4)N(2)C(5). In contrast, however, canonical structures (c) - (g) suggest sp^3 hybridisation of atom N(2), the ideal valency angles of which are closer to the observed value for angle C(4)N(2)C(5). It is thus conceivable that such factors are sufficient to permit a significant contribution of forms (c) - (g) to the overall structure. The corresponding bond angle in six-membered heterocyclic compounds such as (8), (9) and (10) however, could plausibly assume a value approaching 120° and the major contributions to compounds such as (9) may be represented by the canonical forms (h) - (k).



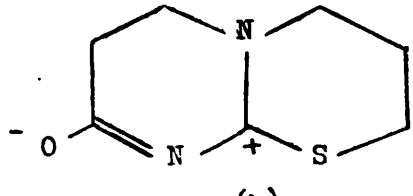
(h)



(i)

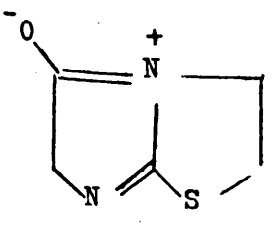


(j)

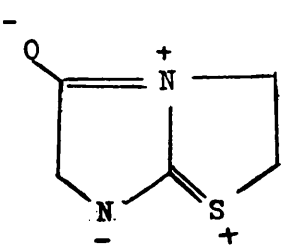


(k)

Comparison of canonical forms (a) - (g) and (h) - (k) suggests that the major contribution to the structure of compound (6) may derive from those forms containing localised carbonyl bonds, whilst in compounds such as (9), there is relatively an increased contribution from canonical forms requiring delocalised carbonyl bonds. The infra-red vibrational frequencies $\nu_{C=O}$ may reflect these differences and similarly, the differences observed in the $\nu_{C=N}$ vibrational frequencies of compounds (6), (8), (9) and (10) may indicate the relative importance of the respective contributions made by those forms containing formal C=N double bonds. (The possible importance of canonical forms (a), (e), (f) and (g) in the structure of the present molecule may also be demonstrated by the previously noted lengthening of the N(2) - C(4) bond relative to the corresponding bonds in the delocalised heterocyclic systems of compounds (14) and (15).) In addition, the C^{13}n.m.r. spectra suggest that, in the present molecule, the carbon atoms of the $\rangle C=O$ and $\rangle C=N$ groups are deshielded with respect to the corresponding atoms in the non-conjugated compound (5). The crystal structure of compound (5) has not been reported but, by analogy, with compounds (3) and (6), it is feasible that canonical forms (m) and (n) may contribute significantly to the overall structure of compound (5).



(m)



(n)

The C^{13}n.m.r. spectra may perhaps be correlated with possible contributions made by canonical structures such as (m) and (n), to the overall structure of compound (5) and with the relative importance of forms such as (e) in the structure of compound (6).

With the exception of those dimensions previously discussed, the remaining features of the molecule agree well with accepted literature values for similar bonding systems.

A diagram representing the crystal-packing arrangements is shown in Figure 3.2.2. and examination of intermolecular non-bonding distances reveals no abnormally short contacts suggesting that molecular packing within the crystal is determined by Van der Waal's forces.

TABLE 3.2.1.

h	k	l	E
-7	5	-2	3.52
6	3	-7	3.37
3	14	0	3.08

TABLE 3.2.2.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
Parameters in calculation; x, y, z, U_{iso} of all non-hydrogen atoms; scale factor; unit weights.	1 - 4	0.122	0.015
x, y, z, U_{iso} of all non-hydrogen atoms; H-atoms in calculation but not refined; scale factor; unit weights.	5 - 6	0.108	0.010
x, y, z, U_{ij} (i, j = 1, 2, 3) of all non-hydrogen atoms; H-atoms in calculation but not refined; scale factors; unit weights.	7 - 9	0.052	0.004
x, y, z, of H-atoms; scale factor; unit weights.	10 - 11	0.049	0.004
x, y, z, U_{ij} (i, j = 1, 2, 3) of all non-hydrogen atoms; H-atoms in calculation but not refined; scale factor; weighting scheme adjusted.	12 - 13	0.045	0.003

TABLE 3.2.3.

(a) Atomic Fractional Coordinates and E.S.Ds for Compound (6)

ATOM	x/a	y/b	z/c
S(1)	0.00345(6)	0.34992(4)	-0.14384(6)
N(1)	0.2479(2)	0.3808(1)	0.0167(1)
N(2)	0.1462(2)	0.2466(1)	0.0564(2)
O(1)	0.3238(2)	0.2057(1)	0.2341(2)
C(1)	0.3415(2)	0.3553(1)	0.1393(2)
C(2)	0.2229(2)	0.4672(1)	-0.0478(2)
C(3)	0.1124(3)	0.4471(2)	-0.1714(2)
C(4)	0.2716(2)	0.2593(1)	0.1517(2)
C(5)	0.1390(2)	0.3195(1)	-0.0141(2)
C(6)	0.5031(2)	0.3436(1)	0.1348(2)
C(7)	0.6141(2)	0.3507(2)	0.2443(2)
C(8)	0.7606(2)	0.3342(2)	0.2418(2)
C(9)	0.7981(2)	0.3103(2)	0.1314(2)
C(10)	0.6878(3)	0.3033(2)	0.0218(2)
C(11)	0.5407(2)	0.3194(1)	0.0231(2)
C(12)	0.3179(2)	0.4211(1)	0.2408(2)
C(13)	0.2350(3)	0.3975(2)	0.3260(2)
C(14)	0.2101(3)	0.4608(2)	0.4139(2)
C(15)	0.2662(4)	0.5470(2)	0.4513(2)
C(16)	0.3502(3)	0.5713(2)	0.3308(3)
C(17)	0.3767(3)	0.5086(2)	0.2443(2)

TABLE 3.2.3. (Cont.)

(b) Hydrogen-atom Fractional Coordinates and E.S.Ds for Compound 6

ATOM	x/a	y/b	z/c
H(20)	0.1828(23)	0.5100(15)	-0.0037(20)
H(21)	0.3095(23)	0.4888(15)	-0.0617(19)
H(30)	0.1580(23)	0.4320(15)	-0.2272(20)
H(31)	0.0494(23)	0.4961(15)	-0.2034(20)
H(7)	0.5876(23)	0.3684(14)	0.3211(20)
H(8)	0.8396(23)	0.3400(14)	0.3156(20)
H(9)	0.9021(23)	0.2944(15)	0.1317(20)
H(10)	0.7128(23)	0.2859(15)	-0.0558(20)
H(11)	0.4626(23)	0.3126(15)	-0.0531(20)
H(13)	0.1963(24)	0.3409(15)	0.3307(20)
H(14)	0.1439(23)	0.4379(15)	0.4690(20)
H(15)	0.2405(23)	0.5925(15)	0.4803(19)
H(16)	0.3997(24)	0.6351(15)	0.3298(20)
H(17)	0.4404(23)	0.5239(15)	0.1910(20)

TABLE 3.2.3. (Cont.)

(c) Anisotropic Temperature Factors ($Å^2$) for Compound (6)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0391	0.0612	0.0500	-0.0068	-0.0056	-0.0035
N(1)	0.0341	0.0317	0.0328	-0.0028	0.0022	0.0017
N(2)	0.0452	0.0356	0.0491	-0.0080	0.0119	-0.0022
O(1)	0.0653	0.0405	0.0536	0.0001	0.0137	0.0140
C(1)	0.0340	0.0300	0.0315	-0.0006	0.0059	0.0011
C(2)	0.0460	0.0354	0.0426	-0.0020	0.0018	0.0055
C(3)	0.0535	0.0511	0.0399	0.0060	0.0002	0.0052
C(6)	0.0431	0.0332	0.0399	-0.0029	0.0157	-0.0002
C(5)	0.0334	0.0383	0.0400	-0.0017	0.0079	-0.0077
C(6)	0.0349	0.0303	0.0331	0.0002	0.0062	0.0027
C(7)	0.0394	0.0494	0.0340	0.0021	0.0048	0.0019
C(8)	0.0381	0.0555	0.0462	0.0038	0.0013	0.0077
C(9)	0.0391	0.0450	0.0611	0.0063	0.0161	0.0102
C(10)	0.0500	0.0418	0.0489	0.0019	0.0211	-0.0014
C(11)	0.0438	0.0387	0.0354	-0.0007	0.0100	-0.0026
C(12)	0.0377	0.0347	0.0320	0.0025	0.0043	-0.0016
C(13)	0.0546	0.0461	0.0413	0.0018	0.0151	-0.0008
C(14)	0.0774	0.0679	0.0477	0.0088	0.0260	-0.0073
C(15)	0.0828	0.0653	0.0457	0.0142	0.0084	-0.0187
C(16)	0.0720	0.0429	0.0575	0.0022	-0.0010	-0.0130
C(17)	0.0541	0.0388	0.0484	-0.0026	0.0102	-0.0051
Average Estimated Standard Deviations ($Å^2$)						
S	0.0003	0.0004	0.0003	0.0002	0.0002	0.0003
N	0.0008	0.0008	0.0008	0.0006	0.0006	0.0006
O	0.0010	0.0008	0.0009	0.0007	0.0007	0.0007
C	0.0010	0.0010	0.0010	0.0009	0.0008	0.0009

TABLE 3.2.4.

Intramolecular Bonded Distances and E.S.Ds (in Å)

ATOM A	ATOM B	Å
C(1)	N(1)	1.468(2)
C(1)	C(4)	1.577(3)
C(1)	C(6)	1.523(2)
C(1)	C(12)	1.529(3)
N(1)	C(5)	1.340(2)
N(1)	C(2)	1.450(3)
C(2)	C(3)	1.525(3)
C(3)	S(1)	1.820(3)
S(1)	C(5)	1.723(2)
C(5)	N(2)	1.317(3)
N(2)	C(4)	1.383(3)
C(4)	O(1)	1.213(3)
C(6)	C(7)	1.391(3)
C(7)	C(8)	1.389(3)
C(8)	C(9)	1.379(3)
C(9)	C(10)	1.387(3)
C(10)	C(11)	1.390(3)
C(11)	C(6)	1.394(3)
C(12)	C(13)	1.385(3)
C(13)	C(14)	1.398(4)
C(14)	C(15)	1.373(4)
C(15)	C(16)	1.388(4)
C(15)	C(17)	1.386(3)
C(17)	C(12)	1.398(3)

TABLE 3.2.5.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	
N(1)	C(1)	C(4)	98.1(1)
N(1)	C(1)	C(6)	112.2(1)
N(1)	C(1)	C(12)	110.2(1)
C(4)	C(1)	C(12)	112.1(1)
C(4)	C(1)	C(6)	109.3(1)
C(12)	C(1)	C(6)	113.9(1)
N(1)	C(2)	C(3)	105.0(2)
C(2)	C(3)	S(1)	107.0(1)
C(3)	S(1)	C(5)	90.8(1)
S(1)	C(5)	N(1)	113.3(1)
S(1)	C(5)	N(2)	128.6(2)
N(1)	C(5)	N(2)	118.2(2)
C(5)	N(2)	C(4)	104.4(2)
N(2)	C(4)	C(1)	110.4(2)
N(2)	C(4)	O(1)	126.3(2)
O(1)	C(4)	C(1)	123.3(2)
C(1)	N(1)	C(5)	108.0(1)
C(1)	N(1)	C(2)	131.6(2)
C(2)	N(1)	C(5)	116.4(2)
C(1)	C(6)	C(7)	120.1(2)
C(1)	C(6)	C(11)	120.5(2)
C(7)	C(6)	C(11)	119.2(2)
C(6)	C(7)	C(8)	120.2(2)
C(7)	C(8)	C(9)	120.7(2)
C(8)	C(9)	C(10)	119.3(2)
C(9)	C(10)	C(11)	120.6(2)
C(10)	C(11)	C(6)	120.0(2)
C(1)	C(12)	C(13)	121.7(2)
C(1)	C(12)	C(17)	119.0(2)
C(13)	C(12)	C(17)	119.2(2)
C(12)	C(13)	C(14)	120.2(2)
C(13)	C(14)	C(15)	120.2(3)
C(14)	C(15)	C(16)	120.1(3)
C(15)	C(16)	C(17)	120.0(2)
C(16)	C(17)	C(12)	120.3(2)

TABLE 3.2.6.

Selected Torsion Angles (°) and E.S.Ds for Compound (6)

C(12)	C(1)	N(1)	C(5)	-108.1(2)
C(12)	C(1)	N(1)	C(2)	48.1(2)
C(6)	C(1)	N(1)	C(5)	123.8(2)
C(6)	C(1)	N(1)	C(2)	-80.0(2)
C(4)	C(1)	N(1)	C(5)	9.1(2)
C(4)	C(1)	N(1)	C(2)	165.3(2)
C(5)	N(1)	C(2)	C(3)	-25.1(2)
C(1)	N(1)	C(2)	C(3)	-179.8(2)
N(1)	C(2)	C(3)	S(1)	27.8(2)
C(2)	C(3)	S(1)	C(5)	-20.5(2)
C(3)	S(1)	C(5)	N(2)	-174.1(2)
C(3)	S(1)	C(5)	N(1)	7.0(2)
C(4)	N(2)	C(5)	N(1)	2.8(2)
C(4)	N(2)	C(5)	S(1)	-176.0(2)
O(1)	C(4)	N(2)	C(5)	-175.8(2)
C(1)	C(4)	N(2)	C(5)	3.8(2)
C(6)	C(1)	C(4)	O(1)	54.6(2)
C(6)	C(1)	C(4)	N(2)	-125.0(2)
C(12)	C(1)	C(4)	O(1)	-72.7(2)
C(12)	C(1)	C(4)	N(2)	107.7(2)
N(1)	C(1)	C(4)	O(1)	171.6(2)
N(1)	C(1)	C(4)	N(2)	-8.0(2)
C(1)	N(1)	C(5)	N(2)	-8.6(2)
C(2)	N(1)	C(5)	N(2)	-168.9(2)
C(1)	N(1)	C(5)	S(1)	170.4(1)
C(2)	N(1)	C(5)	S(1)	10.1(2)
N(1)	C(1)	C(12)	C(13)	104.1(2)
N(1)	C(1)	C(12)	C(17)	-73.4(2)
C(4)	C(1)	C(12)	C(13)	-4.0(3)
C(4)	C(1)	C(12)	C(17)	178.5(2)
C(6)	C(1)	C(12)	C(13)	-128.7(2)
C(6)	C(1)	C(12)	C(17)	53.8(2)
N(1)	C(1)	C(6)	C(7)	157.7(2)
N(1)	C(1)	C(6)	C(11)	-26.8(2)
C(4)	C(1)	C(6)	C(7)	-94.6(2)
C(4)	C(1)	C(6)	C(11)	80.9(2)
C(12)	C(1)	C(6)	C(11)	-152.9(2)
C(12)	C(1)	C(6)	C(11)	-152.9(2)
C(12)	C(13)	C(14)	C(15)	0.7(4)
C(13)	C(14)	C(15)	C(16)	-1.1(4)
C(14)	C(15)	C(16)	C(17)	0.5(4)
C(15)	C(16)	C(17)	C(18)	0.7(4)
C(16)	C(17)	C(12)	C(13)	-1.1(3)
C(17)	C(12)	C(13)	C(14)	0.4(3)
C(6)	C(7)	C(8)	C(9)	-0.4(3)
C(7)	C(8)	C(9)	C(10)	0.5(3)
C(8)	C(9)	C(10)	C(11)	-0.6(3)

TABLE 3.2.6. (Cont.)

C(9)	C(10)	C(11)	C(6)	0.6(3)
C(10)	C(11)	C(6)	C(7)	-0.4(3)
C(11)	C(6)	C(7)	C(8)	-0.6(3)

TABLE 3.2.7.

Least-squares planes for various portions of the molecular framework in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations

Plane (1) = $-0.1689X' - 0.9657Y' + 0.1972Z' = -5.3426$

Plane (2) = $0.6985X' - 0.3012Y' + 0.6491Z' = 1.4305$

Plane (3) = $-0.6563X' + 0.4719Y' + 0.5887Z' = 1.2715$

(b) Deviations (Å) of Atoms from Planes (Starred Atoms Define Plane)

Plane (1) = C(6)* -0.001(2), C(7)* 0.001(2), C(8)* -0.001(3), C(9)* 0.002(2), C(10)* -0.003(2), C(11)* 0.002(2), C(1) 0.097(2)

Plane (2) = C(12)* -0.005(2), C(13)* -0.001(2), C(14)* 0.006(2) C(15)* -0.006(3), C(16)* -0.001(3), C(17)* 0.006(2), C(1) -0.079

Plane (3) = N(1)* 0.002(2), N(2)* 0.002(2), C(5)* -0.006(2), S(1)* 0.002(1), C(1) 0.227(2), C(2) 0.243(2), C(3) -0.205(2), C(4) 0.084(2), O(1) 0.046(2)

(c) Dihedral Angles (°) between Planes

(1) - (2) 72.5° (1) - (3) 103.2° (2) - (3) 102.6°

TABLE 3.2.8.

Intramolecular Non-bonding Distances < 3.6Å

ATOM A	ATOM B		Å
O(1)	C(6)		2.99
O(1)	C(5)		3.31
O(1)	C(12)		3.18
O(1)	C(13)		3.18
O(1)	C(7)		3.42
N(1)	C(11)		2.85
N(1)	C(13)		3.42
N(1)	C(17)		3.13
N(2)	C(6)		3.52
N(2)	C(12)		3.43
C(11)	C(4)		3.26
C(5)	C(6)		3.41
C(5)	C(12)		3.26
C(2)	C(6)		3.42
C(2)	C(11)		3.61
C(2)	C(12)		3.15
C(2)	C(17)		3.24
C(6)	C(17)		3.06
C(7)	C(4)		3.39
C(7)	C(12)		2.93
C(7)	C(17)		3.21
C(4)	C(13)		2.87
Intermolecular Non-bonding Distances < 3.8Å			
C(9)	N(2)	I	3.64
S(1)	C(15)	II	3.73
S(1)	C(16)	II	3.63
C(3)	C(14)	II	3.76
C(3)	C(8)	III	3.58
C(3)	C(9)	III	3.68
C(2)	C(8)	III	3.64
C(2)	C(9)	III	3.40
C(2)	C(10)	III	3.48
O(1)	N(1)	IV	3.57
O(1)	C(5)	IV	3.59
O(1)	S(1)	IV	3.63
O(1)	C(3)	IV	3.31
O(1)	C(2)	IV	3.76
O(1)	C(11)	IV	3.35
O(13)	N(2)	IV	3.54

TABLE 3.2.8. (Cont.)

ATOM A	ATOM B		Å
Intermolecular Non-bonding Distances < 3.8Å			
C(5)	S(1)	V	3.57
C(9)	S(1)	V	3.62

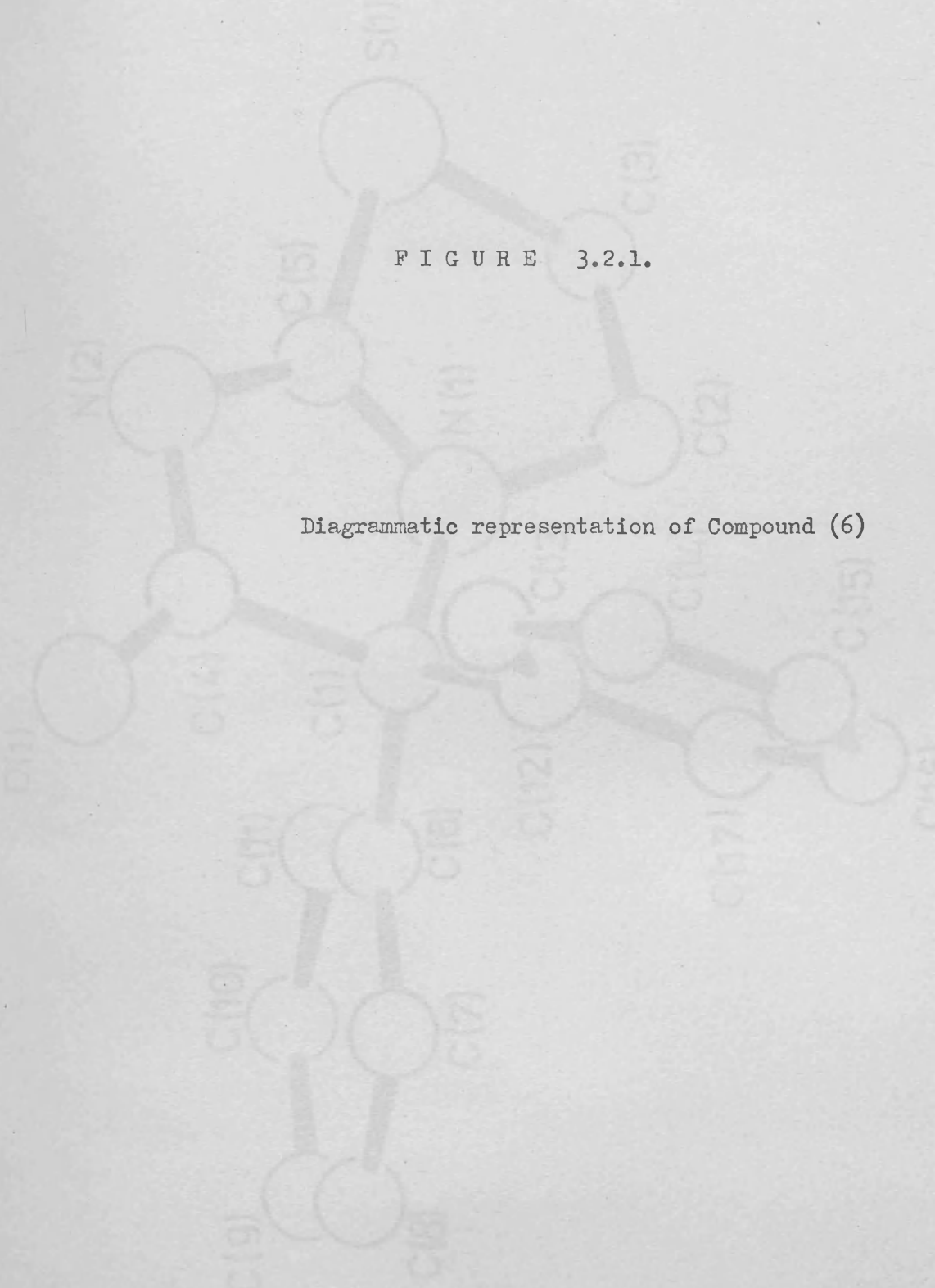
where the position of atom B is given by,

I = 1+x, y, z
II = -x, 1-y, -z
III = 1-x, 1-y, -z
IV = x, $\frac{1}{2}$-y, $\frac{1}{2}$+z
V = 1+x, $\frac{1}{2}$-y, $\frac{1}{2}$+z

TABLE 3.2.9.

Bond	Compound (3)	Compound (6)	Compound (11)
C(5) - N(1)	1.358(6)	1.340(2)	1.381(6)
C(5) - N(2)	1.282(5)	1.317(3)	1.267(6)
C(5) - S(1)	1.744(4)	1.723(2)	1.752(4)
N(2) - C(4)	1.483(6)	1.383(3)	1.497(7)
C(4) - O(1)	-	1.213(3)	-

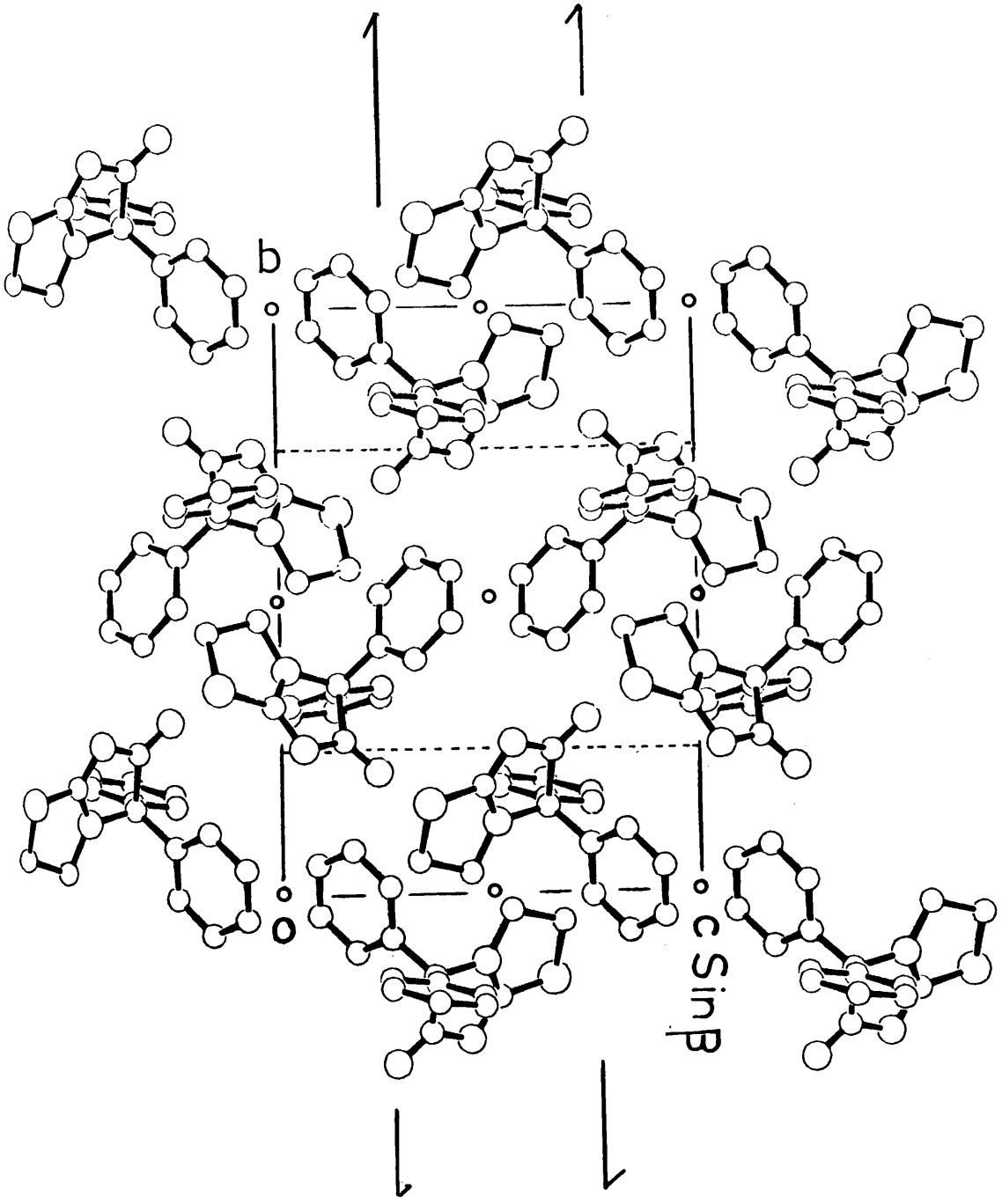
F I G U R E 3.2.1.



Diagrammatic representation of Compound (6)

F I G U R E 3.2.2.

Crystal-packing arrangements for Compound (6)


b
c SinB

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* **Present address - Imperial Chemical Industries Ltd., Pharmaceuticals Division, Mereside, Alderley Park, MACCLESFIELD, Cheshire SK10 4TG.**

PART 4

X-RAY STUDIES OF THREE YLIDES

INTRODUCTION

The term 'ylide' which was devised by Wittig, in 1944[1], and referred to compounds of the type (X^+-C^-<) has now come to represent a complete series of (X^+-Y^-) compounds. An extensive coverage of the reactions, preparations and physical properties of ylides in general was published in a monograph by Johnson in 1966[2] and has since been updated, in a review on the chemistry of ylides, by Hudson.[3]

The chemical stability of ylides relative to reactive anionic species suggests that the presence of the 'onium residue ($-X^+$) adjacent to the negative Y atom must afford some degree of stabilisation within the compound. In addition to such stabilisation effects, almost all stable compounds of this type have an electron-withdrawing group attached to the Y portion of the molecule, which will enhance the stabilisation of the negative atom by virtue of its ability to delocalise the negative charge. It would thus appear that the stability of ylides is dependent on the effectiveness of the stabilising group, the electronegativity of the negative atom Y^- (governing the ability of the atom to successfully bear a negative charge), and also the stabilising effect resulting from the involvement of the 'onium residue X^+.

It has been observed[2,3] that, in general, second-row ylides (X=S,P) are, by far, more stable than first-row ylides (X=O,N), suggesting that stabilisation of the negative Y atom by the 'onium residue may, in second-row ylides be attributed to some involvement other than the simple coulombic intractions available to first-row compounds. Having suggested that 3d-orbitals in second-row elements would be

too diffuse to contribute to molecular binding unless modified sufficiently by molecular environment, Craig et al.[4] proposed that the presence of a formal positive charge on the second-row atom, or the attachment of very electronegative ligands could result in contraction of the 3d-orbitals such that overlap with suitably orientated p-orbitals on an adjacent atom might be feasible. In 1969, Mitchell[5] reviewed the evidence for and against 3d-orbital involvement in bonding, and it would appear that proposals of d-orbital involvement are justified providing a favourable molecular environment exists. Since the σ-bond framework in second-row ylides can be formed without utilising the 3d-orbitals of the 'onium residue, the type of interaction involving the d-orbitals can be assumed to be π in nature. For those second-row ylides in which Y=N-, the π-bonding arrangements may be likened[6-10] to those postulated by Craig and Paddock[11] for cyclic phosphonitrilic compounds and to those suggested by Cruickshank[12] for P-O-P bridged systems, and may best be described by consideration of two equivalent nitrogen-electron lone-pairs interacting with suitable combination of d-orbitals on the 'onium residue, thus forming bonding-overlaps which may theoretically be resolved into two mutually-perpendicular components named, (i)π' in the plane of the σ-bond framework and, (ii)π perpendicular to the plane of the σ-framework. It is also feasible that similar $p\pi - d\pi$ interactions may occur between the nitrogen lone-pairs of electrons and an adjacent second-row atom in the stabilising group, provided the remaining substituents of the stabilising group are sufficiently electronegative to induce the aforementioned contraction of the 3d-orbitals necessary for efficient $p\pi - d\pi$ overlap. Under

these conditions, it is possible that the bonding situation may be regarded as the appropriate 3d-orbitals on the 'onium and stabilising group competing to delocalise the lone pairs of the nitrogen atom and it may be that the availability of the orbitals in the stabilising group will have a marked effect on the $X^{+}-N^{-}$ bond and may also affect the conformations of the systems.

In order to obtain further information regarding the bonding system and conformations exhibited by second-row ylides containing the further possibility of $p\pi - d\pi$ bonding with the stabilising group, the crystal-structure analyses of three such ylides have been carried out and the appropriate dimensions compared with those of other known systems. Section 4.1. concerns the crystal-structure analyses of two phosphonium imines (I and II) whilst section 4.2. investigates the structure of an unusual sulphonium imine (IX).

S E C T I O N 4.1.

THE CRYSTAL AND MOLECULAR STRUCTURES OF

N-DICHLOROPHOSPHINOYL-P-TRIPHENYLPHOSPHAZENE

and

N-DIPHENYLPHOSPHINOYL-P-TRIPHENYLPHOSPHAZENE

INTRODUCTION

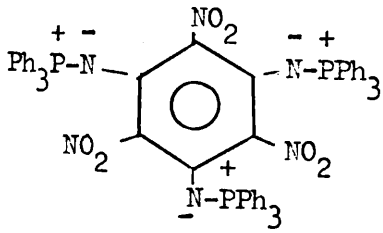
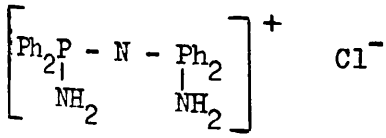
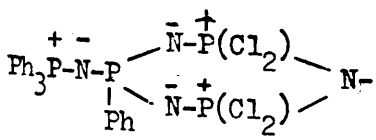
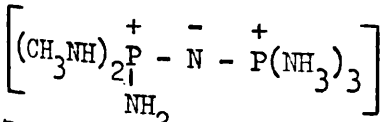
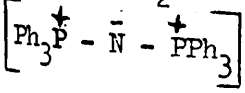
The two compounds I and II may best be regarded as triphenyl phosphonium-imine ylides ($X^{+}=Ph_3P^{+}-$, $Y=N-$), which may afford opportunities for delocalisation of the lone pairs of electrons on the nitrogen atom into vacant 3d-orbitals of suitable energy on the phosphorous atoms of both the stabilising and 'onium groups. In order to investigate the bonding patterns and conformational properties within these molecules and to compare the possible effects of differing stabilising groups on the $X^{+}-Y^{-}$ bond, X-ray analyses of both compounds have been carried out.

$Cl_2P(O)-\overset{-}{N}-\overset{+}{P}Ph_3$

(I)

$Ph_2P(O)-\overset{-}{N}-\overset{+}{P}Ph_3$

(II)

(III)	Reference
(a) $Ph_3\overset{+}{P}-\overset{-}{N}-C_6H_4-pBr$	9
(b) $Ph_3\overset{+}{P}-\overset{-}{N}-SO_2-C_6H_4-pMe$	16
(c) 	19
(d) 	18
(e) 	17
(f) 	20
(g) 	21

(IV)

(a) $MeP(O)Cl_2$	28
(b) $(MeO)_3P(O)$	28

(V) Reference

(a) $(Cl)_2P(O)-N(Ph)-P(S)(Cl)_2$ 29

(b) $(Cl)_2P(O)-N=C=O$ 28

(VI)

(a) $Ph_2P(O)-NH-CH_2-CH_2-Ph$ 30
(2 molecules/asymetric unit)

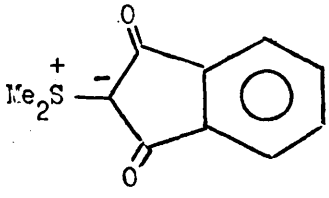
(b) $Ph_2P(O)-N(Me)-CH_2-CH_2-Ph$ 30

(VII)

(a) $Ph_3\overset{+}{P}-C(Cl)-C(O)-Ph$ 35

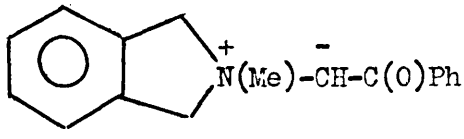
(b) $Et_2\overset{+}{S}-\overset{-}{N}-C(O)-CHCl_2$ 8

(c) $Me_3\overset{+}{N}-\overset{-}{N}-C(O)Ph$ 36, 37

(d)  38

(e) $Me_3\overset{+}{N}-\overset{-}{N}-NO_2$ 36, 37

(f) 39



EXPERIMENTAL

N-dichlorophosphinoyl-P-triphenylphosphazene.

CRYSTAL DATA

$C_{18}H_{15}P_2NOCl_2$; M=394.2; Monoclinic, a=9.218Å, b=10.284Å, c=19.456Å, β=91.18°; U=1843.99Å^3; D_c=1.43 g.cm.$^{-3}$; D_m=1.45 g.cm.$^{-3}$; Z=4; F_{000}=808; Space group $P2_1/c$; μ =5.32 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å; μ=48.62 cm.$^{-1}$; Cu-Kα X-rays; λ=1.5418Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs, taken with Cu-Kα (λ=1.5418Å) radiation and from precession photographs taken with Mo-Kα (λ=0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_1/c$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.2 x 0.3 x 0.2 mm.) rotating about a, to graphite-monochromated Cu radiation (Cu-Kα_1) and by using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 136°$) to collect 3012 independent reflections with $I \geqslant 2\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The structure was determined by centrosymmetric Direct Methods, using the computer programs DATRDN, NORMSF, SINGEN, TANGEN, FOURR, Fc and

CRYLSQ, contained in the X-ray '72 suite of programs.

Phase determination was initiated by assigning phases to five reflections, three of which defined the unit cell origin and were given phase values of 360° and two of which were chosen because of their ability to form a large number of $\sum_2$ phase relationships. Since the phases of the two non-origin defining reflections were unknown, they were given all possible combinations of the values 360° and 180° to initiate a series of calculations utilising the tangent formula of Direct Methods, the correct starting set proving to be that shown in Table 4.1.1., from which the phases of 458 reflections with $E \geqslant 1.4$ were assigned.

An E-map based on these 458 reflections revealed the positions of all non-hydrogen atoms and subsequent structure-factor and electron-density calculations confirmed these positions. An arbitrary temperature factor U_{iso} was assigned to each atom and after each calculation the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Since full-matrix least-squares refinement of the total structure was hindered by the limitations of the computer program (CRYLSQ), the structure was defined in terms of two groups of atoms, and the positional and vibrational parameters of one group were refined by least-squares calculations (utilising structure-factor contributions from all atoms) before refinement of the second group by similar calculations. Details of the refinement are given in Table 4.1.2.(a) which shows convergence of positional, vibrational and scale parameters after 13 cycles of least-squares refinement when R was

0.116 and R' was 0.017.

Hydrogen-atom positions could not be adequately determined by examination of difference syntheses but each position was calculated and assigned a fixed isotropic temperature factor $U_{iso}=0.03\text{Å}^2$. Structure-factor contributions from these atoms were included in subsequent calculations but no refinement of positional or vibrational parameters was carried out.

The degree of refinement thus obtained was insufficient for meaningful interpretation of the relevant geometries and it was suspected that a fault in the diffractometer may have rendered some of the data to be of doubtful value. The data were thus recollected from the same crystal by exposing it to graphite-monochromated Mo-radiation (Mo-Kα_1) and using the θ,ω scan technique (in the range $0<2\theta\leqslant 54^\circ$) to collect 2838 independent reflections with $I\geqslant 2\sigma_i$ ($\sigma_i=\sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made before using the data for subsequent structure refinement.

Refinement of positional, vibrational and scale parameters converged after 9 cycles of least-squares calculations when R was 0.043 and R' was 0.004. Details of refinement are given in Table 4.1.2.(b).

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure factors. The scheme was of the form;

If A $|Fo| > Fc$, $W=10^{-9}$,

otherwise W=X.Y.

with X=1 if $\sin\theta > B$, else $X= \frac{\sin\theta}{B}$

and Y=1 if $|Fo| > C$, else $Y= \frac{C}{|F_o|}$

The most suitable values for A, B and C were found to be 0.75, 0.6 and 10.0 respectively. At the conclusion of refinement, difference syntheses and electron-density calculations revealed no errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (52). Observed and calculated structure factors are listed in Appendix 8. Positional and vibrational parameters with e.s.d.s are given in Table 4.1.3. Values of e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

EXPERIMENTAL

N-diphenylphosphinoyl-P-triphenylphosphazene

CRYSTAL DATA

$C_{30}H_{25}P_2NO$; M=477.46; Orthorhombic, a=17.755Å, b=15.325Å, c=8.973Å; U=2441.33Å^3; D_c=1.30 g.cm.$^{-3}$; D_m=1.31 g.cm.$^{-3}$, Z=4; F_{ooo}=1000; Space group $Pna2_1$; μ=2.07 cm.$^{-1}$; Mo-Kα X-rays; λ=0.7107Å; μ=17.78 cm.$^{-1}$; Cu-Kα X-rays; λ=1.5418Å.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from Weissenberg and oscillation photographs taken with Cu-Kα (λ=1.5418Å) radiation, and from precession photographs, taken with Mo-Kα (λ=0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space groups $Pna2_1$ or Pnma were indicated by systematic absences but subsequent structure solution and refinement verified the space group to be $Pna2_1$.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a small crystal (0.3 x 0.4 x 0.2 mm.) rotating about c, to graphite-monochromated Cu radiation (Cu-Kα_1) and using the θ,ω scan technique (in the range $0<2\theta\leqslant136^\circ$) to collect 2274 independent reflections with $I\geqslant 2\sigma_i$ ($\sigma_i=\sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were made but absorption effects were considered small and no corrections were applied.

STRUCTURE DETERMINATION

The positions of both phosphorous atoms were determined from the

Patterson function, the z-coordinate of one being arbitrarily assigned the value 0.5000 to define the origin in space group $Pna2_1$. This value was held constant throughout subsequent refinement.

Initial attempts at structure determination were hindered by the inevitable presence of pseudo-symmetry resulting from the arbitrary choice of the phosphorous z-coordinate. An electron-density calculation based on those phases appropriate to the phosphorous atoms, revealed several plausible atomic sites. Careful choice of atomic positions from the range of pseudo-symmetrically related peaks, and their inclusion in a subsequent round of structure-factor and electron-density calculations, reduced the extent of the pseudo-symmetry. It hence proved possible to determine all non-hydrogen atomic positions after several rounds of structure-factor and electron-density calculations in which all non-hydrogen atoms had been assigned an arbitrary isotropic temperature-factor $U_{iso}=0.05\text{Å}^2$. After each calculation the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

Since full-matrix least-squares refinement of the total structure was hindered by the limitations of the computer program (CRYLSQ), the structure was defined in terms of two groups of atoms, the positional and vibrational parameters of one group being refined by least-squares calculations (utilising structure-factor contributions from all atoms) before refinement of the second group, by similar calculations. Details of initial refinement are given in Table 4.1.9.(a) which shows the degree of refinement after 11 cycles of least-squares calculations when R was 0.143 and R' was 0.163.

The degree of refinement thus obtained was insufficient for meaningful interpretation of the relevant geometries and it was suspected that a fault in the diffractometer may have rendered some of the data to be of doubtful value. The data were thus recollected from the same crystal by exposing it to graphite-monochromated Mo-radiation (Mo-Kα_1) and using the θ,ω scan technique (in the range $0 < 2\theta \leqslant 60^{o}$) to collect 2952 independent reflections with $I \geqslant 2\,\sigma_i$ ($\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made before using this data in subsequent structure refinement in which positional and vibrational parameters converged after 10 cycles of least-squares calculations, when R was 0.042 and R' was 0.003. Details of this refinement are given in Table 4.1.9.(b).

Difference syntheses revealed atomic positions for all hydrogen atoms which were arbitrarily assigned temperature factors $U_{iso}=0.03\text{Å}^2$ and included in all subsequent calculations.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) analyses of observed and calculated structure-factors. The scheme was of the form;

If $A|Fo| > Fc$, $W=10^{-9}$,

otherwise W=X.Y.

with X=1 if $\sin\theta > B$, else $X=\frac{\sin\theta}{B}$

and Y=1 if Fo C, else $Y=\frac{C}{|F_o|}$

The most suitable values for A, B and C were found to be 0.75, 0.60 and 10.00 respectively. At the conclusion of refinement, difference syntheses and electron-density calculations revealed no errors in the structure.

In all structure-factor calculations, the atomic scattering factors used are given in reference (52). Observed and calculated structure-factors are listed in Appendix 9. Positional and vibrational parameters with e.s.d.s are given in Table 4.1.10. Values of e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

COMPOUNDS I AND II

DISCUSSION

Diagrammatic representations of both molecules (I and II) are given in Figures 4.1.1. and 4.1.2. respectively, hydrogen atoms being omitted for clarity. Details of bond lengths, bond angles, torsion angles, least-squares planes, intramolecular non-bonding distances and intermolecular distances are shown in Tables 4.1.4. to 4.1.8. and Tables 4.1.11. to 4.1.15. for compounds I and II respectively.

In both compounds, the stereochemistry at atoms P(1) and P(2) is approximately tetrahedral, observed distortions from ideal tetrahedral valency angles at atom P(2) [Cl(1)P(2)Cl(2)100.9(1)°, N(1)P(2)O(1)117.6(1)°, C(20)P(2)C(26)102.8(2) and N(1)P(2)O(1) 120.1(1)°] being perhaps attributable to electrostatic repulsions between multiple bonds [P(2) —O(1) and P(2) — N(1)] and to the decrease in bond angle associated with the presence of bonded electronegative substituents[13].

A significant degree of $p\pi$-$d\pi$ bonding is suggested by bond lengths P(1) - N(1) [1.582(2) and 1.556(2)Å respectively for compounds I and II] and P(2) - N(1) [1.557(2) and 1.605(2)Å] which are considerably shorter than those values usually associated with P-N single bonds [1.80 from Pauling's covalent radii[14] and 1.77(2)Å in sodium phosphoramide[15]] but are comparable with corresponding P-N bond-distances reported for compounds, such as (III a-g)[9,16-21] [values range from 1.54(2) - 1.58(1)Å] and several cyclic phosphonitrilic compounds (e.g. the average P-N bond length in

$(Cl_2PN)_4$[22] is, 1.570Å). In addition, bond angles P(1)N(1)P(2) [139.7(2) and 146.0(2)° respectively for compounds I and II] are larger than might otherwise be expected at an sp^2 hybridised nitrogen atom, but agree well with those values reported for compounds such as (III d-g)[18-21] [values range from ca 129 - 147°] and are similar to corresponding values reported in several cyclic phosphonitrilic compounds whose ring size is sufficiently large that the angle is not unduly restricted by requirements of ring geometry e.g. $(Cl_2PN)_4$[22], $(F_2PN)_4$[23] and $(Cl_2PN)_5$[24] have average P-N-P angles in the range 131.3 - 148.6°. Although it has been postulated[25] that large angles between bonds linking first and second-row elements may be related to a partial back-donation of electronic charge from a lone-pair orbital of the first-row atom into appropriate 3d orbitals of the second-row atom, and that the large value of the bond angle may be considered as a means of optimising π-type bonding, it is difficult to differentiate between this effect and the expected bond-angle enlargement resulting from electrostatic repulsions between electron-densities in multiple bonds and possible steric interactions between substituents bonded to the respective P(1) and P(2) atoms. The effects of such steric interactions may be reflected in the increased value of the P-N-P angle in compound II, relative to compound I, the P(2)-bonded phenyl substituents in (II), being perhaps more bulky than the corresponding chlorine atoms in (I).

That electronegative ligands may induce contraction of 3d orbitals, thus enabling possible $p\pi$-$d\pi$ overlap, has previously been noted (see Introduction) and it follows that the greater electronegativity of the chlorine ligands with respect to phenyl ligands may result

in more efficient $p\pi$ -$d\pi$ [P(2)] orbital overlap in compound I relative to II. These effects combined with the greater inductive effect of chlorine ligands may thus afford an explanation for the significantly smaller P(2) - O(1) and P(2) - N(1) bond lengths observed in compound I [1.459(2) and 1.557(2)Å respectively] relative to compound II [1.489(3) and 1.605(2)Å]. That the P(1) - N(1) bond length in I [1.582(2)Å] is significantly larger than the corresponding value in II, [1.556(2)Å] suggests that $p\pi$ [N(1)] - $d\pi$ [P(1)] bonding may be weaker in compound I than in II and that the apparently increased $p\pi$ [N(1)] - $d\pi$ [P(2)] bonding in I relative to II may occur at the expense of $p\pi$ [N(1)] - $d\pi$ [P(1)] bonding in the former compound. These results thus appear to indicate that both the phosphorus atoms of the stabilising and 'onium groups are competing for delocalisation of the lone-pairs of electrons on the nitrogen atom into their respective vacant 3d-orbitals, and that the efficiency of subsequent delocalisation over the P(1) - N(1) - P(2) system is dependent on the availability of the 3d orbitals on the appropriate atom in the stabilising group. Moreover, it has been calculated[26] that a P-N bond length which results from maximum $p\pi$ - $d\pi$ overlap for the formation of one $p\pi$ - $d\pi$ bond in addition to the normal bond, has a value of ca 1.635Å and although such a value may be dependent on the electronegativity of the phosphorus-atom substituents, it is reasonable to assume that the significantly shorter P-N bond lengths observed in compounds I and II may be due to involvement of more than one such $p\pi$ - $d\pi$ interaction resulting from delocalisation of both lone-pairs of electrons on the nitrogen atom over the P(1) - N(1) - P(2) system.

Similar $p\pi$ - $d\pi$ bonding between atoms P(2) and O(1) is also

suggested by bond lengths P(2) - O(1) [1.459(2) and 1.489(3)Å for compounds I and II respectively] which are substantially shorter than might be expected for single bonds [single bonds in phosphates are usually in the range 1.55 - 1.64Å[25], the largest known being 1.68(3)Å in sodium triphosphate[27]] but which are typical of corresponding values reported for compounds such as IV (a) [1.448(5)Å[28]] and IV(b) [1.477(6)Å[28]]. Investigations of P(2) - O(1) bond-lengthening resulting from possible $d\pi - p\pi$ conjugation between this bond and the previously discussed P(1) - N(1) - P(2) system, may be carried out by comparisons of the corresponding P=O bond lengths in compounds, I [1.459(2)Å], V(a) [1.449(6)Å[29]] and V(b) [1.455(10)Å[28]], and II [1.489(3)Å], VI(a) [1.481(4)Å, 1.478(4)Å[30]] and VI (b) [1.489(1)Å[30]], which indicate that any such effects are small.

Table 4.1.16. summarises relevant structural features in several reported cyclic phosphonitrilic compounds[22-24,31-34] and enables comparisons to be made between the geometries of the O(1)P(2)N(1)P(1) system in compounds I and II and the PNPN portion of the cyclic phosphonitrilic compounds. Similarities in corresponding valency angles and P - N bond lengths suggests that $d\pi - p\pi$ bonding in the aforementioned portion of the compounds I and II may be analogous to that postulated for cyclic phosphonitrilic compounds[11], with two lone-pairs of electrons on both the nitrogen and oxygen atoms being delocalised into approximately-orientated 3d orbitals in the phosphorus atoms, in such a way as to form $p\pi - d\pi$ bonds (π and π') in mutually perpendicular planes. While π' -bonding (in-plane) is maximised in planar cyclic molecules e.g.

$(Cl_2PN)_5$ and $(F_2PN)_4$, it has been suggested[11] that the availability of several different d-orbitals at phosphorus is such that the total $p\pi - d\pi$ overlap changes only slowly with distortions from planarity, and Craig and Paddock[11] have calculated that while π' overlap is lost in going from a planar to a tub configuration (in cyclic molecules), some π-bonding is subsequently gained, with the result that such systems may be flexible without gross loss of overall π-bonding efficiency. It would thus seem that the conformations required for such $p\pi - d\pi$ conjugation are less stringently controlled than in the analogous situation of $p\pi - p\pi$ conjugation which imposes a planar requirement for efficient orbital overlap, e.g. benzene. Similarly, it is feasible that, while π' bonding may be maximised in a planar arrangement of atoms P(1)N(1)P(2) and O(1), loss of such bonding due to deviations from planarity may be accompanied by an increase in π-bonding resulting from overlap between nitrogen electron lone-pairs and suitable combinations of 3d-orbitals outwith the plane of the σ framework. Hence, although the maximum amount of π and π' bonding may occur in a planar conformation, the loss of π-energy due to distortions from this ideal arrangement may be less than in $p\pi - p\pi$ conjugated systems. Evidence supporting the suggestion may derive from consideration of the relevant torsion angles in compounds (VII a-f[8,35-39]) which show that in those ylides in which only $p\pi - d\pi$ interactions are possible between the negatively charged Y atom and the stabilising group, the $X^{+} - Y^{-} - Z = O$ system is approximately planar [torsion angle values range from $0^\circ - 8.3^\circ$], whilst the torsion angles P(1)N(1)P(2)O(1) [170.1(2) and $-25.3(4)^\circ$ for I and II respectively] in the

present molecules show a greater deviation from this range of values. The transoid and cisoid nature of the P(1) and O(1) atoms with respect to each other, in compounds I and II respectively, may possibly be attributed to differing non-bonding interactions in the two compounds. Figure 4.1.3. illustrates the conformations of the substituents about bonds P(2) - N(1) in both compounds. The conformation thus adopted by compound I may perhaps be rationalised by consideration of possible electrostatic interactions between the electronegative chlorine ligands and the phosphonium atom P(1) [Cl(1)··· P(1) 3.70Å, Cl(2)···P(1) 3.85Å and possible steric interactions e.g. Cl(2)···C(7) 3.69Å, Cl(2)···C(8) 3.61Å, whilst in II, the cisoid conformation of atoms P(1) and O(1) with respect to each other may represent the minimisation of steric interactions between the phosphonium-bonded phenyl groups and the phenyl ligands of the stabilising group, and between atoms P(1) and O(1) [3.69Å]. Although there are no P(1)-carbon···P(2)-carbon contact distances less than 3.7Å, the enlargement of bond angle P(1)N(1)P(2) relative to I has previously been noted. It would thus appear that the conformation adopted by compounds such as I and II may provide a balance between maximum $p\pi - d\pi$ orbital overlap and non-bonding interactions, and that the range of conformational possibilities arising from $p\pi - d\pi$ conjugation may be greater than is possible in the analogous $p\pi - p\pi$ conjugated systems.

In both compounds, the phosphonium-bonded phenyl groups, which are planar, within experimental error, are arranged in the familiar "propeller" conformation (interplanar angles are 81.7, 96.2 and 117.6° in I and 85.8, 98.1 and 79.9° in II), with the phosphorus atom lying slightly out of plane relative to each ring, as has

been reported for various triphenylphosphine derivatives,[9,10,40-43]. Similarly, those phenyl groups bonded to atom P(2), in II, are planar within experimental error, their orientation with respect to each other being defined by the dihedral angle [98.1°] between their planes. Examination of the previously undiscussed dimensions of compounds I and II, in particular the P - C(phenyl) [mean 1.797(5) and 1.817(4) respectively], P(1)-bonded phenyl C - C [mean 1.387(8) and 1.390(8)Å respectively], P(2)-bonded phenyl C - C [mean 1.389(5)Å] bonds and endocyclic phenyl valency angles [mean 120.0 in all phenyl groups], reveals values which do not differ significantly from accepted values[44].

The absence of short intermolecular contacts in both compounds implies that the crystal-packing arrangements are dominated by Van der Waal's forces. Diagrams illustrating these crystal-packing arrangements are given in Figures 4.1.4. and 4.1.5.

TABLE 4.1.1.

h	k	l	E	Phi	
1	2	-14	3.45	360°	Origin Defining Reflections
2	9	1	3.18	360°	
1	8	1	3.14	360°	
0	1	11	2.49	180°	
4	2	4	2.39	180°	

TABLE 4.1.2.(a)

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} of all non-hydrogen atoms; scale parameter; unit weights.	1 - 4	0.184	0.037
x, y, z, U_{ij} (i, j = 1, 2, 3) of C atoms only; all other atoms were included in the calculation but were not refined; scale parameter; unit weights.	5 - 8	0.147	0.029
x, y, z, U_{ij} (i, j = 1, 2, 3) of P N O Cl atoms only; all other atoms were included in the calculation but were not refined; scale parameter; unit weights.	9 - 13	0.116	0.017

TABLE 4.1.2. (b)

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
Scale parameter; all atoms were included in the calculation but were not refined; unit weights;	1	0.099	0.013
x, y, z, U_{ij} (i, j = 1, 2, 3) of P N O and Cl atoms; H and C atoms in calculation but not refined; scale parameter; unit weights.	2 - 3	0.064	0.007
x, y, z, U_{ij} (i, j = 1, 2, 3) of C atoms; all other atoms in calculation but not refined; scale parameter; unit weights.	4 - 5	0.051	0.004
x, y, z, U_{ij} (i, j = 1, 2, 3) of P N O and Cl atoms; H and C atoms in calculation but not refined; scale parameter; weighting scheme adjusted.	6 - 7	0.045	0.003

TABLE 4.1.2. (b) (Cont.)

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{ij} (i, j = 1, 2, 3) of C atoms; all other atoms in calculation but not refined; scale parameter; weighting scheme adjusted.	8 - 9	0.043	0.004

TABLE 4.1.3.

(a) Atomic Fractional Coordinates and E.S.Ds of Compound (I)

ATOM	x/a	y/b	z/c
P(1)	0.67681(6)	0.28504(6)	0.08953(3)
P(2)	0.67082(7)	0.51012(6)	0.18314(4)
N(1)	0.7170(3)	0.4212(2)	0.1226(1)
O(1)	0.7615(3)	0.6228(2)	0.1991(1)
Cl(1)	0.64863(11)	0.40044(9)	0.26876(4)
Cl(2)	0.46370(9)	0.56988(9)	0.16679(5)
C(1)	0.7716(5)	0.2768(5)	0.0097(2)
C(2)	0.8243(6)	0.3894(5)	-0.0188(3)
C(3)	0.9034(7)	0.3821(6)	-0.0796(3)
C(4)	0.9276(6)	0.2645(6)	-0.1100(3)
C(5)	0.8751(7)	0.1522(6)	-0.0820(3)
C(6)	0.7953(6)	0.1571(6)	-0.0216(3)
C(7)	0.4860(5)	0.2594(5)	0.0725(2)
C(8)	0.3971(5)	0.2317(6)	0.1279(3)
C(9)	0.2488(5)	0.2149(6)	0.1161(3)
C(10)	0.1926(5)	0.2262(7)	0.0505(4)
C(11)	0.2796(6)	0.2553(7)	-0.0047(3)
C(12)	0.4284(5)	0.2720(6)	0.0066(3)
C(13)	0.7383(5)	0.1509(5)	0.1409(2)
C(14)	0.6729(5)	0.0305(5)	0.1383(3)
C(15)	0.7254(7)	-0.0734(6)	0.1765(3)
C(16)	0.8482(7)	-0.0556(7)	0.2180(3)
C(17)	0.9171(6)	0.0643(7)	0.2203(3)
C(18)	0.8641(5)	0.1678(6)	0.1823(3)

TABLE 4.1.3.

(b) Hydrogen-atom Fractional Coordinates

ATOM	x/a	y/b	z/c
H(2)	0.8076	0.4768	-0.0036
H(3)	0.9420	0.4647	-0.1010
H(4)	0.9848	0.2585	-0.1527
H(5)	0.8930	0.0668	-0.1048
H(6)	0.7556	0.0753	-0.0012
H(8)	0.4384	0.2240	0.1756
H(9)	0.1836	0.1943	0.1550
H(10)	0.0858	0.2128	0.0422
H(11)	0.2364	0.2644	-0.0518
H(12)	0.4924	0.2923	-0.0327
H(14)	0.5844	0.0175	0.1080
H(15)	0.6777	-0.1598	0.1743
H(16)	0.8864	-0.1287	0.2469
H(17)	1.0061	0.0756	0.2498
H(18)	0.9152	0.2538	0.1839

TABLE 4.1.3.

(c) Anisotropic Temperature Factors and E.S.Ds ($Å^2$)

ATOM	U_{11}	U_{22}	U_{13}	U_{12}	U_{13}	U_{23}
P(1)	0.0272	0.0385	0.0371	-0.0016	0.0043	0.0005
P(2)	0.0378	0.0363	0.0434	0.0006	0.0017	-0.0008
N(1)	0.042(1)	0.046(1)	0.048(1)	-0.006(1)	0.011(1)	-0.003(1)
O(1)	0.061(1)	0.045(1)	0.085(2)	-0.006(1)	-0.002(1)	-0.013(1)
Cl(1)	0.0800	0.0679	0.0439	0.0154	0.0097	0.0107
Cl(2)	0.0453	0.0720	0.0736	0.0192	0.0026	0.0052
C(1)	0.027	0.053	0.039	-0.001	0.003	-0.001
C(2)	0.051	0.052	0.056	0.001	0.013	0.005
C(3)	0.063	0.073	0.054	-0.003	0.019	0.013
C(4)	0.052	0.088	0.046	0.005	0.014	-0.001
C(5)	0.066	0.073	0.052	0.004	0.014	-0.015
C(6)	0.053	0.057	0.050	-0.007	0.009	-0.006
C(7)	0.028	0.045	0.049	0.001	0.002	0.002
C(8)	0.033	0.066	0.053	-0.007	0.005	0.004
C(9)	0.029	0.077	0.077	-0.006	0.010	0.003
C(10)	0.028	0.077	0.092	-0.001	-0.006	-0.003
C(11)	0.041	0.094	0.070	0.008	-0.018	0.001
C(12)	0.035	0.074	0.053	0.004	-0.001	0.006
C(13)	0.030	0.046	0.040	0.003	0.005	0.001
C(14)	0.040	0.047	0.062	0.001	0.001	0.001
C(15)	0.060	0.054	0.080	0.009	0.021	0.011
C(16)	0.070	0.073	0.060	0.037	0.016	0.016
C(17)	0.048	0.092	0.057	0.029	-0.007	-0.004
C(18)	0.036	0.061	0.057	0.008	-0.002	-0.005
Average E.S.Ds						
P	0.0003	0.0003	0.0003	0.0003	0.0002	0.0003
Cl	0.0005	0.0005	0.0005	0.0004	0.0004	0.0004
C	0.003	0.003	0.004	0.003	0.002	0.003

TABLE 4.1.4.

Intramolecular Bonded Distances and E.S.Ds (Å) for Compound (I)

ATOM A	ATOM B	Å
P(1)	N(1)	1.582(2)
P(1)	C(1)	1.799(4)
P(1)	C(7)	1.803(5)
P(1)	C(13)	1.789(5)
P(2)	N(1)	1.557(2)
P(2)	O(1)	1.459(2)
P(2)	Cl(1)	2.025(1)
P(2)	Cl(2)	2.025(1)
C(1)	C(2)	1.377(7)
C(1)	C(6)	1.393(8)
C(2)	C(3)	1.404(8)
C(3)	C(4)	1.367(9)
C(4)	C(5)	1.369(9)
C(5)	C(6)	1.399(8)
C(7)	C(8)	1.396(7)
C(7)	C(12)	1.384(7)
C(8)	C(9)	1.393(7)
C(9)	C(10)	1.373(9)
C(10)	C(11)	1.385(9)
C(11)	C(12)	1.396(7)
C(13)	C(14)	1.378(7)
C(13)	C(18)	1.410(7)
C(14)	C(15)	1.384(8)
C(15)	C(16)	1.390(9)
C(16)	C(17)	1.387(10
C(17)	C(18)	1.380(9)

TABLE 4.1.5.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	
C(1)	P(1)	N(1)	106.2(2)
C(7)	P(1)	N(1)	115.1(2)
C(13)	P(1)	N(1)	112.7(2)
P(2)	N(1)	P(1)	139.7(2)
C(7)	P(1)	C(1)	108.8(2)
C(13)	P(1)	C(1)	107.0(2)
C(2)	C(1)	P(1)	119.3(4)
C(6)	C(1)	P(1)	120.2(4)
C(13)	P(1)	C(7)	106.7(2)
C(8)	C(7)	P(1)	118.2(3)
C(12)	C(7)	P(1)	120.8(3)
C(14)	C(13)	P(1)	122.6(4)
C(18)	C(13)	P(1)	118.2(4)
O(1)	P(2)	N(1)	117.6(1)
Cl(1)	P(2)	N(1)	109.2(1)
Cl(1)	P(2)	Cl(2)	100.9(1)
Cl(1)	P(2)	O(1)	109.5(1)
Cl(2)	P(2)	N(1)	109.3(1)
Cl(2)	P(2)	O(1)	109.1(1)
C(6)	C(1)	C(2)	120.5(4)
C(3)	C(2)	C(1)	119.2(5)
C(5)	C(6)	C(1)	119.3(5)
C(4)	C(3)	C(2)	120.3(5)
C(5)	C(4)	C(3)	120.8(6)
C(6)	C(5)	C(4)	120.0(6)
C(12)	C(7)	C(8)	120.9(4)
C(9)	C(8)	C(7)	119.2(5)
C(11)	C(12)	C(7)	119.5(5)
C(10)	C(9)	C(8)	119.6(5)
C(11)	C(10)	C(9)	121.7(5)
C(12)	C(11)	C(10)	119.1(5)
C(18)	C(13)	C(14)	119.1(5)
C(15)	C(14)	C(13)	121.7(5)
C(17)	C(18)	C(13)	119.3(5)
C(16)	C(15)	C(14)	118.9(6)
C(17)	C(16)	C(15)	120.2(6)
C(18)	C(17)	C(16)	120.7(5)

TABLE 4.1.6.

Selected Torsion Angles (°) and E.S.Ds

C(1)	P(1)	N(1)	P(2)	170.3(3)
C(7)	P(1)	N(1)	P(2)	49.8(3)
C(13)	P(1)	N(1)	P(2)	-72.9(3)
N(1)	P(1)	C(1)	C(2)	-17.4(4)
N(1)	P(1)	C(1)	C(6)	160.5(4)
C(7)	P(1)	C(1)	C(2)	107.0(4)
C(7)	P(1)	C(1)	C(6)	-75.0(5)
C(13)	P(1)	C(1)	C(2)	-138.0(4)
C(13)	P(1)	C(1)	C(6)	39.9(5)
N(1)	P(1)	C(7)	C(8)	-75.7(4)
N(1)	P(1)	C(7)	C(12)	101.8(4)
C(1)	P(1)	C(7)	C(8)	165.3(4)
C(1)	P(1)	C(7)	C(12)	-17.2(5)
C(13)	P(1)	C(7)	C(8)	50.2(4)
C(13)	P(1)	C(7)	C(12)	-132.3(4)
N(1)	P(1)	C(13)	C(14)	154.5(4)
N(1)	P(1)	C(13)	C(18)	-29.6(4)
C(1)	P(1)	C(13)	C(14)	-89.2(4)
C(1)	P(1)	C(13)	C(18)	86.8(4)
C(7)	P(1)	C(13)	C(14)	27.2(5)
C(7)	P(1)	C(13)	C(18)	-156.8(4)
O(1)	P(2)	N(1)	P(1)	170.1(2)
Cl(1)	P(2)	N(1)	P(1)	44.5(3)
Cl(2)	P(2)	N(1)	P(1)	-64.9(3)
P(1)	C(1)	C(2)	C(3)	177.4(4)
P(1)	C(1)	C(6)	C(5)	-177.1(4)
P91)	C(7)	C(8)	C(9)	178.4(4)
P(1)	C(7)	C(12)	C(11)	-178.1(4)
P(1)	C(13)	C(14)	C(15)	177.5(4)
P(1)	C(13)	C(18)	C(17)	-177.4(4)

TABLE 4.1.7.

Selected least-squares planes in the form, $lX' + mY' + NZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations

Plane (1) - $-0.83582X' + 0.10402Y' - 0.53906Z' = -5.74381$

Plane (2) - $-0.14793X' + 0.97734Y' + 0.15138Z' = 2.16745$

Plane (3) - $0.58873X' - 0.26720Y' - 0.76289Z' = 1.47859$

(b) Deviations (Å) of Atoms from Plane (Starred Atoms Define Plane)

Plane (1) = C(1)* -0.004(4), C(2)* 0.001(6), C(3)* 0.002(6), C(4)* -0.001(6), C(5)* -0.002(6), C(6)* 0.004(6), P(1) -0.076(1)

Plane (2) = C(7)* -0.005(5), C(8)* 0.004(6), C(9)* 0.002(6), C(10)* -0.005(7), C(11)* 0.003(7), C(12) 0.002(6), P(1) 0.043(1)

Plane (3) = C(13)* -0.009(4), C(14)* 0.006(5), C(15)* 0.001(6), C(16)* -0.006(6), C(17)* 0.004(6), C(18)* 0.004(6), P(1) 0.063(1)

(c) Dihedral Angles (°) between Planes

(1) - (2) 81.7° (1) - (3) 96.2° (2) - (3) 117.6°

TABLE 4.1.8.

(a) Intra-molecular Non-bonding Distances < 4.0Å

ATOM A	ATOM B	Å
P(1)	Cl(1)	3.70
P(1)	Cl(2)	3.85
P(2)	C(7)	3.75
P(2)	C(8)	3.95
P(2)	C(13)	3.84
P(2)	C(18)	3.95
N(1)	C(2)	2.96
N(1)	C(6)	3.98
N(1)	C(8)	3.54
N(1)	C(12)	3.78
N(1)	C(18)	3.15
Cl(1)	C(8)	3.96
Cl(1)	C(13)	3.68
Cl(1)	C(18)	3.55
Cl(2)	C(7)	3.69
Cl(2)	C(8)	3.61
C(1)	C(12)	3.16
C(1)	C(14)	3.69
C(1)	C(18)	3.63
C(2)	C(12)	3.88
C(2)	C(7)	3.86
C(6)	C(7)	3.58
C(6)	C(12)	3.63
C(6)	C(13)	3.22
C(6)	C(14)	3.58
C(7)	C(14)	3.17
C(8)	C(13)	3.26
C(8)	C(14)	3.28

TABLE 4.1.8. (Cont.)

(b) Intermolecular Distances < 3.8Å

ATOM A	ATOM B		Å
O(1)	C(15)	I	3.17
O(1)	C(16)	II	3.42
Cl(1)	C(5)	II	3.58
C(17)	C(4)	II	3.74
Cl(2)	C(3)	III	3.79
O(1)	C(9)	IV	3.72
Cl(1)	C(14)	IV	3.75
Cl(1)	C(15)	IV	3.64
Cl(2)	Cl(1)	IV	3.78

where the position of atom B is given by,

I = x, 1+y, z
II = x, $\frac{1}{2}$-y, $\frac{1}{2}$+z
III = 1-x, 1-y, -z
IV = 1-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z

TABLE 4.1.9. (a)

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} of all non-hydrogen atoms; scale factor; unit weights.	1 - 6	0.157	0.031
x, y, z, U_{ij} (i, j = 1, 2, 3) of atoms in group (1); z coordinate of atom P(2) not refined; scale factor; unit weights.	7 - 9	0.146	0.029
x, y, z, U_{ij} (i, j = 1, 2, 3) of atoms in group (2); all other non-hydrogen atoms in calculation but not refined; scale factor; unit weights.	10 - 11	0.143	0.027

NOTE

Group (1) contains atoms P(1), P(2), N(1), O(1), C(20) - C(31)

Group (2) contains atoms C(1) - C(18) and P(1)

TABLE 4.1.9. (b)

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
Scale factor;	1	0.100	0.010
x, y, z, U_{ij} (i, j = 1, 2, 3) of atoms in group (2); all other atoms including H-atoms in calculation but not refined; scale factor; unit weights.	2 - 3	0.081	0.006
x, y, z, U_{ij} (i, j = 1, 2, 3) of atoms in group (1); z coordinate of P(2) not refined; all other atoms in calculation but not refined; scale factor; unit weights.	4 - 6	0.045	0.003
As in cycles 2 - 3 except weighting scheme adjusted.	7 - 8	0.042	0.003
As in cycles 4 - 6 except weighting scheme adjusted.	9 - 10	0.042	0.003

TABLE 4.1.10.

Atomic Fractional Coordinates and E.S.Ds (Å) of Compound (II)

ATOM	x/a	y/b	z/c
P(1)	0.22725(3)	0.05094(4)	0.48578(11)
P(2)	0.08537(3)	0.15967(4)	0.50000(-)
N(1)	0.1571(1)	0.1014(2)	0.5440(3)
O(1)	0.0858(1)	0.2117(2)	0.3599(3)
C(1)	0.2812(2)	0.0156(3)	0.6467(5)
C(2)	0.2879(3)	0.0729(3)	0.7654(6)
C(3)	0.3290(3)	0.0481(4)	0.8908(7)
C(4)	0.3615(3)	-0.0336(4)	0.8967(6)
C(5)	0.3546(3)	-0.0914(3)	0.7808(6)
C(6)	0.3141(2)	-0.0672(3)	0.6534(6)
C(7)	0.2914(2)	0.1152(3)	0.3715(5)
C(8)	0.2623(3)	0.1791(3)	0.2810(6)
C(9)	0.3105(3)	0.2262(3)	0.1868(7)
C(10)	0.3870(3)	0.2078(4)	0.1857(7)
C(11)	0.4161(3)	0.1447(4)	0.2771(6)
C(12)	0.3687(2)	0.0978(4)	0.3711(6)
C(13)	0.2075(2)	-0.0467(3)	0.3780(5)
C(14)	0.2587(3)	-0.0791(3)	0.2723(6)
C(15)	0.2410(3)	-0.1533(4)	0.1915(7)
C(16)	0.1710(4)	-0.1943(3)	0.2156(7)
C(17)	0.1211(3)	-0.1636(3)	0.3206(7)
C(18)	0.1393(2)	-0.0892(3)	0.4027(6)
C(20)	0.0709(2)	0.2312(2)	0.6597(4)
C(21)	0.0317(2)	0.3086(2)	0.6374(5)
C(22)	0.0160(2)	0.3632(2)	0.7585(6)
C(23)	0.0389(3)	0.3408(3)	0.9002(6)
C(24)	0.0781(2)	0.2626(3)	0.9231(5)
C(25)	0.0939(2)	0.2090(2)	0.8028(4)
C(26)	0.0032(1)	0.0901(2)	0.5051(4)
C(27)	-0.0032(2)	0.0216(2)	0.6063(4)
C(28)	-0.0681(2)	-0.0297(2)	0.6106(4)
C(29)	-0.1266(2)	-0.0112(2)	0.5148(5)
C(30)	-0.1219(2)	0.0574(3)	0.4157(5)
C(31)	-0.0569(2)	0.1081(2)	0.4102(4)

TABLE 4.1.10.

(b) Hydrogen-atom Fractional Coordinates

ATOM	x/a	y/b	z/c
H(2)	0.2635	0.1332	0.7769
H(2)	0.3302	0.0974	0.9613
H(4)	0.3812	-0.0596	0.9890
H(5)	0.3741	-0.1490	0.7763
H(6)	0.3132	-0.1130	0.5655
H(8)	0.2021	0.2051	0.2813
H(9)	0.3051	0.2910	0.1525
H(10)	0.4176	0.2370	0.1179
H(11)	0.4716	0.1092	0.2535
H(12)	0.3890	0.0522	0.4338
H(14)	0.3114	-0.0559	0.2551
H(15)	0.2810	-0.1828	0.0968
H(16)	0.1606	-0.2457	0.1440
H(17)	0.0662	-0.1939	0.3476
H(18)	0.1027	-0.0569	0.4818
H(21)	0.0000	0.3221	0.5361
H(22)	-0.0200	0.4167	0.7402
H(23)	0.0240	0.3793	1.0000
H(24)	0.1054	0.2599	1.0156
H(25)	0.1212	0.1524	0.8194
H(27)	0.0413	0.0071	0.6795
H(28)	-0.0725	-0.0796	0.6837
H(29)	-0.1715	-0.0446	0.5241
H(30)	-0.1636	0.0773	0.3424
H(31)	-0.0524	0.1721	0.3505

TABLE 4.1.10.

(c) Anisotropic Temperature Factors and E.S.Ds ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.0267	0.0336	0.0399	0.0003	-0.0007	0.0031
P(2)	0.0302	0.0334	0.0412	0.0019	0.0018	0.0045
N(1)	0.031(1)	0.045(1)	0.057(1)	0.006(1)	0.002(1)	0.004(1)
O(1)	0.048(1)	0.043(1)	0.047(1)	0.001(1)	0.003(1)	0.011(1)
C(1)	0.028	0.041	0.037	-0.001	0.000	0.004
C(2)	0.042	0.045	0.049	-0.002	-0.002	-0.004
C(3)	0.054	0.072	0.050	-0.002	-0.010	-0.012
C(4)	0.047	0.080	0.047	0.003	-0.010	0.015
C(5)	0.048	0.049	0.058	0.006	-0.008	0.013
C(6)	0.040	0.043	0.048	0.005	-0.002	0.003
C(7)	0.034	0.042	0.042	-0.007	0.004	-0.004
C(8)	0.051	0.045	0.061	0.006	0.017	0.012
C(9)	0.081	0.046	0.064	0.003	0.027	0.011
C(10)	0.062	0.062	0.054	-0.024	0.021	-0.007
C(11)	0.039	0.091	0.052	-0.016	0.007	-0.003
C(12)	0.033	0.074	0.053	-0.007	-0.000	0.007
C(13)	0.036	0.038	0.044	-0.000	-0.009	0.001
C(14)	0.045	0.058	0.053	0.002	-0.002	-0.010
C(15)	0.065	0.058	0.062	0.011	-0.007	-0.018
C(16)	0.087	0.040	0.065	0.003	-0.033	-0.003
C(17)	0.055	0.044	0.072	-0.008	-0.017	0.004
C(18)	0.043	0.042	0.058	-0.006	-0.003	0.002
C(20)	0.032	0.038	0.050	-0.002	0.005	-0.002
C(21)	0.048	0.044	0.065	0.006	0.009	-0.001
C(22)	0.067	0.048	0.088	0.003	0.021	-0.011
C(23)	0.069	0.061	0.075	-0.017	0.020	-0.025
C(24)	0.065	0.089	0.053	-0.022	-0.000	-0.013
C(25)	0.048	0.055	0.056	-0.003	-0.005	-0.003
C(26)	0.031	0.038	0.040	0.002	0.003	-0.002
C(27)	0.040	0.049	0.047	-0.004	0.001	0.008
C(28)	0.055	0.051	0.053	-0.014	0.012	-0.002
C(29)	0.041	0.068	0.063	-0.013	0.009	-0.018
C(30)	0.039	0.075	0.063	0.000	-0.012	-0.015
C(31)	0.039	0.054	0.051	0.004	-0.007	-0.002
Average Estimated Standard Deviations						
P	0.0002	0.0002	0.0003	0.0002	0.0003	0.0003
C	0.002	0.002	0.002	0.001	0.002	0.002

TABLE 4.1.11.

Intramolecular Bonded Distances and E.S.Ds (Å) for Compound II

ATOM A	ATOM B	Å
P(1)	N(1)	1.556(2)
P(1)	C(1)	1.815(4)
P(1)	C(7)	1.822(4)
P(1)	C(13)	1.816(5)
P(2)	N(1)	1.405(2)
P(2)	O(1)	1.489(3)
P(2)	C(20)	1.822(3)
P(2)	C(26)	1.808(2)
C(1)	C(2)	1.385(7)
C(1)	C(6)	1.398(6)
C(2)	C(3)	1.394(8)
C(3)	C(4)	1.380(8)
C(4)	C(5)	1.371(8)
C(5)	C(6)	1.400(7)
C(7)	C(8)	1.373(7)
C(7)	C(12)	1.398(5)
C(8)	C(9)	1.403(8)
C(9)	C(10)	1.387(8)
C(10)	C(11)	1.369(8)
C(11)	C(12)	1.391(8)
C(13)	C(14)	1.404(7)
C(13)	C(18)	1.393(5)
C(14)	C(15)	1.385(8)
C(15)	C(16)	1.409(9)
C(16)	C(17)	1.376(9)
C(17)	C(18)	1.395(7)
C(20)	C(21)	1.390(5)
C(20)	C(25)	1.390(5)
C(21)	C(22)	1.399(6)
C(22)	C(23)	1.378(7)
C(23)	C(24)	1.401(6)
C(24)	C(25)	1.385(6)
C(26)	C(27)	1.393(5)
C(26)	C(31)	1.393(4)
C(27)	C(28)	1.395(5)
C(28)	C(29)	1.378(5)
C(29)	C(30)	1.379(6)
C(30)	C(31)	1.392(5)

TABLE 4.1.12.

Valency Angles and E.S.Ds (in DEGREES)

ATOM A	ATOM B	ATOM C	
C(1)	P(1)	N(1)	107.7(2)
C(7)	P(1)	N(1)	114.9(2)
C(13)	P(1)	N(1)	115.7(2)
C(7)	P(1)	C(1)	106.2(2)
C(13)	P(1)	C(1)	106.2(2)
C(13)	P(1)	C(7)	105.5(2)
P(1)	N(1)	P(2)	146.0(2)
O(1)	P(2)	N(1)	120.1(1)
C(20)	P(2)	N(1)	104.7(1)
C(26)	P(2)	N(1)	107.8(1)
C(20)	P(2)	O(1)	110.0(2)
C(26)	P(2)	O(1)	110.0(1)
C(26)	P(2)	C(20)	102.8(2)
C(2)	C(1)	P(1)	117.9(3)
C(6)	C(1)	P(1)	121.7(4)
C(6)	C(1)	C(2)	120.4(4)
C(3)	C(2)	C(1)	119.5(5)
C(4)	C(3)	C(2)	119.8(5)
C(5)	C(4)	C(3)	121.3(5)
C(6)	C(5)	C(4)	119.6(5)
C(5)	C(6)	C(1)	119.3(4)
C(8)	C(7)	P(1)	118.9(3)
C(12)	C(7)	P(1)	120.8(4)
C(12)	C(7)	C(8)	120.3(4)
C(9)	C(8)	C(7)	119.6(5)
C(10)	C(9)	C(8)	119.8(5)
C(11)	C(10)	C(9)	120.6(5)
C(12)	C(11)	C(10)	120.0(5)
C(11)	C(12)	C(7)	119.8(5)
C(14)	C(13)	P(1)	121.7(3)
C(18)	C(13)	P(1)	117.9(3)
C(19)	C(13)	C(14)	120.3(4)
C(15)	C(14)	C(13)	119.8(5)
C(16)	C(15)	C(14)	119.1(5)
C(17)	C(16)	C(15)	121.4(5)
C(18)	C(17)	C(16)	119.5(5)
C(17)	C(18)	C(13)	120.0(4)
C(21)	C(20)	P(2)	118.1(3)
C(25)	C(20)	P(2)	122.5(2)
C(25)	C(20)	C(21)	119.3(3)
C(22)	C(21)	C(20)	119.9(4)
C(23)	C(22)	C(21)	120.6(3)
C(24)	C(23)	C(22)	119.7(4)
C(25)	C(24)	C(23)	119.6(4)
C(24)	C(25)	C(20)	121.0(3)

TABLE 4.1.12. (Cont.)

ATOM A	ATOM B	ATOM C	
C(27)	C(26)	P(2)	121.8(2)
C(31)	C(26)	P(2)	119.1(2)
C(31)	C(26)	C(27)	119.0(3)
C(28)	C(27)	C(26)	120.7(3)
C(29)	C(28)	C(27)	119.3(3)
C(30)	C(29)	C(28)	120.9(3)
C(31)	C(30)	C(29)	119.9(4)
C(30)	C(31)	C(26)	120.2(3)

TABLE 4.1.13.

Selected Torsion Angles (°) and E.S.Ds

C(1)	P(1)	N(1)	P(2)	173.0(3)
C(7)	P(1)	N(1)	P(2)	54.9(4)
C(13)	P(1)	N(1)	P(2)	-68.4(4)
N(1)	P(1)	C(1)	C(2)	-39.9(4)
N(1)	P(1)	C(1)	C(6)	139.0(4)
C(7)	P(1)	C(1)	C(2)	83.6(4)
C(7)	P(1)	C(1)	C(6)	-97.5(4)
C(13)	P(1)	C(1)	C(2)	-164.4(4)
C(13)	P(1)	C(1)	C(6)	14.4(4)
N(1)	P(1)	C(7)	C(8)	-33.8(4)
N(1)	P(1)	C(7)	C(12)	148.7(4)
C(1)	P(1)	C(7)	C(8)	-152.7(4)
C(1)	P(1)	C(7)	C(12)	29.8(4)
C(13)	P(1)	C(7)	C(8)	94.9(4)
C(13)	P(1)	C(7)	C(12)	-82.7(4)
N(1)	P(1)	C(13)	C(14)	154.6(4)
N(1)	P(1)	C(13)	C(17)	-25.2(4)
C(1)	P(1)	C(13)	C(14)	-86.0(4)
C(1)	P(1)	C(13)	C(17)	94.2(4)
C(7)	P(1)	C(13)	C(14)	26.5(4)
C(7)	P(1)	C(13)	C(17)	-153.4(4)
P(1)	N(1)	P(2)	O(1)	-25.3(4)
P(1)	N(1)	P(2)	C(20)	-149.4(3)
P(1)	N(1)	P(2)	C(26)	101.7(3)
N(1)	P(2)	C(20)	C(21)	157.5(3)
N(1)	P(2)	C(20)	C(25)	-26.0(3)
O(1)	P(2)	C(20)	C(21)	27.2(3)
O(1)	P(2)	C(20)	C(25)	-156.4(3)
C(26)	P(2)	C(20)	C(21)	-89.9(3)
C(26)	P(2)	C(20)	C(25)	86.6(3)
N(1)	P(2)	C(26)	C(27)	33.3(3)
N(1)	P(2)	C(26)	C(31)	-149.9(3)
O(1)	P(2)	C(26)	C(27)	165.9(3)
O(1)	P(2)	C(26)	C(31)	-17.3(3)
C(20)	P(2)	C(26)	C(27)	-76.9(3)
C(20)	P(2)	C(26)	C(31)	99.9(3)
P(2)	C(20)	C(21)	C(22)	176.7(3)
P(2)	C(20)	C(25)	C(24)	-176.2(3)
P(2)	C(26)	C(27)	C(28)	178.3(3)
P(2)	C(26)	C(31)	C(30)	-177.7(3)
P(1)	C(1)	C(2)	C(3)	-179.9(4)
P(1)	C(1)	C(6)	C(5)	-179.5(4)
P(1)	C(7)	C(8)	C(9)	-176.8(4)
P(1)	C(7)	C(12)	C(11)	176.7(4)
P(1)	C(13)	C(12)	C(11)	-179.4(4)
P(1)	C(13)	C(17)	C(18)	178.9(4)

TABLE 4.1.14.

Selected least-squares planes in the form, $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations

Plane (1) = $0.83499X' + 0.36900Y' - 0.40820Z' = 1.88366$

Plane (2) = $0.14020X' + 0.67905Y' + 0.72058Z' = 4.33139$

Plane (3) = $0.42611X' - 0.57206Y' + 0.70084Z' = 4.36302$

Plane (4) = $-0.86452X' - 0.48090Y' + 0.14609Z' = -1.92710$

Plane (5) = $0.39138X' - 0.61816Y' - 0.68169Z' = -3.92779$

(b) Deviations (Å) of Atoms from Plane (Starred Atoms Define the Plane)

Plane (1) = C(1)* 0.005(4), C(2)* -0.007(5), C(3)* 0.003(6), C(4)* 0.002(6), C(5)* -0.003(5), C(6)* -0.000(4), P(1) -0.006(1)

Plane (2) = C(7)* -0.005(5), C(8)* 0.002(5), C(9)* 0.003(6), C(10)* -0.005(6), C(11)* 0.002(6), C(12)* 0.003(6), P(1) -0.095(1)

Plane (3) = C(13)* -0.007(4), C(14)* -0.000(5), C(15)* 0.008(6), C(16)* -0.010(6), C(17)* 0.005(5), C(16)* 0.003(6), P(1) -0.036(1)

Plane (4) = C(20)* -0.000(3), C(21)* 0.002(4), C(22)* -0.001(4), C(23)* -0.002(5), C(24)* 0.003(4), C(25)* -0.002(3), P(2) 0.095(1)

Plane (5) = C(26)* 0.007(3), C(27)* -0.008(3), C(28)* 0.001(3), C(29)* 0.005(4), C(30)* -0.006(4), C(31)* -0.000(3), P(2) -0.0497(4)

(c) Dihedral Angle (°) between Planes

(1) - (2) 85.8° (1) - (3) 98.1° (2) - (3) 79.9° (4) - (5) 98.1°

TABLE 4.1.15.

(a) Intramolecular Non-bonding Distances < 4.0Å

ATOM A	ATOM B	Å
P(1)	O(1)	3.69
N(1)	C(21)	3.97
N(1)	C(25)	3.06
N(1)	C(27)	3.15
N(1)	C(31)	3.99
N(1)	C(2)	3.09
N(1)	C(6)	3.93
N(1)	C(8)	3.24
N(1)	C(18)	3.20
P(2)	C(7)	3.90
P(2)	C(8)	3.71
P(2)	C(13)	3.99
O(1)	C(21)	3.05
O(1)	C(25)	3.98
O(1)	C(27)	3.98
O(1)	C(31)	3.02
O(1)	C(7)	3.94
O(1)	C(8)	3.25
C(20)	C(27)	3.50
C(20)	C(31)	3.70
C(21)	C(26)	3.59
C(25)	C(26)	3.61
C(25)	C(27)	3.79
C(26)	C(17)	3.77
C(27)	C(17)	3.55

TABLE 4.1.15. (Cont.)

(b) Intermolecular Distances < 3.8Å

ATOM A	ATOM B		Å
C(3)	C(10)	I	3.74
C(25)	C(29)	II	3.63
C(26)	C(17)	II	3.76
C(27)	C(30)	II	3.76
C(27)	C(31)	II	3.54
C(27)	C(18)	II	3.74
C(27)	C(17)	II	3.58
C(28)	O(1)	II	3.59
C(28)	C(31)	II	3.69
C(28)	C(13)	II	3.64
C(28)	C(18)	II	3.43
C(28)	C(17)	II	3.63
C(29)	C(13)	II	3.67
C(29)	C(14)	II	3.57
C(29)	C(15)	II	3.60
C(29)	C(16)	II	3.71
C(30)	C(15)	II	3.57
C(30)	C(16)	II	3.52
C(31)	C(16)	II	3.65
C(2)	C(29)	II	3.76
C(23)	C(6)	III	3.73
C(25)	C(15)	III	3.75
C(2)	C(16)	III	3.66
O(1)	C(5)	IV	3.28
C(21)	C(4)	IV	3.76
C(3)	C(22)	V	3.78
C(10)	C(31)	V	3.61

where the position of atom B is given by,

I = x, y, 1+z
II = -x, -y, $\frac{1}{2}$+z
III = $\frac{1}{2}$-x, $\frac{1}{2}$+y, $\frac{1}{2}$+z
IV = $\frac{1}{2}$-x, $\frac{1}{2}$+y, $\frac{1}{2}$+z-1
V = $\frac{1}{2}$+x, $\frac{1}{2}$-y, z

TABLE 4.1.16.

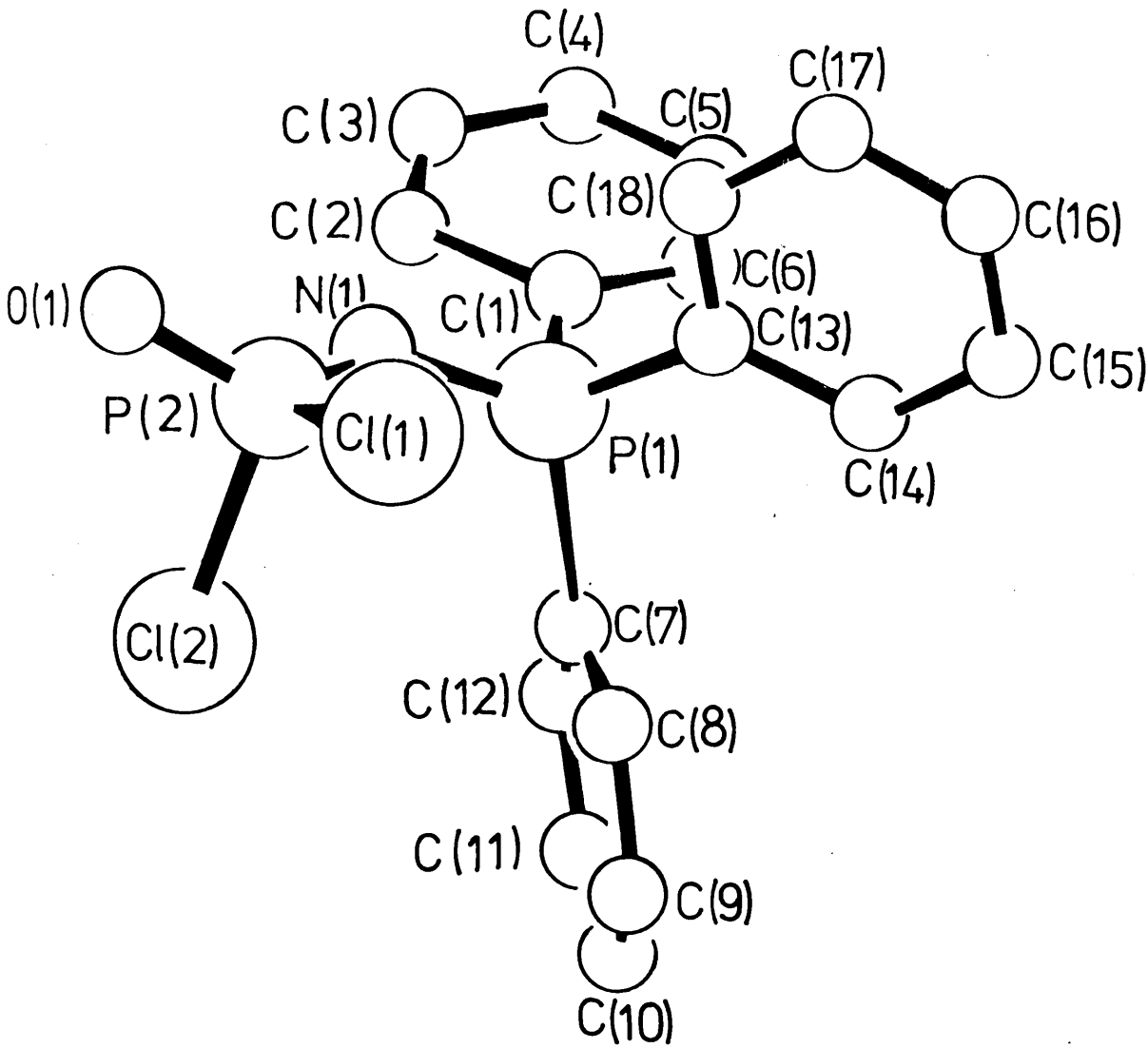
RESULTS OF CYCLIC PHOSPHONITRILIC X-RAY STRUCTURE DETERMINATIONS

Compound	Ref.	Average Distance (P - N)	Average Angle (N - P - N)	(P - N - P)	Configuration
$(F_2PN)_3$	31	1.560	119.4	120.3	Planar
$(F_2PN)_4$	23	1.51	122.7	147.0	Planar
$(Me_2PN)_4$	33	1.596	119.8	131.9	Puckered
$(Me_2N)_8P_4N_4$	34	1.59	121.0	129.0	Planar
$(Cl_2PN)_3$	32	1.59	120.0	119.0	Planar
$(Cl_2PN)_4$	22	1.570	121.2	131.3	Puckered
$(Cl_2PN)_5$	24	1.521	118.4	148.6	Nearly Planar
I	-	1.570	117.6(1)	139.6(2)	
II	-	1.580	120.1(1)	140.1(2)	

TABLE 4.1.16.

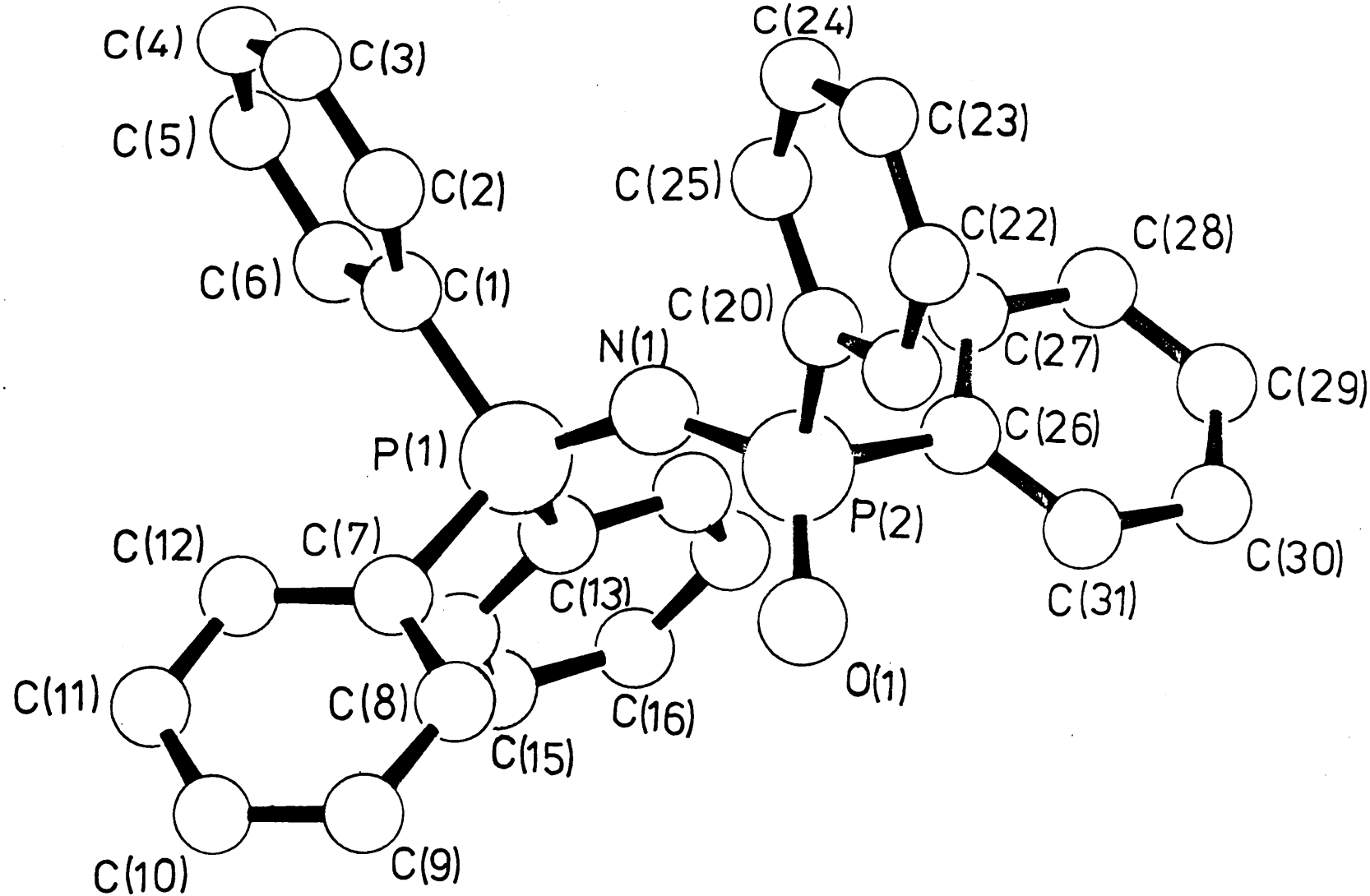
F I G U R E 4.1.1.

Diagrammatic representation of Compound I


C(4)
C(17)
C(3)
C(5)
C(18)
C(2)
C(16)
C(6)
O(1)
N(1)
C(1)
C(13)
C(15)
P(2)
Cl(1)
P(1)
C(14)
Cl(2)
C(7)
C(12)
C(8)
C(11)
C(9)
C(10)

F I G U R E 4.1.2.

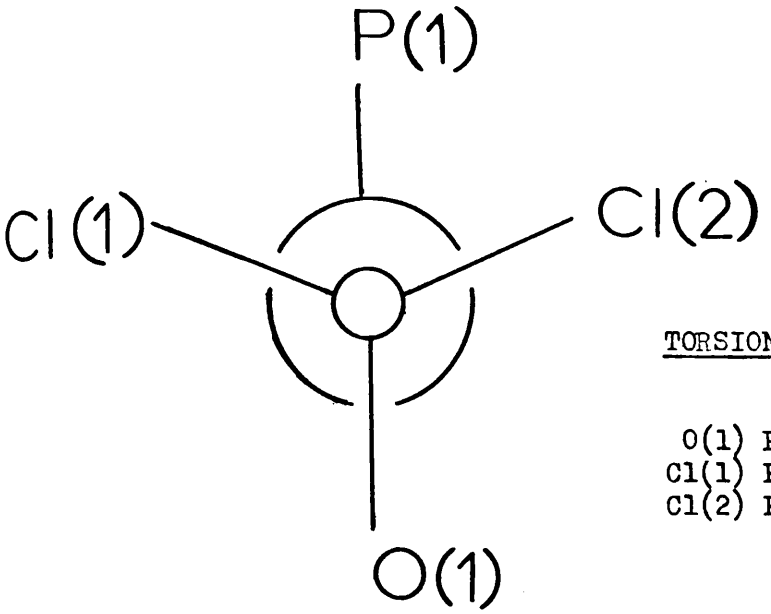
Diagrammatic representation of Compound II


C(4)
C(3)
C(5)
C(2)
C(6)
C(1)
C(24)
C(23)
C(25)
C(22)
C(28)
C(20)
C(27)
N(1)
C(29)
P(1)
C(26)
P(2)
C(12)
C(7)
C(13)
C(31)
C(30)
C(11)
C(8)
C(16)
O(1)
C(15)
C(10)
C(9)

F I G U R E 4.1.3.

Conformations about bond P(2) - N(1)

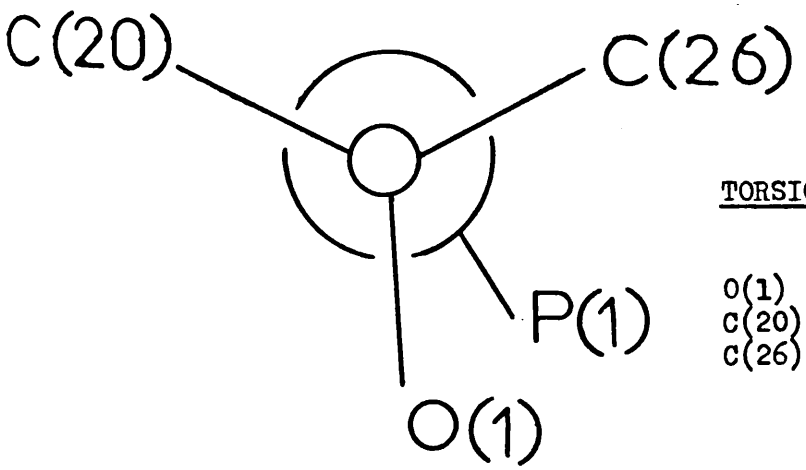
in Compounds I and II



TORSION ANGLES

O(1)	P(2)	N(1)	P(1)	170.1(2)
Cl(1)	P(2)	N(1)	P(1)	44.5(3)
Cl(2)	P(2)	N(1)	P(1)	-64.9(3)

COMPOUND I



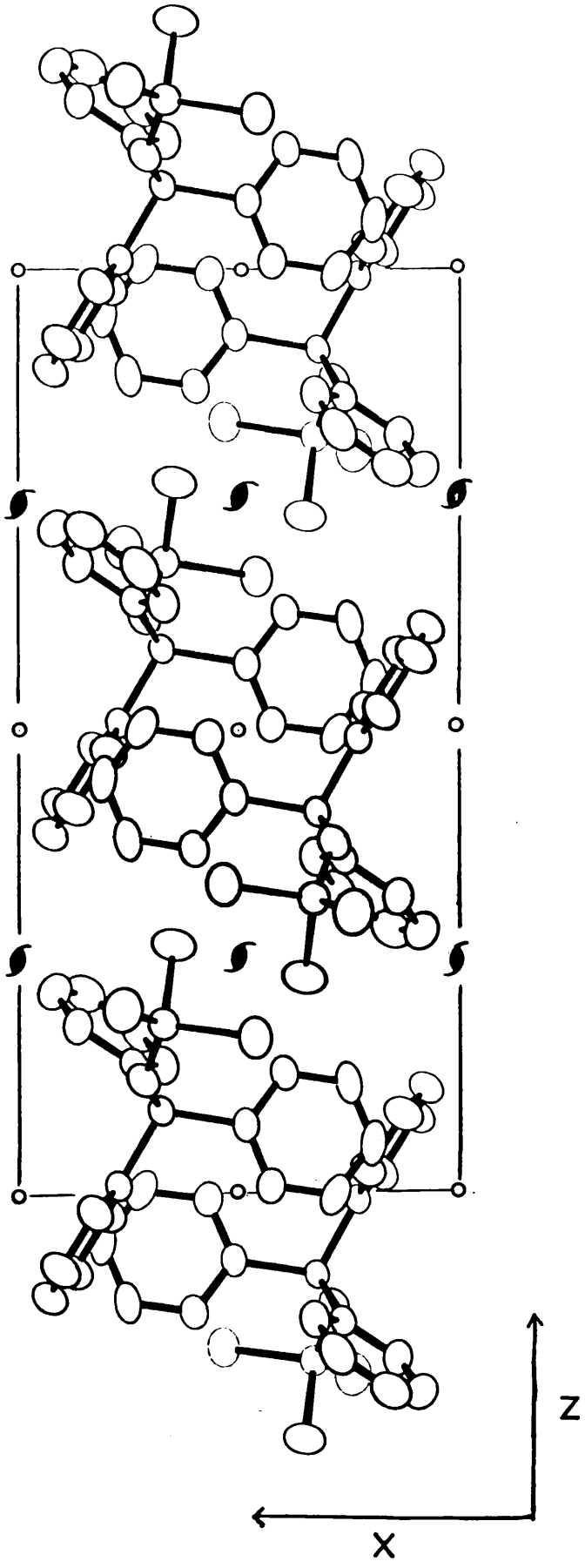
TORSION ANGLES

O(1)	P(2)	N(1)	P(1)	-25.3(4)
C(20)	P(2)	N(1)	P(1)	-149.4(3)
C(26)	P(2)	N(1)	P(1)	101.7(3)

COMPOUND II

F I G U R E 4.1.4.

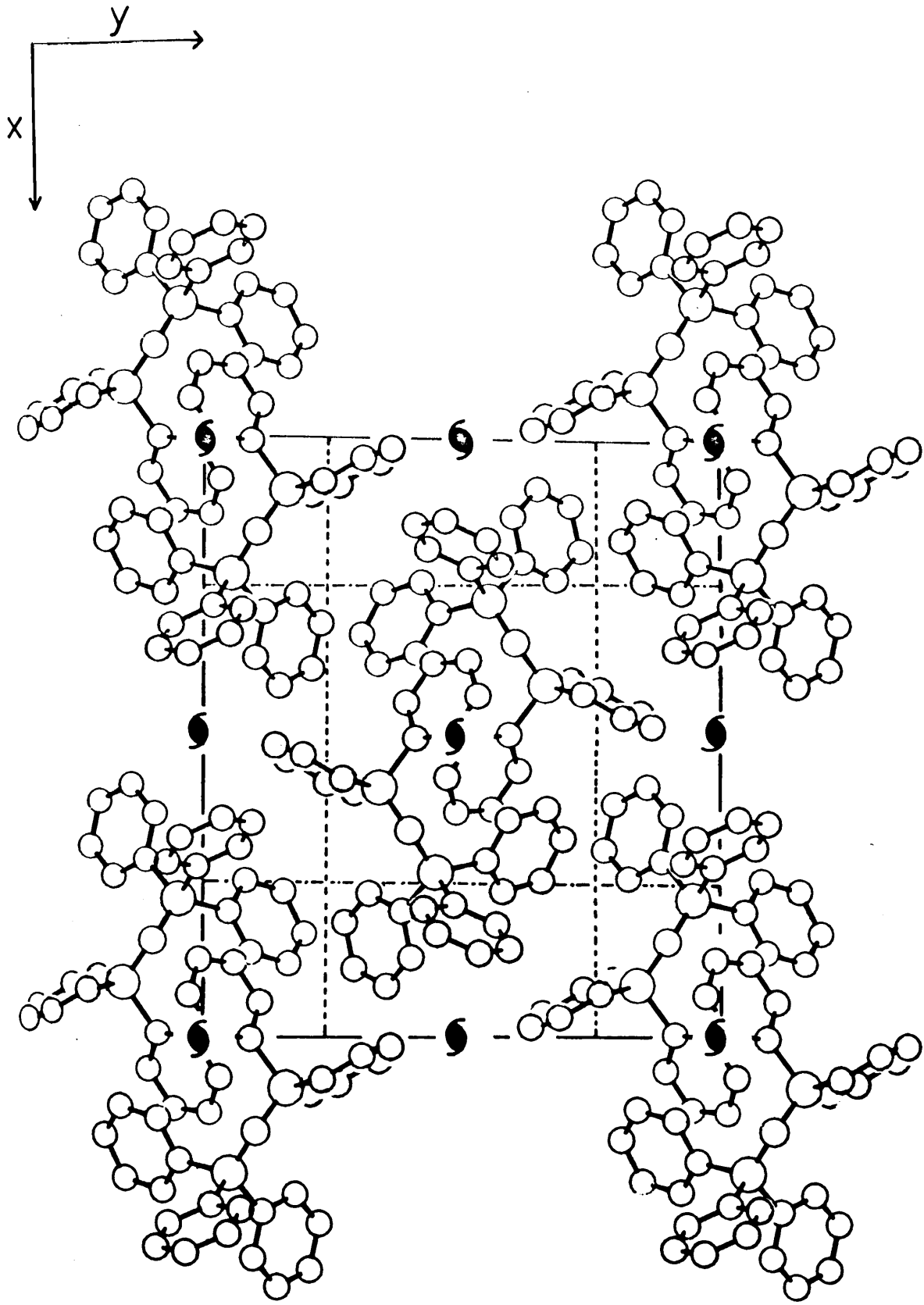
Crystal-packing arrangements for Compound I


Z
X

F I G U R E 4.1.5.

Crystal-packing arrangements for

Compound II

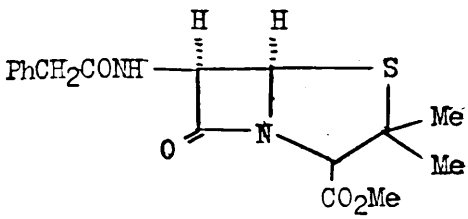

y
x

S E C T I O N 4.2.

THE CRYSTAL AND MOLECULAR STRUCTURE OF AN YLIDE COMPOUND DERIVED FROM METHYL 6β-PHENYL-ACETOAMIDO-PENICILLANATE

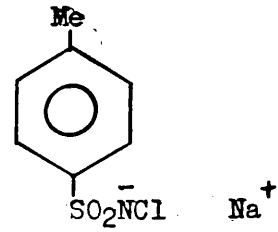
INTRODUCTION

As part of an investigation of the reaction of chloramine T with penicillins,[45,46] with the objective of chemically modifying the thiazolidine ring and forming β-lactams with possible antibiotic activity, a methanolic solution of methyl 6β-phenyl-acetoamido-penicillanate(1) was reacted at room temperature with chloramine T (2) (2 mol. equiv.) in methanol, to yield white crystals. The i.r. spectrum indicated a β-lactam ring (1790 $cm.^{-1}$) and possibly the functional group (3) (1360, 1168, 1150 and 990 $cm.^{-1}$) whilst the n.m.r. spectrum indicated a bicyclic system containing gem-dimethyl, two tosyl units and trans-β-lactam protons. On the basis of elemental analysis and spectroscopic data, three closely-related structures were plausible (VIII, IX and X) for this crystalline product, but these could not be unambiguously distinguished. Since one of the possible structures was the unusual ylide (IX) and since comparison of this compound with similar ylide systems was thought to afford the opportunity for detailed investigations of bonding and conformational patterns within second-row ylide systems, a crystal structure analysis has been carried out, which has confirmed the structure (IX).



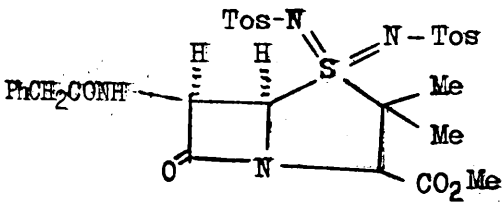
(1)

+

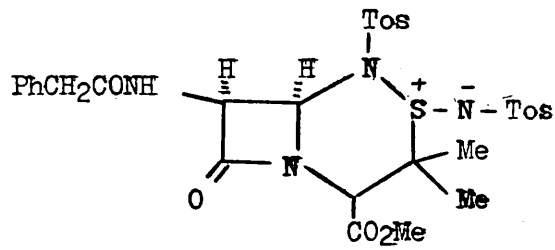


(2)

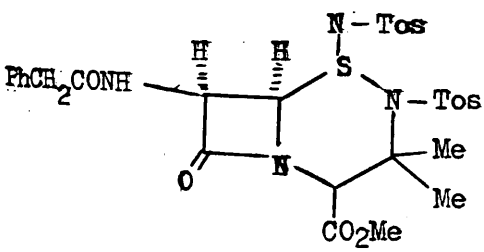
MeOH



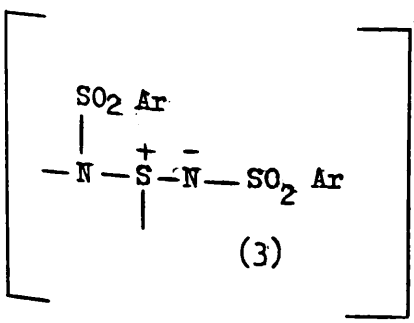
(VIII)



(IX)



(X)



(3)

EXPERIMENTAL

CRYSTAL DATA

$C_{31}H_{34}N_4O_8S_3$; M=686.8; Monoclinic, a=15.613Å, b=7.951Å, c=13.840Å, β=108.98°; U=1624.7Å^3; D_c=1.41 g.cm.$^{-3}$; D_m=1.40 g.cm.$^{-3}$; Z=2; F_{000}=720; Space group $P2_1$; MoKα radiation; λ =0.7107Å; μ (Mo-Kα) = 2.94 cm.$^{-3}$.

CRYSTALLOGRAPHIC MEASUREMENTS

Unit cell parameters were initially determined from oscillation and Weissenberg photographs taken with CuKα (λ =1.5418Å) radiation and from precession photographs taken with MoKα (λ =0.7107Å) radiation, and were subsequently refined by least-squares calculations before data collection. The space group $P2_1$ was indicated by systematic absences.

Intensity measurements were made on a Hilger and Watts Y290 four-circle diffractometer, by exposing a crystal (0.3 x 0.6 x 0.2 mm.) rotating about the unique axis b, to graphite-monochromated Mo-radiation (Mo-Kα_1), and using the θ,ω scan technique (in the range $0<2\theta\leqslant 54^\circ$) to collect 3105 independent reflections ($I \geqslant 2\sigma_i$, $\sigma_i = \sqrt{I+B_1+B_2}$). Appropriate corrections for Lorentz and polarisation factors were applied but absorption effects were considered small and no corrections were made.

STRUCTURE DETERMINATION

The structure was determined by non-centrosymmetric Direct Methods, using the computer program, MULTAN and appropriate programs contained

in the X-ray '72 suite of computer programs.

Phase determination was initiated by assigning phases to those reflections shown in Table 4.2.1. and utilising them in a series of calculations based on the weighted-tangent formula of Direct Methods, from which phases were assigned to those 397 reflections with $E \geqslant 1.4$. An initial E-map, based on these reflections, yielded the positions of the three sulphur atoms. The phases appropriate to these atomic positions were subjected to a phase-refinement procedure (program 'Tangen' of the X-ray '72 system) and from the subsequent E-map based on the same set of reflections, 36 of the non-hydrogen atoms were clearly located. The remaining non-hydrogen atomic positions were revealed by conventional structure-factor and electron-density calculations. Each atom was assigned an arbitrary temperature factor $U_{iso}=0.05\text{Å}^2$ and after each round of calculations, the data were placed on an approximate absolute scale by equating $k\sum|Fo|$ and $\sum|Fc|$.

STRUCTURE REFINEMENT

The refinement of positional, vibrational and overall-scale parameters by least-squares calculations converged after 20 cycles when R was 0.048 and R' was 0.005. Computing limitations forced the use of an arbitrary blocking strategy in which the parameters of groups of atoms were refined simultaneously (considering all off-diagonal elements within the group), while the remaining parameters were held constant. Details of the refinement are given in Table 4.2.2. Where possible, hydrogen-atom positions were located from difference syntheses and each atom was assigned an arbitrary temperature

factor U_{iso} = 0.03$\AA^2$ before inclusion in all subsequent structure-factor calculations, no refinement of these positional and vibrational parameters being carried out.

An appropriate weighting scheme was chosen by examination of a series of bivariate ($|Fo|$ and $\frac{\sin\theta}{\lambda}$) anaylses of observed and calculated structure factors. The scheme was of the form;

If $|Fo| \leqslant 7.5$, then W=1,

else $W = (7.5/Fo)^2$

On convergance of the refinement, calculations of an electron-density distribution and difference synthesis revealed no errors in the structure. In all structure-factor calculations, the atomic scattering factors used are given in reference (52). Observed and calculated structure factors are given in Appendix 10, whilst positional and vibrational parameters, with e.s.d.s, are given in Table 4.2.3. Values of e.s.d.s are derived from the inverse of the least-squares normal-equation matrix and should be regarded as minimum values.

DISCUSSION

A diagrammatic representation of this molecule is given in Figure 4.2.1. whilst the numbering scheme for all non-hydrogen atoms is illustrated in Figure 4.2.2., hydrogen atoms being omitted for clarity. Details of bond lengths, bond angles, torsion angles, least-squares planes, intramolecular non-bonding distances and intermolecular distances are shown in Tables 4.2.4. to 4.2.8.

The detailed geometry of the S(1)-N(1)-S(2) ylide moiety of compound IX may be compared directly with the geometries of the similar molecules (XI a - d)[6,7,47-48]. Whereas the S(1) - N(1) and S(2) - N(1) bond lengths in the latter four molecules lie in the range 1.620(7) - 1.633(9)Å and 1.581(10) - 1.618(7)Å respectively, the value observed for the S(1) - N(1) [1.592(5)Å] bond of IX is comparable with the upper limit of the range for (XI a - d). The length of the S(1) - N(1) bond in IX is intermediate between the values observed in (XI a - d) and the values observed for the corresponding bonds [1.521, 1.524Å] of the double-ylide (XII)[49] and indeed, (IX) may be regarded as an S-alkylated, mono-N-alkylated derivative of the ylide system of (XII). In addition, bond angle S(1)N(1)S(2) [116.3(2)°] is comparable with the range of values observed for the corresponding angles in compounds (XI a -d) [113.4(5) - 116.2(6)°] and is experimentally identical to one of the two corresponding angles in compound XII [116.6 and 125.2°]. It has previously been argued[47] that the S(1) - N(1) and S(2) - N(1) dimensions of compounds (XI a - d) and the corresponding dimensions of XII are consistent with significant levels of sulphur d-orbital participation in delocalised bonding within the ylide systems, and insofar as such arguements are

considered valid, the aforementioned dimensions of the S(1)N(1)S(2) system of IX are compatible with a similar pattern of bonding.

The S(1)N(2)S(3) system of IX is quite different from the S(1)N(1)S(2) system, and may be compared with the N-alkylated derivative XIII[50]. The S(1) - N(2) [1.702(4)Å] bond of IX is significantly longer than the corresponding bond [1.644(5)Å] of XIII, although the S(3) - N(2) bond lengths of the two molecules, respectively 1.676(5) and 1.681(5)Å, are not only experimentally equal, but are also very similar to the values observed for the corresponding bonds [1.683, 1.686Å] of XII. The value of 1.702(4)Å for the S(1) - N(2) bond length of IX is intermediate between the values observed in molecules such as (XI a - d) and (XII), and the value observed for sulphamic acid [1.772(1)Å][51], a feature which suggests minimal double-bond character for the S(1) - N(2) bond in IX. Although the S(1)N(2)S(3) valency angle [121.0(2)°] is considerably larger than the corresponding angle [114.5°] in XIII, the sum of the three valency angles at N(2) [357.7°] and the corresponding sum in XIII [356.0°], indicate that in each case the alkylated nitrogen atoms adopt almost planar configurations. The S(3) - O bond lengths [mean 1.430(4)Å] are not significantly different from those values observed for the S(2) - O bond length [mean 1.447(8)Å], both sets of values being comparable with corresponding dimensions reported in compounds (XI a - d) [mean values range from 1.432 - 1.446Å], and compound (XII) [mean 1.427Å]. Whilst the apparent differences between the observed S(3) - O bond lengths in the present compound [mean 1.430(4)Å] and the corresponding values reported for the analogous compound (XIII)

[mean 1.411(5)Å], may be significant, it is noted that both lengths N(2) - S(3) [1.676(5) and 1.681(5)Å for IX and XIII respectively] and S(3) - C(phenyl) [1.724(6) and 1.746(5)Å respectively] are identical within the limits of experimental accuracy. In the present compound, bond lengths S(2) - C(14) [1.764(5)Å] and S(3) - C(21) [1.724(6)Å] are significantly different, the latter value perhaps suggesting increased $p\pi$ - $d\pi$ interactions between the phenyl group and the 3d-orbitals of atom S(3) [the theoretical S(VI) - C(sp^2) value, calculated from atomic radii and electronegativities is 1.75Å], although possible phenyl-ring distortions resulting from such increased $d\pi$ - $p\pi$ interactions are not observed within the limits of experimental accuracy [mean C - C bond length 1.390(10)Å, mean C - C - C valency angle 120.0(5)°].

Although the differing oxidation states of atoms S(1) [IV] and S(2) [VI] render difficult any direct comparisons between bond lengths S(1) - N(1) [1.592(5)Å] and N(1) - S(2) [1.613(4)Å], it is noted that bond S(1) - N(1) is significantly shorter than bond N(1) - S(2), a feature which differs from that reported for compounds (XI a - c), in which the S(IV) - N bond lengths are significantly longer than the S(VI) - N bonds, but which is in agreement with reported values in compound XII [S(IV) - N 1.521, 1.524Å and S(VI) - N 1.683, 1.686Å]. A contributory factor towards these apparent anomalies may be the greater electronegativity of the nitrogen atoms bonded to S(IV) in compounds IX and XII, relative to the corresponding substituents in the other reported compounds (XI a - c).

The pyramidal stereochemistry of atom S(1) is shown in Figure 4.2.3. which illustrates the conformation of substituents about the N(1) - S(1) bond and indicates the approximate position of the orbital occupied by the lone-pair of electrons on atom S(1). This orbital lies approximately on the S(1)N(1)S(2) plane, possibly destabilising the in-plane d-orbitals of the S(1) atom, as has been suggested in the analogous cases of $(S - N)_n$ cyclic compounds[11]. It is thus feasible that delocalisation of the lone-pairs of electrons on atom N(1), into the in-plane 3d-orbitals of S(1) (π'- bonding), may be adversely affected by such destabilisation effects, and that the observed S(1) - N(1) bond may contain a greater contribution from π-bonding than from π'-bonding, resulting from delocalisation of the appropriate lone-pairs of electrons on the nitrogen atom into those 3d-orbitals on atom S(1) which are least affected by the aforementioned destabilisation i,e, those 3d-orbitals perpendicular to the S(1)N(1)S(2) plane. Support for this suggestion may be derived from a comparison of the relevant S(IV) - N and N - sulphonyl bonds in compounds IX, XI (a - d) and XIII (Table 4.2.9.) It is seen that N-sulphonyl bond lengths in those systems containing two lone-pairs of electrons on the nitrogen atom, appear to lie in the range 1.581(10) - 1.618(7)Å, whilst the corresponding bond lengths in those systems containing only one lone pair of electrons on the nitrogen atom, are 1.676(5) and 1.681(5)Å for compounds IX and XIII respectively i.e. removal of one lone-pair of electrons from the nitrogen atom appears to have a considerable bond-lengthening effect on N - sulphonyl bonds. The $\overset{+}{S} - \overset{-}{N}$ bond lengths in compounds XI (a - d) and XIII however, do not show the same variation with N-alkylation but range from 1.620 - 1.644Å, the

shorter $\overset{+}{S} - \overset{-}{N}$ bond length in IX having been previously noted. These results may possibly be rationalised by consideration of the planar geometry of the N-alkylated systems[50], in which the electron lone-pair orbital is perpendicular to the S - N - S plane and is thus suitably orientated for π-bonding, but not π'-bonding. The apparently small increase in the $\overset{+}{S} - \overset{-}{N}$ bond resulting from N-alkylation may thus imply that π-bonding is dominant in this bond, whilst the bond lengthening observed in the N-sulphonyl bond may possibly reflect the importance of π'-bonding in this bond.

Figure 4.2.4. shows that, whilst the S(1) electron lone-pair orbital lies close to the S(1)N(2)S(3) plane, the N(2) electron lone-pair orbital is approximately perpendicular to this plane, thus allowing the possibility of $p\pi - d\pi$ interactions of the type postulated for the S(1) - N(1) bond (i.e. π-bonding in the plane perpendicular to the S - N - S system). It may therefore be, that both N(1) and N(2) lone-pairs of electrons are competing for delocalisation into the same combination of 3-d orbitals on atom S(1), with the (previously noted), minimal double-bond character in the S(1) - N(2) bond [1.702(4)Å] perhaps suggesting that delocalisation of lone pairs of electrons from the negatively-charged N(1) atom into the 3d-orbitals of atom S(1), occurs at the expense of similar delocalisation from atom N(2).

It has previously been noted[47] that the S(IV) - N - S(VI) = 0 (cis) torsion angles of (XI a - c) lie within a relatively narrow range [31 - 37°], the subsequent analysis of (XI d)[48] revealing a value of 35.3° which is in accord with this observation, and it has been suggested that the value of this torsion angle may be characteristic of such ylide systems. However the corresponding

S(IV)-N-S(VI)= O(cis) angle in (IX) is $-5.3(4)^{\circ}$, such that this grouping of atoms deviates little from coplanarity. Moreover, whereas a value of ca 50° is observed for the S(IV)-N-S(VI) = O (cis) torsion angle of XIII , the corresponding angle in the present molecule $[-9.2(3)^{\circ}]$ again shows a near planar arrangement for this grouping of atoms. (Figure 4.2.5. shows the relevant conformations about bonds S(2) - N(1) and S(3) - N(2)). Further examination of the relevant torsion angles (Table 4.2.10.) in compounds such as (XI a - d) shows that the value of torsion angle S(IV)-N-S(VI) = O (trans) does not differ grossly from 180° $[\text{ca } 160^{\circ} - 180^{\circ}]$, thus revealing a possible tendency towards coplanarity in the S(IV)-N-S(VI) = O system of such ylides, the cis or trans nature of the relevant oxygen atom perhaps being determined by other factors such as non-bonding interactions. In addition, Figure 4.2.6. demonstrates the differing orientation of the respective phenyl groups relative to the N(1) - S(2) - O_2 - R and N(2) - S(3) - O_2 - R systems. Whilst atom O(4) is approximately coplanar with the S(3) - bonded phenyl ring [torsion angle $O(4)S(3)C(21)C(26)1.1(6)^{\circ}$], neither atom O(1) nor O(2) is approximately coplanar with the S(2) - bonded phenyl ring [torsion angles $O(1)S(2)C(14)C(15)32.5(6)^{\circ}$, $O(2)S(2)C(14)C(15)-95.1(6)^{\circ}$] .

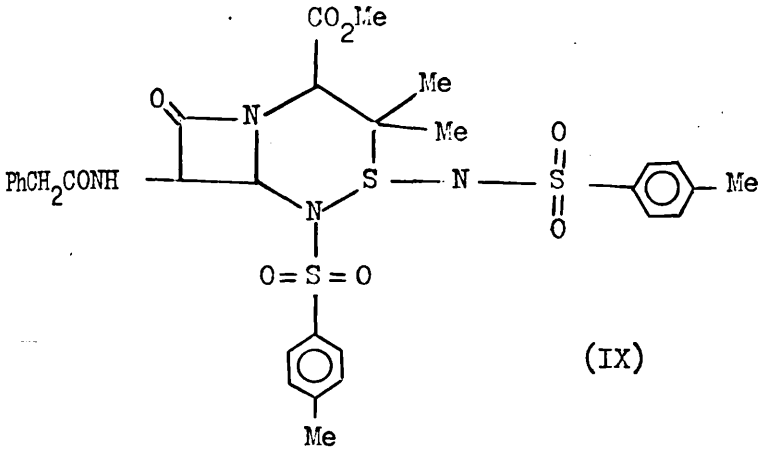
Examination of the relevant conformations of compounds (XI a - d) and XIII(Table 4.2.10,) reveals that, the conformation of the S(IV)-N-S(VI)-O_2Ar portion is analogous to that of the S(1)N(2) S(3)O(3 and 4) Ar moiety of the present molecule, in that one of the oxygen atoms of the $-SO_2$ group is approximately coplanar with

the S - N - S system, whilst the other is approximately coplanar with the phenyl ring. The predominance of this conformation may imply that $p\pi - d\pi$ conjugation is thus maximised and that this is the preferred conformation in the absence of other unfavourable factors, such as steric interactions. In seeking an explanation for the apparently anomalous orientation of the S(2) - bonded phenyl ring, it is noted that the overall conformation of the molecule is such that the S(2) and the S(3) - bonded phenyl rings come into close proximity, both within the molecule and also between screw-axis related molecules, resulting in possible steric interactions between atoms such as C(16)···C(23) [3.55Å], C(17)···C(23) [3.67Å], C(15)···C(22) [3.72Å], C(15)···C(23) [3.66Å and 3.54Å] and C(14)···C(22) [3.57Å]. It is thus feasible that such interactions may contribute towards the observed orientation of the S(2) - bonded phenyl ring.

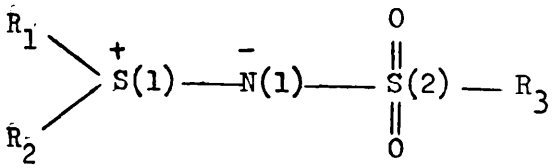
Other aspects of the geometry of IX compare well with literature values for similar bonding systems. The heterocyclic six-membered ring adopts a chair conformation in which S(1) and N(3) are respectively -0.965 and 0.500Å distant from the plane of atoms C(1), C(2), C(5) and N(2). The pseudo-axial and pseudo-equatorial orientations of the S(1) - N(1) and N(2) - S(3) bonds respectively, avoid serious interactions between adjacent ring-bonded atoms. The four-membered ring is significantly non-planar, with an average endocyclic torsion-angle modulus of 11.5°.

Intermolecular distance, O(5)···N(4) [2.88Å], suggests possible interactions between these atoms but since the hydrogen atom bonded to atom N(4) could not be located from difference syntheses no

accurate assessment of possible hydrogen bonding can be made. A diagram representing the crystal-packing arrangements of compound IX is given in Figure 4.2.7.



(IX)



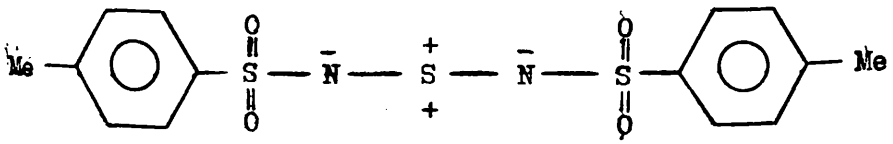
(XI)

(a) $R_1=R_2=R_3=Me$

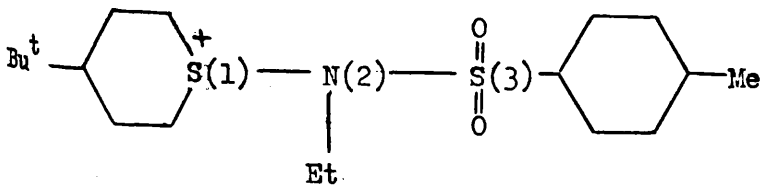
(b) $R_1=R_2=Ph$, R_3=p-tolyl

(c) $R_1=R_2=Me$, R_3=p-tolyl

(d) $R_1=Ph$, $R_2=C_3H_7$, R_3=p-tolyl



(XII)



(XIII)

TABLE 4.2.1.

h	k	l	E	Phi	
13	1	-6	2.64	360°	Origin Defining Reflections
3	0	4	2.29	360°	
16	0	-13	2.26	360°	
3	1	0	2.75	a	
2	1	1	2.77	b	

The choice of the above five reflections was based on their high $|E|$ values, ability to form a considerable number of phase relationships and their ability to adequately define a unit cell origin and enantiomorph. While the origin-defining reflections were arbitrarily assigned phase values of 360°, the unknown phases a and b were respectively assigned values of $\pi/4$, $3\pi/4$ and $(\pm)\ \pi/4$, $(\pm)\ 3\pi/4$, (the enantiomorph being defined by the 3 1 0 reflection) and the correct set of starting phases was found to require values of 135° and 45° respectively for phases a and b.

TABLE 4.2.2.

COURSE OF REFINEMENT

Parameters Refined	Cycle	Final R	Final R'
x, y, z, U_{iso} of all non-hydrogen atoms; scale factor; unit weights.	1 - 3	0.126	0.014
x, y, z, U_{iso} of all non-hydrogen atoms; hydrogen atoms in structure-factor calculations but not refined; scale factor; unit weights.	4 - 5	0.124	0.015
x, y, z, U_{ij} (i, j = 1, 2, 3) for all non-hydrogen atoms in group (1); all other atoms fixed but included in structure-factor calculations; scale factor; unit weights.	6 - 8	0.087	0.009
x, y, z, U_{ij} (i, j = 1, 2, 3) for all non-hydrogen atoms in group (2); all other atoms fixed but included in structure-factor calculations; scale factor; unit weights.	9 - 11	0.073	0.007
x, y, z, U_{ij} (i, j = 1, 2, 3) for all non-hydrogen atoms in			

TABLE 4.2.2. (Cont.)

Parameters Refined	Cycle	Final R	Final R'
group (3); all other atoms fixed but included in structure-factor calculations; scale factor; unit weights.	12 - 14	0.066	0.006
x, y, z, U_{ij} $(i, j = 1, 2, 3)$ for non-hydrogen atoms in group (1); all other atoms fixed but included in structure-factor calculations; scale factor; weighting scheme adjusted.	15 - 16	0.063	0.009
x, y, z, U_{ij} $(i, j = 1, 2, 3)$ for non-hydrogen atoms in group (2); all other atoms fixed but included in structure-factor calculations; scale factor; weighting scheme adjusted.	17 - 18	0.054	0.007
x, y, z, U_{ij} $(i, j = 1, 2, 3)$ for non-hydrogen atoms in group (3); all other atoms fixed but included in structure-factor calculations; scale factor; weighting scheme adjusted.	19 - 20	0.048	0.005

TABLE 4.2.2. (Cont.)

ATOMS IN GROUP (1)	ATOMS IN GROUP (2)	ATOMS IN GROUP (3)
S(3)	S(1)	S(3)
C(14)	S(2)	O(7)
C(15)	O(1)	C(30)
C(16)	O(2)	O(8)
C(17)	S(3)	C(31)
C(18)	O(3)	N(4)
C(19)	O(4)	C(6)
C(20)	N(1)	O(6)
C(21)	N(2)	C(7)
C(22)	C(1)	C(8)
C(23)	C(2)	C(9)
C(24)	C(3)	C(10)
C(25)	C(4)	C(11)
C(26)	C(5)	C(12)
C(27)	N(3)	C(13)
	O(5)	
	C(28)	
	C(29)	

TABLE 4.2.3.

(a) Atomic Fractional Coordinates and E.S.Ds

ATOM	x/a	y/b	z/c
S(1)	0.11300(7)	-0.23955(19)	0.43001(8)
S(2)	0.01079(8)	-0.09498(26)	0.25161(9)
S(3)	0.21765(7)	-0.53880(-)	0.41281(9)
O(1)	-0.0378(3)	-0.2508(9)	0.2450(3)
O(2)	-0.0388(4)	0.0613(10)	0.2462(4)
O(3)	0.1292(3)	-0.5997(5)	0.4030(4)
O(4)	0.2952(3)	-0.6056(6)	0.4898(3)
O(5)	0.4549(2)	-0.0389(6)	0.6182(3)
O(6)	0.4119(3)	0.0104(5)	0.3693(4)
O(7)	0.3238(3)	0.0059(6)	0.7321(2)
O(8)	0.2333(2)	0.2200(4)	0.6620(2)
N(1)	0.0993(3)	-0.0868(7)	0.3521(3)
N(2)	0.2131(3)	-0.3337(6)	0.4385(3)
N(3)	0.3008(2)	-0.1023(5)	0.5280(3)
N(4)	0.4402(2)	-0.2604(6)	0.4163(3)
C(1)	0.1530(3)	-0.1267(7)	0.5542(3)
C(2)	0.2328(3)	-0.0059(6)	0.5545(3)
C(3)	0.3943(3)	-0.1139(7)	0.5580(4)
C(4)	0.3875(3)	-0.2620(7)	0.4838(4)
C(5)	0.2834(3)	-0.2116(6)	0.4394(3)
C(6)	0.4490(3)	-0.1224(6)	0.3633(4)
C(7)	0.5123(4)	-0.1492(9)	0.3007(4)
C(8)	0.4921(3)	-0.0385(7)	0.2091(4)
C(9)	0.4248(4)	-0.0706(10)	0.1166(5)
C(10)	0.4130(5)	0.0327(12)	0.0311(5)
C(11)	0.4692(5)	0.1647(12)	0.0379(5)
C(12)	0.5335(5)	0.2038(11)	0.1270(6)
C(13)	0.5457(4)	0.1044(9)	0.2134(4)
C(14)	0.0555(4)	-0.0881(9)	0.1498(4)
C(15)	0.0069(4)	-0.1646(10)	0.0596(5)
C(16)	0.0388(5)	-0.1625(10)	-0.0223(5)
C(17)	0.1185(5)	-0.0787(10)	-0.0166(5)
C(18)	0.1656(5)	0.0000(10)	0.0733(6)
C(19)	0.1359(5)	-0.0037(10)	0.1573(5)
C(20)	0.1503(7)	-0.0747(14)	-0.1092(6)
C(21)	0.2360(4)	-0.5434(8)	0.2965(5)
C(22)	0.1707(4)	-0.4820(10)	0.2105(5)
C(23)	0.1874	-0.4800(11)	0.1176(5)
C(24)	0.2684(6)	-0.5409(11)	0.1112(5)
C(25)	0.3326(5)	-0.6069(12)	0.1957(6)
C(26)	0.3170(4)	-0.6093(10)	0.2904(5)

TABLE 4.2.3. (Cont.)

ATOM	x/a	y/b	z/c
C(27)	0.2835(9)	-0.5325(18)	0.0084(7)
C(28)	0.0708(3)	-0.0245(10)	0.5569(5)
C(29)	0.1795(4)	-0.2634(9)	0.6355(4)
C(30)	0.2710(3)	0.0708(6)	0.6611(3)
C(31)	0.2571(4)	0.3103(8)	0.7606(4)

TABLE 4.2.3.

(b) Hydrogen-Atom Fractional Coordinates

ATOM	x/a	y/b	z/c
H(2)	0.2057	0.0795	0.5102
H(4)	0.3916	-0.3722	0.5281
H(5)	0.2717	-0.1522	0.3685
H(7)	0.5433	-0.2500	0.3084
H(9)	0.3874	-0.1765	0.1177
H(10)	0.3746	0.0000	-0.0334
H(11)	0.4628	0.2352	-0.0254
H(12)	0.5879	0.2917	0.1357
H(13)	0.5936	0.1667	0.2757
H(15)	-0.0428	-0.2061	0.0523
H(16)	0.0117	-0.2044	-0.0811
H(18)	0.2278	0.0514	0.0904
H(19)	0.1585	0.0738	0.2119
H(20)	0.1088	-0.0833	-0.1763
H(20')	0.1877	0.0244	-0.1051
H(20'')	0.1909	-0.1809	-0.1028
H(22)	0.1153	-0.4489	0.2199
H(23)	0.1432	-0.4 30	0.0548
H(25)	0.3902	-0.6591	0.1934
H(26)	0.3659	-0.6483	0.3434
H(27)	0.2850	-0.6514	-0.0221
H(27')	0.2286	-0.4748	-0.0454
H(28)	0.0173	-0.0998	0.5404
H(28')	0.0857	0.0180	0.6288
H(28'')	0.0470	0.0833	0.5123
H(29)	0.1852	-0.2083	0.7062
H(29')	0.1331	-0.3576	0.6223
H(29'')	0.2334	-0.3333	0.6431
H(31)	0.2283	0.2500	0.8064
H(31')	0.3127	0.2917	0.8004
H(32'')	0.2264	0.4005	0.7503

TABLE 4.2.3.

(c) Anisotropic Temperature Factors ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0332	0.0533	0.0488	-0.0039	0.0188	-0.0059
S(2)	0.0369	0.0929	0.0473	0.0063	0.0122	-0.0015
S(3)	0.0497	0.0420	0.0692	-0.0063	0.0291	-0.0042
O(1)	0.050	0.143	0.062	-0.038	0.016	-0.004
O(2)	0.074	0.157	0.066	0.061	0.024	0.003
O(3)	0.063	0.058	0.129	-0.024	0.056	0.017
O(4)	0.069	0.054	0.067	0.007	0.025	0.014
O(5)	0.039	0.068	0.071	-0.015	0.018	-0.005
O(6)	0.096	0.057	0.118	0.023	0.078	0.025
O(7)	0.070	0.086	0.049	0.021	0.003	-0.006
O(8)	0.066	0.049	0.050	0.002	0.026	-0.006
N(1)	0.049	0.063	0.049	-0.000	0.011	-0.000
N(2)	0.040	0.043	0.067	-0.007	0.027	-0.010
N(3)	0.032	0.044	0.052	-0.004	0.019	-0.009
N(4)	0.047	0.051	0.073	0.002	0.036	0.001
C(1)	0.037	0.058	0.049	-0.004	0.025	-0.006
C(2)	0.035	0.047	0.039	0.004	0.018	-0.003
C(3)	0.035	0.046	0.066	-0.001	0.027	0.004
C(4)	0.037	0.047	0.063	-0.002	0.028	-0.001
C(5)	0.040	0.046	0.055	-0.005	0.031	-0.005
C(6)	0.054	0.053	0.079	0.008	0.042	0.007
C(7)	0.069	0.084	0.086	0.029	0.057	0.024
C(8)	0.047	0.069	0.063	0.004	0.031	-0.004
C(9)	0.059	0.094	0.101	-0.008	0.026	-0.023
C(10)	0.082	0.120	0.058	0.021	0.001	-0.013
C(11)	0.087	0.111	0.082	0.010	0.042	0.015
C(12)	0.086	0.104	0.093	-0.007	0.039	0.013
C(13)	0.067	0.087	0.061	-0.013	0.023	-0.006
C(14)	0.044	0.059	0.044	0.003	0.016	0.002
C(15)	0.043	0.065	0.055	-0.005	0.009	-0.003
C(16)	0.064	0.064	0.050	-0.003	0.018	-0.003
C(17)	0.073	0.057	0.062	0.007	0.029	0.011
C(18)	0.062	0.062	0.071	-0.008	0.029	0.005
C(19)	0.059	0.065	0.056	-0.011	0.015	-0.012
C(20)	0.100	0.100	0.069	-0.006	0.047	-0.014
C(21)	0.041	0.045	0.063	0.002	0.017	-0.014
C(22)	0.051	0.069	0.063	0.016	0.012	-0.009
C(23)	0.068	0.075	0.062	0.025	0.011	-0.006
C(24)	0.083	0.064	0.058	0.003	0.023	-0.019
C(25)	0.065	0.085	0.072	0.010	0.031	-0.019
C(26)	0.048	0.069	0.064	0.018	0.017	-0.003
C(27)	0.176	0.122	0.061	0.035	0.061	0.002
C(28)	0.038	0.081	0.080	0.004	0.026	-0.023

TABLE 4.2.3. (Cont.)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	0.057	0.069	0.060	-0.008	0.031	0.010
C(30)	0.043	0.057	0.047	-0.003	0.022	-0.000
C(31)	0.068	0.070	0.055	-0.007	0.027	-0.016
Average Estimated Standard Deviations						
S	0.0005	0.0007	0.0006	0.0005	0.0005	0.0006
O	0.002	0.003	0.002	0.002	0.002	0.003
N	0.002	0.002	0.002	0.002	0.002	0.002
C	0.004	0.004	0.003	0.003	0.003	0.003

TABLE 4.2.4.

Intramolecular Bonded Distances

ATOM A	ATOM B	Å
S(1)	N(1)	1.592(5)
S(1)	N(2)	1.702(4)
S(1)	C(1)	1.858(5)
S(2)	N(1)	1.613(4)
S(2)	O(1)	1.440(7)
S(2)	O(2)	1.453(8)
S(2)	C(14)	1.764(5)
S(3)	N(2)	1.676(5)
S(3)	O(3)	1.428(4)
S(3)	O(4)	1.431(4)
S(3)	C(21)	1.724(6)
N(2)	C(5)	1.462(6)
N(3)	C(2)	1.450(6)
N(3)	C(3)	1.385(6)
N(3)	C(5)	1.454(6)
N(4)	C(4)	1.432(6)
N(4)	C(6)	1.351(7)
C(1)	C(2)	1.573(7)
C(1)	C(28)	1.530(8)
C(1)	C(29)	1.522(8)
C(2)	C(30)	1.528(6)
C(3)	C(4)	1.543(7)
C(3)	O(5)	1.197(6)
C(4)	C(5)	1.591(6)
C(6)	C(7)	1.525(7)
C(6)	O(6)	1.220(7)
C(7)	C(8)	1.491(8)
C(8)	C(9)	1.392(8)
C(9)	C(10)	1.402(11)
C(10)	C(11)	1.351(12)
C(11)	C(12)	1.351(11)
C(12)	C(13)	1.394(10)
C(13)	C(8)	1.401(9)
C(14)	C(15)	1.374(8)
C(15)	C(16)	1.377(9)
C(16)	C(17)	1.392(10)
C(17)	C(20)	1.517(11)
C(17)	C(18)	1.373(10)
C(18)	C(19)	1.384(10)
C(19)	C(14)	1.398(9)
C(21)	C(22)	1.382(9)
C(22)	C(23)	1.392(10)
C(23)	C(24)	1.384(11)
C(24)	C(27)	1.517(12)
C(24)	C(25)	1.374(11)
C(25)	C(26)	1.408(10)

TABLE 4.2.4. (Cont.)

ATOM A	ATOM B	Å
C(26)	C(21)	1.397(9)
C(30)	O(7)	1.178(6)
C(30)	O(8)	1.325(6)
C(31)	O(8)	1.447(6)

TABLE 4.2.5.

Valency Angles (°) and E.S.Ds

C(1)	S(1)	N(1)	100.9(2)	N(2)	C(5)	C(4)	120.4(3)
C(1)	S(1)	N(2)	97.0(2)	N(3)	C(5)	C(4)	86.3(3)
N(1)	S(1)	N(2)	107.6(2)	N(4)	C(6)	C(7)	113.2(4)
N(1)	S(2)	O(1)	112.1(3)	N(4)	C(6)	O(6)	122.2(3)
N(1)	S(2)	O(2)	107.6(3)	C(7)	C(6)	O(6)	124.6(4)
N(1)	S(2)	C(14)	103.8(2)	C(6)	C(7)	C(8)	113.8(4)
O(1)	S(2)	O(2)	118.2(3)	C(7)	C(8)	C(9)	124.2(5)
O(1)	S(2)	C(14)	108.2(3)	C(7)	C(8)	C(13)	118.9(4)
O(2)	S(2)	C(14)	105.9(3)	C(9)	C(8)	C(13)	116.8(4)
N(2)	S(3)	O(3)	104.1(2)	C(8)	C(9)	C(10)	121.5(4)
N(2)	S(3)	O(4)	106.7(2)	C(9)	C(10)	C(11)	119.4(5)
N(2)	S(3)	C(21)	104.5(3)	C(10)	C(11)	C(12)	121.1(5)
O(3)	S(3)	O(4)	120.2(2)	C(11)	C(12)	C(13)	120.5(5)
O(3)	S(3)	C(21)	110.6(3)	C(12)	C(13)	C(8)	120.6(4)
O(4)	S(3)	C(21)	109.4(3)	S(2)	C(14)	C(15)	117.9(3)
S(1)	N(1)	S(2)	116.3(2)	S(2)	C(14)	C(19)	122.3(3)
S(1)	N(2)	S(3)	121.0(2)	C(15)	C(14)	C(19)	119.8(4)
S(1)	N(2)	C(5)	112.3(3)	C(14)	C(15)	C(16)	120.1(4)
S(3)	N(2)	C(5)	124.4(2)	C(15)	C(16)	C(17)	120.9(5)
C(2)	N(3)	C(3)	138.2(3)	C(16)	C(17)	C(18)	118.4(5)
C(2)	N(3)	C(5)	125.2(3)	C(17)	C(18)	C(19)	121.7(5)
C(3)	N(3)	C(5)	96.0(3)	C(18)	C(19)	C(14)	119.0(5)
C(4)	N(4)	C(6)	122.8(3)	C(16)	C(17)	C(20)	119.6(5)
S(1)	C(1)	C(2)	109.0(2)	C(18)	C(17)	C(20)	122.0(5)
S(1)	C(1)	C(28)	104.3(2)	S(3)	C(21)	C(22)	119.8(3)
S(1)	C(1)	C(29)	105.6(3)	S(3)	C(21)	C(26)	119.5(3)
C(2)	C(1)	C(28)	110.2(4)	C(22)	C(21)	C(26)	120.7(5)
C(2)	C(1)	C(29)	114.1(3)	C(21)	C(22)	C(23)	119.5(5)
C(28)	C(1)	C(29)	113.0(4)	C(22)	C(23)	C(24)	120.3(5)
C(1)	C(2)	N(3)	108.7(3)	C(23)	C(24)	C(25)	120.6(5)
C(1)	C(2)	C(30)	107.9(3)	C(23)	C(24)	C(27)	117.9(6)
N(3)	C(2)	C(30)	111.6(3)	C(25)	C(24)	C(27)	121.6(6)
N(3)	C(3)	O(5)	134.0(3)	C(24)	C(25)	C(26)	120.0(5)
N(3)	C(3)	C(4)	90.6(4)	C(25)	C(26)	C(21)	119.0(5)
C(4)	C(3)	O(5)	135.4(4)	C(2)	C(30)	O(7)	125.4(4)
C(3)	C(4)	N(4)	119.8(4)	C(2)	C(30)	O(8)	109.3(3)
C(3)	C(4)	C(5)	84.7(3)	O(7)	C(30)	O(8)	125.3(3)
N(4)	C(4)	C(5)	118.5(3)	C(30)	C(8)	C(31)	115.4(3)
N(2)	C(5)	N(3)	109.8(3)				

TABLE 4.2.6.

Selected Torsion Angles (°)

(a) Ylide Moiety

C(1)	S(1)	N(1)	S(2)	-139.6(3)
N(2)	S(1)	N(1)	S(2)	119.4(3)
S(1)	N(1)	S(2)	O(1)	-5.3(4)
S(1)	N(1)	S(2)	O(2)	126.3(4)
S(1)	N(1)	S(2)	C(14)	-121.8(3)
N(1)	S(2)	C(14)	C(15)	151.7(5)
N(1)	S(2)	C(14)	C(19)	-30.4(6)
O(1)	S(2)	C(14)	C(15)	32.5(6)
O(1)	S(2)	C(14)	C(19)	-149.6(5)
O(2)	S(2)	C(14)	C(15)	-95.1(6)
O(2)	S(2)	C(14)	C(19)	82.8(6)
N(1)	S(1)	N(2)	S(3)	-123.3(3)
S(1)	N(2)	S(3)	O(3)	-9.2(3)
S(1)	N(2)	S(3)	O(4)	-137.3(3)
O(3)	S(3)	C(21)	C(22)	46.6(6)
O(3)	S(3)	C(21)	C(26)	-133.5(5)
O(4)	S(3)	C(21)	C(22)	-178.9(5)
O(4)	S(3)	C(21)	C(26)	1.1(6)

(b) Six-membered Ring

N(2)	S(1)	C(1)	C(2)*	59.2(3)
N(1)	S(1)	C(1)	C(28)	67.4(4)
N(1)	S(1)	C(1)	C(29)	-173.3(4)
S(1)	C(1)	C(2)	N(3)*	-52.9(4)
C(28)	C(1)	C(2)	C(30)	72.1(5)
C(29)	C(1)	C(2)	C(30)*	-56.3(5)
C(1)	C(2)	N(3)	C(5)	51.2(5)
C(30)	C(2)	N(3)	C(3)*	-20.4(7)
C(2)	N(3)	C(5)	N(2)*	-54.0(6)
C(3)	N(3)	C(5)	C(4)*	11.9(4)
N(3)	C(5)	N(2)	S(1)*	61.5(4)
C(4)	C(5)	N(2)	S(3)*	-38.5(6)
C(5)	N(2)	S(1)	C(1)*	-64.1(4)
S(3)	N(2)	S(1)	N(1)	-123.3(3)

(c) Four-membered Ring

C(5)	N(3)	C(3)	C(4)*	-12.3(4)
C(2)	N(3)	C(3)	O(5)*	-3.0(10)
N(3)	C(3)	C(4)	C(5)*	11.2(3)
O(5)	C(3)	C(4)	N(4)*	-49.5(8)
C(3)	C(4)	C(5)	N(3)*	-10.7(3)
N(4)	C(4)	C(5)	N(2)*	117.3(5)
C(4)	C(5)	N(3)	C(3)*	11.9(4)
N(2)	C(5)	N(3)	C(2)	-54.0(6)

* Endocyclic Values

TABLE 4.2.7.

Least-squares planes for various portions of the molecular framework in the form $lX' + mY' + nZ' = d$, where X', Y' and Z' represent an orthogonalised set of axes.

(a) Plane Equations

Plane (1) = $0.4345X' - 0.8422Y' + 0.3193Z' = 1.2933$

Plane (2) = $-0.3644X' - 0.9072Y' - 0.2104Z' = 2.2615$

Plane (3) = $-0.7756X' + 0.5706Y' + 0.2700Z' = -4.6486$

Plane (4) = $0.3626X' - 0.4468Y' + 0.8179Z' = 6.3563$

(b) Deviations of Atoms from Planes (Starred Atoms Define the Plane)

Plane (1) = C(14)* 0.006, C(15)* -0.011, C(16)* -0.008, C(17)* 0.001, C(18) -0.007, C(19) 0.004, C(20) -0.016, S(2) -0.025

Plane (2) = C(21)* -0.015, C(22)* 0.010, C(23)* 0.003, C(24)* -0.011, C(25)* 0.006, C(26)* 0.007, C(27) -0.044, S(3) -0.073

Plane (3) = C(8)* -0.017, C(9)* 0.004, C(10)* 0.015, C(11)* -0.019, C(12)* 0.005, C(13)* 0.013, C(7) -0.119

Plane (4) = C(1)* -0.013, C(2)* 0.013, C(5)* -0.014, N(1)* 0.014 S(1) -0.965, N(3) 0.500

TABLE 4.2.8.

Relevant Intramolecular Non-bonding Distances (Å)

ATOM A	ATOM B		Å
S(1)	O(1)		2.864
S(1)	O(3)		2.910
O(6)	C(3)		2.888
O(6)	C(5)		3.058
O(6)	O(5)		3.313
O(7)	C(29)		3.081
O(7)	O(5)		2.982
C(14)	C(22)		3.574
C(15)	C(22)		3.716
C(15)	C(23)		3.661
C(16)	C(23)		3.549
C(17)	C(23)		3.673
Intermolecular Distances (Å) < 3.60Å			
O(6)	C(26)	I	3.39
O(8)	O(4)	I	3.17
C(2)	O(4)	I	3.53
C(31)	C(27)	I	3.57
O(2)	C(20)	II	3.59
C(15)	C(23)	II	3.54
C(20)	O(1)	II	3.33
O(2)	C(29)	III	3.43
C(28)	O(3)	III	3.40
C(31)	O(1)	III	3.43
O(5)	C(7)	IV	3.28
O(5)	C(25)	IV	3.52
O(5)	C(26)	IV	3.42
C(7)	O(4)	IV	3.45
C(12)	O(7)	IV	3.42
O(5)	N(4)	IV	2.88

where the position of atom B is given by,

I
II = x, 1+y, z
III = -x, ½+y, -z
IV = -x, ½+y, 1-z
= 1-x, ½+y, 1-z

TABLE 4.2.9.

Compound	Ref.	$\overset{+}{\underset{}{\gtrless}}\text{S} - \overset{-}{\text{N}} -$	$-\overset{-}{\text{N}} - \text{SO}_2 -$	$\overset{+}{\underset{}{\gtrless}}\text{S} - \overset{R}{\underset{|}{\text{N}}} -$	$-\overset{R}{\underset{|}{\text{N}}} - \text{SO}_2 -$
IX	-	1.592(5)	1.613(4)	1.702(4)	1.676(5)
XI(a)	6	1.639(9)	1.581(10)	-	-
XI(b)	7	1.628(7)	1.598(8)	-	-
XI(c)	47	1.636(8)	1.591(8)	-	-
XI(d)	48	1.620(7)	1.618(7)	-	-
XIII	50	-	-	1.644(5)	1.681(5)

TABLE 4.2.10.

Compound	Ref.	τ°_{cis}	τ°_{trans}	$\tau^{\circ}_{\phi\text{-S=O}}$
IX	-	-5.3	-	32.5
	-	-9.2	-	1.1
XI(b)	6	31.7	160.5	-
XI(c)	7	34.9	163.9	14.3
XI(d)	47	36.8	167.2	11.2
XIII	48	35.3	163.7	-15.4
	50	-50.9	180	0.6

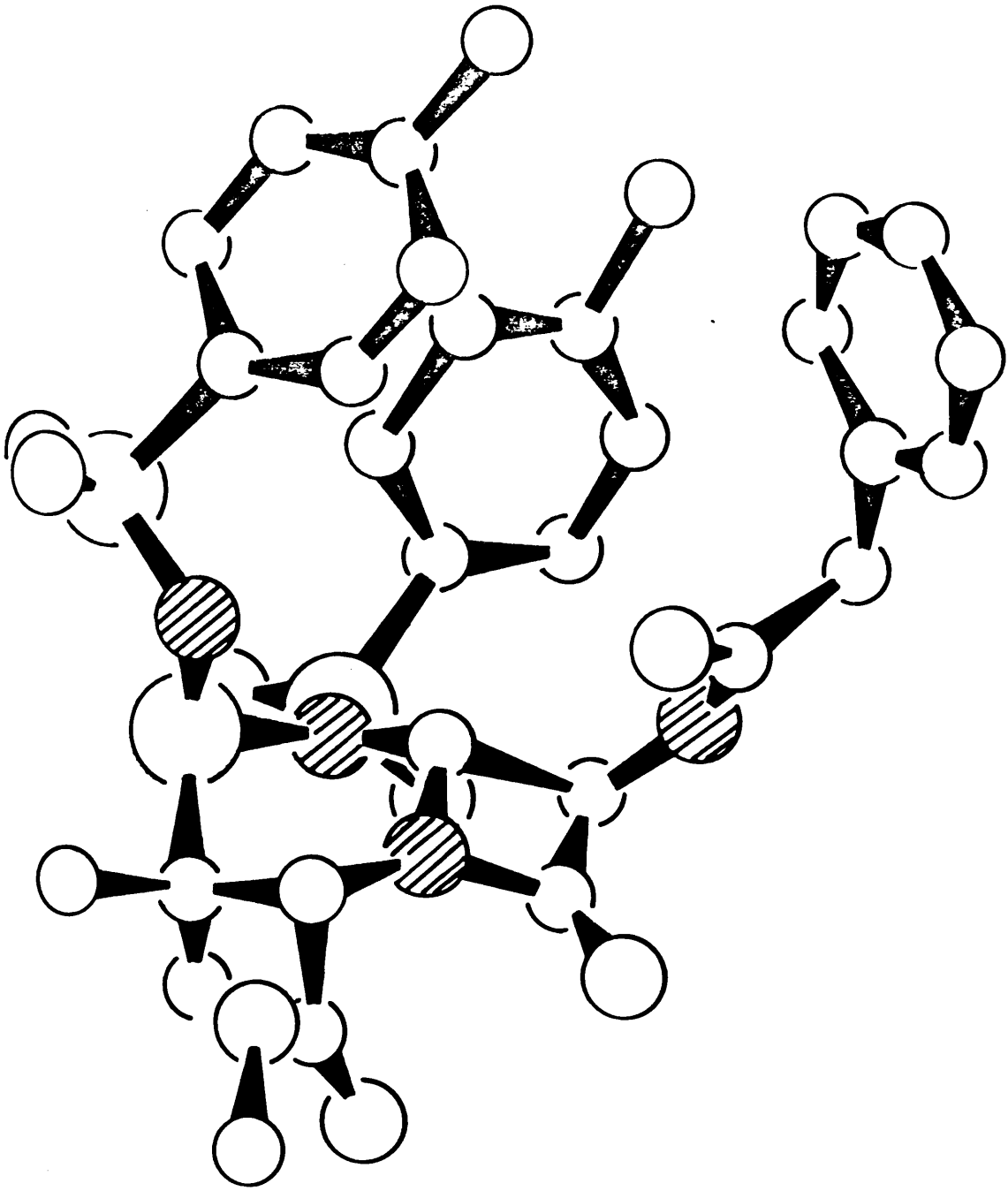
where τ°_{cis} = Torsion Angle $\overset{+}{\text{X}} - \overset{-}{\text{N}} - \text{Z} = 0$ (cis)

τ°_{trans} = Torsion Angle $\overset{+}{\text{X}} - \overset{-}{\text{N}} - \text{Z} = 0$ (trans)

$\tau^{\circ}_{\phi\text{-S=O}}$ = Torsion Angle $\phi - \text{S} = 0$ (cis)

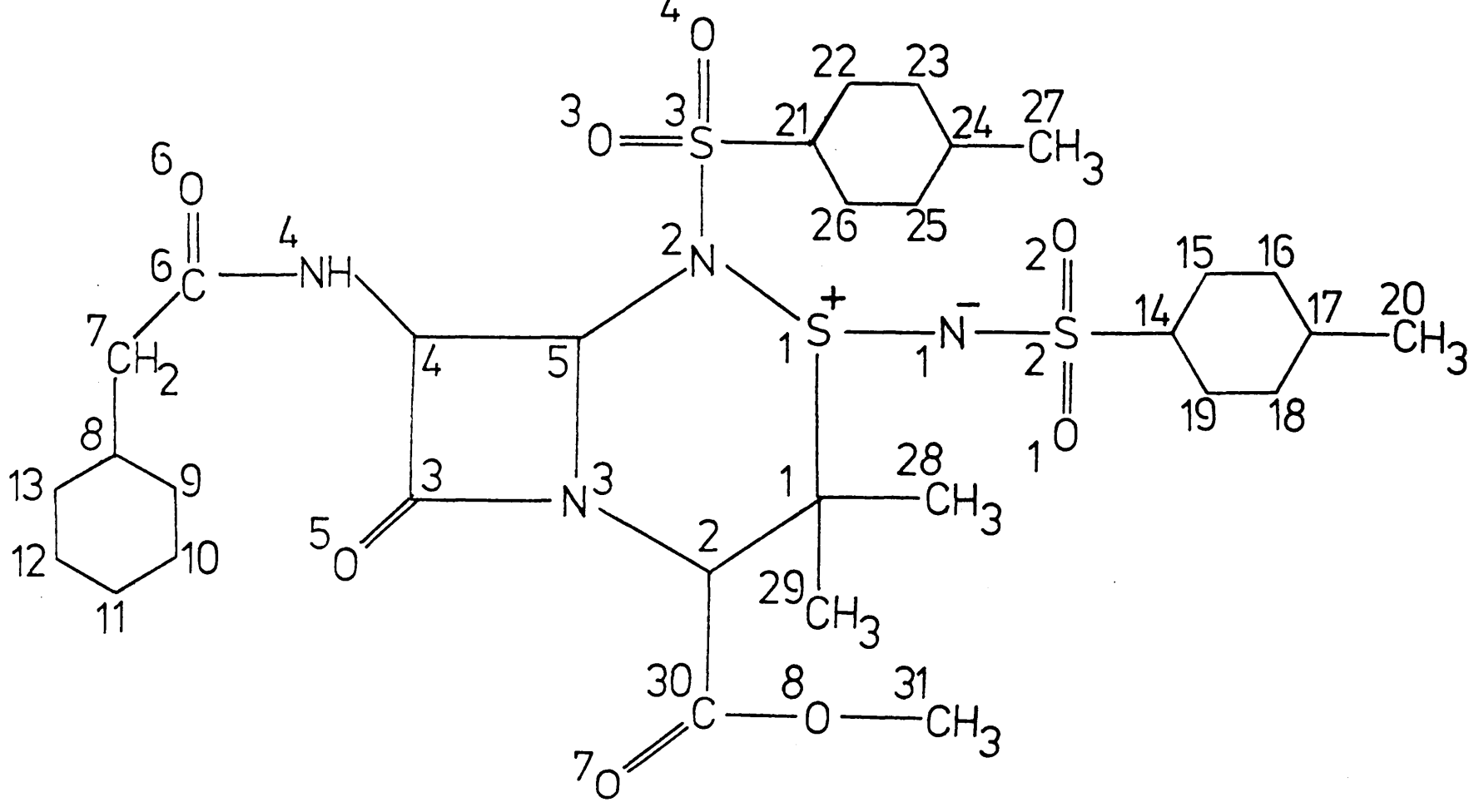
F I G U R E 4.2.1.

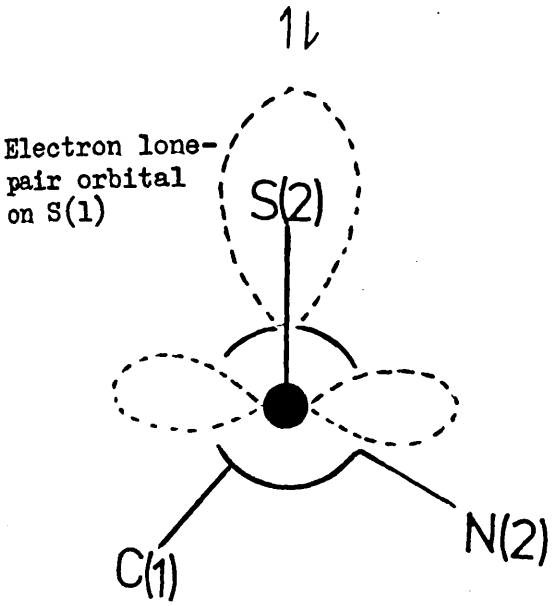
Diagrammatic representation of Compound IX



F I G U R E 4.2.2.

Numbering scheme for Compound IX

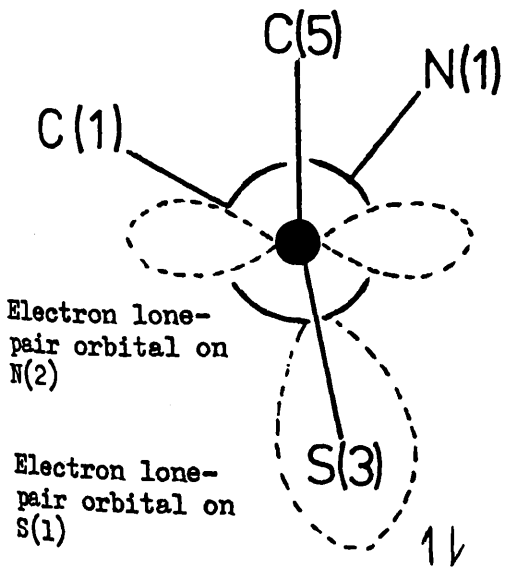




TORSION ANGLES

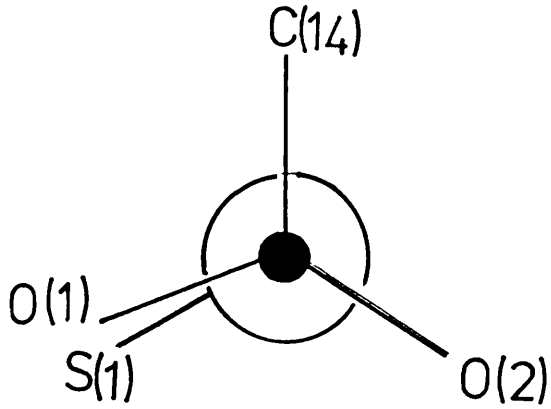
S(2)	N(1)	S(1)	C(1)	-139.6(3)
S(2)	N(1)	S(1)	N(2)	119.4(3)

FIGURE 4.2.3.



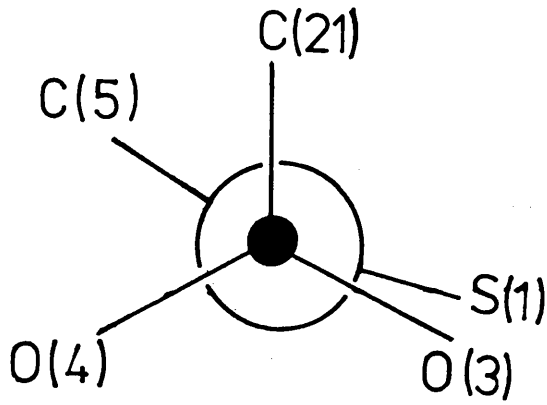
S(3)	N(2)	S(1)	N(1)	-123.3(3)
S(3)	N(2)	S(1)	C(1)	132.8(3)
C(5)	N(2)	S(1)	N(1)	39.7(4)
C(5)	N(2)	S(1)	C(1)	-64.1(4)

FIGURE. 4.2.4.



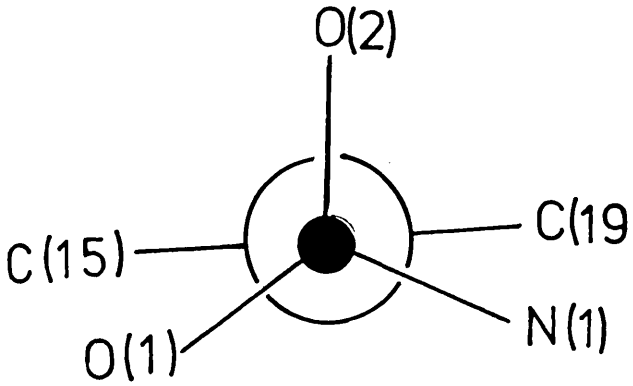
TORSION ANGLES

C(14)	S(2)	N(1)	S(1)	-121.8(3)
O(1)	S(2)	N(1)	S(1)	-5.3(4)
O(2)	S(2)	N(1)	S(1)	126.3(4)



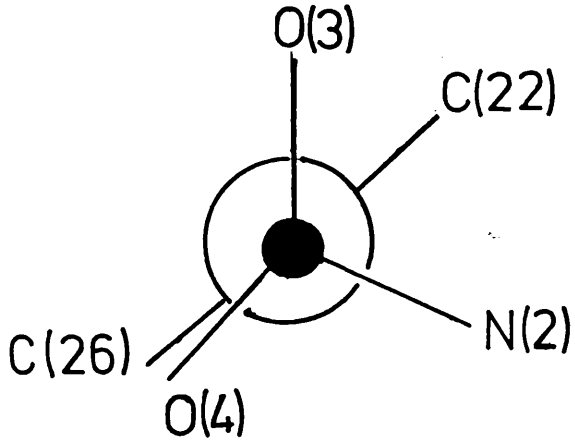
C(21)	S(3)	N(2)	S(1)	107.0(3)
C(21)	S(3)	N(2)	C(5)	-53.9(4)
O(3)	S(3)	N(2)	S(1)	-9.2(3)
O(3)	S(3)	N(2)	C(5)	-170.1(4)
O(4)	S(3)	N(2)	S(1)	-136.3(3)
O(4)	S(3)	N(2)	C(5)	61.9(4)

FIGURE 4.2.5.



TORSION ANGLES

O(2)	S(2)	C(14)	C(15)	-95.1(6)
O(2)	S(2)	C(14)	C(19)	82.8(6)
O(1)	S(2)	C(14)	C(15)	32.5(6)
O(1)	S(2)	C(14)	C(14)	-149.6(5)
N(1)	S(2)	C(14)	C(15)	131.7(5)
N(1)	S(2)	C(15)	C(19)	-30.4(6)

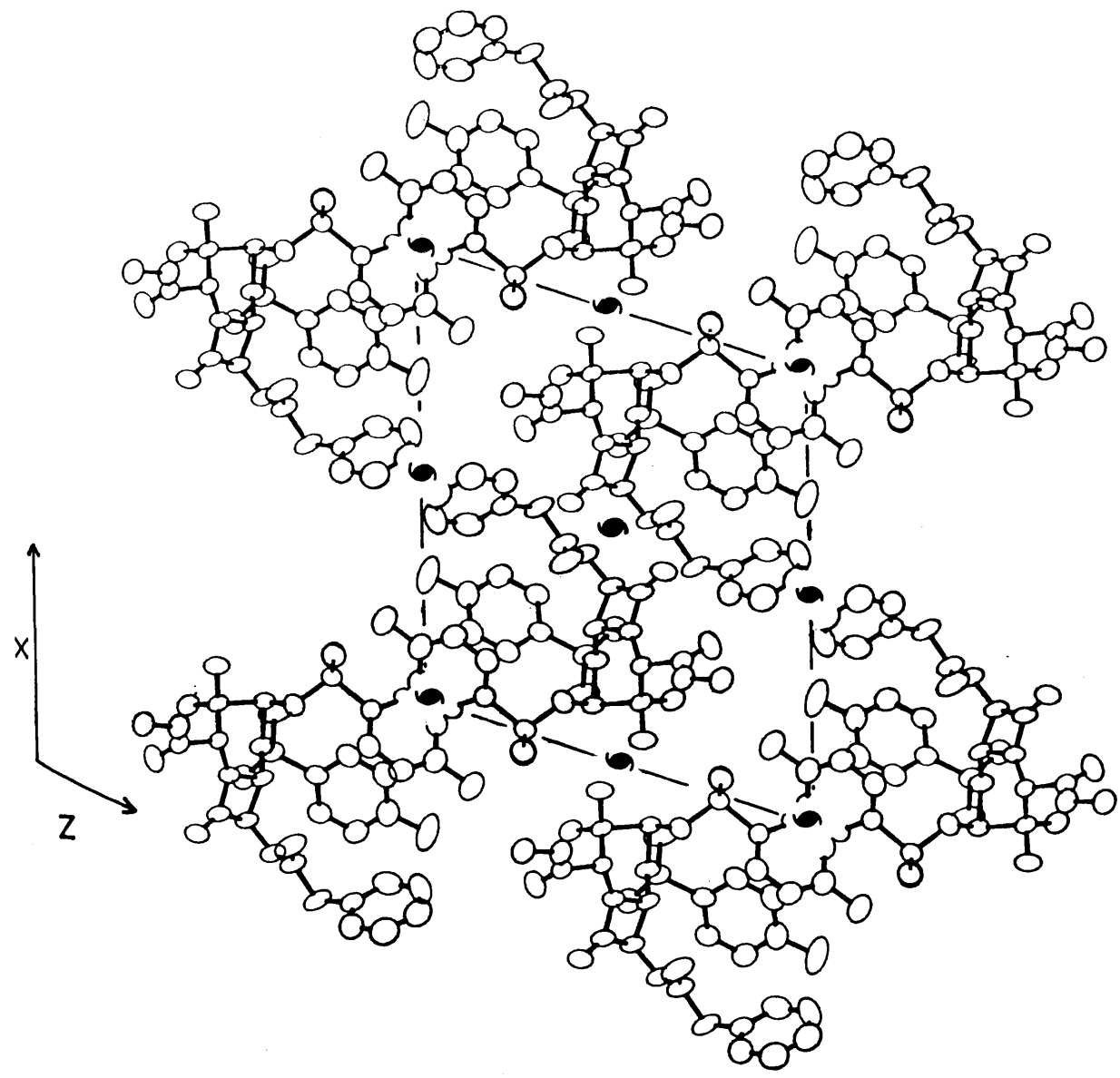


O(3)	S(3)	C(21)	C(22)	46.6(6)
O(3)	S(3)	C(21)	C(26)	-133.5(5)
O(4)	S(3)	C(21)	C(22)	-178.9(5)
O(4)	S(3)	C(21)	C(26)	1.1(6)
N(2)	S(3)	C(21)	C(22)	-65.0(6)
N(2)	S(3)	C(21)	C(26)	115.0(5)

FIGURE 4.2.6.

F I G U R E 4.2.7.

Crystal-packing arrangements for Compound IX


X
Z

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A P P E N D I X 1

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR (+) INDERAL HYDROCHLORIDE

14,2,L

-2	12	14	170

14,5,L

-1	11	14	199
-2	22	13	340

13,0,L

-4	25	18	0

13,1,L

-5	14	9	238

13,4,L

-4	9	11	45

12,0,L

-1	52	51	180
-2	71	73	0
-4	25	21	0
-5	22	24	180

12,1,L

-1	68	67	159
-2	29	24	338
-5	10	18	197

12,2,L

-1	87	88	145

12,3,L

-1	61	59	60
-5	24	20	19

11,0,L

-1	54	54	180
-2	126	125	180
-3	13	12	0

11,1,L

-1	86	84	67
-2	95	97	49
-4	24	18	2

11,2,L

-1	18	21	115
-2	66	64	78
-3	34	35	1
-5	13	18	7

11,3,L

-1	53	49	1
-2	47	44	130
-3	65	66	13

10,0,L

-1	120	121	0
-2	68	68	0
-3	81	84	0
-4	20	14	0
-7	34	29	180

10,1,L

-1	65	66	188
-2	163	164	63
-3	60	57	92
-4	41	41	28
-5	43	49	179

10,2,L

-1	79	79	216
-2	69	69	239
-3	33	33	122
-7	14	15	60

10,3,L

-1	41	42	332
-2	34	37	85
-3	77	74	340
-5	31	33	25

10,4,L

-1	39	35	303
-2	20	18	207

10,5,L

-1	5	3	255

9,0,L

-1	9	0	180
-2	33	30	180
-3	130	130	0
-4	61	62	0
-5	21	17	180

9,1,L

-1	34	36	17
-2	37	36	333
-3	114	112	137
-4	60	59	319
-5	32	33	115
-6	25	21	6

9,2,L

-1	48	46	188
-2	139	138	333
-3	89	90	304
-4	64	60	323
-5	31	33	329

9,3,L

-1	11	18	318
-2	98	98	133
-3	104	106	66
-4	17	7	281
-6	24	28	166
-7	25	22	297

9,4,L

-1	60	53	330
-2	92	95	233
-3	6	8	216
-5	33	35	244

9,5,L

-1	13	9	326
-2	50	52	30
-4	40	38	326

9,6,L

-1	64	80	196

8,0,L

-2	50	47	180
-3	150	148	0
-4	71	69	0
-5	30	32	0
-6	18	21	0

8,1,L

-1	16	16	319
-2	43	41	14
-3	93	90	151
-4	37	37	255
-5	92	92	220
-6	35	35	32

8,2,L

-1	107	101	178
-2	23	23	207
-3	40	46	248
-4	89	89	8
-5	21	25	283

8,3,L

-1	33	32	265
-2	77	79	270
-3	55	57	137
-4	68	69	171
-5	25	23	350
-6	25	23	164

8,4,L

-1	92	79	28
-2	52	51	180
-3	160	157	334
-4	16	19	267
-5	38	38	292

8,5,L

-1	63	70	85
-2	33	38	87
-3	104	112	123
-4	55	55	23

8,6,L

-1	40	43	128
-2	54	53	288

7,0,L

-1	166	163	0
-2	135	133	180
-3	50	49	0
-4	7	2	180
-6	42	42	180

7,1,L

-1	86	85	334
-2	27	31	273
-3	36	32	218
-4	26	27	134
-5	76	75	238
-6	32	32	306
-7	24	20	135

7,2,L

-1	113	111	150
-2	28	28	329
-3	109	107	201
-4	123	121	5
-5	43	44	75
-6	41	38	15
-7	25	19	37
-8	16	19	139

7,3,L

-1	50	48	193
-2	60	63	109
-3	75	74	44
-4	85	84	149
-5	26	26	325
-6	58	60	185
-7	37	32	4

7,4,L

-1	181	171	18
-2	132	127	152
-3	49	48	25
-4	30	29	53
-5	48	44	343
-6	21	19	243

7,5,L

-1	39	46	330
-2	46	43	324
-3	73	75	216
-4	51	50	177
-5	43	41	199
-6	22	21	36
-7	7	15	186

7,6,L

-1	42	58	205
-2	40	50	344
-3	41	45	300

7,7,L

-1	27	43	234
-2	14	20	25
-5	31	31	43

6,0,L

-1	171	171	0
-2	77	75	180
-3	41	42	0
-4	98	93	180
-5	47	45	0
-6	49	47	180

6,1,L

-1	181	178	41
-2	72	71	158
-3	60	59	193
-4	48	49	99
-5	37	33	164
-6	54	52	1
-8	50	44	27

6,2,L

-1	73	71	221
-2	133	131	2
-3	168	168	171
-4	98	96	1
-5	44	40	92
-6	23	22	65

6,3,L

-1	110	99	228
-2	136	135	332
-3	38	40	12
-4	16	26	114

6,3,L

-5	30	28	325
-6	52	53	243

6,4,L

-1	45	43	313
-2	22	26	196
-3	40	40	336
-4	13	12	185
-5	35	35	39
-6	14	10	55

6,5,L

-1	23	33	351
-2	45	44	209
-3	26	29	14
-4	36	34	13
-7	21	24	128

6,6,L

-1	46	61	188
-2	50	59	323
-3	126	136	194
-4	118	119	9
-5	50	53	74

6,7,L

-1	48	70	213
-2	15	28	303
-3	49	58	192

6,8,L

-1	7	23	12

5,0,L

-1	105	101	0
-2	166	160	0
-3	176	171	0
-4	129	130	180
-5	74	69	0
-6	38	35	180
-8	29	26	0

5,1,L

-1	236	233	36
-2	136	125	255
-3	79	66	24
-4	33	31	277
-5	32	32	97
-6	51	50	5

5,2,L

-1	337	316	196
-2	205	194	292
-3	106	108	203
-4	84	79	356
-5	41	42	107
-6	26	26	340

5,3,L

-1	128	126	159
-2	89	87	337
-3	51	51	142
-4	37	38	36
-5	51	53	57
-7	41	40	356

5,4,L

-1	114	130	38
-2	90	99	192
-3	35	34	323
-4	117	116	220
-5	115	115	3
-6	44	43	154

5,5,L

-1	71	93	10
-2	77	94	223
-3	65	63	249
-4	78	78	213
-5	58	59	284
-6	32	35	351

5,6,L

-1	48	68	211
-2	33	44	322
-3	87	99	183
-4	19	23	200

5,7,L

-1	25	54	196
-2	19	27	344
-3	73	86	102

5,8,L

-1	29	47	46
-2	42	64	165

4,0,L

-1	85	91	180
-2	218	216	180
-3	82	90	0
-4	108	110	180
-5	62	57	0
-6	67	67	180
-7	45	43	0

4,1,L

-1	235	239	1
-2	384	376	202
-3	190	180	228
-4	104	105	185
-5	24	27	305
-6	47	47	51
-8	30	28	13

4,2,L

-1	174	159	223
-2	40	44	47
-3	146	142	239
-4	84	84	351
-5	49	44	300
-6	82	84	22
-7	27	31	209
-8	24	18	354

4,3,L

-1	107	111	157
-2	149	148	7
-3	105	105	174
-4	16	18	140
-5	95	92	252
-6	28	33	294

4,4,L

-1	87	94	201
-2	113	116	164
-3	52	47	311

4,4,L

-4	184	189	176
-5	69	69	281

4,5,L

-1	110	147	358
-2	117	125	184
-3	46	39	327
-4	129	128	119
-5	55	58	162
-6	28	27	57

4,6,L

-1	28	45	157
-2	34	39	358
-3	73	70	183
-4	70	68	63
-5	56	57	137
-7	36	34	179

4,7,L

-1	44	73	181
-2	64	75	27
-3	56	62	180

4,8,L

-1	23	53	155
-2	31	36	168

3,0,L

-1	156	150	0
-2	99	89	0
-3	304	284	180
-4	202	185	180
-5	26	23	0
-6	55	54	0
-7	45	40	0

3,1,L

-1	222	235	325
-2	204	208	193
-3	288	277	305
-4	121	118	177
-5	72	73	281
-6	54	61	310

3,2,L

-1	159	140	227
-2	68	65	180
-3	270	269	156
-4	123	128	64
-5	154	154	167
-6	67	62	309
-7	58	56	185

3,3,L

-1	204	222	173
-2	97	98	1
-3	184	182	192
-4	92	90	109
-5	142	145	146
-6	70	69	221

3,4,L

-1	45	48	91
-2	41	41	89
-3	16	19	21
-4	60	62	209
-5	74	75	52
-6	35	32	169

3,5,L

-1	104	153	51
-2	92	106	187
-3	54	54	336
-4	54	53	165
-5	65	65	69

3,6,L

-1	92	140	236
-2	19	19	233
-3	42	41	152
-4	39	38	51
-5	56	57	131
-6	48	45	7

3,7,L

-1	50	79	160
-2	52	54	11
-3	76	77	151
-4	42	38	27
-5	51	54	114
-6	29	23	306

3,8,L

-1	55	86	145
-2	45	47	133
-3	33	30	17

2,0,L

-1	168	155	0
-2	36	36	0
-3	142	138	180
-4	381	371	180
-5	106	104	180
-6	186	185	180
-7	60	59	0

2,1,L

-1	313	324	34
-2	480	480	190
-3	133	137	301
-4	117	115	168
-5	172	171	56
-6	80	75	198
-7	39	35	209

2,2,L

-1	48	47	49
-2	22	33	340
-3	89	87	150
-4	93	84	146
-5	119	114	105
-6	70	74	71
-7	31	28	218

2,3,L

-1	120	124	137
-2	239	234	30
-3	26	24	26
-4	119	121	316
-5	27	30	85
-6	18	16	321

2,4,L

-1	82	96	146
-2	46	43	335
-3	69	68	131
-4	97	97	159

2,4,L

-5	72	74	51
-6	49	48	129
-7	39	37	18
-8	28	29	150

2,5,L

-1	139	157	324
-2	219	210	189
-3	121	118	323
-4	132	131	182
-5	76	74	59
-6	38	40	107

2,6,L

-1	134	149	336
-2	39	40	109
-3	14	17	146
-4	60	58	43
-5	31	34	156
-6	54	56	21

2,7,L

-1	50	51	178
-2	147	143	53
-3	69	68	159
-4	48	47	342
-6	27	26	311

2,8,L

-1	85	104	235
-2	31	25	196
-3	24	22	11
-5	43	40	16
-6	21	20	137

2,9,L

-1	73	87	327

1,0,L

-1	552	589	180
-2	51	47	0
-3	22	4	180
-4	225	221	180
-5	65	66	0
-6	14	13	180

1,1,L

-1	157	155	243
-2	253	263	133
-3	186	190	355
-4	31	34	180
-5	159	158	31
-6	168	168	60
-7	55	59	357

1,2,L

-1	210	219	325
-2	126	129	165
-3	201	199	25
-4	80	76	156
-5	101	100	188
-6	30	29	144
-7	69	73	152

1,3,L

-1	123	125	228
-2	284	297	33
-3	209	211	187
-4	146	149	2
-5	90	90	170
-6	85	89	12

1,4,L

-1	145	148	178
-2	130	126	42
-3	56	55	214
-4	127	125	223
-5	29	29	108
-6	42	45	111
-7	55	53	16

1,5,L

-1	237	232	307
-2	56	57	178
-3	145	149	8
-4	24	19	279
-5	59	61	342
-7	32	32	315

1,6,L

-1	160	159	288
-2	32	25	204
-3	47	45	61
-4	57	58	96
-5	23	21	136
-6	51	53	43

1,7,L

-1	115	109	229
-2	16	20	331
-3	71	70	173
-4	67	68	319
-5	49	53	201
-6	29	26	353

1,8,L

-1	79	78	165
-2	63	65	323
-3	10	8	134

1,9,L

-1	56	55	349
-6	27	29	159

0,0,L

1	123	112	0
2	305	301	0
3	138	135	180
4	54	54	0
5	97	89	180
6	54	51	0
7	57	53	0

0,1,L

1	297	304	148
2	279	281	19
3	118	127	240
4	85	84	27
5	113	113	211
6	96	93	334
7	56	58	256

0,2,L

0	503	490	290
1	247	256	268
2	137	136	153
3	142	134	31
4	16	13	182

0,2,L

5	61	60	221
6	93	93	329
7	63	64	233

0,3,L

1	215	213	107
2	175	175	181
3	100	92	295
4	151	149	168
5	62	66	352
6	89	88	219
7	57	55	215

0,4,L

0	494	463	346
1	199	206	234
2	228	223	294
3	43	44	99
4	42	39	277
5	38	39	221
6	32	32	199
7	37	35	103

0,5,L

1	106	105	114
2	238	235	41
3	75	74	158
4	69	70	335
5	79	76	191
6	25	33	298
7	45	44	147

0,6,L

0	176	158	211
1	105	91	339
2	161	160	187
3	92	86	37
4	60	61	186
5	76	79	219
7	28	21	179

0,7,L

1	52	43	294
2	39	34	239
3	62	58	345
4	115	109	187
5	54	54	44
7	12	14	334

0,8,L

0	50	46	22
1	126	118	175
2	52	51	320
3	14	17	99
5	42	42	105

0,9,L

1	71	61	175
3	44	46	174
6	37	34	343

0,10,L

1	56	50	3
5	20	17	257

0,11,L

4	41	39	173

0,12,L

0	47	46	42

1,0,L

0	126	163	0
1	325	316	0
2	117	125	0
3	167	174	180
4	14	9	180
5	29	26	180
6	25	22	0
7	82	81	0

1,1,L

0	336	333	38
1	612	648	55
2	365	361	46
3	186	186	177
4	52	57	353
5	124	124	188
6	42	41	311
7	36	32	187

1,2,L

0	244	245	16
1	940	1079	340
2	241	236	229
3	342	341	351
4	96	89	88
5	55	58	244
7	32	33	337

1,3,L

0	437	475	352
1	269	268	245
2	59	57	53
3	172	166	22
4	72	71	135
5	64	64	6
6	15	16	178
7	71	71	322

1,4,L

0	298	311	16
1	194	187	201
2	43	42	236
3	156	151	210
4	30	25	30
5	65	69	201
6	41	46	274
7	52	55	317
8	40	43	214

1,5,L

0	67	63	25
1	34	30	161
2	140	135	43
3	55	58	240
4	34	37	23
5	92	91	215
6	62	65	341
7	54	53	215

1,6,L

0	126	128	222
1	159	146	333
2	114	115	191
3	81	73	12
4	80	78	91
6	20	24	196

1,7,L

1	80	65	252
2	60	53	235
3	80	78	21
4	77	74	161
6	38	38	193

1,8,L

0	77	82	36
1	79	76	175
2	101	89	332
3	18	22	215
4	64	66	312
5	16	31	196
6	32	30	199

1,9,L

0	24	21	171
1	30	27	193
5	48	45	173

1,10,L

0	36	31	150
1	47	42	19
2	83	75	181

1,11,L

1	30	27	185
3	25	32	38

1,12,L

0	22	25	347
2	37	35	356

2,0,L

0	322	324	0
1	115	114	0
2	123	118	0
3	144	147	180
4	221	215	0
5	49	47	180
6	11	11	0
7	31	32	0

2,1,L

0	301	285	243
1	392	397	62
2	141	140	46
3	188	177	76
4	49	45	2
5	98	97	172
6	68	69	339

2,2,L

0	705	750	187
1	558	565	63
2	240	244	142
3	123	128	37
4	78	75	192
5	15	18	134
6	67	68	217

2,3,L

0	164	174	9
1	360	342	68
2	61	64	308
3	128	122	11
4	40	38	132
5	56	57	32
6	54	58	226

2,4,L

0	260	276	16
1	219	200	40
3	117	117	196
4	137	140	358
5	61	69	117
7	39	36	58

2,5,L

0	74	73	302
1	193	175	359
2	97	101	209
3	39	39	256
4	51	49	18
5	96	96	188
6	37	38	321

2,6,L

0	26	28	207
1	188	174	10
2	119	113	160
3	102	90	2
4	43	39	171
5	52	55	295
6	11	14	223
7	40	38	292

2,7,L

0	132	143	332
1	21	18	289
2	36	34	243
3	58	50	46
4	63	62	142
5	57	55	66
6	34	35	198
7	26	31	307

2,8,L

0	48	50	10
1	44	39	186
2	76	68	345
3	53	54	224
4	54	50	6

2,9,L

0	38	43	204
1	33	30	182
2	44	39	199
4	48	46	44

2,10,L

1	92	82	349
2	36	31	208
3	42	40	337

2,11,L

0	66	59	351

2,12,L

1	41	35	178

3,0,L

0	177	188	0
1	406	401	180
3	409	403	180
4	11	6	0
5	35	34	180

3,0,L

6	6	12	0

3,1,L

0	229	225	139
1	350	354	6
2	201	199	119
3	150	150	223
4	65	62	89
5	44	47	191
6	43	43	348
8	25	25	9

3,2,L

0	158	155	258
1	219	222	358
2	161	156	114
3	186	186	40
4	44	47	125
5	87	93	352
6	50	49	155
8	21	18	45

3,3,L

0	331	340	300
1	215	210	204
2	110	102	111
3	55	48	134
4	21	16	99
5	41	36	64
6	74	78	199
7	42	45	319

3,4,L

0	141	140	15
1	290	274	141
2	267	257	45
3	132	134	165
4	115	114	352
5	48	49	184
6	49	49	325

3,5,L

0	125	124	185
1	322	299	55
2	167	156	64
3	15	13	250
4	32	27	42
5	53	51	135
7	37	34	181

3,6,L

0	107	111	252
1	204	191	24
2	33	27	24
3	66	67	353
4	17	23	201
5	39	36	314

3,7,L

0	169	175	331
1	24	15	234
2	79	79	285
3	31	33	174
5	51	47	78
6	27	24	192

3,8,L

0	49	44	11
1	5	4	276
2	149	139	344
3	34	36	186
4	64	60	343
5	53	54	184

3,9,L

0	44	49	278
1	73	68	8
2	75	67	117
4	45	39	51

3,10,L

0	24	23	191
1	39	32	66
2	69	66	212
3	31	31	335
4	29	28	156

3,11,L

0	64	54	314
1	39	29	244

4,0,L

0	238	239	0
1	81	75	180
2	131	120	0
3	103	101	180
4	125	129	0
5	11	6	180
6	81	86	0

4,1,L

0	180	179	214
1	338	331	340
2	134	133	140
3	63	64	272
4	114	106	213
5	50	47	166
7	40	43	215

4,2,L

0	49	42	125
1	164	154	353
2	116	111	116
3	104	110	16
4	162	163	177
5	56	60	340
6	41	42	236

4,3,L

0	24	33	22
1	187	182	212
2	161	156	56
3	111	111	131
4	82	79	137
5	75	75	58
6	32	33	140

4,4,L

0	66	56	224
1	221	205	279
2	61	61	335
3	111	107	180
4	71	68	25
5	10	14	183
6	29	32	293

4,5,L

0	47	48	153
1	157	148	310

4,5,L

2	180	177	144
3	19	24	278
4	23	24	143
6	36	31	54

4,6,L

0	100	103	188
1	46	44	66
2	127	122	122
3	167	160	30
4	54	55	172
5	60	61	325
6	63	64	206
7	22	28	270

4,7,L

0	132	142	336
1	45	38	236
2	202	188	50
3	80	71	91
5	54	53	79

4,8,L

0	39	39	148
1	60	57	112
2	68	66	358
3	72	72	245
4	41	39	0
5	40	38	166

4,9,L

0	65	59	203
1	83	76	301
3	40	40	315
4	21	20	40

4,10,L

1	78	71	37
3	24	27	340
4	25	27	174

4,11,L

0	67	62	350

5,0,L

0	93	95	180
1	27	25	0
2	49	47	0
3	82	80	180
4	121	127	0
5	43	37	180
6	59	59	0

5,1,L

0	64	60	155
1	93	106	351
2	144	142	180
3	64	58	69
4	45	50	187
5	24	29	90
6	64	66	46

5,2,L

0	242	215	189
1	126	116	343
2	46	43	289
3	110	107	359
4	59	59	214
5	65	62	324
6	47	49	197
7	31	38	310

5,3,L

0	382	368	347
1	201	198	210
2	146	143	348
3	78	78	135
4	64	66	308
5	44	50	148

5,4,L

0	188	172	142
1	65	60	161
2	55	54	320
3	57	54	212
4	60	62	33
5	61	66	177
6	27	29	333

5,5,L

0	41	43	176
1	171	161	346
2	32	34	121
3	89	81	61
4	67	62	160
5	41	36	91
6	49	51	48

5,6,L

0	62	64	173
1	88	82	60
2	83	82	182
3	30	27	235
4	65	66	187
5	46	49	358
6	43	46	195

5,7,L

0	90	99	328
1	157	149	247
2	91	90	263
3	76	75	113
5	27	27	89

5,8,L

0	38	37	131
1	39	37	6
2	103	102	59
3	43	43	122
4	43	44	32
5	28	30	167

5,9,L

0	88	74	190
1	55	51	347
2	76	70	159
3	71	71	18
5	12	12	343

5,10,L

0	25	24	257
3	41	41	3

6,0,L

0	443	428	180
1	128	126	180
2	16	16	180
3	80	85	180

6,0,L

4	90	89	0
5	23	20	180
7	54	60	180

6,1,L

0	83	72	10
1	343	333	8
2	97	97	204
3	77	76	12
4	45	50	197
5	34	42	30
6	33	38	96
7	30	30	80

6,2,L

0	114	100	139
1	198	187	113
2	22	21	58
3	21	24	346
4	16	16	200
5	54	54	8
6	45	42	187

6,3,L

0	149	136	335
1	109	107	233
2	112	110	345
3	103	102	114
4	62	57	43
5	16	24	115
6	27	29	63
7	40	41	24

6,4,L

0	102	102	176
1	89	82	118
2	58	52	61
3	132	132	192
4	62	64	338
5	37	37	199
6	19	21	344
7	36	36	180

6,5,L

0	33	32	137
1	157	149	330
2	165	162	224
3	107	105	321
4	12	7	207
5	40	39	277

6,6,L

0	67	65	11
1	107	97	108
2	149	142	37
3	75	77	66
4	46	43	199
6	24	27	180

6,7,L

0	63	58	330
1	57	50	219
2	42	38	350
3	82	80	165
6	15	14	41

6,8,L

0	25	20	199
1	29	29	321
2	69	69	358
3	36	40	223
5	42	39	151

6,9,L

0	67	62	176
1	49	49	345
2	69	68	210
4	32	33	133

6,10,L

1	7	6	223
3	41	42	64

7,0,L

0	169	167	180
1	162	154	180
2	104	107	180
3	55	55	180
4	40	43	0
5	24	22	0
7	38	40	180

7,1,L

0	113	111	158
1	186	174	285
2	151	144	185
3	52	50	333
4	77	78	158
5	21	20	344
6	43	46	95

7,2,L

0	61	57	274
1	174	168	138
2	123	121	65
3	75	77	133
4	111	113	207
5	52	52	354
6	41	40	184

7,3,L

0	39	34	359
1	79	81	260
2	108	106	338
3	93	92	228
4	101	104	346

7,4,L

0	69	66	210
1	32	31	53
2	86	81	47
3	81	84	54
4	46	46	90
7	26	27	164

7,5,L

0	106	104	190
1	87	84	356
2	89	89	196
3	29	29	184
4	55	54	171
5	32	38	350

7,6,L

0	44	39	310
1	45	48	146
2	42	40	27
3	48	50	18
4	34	35	229

7,6,L

5	34	34	11
6	29	29	192

7,7,L

0	19	20	0
1	46	44	194
2	50	49	341
3	85	88	171

7,8,L

0	34	31	162
1	49	46	308
2	36	41	64
3	40	37	353

7,9,L

0	57	54	193
3	39	32	343
4	29	26	145

7,10,L

1	26	21	203

7,11,L

0	14	10	59

8,0,L

0	141	131	180
1	14	8	0
2	24	23	180
3	39	42	0
4	83	86	180
5	18	18	180
6	25	26	0
7	40	42	180

8,1,L

0	37	34	137
1	154	151	310
2	170	168	241
3	71	70	292
4	54	58	237
5	78	81	4

8,2,L

0	115	106	30
1	110	109	212
2	45	51	11
3	67	70	22
4	54	55	121

8,3,L

0	75	67	186
1	145	139	211
2	34	25	297
3	135	134	161
4	24	27	222
5	32	33	199

8,4,L

0	86	76	166
1	81	83	280
2	70	67	137
3	65	64	340

8,5,L

0	43	41	146
1	29	35	31
2	60	54	230
3	30	33	358
4	66	65	186

8,6,L

0	74	70	11
1	55	55	195
2	27	26	11
3	31	33	27

8,7,L

0	45	41	245
1	55	54	193
2	49	50	16
3	51	52	162

8,8,L

0	36	31	221

8,9,L

3	24	20	19

8,10,L

1	34	29	184

9,0,L

0	41	36	180
1	32	33	180
2	29	32	180
3	137	139	0
4	102	104	0

9,1,L

0	19	19	35
1	44	40	152
2	142	143	240
3	25	29	302
4	103	105	195
5	32	33	252

9,2,L

0	123	121	15
1	88	92	176
2	88	90	333
3	41	40	285
4	67	70	304
5	24	23	160

9,3,L

0	28	26	91
1	40	41	161
2	97	94	306
3	51	50	231
4	22	21	35

9,4,L

0	62	64	152
1	38	40	304
2	92	91	218
3	36	38	344
6	26	29	12

9,5,L

0	30	27	128
1	32	30	214
2	67	63	215

9,5,L

4	55	60	163

9,6,L

0	51	50	24
1	34	35	170
3	22	27	133

9,7,L

0	40	48	73
1	22	25	193

9,8,L

1	44	42	320
2	34	35	190

9,9,L

3	33	31	5

10,0,L

0	43	41	180
1	69	64	0
2	79	82	180
3	67	71	0
4	33	35	0
5	51	54	0

10,1,L

0	35	33	24
1	50	53	88
2	21	24	245
3	64	66	303
4	40	39	60
5	49	54	357

10,2,L

0	72	71	1
1	56	54	153
2	24	25	264
4	74	73	341
5	37	38	293

10,3,L

0	29	30	49
1	40	40	147
2	22	21	2
3	43	45	246
5	49	47	201

10,4,L

0	43	44	232
1	47	46	10
2	34	38	193
3	41	41	335
5	21	24	258

10,5,L

0	62	58	18
1	32	35	104
3	42	41	304

10,6,L

0	37	30	42
1	50	52	179
2	43	43	313

10,8,L

1	28	26	340

11,0,L

0	68	67	180
1	57	62	0
2	71	72	180
3	36	33	0
5	21	22	0

11,1,L

0	53	47	345
1	28	23	134
2	19	25	144
4	24	31	196

11,2,L

0	38	40	315
1	14	3	245
2	37	36	358
3	32	31	185
4	23	22	12

11,3,L

0	46	43	212
1	53	54	41
3	21	27	303

11,4,L

0	50	47	175
2	56	56	199
3	32	29	344

11,6,L

0	41	43	13

11,7,L

2	16	13	69

11,8,L

2	36	36	211

12,0,L

0	52	52	180
2	9	7	0
4	7	6	180

12,1,L

1	25	20	212

12,2,L

0	48	53	87
1	50	52	174
3	33	35	208
5	16	19	174

12,3,L

0	24	28	172
1	18	26	321
3	5	9	295

12,4,L

3	31	32	346

12,7,L

1 26 18 84

13,0,L

0 10 16 180
2 52 53 180
3 15 16 0

13,1,L

1 40 41 185

13,2,L

3 15 16 223

13,3,L

0 52 49 147

13,5,L

0 37 38 40

13,7,L

0 8 5 165

14,1,L

0 15 23 310

14,4,L

0 28 28 242

15,1,L

1 16 16 221

A P P E N D I X 2

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR

(±) INDERAL HYDROCHLORIDE

15,0,L

-5	51	-47

15,-1,L

-4	41	-36

14,0,L

-4	87	-105

14,-1,L

-5	84	-79

14,-2,L

-1	58	57
-9	58	-45

14,-5,L

-3	49	-45
-5	38	33

13,0,L

-1	68	51
-3	60	-65
-5	32	37
-7	73	65
-11	38	25

13,-1,L

-1	26	25
-2	125	-127

13,-2,L

-3	117	-120
-5	49	58
-6	115	-105
-8	77	68
-10	38	-35

13,-3,L

-1	118	125
-8	35	-43

13,-4,L

-6	29	-16
-7	63	-65
-8	73	65

13,-5,L

-2	70	65

12,0,L

-2	90	-92
-4	169	173

12,-1,L

-1	29	-26
-4	84	-73
-8	48	46
-11	36	32
-13	45	-34

12,-2,L

-2	23	24
-3	125	-123
-5	139	129
-6	90	-87

12,-3,L

-2	55	-62
-10	44	-38

12,-4,L

-1	80	-82
-2	102	100
-3	71	-66
-4	48	-45
-6	66	52
-10	30	24

12,-5,L

-2	59	-53
-3	52	49

11,0,L

-1	214	212
-3	123	-125

11,-1,L

-1	70	-63
-3	83	79
-5	57	-44
-6	69	-69
-7	105	-99
-8	29	36
-10	73	-70
-11	52	-47

11,-2,L

-1	104	105
-2	147	140
-4	123	-117
-5	47	54
-9	55	-59

11,-3,L

-1	98	-99
-3	43	35
-6	58	60
-7	65	67

11,-4,L

-2	110	107
-4	56	-47
-5	105	-88
-6	51	55
-7	89	87

11,-5,L

-2	79	-82
-3	106	108
-4	151	-160
-5	125	-129
-6	78	76

11,-6,L

-2	77	86
-6	86	-77

11,-7,L

-3	69	80
-5	100	-98

10,0,L

-2	54	58
-4	39	-46
-8	116	-114
-10	43	37
-12	77	74

10,-1,L

-1	82	-80
-3	81	-82
-5	88	85
-6	136	129
-7	71	-69
-8	209	-202
-10	74	-69
-11	52	60

10,-2,L

-1	119	-125
-3	43	39
-4	74	-73
-6	145	137
-11	60	-60
-13	62	61

10,-3,L

-2	84	82
-4	140	-141
-6	142	137
-7	101	93
-8	69	-65
-9	84	-78
-10	59	54

10,-4,L

-1	60	63
-2	199	-196
-8	75	-72
-11	55	-46

10,-5,L

-1	141	-156
-5	56	-51
-6	104	98
-7	52	59

10,-6,L

-3	174	-178

10,-7,L

-4	59	-65

9,0,L

-1	71	78
-5	159	164
-7	168	-157
-9	234	229

9,-1,L

-1	92	63
-2	240	242
-3	171	157
-4	125	-112
-5	47	-47
-6	59	56
-7	120	121
-8	138	-132
-9	88	94
-10	241	224
-12	70	-75
-13	45	58

9,-2,L

-1	85	-90
-2	74	-74
-3	55	61
-7	303	-299
-8	147	-159
-9	148	135
-10	62	57
-13	57	-63

9,-3,L

-1	115	-113
-2	101	-103
-4	109	105
-6	91	-102
-7	162	-169
-8	109	-113
-9	81	-81
-10	87	92
-12	94	-90
-14	29	24

9,-4,L

-1	64	59
-4	131	137
-5	173	176
-6	64	71
-8	78	-83
-9	64	-64
-10	53	50

9,-5,L

-1	121	134
-2	169	-177
-3	93	-90
-4	212	218
-5	155	163

9,-6,L

-4	36	-36
-5	64	58
-10	54	-53

9,-7,L

-3	206	-214
-4	52	45
-5	107	118
-7	68	-67

8,0,L

-2	101	108
-4	152	-155
-6	115	118
-8	349	340
-10	32	39
-12	49	-56
-14	58	47

8,-1,L

-1	111	-122
-2	195	-198
-4	211	197
-5	168	-181
-6	169	-177
-7	130	134
-9	140	149
-10	206	213
-11	201	-201
-12	38	50
-13	86	83

8,-2,L

-2	70	-70
-3	169	171
-4	76	-74
-5	266	-265
-6	43	-43
-10	173	-170
-11	117	109

8,-3,L

-1	146	138
-3	47	-54
-4	115	116
-6	237	-230
-8	42	44
-11	36	-44
-12	65	-62
-13	61	63

8,-4,L

-1	51	49
-2	68	67
-3	212	222
-4	110	110
-5	145	-152
-6	212	-222
-8	197	201
-10	74	-70
-12	44	41

8,-5,L

-1	96	99
-4	115	114
-6	132	-142
-8	63	60

8,-6,L

-1	131	-132
-4	104	114
-6	94	-91
-7	87	-84
-8	44	36
-9	57	66
-10	80	-77

8,-7,L

-5	59	-56

8,-8,L

-4	60	-64

7,0,L

-1	605	-629
-3	349	-346
-7	65	-77
-9	150	-155
-11	61	64

7,-1,L

-1	154	157
-2	481	-504
-3	395	-418
-4	184	207
-5	86	-92
-6	116	126
-7	151	163
-8	107	-99
-9	122	-116

7,-2,L

-1	228	223
-2	199	-198
-3	83	84
-4	62	74
-5	164	161
-6	75	-84
-7	88	83
-8	192	186
-10	51	-62

7,-3,L

-1	155	156
-3	121	-123
-4	67	67
-5	67	-69
-6	69	-70
-7	149	139
-11	54	55
-13	87	-87

7,-4,L

-3	231	-246
-5	186	185
-7	252	-249
-8	83	84
-10	33	-33
-11	102	100

7,-5,L

-2	57	53
-3	115	-113
-4	25	-22
-7	66	67
-9	77	-70
-12	50	51

7,-6,L

-1	128	143
-2	77	92
-3	58	-63
-4	109	-120
-5	107	110
-6	144	136
-7	55	-56
-8	45	-63

7,-7,L

-3	49	46

7,-8,L

-1	76	-87
-4	44	-53
-6	77	79

6,0,L

-2	174	-193
-4	164	173
-6	310	-301
-8	80	98
-10	165	-164
-14	64	60

6,-1,L

-1	229	-215
-2	183	206
-3	580	593
-5	328	-361
-6	132	-151
-7	228	224
-8	153	139
-9	144	-151
-12	42	-48

6,-2,L

-2	87	105
-3	217	-243
-4	323	331
-5	114	111
-6	153	-147
-7	114	-113
-8	130	121
-10	53	56
-13	84	-88

6,-3,L

-1	199	-233
-2	62	55
-3	117	117
-4	73	74
-5	136	-135
-8	21	30
-9	52	46

6,-4,L

-1	133	130
-2	245	264
-4	262	-254
-5	79	76
-10	88	-77
-11	51	50
-14	49	-47

6,-5,L

-1	79	-75
-2	137	156
-3	77	75
-8	69	-67
-9	144	145
-10	63	80
-11	65	-60

6,-6,L

-1	186	-200
-2	119	120
-3	215	221
-4	72	-79
-5	66	-70
-10	50	52

6,-7,L

-6	44	47
-8	158	-165
-10	83	80

6,-8,L

-1	91	-103
-2	77	-84
-3	75	77
-5	77	-80

6,-9,L

-2	45	45

5,0,L

-1	683	766
-3	59	-67
-5	280	280
-7	113	101
-11	60	58
-13	64	-69
-15	54	48

5,-1,L

-1	241	-247
-2	235	-281
-3	363	-397
-4	137	162
-5	203	201
-6	65	-64
-7	195	-204
-8	141	160
-10	45	-41
-14	63	63

5,-2,L

-2	53	81
-3	389	-419
-4	162	-163
-6	84	88
-8	90	88
-9	75	-60
-10	89	-96
-12	74	71
-13	38	31

5,-3,L

-1	149	152
-2	106	124
-3	194	-213
-4	234	-239
-5	229	236
-7	90	-96
-8	44	-52
-9	100	96
-10	45	-48
-11	139	-140
-12	61	-62
-15	40	33

5,-4,L

-1	194	-198
-2	137	138
-3	181	183
-9	118	111
-11	107	-113
-12	57	-49

5,-5,L

-2	106	104
-3	62	56
-4	59	-51
-6	209	204
-7	30	-29
-8	57	-44
-10	109	109
-12	24	-28

5,-6,L

-1	102	-100
-2	269	-271
-3	109	113
-9	37	34
-10	77	74

5,-7,L

-1	31	-38
-2	70	66
-5	116	-117

5,-7,L

-6	62	-63
-7	87	87

5,-8,L

-1	94	92
-2	89	-94
-4	131	129
-5	68	-68

5,-9,L

-3	51	55
-4	82	77

4,0,L

-2	556	597
-6	130	-163
-8	54	62
-10	160	-141
-12	138	143
-14	99	-91
-16	47	-45

4,-1,L

-1	417	493
-2	192	196
-4	177	-195
-5	146	186
-6	266	298
-10	31	33
-11	58	61
-12	71	65

4,-2,L

-1	202	-216
-2	175	192
-3	156	165
-4	212	-218
-6	66	-66
-7	104	-120
-8	39	20
-9	163	148
-10	45	-47
-11	84	-77
-12	71	68
-13	74	71

4,-3,L

-1	265	-268
-2	316	336
-3	86	94
-4	329	-339
-5	240	-238
-8	70	-69
-9	77	-70
-15	48	-47

4,-4,L

-1	81	-93
-2	44	29
-3	26	-44
-4	20	-12
-5	55	-51
-6	164	156
-7	48	-38
-8	126	-127
-10	55	50
-11	60	-58

4,-5,L

-1	22	32
-3	262	252
-5	224	-217
-7	212	204
-9	66	-73
-10	70	-59
-13	69	65

4,-6,L

-3	92	86
-4	90	-80
-5	82	-87
-6	71	72
-7	106	97

4,-7,L

-2	64	-71
-4	176	172
-6	151	-145
-7	74	72
-8	135	132

4,-8,L

-2	71	-69
-6	62	-58
-7	73	70
-9	47	-37

4,-9,L

-3	137	-148

3,0,L

-1	113	-135
-3	90	-87
-5	384	446
-7	107	113
-11	106	-104
-13	39	-37
-15	31	32

3,-1,L

-1	196	-197
-2	419	465
-3	241	270
-4	404	-472
-5	75	41
-6	236	249
-7	271	266
-8	35	-33
-9	204	196
-10	135	-128
-14	50	-51
-15	34	-31

3,-2,L

-2	90	79
-4	186	-188
-5	146	-150
-6	447	453
-7	99	108
-8	184	-173
-10	160	147
-11	34	29
-12	47	-42

3,-3,L

-1	375	-389
-2	92	-99
-3	321	352
-4	169	-147
-5	139	-118
-6	116	100
-7	96	-96
-8	89	82
-9	43	-36
-10	96	86
-11	74	-74
-12	52	46
-14	49	45

3,-4,L

-1	81	80
-2	163	175
-4	222	-203
-5	299	-277
-7	225	225
-8	152	-147
-9	157	-149
-10	58	59
-11	53	55
-12	60	-50

3,-5,L

-1	55	39
-2	138	-135
-4	172	167
-5	51	-43
-6	118	-119
-8	85	-77
-12	85	-80

3,-6,L

-1	73	85
-2	133	129
-3	108	104
-4	130	134
-5	83	-87
-9	62	-60
-11	73	75

3,-7,L

-1	209	234
-3	92	-90
-4	54	-54
-5	155	148
-7	43	-53
-9	65	-61
-11	60	59

3,-8,L

-3	83	-87
-5	102	102
-6	97	-99
-8	27	30

3,-9,L

-1	59	63
-2	115	123

2,0,L

-2	406	474
-4	754	-854
-6	229	204
-8	481	-487
-10	109	105

2,-1,L

-1	67	63
-2	870	-963
-3	56	-23
-4	177	-188
-5	468	460
-6	218	-217
-7	329	-312
-8	128	-120
-9	70	77
-12	58	-56
-13	73	77

2,-2,L

-1	119	-130
-2	108	99
-3	279	301
-4	275	268
-5	151	-167
-6	405	377
-7	429	407
-8	264	-272
-9	69	-70
-10	112	107
-11	68	-70

2,-3,L

-1	182	204
-2	456	-440
-3	406	-377
-4	153	129
-5	162	160
-6	278	261
-7	118	-113
-8	76	72
-9	28	-19
-10	61	-62
-12	51	-46

2,-4,L

-2	450	-433
-3	257	-254
-4	54	34
-5	30	-30
-6	186	-178
-7	141	133
-8	125	117
-9	94	-85
-10	43	46
-13	29	35

2,-5,L

-1	308	280
-2	128	-122
-3	352	-327
-4	37	-29
-5	93	103
-6	106	-98
-7	142	132
-8	85	84
-9	88	-83
-10	64	-61
-11	61	54
-12	73	77

2,-6,L

-1	252	255
-2	259	-237
-3	222	-211
-4	146	139
-5	42	35
-6	34	-32
-7	56	-58
-8	30	41
-10	108	-99

2,-7,L

-2	183	174
-4	98	-99
-5	43	31
-6	48	-43
-7	36	-50
-8	144	141
-10	138	-132

2,-8,L

-1	132	130
-2	60	53
-3	92	-90
-5	89	92
-7	42	-37

2,-9,L

-1	85	-81
-3	83	90

1,0,L

-1	138	-252
-3	873	935
-5	739	-708
-7	393	-375
-11	41	-41
-13	61	58

1,-1,L

-1	122	-118
-2	922	932
-3	38	28
-4	133	-135
-5	188	179
-7	34	-39
-8	101	-106
-9	286	-294
-10	155	152
-11	63	53
-12	53	-58

1,-2,L

-1	488	463
-2	807	-762
-3	149	141
-4	877	846
-5	142	-114
-6	338	-331
-7	280	275
-8	200	-191
-9	135	140
-11	23	-24
-12	42	-39

1,-3,L

-1	64	33
-2	142	118
-3	720	642
-4	223	-204
-5	98	84
-6	72	-76
-7	41	40
-8	104	86
-9	63	-53
-10	97	-107
-11	161	165

1,-4,L

-1	107	107
-2	108	-99
-3	285	-247
-4	477	428
-5	111	108
-6	191	-171
-7	126	-116
-9	82	-80
-12	38	45
-13	67	-67
-15	46	42

1,-5,L

-1	138	-107
-2	112	116
-3	86	-57
-4	78	51
-5	89	73
-6	84	-70
-7	197	-185
-8	227	222
-10	57	-56

1,-6,L

-1	175	159
-2	66	55
-3	63	-66
-4	28	-13
-5	78	65
-7	123	115
-8	66	-71

1,-6,L

-9	59	55

1,-7,L

-1	159	-146
-2	104	94
-4	92	-83
-5	94	97
-6	54	62
-7	172	-169
-9	161	169

1,-8,L

-1	116	-114
-2	89	84
-3	67	69
-4	132	-128
-5	114	-115
-6	53	48
-9	56	-75

1,-9,L

-4	64	-64
-5	33	33

0,0,L

-2	525	-545
-4	754	743
-6	223	194
-8	57	51
-10	62	-60
-12	82	-79
-16	58	-51

0,-1,L

-1	766	720
-2	734	717
-3	807	-792
-4	111	91
-5	192	-208
-6	231	-229
-7	196	193
-8	278	270
-9	98	-94
-10	94	-86
-11	53	53

0,-2,L

0	154	124
-1	857	792
-2	1815	-1752
-3	485	413
-4	102	-85
-5	36	-29
-6	274	-254
-7	305	293
-8	109	109
-9	80	-82
-10	93	101
-11	165	167
-12	68	65

0,-3,L

-1	169	165
-2	97	-106
-3	554	-491
-4	229	195
-5	407	384
-6	341	-319
-7	67	-60
-8	100	93
-9	33	35
-10	118	-114
-12	55	58

0,-4,L

0	475	441
-1	58	-67
-2	54	59
-3	51	-46
-4	66	59
-5	456	-421
-6	257	241
-8	57	-55
-9	141	-124
-10	226	-225
-13	68	-64
-14	30	-27

0,-5,L

-1	156	125
-2	304	270
-3	346	-320
-4	275	-262
-5	521	492
-7	205	-205
-8	166	154
-10	36	-35

0,-6,L

0	283	-253
-1	124	-109
-3	232	234
-5	200	-188
-6	113	108
-7	279	282
-8	96	-96
-9	49	49
-11	65	-73

0,-7,L

-1	71	-75
-2	89	81
-4	242	-239
-5	56	52
-6	207	201
-7	58	-68
-9	41	40

0,-8,L

0	116	109
-1	150	-143
-3	71	69
-5	153	-158
-7	64	77
-8	72	-76

0,-9,L

-2	68	68
-4	72	-70
-5	92	-90

-1,0,L

-1	229	-264
-3	929	983
-5	240	-239
-7	228	219
-9	131	-143
-11	83	84
-13	207	-206

-1,-1,L

0	123	-156
-1	103	75
-2	463	-483
-3	152	-138
-4	527	564
-5	273	271
-6	179	-177
-7	313	-307
-8	31	33
-9	81	75
-11	104	107
-13	48	-48

-1,-2,L

-1	1116	-1084
-2	768	749
-3	278	-278
-4	96	-65
-5	23	-28
-6	46	-50
-7	81	-91
-8	94	81
-9	182	-172
-11	162	156
-12	69	65
-14	52	-49

-1,-3,L

0	532	-518
-1	1012	951
-2	77	76
-3	650	-603
-4	130	131
-5	166	165
-6	112	123
-7	79	-77
-8	127	-120
-9	73	74
-10	68	74
-11	60	59
-12	84	80

-1,-4,L

-1	175	-161
-2	94	89
-3	702	647
-4	441	-433
-5	238	230
-6	47	24
-7	109	-107

-1,-4,L

-8	132	-136
-9	163	165
-12	38	33

-1,-5,L

0	418	-378
-1	213	-188
-2	424	388
-3	154	-136
-4	186	-171
-5	42	41
-7	99	-96
-8	183	-186
-9	81	-80

-1,-6,L

0	108	102
-1	151	-139
-2	181	-166
-3	60	-60
-5	81	-73
-6	282	291
-7	167	-173
-8	131	-132
-10	105	108
-11	58	-62

-1,-7,L

0	67	70
-1	79	-76
-3	121	121
-5	72	67
-6	78	70
-7	163	171
-9	52	-61
-10	49	53

-1,-8,L

0	153	154
-1	112	107
-2	108	-101
-6	129	136
-7	100	110
-8	110	-120

-1,-9,L

0	61	54
-1	75	-77
-2	122	-121
-3	81	-82
-6	56	-64

-2,0,L

0	511	-553
-2	811	-828
-4	338	324
-6	55	-72
-8	184	197
-10	79	73
-12	89	-68
-14	102	108
-16	30	38

-2,-1,L

0	683	751
-1	35	0
-2	619	602
-3	550	-580
-4	332	-334
-6	187	183
-7	79	-94
-8	113	-102
-10	175	-176
-11	83	-89
-12	70	-67
-13	118	-122
-14	100	-102
-15	100	105

-2,-2,L

0	254	286
-2	419	418
-3	528	-541
-4	130	-131
-5	243	263
-6	120	-102
-7	281	-287
-8	117	126
-9	174	172
-11	105	-112
-12	195	-200
-13	37	-42
-14	57	52

-2,-3,L

0	934	-961
-1	42	28
-2	319	327
-3	543	513
-4	225	-204
-6	111	105
-7	89	85
-8	84	91
-9	253	255
-10	198	201
-14	25	-32

-2,-4,L

0	127	114
-1	47	-34
-2	129	-127
-3	68	-71
-4	61	-42
-5	254	246
-7	163	-168
-8	187	-184
-9	211	217
-10	225	231
-12	26	-27

-2,-5,L

0	34	-30
-1	264	-256
-3	149	136
-5	224	-217
-6	60	58
-7	239	-233
-8	177	-182
-9	50	41
-12	48	-47

-2,-6,L

0	240	242
-1	47	35
-2	74	72
-3	47	38
-6	59	-62
-7	60	-47
-8	87	-91
-9	106	-108
-10	68	78
-12	51	-55

-2,-7,L

-1	68	66
-2	92	-91
-4	245	236
-5	78	73
-6	54	-45
-8	82	-85
-10	76	85

-2,-8,L

0	34	-31
-2	134	-144
-3	99	95
-4	180	174
-8	49	58

-2,-9,L

0	43	45
-1	56	55
-2	57	-56
-3	160	-169
-4	63	63
-5	126	136

-3,0,L

-1	594	620
-3	644	-656
-5	406	422
-7	77	-77
-9	54	-52
-11	111	-117
-13	191	200

-3,-1,L

0	503	-594
-2	441	460
-3	401	406
-4	71	-60
-5	83	-82
-6	104	107
-7	49	38
-8	66	73
-9	135	122
-10	233	-231
-11	201	-210
-12	149	151
-13	54	-56

-3,-2,L

-1	59	-30
-2	198	228
-4	282	-288
-5	250	242
-6	229	235
-7	99	-107
-8	66	65
-9	32	-23
-10	25	-24
-11	67	-71
-15	72	-74

-3,-3,L

0	127	127
-1	457	-437
-2	275	-274
-3	356	-335
-4	104	-97
-5	169	-164
-6	55	56
-9	84	87
-10	29	-29
-11	107	-111
-13	70	83

-3,-4,L

0	280	275
-3	38	28
-4	162	-165
-6	59	59
-7	277	286
-8	132	131
-13	79	80

-3,-5,L

0	376	371
-1	358	346
-2	68	-59
-3	188	183
-4	58	-47
-5	91	-93
-6	35	-34
-7	125	131
-8	55	52
-9	78	89

-3,-6,L

0	57	54
-1	116	-120
-2	84	-77
-3	171	170
-4	123	122
-5	203	-208
-6	296	-299
-7	105	105
-8	99	103
-10	57	-58

-3,-7,L

0	62	-58
-1	101	103
-2	75	-74
-3	72	-78
-5	99	-94
-6	45	-49
-8	82	76
-9	60	-66

-3,-8,L

0	77	80
-4	107	111
-6	107	-109
-8	78	90

-3,-9,L

0	114	-125
-1	77	84
-2	105	112
-4	26	11

-4,0,L

0	676	-713
-2	313	312
-4	100	81
-6	56	-62
-8	174	-179
-10	190	198
-12	45	50

-4,-1,L

0	326	361
-1	282	-285
-2	55	-38
-3	155	137
-4	464	453
-5	436	446
-6	382	384
-7	385	-394
-8	69	-63
-9	159	170
-10	127	131
-12	75	85

-4,-2,L

0	234	-251
-1	459	-483
-2	176	-180
-3	146	154
-4	90	78
-5	37	-27
-6	58	61
-8	156	-167
-9	148	-162
-11	53	-57
-12	32	-32
-13	43	50
-14	32	-30

-4,-3,L

0	242	222
-1	224	-208
-2	295	-287
-3	98	-87
-4	49	-40
-5	32	-34
-6	116	117
-8	185	-185
-12	39	-42
-13	29	-28

-4,-4,L

0	157	157
-1	229	-214
-2	276	-251
-3	84	75
-4	322	322
-5	101	97
-6	140	-133
-7	44	44
-8	54	58
-9	52	-51
-10	130	134
-12	75	-85

-4,-5,L

-2	258	-241
-3	44	49
-4	150	150
-7	87	84
-11	65	63
-13	74	-77

-4,-6,L

0	180	200
-1	174	181
-2	212	-210
-3	271	-274
-4	91	89
-5	177	179
-7	54	-60
-9	38	-46
-11	70	77

-4,-7,L

0	96	101
-3	55	-53
-10	43	-50

-4,-8,L

0	80	-87
-1	144	146
-2	121	110
-3	129	-138
-4	69	-64
-5	100	108
-7	43	-46

-5,0,L

-1	235	-227
-3	443	428
-5	553	-532
-7	49	51
-13	64	70

-5,-1,L

-1	137	116
-2	180	189
-3	274	255
-4	346	-346
-5	178	-176
-6	133	-124

-5,-1,L

-7	185	185
-8	76	63
-9	81	-90
-10	52	-57

-5,-2,L

0	346	391
-1	88	-91
-2	55	31
-3	404	382
-4	258	246
-5	284	-276
-6	52	-36
-7	214	215
-8	28	-41
-9	72	77
-10	69	73
-12	47	-52
-14	39	50

-5,-3,L

-1	205	-199
-2	139	122
-3	314	311
-4	257	244
-5	282	-276
-6	92	-91
-7	82	79
-8	201	211
-9	94	-99
-10	56	-57
-11	60	58
-13	55	-60

-5,-4,L

0	85	-81
-2	221	-229
-3	106	-96
-4	50	-48
-5	47	-30
-6	50	-39
-7	67	68
-9	109	-106
-10	65	71

-5,-5,L

0	89	-93
-1	66	-52
-2	77	-78
-5	42	-47
-6	140	-148
-7	61	66
-8	121	125
-10	111	-122

-5,-6,L

0	173	-184
-1	114	119
-2	262	268
-4	66	-55
-7	42	44
-8	47	41

-5,-7,L

0	67	-75
-3	67	60
-7	79	-87
-9	76	80

-5,-8,L

0	166	-182
-1	141	-145
-2	87	92
-3	68	71
-4	58	-60
-5	31	32
-7	28	-34

-5,-9,L

0	29	-30
-2	47	41

-6,0,L

-2	298	-302
-4	123	-116
-8	207	-229
-12	99	-104

-6,-1,L

0	285	289
-1	169	-181
-2	191	-188
-3	137	142
-4	154	154
-6	183	-181
-10	27	12

-6,-2,L

0	167	-163
-1	245	244
-2	66	55
-3	53	-36
-4	148	147
-5	56	47
-6	133	131
-9	103	-110
-10	61	73
-11	28	25

-6,-3,L

0	224	237
-1	222	215
-2	396	-384
-3	138	-128
-4	241	222
-5	170	172
-6	114	-101
-8	42	50
-10	31	-26

-6,-4,L

0	128	-124
-2	204	191
-3	91	-91
-4	59	-58
-8	81	83
-10	77	-78

-6,-5,L

0	71	67
-1	114	113
-3	193	-190
-5	68	59
-6	27	-34
-7	139	-140
-8	53	52
-9	29	34

-6,-6,L

0	185	-193
-1	63	-62
-4	80	-75
-5	123	125
-6	71	-73
-7	89	-89
-9	50	49

-6,-7,L

0	47	45
-1	62	54
-6	56	59
-8	64	-74
-9	34	37

-6,-8,L

0	114	119
-1	55	-65
-2	42	40
-6	78	85

-7,0,L

-3	158	148
-5	278	-259
-7	237	224
-11	117	122

-7,-1,L

0	331	338
-2	108	-114
-3	90	-98
-6	76	-67
-7	78	-65
-9	58	-60

-7,-2,L

0	415	-418
-1	174	150
-2	74	-75
-3	62	52
-5	127	-125
-6	139	-131
-7	52	64
-8	70	62
-9	99	-94
-10	93	-99

-7,-3,L

-1	112	116

-7,-3,L

-2	195	190
-3	63	-59
-4	82	-74
-5	123	120
-7	48	38

-7,-4,L

0	114	-115
-2	101	88
-3	85	-86
-4	130	118
-7	57	-53
-9	62	59

-7,-5,L

0	90	-98
-1	167	-164
-2	105	106
-3	87	88
-4	165	-157
-5	32	-15
-6	125	120

-7,-6,L

0	103	-109
-2	95	90
-3	94	-83
-4	141	-128
-5	59	68

-7,-7,L

-3	136	138
-5	149	-155
-7	52	47

-7,-8,L

-2	83	80
-3	72	68

-8,0,L

-2	265	-269
-4	137	134
-6	184	-178
-8	56	52
-12	55	50

-8,-1,L

-1	127	143
-2	118	126
-4	28	-20
-5	32	-18
-9	53	-50
-11	73	69

-8,-2,L

0	221	249
-1	107	116
-2	77	82
-3	48	-45
-4	75	78
-5	129	128
-7	107	-91

-8,-3,L

0	336	-345
-1	88	-93
-2	215	214
-4	93	-97
-6	37	-42

-8,-4,L

0	158	-161
-1	93	92
-2	87	-83
-4	134	-115
-6	118	112
-10	26	17

-8,-5,L

0	156	167
-1	175	-171
-2	75	72
-3	62	62
-6	68	71
-9	70	67

-8,-6,L

-1	78	-74
-2	111	111
-5	130	-134
-6	71	80

-8,-7,L

0	90	94
-2	106	-107

-8,-8,L

-2	44	-37

-9,0,L

-1	185	177
-3	357	-343
-7	111	-112

-9,-1,L

-1	139	143
-2	68	65
-3	94	92
-5	96	93
-9	100	93
-10	39	40

-9,-2,L

0	86	-96
-2	215	213
-3	60	52
-4	105	-100
-5	86	85
-7	46	-43
-8	78	-74
-9	63	66

-9,-3,L

0	78	-73
-3	78	-71
-5	85	86
-6	56	46
-7	158	-161
-8	63	-66

-9,-4,L

0	152	-145
-1	72	-69
-3	94	86
-5	32	-14

-9,-5,L

0	92	90
-2	67	-67
-5	34	46
-6	68	71
-8	94	-91

-9,-6,L

0	84	83
-1	96	-100
-2	68	-66
-3	46	59
-4	57	53

-9,-7,L

-3	77	-77

-9,-8,L

-1	117	107
-2	95	-101

-10,0,L

0	272	-263
-2	281	277
-4	297	-307
-8	99	98
-10	30	-32

-10,-1,L

0	125	-122
-1	119	109
-3	158	-156
-4	103	-99
-5	48	-45
-6	68	-66
-7	43	39
-8	52	-50
-10	75	72

-10,-2,L

-2	107	109
-3	91	86
-4	132	-122
-5	114	-106
-6	110	105
-7	61	-68
-9	91	90

-10,-3,L

0	194	198
-1	139	150
-2	220	214
-3	83	73
-4	87	-91
-5	39	-44
-7	60	58

-10,-4,L

-5	49	-53
-6	44	-39

-10,-5,L

0	122	-129
-3	97	99
-5	99	-96
-7	77	63

-10,-6,L

0	53	57
-1	43	33
-5	43	36

-10,-7,L

-3	26	-26
-4	61	64

-11,0,L

-1	294	-285
-3	261	-249
-5	288	285
-7	143	-147

-11,-1,L

0	94	93
-1	96	-85
-2	269	-271
-3	179	-182
-4	96	90
-5	196	-187
-6	120	110

-11,-2,L

0	227	228
-1	68	68
-2	126	-121
-3	80	-80
-4	77	-69
-5	157	159
-9	29	40

-11,-3,L

0	214	206
-2	135	-129
-3	144	142
-4	106	103
-5	65	-66
-6	65	-61
-7	138	143
-8	49	-49

-11,-4,L

0	133	144
-1	38	32
-3	85	-89
-5	54	55
-7	72	-74
-8	61	60

-11,-5,L

0	106	105
-2	143	-145
-3	64	-64
-4	92	94
-6	62	-65
-7	59	60

-11,-6,L

-1	73	69
-2	27	-11

-11,-7,L

0	31	39
-2	44	24

-12,0,L

-2	166	161

-12,-1,L

-1	135	-129
-2	55	-53
-3	200	201
-5	81	-77
-6	47	-40

-12,-2,L

0	165	-162
-1	120	-115
-6	69	-68
-7	71	62

-12,-3,L

0	68	64
-2	163	-164
-6	90	83

-12,-4,L

-6	67	-66

-12,-5,L

0	49	-43
-1	84	82

-13,0,L

-3	197	191

-13,-1,L

0	104	100
-2	72	-68
-5	47	49

-13,-2,L

-5	52	-62

-13,-4,L

-5	50	48

-14,0,L

-2	57	-47

-14,-2,L

-1	50	46

-14,-3,L

-4	43	47

-14,-5,L

0	50	55

-15,-2,L

0	56	-48

-16,-1,L

0	62	-45

A P P E N D I X 3

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR (±) ERALDIN PERCHLORATE

11,-1,L

1	109	-107

11,-2,L

2	56	60
1	66	-63

10,0,L

-1	33	-44
-2	56	50

10,-2,L

-2	63	-66

10,-3,L

3	78	-77

10,-5,L

4	33	29

9,0,L

-1	88	77
-2	67	68
-5	33	-11

9,-1,L

3	154	158
2	202	-197
0	80	75

9,-2,L

4	69	-60
3	85	93

9,-3,L

2	83	85
0	99	-102
-2	68	74

9,-4,L

1	33	34

8,0,L

-1	58	56

8,-1,L

3	101	-95
1	108	119
-1	112	-113

8,-2,L

6	37	47
4	113	-106
-4	41	-44

8,-3,L

6	50	-45
4	69	-74
-1	60	59

8,-4,L

8	46	39
7	53	-46
5	115	108
4	101	108
3	141	-145
2	109	-115
0	99	98
-1	65	-70

8,-5,L

5	50	-44
2	77	74

8,-6,L

1	44	-52
-2	42	28

7,0,L

-1	74	-71
-2	68	-59
-3	101	93
-4	63	83

7,-1,L

6	132	128
5	126	-126
4	130	141
3	97	-114
0	112	-107
-1	80	-74
-4	73	-69
-6	61	56

7,-2,L

5	169	-177
4	242	249
3	191	207
2	109	-112
1	159	-158
0	70	61
-1	165	155
-2	121	-126
-3	39	-47

7,-3,L

-2	91	-90
-4	59	56

7,-4,L

0	95	-102
-2	40	45

7,-5,L

7	76	71
5	142	-141
4	68	-56
3	53	50
2	113	122
-1	40	31
-4	72	-73

7,-6,L

4	84	100
2	71	-68
-3	95	90

7,-7,L

3	87	-92
1	90	92
-2	65	-70
-3	44	53

7,-8,L

1	43	-43

6,0,L

-1	24	-21
-2	146	152
-4	105	-106
-5	77	81
-7	35	26
-8	34	-34

6,-1,L

7	99	94
4	86	79
2	182	-174
1	117	-117
-1	73	83
-3	120	-113

6,-2,L

5	64	-67
3	82	80
-2	92	-93

6,-3,L

8	64	-62
7	98	-104
6	218	213
5	133	135
4	214	-215
3	157	-166
2	94	104
1	85	83
0	134	-124
-3	136	130
-5	75	-72

6,-4,L

0	174	-178
-1	92	101

6,-5,L

6	83	-79
5	69	76
4	78	69

6,-5,L

2	108	-111
0	127	126
-2	82	-84

6,-6,L

5	63	71
3	65	-50
-1	79	-82
-3	76	85

6,-7,L

-1	87	88

6,-8,L

3	80	77
-1	101	96

6,-9,L

3	46	-52

5,0,L

-1	170	181
-2	147	141
-3	26	36
-4	74	-87
-5	66	70
-7	45	-41

5,-1,L

6	280	-258
5	184	189
4	311	275
3	108	-122
2	161	-170
1	77	74
-1	118	-114
-3	38	-53
-5	95	93
-6	83	-76

5,-2,L

8	119	-109
7	89	94
5	92	75
4	65	-66
2	208	204
-1	387	-393
-3	161	174
-4	110	-103
-5	56	-45

5,-3,L

5	60	-47
4	39	17
3	50	56
2	44	-39
1	173	-164
0	116	103
-2	120	122

5,-4,L

8	95	99
6	127	-118
5	83	-89
4	133	132
3	48	45
2	146	-139
1	49	-53
0	168	175
-2	223	-217
-3	135	-125
-4	101	101
-5	103	95
-7	49	-30

5,-5,L

5	96	103
3	60	-72
-2	110	116
-4	79	-89

5,-6,L

7	94	91
4	171	-190
2	132	146
-1	98	-91
-2	141	134

5,-7,L

6	55	-63
1	133	-130
-2	69	68
-3	79	-78

5,-8,L

5	57	71
3	68	-71
2	72	-71
1	74	68
0	109	110
-1	136	-136
-3	59	59

4,0,L

-1	246	246
-2	90	78
-3	439	-454
-4	227	234
-5	54	-61
-6	54	-51

4,-1,L

8	71	84
3	67	-85
2	112	99
1	174	154
0	192	-187
-1	231	-211
-4	183	180
-7	63	67

4,-2,L

9	70	-67
8	89	-83
7	117	106
6	163	162
3	162	174
1	129	-143
-1	80	82
-2	105	101
-3	133	-133
-4	195	-198
-5	58	-43
-6	76	78

4,-3,L

7	38	37
6	90	-78
5	131	-125
4	97	96
3	42	38
2	107	-121
1	225	-217
0	230	237
-4	122	131

4,-4,L

8	33	-34
6	92	94
5	144	131
3	198	-211
2	149	115
1	175	-177
-2	83	-86
-3	43	-35
-4	124	119

4,-5,L

8	63	-55
6	157	155
4	123	-133
3	50	70
2	265	274
1	33	-8
0	209	-201
-1	68	-77
-2	173	166
-3	59	61
-4	78	-67
-5	122	-118

4,-6,L

5	75	-96
2	66	-71
0	100	101
-1	82	82
-2	110	-105
-4	102	105

4,-7,L

5	111	123
4	139	151
2	82	-84
0	87	91
-1	94	-89
-2	99	-95
-4	54	60

4,-8,L

2	113	105
0	77	89

4,-9,L

4	72	-78
3	60	60
1	177	-174
0	64	60

4,-10,L

0	65	63
-2	42	-47

3,0,L

-1	248	-240
-2	41	49
-3	182	180
-4	188	171
-5	181	-191
-6	108	-112

3,-1,L

9	92	-89
8	109	106
2	110	106
1	169	-191
0	422	-440
-1	203	-199
-3	144	-138
-4	157	152
-5	85	87
-6	37	36

3,-2,L

9	72	-72
8	66	62
5	53	-32
4	194	193
3	297	285
2	296	-281
1	210	205
0	182	-168
-1	74	-55
-2	394	368
-3	217	-228
-4	223	-215
-5	123	119
-7	60	-59
-9	43	36

3,-3,L

7	100	-91
5	61	77
1	507	507
-1	230	-221
-2	205	-213
-3	162	161
-4	174	168
-6	91	-83

3,-4,L

6	105	114
5	69	66
4	103	-122
2	128	-120
1	160	-157
0	111	-124
-2	102	113
-4	137	-136

3,-5,L

8	71	71
7	61	62
6	75	-71
5	148	-155
4	72	70
3	87	103
1	96	99
0	118	109
-1	74	88
-2	49	-46
-3	167	-154

3,-6,L

8	62	58
5	45	42
4	98	94
2	208	-199
1	40	43
0	54	38
-1	97	84
-3	70	-66
-4	62	76

3,-7,L

6	91	92
5	104	115
4	107	-114
1	133	110
0	266	-259
-2	66	68

3,-8,L

7	84	82
5	94	-96
3	142	134
0	189	-183
-1	58	55
-2	133	132
-4	83	-81

3,-9,L

4	49	56
2	114	-100
-1	44	-34
-3	53	52

3,-10,L

5	72	63
3	90	-95
1	67	60

3,-11,L

2	57	50
-1	63	61

2,0,L

-1	752	758
-2	543	-565
-3	547	570
-4	50	12
-5	126	-129

2,-1,L

7	134	118
6	66	54
5	103	-88
4	140	-119
3	69	74
1	428	-462
0	98	119
-1	1147	1126
-2	124	-96
-3	350	-364
-4	204	-206
-5	229	239
-6	95	92
-7	75	-73

2,-2,L

9	33	30
7	32	-28
5	74	71
4	177	193
1	247	225
0	239	-235
-1	374	-353
-2	100	-109
-3	70	81
-5	125	-130
-6	81	-71
-8	52	49

2,-3,L

8	87	-78
5	96	100
4	93	-106
2	263	-276
1	204	202
0	210	230
-3	272	264

2,-4,L

7	116	119
4	121	-112
3	372	365
2	223	-192
1	391	-383
0	125	-107
-1	146	134
-2	122	-120
-3	98	94
-4	101	-101

2,-5,L

6	110	-102
3	117	130
2	26	-33
1	106	108

2,-5,L

-2 223 -227

2,-6,L

8 107 -106
7 76 -79
6 122 121
5 88 99
4 184 -188
2 177 174
0 29 -14
-3 214 210

2,-7,L

5 41 -33
2 79 71
0 99 -92

2,-8,L

9 52 -44
6 85 -78
4 89 83
3 102 111
2 213 -215
1 81 89
0 112 103
-1 45 25
-2 70 -60

2,-9,L

4 59 -53
2 198 -206
1 142 128
-1 65 -56

2,-10,L

4 93 -96
-1 34 32

2,-11,L

1 69 -68
-2 58 54

1,0,L

-1 347 269
-3 78 70
-7 102 -102
-8 56 -56

1,-1,L

7 117 -107
6 79 -81
4 73 70
3 102 -131
2 311 -397
0 81 6
-1 600 535
-2 468 -444
-4 146 178
-5 62 55
-8 89 89

1,-2,L

7 40 -43
5 176 174
4 361 334
3 323 -347
2 762 693
1 1261 1235
0 871 -800
-1 692 -631
-2 235 -186
-4 117 110
-5 90 -99

1,-3,L

5 150 -157
3 73 -83
2 68 44
1 392 -370
0 190 186
-1 251 256
-2 203 228
-3 143 -156
-4 74 -70
-5 70 86
-6 97 101
-7 74 -80

1,-4,L

9 61 66
8 100 93
6 80 -83
5 82 -78
4 111 129
3 86 -71
0 60 -12
-3 177 -176
-4 118 121
-5 150 140

1,-5,L

6 54 54
5 131 138
3 94 -87
1 129 152
-3 83 82
-4 87 -89
-5 158 -153

1,-6,L

8 55 -51
4 108 -120
3 74 -84
2 87 94
-1 208 194
-3 39 42
-7 60 -55

1,-7,L

8 80 82
4 222 218
1 215 -204
-1 159 135
-2 146 -141
-3 93 -99
-5 30 40

1,-8,L

7 52 -46
4 145 159
3 165 -162
2 121 128
0 73 -85
-6 38 -26

1,-9,L

6 74 71
5 63 -65
4 104 -98
3 67 -60
2 135 122
1 49 47
0 110 -104
-1 82 -75
-2 83 90
-3 70 71

1,-10,L

1 97 -105

1,-11,L

1 69 68

1,-12,L

3 64 -75

0,0,L

-2 638 -706
-4 107 120
-5 26 -35
-6 130 -120

0,-1,L

4 51 -52
2 515 395
1 358 -536
-1 499 -543
-2 198 190
-3 41 -26
-4 76 70
-6 64 -70
-7 128 132

0,-2,L

9 92 -91
7 120 120
6 99 100
4 71 -78
3 183 160
2 369 326
1 234 -285
0 225 -209
-1 293 275
-2 271 306
-3 193 -189
-4 253 -249
-6 92 94

0,-3,L

5	119	-137
4	165	135
3	232	198
2	56	-82
1	250	-262
0	181	153
-1	178	189
-2	195	169
-6	88	-95
-7	111	-110

0,-4,L

4	239	233
3	231	-236
2	252	-275
1	31	-21
0	110	76
-1	651	-613
-2	91	84
-3	234	233
-5	51	-48
-6	83	81
-7	70	68
-8	49	-50

0,-5,L

9	89	-90
8	52	-52
7	67	71
6	144	141
5	76	-79
2	146	159
0	233	182
-1	220	-185
-2	179	166
-4	95	-89
-5	114	-115

0,-6,L

6	77	-85
5	190	-197
3	240	253
1	70	-71
0	267	247
-1	57	-47
-3	62	-66
-5	105	110

0,-7,L

7	64	-58
5	121	115
0	63	35
-1	53	-51
-2	134	-132

0,-8,L

6	101	100
3	78	-72
2	214	211
1	130	129
0	169	-162
-1	85	-75
-2	92	100
-4	88	-77
-5	61	-57

0,-9,L

5	113	-109
4	125	126
3	153	-168
2	85	-84

0,-10,L

4	180	183
2	138	-137
0	65	71
-2	77	-86

0,-11,L

6	33	36

-1,0,L

-2	318	276
-3	140	134
-4	121	-128
-5	39	-44

-1,-1,L

8	60	-57
7	66	55
6	106	97
5	112	-105
4	344	-354
3	164	150
2	1199	1237
1	400	-494
0	719	-820
-2	540	527
-3	95	94
-4	70	-83
-5	122	124
-6	135	130
-8	153	-146
-10	44	45

-1,-2,L

8	74	71
7	38	42
6	75	-66
5	210	185
3	80	-83
2	405	397
1	448	-482
0	282	223
-1	168	150
-2	455	-485
-3	254	-277
-4	78	-80
-6	127	-127
-7	111	122

-1,-3,L

9	77	89
7	135	-127
6	130	-136
5	164	176
4	50	58
3	174	-175
2	108	-139
1	783	697
0	456	381
-1	163	-187
-2	127	-133
-3	239	233
-4	175	174
-5	117	121
-6	182	-174
-8	40	33

-1,-4,L

6	68	63
5	121	112
4	182	-186
3	223	-222
0	231	-253
-1	261	231
-2	42	43
-3	46	-49
-4	123	-117
-6	66	65
-7	90	105

-1,-5,L

5	95	-103
3	160	172
2	74	41
1	93	-99
-1	235	242
-3	234	-223
-5	80	80

-1,-6,L

7	86	-84
0	321	290
-1	42	-47
-3	84	78
-4	53	64
-6	90	-85

-1,-7,L

8	45	-42
5	173	171
4	92	-94
1	211	-202
-1	94	-88
-3	53	56
-7	80	78

-1,-8,L

4	134	-127
3	169	161
2	202	210
1	85	-77
0	98	-82
-3	41	-50
-5	43	46
-6	68	-77

-1,-9,L

6	110	-106
4	100	109

-1,-9,L

2	186	-187
0	80	76
-1	53	52
-3	55	-53
-5	74	70

-1,-10,L

6	55	62
4	77	-88
2	59	67
0	63	-58
-1	53	-46

-1,-11,L

0	52	-60

-1,-12,L

4	42	-25

-2,0,L

0	483	-511
-1	58	-114
-2	600	601
-3	174	166
-4	204	-223
-5	175	-184

-2,-1,L

4	141	-138
3	107	121
2	918	-921
1	76	-85
0	465	396
-1	712	652
-2	238	-288
-4	246	234
-5	62	-66
-6	161	158
-8	69	-66

-2,-2,L

7	54	-61
5	171	174
4	240	257
3	138	157
2	429	-400
1	442	403
0	437	385
-1	283	-320
-2	290	-297
-3	71	76
-4	236	227
-5	200	-203
-6	194	-195
-8	104	114

-2,-3,L

4	54	-64
3	55	60
2	124	106
1	78	-109
0	273	-303
-1	123	55
-2	253	220
-3	42	-32
-4	85	-75
-5	108	100
-7	73	-73

-2,-4,L

7	168	156
6	53	-47
5	105	-105
4	56	-44
3	99	119
2	99	-109
1	60	-89
0	265	-298
-1	267	244
-2	242	223
-4	105	-101
-5	119	124
-6	121	113

-2,-5,L

6	115	-124
5	38	34
4	123	132
3	218	190
1	361	310
0	244	-218
-1	192	-181
-2	123	-135
-5	77	-74

-2,-6,L

8	83	-76
3	190	-175
2	217	-211
1	550	527
0	103	91
-1	166	-169
-2	109	90
-3	149	144
-5	110	-115
-6	77	84

-2,-7,L

7	76	77
5	143	-138
3	271	264
2	67	66
1	200	-193
0	80	-59
-3	47	-44
-6	74	83

-2,-8,L

5	98	98
3	55	-55
1	35	42
0	65	61
-2	70	-75
-3	85	-82

-2,-9,L

6	71	-69
5	118	121
3	106	-94
1	55	62
-1	68	-73
-2	83	90
-3	74	79

-2,-10,L

7	73	81
-1	112	-99
-2	66	71

-2,-11,L

6	58	-66
4	64	69
0	77	78

-3,0,L

0	309	333
-1	509	513
-3	184	-188
-4	126	134
-5	231	222
-6	65	-64
-7	246	-232

-3,-1,L

8	68	84
4	151	-156
2	210	-201
1	80	83
0	147	151
-2	119	-129
-3	109	-104
-4	68	-64
-5	68	-53
-6	107	112
-7	70	60

-3,-2,L

8	67	-67
7	61	-58
6	176	178
5	75	76
4	332	-342
3	308	350
2	324	330
0	288	-260
-1	164	-184
-3	167	-130
-4	195	184
-5	141	-143
-7	73	69

-3,-3,L

7	48	48
5	70	-79
4	168	-157
2	311	290
1	159	143
-1	222	225
-2	367	375
-3	374	-349

-3,-3,L

-4	52	-60
-6	78	73
-9	54	-53

-3,-4,L

8	89	78
7	59	-69
3	134	-129
2	246	-232
1	400	-379
0	246	236
-2	147	-167
-3	98	90
-4	242	224

-3,-5,L

7	47	-46
6	86	94
5	153	156
3	207	-199
2	237	208
1	346	315
-1	72	-88
-3	66	72
-5	99	-104
-6	94	-98

-3,-6,L

5	91	-94
3	102	89
2	264	-260
0	143	113
-1	178	170
-2	124	129
-3	74	-73

-3,-7,L

5	131	-123
3	256	253
2	51	-46
1	160	-147
-2	56	-53
-3	126	-143
-4	181	176
-5	30	-25
-6	72	71

-3,-8,L

7	140	-134
6	88	87
5	117	122
1	75	63
-3	56	-61
-4	90	99
-5	156	-152

-3,-9,L

8	31	20
5	67	-61
4	60	-57
2	90	91
0	113	-112
-4	116	119

-3,-10,L

1	89	-83
-3	53	-55
-4	45	-39

-3,-11,L

0	64	65

-3,-12,L

-2	39	39

-4,0,L

0	133	119
-1	277	255
-2	155	136
-3	200	-189
-4	181	-171
-5	90	99
-7	160	-153
-8	59	60

-4,-1,L

7	73	-75
6	128	140
5	68	-73
3	270	-269
2	177	193
1	103	103
-1	271	-282
-2	166	173
-3	708	695
-4	234	-195
-5	244	-217
-6	90	96

-4,-2,L

5	61	-58
4	229	214
1	95	-52
0	270	-268
-1	137	-131
-2	341	-290
-4	70	-66
-5	36	36

-4,-3,L

6	122	-125
4	220	217
3	56	-57
2	288	-282
1	148	162
0	412	412
-1	50	67
-2	65	-70
-4	175	177
-5	74	64
-6	77	-73
-7	75	-74

-4,-4,L

4	55	55
1	332	-294
0	175	-170
-1	84	-89
-4	106	99
-5	66	64

-4,-5,L

9	49	-46
6	118	107
4	80	-74
3	181	-157
2	270	264
1	101	89
0	108	-127
-1	61	68
-2	109	130
-3	106	-107
-4	209	-226
-5	99	95
-6	58	64

-4,-6,L

8	69	61
6	178	-167
5	133	-137
4	187	186
2	105	105
0	42	53
-1	143	165
-2	43	34
-4	151	-162
-5	120	116

-4,-7,L

3	136	-129
2	68	-62
1	133	133
0	55	61
-1	171	-180
-2	105	-115
-3	105	104
-4	125	-114
-6	67	73

-4,-8,L

4	45	-48
2	150	140
0	75	-69
-5	110	-113

-4,-9,L

2	67	-62
-1	89	93
-3	120	-121

-4,-10,L

2	83	-82
0	97	-102
-2	71	78

-4,-11,L

1	124	131

-5,0,L

-1	46	-52
-3	76	-64
-4	133	-107
-5	45	-26
-6	66	-56
-7	65	59

-5,-1,L

5	133	-142
4	40	-19
3	55	41
1	121	-121
-1	47	-44
-3	160	152
-5	34	42
-6	78	67

-5,-2,L

5	116	-127
4	128	129
3	112	109
2	45	-46
0	102	106
-1	268	254
-2	401	-373
-3	188	-161
-4	50	-27
-5	51	50

-5,-3,L

7	92	-87
5	69	64
3	40	-40
2	57	-48
1	41	-46
-1	309	286
-2	151	-137
-3	115	116
-5	67	-63

-5,-4,L

7	68	79
6	159	159
5	126	-134
4	281	-279
3	110	116
2	122	121
1	63	-57
0	177	-180
-1	105	92
-2	148	173
-3	150	161
-4	67	-60
-6	52	61
-7	83	82

-5,-5,L

5	120	125
2	29	-41
1	62	-63
-1	67	85
-3	83	-82
-5	94	-98
-7	47	50

-5,-6,L

6	102	-110
4	108	118
3	121	-103
2	65	-58
1	210	213
0	127	128
-1	65	-73
-2	93	-103
-3	139	150
-4	122	130
-6	88	-96

-5,-7,L

8	60	-61
6	70	69
1	46	-45
0	64	-69
-2	102	-94
-3	149	157
-4	118	-124
-6	47	48

-5,-8,L

5	80	-80
4	57	58
3	126	123
1	82	-75
0	33	-33
-1	58	60
-2	239	-249
-3	131	125

-5,-9,L

1	53	-37
0	69	80
-1	162	168

-5,-10,L

6	33	17
-1	83	-85

-5,-11,L

5	39	-29
3	62	64
-1	38	35

-6,0,L

0	81	-83
-1	81	74
-2	318	320
-4	219	-221
-5	54	56
-6	85	-90

-6,-1,L

7	75	77
6	102	-109
2	130	-131
1	99	-87
-1	86	-73
-2	196	179
-4	67	-71
-5	179	169

-6,-2,L

5	206	208
3	175	-177
1	79	84
0	30	21
-1	214	-211
-2	30	25

-6,-3,L

6	53	-56
4	48	55
3	75	74
2	84	86
1	91	86
-1	147	-148
-2	124	121
-3	108	102
-4	63	-58
-5	69	-47

-6,-4,L

4	99	-109
2	97	-100
1	53	-56
-2	100	-96
-3	67	-63
-5	124	120

-6,-5,L

8	40	46
6	102	-102
5	120	121
4	105	98
1	69	61
0	53	49
-2	75	-69
-4	97	93
-6	104	-112

-6,-6,L

4	126	-128
3	31	-36
2	64	71
1	51	46
0	68	61
-2	119	134
-3	253	-247
-5	101	96

-6,-7,L

1	76	-76
0	102	-91
-1	63	-23
-2	293	319
-4	93	-97

-6,-8,L

0	98	104
-2	107	-114

-6,-9,L

3	93	-92
0	99	-96
-1	83	88

-6,-10,L

0	67	-62

-7,0,L

-1	129	133
-2	43	40
-3	164	-162
-4	75	70
-6	27	33
-7	59	-68

-7,-1,L

5	35	-32
4	41	-46
3	63	-67
1	89	89
0	128	110
-2	68	-72
-3	41	20
-4	71	64

-7,-2,L

6	41	30
5	87	90
3	74	-72
-1	148	-149
-4	109	-109
-5	81	-74

-7,-3,L

7	67	72
5	137	-136
3	145	135
2	51	52
1	143	-138
0	222	214
-2	37	17
-6	46	53

-7,-4,L

4	76	73
3	52	-47
2	103	-108
1	159	-153
0	95	91
-1	45	36
-2	41	41
-5	66	-58

-7,-5,L

6	71	68
4	70	-70
2	82	76
-1	105	-113
-2	73	-64
-3	138	148
-4	63	63
-5	98	-97

-7,-6,L

4	38	-17
2	81	93
-1	158	176
-2	140	145
-3	75	-74
-4	70	-69

-7,-7,L

2	53	-54
-1	286	-286
-3	71	75

-7,-8,L

0	216	216
-1	161	-170

-7,-9,L

1	66	-66
0	72	81

-7,-10,L

2	32	-32

-8,0,L

-3	65	-74
-4	114	126
-5	113	-110

-8,-1,L

6	62	63
4	90	-94
3	98	-97
1	115	111
0	124	-105
-2	149	139
-4	72	68

-8,-2,L

3	120	113
0	145	-153
-3	56	-49
-5	51	47

-8,-3,L

1	70	70
-2	79	-75
-3	90	-103
-5	74	80

-8,-4,L

3	50	-58
0	73	-76
-1	112	-102
-2	130	125
-3	158	152
-5	50	-48

-8,-5,L

-2	149	-156
-3	100	-102

-8,-6,L

6	28	-30
3	27	32
-1	236	238
-3	70	-74
-4	59	56

-8,-7,L

2	35	-30
1	123	118
0	73	-68
-5	32	31

-8,-8,L

0	59	-62

-8,-9,L

1	73	-75

-9,0,L

-2	109	-121
-3	97	100
-7	40	30

-9,-1,L

1	54	-52
-1	86	87

-9,-2,L

2	67	-66
0	39	39
-1	42	-37
-2	76	-71
-7	30	-3

-9,-3,L

2	72	-77
1	80	78
-2	37	30
-4	101	-102

-9,-4,L

4	62	-76
0	95	-86
-1	74	-79
-3	138	145

-9,-5,L

3	84	83
2	109	-104
1	84	-80
0	126	120
-1	69	62
-2	77	-73

-9,-7,L

1	108	97
0	99	-98
-2	77	75

-9,-8,L

2	48	-50
1	98	93
0	60	-54

-9,-9,L

2	79	-81
1	88	90

-10,0,L

0	59	-62
-1	114	114
-4	55	-54

-10,-1,L

1	28	-41
0	67	-62
-1	93	88
-3	67	61

-10,-2,L

3	63	-67
-2	100	-112

-10,-3,L

2	113	105
0	86	-85
-1	43	40
-2	78	80

-10,-4,L

3	30	-26
-2	44	-37

-10,-5,L

-2	67	-67

-10,-6,L

2	77	88

-10,-7,L

1	85	-85

-11,0,L

0	84	74

-11,-1,L

1	62	60
0	39	48
-1	90	-85
-3	49	53

-11,-2,L

-1	29	30

-11,-4,L

-2	56	58

-11,-5,L

-1	78	-79

-11,-6,L

3	40	32

A P P E N D I X 4

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR

(±) VIVALAN OXALATE

14,2,L

-9 39 8

14,1,L

-5 58 44
-14 81 82
-15 67 -66

13,3,L

-5 76 -71

13,2,L

-16 29 36

13,1,L

-4 50 53
-5 42 -33
-7 47 -45
-9 40 42
-10 93 -82
-11 65 61
-12 68 -65
-15 40 -39
-17 68 -66

13,0,L

-10 119 117
-12 46 -58
-16 32 31

12,3,L

-6 54 -50
-8 32 -26

12,2,L

-1 38 -27
-5 42 33
-11 40 23
-14 31 -38
-15 71 -68
-17 75 -70

12,1,L

-9 100 97

-14 70 63
-17 38 50
-18 28 34
-19 42 46
-20 52 49

12,0,L

-4 65 -67
-6 193 -195
-10 165 158
-16 82 -81

11,5,L

-6 46 45

11,4,L

-12 65 60
-15 94 87

11,3,L

-6 52 45
-13 51 62
-15 108 -104
-16 59 67

11,2,L

-1 118 -121
-5 62 -61
-7 79 81
-8 54 -54
-9 64 -69
-10 48 -38
-11 47 49
-18 63 54
-21 69 73

11,1,L

0 39 -34
-2 74 76
-4 60 -60
-6 62 -55
-8 103 104
-9 46 -56
-10 113 -110
-11 54 52
-12 79 84
-14 71 -70

-17 67 -67
-18 44 -46
-25 41 41

11,0,L

0 47 39
-2 101 110
-6 136 -140
-8 93 -100
-10 208 214
-12 94 99
-14 74 71
-20 45 44

10,5,L

-1 44 44
-10 31 19
-11 91 -86
-12 33 35

10,4,L

-3 65 66
-4 115 -113
-10 91 87

10,3,L

-1 92 90
-3 57 -72
-5 63 53
-6 62 -63
-8 41 -32
-11 80 85
-13 77 -85
-15 104 98
-22 41 37

10,2,L

0 138 143
-4 151 -150
-5 85 87
-7 78 -76
-9 87 80
-10 142 148
-13 71 66
-14 34 -34
-15 90 -87
-23 31 -36

10,1,L

0 52 48
-1 38 90
-2 81 72
-3 105 101
-4 32 -41
-5 179 -174
-6 177 -183
-7 58 67
-9 103 103
-10 83 82
-11 117 -122
-14 91 92
-15 65 64
-16 91 -99
-17 195 199
-18 34 41
-20 47 33
-22 39 -35
-23 42 -47

10,0,L

0 42 43
-2 39 42
-4 74 -70
-6 463 -470
-8 279 283
-10 58 -55
-14 153 -150
-18 86 -86
-20 93 -93

9,5,L

0 33 26
-2 132 -135
-8 63 62
-10 49 -46
-11 56 54
-13 55 57

9,4,L

-1 146 -150
-4 78 81
-10 39 -52
-11 91 -86
-18 85 90
-22 66 -69

9,3,L

-3	63	68
-6	101	102
-7	95	-96
-9	96	-92
-11	150	155
-13	91	89
-15	87	-93

9,2,L

-1	77	77
-3	122	-121
-4	44	40
-7	116	116
-8	123	-118
-9	156	-153
-10	87	-85
-11	58	61
-12	71	71
-13	112	-121
-15	85	79
-18	122	112
-19	49	52
-22	102	-104
-24	49	-45

9,1,L

-1	148	151
-2	256	268
-4	194	-190
-6	79	86
-7	147	-150
-8	137	-138
-9	79	-82
-10	82	80
-19	42	-27
-21	70	-64
-24	42	-43
-25	115	112

9,0,L

0	61	-62
-4	170	161
-6	173	189
-8	69	-78
-10	96	90
-12	72	-76
-14	116	126
-16	136	130
-18	116	118
-20	111	109
-24	47	-43
-26	110	103

8,6,L

0	50	-40
-3	43	40
-5	41	-44
-10	47	45

8,5,L

-1	93	86
-4	56	-56
-11	70	-71
-13	68	-62
-15	29	-26

8,4,L

-3	65	68
-6	63	-72
-7	35	-33
-9	76	73
-11	78	81
-13	60	53
-14	31	-26
-17	55	-51
-19	67	-82
-20	54	-54
-21	58	55

8,3,L

0	34	39
-5	61	67
-6	104	-101
-7	112	-104
-9	113	119
-17	114	122
-20	61	60
-24	44	38

8,2,L

0	205	217
-1	168	176
-2	103	101
-6	140	-131
-8	51	45
-9	84	81
-10	88	88
-13	49	-51
-16	51	54
-18	53	49
-21	67	-65
-22	40	-49
-27	91	-87

8,1,L

0	48	49
-1	170	171
-3	55	56
-5	221	-219
-6	179	-173
-7	163	154
-10	44	-46
-13	129	-131
-14	42	37
-15	89	83
-16	54	-58
-17	92	101
-19	107	105
-22	45	-34
-24	57	55
-25	56	-60

8,0,L

0	138	-146
-4	352	-358
-6	56	63
-8	165	165
-10	67	-74
-12	281	-293
-14	163	-160
-18	160	-158

7,6,L

-5	51	49
-12	81	-81
-14	34	-42

7,5,L

-4	84	91
-5	88	-92
-7	69	65
-11	60	59
-16	63	60

7,4,L

-1	115	-122
-2	126	127
-3	85	-85
-4	104	101
-6	26	0
-8	40	34
-9	71	-64
-10	73	-70
-18	83	94
-19	62	-63

7,3,L

-1	57	-57
-5	84	-75
-6	106	99
-9	53	45
-11	53	45
-13	110	-109
-15	35	-51
-17	53	52
-20	99	-89
-22	48	-54

7,2,L

-2	134	134
-3	180	-182
-4	174	168
-6	50	-55
-7	73	71
-8	168	-168
-10	181	-175
-11	102	-98
-12	90	-91
-13	47	-43
-16	93	86
-17	89	82
-19	110	109
-21	109	-110
-22	70	-60
-23	76	77

7,1,L

0	70	71
-1	184	180
-2	99	-97
-3	72	-68
-6	160	153
-8	221	221

7,1,L

-10	55	50
-11	50	-46
-12	101	-103
-13	75	-72
-14	53	133
-17	100	-103
-18	86	84
-19	99	-99
-25	43	52

7,0,L

0	79	-80
-2	37	37
-4	191	182
-6	405	394
-8	103	75
-12	192	-189
-14	199	201
-16	168	165
-18	118	117
-22	115	116

6,6,L

-1	62	62
-3	39	-42
-7	42	-34

6,5,L

0	63	-62
-2	93	101
-4	60	-67
-5	46	42
-6	49	-44
-8	134	-131
-13	69	-74
-16	75	-75

6,4,L

-1	62	61
-3	129	146
-4	56	-58
-6	105	-113
-9	109	101
-10	60	61
-11	65	62
-12	94	90
-13	72	75
-14	106	-111
-15	60	62
-17	65	-68

6,3,L

0	92	104
-5	110	118
-6	113	-106
-7	122	119
-9	109	95
-10	74	-73
-12	90	82
-13	283	-288
-14	66	66
-15	224	-223
-16	44	39
-17	349	352
-20	77	74
-21	77	78
-23	77	-78
-24	65	54

6,2,L

0	96	95
-1	45	38
-2	192	205
-4	86	-85
-6	85	-83
-7	124	124
-9	62	-57
-10	123	132
-11	68	64
-12	154	152
-13	55	50
-14	125	-125
-18	85	84
-19	69	-73
-20	63	-60
-26	91	95
-27	95	-93

6,1,L

0	109	106
-1	234	-249
-2	508	-505
-4	201	-198
-5	86	94
-6	148	-154
-7	168	189
-8	177	169
-9	59	53
-10	183	-173
-13	167	-164
-14	174	-170
-18	235	-231
-19	354	350
-24	41	38

6,0,L

0	231	229
-2	244	-241
-6	233	-238
-8	170	-179
-10	358	329
-12	187	-177
-14	48	-45
-16	255	-257
-22	231	-230
-24	63	61
-26	44	-46

5,7,L

-3	35	-35

5,6,L

0	59	51
-3	31	34
-7	56	53
-12	29	-37
-14	86	-91

5,5,L

-1	77	93
-2	59	62
-3	85	-88
-4	121	119
-5	121	-121
-6	59	64
-7	57	58
-10	82	73
-15	65	67
-16	112	115
-20	41	44

5,4,L

-1	120	-122
-2	108	122
-3	93	-88
-4	145	-141
-5	47	-49
-6	160	159
-7	91	-92
-8	74	74
-10	63	64
-11	68	-64
-12	208	-205
-13	271	-277
-15	71	67

5,3,L

0	33	-30
-3	63	-67
-7	50	57
-9	141	141
-10	90	-88
-12	118	-116
-13	213	-211
-15	159	152
-17	63	-65
-20	123	-122
-21	90	-90
-22	69	-67
-23	107	107

5,2,L

0	67	-56
-2	53	-45
-3	252	-248
-4	157	-146
-5	63	52
-6	86	78
-7	45	51
-8	291	271
-9	134	-130
-11	206	-192
-12	327	-325
-13	296	302
-14	61	53
-15	166	-166
-17	216	223
-19	89	-86
-22	86	85
-23	56	61
-24	52	48
-26	85	-76
-27	48	40

5,1,L

-1	176	161
-3	44	55
-4	71	-74
-5	93	-98
-6	222	223
-7	179	168
-8	552	531
-9	53	-46
-11	293	-293
-12	181	190
-13	228	218
-14	152	153
-15	54	49
-17	71	-65
-18	193	182
-19	270	-267
-20	153	-158
-22	170	173

5,0,L

0	236	224
-4	345	359
-8	411	397
-10	467	-456
-12	177	172
-14	125	-112
-16	235	248
-18	38	31
-20	142	143
-22	178	176
-24	60	-63

4,6,L

-6	52	-48
-7	95	-94
-12	55	50
-15	70	-57

4,5,L

-2	66	-55
-3	87	86
-6	184	-185
-7	48	43
-9	33	39
-10	105	-104
-11	46	-46
-12	47	49
-15	95	-98
-16	124	-128
-19	45	41

4,4,L

0	111	109
-2	110	-100
-3	205	202
-4	130	-126
-5	78	70
-6	72	-72
-7	71	79
-8	84	74
-9	180	182
-10	96	89
-12	118	114
-13	75	75
-14	84	-91
-15	55	-62
-16	76	68
-21	82	73

4,3,L

-1	113	-106
-2	146	140
-3	49	-44
-5	137	134
-6	71	79
-7	52	51
-8	98	-92
-9	67	-59
-11	212	212
-12	124	118
-13	329	-335
-17	100	106
-19	31	38
-20	92	93
-24	50	48

4,2,L

0	190	202
-2	242	-225
-3	39	-26
-4	482	-470
-5	142	133
-6	186	-186
-7	129	115
-8	62	57
-9	557	-561
-10	392	397
-11	277	273
-12	94	82
-13	42	49
-14	241	-234
-15	199	205
-17	174	-171
-18	68	-69
-22	87	-90
-26	77	75

4,1,L

0	319	-340
-1	207	-208
-2	193	-218
-3	125	125
-4	369	-388
-5	98	93
-7	37	-47
-8	631	-623
-9	289	287
-10	51	45
-12	188	-186
-13	51	-44
-14	115	-108
-15	269	-280
-16	54	-49
-17	137	137
-18	195	-197
-19	268	271
-20	37	39
-26	61	-56

4,0,L

0	103	-81
-2	189	169
-4	424	389
-6	423	-403
-8	133	-127
-10	415	412
-12	135	133
-14	170	-161
-16	442	-443
-18	353	348
-20	64	-70
-22	100	-102
-24	70	-69

3,7,L

-1	53	47
-5	116	-118

3,6,L

-1	54	61
-2	99	94
-6	83	77
-7	92	93
-14	86	-82
-15	87	78

3,5,L

0	88	95
-1	76	71
-3	142	-140
-4	53	-58
-5	144	-140
-6	95	97
-7	81	-84
-8	179	174
-9	86	91
-10	53	52
-14	85	83
-16	82	80

3,4,L

-1	148	-147
-2	157	-166
-3	81	-86
-5	116	-111
-7	46	-31
-8	119	119
-9	110	113
-11	245	-250
-12	291	-294
-13	119	-131

3,3,L

-1	148	148
-2	160	-152
-3	184	-169
-4	25	-21
-5	84	84
-7	282	-283
-8	137	135
-9	116	115
-10	92	-101
-11	60	-47
-12	106	-102
-13	181	186
-15	159	155

3,3,L

-19	133	-137
-20	53	-55
-21	59	-60
-23	83	90

3,2,L

0	115	-95
-1	43	48
-2	261	-269
-3	241	-236
-4	57	-55
-5	187	184
-6	133	137
-7	120	104
-8	469	453
-9	383	-393
-10	58	66
-11	116	-115
-12	165	-175
-14	62	67
-16	80	76
-22	83	89

3,1,L

-1	473	493
-2	262	239
-4	597	575
-5	800	-772
-6	474	473
-7	223	236
-10	130	129
-11	172	177
-12	207	201
-13	51	52
-14	54	-53
-16	181	182
-17	131	-135
-18	82	86
-19	201	-207
-20	113	119
-21	53	-58
-22	73	75
-25	83	80

3,0,L

0	1054	-1068
-4	173	-184
-6	758	797
-10	345	-337
-14	370	-368
-16	138	130
-18	31	36
-20	138	135

2,7,L

-4	83	77

2,6,L

-1	52	-48
-3	85	84
-4	122	-119
-7	76	-73
-8	108	-102
-15	54	-60

2,5,L

0	36	-47
-4	76	-72
-6	167	-174
-7	232	234
-10	77	-74
-14	60	-49
-16	77	-66

2,4,L

0	146	159
-1	69	68
-3	206	202
-5	76	78
-6	80	-80
-8	100	109
-9	83	80
-11	101	107
-12	125	127
-13	91	101
-14	72	69
-16	94	95
-21	39	41

2,3,L

-1	311	-325
-2	140	150
-3	115	-102
-7	72	82
-8	211	-208
-10	162	174
-11	187	-189
-16	88	-89
-20	64	51

2,2,L

0	293	311
-1	239	229
-2	103	-107
-3	49	-48
-4	281	-268
-5	315	323
-6	613	-612
-7	143	-120
-9	138	-146
-11	312	306
-12	90	-90
-14	67	66
-16	83	-89
-17	117	-117
-18	86	-92
-19	66	65
-20	99	-98
-22	87	-89
-23	52	60

2,1,L

0	706	-738
-1	405	399
-2	211	-204
-3	808	-832
-4	589	590
-5	723	-759
-6	114	94
-7	184	200
-8	694	-724
-9	665	668
-10	53	61
-11	218	233
-12	163	-162
-13	218	-207
-14	215	-207
-15	195	-183
-16	168	-165
-19	157	152
-21	103	108
-26	83	-89

2,0,L

0	1253	1303
-2	708	726
-4	761	-782
-6	428	421
-8	199	-194
-10	494	496
-12	242	234
-16	47	48
-18	69	77
-20	116	-109
-22	89	-90
-24	29	-29
-26	87	88

1,7,L

-1	61	62
-2	89	-85
-4	41	27
-5	78	-82

1,6,L

0	80	81
-2	89	81
-3	129	-120
-7	53	42
-15	44	38

1,5,L

-1	70	-63
-2	93	86
-3	58	-54
-4	196	-206
-5	172	-177
-6	246	256
-7	149	-146
-8	62	67

1,4,L

0	182	-175
-1	37	-41
-2	147	-128
-3	139	-137
-4	160	176
-5	82	-96
-6	128	-133
-7	177	173
-9	225	-223
-11	90	-85
-12	84	-87
-13	94	-93

1,4,L

-14	79	-79
-16	74	-74
-19	55	-48
-20	69	-58

1,3,L

-1	132	114
-2	191	-188
-4	78	81
-5	258	261
-7	286	-265
-8	180	180
-10	165	-164
-12	58	66
-13	152	151
-15	57	65
-16	60	57
-17	124	134
-19	94	-104
-23	43	-46

1,2,L

0	395	-391
-1	317	-309
-2	171	184
-3	133	-138
-4	541	527
-5	172	-175
-6	190	157
-7	184	-193
-9	352	341
-10	261	243
-11	100	-93
-13	56	47
-15	201	-203
-16	106	118
-18	70	75
-24	55	64
-26	87	89

1,1,L

0	159	173
-1	69	-94
-2	1038	-1069
-3	298	304
-4	1377	1497
-5	590	-604
-6	133	-127
-7	106	-82
-8	320	301
-9	80	-79
-10	166	143
-11	361	358
-13	132	-126
-15	50	46
-18	80	74
-20	110	106
-21	242	-243
-25	57	51

1,0,L

0	251	-305
-4	738	-754
-6	337	-360
-8	451	-452
-10	211	-218
-12	69	-67
-14	164	-162
-16	116	122
-18	85	88
-20	187	-188
-22	177	-175
-24	218	217

0,6,L

0	202	194
-2	126	-126
-4	102	-101
-5	62	-59
-11	50	52
-12	29	-17

0,5,L

-1	92	95
-2	73	78
-5	128	132
-6	99	-91
-7	150	154
-10	59	-68
-15	74	76
-18	75	-78

0,4,L

-2	368	354
-3	174	158
-4	185	-183
-12	87	93
-13	58	58
-14	146	162
-15	91	100
-16	48	39

0,3,L

-1	138	-147
-2	164	142
-5	441	-433
-6	194	-183
-7	429	433
-8	160	-155
-9	181	-167
-13	94	-95
-16	98	-91
-20	51	-52

0,2,L

0	212	214
-1	589	612
-2	342	354
-3	159	-141
-4	712	-702
-5	60	-69
-6	487	-491
-7	388	-392
-8	65	39
-9	390	384
-10	181	-178
-11	278	274
-13	137	129
-15	173	-175
-16	89	-92
-18	116	-120
-19	70	-72
-21	63	65
-24	111	-109

0,1,L

-1	357	371
-2	77	55
-3	878	-938
-7	206	198
-8	423	-416
-9	437	423
-10	186	189
-11	378	-380
-13	69	-74
-14	123	-119
-17	77	71
-19	79	77
-20	153	-161
-21	120	124
-22	110	111
-24	99	-95

0,0,L

-4	550	-577
-6	566	-589
-8	227	216
-10	233	236
-12	156	159
-14	305	303
-16	204	213
-22	134	-137

-1,6,L

-6	68	64
-9	34	29

-1,5,L

-2	108	-109
-6	80	69
-7	129	-138
-9	112	-109
-17	66	63

-1,4,L

-2	165	-166
-3	228	-222
-4	90	83
-5	217	210
-13	106	-112
-14	153	-154

-1,3,L

-1	249	244
-3	335	333
-5	114	-106
-6	104	98
-7	253	-258
-8	93	93
-9	86	-89
-10	79	85
-11	221	221
-12	72	77
-15	128	127

-1,3,L

-16	98	89
-18	48	47
-21	83	-78

-1,2,L

-1	480	-490
-2	127	-142
-3	374	391
-4	346	332
-5	615	-598
-6	111	115
-7	172	173
-8	208	210
-10	255	251
-11	71	62
-12	59	-57
-13	158	-151
-15	73	-79
-16	116	117
-18	62	60
-20	85	78
-21	87	-82
-24	99	96

-1,1,L

-1	271	281
-2	223	231
-3	658	665
-5	414	414
-6	361	-354
-7	188	-173
-8	92	92
-9	193	-195
-10	39	37
-11	247	-247
-15	140	137
-16	135	130
-17	183	191
-18	81	80
-19	108	-108
-20	85	-87
-21	218	-212
-22	51	-52

-1,0,L

-2	181	-187
-4	755	-791
-6	102	-116
-8	209	-196
-10	202	-192
-12	228	-228
-14	113	-104
-18	244	239
-20	275	-278

-2,7,L

-7	46	44

-2,6,L

-4	79	-80
-6	37	-27
-10	59	-64
-13	37	40

-2,5,L

-5	80	98
-7	102	104
-9	105	100
-14	83	86
-16	104	-101

-2,4,L

-2	234	232
-4	39	-36
-7	57	-66
-12	72	-74
-13	141	139
-14	98	97
-16	42	37
-18	72	70

-2,3,L

-1	412	399
-3	176	-164
-4	210	-204
-5	239	-209
-6	160	-165
-7	129	-126
-8	70	-64
-9	88	91
-15	46	-50
-16	83	-84
-18	85	-84

-2,2,L

-1	209	196
-2	171	162
-3	107	94
-4	203	-196
-5	52	-46
-6	173	-174
-7	149	156
-11	57	37
-12	156	-165
-15	99	117
-16	56	50
-17	57	62
-19	49	-52
-21	91	89
-22	70	-65

-2,1,L

-1	120	-110
-2	500	533
-3	120	-117
-5	97	-114
-6	22	-30
-7	275	257
-8	86	-82
-10	80	82
-11	165	-159
-13	95	-99
-14	71	-74
-16	208	212
-17	75	75
-21	75	78

-2,0,L

-2	234	200
-4	165	183
-6	262	284
-8	262	257
-10	122	-125
-12	226	212
-16	65	64
-18	56	53

-3,6,L

-6	99	100
-10	31	23

-3,5,L

-1	44	-43
-3	31	-41
-8	70	80
-9	91	-86
-13	58	-62

-3,4,L

-8	66	63
-12	84	-82
-15	66	-59

-3,3,L

-1	382	364
-2	45	46
-5	82	-85
-6	102	104
-7	38	-19
-8	136	143
-10	179	182
-13	81	84
-14	53	52
-16	61	65
-18	92	98

-3,2,L

-1	90	-85
-3	172	-186
-4	105	121
-5	52	-49
-6	224	210
-7	153	156
-8	203	205
-10	101	-105
-11	89	-87
-12	177	-176
-13	303	-308
-15	125	132
-16	96	98
-18	85	76
-21	35	-40

-3,1,L

-1	144	134
-4	243	-242
-5	182	171
-6	53	36
-7	211	195
-8	247	-234
-9	94	-92
-10	108	98

-3,1,L

-11	150	-140
-12	160	-171
-14	86	-82
-15	96	-100
-16	143	140
-19	71	-75

-3,0,L

-2	908	-920
-4	332	-325
-6	712	678
-8	87	-77
-10	278	-271
-12	130	-134
-16	54	-61
-22	72	67

-4,6,L

-3	71	70

-4,5,L

-2	80	102
-3	31	27
-6	66	79
-9	70	75
-13	43	-42

-4,4,L

-2	98	102
-6	163	-175
-7	108	-115
-9	155	-156
-11	127	132
-12	82	-79
-13	67	65
-18	78	81

-4,3,L

-2	141	-137
-3	148	-153
-5	39	-34
-9	331	343
-10	123	-137
-11	192	-186
-14	67	-68
-15	116	-114
-18	79	-76
-19	68	56

-4,2,L

-1	136	-120
-2	332	336
-3	23	-14
-4	246	249
-5	94	100
-6	202	-203
-7	120	113
-9	117	122
-11	144	-142
-12	174	-181
-13	99	101
-17	43	38
-18	89	82
-20	39	-36
-21	69	70

-4,1,L

-1	370	-380
-2	138	-148
-4	413	398
-5	250	-234
-7	99	118
-8	144	140
-10	82	-91
-11	228	236
-12	85	90
-13	286	-286

-4,0,L

-2	534	520
-4	143	-123
-6	299	271
-8	131	-125
-10	80	82
-12	254	252
-14	168	-169
-16	130	132
-18	112	-100

-5,6,L

-1	39	-43
-2	66	-66
-3	50	-49
-5	63	-61
-8	62	64

-5,5,L

-4	65	-66
-10	68	-68

-5,4,L

-1	88	87
-4	143	-144
-5	107	-107
-6	122	128
-7	150	150
-8	82	82
-15	44	-51

-5,3,L

-3	154	-158
-5	61	-70
-6	130	134
-7	412	422
-8	107	114
-9	102	-109
-11	83	-80
-14	62	64
-15	57	57
-16	58	50
-18	81	77

-5,2,L

-2	171	-172
-3	297	-287
-4	204	-198
-5	174	171
-6	205	206
-7	129	-126
-8	64	65
-9	245	263
-10	122	-112
-11	214	-215
-13	71	-77
-15	37	37
-17	77	-78

-5,1,L

-1	133	-114
-2	548	-538
-3	85	-98
-5	397	384
-8	184	-183
-10	128	129
-11	131	-136
-12	151	-158
-13	109	104
-14	154	158
-16	87	-83
-20	41	-26

-5,0,L

-2	991	-973
-4	98	91
-6	40	-4
-8	101	92
-10	132	-130
-14	104	106
-16	93	-95

-6,6,L

-5	53	52

-6,5,L

-2	49	54
-4	73	77
-5	72	69

-6,4,L

-2	63	-61
-3	92	-85
-5	57	58
-6	109	-106
-7	50	-52
-8	48	42

-6,3,L

-1	150	-153
-4	83	83
-5	199	-200
-7	246	243
-9	114	113
-10	67	-72
-15	55	-61

-6,2,L

-1	230	-232
-2	161	146
-3	338	330

-6,2,L

-5	135	-135
-6	90	-89
-7	58	59
-8	130	126
-10	69	58
-11	31	36

-6,1,L

-2	94	100
-3	78	-74
-5	33	-29
-7	189	-189
-9	77	81
-10	76	-78
-11	68	75
-12	140	147
-13	124	-123

-6,0,L

-2	254	232
-4	170	-155
-8	107	-106
-10	310	309
-12	99	-104

-7,5,L

-10	29	11

-7,4,L

-2	57	-51
-3	197	-200
-4	124	-125
-5	61	59
-6	135	133
-7	90	88

-7,3,L

-1	114	110
-2	89	-90
-3	149	-147
-6	73	74
-7	108	112
-9	40	-35

-7,2,L

-2	267	-262
-3	141	143
-4	172	-157
-11	56	-58

-7,1,L

-1	75	-62
-2	81	-82
-3	104	107
-5	93	89
-6	71	-69
-10	62	-70
-12	37	39
-13	52	47
-15	47	37

-7,0,L

-2	202	-198
-6	88	-97
-8	199	201
-12	82	-82
-18	61	38

-8,5,L

-1	68	-71

-8,4,L

-2	126	-123

-3 77 -79

-8,3,L

-1	94	81
-2	83	94
-3	110	-108
-13	51	39

-8,2,L

-1	74	-71
-3	230	228
-6	81	73
-9	81	-77
-12	58	51

-8,1,L

-2	146	146
-3	115	-117
-5	135	-140
-14	42	-25

-8,0,L

-2	149	147
-8	101	111
-10	60	58

-9,5,L

-1	30	29

-9,3,L

-1	69	75
-2	71	-72
-11	72	-62

-9,2,L

-1	89	83

-9,1,L

-4	70	-78
-5	103	-95
-7	53	60
-9	70	58
-13	62	-49

-9,0,L

-4	35	-20
-6	80	-83
-8	79	70

-10,3,L

-2	60	57

-10,2,L

-7	59	-53
-9	56	48

-10,1,L

-3	129	-128

-10,0,L

-10	78	-66

-11,2,L

-1	62	58

-11,1,L

-5	38	40

-12,3,L

-1	30	22

A P P E N D I X 5

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR

(±) 1-(2,6-DICHLOROPHENOXY)-3-ISOPROPYLAMINOPROPAN-2-OL HYDROCHLORIDE

0,6,L

0	122	99	180
-2	126	135	180
-6	49	57	0
-12	79	91	0

0,5,L

-2	85	72	90
-9	66	74	90
-10	91	97	270
-11	100	108	90
-13	109	109	90
-14	99	107	90

0,4,L

0	298	305	0
-1	213	207	180
-2	313	307	0
-3	94	111	0
-4	73	65	0
-5	254	265	0
-7	140	138	180
-8	135	141	180
-13	134	133	180
-14	116	124	180
-16	140	129	180
-19	120	112	180
-22	115	113	0
-23	92	77	0
-26	66	50	0

0,3,L

-2	379	392	270
-3	45	23	90
-4	345	339	90
-5	180	172	90
-6	82	52	270
-7	74	72	270
-8	385	373	270
-10	162	143	90
-11	336	353	270
-13	171	180	270
-14	243	231	270
-16	303	316	90
-18	104	105	270
-22	124	125	90
-23	105	101	270
-25	48	43	90
-28	85	84	90

0,2,L

0	919	858	180
-1	94	83	0
-2	854	804	180
-4	179	154	180
-5	159	161	0
-6	86	75	180
-7	133	133	0
-8	73	83	0
-10	316	320	0
-11	56	57	180
-12	214	200	0
-13	84	82	0
-14	148	143	0
-15	118	111	0
-16	246	254	0
-17	168	172	180
-18	115	107	180
-21	107	110	0
-22	156	161	180
-23	83	95	180
-24	187	196	180
-27	62	61	0

0,1,L

-1	553	569	90
-2	238	179	90
-3	102	126	90
-4	307	311	90
-5	502	514	270
-6	97	43	270
-7	65	75	270
-8	161	155	270
-9	699	755	90
-10	219	194	90
-11	134	132	90
-12	130	141	270
-13	126	119	270
-15	508	521	90
-16	91	89	90
-17	86	88	270
-18	52	64	270
-19	162	159	270
-20	105	109	270
-21	209	202	90
-26	70	68	90
-33	75	67	90

0,0,L

-4	71	92	0
-6	375	417	0
-8	603	632	180
-10	701	727	180
-12	189	197	0
-14	915	946	180
-18	88	91	0
-22	284	280	0
-24	557	557	0
-28	134	130	180
-30	117	125	0

-1,7,L

-4	70	52	24

-1,6,L

-5	110	114	90
-7	68	78	59
-8	58	59	192
-13	51	51	332

-1,5,L

-3	58	67	27
-4	194	190	195
-6	138	125	142
-10	125	110	202
-21	77	83	313

-1,4,L

0	128	123	270
-2	170	166	9
-3	179	178	293
-4	84	75	2
-5	246	236	253
-6	77	73	325
-7	184	169	255
-9	173	175	289
-10	73	71	44
-11	173	180	226
-13	121	127	111
-15	94	94	100
-17	69	77	61
-19	112	106	114
-20	78	87	172
-21	53	64	45
-22	104	86	155
-31	53	40	217

-1,3,L

-1	244	242	280
-2	262	265	354
-4	264	254	77
-6	316	307	340
-8	287	284	6
-10	214	202	116
-12	97	113	298
-13	119	113	19
-14	150	141	69
-15	123	128	147
-16	197	195	173
-17	135	130	239
-18	87	95	230
-19	82	96	61
-20	93	87	113
-22	76	68	205
-23	146	139	106
-24	128	113	281
-26	91	79	81

-1,2,L

0	242	234	90
-1	635	594	99
-2	161	168	290
-3	419	370	59
-4	411	390	261
-5	203	193	22
-6	525	497	104
-7	660	652	90
-8	77	85	343
-9	282	265	139
-10	313	317	195
-11	181	188	306
-12	228	222	68
-13	244	245	80
-14	193	193	335
-15	206	202	242
-16	92	95	242
-17	266	262	252
-18	149	150	100
-19	191	195	8
-20	262	251	304
-21	136	149	249
-23	88	87	254
-24	178	179	22
-25	97	82	74
-28	59	47	196
-30	68	50	82

-1,1,L

0	187	194	90
-1	446	433	239
-2	623	595	182
-3	813	799	33
-4	315	296	236
-5	797	783	206
-6	679	663	145
-7	352	365	93
-8	573	543	185
-9	483	478	6
-10	187	189	283
-11	327	334	205
-12	239	231	290
-14	62	53	292
-15	248	257	15
-16	248	255	17
-17	252	252	236
-18	163	170	11
-19	75	88	112
-20	65	77	270
-21	124	122	295
-22	82	92	10
-23	213	226	268
-26	109	102	182
-27	64	53	15
-29	62	60	150
-34	71	58	324

-1,0,L

-2	615	704	180
-3	140	219	270
-4	879	883	0
-5	440	442	270
-6	359	313	180
-7	213	182	270
-8	520	524	180
-9	598	622	270
-10	282	259	0
-11	99	129	270
-12	202	209	180
-14	98	103	0
-16	157	159	0
-17	242	228	90
-19	92	79	90
-20	129	151	180
-22	97	90	180
-23	137	160	90
-24	140	142	180
-26	170	169	180
-27	70	62	270
-28	120	128	0

-2,6,L

-10	95	81	31

-2,5,L

0	82	57	0
-1	223	234	280
-3	105	121	301
-5	113	115	205
-6	81	94	342
-10	71	68	75
-13	83	86	64
-15	98	86	68

-2,4,L

0	120	122	0
-1	95	90	196
-2	127	112	84
-4	147	152	305
-6	126	124	41
-7	143	134	168
-8	144	154	120
-10	216	209	206
-11	114	92	329
-12	179	179	184
-13	161	157	173
-14	149	144	162
-15	91	104	279
-16	89	102	285
-17	57	66	29
-21	59	43	352
-23	63	45	325

-2,3,L

0	111	119	0
-1	508	506	100
-2	75	89	241
-3	515	486	80
-4	196	203	88
-5	208	211	341
-6	138	143	28
-7	177	174	221
-8	120	117	209
-9	141	135	273
-10	142	135	113
-11	198	194	304
-12	146	132	296
-13	180	184	232

-2,3,L

-14	151	140	212
-15	132	134	258
-16	69	61	241
-17	142	148	306
-18	71	76	344
-19	112	108	143
-20	66	71	250
-21	110	122	124
-23	164	173	59

-2,2,L

0	369	356	0
-1	193	201	254
-2	351	346	234
-3	248	246	291
-4	284	275	151
-5	158	156	125
-6	316	324	65
-7	209	195	71
-8	375	356	271
-9	163	170	278
-10	328	327	44
-11	191	191	78
-12	410	408	3
-13	230	226	109
-14	145	146	285
-15	84	90	263
-16	119	113	64
-17	103	93	83
-18	92	97	336
-19	62	66	98
-20	170	174	225
-21	124	110	258
-22	197	215	60
-24	100	106	290

-2,1,L

0	924	923	180
-1	1544	1558	296
-2	656	665	270
-3	262	304	194
-4	593	579	33
-5	189	182	310
-6	590	595	209
-7	101	105	301
-8	307	292	316
-9	376	380	118
-10	403	398	39
-11	231	243	201
-12	190	174	328
-13	360	348	35
-14	198	197	12
-15	183	179	100
-16	208	217	82
-18	173	179	202
-20	124	127	46
-21	104	122	341
-22	60	57	74
-23	275	269	253
-24	215	213	201
-25	117	127	286
-26	77	73	323
-27	56	31	46

-2,0,L

0	810	871	180
-1	449	423	90
-3	343	336	90
-6	842	848	0
-8	708	708	180
-9	89	92	90
-10	533	546	180
-11	802	802	270
-12	135	134	180
-13	654	672	270
-14	319	294	180
-15	216	210	90
-16	145	137	180
-18	308	300	0
-19	118	117	270
-20	115	118	180
-21	128	136	90
-22	96	98	180
-23	91	112	90
-26	46	42	180
-28	64	76	0

-3,6,L

-7	49	41	94

-3,5,L

0	98	99	90
-2	81	93	188
-4	136	115	179
-6	150	150	156
-8	98	109	195
-10	101	98	191
-14	83	79	357
-18	96	96	24
-20	57	49	4

-3,4,L

0	301	294	90
-1	83	92	158
-2	130	119	272
-3	219	221	332
-5	227	228	255
-8	103	107	273
-9	163	161	344
-10	69	81	279
-11	66	70	131
-12	58	70	70
-13	73	58	211
-14	92	87	293
-15	145	152	358
-17	99	102	133
-19	68	71	101
-21	66	65	357

-3,3,L

0	158	150	270
-2	239	246	31
-3	169	165	12
-4	146	142	23
-5	95	94	185
-6	188	205	317
-7	78	80	1
-8	280	264	3
-9	104	89	2
-10	177	172	11
-11	201	213	177
-12	206	204	281
-13	138	136	189
-14	102	101	183
-15	121	119	359
-16	113	104	151
-18	107	114	239
-19	48	63	229
-20	71	75	153
-22	110	113	159

-3,2,L

0	45	43	90
-1	203	212	46
-2	254	239	308
-3	327	343	159
-4	344	333	106
-5	140	134	31

-3,2,L

-6	115	105	277
-7	576	572	89
-8	125	127	276
-9	182	173	194
-10	141	150	115
-12	198	203	127
-14	97	107	306
-15	187	197	240
-17	102	104	298
-18	135	131	273
-20	110	126	91
-22	131	115	230
-24	96	92	203
-26	66	44	31
-27	64	73	188

-3,1,L

0	149	130	270
-1	667	678	133
-2	128	135	300
-3	291	286	315
-4	825	819	176
-5	518	514	293
-6	421	410	191
-7	293	301	155
-8	364	360	137
-9	276	273	346
-10	447	444	181
-11	230	230	255
-12	228	240	107
-13	390	391	79
-14	180	185	11
-15	112	117	18
-16	101	106	327
-17	175	168	221
-18	208	216	6
-19	233	232	74
-20	151	148	358
-21	89	99	24
-22	76	59	268
-23	224	232	174
-24	70	77	3
-25	131	139	51
-28	93	94	181
-29	86	81	286

-3,0,L

-1	265	287	90
-2	388	410	180
-3	691	654	270
-4	490	501	0
-5	787	792	270
-6	106	49	180
-7	177	180	90
-8	226	215	180
-9	178	163	270
-10	342	333	0
-11	161	161	270
-12	251	229	0
-13	404	397	90
-14	222	218	180
-16	239	236	0
-19	286	290	90
-20	60	84	180
-22	120	130	0
-24	88	95	0
-26	95	102	180

-4,6,L

0	122	133	180
-2	81	84	195
-16	64	44	352

-4,5,L

0	81	74	0
-1	77	79	287
-3	69	80	190
-5	102	96	274
-7	63	58	338
-9	157	156	89
-13	84	94	69
-14	75	82	178
-16	59	53	149
-19	57	33	283

-4,4,L

0	329	323	0
-2	115	114	6
-5	71	65	200
-6	94	105	287
-8	73	69	203
-10	45	52	150
-11	92	91	154
-14	68	70	143
-15	53	52	109

-4,3,L

0	94	82	180
-1	153	148	182
-2	196	200	175
-3	280	293	184
-4	132	122	180
-6	87	101	272
-7	128	138	199
-8	159	157	44
-9	88	85	263
-11	314	307	284
-12	222	232	334
-13	201	202	263
-14	77	95	10
-16	73	61	322
-17	96	94	329
-20	106	109	130

-4,2,L

0	290	299	180
-1	333	349	126
-2	521	527	189
-3	249	244	273
-4	402	403	137
-5	324	323	24
-6	467	461	346
-7	319	327	184
-8	92	102	161
-9	280	271	321
-10	118	105	100
-11	124	134	4
-12	182	192	349
-13	152	142	221
-14	137	127	250
-15	133	133	278
-16	91	94	27
-17	129	120	31
-18	161	154	0
-19	96	96	171
-20	152	142	195
-22	137	137	195
-23	97	88	44
-25	76	63	141
-26	91	97	206
-33	56	33	307

-4,1,L

0	257	233	0
-1	125	132	287
-2	436	405	295
-3	423	428	302
-4	283	283	118

-4,1,L

-5	234	219	210
-6	130	85	19
-7	403	411	31
-8	212	225	285
-9	165	161	354
-10	303	307	189
-11	681	657	99
-12	334	332	184
-13	437	437	97
-14	216	226	230
-15	91	82	193
-16	168	167	74
-17	166	161	172
-19	182	185	33
-20	87	83	219
-21	174	168	220
-22	97	92	10
-24	78	94	313

-4,0,L

0	439	426	0
-1	269	226	270
-2	594	577	0
-3	256	244	90
-4	272	262	0
-7	284	268	270
-8	269	285	180
-9	94	103	90
-10	75	63	0
-11	457	442	90
-13	177	171	90
-14	181	174	180
-15	85	76	90
-16	110	112	180
-17	135	136	270
-21	80	85	90
-22	282	255	0
-23	114	102	270

-5,6,L

-7	133	128	96
-17	73	69	265

-5,5,L

-9	96	90	221
-11	83	73	300

-5,4,L

-2	56	47	220
-3	141	142	271
-5	177	176	266
-6	133	127	61
-7	155	156	254
-8	93	100	310
-9	203	201	270
-10	63	63	233
-11	79	78	272
-12	102	106	107
-13	95	79	92
-15	57	75	111
-16	64	59	230
-17	101	101	112
-18	106	97	103
-21	46	41	95
-26	57	39	231

-5,3,L

0	134	140	90
-1	290	294	140
-2	141	129	29
-3	293	297	353
-5	141	134	190
-6	270	274	341
-7	121	117	152
-8	139	150	60
-9	274	279	14
-10	79	65	231
-11	58	76	131
-13	100	96	76
-15	100	98	340
-16	70	69	160
-17	136	141	171
-22	48	51	60
-23	92	94	194

-5,2,L

-1	139	158	46
-2	151	155	156
-3	222	233	48
-5	359	363	117
-7	142	139	66
-8	98	96	123
-9	279	298	72
-10	136	134	18
-11	194	190	142
-12	145	147	285
-14	66	62	153

-15	165	178	270
-16	97	99	90
-17	68	62	210
-19	115	108	250
-20	81	86	288
-21	108	117	297
-22	116	113	51
-29	78	53	112

-5,1,L

0	237	239	270
-1	129	131	32
-3	196	209	316
-4	405	410	170
-5	234	223	297
-6	242	248	218
-7	143	139	315
-8	82	97	345
-9	102	88	265
-10	234	244	153
-11	178	180	269
-12	71	71	2
-13	104	104	280
-14	158	152	22
-16	78	73	262
-17	136	127	196
-18	73	72	277
-19	69	74	330
-23	179	173	16

-5,0,L

-1	442	478	90
-2	75	72	180
-3	107	88	270
-4	169	165	180
-5	801	781	270
-6	68	55	0
-7	82	53	90
-8	123	125	180
-9	244	218	270
-10	175	186	0
-11	538	495	270
-12	180	181	180
-13	430	424	90
-14	99	102	180
-16	63	62	0
-17	57	47	270
-19	284	294	90
-21	59	62	270
-23	76	73	270
-24	128	130	180

-5,6,L

-25	194	158	93
-27	196	99	227
-34	72	38	151

-6,6,L

-10	70	78	2

-6,5,L

-1	147	145	255
-7	54	60	177
-20	52	24	238

-6,4,L

0	118	130	0
-2	133	138	322
-4	100	93	51
-6	70	75	28
-8	146	150	198
-10	136	146	171
-11	78	86	192
-12	97	111	174
-14	166	165	209
-16	73	81	154

-6,3,L

-1	242	245	45
-2	55	60	125
-3	129	136	114
-5	75	70	184
-6	85	99	347
-7	173	179	339
-8	115	126	210
-9	59	70	96
-10	88	79	306
-11	87	91	210
-13	101	97	357
-17	100	92	229
-21	84	83	93

-6,2,L

0	98	96	0
-1	210	220	214
-2	322	326	175
-3	77	71	169
-4	199	204	162
-5	124	141	303
-6	78	84	8
-7	101	108	185
-8	51	43	94
-9	120	126	132
-10	270	261	3
-11	127	131	38
-12	480	483	355
-13	93	104	184
-14	97	96	8
-15	134	135	64

-6,1,L

0	228	226	0
-1	160	152	270
-2	103	94	214
-3	390	385	268
-4	272	265	90
-6	156	164	341
-7	141	144	80
-8	162	172	236
-9	79	64	158
-10	192	195	81
-11	93	82	262
-12	135	129	346
-14	108	104	278
-16	141	134	119
-17	99	100	76
-20	94	86	247
-21	116	114	273
-22	61	66	133
-27	66	69	259
-28	66	48	149
-29	49	39	58
-30	54	49	335
-33	62	25	291

-6,0,L

0	606	588	0
-1	376	373	90
-3	216	239	270
-4	137	139	0
-5	188	193	90
-7	127	120	90
-8	90	89	180
-9	416	404	270
-10	249	241	180
-11	125	123	270
-12	433	432	180
-14	254	255	180
-15	384	393	270
-16	134	134	0
-17	196	201	90
-18	152	157	180
-21	87	63	270
-23	122	138	90
-24	75	82	0

-7,5,L

-7	53	43	135

-7,4,L

0	72	82	90
-2	47	70	336
-4	78	90	4
-7	78	74	324

-7,3,L

-2	83	93	313
-4	147	140	355
-5	51	59	266
-6	172	170	38
-7	135	131	102
-8	192	203	333
-9	45	71	297
-11	93	101	283
-13	44	56	108
-16	141	134	212

-7,2,L

-1	228	238	139
-2	212	208	155
-3	261	272	32
-4	113	119	340
-5	95	104	132
-6	101	103	173
-7	253	252	121
-8	184	199	180
-9	105	100	336
-12	99	111	218
-13	82	90	90
-15	66	67	295
-16	92	94	353
-23	65	61	191

-7,1,L

0	97	91	270
-1	181	180	257
-2	95	104	119

-7,1,L

-3	127	114	7
-4	161	176	176
-5	163	169	155
-6	187	204	208
-7	130	136	261
-8	188	195	143
-10	154	170	157
-11	168	160	121
-12	220	224	264
-14	203	190	31
-15	72	72	31
-16	92	93	93
-17	77	68	143
-18	143	142	333
-23	81	82	94

-7,0,L

-1	84	97	90
-3	258	265	270
-4	113	109	0
-5	362	350	270
-7	96	100	270
-8	109	113	0
-9	190	193	270
-12	100	104	0
-14	199	186	0
-15	104	103	90
-17	128	118	90
-18	100	104	180
-19	98	95	90
-20	78	63	0
-21	58	52	90
-29	75	64	270

-8,5,L

-11	78	71	77
-13	62	89	100

-8,4,L

0	137	142	0
-2	115	115	317
-3	80	76	84
-4	100	88	85
-8	92	81	249
-14	55	44	234
-22	78	59	41

-8,3,L

-1	93	111	55
-2	85	88	248
-3	124	117	56
-4	91	93	96
-5	95	103	145
-9	131	130	266
-11	163	163	254
-12	91	93	339
-13	134	136	292
-15	113	111	290

-8,2,L

0	158	161	180
-1	139	134	295
-2	124	126	175
-3	74	77	274
-4	93	94	228
-5	85	94	159
-6	53	67	94
-20	95	87	148
-28	53	42	317

-8,1,L

0	103	105	0
-1	266	267	295
-2	128	135	243
-4	103	104	110
-5	102	105	287
-6	173	168	352
-7	42	32	331
-8	112	107	179
-9	265	265	100
-10	100	111	153
-11	251	248	93
-12	147	154	329
-13	212	225	70
-14	148	158	155
-15	128	131	105
-16	68	84	199
-18	91	85	352
-23	76	72	274

-8,0,L

0	190	194	0
-1	207	213	90
-3	173	165	270
-5	133	128	90
-6	144	125	0
-7	133	131	90
-8	131	121	180
-9	159	156	270
-12	175	179	0
-16	90	114	180
-18	83	61	0
-21	94	94	270

-9,4,L

-5	91	97	269
-6	49	67	282

-9,3,L

-2	120	129	13
-4	89	90	5
-6	98	97	17
-7	104	104	56
-8	90	84	358

-9,2,L

0	75	94	90
-1	76	89	95
-2	85	78	246
-7	224	226	98
-8	84	94	216
-9	79	93	51
-10	84	76	344
-12	119	116	86
-14	56	66	233
-15	133	114	318
-17	79	86	252

-9,1,L

0	159	148	270
-2	167	167	159
-3	140	137	325
-5	83	77	281
-6	181	174	225
-9	153	156	142
-11	89	90	235
-14	86	88	165
-16	121	117	359

-9,0,L

-1	94	100	270
-3	134	131	270
-7	117	112	270
-8	57	60	0

	-9,5,L		
-9	149	159	273
-17	147	112	93
	-10,5,L		
0	60	62	0
	-10,3,L		
-1	110	97	95
-2	106	118	221
-6	55	42	303
-8	74	63	286
	-10,2,L		
0	86	82	180
-2	69	67	198
-4	84	72	122
-10	159	154	25
-12	75	84	345
-16	72	65	37
	-10,1,L		
0	170	156	0
-1	184	183	279
-2	119	119	11
-5	83	96	201
-12	65	83	180
-18	56	40	227

-21	51	41	197
	-10,0,L		
0	105	100	0
-5	78	86	90
-6	176	164	0
-8	161	156	180
-10	185	181	183
-11	90	85	90
-14	162	152	180
-16	92	70	0
	-11,4,L		
-5	62	71	268
	-11,3,L		
-7	63	41	52
-12	56	30	283
	-11,2,L		
-3	86	97	94
-4	58	65	207
	-11,1,L		
-4	49	35	167
-5	76	69	224
-8	120	103	194

	-11,0,L		
-3	95	86	270
-4	149	153	0
-5	66	65	270
-7	150	133	270
-10	161	160	0
-14	53	56	180
-17	86	64	90
-19	60	55	90
	-12,2,L		
0	63	63	180
-2	197	196	278
-3	99	94	263
	-12,0,L		
0	132	138	0
-2	81	91	0
	-13,2,L		
-3	50	9	105
-7	48	41	81
	-13,0,L		
-3	47	2	270

APPENDIX 6

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR 6β-(1-ETHYL-1-HYDROXYPROPYL)-5α-PHENYL-2,3,5,6-TETRAHYDROIMIDAZO [2,1-b] THIAZOLE

,14,L

2	62	62	180
-2	29	31	0

0,13,L

-1	41	40	270
-4	32	39	270
-6	69	60	90

0,12,L

0	51	46	0
-1	58	48	0
-3	58	67	180
-5	39	30	180

0,11,L

-2	39	41	270
-5	67	66	90
-6	33	34	270
-7	42	43	270

0,10,L

0	192	193	0
-1	90	88	180
-2	78	81	180
-3	45	50	0
-4	45	47	180
-6	75	77	180
-8	35	39	180
-9	47	48	0
-10	32	33	0

0,9,L

-1	66	71	270
-2	131	123	90
-3	84	78	90
-4	76	65	90
-6	46	40	90
-8	25	8	270
-12	46	47	90

0,8,L

0	95	100	180
-1	54	63	180
-2	168	181	0
-3	85	94	180
-4	218	234	180
-5	214	217	180
-6	123	131	180
-7	53	59	180
-8	126	128	0
-10	72	66	180

,7,L

-1	175	192	90
-2	38	45	90
-3	176	188	270
-4	91	95	270
-5	32	34	90
-7	61	66	270
-8	72	68	270
-9	53	58	90
-13	42	35	270

0,6,L

0	279	299	0
-1	82	73	0
-2	42	51	180
-3	158	169	180
-4	133	124	0
-7	83	93	0
-8	176	193	180
-10	45	50	0
-11	63	67	0
-12	30	32	180

0,5,L

-1	171	155	90
-2	591	593	270
-3	184	159	90
-4	170	176	90
-5	177	160	90
-6	155	166	270
-7	107	105	90
-8	197	188	90
-9	75	62	90
-11	27	27	90

0,4,L

0	55	56	0
-1	388	386	180
-2	469	461	0
-3	50	53	180
-4	117	99	0
-5	86	77	180
-7	187	176	180
-8	96	109	180
-9	107	98	0
-10	118	109	180
-11	31	38	180
-13	60	60	0

0,3,L

-1	257	259	90
-2	244	284	90
-3	309	281	90
-4	204	208	270
-5	67	80	90
-6	246	235	90
-7	295	278	90
-9	77	75	270
-12	62	67	90

0,2,L

0	64	60	0
-1	260	233	0
-2	616	622	0
-3	461	429	180
-4	94	80	180
-5	104	85	0
-6	78	89	180
-8	99	113	0
-9	173	170	180
-10	100	97	180
-11	80	73	0
-12	69	74	0
-13	58	61	180

0,1,L

-1	539	568	270
-2	229	224	90
-3	30	26	270
-4	129	137	270
-5	331	318	90
-6	100	108	270
-8	39	55	270
-9	94	104	270
-10	78	90	90
-11	66	62	90
-14	26	28	90
-15	46	53	90

0,1,L

-4	77	67	186
-6	221	170	186
-8	112	126	189
-10	225	239	0
-12	187	187	180

-1,14,L

-1	42	37	253

-1,13,L

-1	33	32	49
-3	38	38	216
-5	36	27	334
-7	42	45	208

-1,12,L

0	59	64	270
-1	39	35	140
-2	45	42	111
-6	61	58	207

-1,11,L

-1	44	43	204
-2	64	61	240
-4	56	55	35
-5	70	72	205

-1,10,L

0	49	58	90
-1	84	81	54
-2	89	84	249
-3	114	117	316
-4	32	37	72
-5	27	26	68
-6	36	44	65
-7	29	33	62
-8	42	48	282
-9	52	50	234
-10	29	29	149

-1,9,L

0	57	67	90
-1	42	45	292
-2	85	83	70
-3	68	68	164
-4	113	116	133
-5	49	54	231
-6	60	59	43
-13	33	42	298

-1,8,L

0	98	77	90
-1	207	208	267
-2	124	127	166
-3	139	145	107
-4	50	39	167
-5	69	66	167
-6	64	53	342
-7	49	41	258
-9	142	141	101
-11	67	63	297

-1,7,L

0	184	190	270
-1	75	71	278
-2	78	76	217
-3	190	179	197
-4	129	116	354
-6	53	59	161
-7	72	71	139
-9	48	46	313

-1,6,L

0	41	53	90
-1	256	235	58
-2	295	278	47
-3	149	134	273
-4	55	59	262
-5	60	55	222
-6	89	86	197
-7	102	94	112
-8	92	76	133
-9	105	100	251
-10	43	45	294
-11	47	45	85
-12	52	50	116
-14	33	16	185

-1,5,L

0	52	59	90
-1	58	58	232
-2	282	284	63
-3	214	214	338
-4	130	141	100
-5	265	261	196
-7	161	173	345
-8	165	169	284
-9	72	75	179
-10	87	92	275
-12	34	31	315

-1,4,L

0	228	213	90
-1	147	117	34
-2	315	289	337
-3	223	249	76
-4	346	348	102
-5	48	61	283
-6	143	141	93
-7	68	76	195
-8	130	129	237
-9	36	33	119
-10	118	121	58
-12	58	61	272

-1,3,L

0	188	184	270
-1	317	311	345
-2	373	356	93
-3	547	548	229
-4	347	347	143
-5	213	217	339
-6	161	146	32
-7	142	140	224
-8	51	55	195
-9	98	84	355
-10	70	73	273
-11	91	86	31

-1,2,L

0	313	272	270
-1	865	899	237
-2	619	628	78
-3	151	134	111
-4	229	232	9
-5	228	217	35
-6	71	69	301
-7	159	152	186
-8	91	93	77
-9	112	116	72
-10	82	83	267
-11	120	130	242
-12	79	87	88

-1,1,L

0	605	653	90
-1	461	475	59
-2	479	495	1
-3	397	397	30
-4	442	433	41
-5	177	170	110
-6	141	139	196
-7	77	81	19
-8	83	91	274
-9	95	95	46
-10	48	54	292
-11	94	96	89
-12	73	74	244
-13	33	33	326

-1,0,L

-1	833	964	90
-2	632	654	180
-3	376	387	270
-4	208	220	0
-5	271	275	90
-6	33	49	0
-7	107	119	90
-9	198	188	270
-10	237	247	180
-11	145	153	90
-12	57	52	180
-13	67	59	270

-2,14,L

-3	36	38	33

-2,13,L

-4	29	32	280

-2,12,L

-1	28	36	22
-2	41	33	115
-3	25	30	236
-4	53	50	184
-7	52	51	344

-2,11,L

0	43	34	180
-1	37	39	165
-2	70	69	292
-3	76	75	312
-4	62	61	57
-6	96	55	290
-8	43	53	96

-2,10,L

-1	51	54	241
-2	66	75	175
-3	70	61	70
-4	107	116	53
-5	59	58	84
-6	39	44	349
-8	60	53	148
-9	24	34	280
-11	47	40	204

-2,9,L

-2	92	95	304
-3	94	91	117
-4	115	115	267
-5	110	117	262
-7	57	56	88
-9	35	33	251
-10	42	49	267

-2,8,L

0	365	358	180
-1	118	115	306
-2	118	133	353
-3	84	79	346
-4	68	76	8
-5	124	124	17
-6	44	57	45
-7	80	80	21
-8	55	58	352
-10	80	79	194
-12	50	54	357

-2,7,L

0	120	125	180
-1	42	22	270
-2	44	42	152
-3	48	54	211
-4	87	83	321
-5	183	191	79
-6	140	142	75
-8	35	45	239
-9	38	28	236
-10	30	35	46
-13	28	15	296

-2,6,L

0	207	196	0
-1	225	223	317
-2	300	301	175
-3	86	75	195
-4	133	128	184
-5	66	61	17
-6	122	124	110
-8	66	66	148
-9	97	96	295
-10	125	119	346
-11	46	39	16

-2,5,L

0	125	121	0
-1	120	94	231
-2	98	103	270
-4	255	238	118
-5	98	115	292
-6	193	181	270
-7	94	87	219
-8	24	25	16
-9	40	37	305
-11	35	34	255
-12	35	32	251
-14	32	40	123

-2,4,L

0	195	193	0
-1	289	279	176
-2	190	175	171
-3	354	346	353
-4	224	225	186
-5	102	103	297
-6	98	109	237
-7	166	159	112
-8	134	134	359
-9	85	82	353
-10	106	108	4
-11	104	101	184
-13	33	41	310

-2,3,L

-1	303	296	63
-2	550	561	121
-3	419	412	203

-2,3,L

-4	316	292	296
-5	272	270	259
-6	136	146	69
-7	44	36	338
-8	222	228	259
-9	54	56	113
-10	45	43	251
-11	70	73	5
-14	45	41	293

-2,2,L

0	922	968	180
-1	882	914	267
-2	602	615	72
-3	182	178	149
-4	110	115	277
-5	316	304	93
-6	196	178	51
-7	201	192	15
-8	145	144	328
-9	34	37	144
-10	128	138	153
-11	75	68	36
-12	63	59	339
-13	47	43	124
-14	29	23	193

-2,1,L

0	474	453	0
-1	396	410	108
-2	527	513	245
-3	256	258	304
-4	121	135	96
-5	353	329	120
-6	76	78	276
-7	127	117	265
-8	149	141	80
-9	71	75	66
-10	65	66	303
-11	36	32	204
-12	71	74	215
-13	73	69	299

-2,0,L

0	801	828	180
-1	272	281	270
-2	1094	1229	180
-3	288	294	90
-4	153	188	2
-5	124	183	90
-6	186	191	3
-7	75	68	270
-8	175	168	180
-9	89	81	90
-10	139	149	0
-14	47	49	0

-3,14,L

0	49	49	90

-3,13,L

-3	37	36	152
-5	28	31	25

-3,12,L

-1	28	34	293
-2	42	49	145
-8	66	63	64

-3,11,L

0	51	53	90
-1	36	34	198
-3	116	117	12
-5	50	48	129
-7	91	86	34
-8	26	13	241

-3,10,L

0	63	58	90
-1	88	94	94
-2	55	63	13
-5	40	35	192

-3,9,L

0	148	153	270
-1	51	51	73
-2	43	50	340
-3	53	49	126
-4	121	122	197
-5	101	101	357
-6	109	116	347
-8	53	49	191
-12	35	35	91

-3,8,L

0	163	163	270
-1	181	177	206
-2	64	62	280
-5	122	126	337
-6	45	42	76
-7	63	58	288
-8	26	24	56
-11	60	51	214
-13	29	23	149

-3,7,L

0	59	59	270
-1	149	137	27
-2	30	30	176
-3	64	67	4
-4	108	109	32
-5	174	176	9
-6	119	110	178
-7	61	60	166
-9	22	19	291
-11	30	36	170

-3,6,L

0	401	416	270
-1	267	270	108
-2	59	70	38
-3	78	74	286
-4	87	86	323
-5	73	73	35
-6	40	37	326
-7	61	57	64
-8	105	106	13
-9	80	79	281
-10	65	63	265
-11	45	46	98
-12	45	36	57

-3,5,L

-1	249	254	186
-2	240	232	250
-3	254	256	29
-4	159	155	155
-5	92	94	159
-6	37	38	42
-7	133	126	354
-8	37	42	152
-9	56	51	113
-10	85	92	113

-3,5,L

-11	50	46	149
-13	52	53	11

-3,4,L

0	64	65	90
-1	156	170	256
-2	571	558	247
-3	382	361	289
-4	83	70	260
-5	115	114	155
-6	201	192	358
-8	106	108	316
-9	72	69	221
-10	78	76	128
-12	69	69	249
-15	31	38	95

-3,3,L

0	596	579	270
-1	406	399	322
-2	103	84	316
-3	215	206	184
-4	204	167	270
-5	357	370	32
-6	39	57	307
-7	347	339	164
-8	109	116	54
-11	48	50	238
-12	46	43	32
-13	49	50	171

-3,2,L

0	281	258	90
-1	553	534	282
-2	166	174	229
-3	133	134	359
-4	216	186	279
-5	255	252	303
-6	200	195	251
-7	105	123	263
-8	115	126	92
-9	140	142	80
-10	59	65	339
-11	36	34	272

-3,1,L

0	97	93	270
-1	615	552	108
-2	537	548	217
-3	233	238	35
-4	214	212	352
-5	216	218	187
-6	347	333	166
-7	133	129	310
-8	106	102	351
-9	213	215	206
-10	55	54	145
-11	43	41	191
-12	46	38	81
-14	54	55	25

-3,0,L

-1	514	537	90
-2	155	141	180
-3	65	56	270
-4	104	109	0
-5	210	196	270
-6	238	208	0
-8	118	125	0
-9	143	130	270
-10	100	100	0
-11	77	78	90
-12	57	53	0

-4,14,L

-1	28	37	220

-4,12,L

-1	45	45	13
-2	52	57	328
-6	44	48	12

-4,11,L

-2	52	46	257
-3	52	53	121
-4	101	100	94
-5	67	69	97
-6	36	41	256
-8	32	33	114

-4,10,L

0	140	137	0
-2	59	53	240
-3	46	41	31
-4	37	34	314
-5	68	77	281
-7	61	56	142
-10	48	45	351

-4,9,L

0	28	34	0
-1	48	45	62
-2	145	147	97
-3	61	62	121
-4	24	17	6
-5	127	134	264
-6	56	64	114
-7	68	67	59

-4,8,L

0	76	70	180
-1	162	162	124
-2	159	158	15
-3	74	78	244
-4	73	65	300
-8	54	57	324
-9	39	34	121
-10	79	82	128
-11	36	36	176

-4,7,L

0	147	145	0
-1	45	41	208
-2	117	117	92
-3	200	187	268
-4	46	44	336
-5	92	95	80
-6	34	33	129
-7	114	118	286
-8	54	62	237
-13	46	41	273

-4,6,L

0	223	207	0
-1	153	140	61
-3	213	209	163
-4	165	154	308
-5	66	56	89
-6	210	210	316
-7	91	94	331
-8	49	54	258
-10	54	56	57
-11	48	48	306

-4,5,L

0	46	45	0
-1	239	215	172
-2	190	167	283
-3	174	166	0
-4	217	210	172
-5	227	235	282
-6	95	95	265
-7	47	44	80
-8	191	212	81
-9	45	37	11
-11	57	49	219
-12	59	59	288

-4,4,L

0	414	410	180
-1	51	51	197
-2	131	111	181
-3	286	279	0
-4	254	246	17
-5	55	55	19
-6	84	85	334
-7	100	108	220
-8	128	129	132
-9	56	57	353
-10	70	72	204
-12	29	29	104
-13	42	46	39

-4,3,L

0	128	165	0
-1	457	431	288
-2	423	394	38
-3	173	173	101
-4	240	215	265
-5	62	73	346
-6	372	356	79
-7	84	72	336
-8	59	59	267
-9	118	118	245
-10	76	82	124
-11	33	38	245
-12	52	55	71

-4,2,L

0	492	482	180
-1	438	403	66
-2	337	322	280
-3	96	110	92
-4	218	243	211
-5	182	184	196
-6	124	123	291
-7	131	122	270
-8	69	75	44
-9	122	133	237
-10	123	122	293
-11	52	49	315
-15	25	23	175

-4,1,L

0	181	174	0
-1	396	400	291
-2	148	142	47
-3	520	490	273
-4	443	375	113
-5	312	312	62
-6	153	162	280
-7	168	178	283
-8	45	47	90
-9	72	74	60
-10	35	41	6
-13	47	49	243
-15	47	44	79

-4,0,L

0	267	224	0
-1	264	276	90
-2	235	213	180
-3	56	40	270
-4	78	99	0
-5	617	606	270
-6	50	54	180
-8	143	134	180
-10	96	98	0
-11	22	23	90
-12	53	59	180
-14	30	35	180

-5,13,L

-3	28	20	138
-5	41	36	333

-5,12,L

-2	60	52	85

-5,11,L

-1	36	32	107
-2	61	54	359
-3	50	48	331
-4	52	44	351
-5	57	58	221
-7	43	46	319

-5,10,L

0	25	25	270
-1	107	113	93
-3	56	54	220
-4	52	56	142
-6	27	27	359
-8	44	43	256
-9	41	39	321

-5,9,L

0	107	98	90
-1	80	80	350
-2	67	74	53
-3	62	65	215
-4	63	67	189
-5	64	60	9
-6	77	77	354
-7	48	45	186
-8	45	44	81
-10	38	31	107

-5,8,L

0	150	149	90
-1	177	186	239
-2	38	39	266
-3	51	62	151
-4	69	57	7
-6	96	101	227
-7	38	40	178
-9	44	36	75

-5,7,L

0	71	73	90
-1	59	62	204
-2	82	75	118
-4	183	193	0
-6	177	191	191
-8	76	71	12
-9	30	40	350
-11	40	41	2

-5,6,L

-1	111	110	12
-2	129	127	135
-3	117	113	75
-4	237	235	222
-5	78	80	264
-6	137	135	240
-7	48	49	258
-8	53	55	124
-9	48	57	271
-10	38	33	180
-12	36	35	87

-5,5,L

0	168	157	90
-1	206	188	183
-2	122	124	299
-3	286	279	338
-4	26	36	78
-5	165	149	196
-6	206	200	3
-7	213	215	352
-8	31	24	257
-9	83	89	212

-5,4,L

0	125	153	90
-1	104	83	62
-2	70	94	246
-3	171	170	78
-4	85	69	136
-5	79	76	60
-6	147	148	140
-7	91	84	21
-8	126	129	254
-9	68	67	20
-11	49	55	15

-5,3,L

0	329	342	90
-1	101	105	225
-2	390	387	60
-3	428	425	168
-4	75	77	203
-5	215	208	350
-6	100	94	303
-7	139	137	186
-8	165	173	173
-9	119	139	25
-10	34	41	325
-11	54	51	14

-5,2,L

0	473	455	270
-1	134	132	125
-2	196	177	163
-3	259	238	96
-4	50	40	339
-5	134	126	194
-6	111	108	180
-7	142	135	313
-8	33	37	162
-9	60	61	71
-10	80	82	254
-11	38	41	273
-12	58	62	106
-14	28	32	7

-5,1,L

0	98	104	90
-1	272	310	219
-2	216	222	205
-3	109	120	154
-4	489	506	335
-5	64	55	206
-6	76	70	210
-7	110	113	7
-8	93	90	2
-9	45	48	21
-11	31	34	121
-12	43	48	215
-13	37	37	64
-14	55	57	317

-5,0,L

-1	540	552	90
-2	60	74	180
-3	102	95	270
-4	486	436	180
-5	275	257	90
-6	40	52	180
-7	178	165	90
-8	164	166	180
-9	146	152	270
-10	25	20	180

-6,13,L

-2	49	38	82

-6,12,L

-3	57	58	106

-6,11,L

0	48	58	0
-1	33	31	248
-2	50	49	251
-3	72	71	303
-6	43	45	266

-6,10,L

0	106	138	0
-1	67	69	173
-2	77	78	135
-9	41	34	29

-6,9,L

0	64	69	180
-1	49	58	247
-3	48	46	10
-4	93	96	267
-5	74	78	263
-6	25	24	75
-7	45	43	105

-6,8,L

0	164	168	180
-1	26	30	213
-2	66	64	328
-3	101	105	345
-4	52	51	174
-5	101	106	105
-7	63	61	239
-10	73	70	221

-6,7,L

-1	102	108	357
-2	33	34	15
-3	64	60	259
-4	123	129	197
-5	227	230	91
-7	87	75	273
-8	33	28	298
-10	23	21	296
-11	33	32	9

-6,7,L

-12	31	27	14

-6,6,L

0	100	95	0
-1	180	178	359
-2	117	98	206
-3	31	28	55
-4	190	208	157
-5	184	163	264
-6	54	53	153
-7	75	84	95
-8	73	78	146
-10	50	46	340
-11	74	68	31

-6,5,L

0	71	77	180
-1	115	122	266
-2	126	117	227
-3	55	46	184
-4	173	175	50
-5	104	92	235
-6	267	283	274
-7	123	130	148
-8	60	62	184

-6,4,L

0	136	133	0
-1	147	155	155
-2	179	193	41
-3	45	22	51
-4	31	27	222
-5	73	60	193
-6	73	50	147
-7	111	111	177
-8	103	108	258
-9	46	44	8
-10	26	27	296
-11	60	56	169

-6,3,L

0	37	40	180
-1	103	91	5
-2	277	287	115
-3	211	202	97
-4	283	297	261
-5	163	172	246
-7	112	113	72
-8	213	224	293
-11	43	48	326
-11	59	61	70

-6,2,L

0	118	138	180
-1	138	115	7
-2	138	130	31
-3	386	378	220
-4	83	79	159
-5	144	139	59
-6	61	47	211
-7	206	197	0
-8	128	126	4
-9	90	94	105
-10	65	61	97
-11	31	31	32
-12	41	43	350

-6,1,L

0	35	3	180
-1	242	295	105
-2	328	320	286
-3	161	173	293
-4	100	93	304
-5	186	171	117
-6	90	97	270
-7	117	120	219
-8	63	68	181
-9	93	82	103
-13	52	37	288
-14	41	38	109

-6,0,L

0	480	494	0
-1	289	290	270
-2	180	165	180
-3	284	268	90
-4	185	178	0
-5	24	34	90
-6	50	51	180
-7	100	95	90
-8	139	137	180
-9	29	33	270
-10	73	66	0
-12	53	51	180
-13	26	23	90
-14	33	44	0
-15	43	41	270

-7,13,L

-3	38	34	195
-5	33	12	5

-7,12,L

-3	42	36	355
-4	25	39	293

-7,11,L

-2	60	53	229
-5	57	56	144

-7,10,L

0	51	54	90
-1	38	33	53
-2	41	41	271
-3	41	42	301
-9	40	40	218

-7,9,L

-1	79	83	238
-2	64	69	287
-3	41	46	200
-4	92	82	179
-6	65	61	327
-8	37	42	236

-7,8,L

0	59	55	270
-1	123	127	298
-3	76	75	52
-4	106	108	22
-5	50	49	181
-6	65	61	162
-9	52	47	107

-7,7,L

0	146	149	270
-1	44	44	309
-2	35	37	163
-3	106	106	135
-4	133	131	328
-5	85	84	248
-6	68	77	178

-7,7,L

-7	74	76	2.8

-7,6,L

0	90	83	270
-1	109	109	62
-2	184	190	63
-3	77	82	284
-4	31	40	108
-5	99	96	157
-6	197	194	17
-7	73	72	68
-8	38	40	116
-9	47	50	255
-10	75	75	308
-11	56	55	137
-12	30	25	93

-7,5,L

0	69	72	90
-1	28	33	76
-2	32	43	137
-3	138	139	308
-4	116	110	194
-5	196	197	155
-6	79	73	97
-7	71	79	74
-8	53	47	214
-11	34	22	104

-7,4,L

0	244	239	90
-1	33	36	274
-2	322	314	324
-3	166	164	190
-4	130	138	51
-6	105	96	103
-7	179	181	189
-8	54	49	206
-9	33	34	227
-10	103	101	73
-12	31	27	254

-7,3,L

0	123	120	270
-1	296	293	25
-2	103	105	183
-3	118	104	223
-4	139	135	216
-5	120	115	337
-6	118	113	311
-7	124	120	204
-9	51	53	355

-7,2,L

0	193	197	90
-1	221	204	252
-2	280	255	79
-3	103	89	26
-4	295	270	342
-5	103	96	2
-6	59	58	280
-7	45	47	147
-8	128	130	49
-9	108	109	121
-10	56	51	215
-11	62	66	234
-12	45	37	125
-13	36	39	18

-7,1,L

0	156	143	90
-1	174	177	0
-2	149	141	156
-3	113	104	347
-4	273	260	41
-5	77	67	143
-6	159	165	173
-7	87	90	61
-8	77	88	341
-9	46	49	248
-11	38	38	284
-13	29	29	358
-14	38	38	47

-7,0,L

-1	320	336	90
-2	322	291	0
-3	216	225	270
-4	37	31	180
-5	97	82	270
-6	140	142	0
-7	69	71	90
-8	41	37	0
-9	65	67	270
-11	94	93	90
-12	41	42	0
-14	32	41	180

-8,12,L

0	25	32	0
-1	45	46	352

-8,11,L

-2	36	33	233
-5	55	55	97

-8,10,L

-1	45	44	210
-3	32	35	357
-7	55	57	183
-8	44	36	156

-8,9,L

-3	95	89	99
-5	67	66	250
-7	35	40	89
-9	45	46	279

-8,8,L

0	101	96	180
-1	70	72	300
-2	63	68	6
-3	79	85	226
-4	61	61	196
-5	65	72	64
-7	45	51	310
-10	45	40	187

-8,7,L

-1	123	126	67
-2	50	49	65
-3	74	73	219
-4	61	63	203
-6	87	92	91
-7	29	22	287
-10	34	34	72
-11	25	20	42

-8,6,L

0	209	204	0
-1	48	53	319
-2	84	79	196

-8,6,L

-3	193	192	182
-4	119	110	10
-5	101	104	293
-6	29	34	331
-7	83	72	22
-8	65	64	152
-9	74	66	194
-10	42	39	25
-12	39	42	193

-8,5,L

0	54	42	180
-1	103	109	92
-2	179	189	235
-3	180	181	55
-4	42	47	92
-5	69	64	53
-6	79	72	142
-7	28	29	173
-8	71	71	124
-12	58	50	264

-8,4,L

0	50	45	0
-1	246	258	213
-2	65	58	129
-3	261	271	2
-4	36	31	231
-5	48	57	109
-6	63	78	82
-7	57	56	177
-8	62	64	330
-9	113	103	347
-11	57	46	186
-13	43	50	13

-8,3,L

-1	62	69	42
-2	86	90	76
-3	100	104	153
-4	40	43	176
-5	85	78	176
-6	249	252	110
-8	51	53	103
-9	38	50	170

-8,2,L

0	220	214	180
-1	242	253	12
-2	253	256	336
-3	141	135	301
-4	69	70	22
-5	151	161	118
-6	40	36	345
-7	40	39	198
-8	34	34	355
-9	107	103	159
-10	77	83	191
-11	54	55	6
-14	38	36	172

-8,1,L

0	99	103	180
-1	71	64	220
-3	102	108	319
-4	172	170	91
-5	236	237	86
-7	154	141	256
-8	80	83	126
-10	26	31	309
-14	25	17	256

-8,0,L

0	324	323	0
-1	135	112	90
-2	43	53	180
-3	205	200	90
-4	68	66	0
-5	79	67	270
-6	73	80	0
-7	44	57	90
-8	24	11	180
-10	144	137	0
-13	55	51	90

-9,12,L

0	56	49	270
-2	25	29	122

-9,11,L

-5	33	30	210

-9,10,L

0	56	50	90
-2	38	41	287
-4	44	45	151
-6	45	50	51
-9	32	29	340

-9,9,L

-2	53	51	26
-4	59	58	183
-6	45	41	15
-8	53	50	154

-9,8,L

-1	88	93	238
-2	56	56	144
-3	44	45	113
-5	57	69	333
-6	50	51	180
-7	51	54	229
-9	49	52	86

-9,7,L

-1	66	74	49
-2	112	118	165
-3	25	26	109
-5	80	82	35
-7	42	48	127
-9	39	28	320
-10	28	30	255

-9,6,L

0	71	64	270
-1	152	143	150
-2	108	109	127
-3	172	180	277
-4	105	113	217
-5	32	24	354
-7	62	63	74
-8	47	48	107
-9	54	54	266
-10	46	46	201

-9,5,L

0	45	47	90
-1	57	53	166
-2	154	156	286
-3	80	88	338
-4	61	58	101
-5	33	36	313

-9,5,L

-6	45	48	83
-7	52	53	350
-8	52	57	294

-9,4,L

0	218	214	90
-1	113	105	350
-2	216	219	239
-3	62	53	213
-4	120	115	102
-5	23	25	236
-7	31	23	8
-8	77	74	298
-10	66	65	86
-12	61	62	269
-13	34	28	174

-9,3,L

0	54	46	270
-1	44	58	344
-2	136	145	84
-3	131	132	118
-4	48	48	111
-5	91	88	358
-6	60	64	18
-8	74	71	101
-9	41	42	105
-10	40	40	225

-9,2,L

0	256	235	270
-1	270	281	254
-2	144	139	156
-3	106	104	195
-4	69	67	225
-5	118	122	198
-6	109	106	188
-7	81	72	338
-8	81	73	105
-9	47	51	67
-10	66	65	274
-11	49	57	261
-13	43	39	116

-9,1,L

0	90	91	270
-1	60	71	68
-2	42	40	321
-3	118	127	39
-4	131	128	5
-5	67	76	207
-6	190	188	158
-9	48	45	243
-10	28	17	92

-9,0,L

-1	229	236	90
-2	76	92	0
-3	34	30	270
-4	230	250	180
-5	45	40	270
-6	84	84	0
-8	41	38	180
-9	90	99	270
-11	69	72	90

-10,12,L

-3	56	48	189

-10,11,L

-3	31	33	261

-10,10,L

-1	67	58	175
-3	47	49	66

-10,9,L

-3	50	47	118
-5	49	34	295
-7	50	46	42

-10,8,L

0	51	47	180
-1	54	59	50
-2	84	88	45
-5	43	46	126
-6	47	44	79
-8	48	51	337
-10	35	37	128

-10,7,L

0	60	63	0
-3	54	46	260
-4	46	54	307
-5	93	95	93
-8	55	51	222

-10,6,L

0	33	41	180
-1	106	108	8
-2	106	104	196
-3	45	37	95
-6	42	42	303
-7	48	47	270
-10	52	46	16
-11	50	52	347

-10,5,L

-1	186	195	230
-2	74	83	345
-3	86	85	341
-4	93	88	74
-6	72	77	276
-9	53	56	346

-10,4,L

-1	190	186	177
-2	51	53	18
-3	67	71	6
-7	50	45	202
-9	61	52	357
-11	58	62	182
-12	36	27	83

-10,3,L

0	106	98	180
-1	87	87	36
-2	95	101	358
-3	93	87	194
-4	154	153	284
-5	134	133	295
-6	65	58	309
-7	131	132	22
-8	64	71	282
-10	28	33	197

-10,2,L

0	192	185	180
-1	77	72	14
-2	78	76	273

-10,2,L

-3	199	204	184
-4	45	40	160
-5	103	109	42
-7	117	121	350
-8	31	32	76
-9	50	53	231
-10	42	46	164
-12	46	49	7

-10,1,L

0	109	104	0
-1	51	46	209
-2	76	77	239
-3	111	105	279
-4	76	75	217
-5	141	137	47
-7	39	44	304
-9	47	36	69
-10	48	52	9

-10,0,L

0	218	211	0
-2	246	240	180
-3	33	32	270
-4	34	27	180
-5	197	184	270
-7	62	67	90
-8	70	76	180
-12	57	57	180

-11,10,L

0	57	55	90
-2	43	37	292

-11,9,L

-5	51	43	3

-11,8,L

-1	61	62	312
-2	37	35	182
-4	47	43	26

-11,7,L

-1	46	42	105
-3	29	28	217
-4	96	90	357
-6	64	65	179
-8	52	46	44

-11,6,L

0	79	82	270
-1	105	104	45
-2	41	41	45
-3	83	94	48
-4	40	46	275
-6	24	25	321
-8	46	44	14
-10	29	30	284

-11,5,L

0	77	81	90
-2	104	104	321
-3	62	61	63
-5	82	93	185
-6	37	47	43
-7	66	66	350
-9	55	49	118
-10	48	49	93

-11,4,L

0	92	116	90
-1	58	55	64
-2	81	84	254
-3	134	145	87
-6	49	52	333
-7	43	42	286
-8	85	84	266

-11,3,L

0	164	159	270
-1	87	88	272
-2	39	41	80
-3	90	92	211
-4	152	161	227
-5	36	24	24
-6	107	111	305
-7	45	38	157
-8	32	32	126
-9	27	27	41

-11,2,L

0	168	171	270
-1	49	47	289
-2	154	151	66
-3	117	118	33
-4	113	124	339
-5	97	96	13
-9	28	14	90
-10	49	45	306
-11	38	35	245
-12	43	34	115

-11,1,L

-1	167	160	136
-2	121	123	238
-4	99	103	352
-6	52	53	208
-8	88	92	324
-9	40	40	285

-11,0,L

-1	130	142	90
-2	56	57	180
-3	58	54	270
-4	77	77	180
-5	126	123	90
-6	83	84	0
-7	80	78	90
-8	41	39	0
-11	41	35	90
-13	46	40	270

-12,10,L

0	46	46	0
-3	42	44	47
-4	31	30	85

-12,9,L

0	59	68	180
-2	41	37	63
-5	54	44	233

-12,8,L

0	28	25	180
-5	34	35	112

-12,7,L

-1	34	37	35
-3	80	81	268

-12,7,L

-4	26	39	53
-5	32	38	69
-6	32	30	25
-7	72	68	282

-12,6,L

0	47	41	0
-2	54	56	296
-3	58	66	153
-4	46	43	64
-7	34	25	57
-8	30	29	127
-9	29	24	148

-12,5,L

-1	67	67	143
-2	37	39	270
-3	29	29	74
-4	45	52	92
-5	66	64	271
-6	50	47	292
-7	73	69	147
-8	46	44	35

-12,4,L

-1	89	86	162
-2	67	69	87
-3	70	71	337
-5	71	77	274
-7	53	58	128
-9	33	32	354

-12,3,L

0	50	56	180
-1	94	99	335
-2	85	78	100
-3	94	101	155
-4	54	58	330
-6	87	90	78
-7	39	31	62
-9	63	63	221

-12,2,L

-1	128	129	325
-2	40	25	21
-3	58	59	256
-4	30	28	222
-5	46	47	112
-7	52	51	236
-8	41	36	290
-9	51	50	197
-10	44	38	143
-11	29	30	24

-12,1,L

0	213	219	0
-1	78	78	152
-2	60	67	99
-3	96	101	285
-4	52	52	72
-5	127	120	125
-6	46	41	263
-7	84	90	242
-8	34	33	190
-9	26	33	15

-12,0,L

-3	47	50	90
-4	54	57	0
-6	27	36	0
-7	48	45	270
-11	41	37	270

-13,9,L

-3	46	43	158
-4	44	40	184

-13,8,L

0	45	40	270

-13,7,L

0	24	33	270
-2	50	46	137
-4	53	44	358
-6	51	55	188

-13,6,L

0	35	38	270
-1	33	36	172
-2	72	73	54
-3	37	39	314
-4	41	37	205

-13,5,L

-4	66	62	148
-7	35	32	310
-8	42	45	258
-9	28	27	210

-13,4,L

0	57	63	90
-1	52	45	336
-2	87	91	300
-3	97	101	252
-4	36	36	97
-5	31	41	25
-7	32	34	138
-10	35	38	68

-13,3,L

-2	120	117	59
-5	74	78	5
-7	67	65	208

-13,2,L

0	43	40	270
-3	50	54	98
-4	48	53	358
-6	65	67	181
-9	34	31	50

-13,1,L

0	99	93	90
-1	97	99	66
-2	93	93	187
-3	54	51	346
-4	97	89	16
-5	56	59	182
-6	107	108	176
-8	34	35	332
-9	36	38	254
-10	43	42	191
-11	40	41	58

-13,0,L

-4	61	58	180
-5	67	55	270
-7	45	43	270
-9	44	33	270

-13,-,L

-10	36	36	180

-14,2,L

-5	48	48	291

-14,8,L

0	54	52	180

-14,7,L

0	41	39	0
-3	31	29	229

-14,6,L

-2	44	46	207
-4	38	38	162

-14,5,L

-3	62	57	24
-5	42	42	298

-14,4,L

-1	73	75	192
-2	46	46	139
-4	49	53	271

-14,3,L

-1	41	41	352
-4	63	63	234
-6	42	38	105
-10	32	26	178

-14,2,L

-1	54	59	66
-2	45	48	280
-4	37	31	148
-5	41	42	83
-7	44	40	1
-8	44	42	51

-14,1,L

-1	83	94	83
-2	80	85	220
-3	86	86	284
-4	36	37	132
-5	63	68	73
-7	59	57	255
-8	44	44	127
-9	56	56	103

-14,0,L

0	113	111	180
-2	33	30	180
-3	51	48	90
-5	73	81	270
-7	37	46	90
-8	29	29	180

-15,8,L

-2	29	23	70

-15,7,L

-4	43	41	342
-6	50	44	201

-15,6,L

-5	32	36	182

-15,5,L

-2	46	45	282
-5	45	42	152

-15,4,L

0	70	64	90
-2	38	42	250
-3	57	62	163
-7	49	44	193

-15,3,L

-1	40	50	305
-4	28	25	211
-5	39	29	353

-15,2,L

-1	47	43	203
-2	56	60	136
-3	36	38	2
-5	47	43	201

-15,1,L

-2	52	49	174
-3	33	25	318
-4	64	63	3
-6	46	44	119
-8	54	53	16

-15,0,L

-2	85	89	0
-3	48	51	270
-7	69	63	90

-16,7,L

-3	32	28	252

-16,5,L

-4	32	26	67

-16,4,L

-1	37	37	174
-2	48	46	46

-16,3,L

-4	34	33	220

-16,2,L

-1	57	55	18
-3	47	43	219
-4	28	45	102

-16,1,L

-3	32	30	258
-5	24	27	65
-7	32	29	273

-16,0,L

0	102	104	0
-3	79	73	90

-17,4,L

-1	29	31	350

-17,4,L

-4	26	22	110

-17,2,L

0	75	77	270
-2	33	31	133
-3	35	27	14

-4	31	28	326

-17,1,L

-6	37	32	197

-17,0,L

-1	61	59	98

-18,2,L

0	26	31	150

-19,1,L

-1	41	34	95

A P P E N D I X 7

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR 5,5-DIPHENYL-6-OXO-2,3,5,6-TETRAHYDROIMIDAZO [2,1-b] THIAZOLE

12,8,L

-2 68 71
-4 66 -63

12,7,L

-1 79 -76
-3 79 73

12,6,L

-4 50 -41
-6 54 55

12,5,L

0 54 54
-6 46 -41

12,4,L

0 97 -97
-1 46 -37
-6 47 -46

12,3,L

-1 58 55
-3 97 -92
-7 36 34

12,2,L

-3 27 -35
-4 37 38
-9 26 -19

12,1,L

-7 34 -34
-8 36 -38

12,0,L

0 69 68
-4 61 -56
-6 38 47
-8 79 69

11,11,L

-2 46 39

11,10,L

0 47 -43
-1 37 -35
-6 50 -49

11,9,L

-1 41 -35
-2 55 -47

11,8,L

0 46 46
-1 46 46
-3 27 22
-5 47 -49
-7 26 -32
-8 36 40

11,7,L

-4 60 64
-6 46 47
-7 25 -25
-8 28 26

11,6,L

-1 36 -35
-2 63 -62
-5 57 57
-8 37 -30

11,5,L

0 54 -48
-2 89 87
-3 51 47
-4 32 -34
-6 98 -93

11,4,L

-3 45 -48
-5 53 53
-7 40 41
-8 38 39
-10 35 32

11,3,L

-3 93 -92
-4 51 60
-6 57 58
-8 23 8
-9 95 -95

11,2,L

-1 54 50
-2 53 47
-4 47 50
-5 66 -67
-7 72 -65
-8 27 28

11,1,L

0 69 67
-1 48 39
-3 80 81
-8 58 53
-9 49 51

11,0,L

-2 123 -121
-4 137 -132
-6 71 70
-8 51 -48
-10 58 -51

10,13,L

-1 52 -49
-4 52 -49

10,12,L

-5 55 59

10,11,L

-2 60 57
-5 30 26
-8 42 36

10,10,L

0 38 -44
-3 23 27
-5 33 -34
-6 30 -39
-9 28 26

10,9,L

-1 30 31
-2 119 -122
-3 76 -79
-8 31 -29

10,8,L

-1 94 98
-7 39 44

10,7,L

0 61 -64
-4 48 48
-5 55 59
-10 52 52

10,6,L

0 89 88
-1 50 -58
-3 42 -43
-4 133 -131
-5 56 56
-7 30 -22
-9 55 -60
-10 54 -58

10,5,L

-1 63 62
-3 48 -45
-4 92 -89
-5 60 71
-7 25 -30
-8 64 69
-9 39 43

10,4,L

0 52 -50
-1 58 -52
-4 77 73
-5 33 20

10,3,L

0 92 -88
-3 123 -130

10,3,L		
-4	27	35
-5	64	-60
-7	40	37
-8	23	-33
-11	47	-54
-12	49	-46

10,2,L		
-1	100	98
-2	41	38
-3	28	30
-4	44	44
-5	59	-53
-6	62	-66
-7	81	82
-9	44	38
-11	33	-32

10,1,L		
0	84	-83
-2	63	-60
-3	129	124
-4	36	-37
-5	33	39
-8	56	-58
-9	27	35

10,0,L		
0	57	48
-2	148	-152
-4	122	-136

9,15,L		
-3	45	30

9,14,L		
0	31	19
-1	25	-18
-2	27	-31
-4	59	-52
-5	61	-61

9,12,L		
0	33	-45
-1	50	-47
-3	38	43
-5	65	66

9,11,L		
-1	32	34
-2	61	64
-3	54	-51
-4	70	-65
-6	70	-72

9,10,L		
-4	51	49
-5	53	48
-6	30	-41
-10	32	33

9,9,L		
0	23	-23
-2	89	-91
-3	41	-42
-9	71	-70

9,8,L		
0	65	-71
-1	91	95
-2	62	59
-4	44	-34
-5	65	-65
-6	78	78
-10	53	57

9,7,L		
0	41	36
-3	94	93
-7	50	-42

9,6,L		
0	78	74
-2	38	45
-3	67	-72
-4	142	-142
-7	38	42
-10	29	-35
-12	35	-27

9,5,L		
0	47	48
-1	56	-56
-2	34	38
-4	80	-86
-6	41	-31
-7	53	57
-8	37	38
-10	63	64

9,4,L		
0	127	-126
-1	119	-132
-2	88	80
-3	42	46
-4	81	85
-6	61	-65
-9	41	-34
-10	29	34
-11	71	65

9,3,L		
0	57	57
-1	57	56
-2	53	-51
-3	34	-26
-5	64	-68
-6	58	-59
-7	96	95

9,2,L		
-1	196	197
-2	24	-26
-3	52	49
-4	44	-42
-5	71	-70
-7	66	70
-8	95	-97
-9	66	67

9,1,L		
0	104	-108
-1	90	-90
-2	250	-252
-4	89	94
-5	27	30
-6	30	-34
-7	83	-87
-8	71	-66
-10	44	43
-11	30	22
-12	60	56

9,0,L		
0	216	216
-6	61	58
-8	45	44
-10	22	-14

8,16,L		
0	31	-29
-2	46	48
-4	38	36

8,15,L		
0	50	50

8,14,L		
-2	87	-85
-3	56	-56
-4	71	-70

8,13,L		
0	78	-79
-3	101	98
-5	52	50
-7	52	-50
-9	45	44

8,12,L		
0	61	57
-5	82	80
-8	39	39
-9	45	50

8,11,L		
0	78	76
-1	61	66
-3	80	-74
-7	79	79
-9	35	-42

8,10,L		
0	191	-189

8,10,L

-1	61	-63
-2	42	47
-3	64	-63
-4	36	33
-5	41	-37
-6	67	-68
-7	57	-58
-8	65	-56
-9	60	-60
-10	64	68

8,9,L

0	51	58
-1	30	18
-2	49	53
-3	78	-78
-4	44	37
-6	85	90
-7	61	62
-9	50	-46
-10	61	60

8,8,L

0	154	154
-1	56	55
-3	107	108
-4	61	62
-5	92	-93
-7	40	39
-8	55	51
-10	68	-66
-11	34	22

8,7,L

-1	61	-64
-2	51	-50
-3	98	102
-4	61	-69
-5	51	-53
-6	111	-113
-7	114	-113
-8	166	-167
-10	100	-100
-11	47	42
-12	28	-18

8,6,L

0	144	138
-1	48	40
-2	204	-224
-3	25	26
-4	67	69
-6	57	-60
-7	77	73
-8	76	74
-9	85	89
-10	36	-35
-11	27	28
-12	59	55
-13	76	80

8,5,L

0	24	10
-1	39	-34
-2	167	170
-3	100	95
-4	60	59
-6	99	-104
-7	35	36
-8	65	62
-9	42	-50
-13	34	-33

8,4,L

0	178	-190
-1	36	-32
-2	105	107
-3	142	-144
-4	89	86
-6	115	-118
-7	185	-197
-8	31	-29
-9	55	-47
-11	56	-51
-12	53	-50

8,3,L

0	167	165
-1	87	95
-3	128	-137
-4	41	25
-6	44	50
-8	42	-41
-12	64	66
-13	57	53

8,2,L

-1	122	115
-3	119	113
-5	89	-86
-7	49	47
-8	35	-33
-9	55	56
-11	47	37

8,1,L

0	93	-82
-1	53	-45
-2	194	-194
-3	27	37
-4	78	66
-5	72	-62
-6	45	-42
-7	90	-89
-8	79	-84
-14	28	-36

8,0,L

0	319	321
-2	72	73
-4	65	-62
-6	168	175
-8	121	126
-10	139	-141
-12	48	44

7,17,L

-2	45	41

7,16,L

0	54	47
-5	57	-57

7,15,L

0	122	-123
-2	73	-73
-3	51	-55
-5	49	50
-8	92	-92

7,14,L

-1	71	75
-4	36	-34
-9	53	54

7,13,L

-1	60	-62
-2	70	67
-3	79	77
-4	31	-33
-5	53	-49
-8	48	46

7,12,L

0	56	53
-1	122	-121
-3	82	-82
-6	35	28
-9	97	-94
-11	43	43

7,11,L

0	85	90
-2	126	123
-3	71	-70
-5	68	-66
-6	25	-30
-7	42	50
-8	83	86

7,10,L

0	99	-101
-1	39	-40
-6	60	-61
-7	22	29

7,9,L

0	38	-39
-1	152	154
-2	74	-68
-3	67	-65
-4	124	131
-5	95	96
-6	52	51
-8	35	-36
-9	58	55

7,8,L

0	52	47

7,8,L

-1	177	182
-2	24	-25
-3	54	56
-4	76	-89
-5	137	-137
-9	119	122
-10	46	-49
-11	68	-73

7,7,L

0	51	-48
-1	43	-44
-2	45	-44
-3	41	36
-4	86	91
-6	97	99
-8	90	-92
-9	33	-29

7,6,L

0	24	-22
-1	197	-194
-3	71	74
-5	62	65
-6	109	106
-7	50	-50
-8	48	-48
-9	79	-86
-10	55	58

7,5,L

0	52	57
-1	102	100
-2	204	205
-3	158	-157
-4	56	-57
-5	53	58
-6	72	-70
-7	80	-77
-8	100	96
-9	44	50
-12	90	-85

7,4,L

-1	125	-126
-4	89	89
-5	191	195
-6	58	51
-7	33	31
-8	29	-32
-9	98	-98
-12	31	31
-13	50	45

7,3,L

-1	118	121
-2	78	-81
-3	67	-67
-4	64	61
-5	136	137
-6	94	92
-7	100	-101
-8	162	-171
-9	61	-60
-11	71	-70
-12	45	42

7,2,L

0	219	-213
-1	136	135
-3	48	-44
-5	264	-278
-6	37	-45
-7	93	-97
-8	142	151
-9	87	92
-10	46	43
-11	60	-68

7,1,L

-1	88	-85
-2	83	79
-3	175	174
-4	93	92
-6	405	414
-8	96	-102

7,0,L

0	81	88
-2	143	145
-4	124	-128
-6	154	149
-8	147	-153
-10	66	-79
-12	69	-65

6,18,L

0	71	-63
-3	57	57

6,17,L

0	64	66
-1	50	50
-5	57	-53

6,16,L

0	38	-33
-3	31	-30
-4	69	75
-8	49	-42

6,15,L

-1	44	-39
-4	82	80
-6	56	-60

6,14,L

0	151	153
-1	45	40
-4	38	-40
-5	58	-59
-8	38	39
-10	88	-81

6,13,L

-2	33	36
-3	36	35
-5	49	43
-7	53	-49
-10	37	-38
-11	71	62

6,12,L

0	88	98
-2	51	44
-3	25	28
-5	44	42
-6	35	38
-7	37	-34
-9	33	-27

6,11,L

0	91	-93
-3	89	-98
-4	110	-109
-5	152	-157
-7	38	-41
-8	37	38
-9	31	-45
-10	37	33
-11	47	-46

6,10,L

0	109	-114
-1	35	40
-3	21	22
-4	285	283
-6	48	-57
-9	43	47
-10	66	62

6,9,L

-1	78	76
-2	83	-82
-3	58	52
-4	175	170
-5	88	-95
-7	190	184
-10	45	-41

6,8,L

0	80	-88
-2	40	-42
-3	80	-87
-4	205	-205
-6	157	-160
-8	159	-156
-11	29	-37
-12	74	-76

6,7,L

0	69	-72
-1	109	-116
-2	158	-152
-3	261	262
-4	25	21
-5	102	100
-6	22	26
-7	79	-84

6,7,L

-8	105	107
-9	52	53
-10	81	-84
-11	78	86

6,6,L

0	187	193
-1	71	-64
-2	99	102
-4	226	-221
-5	94	92
-6	348	346
-7	121	-121
-8	167	162
-11	42	-51
-13	76	-79
-14	87	81

6,5,L

0	61	64
-1	103	-91
-2	72	78
-3	105	-110
-4	93	-91
-5	213	-206
-6	249	246
-7	71	-68
-8	42	44
-9	92	-92
-10	37	-44
-11	73	-69
-13	37	-38
-14	30	30

6,4,L

0	128	-126
-1	243	-237
-2	26	30
-3	116	106
-4	245	246
-5	147	-147
-6	115	-108
-7	142	144
-8	111	-110
-9	50	-50
-10	78	84
-12	46	52
-14	57	-47

6,3,L

0	180	-88
-1	78	93
-6	37	-43
-7	464	466
-8	73	76
-9	53	-49
-10	42	-46

6,2,L

0	251	-253
-1	200	231
-4	96	-88
-6	99	-100
-7	101	99
-9	38	36
-11	54	-57
-12	49	-55
-14	42	-31

6,1,L

0	154	155
-1	160	-167
-2	182	-185
-3	187	181
-4	83	86
-5	153	152
-7	167	-170
-9	27	23
-10	69	-73
-13	77	-77

6,0,L

0	330	331
-2	271	-272
-4	119	-121
-6	121	108
-8	224	228
-10	51	-48
-14	89	84

5,19,L

0	43	-34

5,18,L

-3	82	-85
-4	74	78
-5	39	44
-12	49	-39

5,17,L

-2	58	63
-3	72	-74
-6	38	-42

5,16,L

0	58	-60
-5	32	31
-8	57	61

5,15,L

0	35	-18
-2	117	-121
-3	81	79
-5	27	-33
-6	67	72

5,14,L

-1	107	103
-5	92	-94
-6	103	106
-10	58	-54

5,13,L

-1	67	70
-2	104	103
-4	109	105
-9	40	31

5,12,L

-1	107	-112
-2	59	-55
-3	114	-113
-5	159	160
-9	38	-41
-11	33	-28

5,11,L

0	115	-116
-1	97	99
-4	135	-137
-5	116	119
-6	141	-136
-8	44	40

5,10,L

0	112	-110
-1	162	157
-3	133	129
-4	53	53
-5	90	85
-7	75	77

5,9,L

0	71	-70
-1	92	-85
-2	222	-225
-3	65	-68
-4	144	-152
-8	185	-187
-6	177	175
-9	116	-114
-12	27	26

5,8,L

0	188	194
-1	73	70
-2	92	-91
-4	168	175
-5	206	-207
-10	52	47
-11	36	36
-12	50	51
-13	86	-83

5,7,L

0	197	184
-5	87	-81
-2	53	-53
-7	118	-121
-6	137	130
-8	106	106
-12	51	44
-9	87	82

5,6,L

0	308	319

5,6,L

-1	212	-204
-2	349	-345
-3	235	-231
-4	68	74
-5	97	93
-8	38	40
-10	164	-169
-12	69	76
-13	45	37
-14	27	-30

5,5,L

0	41	-29
-2	251	255
-3	193	193
-4	130	-128
-6	301	-296
-7	110	114
-8	91	91
-10	62	67
-11	74	71
-14	52	-54

5,4,L

0	234	-245
-1	120	120
-2	185	182
-3	47	-37
-4	150	-135
-5	258	259
-6	322	-323
-7	80	-79
-8	31	45
-9	77	79
-10	52	58
-12	59	-59

5,3,L

0	221	-204
-2	258	-247
-3	445	-438
-4	213	-204
-5	56	33
-7	86	77
-8	108	111
-9	45	31
-13	88	86

5,2,L

0	159	153
-1	45	57
-2	169	169
-3	397	401
-4	164	170
-5	263	-266
-7	24	-24
-9	200	201
-13	72	-73

5,1,L

0	211	213
-1	84	71
-2	331	-327
-3	94	-89
-4	282	284
-5	47	47
-6	97	-91
-7	90	-94
-8	76	-69
-9	93	84
-10	88	-92
-11	44	43
-12	43	33
-13	53	-46

5,0,L

0	148	165
-2	363	-350
-4	338	-338
-6	86	-83
-8	119	115
-10	52	-53
-12	95	97

4,19,L

-1	60	64
-3	28	-12
-5	28	36

4,16,L

0	99	-110
-5	61	-59
-7	57	51
-9	62	62

4,15,L

0	57	-63
-2	71	-69
-6	75	75
-8	91	-90

4,14,L

0	72	-84
-4	73	-74
-5	45	43
-6	23	21
-8	42	-46
-9	35	31

4,13,L

-1	142	-146
-3	225	227
-6	76	-73
-7	43	-44
-10	52	47

4,12,L

-1	185	-182
-2	169	-167
-4	135	-140
-6	60	63
-8	89	89

4,11,L

0	51	60
-1	52	61
-2	87	80
-7	108	118
-8	59	63
-9	33	-36
-11	32	-25

4,10,L

0	125	-117
-2	67	71
-4	82	89
-5	39	-36
-8	145	-145
-11	42	38

4,9,L

0	83	66
-1	92	92
-2	161	-162
-3	235	-237
-6	154	-158
-7	35	39
-8	51	-51
-10	64	-67
-11	61	-57

4,8,L

0	91	96
-1	269	273
-3	70	71
-4	117	-110
-5	142	-139
-6	206	197
-7	85	90
-8	69	79
-9	104	97
-11	59	-61

4,7,L

0	45	-46
-1	204	-195
-2	145	145
-3	160	164
-7	148	-143
-8	37	-32
-12	56	55

4,6,L

0	222	222
-1	256	-245
-2	145	137
-4	149	-137
-6	45	31
-7	63	61
-9	96	-106
-10	46	-43
-11	109	118
-12	36	-52

4,5,L

0	272	257
-1	183	177
-2	362	363
-4	435	-423
-5	191	176

4,5,L

-6	309	-294
-7	62	-68
-9	71	-69
-10	55	-52
-12	95	-94
-13	32	40

4,4,L

0	429	-416
-1	99	-97
-3	68	70
-5	415	408
-6	148	-153
-7	184	-184
-8	115	-119
-9	73	71
-10	48	38
-11	130	134
-13	36	37

4,3,L

0	86	78
-1	421	417
-2	212	-208
-3	188	-198
-4	138	138
-5	205	-176
-6	161	158
-7	122	119
-8	109	-111
-9	39	34
-10	36	43
-11	54	-52
-12	43	49
-13	38	43

4,2,L

0	101	-99
-1	158	156
-2	324	313
-3	189	-161
-4	381	376
-5	209	-217
-6	105	-107
-7	77	-77
-8	158	-159
-10	48	55
-11	93	-98
-13	64	-62

4,1,L

0	280	-271
-1	289	-277
-2	250	238
-4	111	97
-5	135	-96
-6	96	106
-7	147	-145
-8	176	-178
-9	91	-99
-10	158	164
-11	120	124
-12	92	92
-13	34	34

4,0,L

0	459	455
-2	512	529
-4	508	-502
-6	195	196
-10	66	71
-12	85	-100
-14	92	96

3,20,L

-1	57	54

3,18,L

0	56	-53
-1	60	-66
-2	31	22
-6	51	-53

3,1,L

-3	359	351

3,17,L

-4	36	-30
-6	31	-34
-7	137	135
-8	45	35

3,16,L

0	53	-54
-1	72	71
-2	54	-56
-7	46	42
-8	61	-63

3,15,L

0	30	31
-1	70	-69
-2	118	-114
-3	75	-79
-4	49	42
-5	48	45

3,14,L

0	316	322
-2	64	-74
-3	83	86
-5	78	-77
-8	93	98
-9	43	44
-11	48	39

3,13,L

0	47	45
-1	89	-96
-2	79	-72
-3	70	72
-4	80	-81
-7	51	-54
-11	65	48

3,12,L

-2	157	-158
-3	155	-155
-4	98	-100
-5	58	56
-12	48	41

3,11,L

0	131	139
-2	166	158
-3	45	-47
-4	128	129
-7	177	186
-10	49	51

3,10,L

-1	144	-137
-2	73	67
-3	156	-153
-4	71	74
-5	77	71
-6	223	-232
-7	117	-123
-13	29	26

3,9,L

0	152	163
-1	105	-96
-2	81	-78
-3	68	-69
-4	87	89
-5	109	-108
-6	59	-58
-7	54	56
-9	50	49
-10	51	-55
-12	31	34

3,8,L

0	103	105
-1	101	104
-3	135	125
-4	181	-181
-5	178	-169
-6	190	185
-7	36	41
-8	113	113
-9	104	105

3,7,L

0	268	-254
-1	247	-244
-2	82	80
-3	410	407
-4	254	249
-5	20	16
-7	101	-100
-8	105	-104
-11	87	93
-12	35	-37

3,6,L

0	78	81
-1	153	138

3,6,L

-4	248	-255
-5	231	234
-6	102	-95
-7	123	-115
-8	33	-33
-9	40	45
-10	62	-66
-12	62	-65

3,5,L

-1	146	-133
-2	359	359
-3	121	120
-4	313	-300
-5	36	-35
-6	245	-239
-7	21	30
-8	143	142
-10	50	-39
-11	36	-43
-12	67	-70
-14	46	52

3,4,L

0	332	-328
-1	546	-570
-2	110	-107
-4	602	604
-5	138	134
-6	99	93
-7	170	164
-9	219	-218
-10	154	155
-11	95	97
-12	43	41

3,3,L

0	303	285
-1	70	74
-2	408	403
-3	261	-290
-4	323	317
-5	186	-180
-6	103	104
-9	278	-275
-10	67	-73
-11	70	-69

3,2,L

-1	370	373
-2	351	353
-3	214	-222
-4	228	223
-5	414	-396
-6	22	-24
-7	33	28
-13	51	-49
-14	32	20

3,1,L

0	171	178
-1	190	184
-2	364	-378
-3	359	351
-4	83	-90
-5	49	56
-6	393	391
-7	46	46
-8	99	-101
-9	83	-79
-10	27	-27
-11	52	57
-12	94	92
-14	56	52

3,0,L

0	414	401
-2	705	-756
-4	246	235
-6	68	-60
-8	81	80
-10	288	-291

2,20,L

-3	30	-34

2,19,L

0	36	-25
-1	86	-83
-2	71	67
-3	73	81
-6	52	-49

2,18,L

0	41	40
-6	39	-39

2,17,L

-1	72	75
-2	100	-101
-3	104	-108
-5	50	49
-7	42	42

2,16,L

0	87	-76
-3	72	78
-4	127	128
-6	57	-55
-7	68	-63
-8	47	-45

2,15,L

0	100	100
-1	69	78
-2	62	69
-4	57	58
-5	67	-67

2,14,L

0	165	167
-1	46	50
-3	70	-77
-4	134	-137
-5	92	-86
-10	59	-59
-11	54	-58

2,13,L

0	93	-90
-1	47	-35
-4	71	-73
-6	57	51
-7	132	-131
-10	35	37

2,12,L

0	158	160
-1	76	68
-2	230	233
-3	33	29
-5	89	97
-6	47	42
-8	23	22
-9	40	-45

2,11,L

0	102	106
-1	73	70
-2	107	117
-3	221	-216
-4	69	-67
-6	82	-84
-7	108	-112
-9	52	55
-10	70	-76
-12	41	-43
-13	72	65

2,10,L

0	237	-235
-1	125	-121
-2	122	116
-4	51	47
-5	129	-134
-6	234	-231
-7	28	29
-12	61	51
-13	39	32

2,9,L

0	138	-143
-1	190	188
-2	68	72
-5	46	48
-6	350	352
-7	82	79
-8	131	-127
-10	97	100

2,8,L

0	102	94
-1	148	163
-2	151	-153
-3	95	-96
-6	88	-80
-7	123	-119
-11	29	-31

2,7,L

-1	149	-143
-2	73	-71
-3	292	285
-4	99	92
-5	159	149
-7	232	-218
-9	83	78
-11	133	132
-13	59	-53

2,6,L

0	551	546
-1	110	-116
-2	286	-261
-4	326	-308
-5	140	149
-6	232	220
-7	51	-51
-9	70	-78
-10	103	-98
-14	55	46

2,5,L

0	302	-292
-1	66	-49
-3	76	-60
-4	367	332
-5	122	-114
-6	119	-115
-7	52	58
-8	240	240
-9	103	-101
-10	70	72
-13	51	-36
-14	39	-34

2,4,L

0	456	-461
-1	423	-418
-3	556	-556
-4	628	615
-5	34	-30
-8	32	35
-9	166	-158
-10	134	139
-14	90	-87

2,3,L

0	274	-289
-1	498	512
-2	636	647
-3	836	-819
-4	105	99
-5	391	361
-6	66	-56
-7	125	135
-8	32	36
-9	35	-37
-10	59	-62
-11	191	-185
-12	79	-77
-13	60	62

2,2,L

0	216	-215
-1	664	699
-2	465	-484
-3	418	407
-4	105	-87
-5	46	-58
-6	139	-148
-8	55	49
-9	232	226
-11	49	-45

2,1,L

0	430	-438
-1	314	327
-2	1045	-1176
-3	494	490
-4	143	-131
-5	69	59
-9	139	128
-10	126	-126
-11	103	-102
-12	63	64
-13	26	-24

2,0,L

0	1016	-1216
-2	485	-547
-4	204	-202
-6	416	382
-8	90	94
-10	92	-98
-12	70	-68

1,20,L

-3	33	32

1,19,L

0	45	39
-3	56	-61
-4	66	-62
-6	45	-44

1,18,L

-1	37	-34
-2	49	-51
-4	62	61
-5	122	123
-7	44	44

1,17,L

-5	39	-42

1,16,L

-2	24	18
-4	50	47
-5	64	-60
-6	33	31

1,15,L

0	53	58
-2	51	-53
-3	61	65
-4	93	97
-5	53	-58
-6	137	135
-8	64	-53

1,14,L

0	71	-66
-1	79	85
-2	100	101
-4	51	-51
-5	68	-67
-6	84	77
-9	54	55
-10	42	48
-11	57	-55

1,13,L

0	37	-36
-1	143	-141
-2	32	-35
-5	39	36
-6	60	-55
-7	47	-54
-8	58	67
-9	48	-47

1,12,L

-1	301	-296
-2	153	149
-3	224	235
-4	95	100
-5	142	138
-9	62	-62
-10	50	-47
-11	74	72
-12	56	-49

1,11,L

0	47	-48
-1	61	56
-2	292	291
-3	152	145
-4	261	-260
-6	120	-117
-7	45	41
-8	81	76
-11	40	45
-12	68	-68

1,10,L

0	226	-232
-1	56	48
-2	77	-77
-3	86	95
-5	82	-79
-7	81	86
-8	120	-115
-9	79	-79
-10	34	33
-11	73	-69

1,9,L

0	236	-234
-1	67	-66

1,9,L

-2	563	-558
-4	364	356
-6	64	,71
-7	51	-48
-9	154	-152
-11	25	7
-12	128	129
-13	25	-26

1,8,L

0	103	97
-1	537	527
-2	545	525
-3	95	96
-4	154	146
-5	233	-229
-6	32	33
-8	132	136
-9	110	100
-11	46	-45
-13	62	-60

1,7,L

0	437	416
-1	75	-86
-2	326	-320
-3	75	-54
-4	51	-51
-7	110	-99
-8	32	-32
-10	120	-118
-12	34	34
-14	27	-21

1,6,L

0	71	-68
-1	550	-546
-2	185	-184
-3	163	-154
-4	475	-466
-5	93	89
-6	45	54
-7	82	75
-8	32	-26
-9	234	-240
-10	101	-97
-11	102	102
-12	49	50

1,5,L

0	479	-487
-1	666	666
-2	733	729
-4	181	-180
-5	200	197
-6	53	30
-7	144	134
-8	195	198
-9	116	120
-10	277	274
-11	62	59
-12	114	-111

1,4,L

-1	160	168
-2	205	198
-3	437	-415
-4	200	-187
-5	279	265
-6	63	-56
-7	182	-163
-8	66	-65
-9	136	-134
-11	93	-104
-12	59	-59

1,3,L

0	199	-208
-1	633	-630
-2	676	-690
-3	34	26
-4	32	-24
-5	478	-447
-6	67	-66
-7	359	355
-8	119	-116
-9	70	-68
-12	47	52

1,2,L

0	34	-28
-1	899	1028
-2	631	-645
-3	395	378
-4	50	-42
-5	186	-175
-6	46	-63
-7	158	141
-9	284	281
-10	189	192
-12	53	51

1,1,L

0	536	-575
-1	506	-525
-2	754	-816
-3	200	204
-4	274	272
-5	30	22
-6	22	34
-7	56	-57
-8	186	-178
-9	150	144
-10	92	-90
-13	60	-66
-14	74	-81

1,0,L

0	74	-107
-2	242	-253
-4	689	-704
-6	210	210
-8	149	-152
-10	109	105
-12	120	-119

0,20,L

0	67	70
-2	35	-42
-4	72	-71

0,19,L

-1	34	32
-3	41	44

0,18,L

0	77	-76
-2	26	-20

0,17,L

-2	97	99
-3	79	-75
-4	26	-16
-5	82	-84
-8	48	51

0,16,L

-1	58	60
-2	90	97
-3	37	-42
-4	79	88
-6	50	55

0,15,L

-2	71	-68
-3	24	-26
-4	66	-62

0,14,L

-1	86	-88
-2	270	-278
-3	105	106
-4	58	-59
-7	67	63
-8	107	105
-10	67	-64
-11	54	55

0,13,L

-1	30	34
-3	283	288
-5	114	117
-8	35	32
-11	65	74

0,12,L

0	104	104
-1	56	-48
-2	144	-143
-3	130	-129
-5	145	146
-7	111	-108
-8	63	69
-10	84	-82

0,11,L

-1	37	-40
-2	72	-75
-3	268	-264
-7	103	105

0,11,L

-9	103	-104
-10	52	52
-11	31	-40
-12	46	48

0,10,L

0	317	-311
-1	127	118
-3	109	-106
-4	415	421
-5	193	201
-7	102	-97
-9	70	67
-10	144	146
-11	43	-46

0,9,L

-1	119	105
-2	141	-153
-3	226	-220
-4	78	86
-5	57	58
-6	31	-30
-7	109	110
-10	62	-64
-11	83	-87

0,8,L

0	172	-158
-1	39	31
-3	221	213
-4	112	-121
-5	164	-163
-6	22	32
-7	190	185
-9	23	30
-10	86	-82

0,7,L

-1	371	-351
-2	161	-163
-3	355	327
-4	174	-159
-5	38	39
-6	83	-89
-7	150	-152
-8	103	-103
-10	35	35
-11	108	103
-13	53	-53

0,6,L

0	623	619
-1	411	401
-2	35	-41
-3	236	-232
-5	258	260
-6	48	48
-7	35	41
-8	325	315
-10	88	-81
-11	37	-46
-12	59	-53
-13	40	41

0,5,L

-1	559	-574
-2	183	192
-3	37	26
-4	103	-107
-5	122	-129
-6	121	-127
-7	182	-172
-8	75	75
-9	65	64
-10	67	-70
-12	61	-60
-14	26	10

0,4,L

0	369	-367
-1	333	335
-2	310	305
-3	268	230
-4	215	209
-5	97	-87
-6	398	-392
-7	124	122
-8	244	-247
-9	44	38
-10	53	49

0,3,L

-1	1097	1267
-2	580	-592
-3	104	-91
-4	46	67
-5	159	-169
-6	65	-68
-7	499	501
-8	119	-119
-9	96	98
-10	56	52
-11	89	-102
-12	47	46
-13	64	71

0,2,L

0	447	-462
-1	337	-340
-2	202	-200
-3	211	198
-5	300	-294
-6	199	-190
-7	104	104
-8	222	-226
-9	127	-129
-10	89	94
-11	39	-46
-12	71	74
-13	66	-68
-14	52	-54

0,1,L

-1	627	-705
-2	459	456
-3	51	-45
-4	207	195
-5	271	-266
-6	190	171
-7	328	-310
-9	50	-54
-10	164	170
-11	189	192
-12	34	-29

0,0,L

-2	321	-315
-4	208	201
-6	244	251
-8	373	361
-10	351	-349
-12	124	120

-1,19,L

-1	47	-41
-2	79	77
-3	57	54

-1,18,L

-1	92	-90
-4	27	-27

-1,17,L

-2	37	47
-4	31	39
-5	39	37
-6	66	-70

-1,16,L

-1	54	51
-3	55	60
-6	72	-73
-9	33	35

-1,15,L

-1	22	-31
-2	163	-168
-3	42	44
-5	50	45

-1,14,L

-1	82	73
-3	73	78
-4	79	-76
-5	38	-41
-6	54	53
-7	58	-52
-9	55	49

-1,13,L

-1	77	76
-2	182	185
-4	107	-107
-5	48	-50
-7	32	-22
-8	58	-56
-9	101	99
-10	24	-23

-1,12,L

-2	46	-50
-3	227	-239
-4	93	-91
-5	146	147
-7	121	120
-9	81	-83
-10	46	54
-11	56	49

-1,11,L

-1	66	66
-2	153	166
-3	226	-225
-4	22	-28
-5	93	92
-6	161	-158
-8	78	81
-9	58	-55
-10	65	66
-11	59	-58

-1,10,L

-1	151	-145
-2	81	88
-3	34	-42
-5	94	-91
-6	104	-102
-7	30	-35
-8	142	141
-9	46	-40
-10	62	64

-1,9,L

-1	173	168
-2	152	147
-3	202	-208
-4	108	-113
-5	25	20
-6	390	394
-7	145	141
-8	124	-120
-9	37	35
-10	36	-37

-1,8,L

-1	205	200
-2	286	-268
-3	132	129
-4	100	-95
-5	230	-231
-8	168	-175
-9	227	236
-10	48	-49
-12	42	-43

-1,7,L

-1	69	-72
-2	214	-201
-3	23	12
-4	118	-101
-6	86	-82
-7	64	-64
-8	177	-177
-9	83	82
-11	86	82
-12	33	-41
-13	37	-37

-1,6,L

-1	178	-178
-3	157	139
-5	192	182
-6	248	231
-7	184	190
-8	62	65
-9	43	41
-10	76	78
-12	26	-23
-13	55	50
-14	49	48

-1,5,L

-1	430	-433
-2	222	216
-3	63	57
-4	140	130
-5	129	-123
-6	383	-374
-7	96	-93
-8	141	142
-9	175	-186
-12	68	-61
-13	63	-67
-14	52	-51

-1,4,L

-1	694	-694
-2	127	120
-3	222	-207
-4	337	334
-5	44	34
-6	113	-111
-7	33	26
-8	68	-64
-9	180	-182
-10	92	91
-14	27	-19

-1,3,L

-1	565	568
-2	322	-315
-3	557	-555
-4	192	185
-5	301	273
-6	167	157
-7	165	-159
-8	31	-41
-9	64	61
-10	69	59
-11	64	-60
-13	100	102

-1,2,L

-1	378	359
-2	715	736
-3	66	56
-4	211	214
-5	330	-328
-6	124	131
-7	116	-114
-9	285	286
-10	96	-96
-11	44	-46
-12	50	-54

-1,1,L

-1	212	211
-2	634	-638
-3	492	478
-4	360	336
-5	133	-131
-6	267	252
-7	189	-179
-8	226	-230
-9	43	40
-10	173	-175
-11	42	-39
-12	61	62

-1,0,L

-2	845	925
-4	388	-382
-6	313	303
-8	70	-60
-10	121	-120
-12	68	68
-14	57	63

-2,20,L

-1	39	-29

-2,19,L

-3	55	55

-2,18,L

-3	43	-46

-2,17,L

-2	32	-32
-3	32	-32
-4	66	64

-2,16,L

-2	34	-33
-4	43	40
-6	78	-79
-8	76	-80

-2,15,L

-2	82	-84
-4	28	18
-5	36	38
-7	48	49

-2,14,L

-1	110	116
-2	29	27
-3	61	-58
-4	73	-73
-5	36	20

-2,14,L

-6	59	62
-7	39	-39

-2,13,L

-1	225	-235
-2	119	118
-3	50	51
-4	67	63
-7	121	-123
-8	66	70

-2,12,L

-1	171	-176
-2	80	77
-3	65	-64
-7	54	-57
-9	87	-79
-10	46	52
-11	45	43

-2,11,L

-2	185	182
-4	70	-67
-5	187	-191
-6	50	-44
-7	90	94
-8	85	79

-2,10,L

-1	36	36
-2	73	69
-3	168	173
-4	113	113
-5	90	-90
-6	105	-102
-7	127	124
-8	181	-180
-10	57	56
-11	67	73

-2,9,L

-1	370	364
-2	299	-296
-4	189	191
-5	139	-142
-6	131	-124
-7	210	214
-8	117	-119

-2,8,L

-1	93	109
-2	264	-259
-3	59	-46
-4	116	-110
-5	191	-196
-6	190	-193
-7	77	-75
-8	69	65
-9	68	65
-11	46	-44

-2,7,L

-1	87	-80
-2	62	54
-3	277	280
-4	315	300
-5	39	30
-6	175	172
-7	154	-151
-8	126	136
-9	25	-20
-10	49	51
-11	54	55
-12	72	68

-2,6,L

-1	394	-387
-2	138	125
-3	68	-56
-4	205	-196
-5	215	-206
-6	184	185
-7	132	-131
-8	116	114
-9	84	-85
-10	84	-88
-11	25	27

-2,5,L

-1	116	114
-2	275	261
-3	256	-233
-4	286	-252
-5	28	29
-7	51	41
-8	42	-44
-9	84	-80
-10	28	31
-12	62	-66

-2,4,L

-1	107	104
-2	138	-119
-4	282	267
-5	345	332
-7	29	-28
-8	83	-86
-10	122	128
-11	54	53
-12	51	52
-13	73	72

-2,3,L

-1	219	-201
-2	294	-290
-3	103	101
-4	169	-157
-5	304	-287
-6	107	107
-7	210	213
-8	34	-39
-9	119	-114
-10	41	-40
-11	79	-77
-13	51	-55
-14	38	-46

-2,2,L

-1	573	587
-2	281	-272
-3	332	-318
-4	310	295
-5	443	-435
-6	213	205
-7	52	59
-8	60	54
-9	126	123
-11	83	-82

-2,1,L

-1	742	-778
-3	683	669
-4	405	378
-5	290	263
-6	215	220
-7	105	-110
-8	185	-189
-10	47	-63
-12	119	122

-2,0,L

-2	161	165
-4	813	-800
-6	144	156
-8	53	54
-12	131	-128
-14	68	74

-3,20,L

-1	48	44

-3,18,L

-2	64	63
-5	33	34

-3,17,L

-1	47	52
-2	63	56
-3	83	-80
-4	54	-57

-3,15,L

-1	26	22
-4	27	27
-5	57	-54
-6	107	108

-3,14,L

-5	74	-75
-6	41	43

-3,13,L

-1	101	-107
-2	32	-39
-3	75	85
-4	33	32
-6	51	-61
-8	41	37

-3,12,L

-7	55	-51
-9	42	-43

-3,11,L

-1	245	250
-2	73	70
-3	85	-77
-4	23	-19
-7	45	43
-8	58	56
-11	54	-57

-3,10,L

-1	120	119
-3	107	-103
-4	388	391
-5	168	175
-6	101	-102
-8	120	-126
-10	51	48

-3,9,L

-1	71	-61
-2	184	-179
-3	54	-57
-4	39	31
-6	41	-51
-7	42	-41
-8	86	-84
-11	40	-40

-3,8,L

-1	163	159
-2	36	27
-3	168	174
-4	62	-63
-5	131	-138
-6	54	52
-7	93	-92
-8	58	59
-9	60	56
-11	24	-22

-3,7,L

-1	80	-74
-2	105	-113
-3	351	362
-4	127	121
-6	302	309
-7	150	-147
-12	74	73

-3,6,L

-2	100	-99
-3	219	-219
-4	51	-53
-5	61	65
-6	31	22
-7	198	-196
-9	100	-101
-10	75	-74
-11	35	-21

-3,5,L

-1	343	336
-2	543	521
-3	137	-127
-4	133	-137
-5	136	136
-6	159	-155
-8	97	91
-9	105	105
-10	77	77
-11	44	-49

-3,4,L

-1	257	-245
-2	84	-80
-3	271	276
-4	29	-18
-5	40	55
-6	190	-190
-7	57	58
-9	73	-70
-10	44	45

-3,3,L

-1	130	134
-2	71	83
-3	328	-318
-4	105	-97
-5	64	62
-6	95	98
-7	274	274
-8	24	-21
-10	57	-52

-3,2,L

-1	461	470
-2	67	-83
-3	608	597
-4	76	-75
-5	362	-362
-6	85	-84
-9	131	137

-3,1,L

-1	177	-178
-2	185	-166
-4	148	-127
-5	149	153
-6	119	120
-7	111	-112
-8	118	-120
-11	60	54
-13	103	-99

-3,0,L

-2	858	-894
-4	239	-247
-8	328	337
-10	105	-102
-12	84	79

-4,19,L

-1	40	-45
-2	78	76

-4,18,L

-1	79	-74

-4,17,L

-2	27	-31
-3	33	-29

-4,16,L

-1	97	93
-2	31	20
-3	46	43
-4	63	61

-4,15,L

-2	125	-121
-4	74	75
-5	80	-79
-8	43	-35

-4,14,L

-2	83	85
-3	25	22
-4	49	-56
-5	56	-58
-6	52	48
-7	42	38

-4,13,L

-2	49	54
-3	114	110
-4	57	-54
-5	56	63
-7	95	-94
-9	51	52

-4,12,L

-1	66	-63
-2	93	-96
-4	90	-91
-5	43	38
-6	42	50
-7	35	35
-8	30	25
-9	80	-82
-10	44	-41

-4,11,L

-1	89	91
-3	34	-32
-5	67	68
-6	47	-48
-7	53	55
-10	47	48

-4,10,L

-1	87	84
-2	34	41
-4	142	144
-5	28	29

-4,10,L

-8	67	-68
-10	46	49

-4,9,L

-1	121	-114
-2	99	-103
-3	114	-110
-4	138	-140
-5	110	-110
-6	150	150
-7	58	61
-8	55	-61
-9	53	-62
-11	68	-64

-4,8,L

-1	133	129
-2	33	30
-3	117	118
-5	113	-111
-6	287	295
-8	41	-35
-9	35	29
-10	63	61

-4,7,L

-1	170	-165
-2	34	-37
-3	99	105
-5	33	33
-6	86	87
-7	131	-137
-9	30	35

-4,6,L

-1	249	-241
-2	73	-73
-3	122	127
-4	268	-264
-5	245	233
-7	40	41
-8	30	-33
-9	62	-66
-10	89	-90
-11	29	21
-12	60	-53

-4,5,L

-1	116	-125
-2	96	107
-3	334	324
-4	178	-175
-6	210	-209
-7	107	107
-8	79	77
-9	28	28
-11	67	65
-12	47	-48

-4,4,L

-1	198	-205
-2	43	38
-3	31	33
-4	28	24
-5	180	180
-6	112	-112
-7	30	32
-8	85	-81
-10	62	69

-4,3,L

-1	244	237
-2	103	-93
-3	424	-418
-4	282	282
-6	83	92
-7	164	173
-8	40	-39
-11	70	-73
-12	41	40

-4,2,L

-1	129	-115
-2	462	447
-3	309	307
-4	33	-36
-5	109	-105
-6	178	-179
-7	168	-172
-8	81	-86
-9	82	72
-10	79	78
-11	56	-52
-13	92	-96

-4,1,L

-1	48	-63
-2	553	-559
-4	57	66
-5	35	34
-6	60	62
-7	171	-178
-8	78	87
-9	80	88
-12	87	89

-4,0,L

-2	32	29
-4	341	-348
-6	180	177
-8	106	104
-10	146	-149

-5,17,L

-1	45	43

-5,16,L

-1	70	67
-2	64	-62
-5	51	-46

-5,15,L

-2	59	-56
-3	33	29
-4	84	79
-5	67	63

-5,14,L

-1	124	125
-3	63	62
-4	53	-54

-5,13,L

-1	103	-105
-2	92	-93
-4	81	-74

-5,12,L

-1	68	-78
-2	55	-51
-3	46	-44
-4	44	42
-5	167	167
-6	31	32
-8	25	26

-5,11,L

-2	210	218
-3	70	73
-4	34	40
-6	148	-149
-7	49	42
-8	63	61

-5,10,L

-1	148	-150
-3	54	-54
-4	154	-151
-5	127	-131
-8	62	-55

-5,9,L

-1	127	130
-2	220	-219
-3	48	-40
-4	162	166
-5	27	-39
-6	104	106
-7	63	64
-9	43	44

-5,8,L

-1	149	156
-3	146	145
-4	85	90
-5	167	-161
-7	81	78
-8	55	53
-9	110	111
-10	62	-62

-5,7,L

-1	240	-233
-2	62	-51
-3	99	93
-4	164	-160
-5	34	-23
-6	110	-112

-5,7,L

-7	46	-39
-8	63	-63
-10	74	-71

-5,6,L

-1	158	-164
-2	121	-116
-4	143	-147
-5	265	264
-6	68	-70
-7	88	84
-8	123	125
-10	86	-78
-11	57	61

-5,5,L

-1	44	41
-2	156	160
-3	102	103
-4	217	-222
-5	28	-34
-6	109	-106
-8	176	184
-9	35	-36

-5,4,L

-1	145	-151
-2	64	73
-3	452	-452
-4	297	298
-5	246	252
-7	114	-116
-8	59	-58
-9	49	-53
-10	76	75

-5,3,L

-3	204	-205
-4	88	82
-5	172	-178
-6	97	93
-7	54	35
-12	35	30

-5,2,L

-1	137	122
-2	89	92
-4	164	159
-5	162	-171
-6	63	-61
-7	52	56
-9	117	118

-5,1,L

-1	112	-98
-2	362	-357
-3	103	96
-4	28	-31
-5	40	42
-6	201	207
-8	153	-158
-9	50	-58
-11	94	92
-12	73	71

-5,0,L

-2	95	69
-4	111	-109
-6	47	45
-10	69	-70
-12	78	-74

-6,17,L

-1	76	79
-3	54	-54

-6,16,L

-2	27	17

-6,15,L

-2	29	24
-4	48	-54
-6	65	63

-6,14,L

-2	98	-95
-3	46	41
-4	61	-57
-6	57	53

-6,13,L

-1	91	-90
-3	92	86
-7	71	-65

-6,12,L

-1	35	-31
-2	111	107
-3	61	-62
-4	73	-75

-6,11,L

-2	48	51
-3	101	-100
-7	48	55

-6,10,L

-3	33	-27
-4	118	120
-6	148	-147
-8	47	-50

-6,9,L

-1	183	178
-2	91	-87
-3	83	-85
-4	50	47

-6,8,L

-4	76	-77
-7	77	-79
-9	70	69
-10	32	-33

-6,7,L

-1	151	-157
-2	104	99
-3	290	297
-5	51	55
-7	179	-182
-9	53	58

-6,6,L

-1	29	-27
-3	171	-169
-4	276	-286
-6	141	149
-8	26	23
-10	39	-35

-6,5,L

-1	75	-77
-2	154	158
-3	184	-183
-4	36	31
-5	113	118
-6	73	-74
-7	92	-92
-8	90	89
-11	25	-18

-6,4,L

-1	136	-143
-2	146	153
-3	47	47
-4	376	386
-5	62	-68
-6	85	-82
-7	48	55
-9	56	-63
-10	85	90
-11	59	57

-6,3,L

-1	349	340
-2	114	106
-3	346	-359
-4	190	-196
-5	109	-106
-7	102	100
-9	49	-53
-11	132	-135

-6,2,L

-1	183	177
-2	163	-162
-3	83	-88
-4	120	118
-5	71	-68
-6	28	25
-9	91	96
-10	48	39

-6,1,L

-1	45	-52

-6,1,L

-2	78	67
-3	180	185
-5	30	31
-6	126	129
-8	87	-95
-11	61	58

-6,0,L

-2	62	65
-4	256	-265
-6	68	71
-8	101	94
-10	120	-123

-7,17,L

-1	41	-37

-7,16,L

-1	33	-26
-2	60	58

-7,15,L

-2	108	-104
-4	61	59

-7,14,L

-1	33	-32
-3	25	21
-5	58	-62

-7,13,L

-2	56	55
-5	59	61

-7,12,L

-2	95	95
-5	49	48

-7,11,L

-1	54	-62
-2	72	71
-3	100	-98
-4	89	-94
-6	40	-44

-7,10,L

-2	59	52

-7,9,L

-1	79	-82
-3	74	80
-4	62	58
-5	39	-38
-6	114	113
-7	30	34

-7,8,L

-1	158	160
-3	60	60
-4	132	-132
-5	136	-140
-6	41	41
-7	56	-51
-8	51	-46
-9	60	62

-7,7,L

-2	181	-186
-3	47	43
-4	62	65
-5	66	66
-6	35	30
-7	65	-65
-9	36	24

-7,6,L

-1	32	-37
-2	65	65
-3	86	-82
-4	42	-39
-5	68	72
-6	119	122
-7	25	-32
-8	24	22
-9	106	-102

-7,5,L

-1	119	-119
-2	433	435
-3	55	-51
-4	51	60
-5	60	-61
-6	112	-118
-8	97	95
-9	60	-56
-10	111	105

-7,4,L

-1	191	-197
-2	35	34
-3	108	-113
-6	51	-47
-8	49	-53
-9	133	-133

-7,3,L

-1	109	111
-2	127	-124
-3	112	118
-4	46	53
-7	176	178

-7,2,L

-1	359	376
-2	163	-169
-3	250	253
-5	137	-134
-6	41	-37
-8	39	-36
-9	127	127
-10	42	45

-7,1,L

-2	392	-407
-3	21	25
-4	141	140
-7	100	-104
-10	122	-116

-7,0,L

-2	83	88
-6	87	90
-8	91	91

-8,13,L

-1	72	-77
-3	63	57
-5	36	38

-8,12,L

-1	61	-62
-2	36	-32
-5	46	41

-8,11,L

-1	68	70
-3	59	-55

-8,10,L

-4	95	89

-8,9,L

-1	50	55
-2	47	-43
-3	90	-95
-4	51	47
-5	43	-44
-6	36	37

-8,8,L

-1	57	53
-3	57	58
-5	90	-93
-7	54	55
-8	54	56

-8,7,L

-1	168	-173
-2	64	-69
-3	64	61
-6	29	24
-7	74	-74

-8,6,L

-4	44	-47
-5	92	94
-6	51	-57
-8	138	140

-8,5,L

-1	117	119

-8,5,L

-2	84	80
-3	57	58
-4	46	-46
-6	67	-59
-7	48	42
-8	59	59

-8,4,L

-1	150	146
-2	80	-84
-3	126	-129
-5	154	157
-6	70	-75
-8	114	-107

-8,3,L

-1	138	142
-2	95	-94
-3	80	-81
-4	81	85
-7	121	119

-8,2,L

-1	36	38
-3	85	87
-4	57	61
-5	136	-138
-7	29	18

-8,1,L

-1	129	-126
-3	80	86
-4	43	52
-5	40	41
-6	85	87
-7	66	-68
-8	46	-46

-8,0,L

-2	124	-122
-4	122	-123
-6	47	55
-8	35	38

-9,14,L

-1	40	44

-9,12,L

-1	92	-89

-9,11,L

-1	26	28
-2	70	67
-3	46	-46

-9,10,L

-3	47	-41
-4	56	58

-9,9,L

-1	100	100
-2	118	-122
-3	64	-59
-5	40	42

-9,8,L

-1	75	71
-3	77	73
-4	74	-73
-5	35	-35

-9,7,L

-1	64	-64
-3	67	71
-6	46	36
-7	69	-72

-9,6,L

-1	47	-41
-2	61	63
-6	68	69

-9,5,L

-2	37	35
-3	50	-49
-4	36	-41
-6	115	-110
-7	47	-52

-9,4,L

-1	29	-26
-4	97	88
-5	50	47
-6	69	-68
-7	87	88

-9,3,L

-1	98	100
-2	44	-41
-3	105	-103
-6	38	38
-7	75	74

-9,2,L

-2	57	55
-5	117	-114
-7	60	-53

-9,1,L

-1	88	-86
-3	62	70
-6	148	142

-9,0,L

-4	126	-124
-6	102	103

-10,12,L

-1	43	-35

-10,9,L

-1	34	29
-2	64	-61

-10,8,L

-3	40	42

-10,7,L

-3	66	67

-10,6,L

-1	54	-57
-3	68	-66
-4	68	-72
-5	28	26

-10,5,L

-1	93	-93
-3	24	20
-6	81	-84

-10,4,L

-2	63	65
-4	77	79

-10,3,L

-2	74	-70
-3	129	-126
-4	24	14
-5	76	-75
-6	26	28

-10,2,L

-2	26	25
-3	35	37
-4	75	72
-5	75	-75

-10,1,L

-1	28	-32
-2	88	-84
-3	87	82

-10,0,L

-2	49	-45
-4	144	-143

-11,8,L

-2	30	-28

-11,7,L

-1	46	-42

-11,6,L

-1	62	-63

-11,5,L

-2	97	94
-4	33	-38

-11,4,L

-2	48	-43

-11,3,L

-1	81	79
-3	37	-39

-11,2,L

-1	151	143
-3	32	27

-11,1,L

-1	42	-38
-2	87	-85
-5	45	35

-11,0,L

-2	55	56
-4	101	-101

-12,5,L

-1	59	59

-12,1,L

-2	65	-57

A P P E N D I X 8

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR N-DICHLOROPHOSPHINOYL-P-TRIPHENYLPHOSPHAZENE

0,0,L

-2	390	-358
-4	233	-253
-6	473	491
-8	88	70
-10	566	572
-12	529	537
-14	43	-50
-20	249	-243
-22	255	253

0,-1,L

-1	366	-425
-2	554	-594
-3	229	246
-4	651	-694
-5	50	-79
-6	642	657
-7	349	-354
-8	42	47
-9	610	633
-10	90	100
-11	799	-823
-12	50	-43
-13	351	351
-14	138	146
-15	64	-64
-16	207	-214
-17	31	-34
-18	72	74
-20	88	86
-21	53	46
-23	47	-39
-24	123	-119

0,-2,L

0	463	-500
-1	244	-247
-2	1544	-1997
-3	195	-213
-4	116	128
-5	824	868
-6	558	596
-7	769	-798
-8	437	-432
-9	125	125
-10	336	-326
-11	32	32
-12	148	-146
-13	62	71
-14	195	-205
-15	109	116
-16	72	71
-17	43	-41
-18	103	113
-19	41	39
-20	164	-158
-21	89	-88
-23	59	55
-24	100	-96

0,-3,L

-1	126	-135
-2	1163	1322
-3	571	608
-4	196	-228
-5	348	-387
-6	774	778
-7	178	-179
-8	199	-203
-9	396	401
-10	303	-304
-13	186	191
-14	498	510
-15	73	68
-16	52	-54
-17	242	-239
-18	158	153
-19	166	167
-20	93	-89
-23	52	47
-24	52	51

0,-4,L

0	349	352
-2	608	619
-3	347	-354
-4	426	-451
-6	197	207
-7	296	-281
-8	72	-91
-9	274	281
-10	323	316
-11	187	186
-12	116	114
-13	365	-379
-14	97	-98
-15	256	-255
-16	172	164
-19	88	87
-20	70	68
-22	96	89

0,-5,L

-1	51	-68
-2	140	-131
-3	26	-17
-4	727	-710
-5	236	-228
-7	425	435
-8	274	286
-9	233	-237
-10	203	-185
-11	247	-249
-13	224	-223
-14	38	-38
-15	186	185
-16	234	-229
-17	79	-76
-19	129	125
-21	189	-181

0,-6,L

0	613	-623
-1	135	-149
-3	245	250
-4	121	-120
-5	200	187
-6	212	217
-7	53	-78
-8	308	-305
-9	309	-318
-11	116	126
-12	55	-59
-13	90	84
-14	150	-152
-15	258	256
-16	103	107
-17	55	59
-18	217	-208
-19	120	-115
-20	57	46

0,-7,L

-1	317	320
-3	173	181
-4	122	121
-5	387	-406
-6	60	-61
-7	213	217
-8	107	112
-9	33	42
-10	186	-180
-11	156	156
-12	126	126
-13	240	233
-14	102	-99
-15	44	-43
-16	55	45
-17	155	-150
-19	48	36

0,-8,L

0	190	192
-1	312	-319
-2	57	50
-4	141	138
-7	116	129
-8	47	-60
-9	114	117
-10	94	93
-11	67	52
-13	91	-89
-15	64	-61
-16	158	158
-18	95	-87
-19	55	48

0,-9,L

-1	313	-321
-4	76	77
-5	98	-95
-7	120	116
-8	97	-99
-10	60	-63
-11	333	-330
-12	200	188
-14	40	-37
-15	55	-56
-17	114	103

0,-10,L

0	119	127
-1	80	-79
-2	110	-105
-3	55	47
-4	50	49
-5	83	78
-6	79	-69
-7	77	-73

-1,-4,L		
2	588	-532
1	271	-196
0	462	-454
-1	329	364
-2	229	-214
-3	282	273
-4	276	260
-5	598	-616
-6	271	269
-8	73	69
-9	54	51
-10	322	-328
-11	154	-144
-13	321	320
-14	294	298
-15	120	-120
-16	101	-97
-17	62	-65
-18	301	299
-19	47	-39
-20	108	-107
-21	120	114

-1,-5,L		
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19	205	-206
17	98	94
16	141	-135
14	119	118
13	413	424
11	128	127
10	75	-61
9	237	-240
8	261	253
5	55	29
4	384	-392
3	633	640
2	135	-132
1	298	323
0	219	-204
-1	113	100
-2	117	-125
-3	369	-379
-4	61	64
-5	169	188
-6	371	-357
-7	599	-596
-8	140	-141
-9	425	438
-10	193	209
-11	93	91
-13	207	-216
-14	74	-75
-15	69	-67
-17	61	-64
-21	139	128

-1,-6,L		
22	39	-40
19	52	-44
18	77	-77
17	38	46
16	85	80
15	129	137
14	87	92
13	95	-95
12	223	216
9	321	-326
7	97	98
6	109	-115
5	245	252
4	316	320
3	359	362
2	195	-207
1	527	-525
0	311	310
-1	155	-157
-2	185	181
-4	368	-384
-6	135	144
-7	336	339
-8	82	75
-9	69	-78
-10	143	-152
-11	89	-96
-12	120	122
-13	108	-110
-16	175	-179
-17	47	54
-18	153	155
-20	154	-147
-21	66	-71

-1,-7,L		
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17	106	106
16	52	59
15	95	-90
13	81	-80
12	50	38
11	61	-65
10	152	-149
9	96	-94
8	48	39
7	421	431
6	198	199
5	58	-48
4	77	-86
3	362	-371
2	260	253
1	152	-147
0	39	-41
-1	178	-188
-3	419	429
-4	175	-178
-5	159	169
-6	170	156
-7	433	-441
-8	79	-87
-9	173	168
-10	144	145
-11	43	-34
-12	157	-161
-13	189	-183
-14	126	128
-15	218	215
-18	59	-57
-19	112	-113

-1,-8,L		
19	64	-59
17	106	-102
16	79	-72
14	66	60
13	118	-111
12	44	-50
11	228	232
10	86	87
8	84	-83
7	194	210
5	337	-333
4	99	109
3	211	-215
2	36	33
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-1	582	600
-2	84	97
-3	56	-64
-4	330	-333
-5	29	-8
-6	146	151
-8	89	89
-9	108	-96
-13	167	-166
-11	218	223
-12	151	149
-14	94	-89
-15	115	118
-16	76	-78
-17	78	-74
-19	70	-68

-1,-9,L		
12	62	52
11	94	88
10	109	-107
9	208	-206
8	44	41
5	95	-94
1	391	393
0	174	-179
-1	397	-394
-2	182	191
-3	102	103
-4	72	-77
-7	58	-57
-8	62	68
-9	125	124
-10	94	-82
-11	135	129
-12	109	-106
-13	120	-120
-14	97	96
-15	63	75

-1,-10,L		
15	115	105
14	67	59
12	153	-158
11	76	-79
10	103	102
9	119	-123
5	198	187
4	67	-57
3	89	-82
1	43	-45
0	109	-110
-1	104	-104
-2	181	184
-3	264	-267
-5	111	111
-6	50	50
-10	216	-210

-1,-10,L

-12	135	131
-13	146	-145
-14	47	34

-1,-11,L

13	123	-111
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7	91	92
6	96	-97
3	189	-191
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-1	97	-93
-2	123	122
-3	54	47
-5	85	78
-6	153	-149
-7	40	26
-8	86	82
-9	94	-87
-12	71	79

-1,-12,L

9	56	58
8	38	-51
7	53	-56
6	53	-46
4	69	72
3	144	-139
1	75	75
0	49	-39
-1	55	48
-3	68	-68
-4	107	-100
-6	50	-46
-7	56	-52
-8	130	122
-9	40	-39

-1,-13,L

1	94	86
0	44	-51
-2	59	-60

-2,0,L

24	113	108
22	196	-191
20	133	-131
18	72	75
16	169	167
14	56	-60
12	740	746
10	1001	-995
8	245	-213
6	737	-701
4	949	909
2	622	569
0	1658	-1535
-2	1061	-1008
-4	1356	-1367
-6	178	195
-8	366	-352
-10	149	134
-12	365	-398
-14	85	75
-16	334	-332
-18	252	253
-20	116	115
-22	142	-139

-2,-1,L

23	115	-113
22	103	-97
21	189	191
19	137	-141
18	130	126
16	276	271
15	221	223
14	44	-47
13	351	-355
12	97	-102
10	286	282
9	480	469
8	90	91
7	116	-120
6	1263	1260
5	571	-559
4	292	-285
3	995	961
2	118	-109
1	1110	-1072
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-1	738	681
-2	1184	1142
-3	377	-360
-4	228	222
-5	496	487
-6	84	-79
-7	414	-401
-8	114	90
-9	79	71
-10	164	141
-11	264	266
-13	184	-186
-14	77	86
-15	91	88
-16	157	164
-18	73	-82
-20	76	-78
-21	109	-105
-22	90	-92
-23	122	120
-24	59	44

-2,-2,L

24	77	68
23	49	47
21	119	-118
20	69	67
19	170	177
18	241	248
17	246	-246
16	165	-170
15	95	96
14	313	-320
12	394	405
11	239	239
10	89	-95
9	300	-304
8	647	627
7	109	113
6	153	-146
5	278	-276
4	423	-429
3	248	-242
2	412	398
1	520	509
0	217	200
-1	324	-317
-2	418	410
-3	352	-332
-4	571	552
-5	247	-241
-6	173	132
-7	156	161
-8	332	-335
-9	316	-315
-10	125	129
-11	485	492
-12	30	-28
-13	394	-401
-14	382	387
-16	217	-225
-18	192	-197
-19	61	-55
-20	110	106
-23	87	91
-24	61	55

-2,-3,L

22	79	67
19	141	-140
18	252	-253
16	96	-94
15	135	131
14	42	49
13	73	-81
12	306	306
11	163	-158
10	392	390
9	59	55
8	915	-908
7	266	-282
6	182	166
4	127	-125
3	158	144
2	583	583
1	165	174
0	467	-463
-1	79	80
-2	632	639
-3	244	-235
-4	227	-249
-5	63	62
-6	600	-577
-7	466	482
-8	70	-60
-9	170	-178
-10	46	-27
-11	32	31
-12	49	-39
-13	128	-127
-14	103	-111
-15	93	-87
-16	93	-102
-17	154	153
-18	147	-135
-20	126	124

-2,-4,L

23	85	-80
21	102	-93

-2,-4,L

20	195	-187
19	277	277
16	259	-257
14	152	152
13	197	-197
12	138	-130
11	206	-214
10	198	-183
9	75	-83
8	112	-105
7	443	452
6	127	142
5	256	-252
4	371	-358
2	157	172
1	320	317
0	62	50
-1	741	-738
-2	439	-455
-3	251	260
-4	419	444
-5	394	381
-6	248	-257
-7	199	206
-8	316	333
-9	274	-290
-11	77	79
-12	226	-243
-14	46	48
-15	171	170
-16	189	197
-17	154	152
-18	65	-63
-20	138	136
-21	67	-70
-22	155	-144

-2,-5,L

21	126	115
19	44	49
18	108	98
16	203	199
14	116	-118
13	57	-57
12	236	-244
11	287	286
9	279	283
8	71	75
7	322	-339
6	184	186
5	569	574
4	110	128
3	425	-455
2	267	-282
0	254	-240
-1	143	161
-2	171	170
-3	42	39
-4	157	139
-5	261	-265
-7	138	138
-8	264	247
-9	601	-603
-10	72	50
-11	273	284
-12	55	58
-13	346	347
-15	279	-276
-16	99	101
-17	78	82
-19	162	-161
-20	78	72

-2,-6,L

21	46	38
19	124	-113
18	155	149
17	96	-86
16	79	-86
14	140	142
13	256	260
12	171	-175
11	73	81
10	126	119
8	182	184
7	139	-145
5	262	-260
4	167	-175
2	348	364
1	327	319
0	194	-202
-1	102	-99
-2	77	-73
-3	88	-97
-4	508	516
-5	150	-153
-6	430	-452
-7	183	-172
-8	250	255
-9	200	207
-10	57	54
-12	44	-42
-13	76	66
-15	265	-262
-18	76	-77
-20	84	86
-21	37	32

-2,-7,L

20	48	-32
17	78	79
15	148	144
14	143	-133
13	165	-158
12	134	131
11	138	143
10	51	-54
9	227	-235
8	68	-61
7	455	-459
6	123	-125
5	502	517
4	194	194
3	97	-93
2	307	-322
0	82	85
-2	210	-215
-3	467	-481
-4	128	132
-5	125	141
-6	54	-47
-7	354	360
-8	128	-125
-9	229	-232
-12	62	-62
-14	74	-80
-15	256	-257
-16	57	56
-17	205	197

-2,-8,L

17	82	82
14	38	44
11	95	-93
10	124	-127
9	138	131
8	167	160
6	102	-99
5	326	331
4	243	-248
3	131	134
2	290	287
1	297	-313
0	156	-161
-1	206	212
-3	218	226
-4	106	106
-5	61	61
-6	370	-371
-7	63	-62
-10	112	112
-11	190	-184
-12	142	-137
-13	137	139
-14	71	65
-17	89	90

-2,-9,L

17	100	-82
15	64	-42
13	149	-157
12	162	162
11	199	202
7	62	60
5	132	130
3	230	-230
2	90	97
1	80	-83
0	235	238
-1	415	421
-2	166	-167
-3	43	-50
-5	144	134
-6	49	-56
-8	50	-57
-9	130	-124
-10	188	189
-11	98	101
-13	154	158

-2,-10,L

15	71	60
13	47	58
12	61	59
10	193	-191
9	58	50
8	75	84
7	223	-221
6	75	70
3	131	142
2	160	161
1	244	-243
0	134	-136

-2,-10,L

-1	116	110
-2	78	-81
-4	84	79
-5	243	-235
-7	59	66
-9	78	75
-10	90	81
-12	160	-162
-14	64	55
-15	69	-65

-2,-11,L

7	68	-67
6	137	139
4	126	-127
3	62	60
1	78	-72
0	43	-51
-1	83	86
-2	52	-47
-3	128	-124
-4	148	146
-6	130	125
-7	141	136
-8	131	-130

-2,-12,L

4	110	-106
3	89	85
1	160	-148
-2	66	58
-3	105	91
-5	60	-58
-6	92	-81
-7	81	76
-8	73	-72
-9	43	-31

-3,0,L

22	281	279
16	84	91
12	68	64
10	60	51
8	333	299
6	739	-703
4	625	-571
2	509	437
0	301	294
-2	1944	-1828
-4	183	-166
-6	301	-281
-8	248	225
-10	333	325
-14	228	-246
-18	210	-221
-22	224	227

-3,-1,L

24	66	55
22	117	-114
20	71	-89
18	81	-78
17	65	62
16	157	160
15	154	-153
13	318	317
12	275	261
11	482	-475
9	202	204
8	504	-482
7	114	108
6	618	-565
5	228	210
4	149	143
3	69	-56
2	131	-110
1	531	-467
0	396	362
-1	564	492
-2	897	-816
-4	372	-368
-6	131	124
-7	375	371
-8	255	-234
-9	66	-66
-10	169	178
-11	274	-273
-12	199	-198
-13	376	385
-14	291	-300
-15	135	-130
-16	182	-186
-18	245	251
-19	133	127
-21	34	-21
-23	81	-81

-3,-2,L

21	91	100
20	128	-122
19	97	-97
17	215	223
16	181	184
15	67	-70
14	168	-170
13	195	-192
12	149	-156
11	77	77
10	359	-337
9	239	247
8	52	-33
7	122	-122
6	321	313
5	116	-118
4	97	-98
3	306	294
2	162	-156
1	756	-715
0	380	347
-1	653	615
-2	256	-254
-4	524	490
-5	74	-68
-6	267	273
-7	88	-91
-8	429	-410
-9	223	217
-10	75	78
-11	167	-174
-12	137	-153
-13	210	215
-14	53	-43
-15	42	-53
-16	423	441
-20	82	-78
-21	45	-57
-22	67	60
-23	50	49

-3,-3,L

23	39	39
20	176	173
19	87	85
17	173	-172
16	50	49
15	41	-49
14	70	-74
13	234	234
12	291	309
11	192	183
9	118	-98
8	267	260
7	155	143
6	154	137
5	365	-368
4	199	173
3	276	276
2	60	-76
1	161	151
0	602	576
-1	246	226
-2	605	-567
-3	97	108
-4	260	233
-5	588	-589
-6	144	139
-7	67	-53
-8	750	-751
-9	138	141
-10	102	88
-11	142	-136
-12	194	196
-13	44	48
-14	215	220
-16	145	-154
-17	237	-244
-19	57	65
-20	251	-252
-22	88	74
-23	44	41

-3,-4,L

22	102	93
20	61	65
19	229	-231
18	149	-156
15	58	45
14	144	-149
13	87	-90
12	351	343
11	178	-183
10	394	395
9	143	-142
8	117	-125
7	105	-114
6	294	283
4	187	-179
3	132	153
2	80	-74
1	218	-203
0	466	464
-2	228	211

-3,-4,L

-3	244	-235
-4	513	-517
-5	125	-127
-6	450	450
-7	70	75
-8	410	-419
-9	440	439
-10	277	283
-11	278	-282
-13	79	-85
-14	203	-207
-17	37	-38
-18	174	-174
-19	119	122
-20	65	-67

-3,-5,L

22	53	-52
21	121	-124
19	146	136
17	47	-49
16	129	-125
15	282	279
14	40	-42
13	226	-228
12	65	-56
11	322	-326
10	139	-143
7	378	377
6	42	-29
5	424	-413
4	306	-273
3	385	399
2	35	50
1	430	-426
0	87	78
-1	452	-451
-2	245	-222
-3	421	438
-4	130	107
-5	153	-147
-6	384	378
-7	286	279
-9	110	103
-10	104	-109
-11	246	-250
-12	46	41
-13	38	23
-14	106	-113
-15	257	265
-17	64	-66
-18	141	137
-19	164	167
-21	89	-88

-3,-6,L

19	116	112
18	103	-95
16	178	178
14	125	-123
13	105	-109
11	171	172
9	278	288
8	381	-384
7	61	60
6	359	364
4	55	-64
3	274	-286
2	275	-277
1	268	254
0	119	122
-1	88	80
-2	178	183
-3	388	401
-4	203	-196
-6	341	345
-7	139	-140
-8	266	-262
-9	83	-83
-11	30	26
-12	149	145
-13	80	77
-14	37	-25
-15	179	180
-17	122	-121
-18	76	69
-19	84	-83
-20	47	46

-3,-7,L

19	94	89
17	207	-202
15	64	69
14	82	84
13	62	62
12	188	-190
11	82	-85
10	162	162
9	295	297
8	115	-111
7	174	-178
6	91	86
5	495	-507
3	386	385
2	67	63
1	139	136
0	73	-75
-1	117	-114
-2	52	52
-3	89	78
-4	183	-189
-5	388	-395
-6	54	68
-7	35	-21
-8	116	103
-9	116	129
-10	156	-155
-12	232	240
-14	110	-115
-16	52	42
-17	149	-149

-3,-8,L

16	100	101
15	91	84
14	120	-122
13	103	90
10	64	57
9	157	-161
8	213	-226
7	114	-127
6	285	289
3	91	96
2	235	-230
1	223	228
0	167	167
-1	489	-502
-2	270	-278
-3	116	-121
-4	29	-26
-5	117	-101
-6	139	135
-10	72	-75
-11	47	51
-13	167	-173
-14	85	-89
-15	64	-65

-3,-9,L

13	49	51
12	133	-131
11	248	-240
10	236	232
9	222	222
7	51	61
6	81	-76
3	47	59
2	96	-89
1	77	-84
-1	96	-96
-2	181	177
-3	260	269
-5	109	107
-9	65	70
-10	106	-104
-11	156	-159
-12	89	95
-15	50	47

-3,-10,L

13	42	42
12	87	87
10	94	93
8	154	-154
7	191	192
5	163	-157
2	154	-154
1	135	129
0	276	267
-1	87	-88
-2	60	-62
-3	181	188
-5	181	179
-6	135	-143
-7	93	-95
-11	51	47
-12	81	76
-13	73	74

-3,-11,L

9	59	52
7	66	-71
6	91	-83
4	156	152
3	54	49
-3	60	59
-4	150	-143
-5	107	-111
-7	86	-80
-8	102	104
-9	98	100
-11	63	-48

-3,-12,L

7	93	84
5	91	-86
4	55	60
2	70	-62
-1	59	-55
-2	91	-90
-3	99	-85
-4	75	71
-5	86	85
-6	128	119

-4,0,L

22	86	-90
20	198	204
14	114	-107
12	399	-392
10	308	307
8	396	-375
6	657	614
4	81	-66
2	746	-661
0	63	26
-2	1595	1455
-4	417	-368
-6	646	634
-8	416	414
-10	404	-399
-12	280	279
-14	177	190
-16	128	143
-18	76	100
-22	174	-170

-4,-1,L

22	140	143
21	66	-57
19	67	74
17	99	-99
16	98	-86
15	31	-13
14	137	150
13	90	95
12	194	-182
11	199	195
10	348	351
9	364	-367
8	206	-186
7	433	421
6	842	-804
5	388	-350
4	37	-30
3	206	172
2	90	87
1	457	423
0	720	657
-1	734	-658
-3	523	484
-4	774	-707
-6	583	-566
-7	66	-74
-8	220	220
-11	254	252
-12	199	202
-13	415	-409
-15	228	235
-16	117	-109
-17	55	-61
-18	122	-128
-19	96	-91
-21	116	106
-22	70	64

-4,-2,L

21	35	-41
18	174	-179
16	109	106
14	105	101
13	116	113
12	105	-106
11	364	-373
10	87	74
8	450	-440
7	83	-86
6	57	41
5	537	509
4	429	402
3	504	-473
2	255	-228
1	460	423
0	297	-264
-1	576	-519
-2	63	70
-3	54	45
-4	1092	-1051
-5	316	298
-7	186	184
-8	292	300
-9	67	-63
-10	170	-167
-11	88	-90
-12	156	160
-13	138	131
-14	271	-278
-15	165	-154
-16	195	-204
-17	181	186
-18	110	99
-20	63	60

-4,-3,L

20	171	-171
18	98	103
17	183	183
15	194	-196
14	274	270
12	468	-473
11	200	204
10	192	181
9	144	-141
7	226	228
6	237	-230
5	111	108
4	560	535
3	264	-266
2	403	-372
1	234	228
0	437	-423
-1	230	-228
-2	269	-267
-4	209	203
-5	503	491
-6	125	-133
-7	566	-561
-8	496	494
-9	50	-51
-10	341	-337
-11	139	144
-12	144	-150
-13	119	-113
-14	123	116
-15	192	191
-16	65	68
-17	59	58
-19	144	-146
-20	75	76
-21	33	35

-4,-4,L

20	149	148
17	130	-130
15	188	-183
14	59	55
13	222	233
12	137	143
11	168	163
10	222	222
9	104	108
8	303	313
6	513	-508
5	235	226
4	456	434
3	570	-561
2	162	-168
1	441	432
-1	252	242
-2	643	618
-4	174	173
-5	90	93
-6	127	-121
-7	303	-291
-8	53	-60
-10	286	-294
-11	216	219
-12	167	173
-13	129	122
-14	105	106
-15	194	-194
-18	105	115
-19	116	-114
-20	176	-172

-4,-5,L

19	180	-180
17	138	146
16	90	-83
15	139	-136
13	179	190
12	35	-25
11	73	-78
10	140	148
9	384	-384
8	88	88
7	82	-79
6	152	-149
5	79	81
3	225	-204
2	64	79
1	177	174
0	239	221
-2	276	274
-3	450	-447
-5	139	131
-6	448	-459

-4,-5,L

-7	201	-204
-8	242	250
-9	497	504
-10	58	61
-12	219	-223
-13	166	-160
-14	146	153
-15	113	-118
-18	64	-68
-20	50	-50
-21	90	91

-4,-6,L

20	86	77
18	78	-75
16	60	-63
15	124	122
14	131	132
12	183	-183
11	91	-97
10	135	-135
9	248	-248
8	299	294
7	80	82
6	363	-364
5	271	272
4	301	296
1	221	-224
0	244	-237
-1	115	115
-2	64	-59
-3	355	-356
-5	279	285
-6	86	-87
-7	159	160
-8	152	161
-9	135	-134
-10	29	-27
-11	102	-97
-12	95	-100
-13	117	-109
-16	117	-118
-17	148	151

-4,-7,L

18	94	-96
17	115	112
15	204	-205
12	46	43
10	86	-85
8	160	160
7	337	341
5	72	70
4	77	-82
3	311	-309
2	80	89
0	217	-214
-2	124	127
-3	103	101
-4	90	86
-5	185	183
-6	74	78
-7	77	-93
-11	112	-111
-12	101	-103
-13	109	107
-14	138	137
-15	201	193
-16	53	-63

-4,-8,L

16	61	-60
14	164	156
13	80	-82
12	117	-115
11	194	188
8	40	-43
7	56	-63
6	177	-174
5	224	-231
4	108	102
2	103	101
0	102	-89
-1	247	255
-3	247	-244
-5	160	-157
-6	46	50
-9	63	-62
-11	165	155
-13	71	67
-17	120	-117

-4,-9,L

14	78	71
13	80	84
11	145	144
10	248	-233
9	173	-170
8	61	61
7	46	-40
6	81	76
5	45	24
4	64	-70
2	112	115
1	130	135
0	95	-93
-1	71	-74
-2	43	-40
-3	106	-111
-4	58	-58
-5	112	-108
-6	49	44
-9	53	45
-10	61	50
-11	71	76
-13	159	-159
-15	60	-54

-4,-10,L

13	111	-106
12	163	-162
10	112	113
9	66	-61
8	55	59
5	125	126
0	110	-103
-2	95	91
-5	52	55
-7	147	144
-10	79	-72
-11	78	-79
-13	90	-83

-4,-11,L

8	50	47
7	61	55
4	131	-130
3	54	-54
2	37	38
1	88	87
0	56	51
-1	51	-63
-3	84	82
-5	76	79
-6	92	-92
-7	85	-71
-8	44	-39

-4,-12,L

5	56	54
4	53	60
3	58	-49
-1	63	63
-2	42	31
-4	123	-115
-5	65	-59

-5,0,L

22	181	-183
20	62	70
14	70	61
12	67	59
10	752	-732
8	485	461
6	38	24
4	493	462
2	878	814
0	805	-722
-2	264	-245
-4	714	676
-6	351	357
-8	189	187
-10	357	353
-12	593	-593
-16	104	108
-18	75	81
-20	86	81

-5,-1,L

22	77	-81
21	112	105
20	112	117
19	113	-115
18	143	138
17	118	121
14	116	-121
13	320	-322
12	190	-187
11	431	434
10	175	-164
8	259	247
7	195	-197
6	286	270
5	56	57
4	244	-219
2	113	-100
1	367	-350
0	439	-402
-1	735	656
-3	344	-308

-5,-7,L

-1	234	-234
-2	85	-89
-4	173	173
-5	229	234
-6	43	-59
-7	64	65
-8	65	58
-9	61	59
-10	54	54
-11	83	75
-13	122	-119
-15	73	-79
-17	162	156

-5,-8,L

15	43	-39
14	92	-87
11	230	-228
10	65	-66
9	133	121
8	80	81
7	104	114
5	44	61
3	164	-169
2	62	-57
1	209	-214
-1	52	62
-2	33	27
-3	122	128
-5	75	65
-8	110	104
-11	150	-147
-12	82	-82
-13	52	54
-14	85	82

-5,-9,L

14	56	-57
12	68	74
11	89	91
9	85	79
8	82	-85
7	80	-83
6	71	-71
5	186	-190
3	109	-122
0	41	44
-1	202	210
-2	76	-66
-3	143	-153
-6	40	-40
-7	184	-183
-8	63	71
-9	134	-131
-11	66	67
-13	74	65

-5,-10,L

11	46	31
10	135	-133
9	68	-62
8	50	51
7	51	-52
6	65	-65
3	45	37
2	77	69
1	79	73
0	68	-59
-1	39	41
-3	98	-99
-5	62	-64
-10	56	55
-11	78	65

-5,-11,L

8	47	-40
6	77	74
5	95	96
3	64	64
1	89	-84
0	105	-105
-1	48	45
-3	154	-153
-4	62	62
-5	89	88
-7	101	100
-8	86	-86

-6,0,L

20	181	-186
16	181	-184
14	164	-175
12	297	298
10	332	322
8	548	-528
6	163	-167
4	116	108
0	362	327
-2	378	-345
-4	85	-76
-6	164	-159
-8	214	-241
-10	260	-283
-12	218	217
-14	104	-103
-18	148	-152

-6,-1,L

20	81	-79
19	108	101
18	58	-65
17	86	-90
16	88	85
15	48	60
14	105	102
13	239	237
12	96	103
11	442	-445
10	346	-344
9	260	259
8	78	-75
7	142	135
6	97	99
5	212	-198
4	792	747
2	270	260
1	213	205
0	146	-132
-1	476	-444
-3	353	325
-4	127	117
-6	66	67
-7	241	-235
-8	464	465
-9	139	122
-10	384	391
-11	134	-123
-12	63	-53
-13	46	45
-18	156	162
-20	70	72

-6,-2,L

21	44	35
18	159	165
15	264	-273
14	143	-135
13	146	153
12	156	-160
10	127	130
9	123	114
8	81	87
7	267	258
6	560	537
5	75	-62
4	87	75
3	221	-211
2	418	-381
1	153	-152
0	313	286
-1	387	364
-3	269	-257
-4	94	90
-5	284	274
-6	432	421
-7	285	-280
-8	222	243
-9	75	-79
-10	56	-53
-14	41	-28
-16	166	173
-19	37	-47

-6,-3,L

20	59	58
17	237	-245
15	48	55
14	232	-243
13	138	127
11	209	-222
8	265	263
6	449	-434
5	468	-456
4	61	52
3	199	183
2	310	-296
0	160	-153
-1	100	103
-2	165	157
-3	36	38
-4	203	202
-5	406	-390
-6	178	-159
-7	189	187
-8	237	-235
-9	171	177
-10	53	-61
-11	75	-85
-12	172	-171
-13	128	127
-14	149	149

-6,-3,L

-15	77	-72
-16	109	-112
-17	86	-89
-18	76	-69
-20	65	-59

-6,-4,L

19	87	-92
18	236	-245
17	176	180
16	53	33
15	51	-58
13	175	173
12	131	127
10	79	-68
9	198	-194
8	467	-469
6	106	-107
5	64	-63
4	213	-210
3	69	72
1	322	313
0	197	199
-1	67	66
-2	223	-220
-3	626	-616
-4	279	-276
-5	363	359
-7	141	136
-8	306	-304
-10	156	164
-11	41	31
-13	59	-64
-17	49	51
-18	78	-80
-19	99	97

-6,-5,L

19	155	157
18	75	-74
16	98	95
14	127	123
13	105	-109
10	56	57
9	46	46
7	326	328
6	179	-177
5	109	106
4	331	328
3	347	346
2	111	106
1	347	-341
0	86	-70
-3	214	199
-4	107	-116
-5	62	62
-6	108	119
-7	276	274
-9	165	-159
-10	177	172
-11	227	-225
-12	53	59
-13	113	114
-15	76	75
-17	52	-43

-6,-6,L

16	161	165
15	113	-110
14	72	-78
13	69	-66
11	30	32
8	94	89
7	201	195
6	309	310
5	156	-153
4	179	-181
3	303	-301
0	84	78
-2	66	-75
-3	102	105
-4	104	105
-6	141	141
-7	181	-184
-8	182	-189
-9	167	-174
-10	246	248
-11	74	75
-12	47	-59
-13	73	69
-14	130	-123
-16	128	121
-17	120	-121

-6,-7,L

17	96	-93
14	67	57
12	120	-119
11	165	170
10	146	143
9	39	42
7	267	-266
6	50	-51
5	198	-203
4	85	-85
3	64	68
0	79	-81
-1	125	133
-2	57	55
-5	319	-314
-7	66	64
-8	87	-89
-10	96	-93
-13	69	78
-14	73	-74
-15	72	-60

-6,-8,L

9	140	-135
7	57	-62
6	71	76
5	94	103
4	65	-59
3	237	239
1	146	144
0	59	56
-1	194	-196
-2	102	-90
-3	87	98
-4	93	85
-6	63	72
-7	195	196
-8	163	-159
-9	157	156
-13	70	-63
-14	117	-109

-6,-9,L

11	133	-131
10	91	91
9	87	87
6	40	47
5	135	136
3	78	75
1	147	-152
0	75	72
-3	129	127
-7	120	122
-11	153	-146
-12	105	108

-6,-10,L

9	98	99
8	60	-56
5	59	-53
3	87	-86
1	95	-88
0	175	172
-1	55	-45
-2	102	-94
-3	137	136
-7	168	-167

-6,-11,L

5	121	-111
0	40	48
-2	88	-90
-4	68	-58

-7,0,L

20	215	212
14	51	68
12	191	-183
10	159	161
8	451	438
6	421	430
4	401	-378
2	107	-116
0	182	-177
-2	265	250
-4	67	58
-8	235	-245
-10	77	-83
-12	187	186
-16	108	96

-7,-1,L

16	188	-188
14	88	-96
12	118	113
11	229	228
10	302	291
9	349	-349
8	55	57
6	139	-131
5	145	146
4	343	-326
3	137	-149
2	78	61

-7,-1,L

1	49	59
0	306	286
-2	91	-78
-3	39	-26
-5	70	-74
-8	62	61
-10	66	56
-11	117	128
-12	69	60
-13	115	-108
-15	113	112
-17	77	-79

-7,-2,L

18	88	-88
17	82	86
15	95	89
14	180	175
12	52	-49
11	131	-129
9	203	202
8	216	-216
6	340	-337
5	43	36
4	75	58
2	265	256
1	163	-155
-1	184	-178
-3	277	257
-4	279	-270
-5	123	-123
-6	74	66
-8	175	168
-10	88	-85
-11	64	-55
-13	100	-102
-14	187	-194
-17	47	42
-18	90	96

-7,-3,L

19	70	80
18	197	189
17	98	96
15	210	-213
12	63	-56
11	76	76
10	134	-126
8	134	-121
7	159	155
6	393	382
5	85	86
4	238	238
3	140	-123
2	31	-17
1	42	36
0	50	37
-1	103	-96
-2	193	-187
-3	295	292
-4	110	101
-5	127	124
-6	240	241
-7	180	-182
-9	112	112
-10	192	-197
-11	118	-119
-12	67	70
-15	112	112

-7,-4,L

17	144	-141
16	55	-63
12	150	-144
9	68	58
8	92	94
7	252	-247
5	97	-89
4	404	408
2	411	-404
1	52	-52
-1	167	165
-2	259	256
-3	47	44
-5	256	-252
-7	120	-113
-8	119	120
-10	62	-54
-11	108	107
-12	173	181
-14	56	47

-7,-5,L

17	64	71
16	104	-103
13	216	210
12	127	128
11	59	-61
9	105	-103
7	105	105
6	135	-130
4	194	-192
2	114	-115
1	303	295
0	199	194
-1	214	-206
-3	132	-135
-4	281	-289
-5	59	64
-6	124	132
-7	238	-233
-8	101	105
-9	316	321
-10	53	-58
-13	144	-147

-7,-6,L

15	133	137
13	77	-83
12	48	-46
11	144	-147
10	99	101
9	50	-50
8	122	-123
7	189	195
6	280	-285
5	118	119
4	202	207
3	37	39
2	208	-210
1	106	-111
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-3	98	-101
-4	163	-169
-5	207	207
-7	95	98
-9	77	79
-10	183	-181
-11	52	-57
-12	62	52
-13	115	-114
-15	85	84
-16	114	-109

-7,-7,L

15	99	-92
12	72	73
10	115	-121
9	98	95
8	97	94
7	185	184
6	56	-58
5	193	-197
4	36	24
3	173	-174
1	139	136
0	72	-75
-1	81	-78
-2	101	99
-4	96	-97
-5	247	246
-6	64	-67
-7	212	-213
-8	45	-47
-9	64	-67
-12	58	-57
-14	65	69

-7,-8,L

12	34	-38
11	154	160
10	91	90
5	98	-104
4	211	212
1	97	98
0	120	-126
-1	95	97
-2	170	172
-3	88	-95
-4	133	-135
-5	60	57
-7	135	-134
-8	130	125
-9	61	-63
-10	87	-86
-11	112	103

-7,-9,L

10	49	-43
9	182	-183
8	83	92
7	47	46
1	133	136
0	132	-131
-1	73	-65
-2	49	53
-3	81	-79
-4	45	61
-9	103	101

-7,-10,L

3	86	-81
0	93	-91
-2	189	184
-3	97	-99
-4	45	-48
-5	71	79

-8,0,L

16	200	207
12	48	55
10	163	-165
8	33	26
6	43	-44
4	125	109
2	196	-204
0	224	-210
-8	178	171
-10	76	-82
-12	248	-241
-14	130	133

-8,-1,L

18	70	66
15	43	-28
14	144	-143
12	117	-123
8	85	74
7	69	-76
6	77	-92
5	67	-63
4	165	-165
2	90	-87
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-3	291	-265
-4	80	75
-5	191	185
-8	255	-270
-9	148	-135
-10	165	-185
-11	192	195
-12	127	-142
-14	68	62
-15	74	-79
-17	93	97

-8,-2,L

17	45	-50
16	139	-140
14	105	-108
13	44	45
12	92	95
11	203	205
9	237	-237
8	91	84
7	46	41
6	146	-143
5	160	-161
3	51	47
2	117	105
1	67	67
0	66	-71
-2	253	241
-3	114	-105
-4	91	105
-6	335	-323
-7	95	89
-9	107	-107
-10	106	91
-11	103	100
-14	126	125
-16	106	-108
-17	48	-50

-8,-3,L

16	117	120
15	125	119
14	96	98
13	80	-78
11	43	28
10	66	73
8	204	204
7	68	-66
5	293	287
2	290	285
-1	97	-94
-2	199	214
-3	106	-99
-4	118	-124
-5	177	171
-7	64	51
-8	105	110
-9	181	-198
-10	261	275
-12	83	-89
-13	84	-79
-14	56	-55
-15	79	-90
-16	62	60

-8,-4,L

15	53	-50
14	110	113
13	113	-111
12	63	-67
10	94	-93
9	118	-133
8	106	109
7	116	114
5	71	77
4	44	-39
3	75	-67
2	325	320
1	280	-288
0	284	-282
-1	107	100
-2	121	-124
-3	69	77
-4	220	218
-5	68	-75
-7	97	95
-8	104	99
-9	223	-222
-12	112	-114
-13	51	58

-8,-5,L

15	32	-14
14	61	-59
13	161	-157
11	204	200
10	54	-58
9	162	171
8	59	-69
7	185	-197
6	117	-115
5	52	47
3	298	-301
2	67	67
0	213	-222
-1	239	229
-2	62	69
-4	68	67
-5	118	-117
-6	128	-122
-9	86	-91
-11	146	145
-12	63	-56
-13	91	89

-8,-6,L

13	117	124
11	94	94
10	78	-80
7	181	-177
5	103	110
4	178	-176
3	175	176
2	201	206
-1	88	92
-2	123	-122
-4	148	142
-5	93	-93
-6	104	-100
-7	153	165
-9	67	68
-10	84	86
-11	64	52

-8,-7,L

12	58	59
9	107	-117
7	127	-126
6	82	83
5	297	305
4	71	-74
1	173	-173
0	54	54
-2	73	-75
-3	60	-59
-4	127	128
-7	129	126
-9	60	-63
-10	58	64
-11	90	-82

-8,-8,L

10	64	-71
9	141	139
8	106	110
4	155	-167
3	95	-99
2	89	84
1	140	-149
-2	96	-103
-3	54	58
-4	138	133
-6	96	-96
-8	45	-48

-8,-9,L

0	91	101
-1	146	143
-2	125	-130

-9,0,L

16	146	-140
12	192	184
8	309	-303
2	85	79
0	298	296
-2	235	-227
-6	71	71
-10	212	209
-12	176	201
-14	186	-190

-9,-1,L

14	141	142
12	124	141
11	128	-144
10	168	-174
9	167	179
8	76	-73
6	199	202
4	207	207
3	136	133
2	38	-54
1	153	-136
-2	100	-82
-3	233	229
-5	268	-271
-6	180	177
-7	157	168
-8	77	70
-9	88	97
-10	68	-81
-11	206	-206
-12	96	-103
-13	104	100
-14	102	-103

-9,-2,L

15	82	-72
10	56	-60
8	69	78
6	240	231
5	177	-180
4	196	-189
2	136	-135
0	101	97
-2	216	-225
-3	62	62
-4	126	116
-6	110	111
-7	166	-163
-8	220	-221
-9	74	73
-10	106	-112
-15	88	86

-9,-3,L

15	61	65
14	160	-163
13	73	80
11	77	-82
9	132	142
6	46	-55
5	188	-194
4	153	-167
3	167	160
2	224	-227
0	138	125
-2	61	59
-4	139	-139
-5	166	-169
-8	107	-111
-9	107	110
-12	167	176
-13	82	85

-9,-4,L

14	54	-57
12	132	127
11	59	-58
8	85	-73
6	100	98
5	84	-85
3	315	319
1	75	76
0	181	181
-1	267	-271
-2	126	-117
-4	71	-76
-5	68	75
-6	122	125
-9	135	140
-10	120	121
-11	40	-48
-13	85	-90

-9,-5,L

11	115	-113
8	72	-73
7	64	59
6	115	122
4	144	151
3	38	41
1	210	-217
-1	75	-70
-3	54	45
-5	104	111
-6	131	137
-9	79	-88
-10	69	-68
-11	114	-113

-9,-6,L

10	57	64
9	45	44
8	72	-76
7	88	92
6	58	62
5	199	-210
2	127	-128
0	121	123
-2	62	69
-3	151	163
-4	94	-101
-7	136	-143
-9	92	-90

-9,-7,L

9	42	-32
8	108	-120
5	74	-70
3	133	144
1	124	124
-4	84	-89
-5	76	-68

-9,-8,L

5	50	53
2	103	-102
1	54	56
-1	116	-120

-10,0,L

12	156	-164
10	183	188
6	171	-171
2	119	-106
0	99	-91
-2	447	463
-10	197	-194
-12	72	75

-10,-1,L

13	74	86
12	60	64
11	50	45
9	200	-208
8	105	-111
7	182	191
6	108	-104
4	34	-23
3	52	-57
2	179	172
1	190	190
0	126	124
-1	157	-156
-2	77	89
-5	102	106
-6	163	-164
-7	102	-105
-10	93	103
-12	127	145

-10,-2,L

13	75	-69
9	83	-75
8	101	-104
6	72	-70
5	203	218
4	237	237
3	133	-134
2	51	61
0	123	-127
-1	86	87
-4	211	-215
-7	109	112
-8	210	224

-10,-3,L

12	95	-99
7	137	146
4	74	-85

-10,-3,L

3	246	-261
1	59	56
0	263	-271
-4	155	163
-5	60	55
-7	133	-136
-8	52	46
-10	73	-78

-10,-4,L

11	112	117
8	71	84
3	120	-135
2	180	-200
1	142	153
-1	120	123
-2	144	154
-3	72	-73
-5	102	-103
-7	65	75
-10	85	-90

-10,-5,L

9	85	-96
8	60	60
7	95	-102
6	57	-48
3	86	102
2	201	205
1	59	62
-3	87	-85
-5	35	6
-6	74	-79

-10,-6,L

7	97	103
5	100	111
4	153	173
3	75	-92
1	98	-95
-1	34	-34
-3	33	-35

-11,0,L

8	96	100
6	124	140
2	104	105
0	90	-84
-2	167	-188
-4	112	108

-11,-1,L

9	86	93
8	68	83
7	134	-137
6	85	96
2	145	-154
-1	72	66
-2	90	99

-11,-2,L

8	61	60
6	63	-73
4	180	-180
3	165	176
2	66	72
0	114	118
-6	97	-85

-11,-3,L

7	65	-93
6	60	-59
5	98	101
2	72	78
1	74	-79
0	92	96
-4	142	-150
-5	55	67

-11,-4,L

0	159	-169
-3	154	160

A P P E N D I X 9

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR N-DIPHENYLPHOSPHINOYL-P-TRIPHENYLPHOSPHAZENE

24,5,L

1	128	131	71

24,4,L

2	35	41	170
1	41	39	175
0	69	63	180

24,3,L

1	30	31	26

24,2,L

2	59	60	170
0	48	54	180

24,1,L

1	51	52	273

24,0,L

3	81	83	250
2	54	56	285
1	57	63	186
0	88	89	0

23,8,L

1	78	80	278
0	67	60	180

23,7,L

2	68	61	13
1	67	74	85

23,6,L

2	96	94	137
1	36	37	216
0	117	120	180

23,5,L

0	55	57	0

23,4,L

4	87	84	152
2	105	105	168
1	52	45	70

23,3,L

3	50	49	258
1	90	91	255
0	72	71	180

23,2,L

4	31	33	169
3	99	99	266
1	61	61	280

23,1,L

4	99	101	7
3	75	79	267
2	70	65	0
1	75	77	296

22,10,L

1	59	55	284
0	76	69	180

22,9,L

2	33	30	358
1	54	57	271
0	41	36	0

22,8,L

3	54	54	39
2	70	69	176
1	48	46	235
0	92	91	180

22,7,L

4	80	79	37
3	51	46	261
1	150	153	273
0	43	44	0

22,6,L

3	55	51	76
1	65	62	66
0	43	54	0

22,5,L

2	51	46	162
1	62	60	247
0	96	101	180

22,4,L

5	56	51	216
4	28	26	113
3	54	53	269
1	50	54	306

22,3,L

5	92	94	238
3	58	58	283
2	56	55	30
1	90	93	257
0	116	116	180

22,2,L

5	41	36	255
4	74	71	284
2	84	79	40
1	66	70	279
0	70	77	0

22,1,L

5	66	74	274
4	35	42	280
3	69	79	265
2	63	72	14
1	86	88	240

22,0,L

5	44	51	56
4	137	134	345
2	174	171	345
1	34	33	53
0	184	181	0

21,11,L

2	48	37	38
1	82	74	291

21,10,L

2	42	45	163

21,9,L

4	61	57	178
3	156	154	281
2	60	62	239
1	144	141	276
0	33	42	0

21,8,L

4	125	123	356
2	138	141	17
1	61	63	293
0	153	147	0

21,7,L

4	44	42	220
2	52	55	120

21,6,L

3	44	52	333
2	110	106	339
1	45	45	352
0	67	69	0

21,5,L

6	41	37	281
5	38	41	131
2	54	56	111
1	31	32	123

21,4,L

5	39	47	239
4	53	54	260
3	45	50	20
1	40	47	346
0	34	33	0

21,3,L

5	56	59	324
3	48	52	224
2	64	62	140
1	88	90	219

21,2,L

6	77	82	335
5	46	34	308
4	112	109	354
3	28	22	259
2	122	124	321
1	70	72	307
0	161	158	0

21,1,L

6	34	37	343
5	117	119	50
3	71	65	75
1	134	131	90

20,12,L

2	40	44	7
0	51	50	0

20,11,L

3	72	72	266
2	85	86	188
1	67	67	268
0	52	54	180

20,10,L

4	95	96	355
3	131	134	285
2	109	111	337
1	66	65	286
0	142	149	0

20,9,L

5	54	53	71
3	59	59	88
2	122	119	336

20,8,L

4	33	36	305
3	77	80	254
2	94	88	343
1	48	43	322
0	70	67	0

20,7,L

6	85	80	25
5	70	74	69
3	114	110	62
2	108	105	3
1	118	121	84
0	147	153	0

20,6,L

5	66	67	73
4	67	74	236
3	87	92	135
1	110	113	117
0	49	52	180

20,5,L

6	73	72	195
5	64	70	53
3	48	49	31
2	132	135	196
1	86	86	68

20,4,L

4	51	51	96
3	82	81	234
2	60	65	204
1	35	39	218
0	119	110	180

20,3,L

4	41	42	277
3	112	108	50
1	61	65	35
0	78	78	0

20,2,L

7	40	46	293
6	49	51	149
5	68	64	324
4	74	78	159
3	43	45	281
2	100	100	164
0	57	59	180

20,1,L

7	32	37	62
6	70	67	11

20,1,L

5	56	60	50
2	107	107	322
1	48	53	116
0	139	146	0

20,0,L

7	99	96	67
6	135	130	152
4	102	101	124
3	151	152	53
2	112	111	181
1	141	143	104
0	187	196	180

19,14,L

0	43	45	0

19,13,L

3	85	79	86
2	31	32	190
1	59	57	63
0	60	61	180

19,12,L

1	137	137	281

19,11,L

5	69	65	59
4	37	42	9
3	68	70	74
2	53	53	16
1	70	69	91

19,10,L

3	61	64	287
2	63	63	231
1	48	42	341
0	36	39	180

19,9,L

4	124	123	356
3	55	56	40
2	124	125	359
0	83	88	0

19,8,L

5	66	67	100
4	79	77	24
3	132	134	71
2	36	47	134
1	132	133	93

19,7,L

7	66	62	51
6	70	66	196
5	105	106	79
3	136	131	101
2	74	75	214
1	94	93	90
0	75	73	180

19,6,L

6	75	75	151
4	89	87	136
3	54	42	16
2	114	117	192
1	67	73	71
0	164	162	180

19,5,L

6	85	81	212
5	59	64	133
4	51	52	189
3	81	78	111
2	79	80	195
0	115	119	180

19,4,L

6	94	94	160
5	74	70	352
4	154	157	188
3	60	61	270
2	137	138	146
1	51	53	270
0	292	297	180

19,3,L

7	71	69	271
6	70	74	49
5	97	97	253
3	152	142	247
1	126	129	271
0	25	26	0

19,2,L

7	89	86	72
5	69	70	71
4	52	56	55
3	69	73	40
1	62	65	126

19,1,L

8	35	41	95
7	81	84	219
6	87	81	154
5	124	119	241
4	120	118	153
3	51	56	292
2	82	82	180

18,14,L

0	62	64	180

18,13,L

4	45	43	10
3	87	88	82
0	70	73	0

18,12,L

5	59	65	79
4	105	103	157
3	42	41	107
2	100	99	174
1	47	48	70
0	136	130	180

18,11,L

5	45	46	274
4	41	34	14
3	65	70	307
2	45	48	142
1	63	61	285

18,10,L

3	51	51	97
2	60	56	86

18,10,L

1	47	52	92

18,9,L

5	42	51	125
4	37	34	335
3	67	68	65
1	49	40	39
0	87	94	180

18,8,L

7	62	50	6
6	36	26	177
5	44	42	120
4	105	103	162
3	130	131	91
2	74	83	137
0	48	55	180

18,7,L

7	62	61	179
5	35	32	201
4	37	40	208
2	76	73	195
1	80	74	68

18,6,L

8	71	74	174
7	54	54	75
6	90	96	181
5	70	67	86
4	197	197	185
3	66	65	84
2	199	198	175
1	99	107	162
0	117	115	180

18,5,L

8	53	51	189
7	114	117	248
6	99	101	155
5	199	201	240
4	66	59	163
3	190	181	275
2	74	70	215
1	255	255	273
0	199	206	180

18,4,L

8	68	68	358
6	83	79	311
5	94	93	233
4	75	76	359
3	43	50	13
2	52	57	62
0	138	140	0

18,3,L

8	80	75	156
7	66	64	263
5	47	54	238
4	64	68	191
3	90	91	249
2	31	30	42
1	173	169	280
0	103	116	180

18,2,L

8	81	83	350
7	47	47	217
6	131	131	329
5	42	41	268
4	57	56	341
3	129	131	245
2	166	163	8
1	40	35	80
0	265	270	0

18,1,L

7	71	67	104
5	67	68	98
4	40	47	73
3	51	43	172
2	51	37	255
1	57	54	54
0	48	47	0

18,0,L

8	62	70	255
7	92	95	220
5	42	41	260
4	35	41	278
3	95	93	198
2	120	126	43
1	82	76	60
0	52	53	180

17,15,L

2	49	54	1

17,14,L

4	59	59	155
3	93	84	62
2	75	73	179
1	131	126	84
0	86	92	180

17,13,L

5	35	34	220
3	37	37	292
2	102	103	187
1	90	80	254
0	91	89	180

17,12,L

5	34	32	84
2	51	48	113
1	30	31	247

17,11,L

5	36	33	273
4	48	50	180
3	68	66	214
2	53	61	178
1	69	71	249

17,10,L

2	46	46	330
1	62	62	240

17,9,L

7	28	29	194
5	28	21	190
3	95	100	201
2	54	58	9
1	74	70	227
0	29	35	0

17,8,L

6	66	62	355
5	121	120	88
4	72	74	238
3	69	65	108
1	93	100	82

17,7,L

8	65	60	165
7	40	45	190
6	85	82	145
5	58	62	275
4	187	181	166
3	158	167	269
2	186	184	195
1	51	39	166

17,6,L

8	39	42	356
7	43	47	235
6	74	72	307
5	93	84	227
4	84	77	316
3	39	73	232
2	134	135	318
1	163	163	295
0	133	133	0

17,5,L

6	46	44	209
5	67	64	316
4	71	77	195
2	145	148	88
1	62	57	61
0	105	106	180

17,4,L

8	72	67	20
7	117	116	272
6	69	70	317
5	60	59	276
4	123	122	315
3	187	181	231
2	118	121	2
1	360	359	241
0	264	269	0

17,3,L

8	67	65	341
7	73	76	63
6	122	117	335
5	113	110	53
4	186	186	6
3	36	43	118
2	236	237	9
1	199	207	88
0	183	185	0

17,2,L

7	65	62	51
6	26	37	253
5	113	118	132
4	56	56	353
3	161	167	126
1	65	70	237
0	120	119	0

17,1,L

7	75	78	46
6	80	77	260
3	128	130	84
2	43	37	358
1	185	185	124
0	163	164	0

16,16,L

1	85	88	78

16,15,L

4	46	45	163
3	36	39	284
2	87	84	177
0	111	110	180

16,14,L

2	47	51	53
1	26	27	279

16,13,L

6	71	68	132
4	98	97	184
3	51	55	203
2	74	77	190
0	76	75	180

16,12,L

5	118	116	242
3	120	99	285
2	65	68	260
1	129	129	255
0	63	56	0

16,11,L

7	31	42	198
6	51	55	18
5	80	80	261
3	75	78	268
2	73	69	358
1	57	58	235

16,10,L

7	61	59	144
6	63	66	0
5	52	48	214
4	143	142	345
2	199	199	337
1	70	72	188
0	82	82	0

16,9,L

7	37	30	87
5	72	74	80
3	88	92	87
1	67	61	48

16,8,L

8	51	58	311
7	73	72	231
6	60	53	341
5	54	55	232
4	87	87	2
3	115	116	246
2	80	81	357
1	105	114	357
0	91	87	0

16,7,L

7	128	126	71
6	78	73	285
5	128	127	53

16,7,L

4	55	61	318
3	99	97	78
2	59	62	38
1	173	176	100
0	47	40	180

16,6,L

8	75	73	228
7	75	67	239
6	75	70	175
5	89	92	293
4	106	112	78
3	174	180	236
2	43	51	207
1	115	117	286
0	135	121	180

16,5,L

8	115	115	328
6	158	156	339
5	60	64	11
4	237	247	0
3	33	34	345
2	163	167	8
1	96	93	184
0	206	210	0

16,4,L

9	49	46	97
5	98	91	59
4	74	79	38
3	178	171	82
2	120	118	52
1	119	115	109
0	64	62	0

16,3,L

8	59	51	323
7	58	49	34
6	50	46	1
5	127	128	67
4	49	50	288
3	141	147	148
2	69	73	286
1	84	82	131
0	236	238	0

16,2,L

9	51	54	36
8	31	34	20
7	135	135	55
6	62	67	171
5	126	130	82
4	97	93	125
3	106	105	98
2	59	56	320
1	175	183	116
0	79	72	0

16,1,L

7	80	84	76
6	73	74	203
5	104	103	99
4	83	81	151
3	84	81	129
2	33	29	274
1	147	152	106
0	191	186	180

16,0,L

9	69	73	332
8	98	106	160
7	108	109	5
6	126	120	166
4	217	214	206
3	79	79	88
2	152	157	152
1	80	80	234
0	138	131	180

15,16,L

3	56	53	268
2	86	88	352
1	88	80	255

15,15,L

3	60	56	88
2	30	26	348
1	86	83	114

15,14,L

5	50	49	241
3	42	46	238
2	55	55	237
1	78	77	298
0	55	54	180

15,13,L

5	54	48	265
3	78	75	273
2	63	64	325
1	72	67	335
0	43	42	0

15,12,L

7	61	59	211
6	73	68	310
5	46	49	237
4	95	92	356
3	60	62	282
2	50	51	342
1	46	44	243
0	106	106	0

15,11,L

6	91	91	313
5	70	73	40
4	121	118	347
2	105	105	347
1	111	111	38
0	130	127	0

15,10,L

6	31	31	12
5	41	36	217
4	121	124	352
2	67	60	25
1	28	34	344
0	107	111	0

15,9,L

8	48	63	311
7	93	95	41
6	132	130	332
5	128	125	86
4	173	180	337
3	238	236	88
2	180	190	31
1	87	91	83
0	55	63	0

15,8,L

6	143	139	152
5	102	105	54
4	162	161	152
3	84	76	53
2	122	120	196
1	156	156	98
0	139	129	180

15,7,L

6	63	62	297
5	140	144	229
4	73	77	36
3	160	175	352
2	42	49	339
1	54	55	207
0	83	76	0

15,6,L

9	87	82	50
8	34	34	114
7	63	63	57
6	97	98	120
5	51	47	113
3	206	207	54
1	97	95	80

15,5,L

7	56	60	293
5	139	138	241
4	100	111	143
3	81	81	65
2	114	112	108
1	63	60	347
0	102	100	0

15,4,L

9	59	56	55
7	71	66	90
6	84	89	49
5	67	65	3
4	88	89	117
2	142	144	286
1	240	238	55
0	37	18	0

15,3,L

9	66	65	52
7	74	71	153
6	84	89	114
5	110	115	97
4	90	86	149
3	58	52	103
2	60	59	87
1	133	133	83

15,2,L

9	96	90	47
8	85	83	195
7	58	59	129
6	163	159	176
5	97	102	166
4	163	163	184
3	136	128	6
2	210	206	168
1	211	225	68
0	439	452	180

15,1,L

10	62	59	76
9	60	59	264
8	66	65	106
7	147	150	288
6	116	117	192
5	92	98	286
4	167	169	172
3	226	233	234
2	87	91	147
1	348	355	270

14,17,L

2	111	106	352
1	57	50	76
0	170	165	0

14,16,L

3	57	57	97
0	81	84	180

14,15,L

5	33	23	249
4	44	45	280
3	64	57	45
2	68	71	2
1	31	31	307

14,14,L

4	53	56	19
0	62	55	180

14,13,L

6	49	50	298
4	43	46	287
0	72	77	0

14,12,L

5	50	55	312
4	61	59	352
3	55	62	306
2	55	58	78
1	47	45	358

14,11,L

8	73	69	345
7	63	53	53
6	88	81	335
5	56	53	85
4	171	170	357
3	78	78	94
2	166	166	2
1	56	47	154
0	102	92	0

14,10,L

7	123	123	43
6	71	70	139
5	180	183	59
4	101	98	162
3	208	203	79
2	58	58	246
1	138	139	113

14,9,L

5	61	57	141
4	124	130	149
3	50	49	134
2	59	62	173
1	56	59	289
0	32	42	0

14,8,L

8	51	46	99
7	97	96	66
5	113	112	27
4	147	147	296
3	107	106	72
2	122	124	136
1	149	146	107
0	121	125	0

14,7,L

8	105	103	126
7	38	39	206
6	195	192	151
5	39	38	166
4	176	170	173
3	136	130	241
2	206	194	180
1	54	46	281

14,6,L

8	36	38	284
6	60	55	288
5	70	71	261
3	189	186	268
2	121	129	72
1	71	65	345
0	133	133	180

14,5,L

8	51	53	26
6	71	74	42
5	125	127	218
4	109	104	112
3	53	53	35
2	110	120	72
1	158	156	344
0	79	75	180

14,4,L

9	40	39	165
7	66	62	142
6	85	88	268
5	60	50	217
4	153	158	196
3	73	73	18
2	131	134	95
1	174	183	116
0	43	23	0

14,3,L

9	57	58	288
8	88	80	172
7	59	60	252
5	63	59	250
4	191	179	173
3	107	111	273
2	279	284	152
1	213	220	250
0	248	251	180

14,2,L

8	73	69	331
7	41	37	131
5	175	170	239
3	67	63	241
2	45	51	83
1	169	178	266
0	285	283	0

14,1,L

10	58	53	161
8	81	77	181
7	77	78	287
6	170	173	196
5	126	128	283
4	71	61	188
3	32	9	203
2	294	301	149
1	192	207	260
0	457	457	180

14,0,L

10	40	42	314
9	108	101	252
8	169	164	2
7	284	277	266
6	75	72	314
5	123	126	316
4	46	45	90
3	528	534	247
2	281	292	337
1	566	568	272
0	451	448	0

13,18,L

1	73	80	86
0	91	94	0

13,16,L

5	68	63	60
3	43	45	60
1	102	102	103
0	69	69	0

13,15,L

4	43	44	172
3	55	54	95
2	91	85	200
1	59	55	138
0	86	82	180

13,14,L

5	50	51	323
4	109	112	176
3	43	40	345
2	78	78	167
0	84	83	180

13,13,L

6	69	69	47
5	76	83	276
4	38	44	280
3	40	37	286
1	116	113	235

13,12,L

8	44	44	316
7	59	60	56
6	41	38	46
5	111	109	54
4	44	47	166
3	77	73	67
1	90	95	58

13,11,L

8	38	42	103
6	140	136	143
5	72	71	269
4	92	96	154
3	74	71	288
1	52	48	236

13,11,L

0	102	106	180

13,10,L

8	47	38	23
6	64	68	344
5	111	110	95
3	78	83	101
2	81	92	36
1	54	48	131
0	84	93	0

13,9,L

8	115	114	159
6	132	157	144
5	68	70	45
4	243	244	158
3	72	75	209
2	259	256	183
1	34	39	101
0	115	112	180

13,8,L

9	80	73	224
8	68	68	198
7	100	95	228
6	52	50	227
5	191	195	258
4	52	49	199
3	144	140	259
2	84	81	119
1	117	119	285
0	55	50	180

13,7,L

9	59	59	268
7	39	38	255
6	145	144	179
5	94	91	297
4	46	51	98
3	147	142	245
2	91	81	306
1	132	146	260
0	198	197	180

13,6,L

9	83	75	234
7	118	117	227
6	149	153	290
5	48	42	233
4	146	158	345
3	113	112	242
2	298	301	72
1	158	149	239

13,5,L

9	39	48	201
7	121	121	278
6	53	51	261
5	163	165	30
4	63	67	214
3	167	165	215
2	157	158	167
1	83	89	208
0	77	37	0

13,4,L

9	94	92	209
8	74	71	335
6	183	185	320
5	129	129	266
4	248	248	35
3	200	209	276
2	39	40	93
1	100	117	230
0	194	202	0

13,3,L

9	56	49	65
8	88	85	247
7	116	114	103
6	194	195	237
5	65	62	61
4	126	128	77
3	171	177	111
2	110	115	191
1	161	160	50
0	166	157	180

13,2,L

10	76	73	207
9	86	82	235
8	65	60	281
7	220	223	255
5	237	233	286
4	73	74	185
3	340	341	270
2	263	261	137
1	363	371	275
0	123	137	180

13,1,L

10	61	70	331
9	47	46	327
8	166	171	317
7	81	79	68
6	214	210	354
5	149	153	226
4	167	171	335
3	259	263	322
2	444	450	20
1	92	89	188
0	394	403	0

12,18,L

3	40	42	114
2	42	43	38

12,17,L

1	87	91	94
0	105	99	180

12,16,L

5	42	40	70
4	78	74	194
3	31	26	57
2	110	109	189
0	128	129	180

12,15,L

6	68	59	168
5	45	34	272
4	77	74	138
3	70	70	230
2	116	118	169
1	153	153	265
0	94	93	180

12,14,L

5	27	30	308
4	56	52	184
3	55	57	243

12,14,L

2	82	87	255
0	42	43	0

12,13,L

6	68	71	181
5	78	80	278
4	108	106	121
3	154	160	288
2	135	141	164
1	104	103	262
0	101	98	180

12,12,L

8	54	62	13
7	62	67	232
6	83	78	7
5	117	115	258
4	120	122	343
3	130	128	268
2	167	168	11
1	102	103	243
0	99	106	0

12,11,L

9	68	59	98
7	77	79	105
6	48	44	118
5	104	99	69
3	47	35	85
2	91	98	109
1	156	163	58
0	26	29	180

12,10,L

9	54	44	226
8	72	71	212
7	116	112	252
6	66	68	162
5	133	127	215
4	94	99	116
3	96	96	230
2	105	103	231
1	167	169	273
0	72	76	180

12,9,L

8	33	34	340
6	51	50	271
5	45	42	245
4	93	99	199
3	62	57	10
2	104	104	334
0	97	93	0

12,8,L

9	42	34	235
8	40	40	170
7	89	87	238
6	98	104	227
5	99	92	236
4	46	54	224
3	136	141	221
1	170	164	274

12,7,L

10	73	69	345
9	83	83	246
8	102	95	311
5	90	87	330
4	123	119	269
3	62	66	181
2	282	288	326
1	198	194	216
0	131	142	0

12,6,L

10	71	69	324
8	109	111	334
7	84	82	266
5	125	122	235
4	138	145	354
3	75	78	6
2	70	72	321
1	213	216	291
0	118	119	0

12,5,L

10	100	99	328
9	87	87	116
8	87	91	337
6	88	89	318
5	193	191	72
4	198	199	329
3	188	193	70
2	197	195	339
1	341	318	72
0	462	465	0

12,4,L

8	77	71	233
7	50	51	47
6	173	176	170
5	36	41	116
4	371	379	181
3	135	144	31
2	264	273	229
1	62	57	43
0	82	93	180

12,3,L

10	64	58	324
9	59	52	343
8	106	107	319
7	65	69	135
6	121	115	286
5	103	100	272
4	282	284	34
3	276	272	311
2	228	220	334
1	26	35	25
0	100	111	0

12,2,L

9	79	78	39
8	82	87	207
7	40	32	75
6	101	103	226
5	139	139	75
4	118	115	134
3	217	198	47
2	244	242	105
1	257	251	82
0	411	410	180

12,1,L

9	64	57	246
7	114	114	294
6	60	52	24
5	273	285	278
4	119	127	296
3	103	104	302
2	134	148	68
1	282	285	281

12,0,L

11	73	76	8
10	77	75	21
9	56	50	39
8	69	71	307
7	68	61	64
6	115	123	331
5	161	154	64
4	425	416	21
3	226	248	104
2	253	265	62
1	267	263	48
0	250	250	0

11,18,L

1	45	45	0

11,17,L

4	48	47	172
2	72	70	166
0	134	134	180

11,16,L

5	38	41	198
3	77	71	234
2	40	34	301
1	98	98	293
0	77	80	180

11,15,L

6	58	54	181
5	30	34	269
4	73	73	168
3	52	52	279
2	117	115	192
1	58	61	350
0	88	85	180

11,14,L

7	122	116	250
6	37	40	11
5	165	162	251
4	29	32	22
3	210	213	268
2	50	47	47
1	274	275	264

11,13,L

8	78	77	347
7	47	47	151
6	85	80	333
4	148	150	358
3	42	45	23
2	196	199	348
1	105	103	56
0	116	115	0

11,12,L

6	46	47	220
5	51	58	215
4	54	56	73
2	106	107	93
1	104	109	254
0	103	105	180

11,11,L

8	64	69	341
6	122	116	313
5	53	52	221
4	167	169	347
3	57	74	157
2	79	76	24
1	80	80	22
0	270	272	0

11,10,L

7	46	37	42
6	74	69	211
5	141	136	88
4	66	67	64
3	93	92	111
2	108	101	159
1	56	40	60

11,9,L

10	65	66	239
9	55	57	269
8	71	66	286
6	99	99	309
5	61	65	185
4	86	86	190
3	112	115	284
2	67	71	221
1	101	105	166
0	152	158	0

11,8,L

10	75	73	336
9	79	85	345
8	73	74	3
6	64	67	298
3	179	176	335
2	210	220	254
0	298	299	0

11,7,L

10	60	55	358
9	44	43	99
8	94	90	342
7	79	82	27
6	102	94	339
5	118	119	164
4	193	195	278
3	239	225	78
2	390	397	13
1	68	62	248
0	136	146	0

11,6,L

9	74	69	32
8	65	69	353
7	153	151	34
5	241	237	75
4	286	290	190
3	413	423	93
2	120	116	296
1	151	156	38
0	92	83	0

11,5,L

7	84	85	121
5	55	52	22
4	200	201	196
3	143	147	314
1	135	133	74
0	280	273	0

11,4,L

9	118	121	36
8	82	82	212
7	162	157	48
6	137	138	108

11,4,L

5	362	355	61
4	191	184	224
3	374	365	88
2	116	113	35
1	254	254	91
0	95	99	180

11,3,L

10	76	78	151
8	157	154	168
7	85	81	274
6	291	280	180
5	91	84	186
4	285	289	174
3	75	87	18
2	455	431	155
1	209	199	304
0	452	451	180

11,2,L

9	66	64	285
7	185	180	293
6	66	70	335
5	110	98	342
4	110	109	72
3	89	81	83
2	227	227	23
1	273	269	270
0	148	151	0

11,1,L

8	61	66	44
7	62	62	260
6	51	45	153
5	169	161	76
4	229	223	121
3	319	313	128
2	195	201	159
1	41	54	262
0	20	1	0

10,19,L

0	84	85	0

10,18,L

2	31	25	260

10,17,L

5	31	34	68
4	45	45	247
0	49	53	180

10,16,L

6	71	75	165
5	83	87	259
4	68	68	193
3	63	68	252
2	66	60	197
1	129	126	299
0	40	34	180

10,15,L

7	43	40	269
6	116	118	339
4	99	97	306
3	58	62	256
2	131	133	14
1	116	115	260
0	199	199	0

10,14,L

7	46	48	52
6	32	28	238
3	60	56	33
1	71	65	90
0	123	132	0

10,13,L

8	82	73	338
6	88	90	318
5	67	64	226
4	127	124	0
2	113	112	6
1	99	106	301
0	192	191	0

10,12,L

9	79	80	72
7	106	105	70
6	75	71	336
5	185	181	74
4	112	112	351
3	178	185	88
2	200	208	29
1	232	231	115
0	41	46	180

10,11,L

9	49	49	143
8	43	39	270
7	41	46	214
6	31	30	183
5	93	90	100
4	142	142	153
3	163	160	78
2	57	62	196
1	89	86	69
0	78	79	180

10,10,L

9	48	52	355
8	68	65	243
7	110	109	46
6	46	45	351
5	47	56	111
4	90	90	199
3	68	65	119
2	85	94	136
1	147	148	38
0	121	124	180

10,9,L

7	50	53	163
6	67	63	309
5	50	55	228
4	70	69	232
3	148	151	23
2	208	212	78
1	70	68	340
0	30	31	180

10,8,L

9	58	60	31
8	46	43	298
7	162	165	82
6	79	71	223
5	197	195	62
3	50	59	158
2	49	42	188
1	290	305	121

10,7,L

9	32	42	14
6	68	70	272
4	134	128	74
3	164	171	325
2	180	171	144
1	149	152	307
0	114	110	180

10,6,L

11	46	51	84
9	91	82	102
8	27	31	13
7	124	125	97
6	43	44	297
5	233	234	61
4	143	152	56
3	317	317	88
2	115	125	358
1	297	296	85
0	162	154	0

10,5,L

11	45	44	30
10	140	133	157
9	41	52	93
8	188	185	136
7	93	88	123
6	289	286	182
5	119	124	83
4	450	446	183
3	135	141	51
2	456	475	167
1	227	233	69
0	140	146	180

10,4,L

9	105	103	227
8	116	109	156
7	59	60	244
6	122	117	170
5	61	60	310
4	183	180	179
3	224	234	245
2	126	128	187
1	215	208	246
0	206	196	0

10,3,L

10	65	67	128
9	41	44	295
7	45	52	202
6	150	161	139
5	88	85	231
4	235	236	170
2	243	258	132
1	152	159	359
0	139	127	180

10,2,L

11	50	54	215
9	150	149	216
7	180	180	252
6	81	84	213
5	196	194	261
4	109	112	195
3	164	169	271
2	193	180	101
1	224	240	257
0	187	202	180

10,1,L

9	91	84	259
8	41	47	85
7	149	138	254
6	165	162	22
5	108	111	19
4	105	99	166
3	297	293	251
2	175	171	302
1	156	158	200
0	406	360	0

10,0,L

9	27	30	193
8	138	138	327
7	209	210	147
6	248	240	5
5	211	217	194
4	94	101	42
3	60	63	336
2	103	114	57
1	86	85	51
0	233	245	0

9,20,L

0	40	42	0

9,19,L

1	54	54	61
0	99	103	0

9,18,L

5	71	71	51
2	45	42	125
1	79	74	133
0	68	67	180

9,17,L

5	52	55	259
4	62	55	314
3	31	31	298
2	42	37	17
0	42	33	0

9,16,L

7	83	83	39
6	48	58	219
5	88	87	69
3	111	116	78
2	76	76	230
1	62	63	158
0	73	68	0

9,15,L

5	83	77	259
4	64	60	166
3	86	91	274
2	55	60	25
1	47	43	229

9,14,L

8	45	49	17
7	52	51	70
6	95	89	344
5	101	104	41
4	118	111	334
3	81	73	74
2	87	88	3
1	97	96	89
0	224	232	0

9,13,L

7	63	67	66
6	83	84	105
5	169	168	76
4	48	49	155
3	155	155	99
2	26	16	202
1	155	150	123

9,12,L

6	65	64	221
5	92	89	87
4	139	135	188
3	119	115	73
1	144	147	64
0	127	133	180

9,11,L

8	42	43	144
7	84	88	21
5	87	82	71
4	85	77	128
3	150	150	127
2	155	156	128
1	116	122	215
0	232	238	180

9,10,L

10	54	49	216
7	92	97	156
5	58	56	73
4	181	173	189
3	52	60	34
2	157	159	155
1	88	73	77

9,9,L

9	50	45	306
8	69	69	184
7	51	55	289
6	143	146	198
5	99	102	279
4	178	184	74
3	133	131	266
2	257	246	158
1	172	173	311
0	449	449	180

9,8,L

10	88	81	31
8	55	59	3
7	86	84	182
6	65	68	14
5	38	35	151
4	140	139	351
3	139	130	263
2	308	312	16
1	211	208	312
0	147	149	0

9,7,L

10	29	28	126
9	110	107	78
8	90	86	180
6	99	93	139
5	283	281	87
4	55	71	107
3	295	286	100
2	232	229	148
1	171	176	82
0	134	117	180

9,6,L

10	63	55	119
9	92	86	212
8	63	58	180
7	113	106	218
6	54	57	160
5	55	47	216
4	241	242	167
3	238	229	261
2	87	87	159
1	289	287	269
0	33	26	0

9,5,L

9	39	32	113
7	172	168	121
6	162	153	154
5	90	82	221
4	142	136	111
3	139	140	42
2	294	275	291
1	364	354	80
0	136	116	0

9,4,L

10	33	23	144
9	118	116	257
8	122	125	156
7	182	178	173
6	384	370	187
5	298	292	240
4	75	88	168
3	239	239	301
2	263	234	202
1	304	292	235
0	520	510	180

9,3,L

10	76	72	306
9	92	89	236
8	77	81	325
7	217	206	252
6	75	75	113
5	200	205	260
4	144	136	335
3	213	186	289
2	198	188	334
1	307	291	306
0	359	372	0

9,2,L

10	90	96	346
9	100	102	227
8	136	133	35
7	118	110	230
6	82	86	303
5	341	333	228
4	168	158	7
3	315	354	300
2	275	259	248
1	127	125	32
0	806	790	0

9,1,L

10	125	124	343
8	135	135	314
7	139	131	111
6	214	206	342
5	53	51	81
4	206	202	331
3	98	84	349
2	557	542	339
1	215	210	115

9,1,L

0	256	243	0

8,20,L

1	69	65	87

8,19,L

4	27	28	68

8,18,L

5	75	72	58
3	83	85	79
2	30	12	107
1	141	142	87
0	56	59	180

8,17,L

6	122	119	147
4	101	96	164
2	97	94	184
0	162	155	180

8,16,L

7	70	73	267
4	39	43	359
2	65	74	2
1	56	48	271

8,15,L

6	56	60	102
5	54	54	71
4	104	103	145
3	74	69	67
2	52	50	245
1	115	120	40

8,14,L

7	44	43	176
6	51	50	145
1	72	72	49

8,13,L

9	39	32	204
6	73	78	147
3	110	109	29
2	49	42	154
1	72	74	93
0	130	117	180

8,12,L

9	51	49	164
7	33	30	142
6	63	64	139
4	118	123	124
3	72	65	131
2	144	140	219
1	24	32	266
0	91	96	0

8,11,L

8	97	92	191
7	99	99	199
6	163	173	179
4	168	161	152
3	151	140	340
2	326	332	201
1	34	27	159
0	188	190	180

8,10,L

9	99	93	268
8	83	87	44
7	188	188	257
6	33	25	24
5	230	233	247
4	43	44	95
3	272	269	289
2	73	79	45
1	448	451	262
0	82	64	0

8,9,L

7	87	93	106
6	98	105	308
5	149	149	94
4	174	159	357
3	168	170	135
2	250	264	36
1	116	101	343
0	36	16	0

8,8,L

9	81	81	215
7	105	105	258
6	78	73	73
5	136	136	278
4	69	74	150
3	197	203	235
2	151	154	119
1	295	300	274
0	112	106	180

8,7,L

10	63	67	326
9	46	49	281
8	153	157	315
6	191	182	358
5	284	268	120
4	447	439	20
3	130	121	116
2	362	354	5
1	226	218	249
0	221	208	0

8,6,L

11	50	57	116
10	59	53	164
9	64	66	113
8	105	109	166
7	53	49	166
5	183	186	156
4	187	179	189
3	320	323	70
2	310	310	144
1	291	282	63
0	64	64	0

8,5,L

10	65	60	263
9	115	113	268
8	64	63	248
7	109	108	242
6	84	90	240
5	65	65	184
4	54	54	262
3	111	114	211
2	173	177	244
1	612	589	250
0	311	309	0

8,4,L

10	46	41	17
9	82	85	340
7	54	46	241
5	121	110	174
4	95	87	19
3	104	111	253
2	382	368	358
1	22	29	270
0	194	194	180

8,3,L

10	83	77	346
9	52	57	226
8	134	137	294
7	185	182	273
6	184	177	320
5	66	68	232
4	253	263	301
3	106	96	108
2	397	372	23
1	467	460	297
0	354	331	180

8,2,L

9	59	54	32
8	64	63	354
7	162	152	348
6	82	81	4
5	202	191	53
4	190	175	308
3	284	288	108
2	371	355	340
1	232	224	337
0	594	584	0

8,1,L

10	77	77	13
8	143	139	315
6	220	208	5
5	114	117	114
4	175	174	338
3	108	96	232
2	471	455	330
1	112	113	340
0	149	195	0

8,0,L

11	89	89	84
9	244	241	34
7	374	376	73
6	79	77	254
5	362	364	96
4	452	440	29
3	606	589	62
2	231	226	286
1	329	360	93
0	241	227	0

7,20,L

3	75	75	96
2	50	51	359
1	53	54	69
0	48	48	0

7,19,L

4	81	82	165
3	89	87	79
2	104	100	152
1	63	58	66
0	160	152	180

7,18,L

4	38	34	161
2	72	67	122
1	77	75	249

7,17,L

5	42	47	80
4	64	61	141
2	90	92	207

7,16,L

7	68	65	230
5	120	115	224
4	79	77	165
3	80	75	273
2	96	95	157
1	138	143	302

7,15,L

8	50	54	24
5	69	72	239
4	53	51	308
1	65	70	247
0	93	92	0

7,14,L

8	43	51	42
7	107	98	198
6	47	41	142
5	30	38	185
4	38	46	119
3	116	120	310
2	128	127	335
1	124	122	16
0	98	103	180

7,13,L

6	91	87	204
5	68	74	132
4	67	64	203
3	83	88	130
2	84	85	269
1	94	93	354
0	69	75	0

7,12,L

9	41	44	239
8	61	57	165
7	141	142	246
6	70	65	152
5	160	154	243
4	92	94	206
3	105	107	321
2	162	154	166
1	305	313	301

7,11,L

8	115	114	351
7	70	68	242
6	128	117	359
5	44	46	320
4	94	93	328
3	187	203	246
2	180	188	355
1	100	109	312
0	421	424	0

7,10,L

9	82	73	257
7	56	56	224

7,10,L

6	64	69	181
5	67	66	226
4	82	75	96
3	186	180	7
2	131	126	237
1	149	146	247
0	52	48	180

7,9,L

10	98	96	340
9	83	78	252
8	196	194	338
7	110	115	236
6	226	226	13
5	265	259	269
4	248	242	348
3	340	328	303
2	543	551	5
1	249	253	245
0	296	353	0

7,8,L

11	94	86	80
9	45	43	83
8	115	112	14
7	153	153	65
6	66	63	305
5	422	423	108
4	306	319	6
3	593	596	83
2	278	269	8
1	183	201	125
0	163	165	0

7,7,L

10	55	68	239
9	79	78	203
8	54	51	271
7	38	38	20
6	133	134	337
4	245	233	158
3	107	108	148
2	113	117	207
1	113	116	230
0	124	126	0

7,6,L

9	76	77	359
8	67	63	262
7	115	114	113
6	207	199	349
5	197	199	83
4	51	42	348
3	201	213	83
2	203	192	106
1	243	245	47
0	335	321	0

7,5,L

8	48	56	199
7	88	90	91
6	161	164	232
4	88	86	281
3	101	96	208
2	218	206	138
1	270	244	144
0	312	299	180

7,4,L

11	70	66	343
9	59	55	34
8	110	111	246
7	153	155	281
6	125	122	335
5	257	238	32
4	87	73	241
3	74	67	124
2	250	239	48
1	459	422	326
0	591	600	180

7,3,L

9	59	61	309
8	70	75	26
7	93	89	271
6	192	185	2
5	136	122	299
4	103	94	349
3	64	46	351
2	336	308	74
1	168	146	259
0	222	227	0

7,2,L

9	95	97	74
8	142	133	2
7	120	114	87
6	172	174	330
5	261	261	56
4	145	119	329
3	293	278	33
2	88	86	323
1	438	452	59
0	594	603	0

7,1,L

10	130	131	139
9	127	125	63
8	194	190	133
7	144	145	37
6	155	158	186
5	154	150	62
4	203	209	117
3	110	126	69
2	457	439	126
1	358	348	34
0	134	165	180

6,20,L

3	34	36	231
2	56	58	169
1	65	66	257

6,19,L

5	54	44	91

6,18,L

6	62	58	177
5	52	51	228
4	98	93	164
2	98	99	167
1	57	48	281
0	151	149	180

6,17,L

7	51	53	257
6	57	59	306
5	80	86	259
4	60	61	3
3	111	103	231
1	158	166	278
0	48	47	0

6,16,L

3	36	24	242
2	43	36	80
1	103	100	256
0	90	88	0

6,15,L

7	63	56	147
6	130	127	306
4	140	138	350
3	67	70	324
2	145	146	53
1	66	72	196
0	67	76	0

6,14,L

6	46	48	251
4	43	41	285
2	45	44	72
1	69	74	190
0	71	79	180

6,13,L

8	33	30	23
7	56	54	256
6	77	75	323
4	152	157	336
3	34	32	350
2	142	132	39
1	166	169	265
0	155	165	0

6,12,L

10	32	25	232
8	64	62	238
7	54	52	14
5	81	80	54
4	97	103	154
3	69	66	32
2	62	74	277
1	165	167	66

6,11,L

9	115	113	266
8	53	52	66
7	86	82	259
5	208	201	259
4	87	99	203
3	167	166	301
2	177	175	306
1	365	354	297
0	244	242	0

6,10,L

10	76	78	343
9	57	55	40
8	114	117	340
6	178	176	344
5	73	71	31
4	382	384	351
3	180	178	39
2	410	418	18
1	208	208	75
0	431	452	0

6,9,L

9	57	60	70
7	77	78	163
6	107	106	71
5	352	352	81
4	247	243	208
3	108	102	121
2	69	64	27
1	144	154	82
0	113	106	0

6,8,L

10	63	57	312
9	68	73	62
8	99	100	304
7	82	76	78
6	73	76	329
5	93	107	315
4	310	306	29
3	75	80	49
2	148	147	321
1	324	310	54
0	138	151	0

6,7,L

11	36	44	32
9	85	89	83
8	61	62	93
7	148	145	109
6	131	129	101
5	340	335	88
4	133	143	162
3	410	397	97
2	129	124	193
1	501	477	55
0	215	223	180

6,6,L

8	113	111	206
7	42	39	74
6	252	246	194
5	85	77	57
4	302	286	203
3	160	144	290
2	215	194	196
1	164	171	42
0	487	483	180

6,5,L

11	77	83	332
9	118	127	287
8	90	90	107
7	77	73	81
6	192	181	141
5	158	149	248
4	276	254	134
3	353	333	339
2	337	321	201
1	314	301	220
0	76	95	180

6,4,L

10	87	89	356
8	45	37	340
7	76	82	3
6	27	26	310
5	131	128	280
4	181	164	338
3	112	84	203
2	94	89	144
1	546	535	237
0	217	196	180

6,3,L

11	68	66	50
8	112	104	100
7	61	60	10
6	159	164	151
5	204	198	356

6,3,L

4	177	160	135
3	437	410	26
2	318	321	175
1	134	154	77
0	49	41	180

6,2,L

9	121	130	213
8	126	122	85
6	105	102	73
5	265	243	301
4	283	259	151
3	535	500	234
2	386	383	277
1	538	506	206
0	818	808	0

6,1,L

9	116	119	42
7	273	270	109
6	105	101	119
5	232	220	61
4	213	196	52
3	96	92	24
2	190	188	217
1	377	376	65
0	233	211	180

6,0,L

10	106	116	133
9	103	99	204
8	119	119	160
7	213	211	235
6	452	446	142
5	223	208	264
4	359	338	175
3	553	490	270
2	382	391	101
1	166	152	1
0	776	745	180

5,21,L

0	126	124	0

5,20,L

3	58	53	64

5,19,L

3	90	90	252
2	60	61	135
1	81	82	271

5,18,L

4	68	69	3
2	78	78	329

5,17,L

4	44	42	30
3	25	37	242
2	76	78	317
1	80	77	291

5,16,L

7	60	60	24
6	102	99	323
4	106	106	0
3	64	71	30
2	54	56	34
1	80	80	199
0	62	60	0

5,15,L

6	75	75	22
5	81	85	15
4	84	83	338
2	84	90	23

5,14,L

8	66	66	254
7	95	98	73
5	191	190	61
4	99	103	342
3	209	219	88
2	83	81	325
1	112	118	110

5,13,L

9	45	47	347
8	76	70	180
7	34	31	318
6	129	128	178
5	47	44	153
4	168	166	150
3	93	94	0
2	93	91	199
1	74	78	294
0	296	285	180

5,12,L

8	43	42	358
6	121	121	346
5	103	129	32
4	70	68	7
3	130	136	247
2	257	258	5
1	86	87	324
0	125	134	0

5,11,L

9	39	37	22
7	99	103	110
6	90	90	108
5	41	50	270
4	58	60	188
3	201	202	20
2	153	150	160
1	306	306	82
0	57	68	180

5,10,L

7	80	80	152
5	42	48	295
4	169	183	6
3	242	251	300
2	101	100	296
1	71	81	348
0	87	86	0

5,9,L

10	76	78	55
9	111	114	81
8	66	65	93
6	41	44	221
5	37	36	150
4	137	145	27
3	385	399	70
2	128	131	47
0	25	20	180

5,8,L

8	68	63	159
7	94	99	124
6	126	125	130
5	239	230	89
4	182	181	188
3	294	290	99
2	315	315	190
1	83	76	132
0	275	256	180

5,7,L

10	79	83	188
9	75	69	356
8	160	154	153
7	68	65	312
6	222	226	193
5	99	101	90
4	351	347	171
3	177	178	314
2	522	521	181
1	42	36	130
0	104	140	180

5,6,L

9	93	101	251
8	56	54	140
7	140	144	196
6	70	82	150
5	191	192	248
4	94	113	109
3	288	284	271
2	184	185	169
1	214	193	302
0	597	583	180

5,5,L

8	67	68	207
7	188	184	354
6	297	286	172
5	138	125	30
4	236	234	259
3	389	375	178
2	237	251	170
1	562	534	280
0	304	264	180

5,4,L

9	151	159	244
7	314	315	269
6	150	148	103
5	296	291	237
4	408	383	69
3	452	441	289
2	293	254	213
1	873	898	280
0	253	276	180

5,3,L

10	99	101	337
9	56	52	62
8	209	216	331
7	64	60	284
6	254	247	356
5	69	64	80
4	238	241	66
3	224	201	194
2	600	593	311
1	322	316	300
0	783	797	0

5,2,L

10	74	73	151
8	127	130	156
7	148	153	94
6	291	282	123
5	269	255	220
4	365	370	191
3	451	412	22
2	167	143	53
1	367	382	197
0	245	281	180

5,1,L

11	72	72	201
10	75	77	317
9	153	163	250
8	162	157	267
7	111	117	270
6	32	33	40
5	415	399	244
4	150	120	1
3	308	313	243
2	346	317	2
1	775	777	220
0	572	602	180

4,20,L

2	58	62	353

4,19,L

3	64	62	55

4,18,L

3	51	49	349
2	58	56	302
1	27	26	188

4,17,L

6	71	69	44
5	69	68	58
4	27	28	201
2	64	64	320
1	83	83	320

4,16,L

7	75	73	77
6	38	41	340
5	96	93	102
4	64	65	45
3	157	163	84
2	68	71	292
1	73	68	38
0	184	186	0

4,15,L

8	39	43	158
7	57	56	54
6	109	104	160
5	115	116	65
4	112	107	157
3	105	106	97
2	136	137	189
1	161	168	31
0	168	183	180

4,14,L

6	66	70	154
5	62	64	90
3	76	78	203
2	47	54	135
1	134	136	285
0	45	44	180

4,13,L

7	37	44	66
6	121	122	137
5	145	141	88
4	134	140	138
3	164	157	72
2	195	194	216
1	68	66	146
0	75	91	180

4,12,L

9	79	76	279
8	88	89	151
7	117	119	258
6	126	129	158
5	151	152	240
4	106	106	183
3	167	166	286
2	259	253	165
1	220	225	279
0	148	151	180

4,11,L

9	67	61	296
8	43	44	81
7	32	33	313
6	50	54	125
5	89	103	189
4	230	230	354
3	126	132	7
2	243	239	342
1	113	113	278

4,10,L

9	85	81	210
8	56	63	94
7	26	14	227
6	79	80	243
5	107	108	73
4	118	109	152
3	253	263	131
2	59	71	75
1	130	112	214
0	222	192	180

4,9,L

11	48	44	74
9	43	43	147
8	60	55	234
7	46	52	170
6	39	33	181
5	34	36	6
4	69	92	40
3	104	98	37
2	201	182	219
1	73	74	349
0	147	147	180

4,8,L

9	67	67	220
8	81	82	176
7	113	99	258
6	131	130	123
5	27	43	85
4	285	273	190
3	88	78	228
2	214	220	195
1	173	144	198
0	104	103	180

4,7,L

10	65	69	230
9	51	55	174
8	77	86	235
7	92	96	187
6	59	61	332
5	230	226	241
4	135	125	279
3	461	445	18
2	104	99	237
1	175	173	287
0	346	315	180

4,6,L

10	64	69	181
9	93	95	270
8	126	130	153
7	61	57	302
6	256	249	168
5	290	297	267
4	548	545	196
3	339	329	252
2	291	257	160
1	457	437	270
0	134	126	0

4,5,L

10	83	84	351
9	117	131	253
8	153	158	330
7	254	252	243
6	268	277	346
5	269	283	246
4	504	507	356
3	674	672	277
2	534	517	7
1	484	484	297
0	46	6	1

4,4,L

11	63	65	95
9	105	107	59
8	70	69	307
7	130	133	46
6	159	156	299
5	112	111	139
4	183	167	112
3	359	328	53
2	272	239	32
1	184	172	110
0	159	171	180

4,3,L

11	68	67	246
10	29	20	147
9	58	55	208
8	118	119	145
7	301	322	239
6	172	170	326
5	92	86	319
4	204	213	307
3	554	523	229
2	281	275	86
1	673	663	349
0	812	829	0

4,2,L

10	73	67	299
9	173	178	59
8	171	173	307
7	172	180	86
6	315	321	330
5	117	115	178
4	223	214	7
3	134	132	12
2	282	278	116

4,2,L

1	661	648	84
0	547	545	0

4,1,L

10	50	50	172
9	58	54	66
8	121	114	191
7	112	112	154
6	235	246	207
5	160	139	234
4	338	325	60
3	267	228	103
2	197	180	66
1	443	452	344
0	1235	1421	180

4,0,L

10	92	93	249
9	78	77	99
8	207	194	322
7	418	412	264
6	349	320	272
5	343	319	293
4	310	292	344
3	233	217	63
2	912	907	108
1	1122	1209	16
0	375	403	180

3,21,L

1	83	78	66
0	78	71	180

3,20,L

4	71	68	190
2	43	45	167
1	39	29	23
0	47	49	180

3,19,L

2	48	48	181
0	74	74	180

3,18,L

3	49	50	297
0	106	110	0

3,17,L

6	47	47	124
5	41	39	115
4	55	61	197
3	100	101	51
2	71	73	191
1	126	124	54
0	28	15	180

3,16,L

4	69	69	166
3	113	110	298
2	117	110	111
1	79	75	289
0	140	140	180

3,15,L

7	69	74	108
5	132	127	86
4	40	43	116
3	79	81	62
1	172	173	114
0	61	65	180

3,14,L

9	56	54	300
8	125	130	163
7	46	37	230
6	184	184	166
5	73	70	207
4	258	257	172
2	302	301	191
1	202	196	272
0	283	289	180

3,13,L

9	85	89	251
7	103	104	283
6	75	80	331
5	135	132	243
4	104	117	347
3	118	118	208
2	181	185	105
1	394	394	266
0	90	95	0

3,12,L

9	51	51	257
8	80	79	79
7	50	55	295
6	40	42	346
5	79	79	180
4	93	100	207
3	69	69	145
2	132	132	162
1	162	156	255
0	117	116	0

3,11,L

9	72	70	220
8	82	78	336
7	120	121	224
6	100	102	289
5	75	80	349
4	155	158	25
3	284	287	243
2	127	130	290
1	149	146	264
0	46	43	0

3,10,L

8	33	39	2
7	63	65	296
6	68	73	48
5	112	112	127
4	149	155	320
3	88	90	46
2	177	181	12
1	110	102	290
0	85	80	180

3,9,L

10	61	57	324
9	90	93	157
8	57	58	299
7	43	47	240
6	76	85	0
5	119	120	121
4	139	134	249
3	108	103	149
2	121	124	296
1	43	51	196
0	306	281	0

3,8,L

9	58	55	82
8	85	79	199
7	70	70	54
6	61	60	304
5	37	27	26
4	197	196	169
3	254	250	50
2	312	315	206
1	213	184	342
0	59	54	0

3,7,L

11	93	90	241
10	35	31	76
9	132	138	257
8	71	73	275
7	57	57	198
6	83	81	193
5	466	473	250
4	170	148	191
3	262	254	291
2	267	227	357
1	315	313	252
0	219	195	180

3,6,L

12	63	69	308
10	71	70	327
9	83	88	41
8	68	74	346
7	74	71	137
6	237	231	300
5	210	201	39
4	508	507	342
3	298	276	318
2	462	449	12
1	284	261	69

3,5,L

9	38	40	180
8	95	99	185
7	74	78	304
6	82	87	163
5	124	128	18
4	157	145	193
3	371	338	189
2	324	285	71
1	211	196	205
0	300	288	180

3,4,L

10	138	143	331
9	49	50	270
8	153	162	332
7	60	63	350
6	337	357	359
5	123	126	17
4	503	485	329
3	293	261	141
2	580	583	342
1	424	419	349
0	856	861	0

3,3,L

10	60	63	92
9	166	171	74
8	42	46	81
7	321	336	91
6	152	152	204
5	273	270	82
4	260	236	179
3	317	317	63
2	446	431	144
1	1189	1306	90
0	733	731	0

3,2,L

10	38	34	174
9	87	89	278
8	41	42	155
7	52	48	332
6	295	282	203
5	210	188	66
4	264	236	215
3	276	250	137
2	629	611	280
1	1085	1117	189
0	86	97	180

3,1,L

10	29	30	282
9	54	62	81
8	101	99	50
7	107	109	45
6	122	131	233
5	241	228	339
4	443	430	186
3	58	55	286
2	484	440	160
1	696	688	95
0	364	360	0

2,20,L

4	36	27	121
3	46	46	287
2	73	77	183
1	54	54	261

2,18,L

5	86	90	283
3	52	50	303
2	58	59	201
1	87	91	299
0	102	102	180

2,17,L

6	44	49	4
5	35	39	193
4	127	126	6
3	52	51	314
2	102	99	14
1	29	18	255
0	103	102	0

2,16,L

8	78	80	173
7	64	63	139
6	70	68	160
5	85	84	92
4	68	71	198
3	61	59	36
2	115	114	160
1	166	170	84
0	184	178	180

2,15,L

9	87	92	228
7	81	86	227
6	30	34	243
5	163	161	259
4	42	42	260
3	189	190	274
2	104	105	109
1	196	194	252

2,15,L

0	112	120	180

2,14,L

9	34	43	176
8	46	38	300
6	53	52	77
5	25	22	95
4	67	60	49
3	84	75	147
2	144	147	283
0	38	44	0

2,13,L

9	69	73	241
8	57	51	276
7	106	106	224
6	53	49	312
5	139	143	263
4	121	117	173
3	264	266	267
2	151	159	229
1	146	149	269
0	48	43	180

2,12,L

10	74	72	334
9	73	72	320
8	94	96	329
7	50	51	147
6	160	164	20
5	133	131	267
4	146	149	318
3	177	183	317
2	400	401	345
1	88	84	224
0	151	163	0

2,11,L

8	78	76	5
7	64	66	139
6	141	143	6
5	95	97	85
4	263	265	303
3	118	117	186
2	199	206	30
1	35	39	21
0	95	101	0

2,10,L

10	59	61	310
9	117	122	79
8	92	94	302
7	169	176	70
6	123	128	354
5	172	177	111
4	129	129	289
3	215	219	58
2	188	174	347
1	192	175	80
0	200	201	0

2,9,L

10	58	61	188
8	58	57	153
7	96	105	114
6	78	83	285
5	155	163	1
4	202	196	104
3	68	58	202
2	211	203	166
1	195	188	78
0	209	220	180

2,8,L

10	86	96	303
9	77	87	69
8	84	84	349
7	107	115	101
6	132	137	250
5	40	38	145
4	311	309	351
3	74	86	70
2	170	145	256
1	433	408	47
0	521	512	0

2,7,L

11	40	48	44
10	76	84	174
9	37	41	50
8	164	176	169
7	71	78	325
6	116	114	183
5	321	327	50
4	77	71	80
3	109	108	54
2	380	364	165
1	154	143	114
0	209	208	180

2,6,L

10	70	68	303
9	31	27	315
8	139	136	352
7	164	166	247
6	64	66	287
5	36	44	324
4	206	186	56
3	273	253	214
2	135	143	317
1	145	143	227
0	545	541	0

2,5,L

10	59	59	8
9	64	57	94
8	91	89	359
7	326	336	33
6	125	117	76
5	263	266	79
4	189	183	309
3	803	783	86
2	351	343	350
1	246	260	136
0	96	79	180

2,4,L

10	48	45	180
9	98	107	162
8	93	105	199
7	115	127	6
6	132	130	175
5	259	251	89
4	382	390	153
3	801	778	121
2	336	318	142
1	273	275	106
0	124	126	180

2,3,L

9	110	114	334
8	77	71	56
7	239	254	66
6	208	209	158

2,3,L

5	109	128	108
4	632	589	193
3	130	146	39
2	1177	1249	272
1	554	569	171
0	394	374	0

2,2,L

10	91	93	71
9	64	68	292
8	193	195	204
7	253	252	93
6	237	239	163
5	136	131	74
4	158	139	97
3	383	379	229
2	678	683	118
1	863	908	157
0	1019	1210	180

2,1,L

9	46	40	344
8	143	140	200
7	183	183	286
6	261	250	151
5	51	51	189
4	349	364	229
3	165	143	3
2	774	767	185
1	343	341	332
0	336	344	180

2,0,L

12	72	75	53
11	81	87	234
10	192	195	76
9	142	143	217
7	311	290	290
6	114	105	187
5	392	376	286
4	356	316	151
3	185	168	262
2	605	581	13
1	576	573	267
0	440	471	180

1,20,L

2	40	41	146
1	76	72	272
0	97	92	180

1,19,L

5	60	58	290
4	81	83	14
3	109	105	258
2	81	80	317
1	136	137	262
0	115	109	0

1,18,L

6	54	53	344
5	70	65	117
3	97	103	72
2	117	119	1
1	80	76	97
0	27	28	0

1,17,L

5	77	73	238
2	47	58	179
1	76	77	274
0	53	60	180

1,16,L

6	56	62	346
5	49	45	33
4	136	128	340
3	73	61	61
2	109	111	4
1	83	90	111
0	142	144	0

1,15,L

8	67	61	201
6	91	92	157
5	58	64	132
4	60	63	191
3	41	45	80
2	145	148	235
1	109	104	61
0	200	193	180

1,14,L

7	93	102	274
6	74	70	266
5	73	71	251
4	69	71	20
3	117	128	281
2	186	191	282
1	196	202	297
0	34	33	0

1,13,L

8	70	70	8
6	153	160	6
5	55	56	123
4	80	85	346
2	157	154	15
1	60	65	2
0	114	114	0

1,12,L

10	67	69	335
8	79	80	304
7	117	122	120
6	64	63	316
5	97	99	8
4	234	215	339
3	66	63	288
2	105	101	333
1	192	188	84
0	50	57	0

1,11,L

9	95	98	31
8	32	31	101
7	150	157	48
6	92	99	112
5	138	135	69
4	127	126	5
3	222	231	72
2	85	83	308
1	102	115	82
0	85	83	0

1,10,L

9	74	74	112
8	42	46	337
7	58	58	92
6	64	61	191
5	118	113	111
4	217	222	18

1,10,L

3	256	254	92
2	204	201	331
1	65	51	69
0	306	312	180

1,9,L

11	73	81	68
9	101	104	60
8	88	88	133
7	162	168	46
6	130	138	171
5	452	450	65
4	245	253	174
3	329	331	99
2	125	135	185
1	231	240	81

1,8,L

10	59	56	187
9	101	102	261
8	140	140	185
7	90	85	221
6	250	261	100
5	90	90	235
4	341	343	179
3	239	238	270
2	332	334	191
1	152	146	169
0	50	59	180

1,7,L

9	51	41	350
8	50	50	302
7	105	108	77
6	134	128	334
5	47	38	261
4	114	118	333
3	202	182	63
2	438	440	58
1	172	165	87
0	76	70	180

1,6,L

10	67	77	132
9	82	85	158
8	58	52	94
7	39	42	26
6	294	301	139
5	24	20	23
4	256	258	164
3	417	398	124
2	183	170	254
1	98	102	56
0	385	371	180

1,5,L

10	45	47	248
8	142	154	312
7	99	100	203
6	115	118	327
5	194	192	187
4	378	361	80
3	210	182	354
2	444	443	196
1	555	533	138
0	358	398	0

1,4,L

9	97	102	40
8	192	203	106
7	146	147	137
6	101	94	185
5	122	116	161
4	245	234	156
3	428	420	359
2	579	585	212
1	261	278	108
0	155	127	0

1,3,L

10	42	35	199
9	109	108	132
8	48	40	152
7	76	82	183
6	342	345	201
5	302	291	212
4	222	194	201
3	290	283	122
2	581	606	113
1	1044	1112	16
0	200	207	0

1,2,L

11	92	100	285
10	90	91	111
9	82	79	262
8	208	205	160
7	214	208	304
6	264	258	180
5	166	166	263
4	487	469	211
3	696	696	246
2	597	608	170
1	818	871	287
0	465	467	180

1,1,L

11	99	108	167
10	138	137	34
9	106	105	215
8	114	111	306
7	358	356	259
6	183	206	1
5	233	230	257
4	154	126	51
3	167	178	293
2	1002	1085	15
1	794	833	256
0	598	707	0

0,21,L

1	94	89	275

0,20,L

4	77	80	339
2	137	137	332
0	99	99	0

0,19,L

5	83	83	73
3	27	29	132

0,18,L

6	105	111	22
4	81	79	328
2	191	191	334
0	134	134	0

0,17,L

7	80	82	108
5	150	148	76
3	247	245	95

0,17,L

1	200	195	65

0,16,L

6	74	68	222
4	37	32	246
2	108	105	152
0	196	201	180

0,15,L

7	55	53	282
5	81	80	32
3	25	28	41
1	90	90	42

0,14,L

6	83	87	340
4	65	68	357
2	195	207	167

0,13,L

7	123	125	4
5	51	46	224
3	235	251	35
1	58	58	325

0,12,L

10	62	66	69
8	112	112	85
6	55	55	298
4	239	239	24
2	97	99	64
0	39	33	0

0,11,L

9	67	72	73
7	118	122	54
5	352	361	86
3	455	458	96
1	169	184	164

0,10,L

10	139	112	143
8	148	150	156
6	187	199	142
4	332	344	146
2	361	396	161
0	213	209	180

0,9,L

7	26	30	268
5	268	287	200
1	96	104	14

0,8,L

10	82	82	140
8	97	104	158
6	178	183	150
4	233	225	172
2	227	227	86
0	593	614	180

0,7,L

9	99	103	246
7	173	178	202
5	454	466	227
3	352	370	266
1	350	364	322

0,6,L

10	106	114	44
8	101	107	295
6	198	202	334
4	233	232	51
2	377	370	90
0	189	192	180

0,5,L

9	91	97	100
7	235	249	197
5	132	125	87
3	300	283	224
1	237	227	121

0,4,L

10	50	58	125
8	120	121	221
6	135	149	307
4	699	698	213
2	786	787	80
0	330	336	180

0,3,L

11	101	107	258
9	77	75	261
7	75	78	192
5	320	305	280
3	771	779	235
1	872	926	268

0,2,L

12	54	56	267
10	66	72	309
8	270	262	2
6	215	212	213
4	48	15	141
2	1057	1151	349
0	512	551	0

0,1,L

11	38	35	161
9	179	188	252
7	351	345	271
5	355	319	299
3	288	312	274
1	864	987	287

0,0,L

12	58	62	344
10	282	280	324
8	551	552	31
6	370	368	358
4	355	331	278
2	952	941	264

APPENDIX 10

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR AN YLIDE COMPOUND DERIVED FROM METHYL 6β-PHENYL-ACETOAMIDO-PENICILLANATE

18,4,L

-3	68	66	129
-5	27	33	303
-6	66	72	165
-7	49	54	7
-8	56	60	206

18,3,L

-2	68	71	177
-3	108	116	10
-4	78	78	220
-5	74	75	39
-6	55	53	179
-8	82	86	40
-9	103	115	181
-10	72	71	357

18,2,L

1	43	39	30
0	44	50	247
-1	62	64	326
-2	40	46	166
-3	39	39	143
-4	59	63	9
-5	108	109	251
-6	59	58	76
-7	69	68	179

18,1,L

1	54	52	313
0	75	73	51
-1	60	62	209
-3	80	81	154
-4	89	87	356
-5	68	67	164
-6	70	65	272
-7	52	51	118
-8	50	50	84
-10	67	72	195
-11	57	68	15
-12	57	58	123

18,0,L

1	113	112	180
0	144	145	0
-1	67	66	180
-2	75	79	0
-3	119	120	180
-5	148	162	0
-6	125	118	180
-7	35	32	0
-8	87	89	180
-9	121	115	0
-10	28	26	180
-11	56	63	180
-12	54	58	0

17,5,L

-3	49	42	235
-7	41	53	36

17,4,L

0	37	33	339
-1	59	63	190
-2	57	57	5
-5	61	64	165
-7	66	67	30
-8	91	104	193
-9	110	119	2
-10	91	99	168

17,3,L

2	44	43	2
1	49	52	262
0	68	67	39
-1	34	40	206
-2	50	49	164
-4	63	66	297
-5	111	117	87
-6	92	92	222
-7	142	147	45
-8	40	41	232
-10	51	60	63
-11	58	59	218
-12	102	107	20

17,2,L

0	40	41	249
-1	60	54	355
-2	28	26	229
-3	60	60	125
-4	50	56	308
-5	54	55	244
-7	45	46	137
-8	47	47	306
-10	37	41	54
-11	49	53	104
-12	57	67	275

17,1,L

3	36	40	312
2	67	62	208
1	72	71	21
0	61	56	120
-1	45	49	336
-2	58	68	216
-3	83	88	260
-4	93	93	37
-5	75	83	156
-6	87	88	294
-7	99	99	136
-8	48	49	331
-10	56	58	183
-11	61	66	2
-12	38	41	126
-13	46	51	311

17,0,L

3	66	69	0
1	54	53	180
0	59	60	0
-1	31	33	0
-2	117	116	0
-3	135	136	180
-4	75	78	0
-8	37	37	180
-9	113	117	0
-10	93	89	180

16,6,L

-4	50	48	223
-5	46	48	126

16,5,L

1	44	51	51
0	46	47	219
-1	44	45	84
-3	41	38	179
-4	80	82	353
-5	39	42	179
-6	52	52	20

16,4,L

-1	77	77	206

16,4,L

-2	73	75	32
-3	38	41	153
-5	56	58	198
-7	42	43	8
-8	78	79	179
-9	84	96	346
-12	43	44	198

16,3,L

2	34	36	305
1	30	31	232
0	62	64	25
-1	89	97	186
-2	23	24	188
-3	40	40	332
-4	54	55	50
-5	52	56	66
-6	141	139	179
-7	123	128	17
-8	41	37	246
-9	68	64	93
-10	59	58	209
-11	52	60	318
-12	41	43	89
-13	48	46	261

16,2,L

4	76	80	350
3	69	73	233
2	58	61	109
1	66	69	11
0	49	55	232
-1	95	91	297
-2	72	70	139
-3	71	71	99
-4	105	101	257
-6	39	40	241
-7	42	41	113
-8	87	94	334
-10	64	70	68
-11	50	57	187
-13	69	73	302

16,1,L

3	49	49	53
2	88	88	250
1	50	48	15
0	51	49	86
-1	77	75	259
-2	93	91	226
-3	30	29	127
-4	154	156	53
-5	133	134	203
-6	43	45	304
-7	59	57	145
-8	40	39	42
-10	115	116	245
-11	54	53	77
-12	38	37	77

16,0,L

5	46	45	180
3	59	54	0
2	77	76	180
1	25	25	0
-1	33	38	0
-3	132	126	180
-4	121	114	0
-5	26	29	180
-6	33	29	0
-7	29	23	180
-8	41	41	0
-9	62	65	0
-10	68	67	180
-12	51	48	180
-13	123	129	0

15,6,L

-3	69	76	337
-4	68	69	151
-5	29	24	7
-7	39	40	73
-9	43	46	142

15,5,L

2	44	49	163
1	70	74	30
0	99	98	189
-1	98	93	1
-2	87	86	152
-3	55	50	329
-5	60	61	149
-6	91	91	16
-7	89	85	213
-8	52	46	9
-10	65	66	294
-11	26	30	79

15,4,L

4	48	51	220
2	47	50	305
0	61	62	185
-1	58	57	301
-2	49	48	72
-3	40	36	209
-4	72	70	33
-5	168	170	202
-6	155	156	11
-7	54	51	194
-8	84	92	332
-9	51	51	116
-10	51	52	221
-11	58	59	0
-12	52	45	190

15,3,L

5	30	35	312
4	46	48	315
2	36	28	212
0	57	52	340
-1	103	108	160
-2	37	36	58
-4	68	67	49
-5	95	95	182
-6	81	84	99
-7	60	61	324
-8	44	39	229
-9	68	74	96
-10	62	58	193
-11	88	95	17
-12	71	67	304
-13	96	105	156

15,2,L

6	47	60	97
5	38	38	154
4	46	38	346
3	40	40	219
2	75	77	41
1	87	90	176
0	40	36	357
-1	65	67	301
-2	117	120	156
-3	132	131	20
-4	160	162	179
-5	193	193	315
-6	54	57	94

15,2,L

-7	51	54	96
-8	100	101	346
-9	62	57	205
-11	46	45	117
-12	63	67	335
-13	98	101	275
-14	75	86	126

15,1,L

6	33	33	239
4	86	85	35
3	56	54	243
2	67	76	231
1	74	76	49
0	62	60	152
-1	123	122	32
-2	189	183	224
-3	53	52	24
-4	117	110	75
-5	134	140	233
-6	28	25	147
-7	117	123	248
-8	68	63	13
-9	72	72	188
-10	51	50	288
-11	45	43	65
-14	91	103	214
-15	38	43	1

15,0,L

6	60	67	180
5	52	51	180
3	51	47	0
2	33	33	180
0	35	21	180
-1	142	143	0
-2	29	28	180
-3	69	68	180
-5	107	106	0
-6	132	131	0
-7	112	107	180
-8	78	79	0
-9	42	42	0
-10	50	54	180
-13	73	72	0
-14	52	55	180
-15	30	19	180

14,7,L

-2	34	35	66
-6	35	36	334
-7	51	55	125

14,6,L

1	43	50	175
0	60	61	332
-1	74	76	161
-2	60	62	348
-4	40	37	137
-5	50	50	317
-6	38	43	130
-7	66	67	313
-8	56	53	158

14,5,L

3	51	50	190
2	43	43	54
0	35	38	209
-1	61	66	41
-2	69	65	190
-3	97	98	16
-4	85	79	210
-5	91	93	7
-7	44	44	237
-8	94	105	12
-9	87	90	181
-10	76	75	18
-11	66	63	240
-12	43	42	38

14,4,L

3	38	42	39
1	65	67	16
0	83	89	220
-1	40	43	100
-2	61	60	19
-3	75	83	87
-4	79	79	190
-5	136	133	303
-6	118	120	72
-7	40	31	295
-8	42	53	224
-9	55	55	219
-10	53	47	324
-11	70	71	61
-12	112	119	223
-13	50	53	35

14,3,L

6	52	47	198
5	70	74	340
3	44	43	229
2	56	57	105
1	29	21	65
0	120	118	338
-1	142	149	182
-2	62	61	164
-3	123	123	359
-5	91	90	162
-6	36	33	261
-9	47	39	314
-10	106	108	173
-11	97	102	350
-14	49	51	202

14,2,L

7	44	42	329
6	57	61	115
5	46	48	70
4	30	25	141
3	28	25	254
2	98	95	6
1	111	107	154
0	137	138	335
-1	92	95	227
-2	41	42	68
-3	190	191	124
-4	135	145	278
-5	146	137	345
-6	103	99	155
-7	102	99	36
-8	72	76	267
-10	50	48	352
-11	180	184	152
-12	109	109	340
-13	31	33	195

14,1,L

7	40	43	219
6	59	58	271
5	18	20	205
4	104	106	31
3	98	99	251
2	78	75	80
0	82	78	52
-1	97	99	253
-2	146	143	229

14,1,L

-3	151	147	70
-4	61	64	243
-5	21	-21	341
-6	142	141	242
-7	89	92	196
-8	71	66	44
-9	92	90	206
-11	32	35	152
-12	32	30	187
-13	79	81	39
-14	123	128	233
-15	48	60	35

14,0,L

7	52	51	0
4	108	112	180
3	92	87	0
2	46	43	0
1	54	51	180
0	41	34	180
-2	48	50	0
-3	239	240	180
-4	129	128	0
-5	69	69	0
-6	47	50	180
-11	90	86	180
-13	88	97	0
-14	73	72	180
-15	70	76	0

13,7,L

-1	29	29	345
-3	44	48	215
-6	30	32	342
-7	36	36	143

13,6,L

0	45	49	23
-1	39	40	196
-2	51	54	23
-3	56	62	325
-7	46	46	344
-8	67	71	177
-9	55	48	31
-10	35	48	199

13,5,L

4	20	23	14
3	67	65	146
2	75	80	62
1	94	99	206
0	46	44	5
-1	71	70	77
-2	69	75	219
-3	86	88	357
-4	99	97	216
-5	98	100	11
-6	67	66	119
-7	42	43	183
-8	46	44	314
-9	68	70	197
-10	97	102	27
-11	78	79	211
-12	49	49	33
-13	41	45	183

13,4,L

7	46	50	216
6	62	62	12
3	86	85	273
1	128	126	55
0	171	174	235
-1	88	93	67
-3	109	106	41
-4	85	93	260
-5	67	61	183
-6	135	136	26
-7	66	65	257
-8	61	59	116
-9	95	101	237
-10	94	91	62
-11	21	16	57
-12	62	65	260
-13	42	41	116

13,3,L

7	39	50	169
6	67	64	226
5	97	104	347
3	36	41	127
1	69	68	223
0	68	68	8
-1	84	83	164
-2	32	34	232
-3	63	68	41
-4	94	97	346
-5	65	61	130
-6	180	188	162
-7	138	138	341
-8	117	111	145
-10	92	86	156
-11	54	63	30
-12	59	56	10
-13	53	53	190
-14	62	65	167
-15	47	56	358

13,2,L

7	75	75	342
6	123	123	161
5	85	88	59
3	72	72	289
2	52	56	30
1	255	256	146
0	170	177	321
-1	111	107	143
-2	38	40	352
-3	134	127	116
-4	92	106	303
-5	137	133	348
-6	199	199	151
-7	182	177	8
-8	251	249	173
-9	106	98	338
-10	127	128	121
-12	97	99	319
-13	64	64	204
-14	93	99	28
-15	96	113	161

13,1,L

6	59	57	308
5	52	54	182
4	165	168	46
3	82	79	204
2	128	136	60
1	134	123	238
0	114	117	84
-1	73	71	336
-2	154	155	230
-3	225	216	49
-4	190	190	212
-5	206	201	55
-6	341	337	242
-7	67	67	145
-8	119	121	16
-9	158	165	201
-10	103	108	344

13,1,L

-11	62	66	187
-12	141	141	49
-13	162	169	232
-14	41	42	58

13,0,L

8	46	46	0
6	52	52	180
5	95	96	180
3	99	103	0
2	69	66	180
1	118	110	180
0	86	80	0
-1	62	78	180
-2	170	165	0
-3	260	238	180
-4	227	230	0
-5	93	85	180
-6	113	125	0
-7	32	30	180
-8	161	170	180
-10	117	120	180
-11	87	92	0
-13	52	48	0
-14	65	73	180
-16	20	14	0

12,8,L

-2	74	75	231
-3	62	61	30
-4	62	66	222
-5	73	76	44

12,7,L

2	29	25	273
1	50	46	36
0	46	50	250
-1	42	47	127
-2	58	61	339
-3	58	60	181
-4	43	47	321
-6	41	41	101
-7	48	49	282
-8	35	41	162
-10	28	29	90

12,6,L

5	43	44	68
4	18	16	193
2	36	32	78
1	71	70	254
0	78	80	33
-1	61	65	176
-2	83	85	344
-3	76	76	157
-4	80	81	328
-5	88	89	112
-6	65	64	239
-7	52	49	63
-8	55	54	216
-9	23	15	327
-10	32	35	145
-12	35	33	173

12,5,L

6	32	35	146
4	40	42	165
2	71	69	74
1	88	87	204
0	92	91	334
-1	116	112	181
-2	103	98	45
-3	93	93	268
-4	26	26	276
-5	141	141	33
-6	205	197	214
-7	167	164	17
-8	89	86	217
-9	83	78	39
-10	44	46	112
-11	51	48	247
-12	56	55	358
-13	60	63	143

12,4,L

8	51	47	259
7	46	52	193
6	85	90	2
5	42	48	163
4	39	40	15
3	53	53	226
2	92	94	79
1	60	58	318
0	54	54	124
-1	79	81	298
-2	77	77	77
-3	122	114	43
-4	156	149	243
-5	95	91	82
-6	61	58	4
-7	127	125	157
-8	144	143	50
-9	180	186	236
-10	128	130	20
-12	48	39	223
-15	43	46	66

12,3,L

8	63	68	7
7	77	84	200
6	50	50	102
5	72	75	340
4	30	28	258
3	132	132	55
2	219	219	187
1	196	204	351
0	76	83	256
-1	60	70	192
-2	63	64	109
-3	89	80	254
-4	270	269	2
-5	276	283	156
-6	99	97	260
-7	36	37	68
-8	144	138	357
-9	153	154	170
-11	72	71	281
-12	25	31	81
-14	27	32	186

12,2,L

9	38	34	126
8	50	45	293
7	58	55	356
6	55	57	125
5	107	105	107
4	67	69	286
3	62	62	27
2	129	127	140
1	34	35	15
0	122	117	345
-1	191	187	255
-2	269	266	59
-3	219	206	173
-4	203	207	333
-5	52	49	269
-6	169	178	127
-8	265	267	145

12,2,L

-9	333	335	329
-10	196	193	159
-11	151	161	26
-12	64	69	231
-13	44	42	145
-14	77	72	359
-15	127	136	151
-16	68	71	329

12,1,L

8	45	46	125
7	55	51	282
5	65	71	57
4	61	63	19
3	220	223	88
2	169	160	286
1	58	55	185
0	188	187	16
-1	156	158	230
-2	113	111	167
-3	239	231	4
-4	197	188	175
-5	157	146	338
-6	274	262	216
-7	157	152	37
-8	88	95	187
-9	134	133	241
-10	58	57	67
-11	141	140	222
-12	205	208	43
-13	201	206	217
-14	101	95	17
-15	42	45	196

12,0,L

9	30	29	180
8	65	51	0
6	69	68	0
5	215	208	180
4	130	132	0
2	142	142	180
1	109	107	0
0	145	141	180
-1	331	324	0
-2	390	382	180
-3	227	213	0
-4	48	54	180
-6	160	169	180
-7	217	212	180
-8	106	105	180
-10	46	55	0
-11	32	31	180
-12	68	72	0
-15	62	57	180
-16	25	23	0

11,8,L

-3	21	28	339
-5	31	35	62
-6	60	55	218

11,7,L

3	35	31	345
1	53	57	26
0	75	78	227
-1	92	94	41
-2	65	63	211
-5	65	67	227
-6	61	58	66
-7	70	66	234
-8	43	41	65

11,6,L

5	26	37	97
4	64	64	259
3	58	62	115
2	62	65	270
1	59	62	27
0	39	40	164
-1	50	50	308
-2	70	71	37
-3	88	86	244
-4	80	75	99
-5	52	51	208
-6	41	42	256
-9	32	31	85
-10	52	48	315
-13	23	21	328

11,5,L

3	34	30	56
2	47	46	202
1	43	45	243
0	66	67	335
-1	97	104	120
-2	52	51	338
-3	63	57	251
-4	98	94	343
-5	101	101	178
-6	106	101	28
-7	43	47	288
-8	85	77	192
-9	108	112	17
-10	81	84	195
-11	52	48	6
-13	34	40	185
-14	43	55	32

11,4,L

9	33	34	34
8	66	68	244
6	70	65	26
5	48	49	148
4	54	64	321
3	139	137	195
2	175	170	353
1	70	68	232
0	93	96	122
-1	92	95	292
-2	103	109	96
-3	87	93	331
-4	200	207	194
-5	39	37	352
-6	104	103	231
-7	161	172	31
-8	162	153	251
-9	55	60	106
-10	145	150	12
-11	36	40	246
-12	25	30	107
-13	58	59	270
-14	53	61	69

11,3,L

8	66	61	24
7	85	83	204
5	39	40	317
4	126	127	4
3	69	65	306
2	284	282	200
1	296	297	342
0	111	105	241
-1	155	150	114
-2	70	61	245
-3	117	120	26
-4	76	80	5
-5	131	125	245
-6	246	252	89

11,3,L

-7	68	66	211
-8	141	147	336
-9	167	167	131
-10	45	55	121
-11	134	133	12
-12	68	69	189
-14	59	62	141
-15	59	71	336

11,2,L

10	46	55	69
9	26	21	86
8	56	57	302
7	29	27	237
6	65	66	86
5	82	79	88
4	52	53	232
3	144	136	318
2	60	60	183
1	88	85	44
0	123	121	161
-1	101	96	312
-2	115	121	130
-3	50	51	198
-4	51	45	16
-5	174	167	203
-6	156	152	2
-7	393	406	133
-8	174	176	314
-9	86	85	6
-10	121	126	97
-11	62	68	26
-12	57	55	249
-13	83	81	331
-14	94	94	145
-15	33	41	60
-16	47	55	307

11,1,L

10	36	38	221
8	55	48	99
7	73	66	301
6	77	75	204
5	190	186	56
4	95	93	63
2	250	253	269
1	166	155	114
0	223	213	347
-1	174	164	175
-2	158	147	14
-3	146	139	182
-4	288	278	61
-5	273	262	247
-6	182	175	121
-7	123	120	323
-8	145	145	201
-9	173	176	29
-10	132	138	212
-11	128	130	56
-12	62	60	287
-13	78	77	194
-14	44	39	351
-16	56	56	15

11,0,L

10	54	55	180
8	52	48	0
7	83	81	180
6	24	29	0
5	160	155	180
4	76	77	0
3	65	63	180
2	178	171	0
0	144	128	180
-1	224	207	0
-2	311	303	180
-3	258	241	0
-4	335	321	180
-5	248	215	0
-6	61	66	180
-7	296	302	180
-8	163	155	0
-10	47	50	0
-11	169	155	180
-12	106	107	0
-14	44	35	180
-16	19	14	0
-17	29	37	0

10,8,L

1	40	40	256
-2	35	32	89
-8	45	38	311

10,7,L

5	50	50	165
1	68	71	327
0	65	62	160
-1	53	50	356
-2	56	58	240
-4	28	27	227
-5	35	29	174
-6	88	91	356
-7	97	97	178
-8	56	59	340
-9	44	42	226
-10	21	21	60

10,6,L

7	37	35	231
5	43	44	324
4	64	59	168
3	54	52	18
2	92	96	218
1	126	126	18
0	47	46	176
-3	41	45	261
-4	112	113	118
-5	109	111	251
-6	38	38	70
-8	38	36	142
-10	18	21	267
-11	33	38	69
-12	59	69	185

10,5,L

8	27	30	192
7	51	54	88
4	64	63	253
3	69	68	117
2	69	80	255
1	73	77	338
0	114	114	141
-3	85	79	245
-4	46	50	342
-5	47	37	136
-6	46	48	56
-7	121	125	292
-8	73	75	23
-9	64	65	17
-11	40	41	288
-12	19	23	268
-13	54	51	69

10,4,L

8	89	82	184
7	29	31	318
5	92	94	18

10,4,L

4	169	175	262
3	125	121	164
2	136	137	347
1	139	145	69
0	70	65	240
-1	81	78	196
-2	122	117	92
-3	167	156	345
-4	218	213	187
-5	172	170	300
-6	115	107	60
-7	188	179	84
-8	179	174	294
-9	53	57	57
-10	95	93	20
-11	32	32	146
-12	66	66	253
-13	49	49	171
-14	67	72	9

10,3,L

10	56	49	207
9	53	52	32
8	69	67	334
7	160	166	167
6	136	134	5
5	110	108	197
4	163	164	358
3	149	151	209
2	67	71	218
1	243	253	9
0	45	35	195
-1	34	26	91
-2	173	171	173
-3	261	253	349
-4	59	50	71
-5	218	204	165
-8	314	313	23
-9	46	38	300
-10	141	145	178
-11	63	64	13
-12	75	78	282
-13	43	50	97
-14	78	81	200
-15	89	91	354

10,2,L

8	48	49	15
7	56	55	212
6	31	35	107
5	116	117	63
4	124	126	275
3	91	92	325
1	219	218	84
0	152	161	259
-1	153	153	311
-2	241	234	145
-3	115	118	42
-4	204	210	296
-5	61	56	250
-6	112	106	27
-7	205	198	113
-8	209	202	333
-9	91	87	61
-10	32	28	113
-11	85	87	122
-12	42	39	219
-13	81	80	359
-14	89	96	159
-15	55	53	356
-16	50	49	143

10,1,L

11	33	33	169
8	72	70	96
7	64	54	328
6	107	101	139
5	118	121	341
4	173	170	90
3	111	115	310
2	144	148	289
1	291	271	71
0	22	30	327
-1	140	130	100
-2	114	109	2
-3	87	77	179
-4	174	170	11
-5	172	171	229
-6	63	65	169
-7	122	113	3
-8	274	269	108
-9	117	113	16
-10	141	140	207
-11	80	77	82
-12	108	112	256
-13	61	59	61
-14	66	59	255
-15	46	55	99
-16	40	42	45

10,0,L

11	49	47	0
10	56	51	180
9	60	55	0
8	87	90	180
7	72	73	0
6	48	40	180
5	76	72	180
4	244	222	0
3	207	208	180
2	384	395	0
1	395	372	180
0	167	151	0
-2	151	159	180
-3	216	224	0
-4	38	43	180
-5	62	43	180
-6	106	107	180
-7	100	96	180
-8	159	156	0
-9	188	200	180
-10	83	79	0
-11	88	82	180
-12	83	67	0
-13	106	111	180
-17	51	52	0

9,9,L

-4	53	50	97

9,8,L

2	22	17	164
-1	26	26	104
-2	39	42	241
-5	21	21	345
-6	34	30	119
-8	32	32	115
-9	38	39	24

9,7,L

4	39	38	346
3	54	56	206
2	140	148	14
1	94	95	169
-1	61	67	9
-2	107	110	168
-3	132	133	339
-4	147	143	173
-5	107	109	9

9,7,L

-7	65	67	158
-8	56	55	320
-9	61	62	174
-10	54	55	341
-11	58	60	202

9,6,L

5	48	51	255
4	64	69	124
2	53	56	252
1	116	119	88
0	107	110	216
-1	79	82	94
-2	144	145	306
-3	96	100	145
-4	52	48	336
-5	119	121	196
-6	132	126	52
-7	119	119	257
-8	55	57	60
-9	60	59	146
-10	57	63	247
-12	43	46	231
-13	28	34	26

9,5,L

6	55	58	151
5	45	45	319
4	59	59	290
2	166	166	74
1	135	138	245
-1	110	114	85
-2	77	80	265
-3	42	39	0
-4	77	72	248
-5	164	169	63
-7	65	62	321
-8	130	131	278
-9	78	79	109
-11	111	114	282
-12	55	60	143
-13	33	30	12
-14	24	27	170

9,4,L

9	34	33	14
8	89	88	188
7	93	102	344
6	47	43	98
5	72	75	12
4	101	99	182
3	171	184	277
2	131	132	28
1	251	246	135
0	211	219	278
-1	262	245	162
-2	246	235	14
-3	94	97	200
-4	90	89	161
-5	210	214	277
-6	177	164	159
-7	373	362	348
-8	165	167	184
-9	74	75	257
-11	38	38	158
-12	99	92	324
-13	82	83	174
-14	56	60	9
-15	21	15	106

9,3,L

10	80	83	163
9	92	98	8
8	46	46	241
7	73	76	154
6	96	101	197
5	125	122	330
4	203	204	347
3	211	211	228
2	81	82	53
1	145	133	229
0	150	143	346
-1	141	141	48
-2	347	336	205
-3	277	277	357
-4	121	114	275
-5	160	151	101
-6	78	73	66
-7	34	37	280
-8	300	302	15
-9	297	295	173
-10	101	90	0
-11	74	84	259
-12	66	62	11
-13	55	55	136
-14	66	58	205
-15	87	79	25

9,2,L

11	44	49	333
10	24	22	24
9	105	107	145
8	115	112	325
6	77	73	55
5	56	57	160
4	88	93	330
3	281	277	317
2	158	157	135
1	175	174	144
0	88	92	269
-1	98	87	257
-2	188	194	100
-3	188	175	236
-4	158	155	73
-5	201	198	303
-6	165	151	146
-7	173	185	79
-8	203	195	342
-9	225	211	157
-10	62	59	12
-11	86	87	124
-12	85	86	223
-13	90	89	11
-14	91	93	137
-17	48	48	289

9,1,L

12	54	56	36
11	71	72	201
10	44	46	4
9	71	71	111
8	87	91	278
6	45	46	200
5	111	111	15
4	78	74	103
3	171	165	319
2	194	194	137
1	167	170	352
0	76	84	150
-1	155	137	91
-2	297	283	332
-3	339	322	175
-4	187	171	339
-5	186	170	153
-6	81	85	45
-7	32	32	5
-8	255	250	77
-9	207	201	257
-10	54	51	208
-11	199	198	5

9,1,L

-12	146	148	185
-13	42	45	305
-15	62	58	67
-16	53	50	29

9,0,L

12	57	64	0
8	56	63	180
7	129	122	0
6	185	177	180
5	124	128	0
4	59	50	180
3	246	241	0
2	85	94	180
1	141	132	180
0	350	332	0
-1	457	449	180
-3	175	164	0
-4	243	237	180
-5	447	422	0
-6	436	415	180
-7	330	315	0
-8	41	37	180
-9	108	106	180
-10	150	154	180
-11	101	96	180
-12	102	94	0
-13	130	131	180
-14	21	9	180

8,9,L

1	49	44	104
0	37	38	285
-2	31	30	307
-6	39	36	84

8,8,L

5	29	37	62
2	42	41	30
1	52	55	206
-2	27	34	4
-3	58	53	158
-4	26	34	306
-5	90	92	89
-6	38	40	269
-7	40	41	347
-8	73	72	120

8,7,L

5	20	22	289
2	46	47	65
1	56	61	154
0	40	37	19
-1	47	46	253
-3	39	35	78
-4	57	58	238
-5	119	116	32
-6	124	123	168
-7	84	83	319
-8	70	69	190
-9	40	41	228
-11	57	62	207
-12	60	66	15

8,6,L

7	39	38	160
6	58	64	349
3	68	74	175
2	68	60	63
0	98	96	216
-1	136	130	19
-2	78	85	212
-3	45	44	71
-4	33	29	195
-5	71	71	177
-6	80	79	7
-7	59	60	229
-8	97	97	128
-9	106	109	215
-11	35	39	181
-13	47	50	93
-14	70	73	279

8,5,L

10	56	58	52
9	64	66	247
8	53	53	106
6	40	37	89
5	33	28	279
4	148	153	231
3	141	144	83
2	172	173	153
1	52	60	131
0	45	44	286
-1	110	103	195
-2	138	139	31
-3	123	122	215
-4	86	92	353
-5	78	79	110
-6	106	100	190
-8	73	77	325
-9	88	88	199
-10	62	66	298
-11	50	48	334
-13	35	35	71

8,4,L

10	39	39	358
9	31	34	118
8	53	61	256
7	53	61	200
6	106	96	2
5	63	63	272
4	38	41	189
3	215	213	213
2	174	182	64
1	100	102	210
0	52	46	236
-1	64	60	250
-2	94	101	354
-3	74	73	117
-4	223	202	287
-5	117	111	155
-6	166	165	2
-7	163	170	22
-8	248	241	180
-9	251	247	309
-10	51	53	213
-12	54	52	4
-13	83	81	210
-14	109	111	12
-15	62	57	172
-16	34	32	310

8,3,L

12	40	37	75
10	61	66	161
9	67	66	313
8	44	44	181
7	102	101	338
6	143	150	164
5	137	140	320
4	211	198	312
3	335	338	164
2	40	47	160
1	14	9	131
0	172	166	349
-1	67	60	201

8,3,L

-2	121	121	169
-3	179	181	46
-4	91	84	330
-5	198	197	117
-6	430	428	184
-7	317	318	347
-8	75	73	117
-9	179	181	261
-10	80	73	44
-11	132	131	242
-12	140	140	29
-13	81	78	194
-16	70	75	276

8,2,L

12	44	49	233
11	39	43	317
9	51	58	159
7	65	72	276
6	125	125	74
5	100	104	203
4	34	37	312
3	150	152	287
2	213	215	136
1	53	52	278
0	241	233	218
-1	220	206	348
-2	26	33	111
-3	113	110	28
-4	217	204	259
-5	327	316	321
-6	340	346	63
-7	47	45	174
-8	70	67	311
-9	163	172	307
-10	49	54	103
-11	77	84	98
-12	43	43	358
-13	39	43	242
-14	68	67	16
-15	59	63	116
-16	47	52	265
-17	37	41	337

8,1,L

11	52	53	236
10	50	47	274
9	38	36	103
8	61	56	243
7	24	26	62
6	89	91	283
5	153	148	61
4	103	94	303
3	183	163	270
2	85	89	152
1	260	257	29
0	260	259	73
-1	267	263	233
-2	168	145	19
-3	252	246	51
-4	79	72	308
-5	314	300	210
-6	165	147	315
-7	210	209	108
-8	150	143	292
-9	99	97	204
-10	79	75	102
-11	97	106	328
-12	83	79	126
-13	60	57	287
-14	46	49	141
-15	31	30	54

8,0,L

12	95	90	0
11	40	41	180
8	50	41	180
7	61	58	0
6	98	109	180
5	113	129	0
4	63	64	180
3	196	176	0
2	302	285	180
0	116	78	0
-1	74	67	180
-2	290	257	0
-3	37	36	180
-4	404	385	0
-5	228	208	180
-6	104	93	180
-7	104	96	0
-8	228	228	180
-9	289	287	0
-10	280	289	180
-11	58	55	0
-12	66	60	0
-13	45	47	180
-15	69	70	180
-16	110	116	0

7,9,L

3	69	68	323
2	38	38	161
0	56	60	257
-3	34	33	126
-4	20	20	337
-7	36	38	245

7,8,L

5	48	41	16
1	107	113	246
0	113	108	53
-1	77	80	225
-2	64	68	59
-5	40	40	70
-6	50	47	235

7,7,L

7	52	57	14
6	33	33	151
4	19	16	189
3	87	96	58
2	34	38	103
1	37	35	173
0	111	113	8
-1	48	43	173
-2	81	87	3
-3	97	92	175
-4	66	68	336
-5	50	48	104
-6	33	29	228
-7	38	24	347
-8	63	70	196
-9	56	57	337
-12	48	50	40

7,6,L

9	24	25	124
8	37	39	322
7	51	52	143
6	82	82	329
5	82	78	133
4	31	34	64
3	90	83	215
2	99	103	83
1	211	224	294
0	176	177	134
-1	146	149	337
-2	98	100	191

7,6,L

-3	147	150	18
-4	162	155	184
-5	96	98	47
-6	111	112	309
-7	84	87	158
-8	48	53	196
-9	143	141	228
-10	59	56	57
-11	48	49	245
-12	52	51	109
-13	30	27	254

7,5,L

10	60	58	28
9	81	88	205
8	70	73	1
7	68	68	131
6	66	67	217
5	72	74	332
4	190	185	174
3	284	285	59
2	305	304	207
1	136	126	45
0	52	49	321
-1	51	49	138
-2	110	105	46
-3	221	219	256
-4	245	233	67
-5	170	170	200
-6	189	184	34
-7	179	175	253
-8	48	51	216
-9	88	95	348
-10	45	51	138
-11	75	75	31
-12	54	53	176
-14	30	28	188

7,4,L

11	53	60	233
8	73	81	298
7	52	53	107
5	215	224	62
4	178	174	218
3	45	46	327
2	154	158	137
1	309	296	338
0	207	199	149
-1	142	143	263
-2	144	126	0
-3	146	138	86
-4	127	126	231
-5	58	57	150
-6	124	124	341
-7	99	96	340
-8	335	336	241
-9	71	68	148
-10	100	100	305
-11	69	68	357
-12	85	85	197
-13	67	59	315
-14	53	58	56
-15	43	38	194
-16	55	56	310

7,3,L

11	70	78	166
10	39	44	134
9	61	57	297
8	40	43	54
6	159	168	225
5	61	67	325
4	190	197	321
3	296	289	151
2	166	173	264
1	92	93	217
0	299	280	359
-1	222	209	218
-2	30	25	50
-3	179	190	291
-4	86	75	178
-5	187	170	323
-6	320	323	175
-7	194	179	20
-8	206	204	275
-10	115	118	109
-11	70	65	339
-12	76	77	47
-13	80	75	200
-14	54	53	34

7,2,L

11	67	73	315
10	82	84	151
8	148	146	337
7	139	150	198
6	213	217	20
5	285	286	141
4	276	262	318
3	124	127	256
2	166	164	180
1	307	283	38
0	320	307	267
-1	279	270	3
-2	431	406	271
-3	522	497	58
-4	239	228	190
-6	204	201	34
-7	170	163	140
-8	256	249	324
-9	120	120	231
-10	170	167	63
-11	33	32	287
-12	49	49	358
-13	31	31	128
-14	48	44	130
-15	39	40	50
-16	76	76	264
-17	56	60	340

7,1,L

13	37	48	44
12	35	32	94
11	75	75	226
9	98	104	254
8	202	210	47
7	169	170	197
6	161	151	312
5	124	128	51
4	125	109	204
3	157	144	49
2	176	179	205
1	245	242	42
0	17	10	302
-1	239	235	299
-2	268	250	137
-3	150	136	324
-4	231	216	146
-5	309	286	249
-6	236	216	259
-7	200	189	94
-8	124	114	322
-9	157	149	288
-10	76	81	188
-11	208	205	51
-12	54	48	174
-13	53	59	27
-14	63	59	221
-15	98	97	33
-17	30	30	240

7,0,L

11	27	29	0
10	58	54	180
8	170	165	0
7	128	129	180
6	100	96	180
4	17	28	0
3	133	138	0
2	171	167	180
1	290	297	0
0	433	437	0
-1	115	130	180
-2	506	499	0
-3	225	230	180
-4	207	208	0
-5	107	104	180
-6	17	11	180
-7	85	77	0
-8	229	227	0
-9	59	65	180
-10	108	100	180
-11	29	30	0
-13	40	31	0
-14	81	73	180
-15	48	44	180
-16	127	133	0
-17	38	46	180

6,9,L

1	90	94	327
-4	31	37	325
-5	50	48	153
-6	57	60	345

6,8,L

4	46	51	200
3	97	90	36
2	138	136	228
1	74	76	8
0	43	41	43
-1	57	58	245
-2	73	70	69
-3	98	93	226
-4	96	88	45
-5	66	64	227
-6	29	31	311
-7	45	48	84
-8	37	43	246
-9	66	69	65

6,7,L

8	28	27	222
6	31	26	248
5	40	39	86
4	26	15	166
3	85	91	43
2	94	98	105
1	142	142	333
0	49	43	88
-1	41	49	182
-2	87	91	8
-3	102	98	187
-4	83	83	34
-7	24	20	182
-8	66	68	220
-9	156	156	25
-10	69	71	160
-11	23	27	57

6,6,L

9	58	63	355
8	55	60	156
7	53	59	16
6	39	31	332
5	37	43	204
4	31	25	62
3	75	80	183
2	213	215	325
1	28	31	112
0	141	134	65
-1	146	150	307
-2	162	170	130
-3	145	138	326
-4	142	150	163
-5	41	41	31
-6	214	200	272
-7	163	170	108
-8	86	87	236
-9	81	87	148
-10	71	72	28
-11	109	106	186
-12	64	64	28
-13	74	71	198
-14	41	37	30

6,5,L

11	70	74	48
10	33	37	258
8	97	97	354
7	131	136	167
6	133	132	27
5	147	147	238
3	239	241	107
2	99	97	174
1	199	198	24
0	292	288	206
-1	207	201	47
-2	173	169	181
-3	62	62	272
-4	96	96	0
-5	247	240	173
-6	231	223	47
-7	273	269	235
-8	117	111	34
-9	162	157	95
-10	38	42	166
-12	49	52	216
-13	76	76	54
-14	54	58	214
-15	39	42	355

6,4,L

11	67	72	190
10	75	84	33
8	36	36	71
5	117	110	45
4	302	299	230
3	128	137	94
2	41	37	180
1	283	280	15
0	253	253	172
-1	199	191	320
-2	239	214	123
-3	69	68	244
-4	95	95	17
-5	303	296	231
-6	274	261	26
-7	246	232	143
-8	263	244	297
-10	75	72	168
-11	156	155	6
-12	96	95	186
-13	77	71	326
-14	39	37	127
-15	50	48	352
-16	38	39	192

6,3,L

12	58	66	344
11	64	67	154

6,3,L

10	46	48	226
9	61	59	11
8	67	74	276
7	58	53	5
6	116	111	197
5	158	162	2
4	89	87	258
3	81	86	139
2	205	204	155
1	113	112	323
0	320	290	319
-1	295	294	183
-2	274	258	65
-3	184	169	229
-4	340	327	61
-5	284	265	204
-6	256	253	151
-7	310	314	347
-8	162	155	203
-9	240	227	60
-10	279	265	211
-11	140	140	74
-12	103	104	330
-13	83	82	168
-14	31	30	309
-15	53	53	248
-16	70	78	23

6,2,L

12	55	56	278
11	49	45	322
10	83	78	179
9	82	93	42
8	100	96	146
7	70	71	357
6	125	122	159
5	149	151	136
4	291	272	332
3	388	381	199
2	252	245	48
1	257	243	172
0	188	193	291
-1	366	343	4
-2	678	654	179
-3	164	145	80
-4	371	335	288
-5	135	121	3
-6	62	66	140
-7	192	175	144
-8	125	124	336
-9	78	83	199
-10	165	156	19
-11	144	149	179
-12	177	170	22
-13	84	84	254
-14	65	67	116
-15	66	62	353

6,1,L

13	54	56	38
12	53	56	216
11	65	70	277
9	81	72	190
8	125	132	3
7	134	121	199
6	147	148	14
5	51	54	145
4	301	278	29
3	226	205	208
2	240	240	348
1	188	185	76
0	330	310	239
-1	474	466	23
-2	261	265	144
-3	380	370	341
-4	325	319	73
-5	561	536	231
-6	284	266	41
-7	60	56	237
-8	46	40	290
-9	213	197	146
-10	126	125	340
-11	155	149	105
-12	35	37	46
-13	32	30	355
-14	68	62	184
-15	55	62	21
-16	41	44	155
-17	44	52	260

6,0,L

12	69	65	0
10	52	52	0
9	118	116	180
8	74	70	0
7	26	33	180
6	131	120	180
4	315	293	0
3	86	72	180
2	589	544	180
1	529	520	0
0	86	70	180
-1	469	464	0
-2	315	304	180
-3	371	343	180
-4	615	598	0
-5	454	460	180
-6	279	255	180
-7	245	244	180
-8	89	88	0
-9	215	220	180
-10	51	47	180
-11	201	204	0
-12	195	200	180
-13	122	112	0
-14	140	141	180
-15	62	61	0
-16	67	66	0

5,9,L

4	34	42	350
3	18	19	221
0	47	49	143
-1	67	68	314
-2	53	54	171
-3	71	67	23
-4	37	40	213
-5	35	32	345
-7	45	48	151

5,8,L

5	20	20	327
3	50	47	353
2	87	85	275
1	94	97	60
0	90	92	258
-1	100	98	89
-2	85	81	239
-4	50	53	68
-5	64	64	236
-6	70	75	3
-7	76	76	161
-9	85	93	66
-10	41	42	209

5,7,L

5	59	61	130
3	54	64	33
2	85	82	347
1	68	65	165

5,7,L

0	44	42	188
-1	36	37	349
-2	79	76	74
-3	83	80	212
-4	35	35	41
-5	39	43	98
-6	61	65	328
-7	52	47	168
-8	34	37	43
-9	72	72	48
-10	94	95	160
-11	94	91	10
-12	73	71	204

5,6,L

11	28	29	88
9	54	59	7
8	52	56	165
6	44	51	253
5	40	38	33
4	96	97	146
2	232	237	358
1	122	118	137
0	140	150	12
-1	118	109	178
-2	85	85	334
-3	35	38	192
-4	88	91	190
-5	111	110	35
-6	36	37	42
-7	43	42	315
-8	103	108	180
-9	143	135	87
-10	110	106	268
-13	47	49	233
-14	43	45	71

5,5,L

12	41	39	225
11	56	61	18
10	68	63	202
9	60	60	60
8	62	61	245
6	108	108	111
5	153	148	225
4	203	207	49
3	219	211	179
2	195	182	41
1	221	222	253
0	173	174	206
-1	174	174	50
-2	233	225	163
-3	92	96	9
-4	160	153	223
-5	198	192	63
-7	71	75	278
-8	78	79	345
-9	182	191	146
-10	72	71	66
-11	74	73	166
-12	77	73	272
-13	60	58	95
-14	55	50	231

5,4,L

13	27	31	98
12	59	67	235
11	79	88	174
10	127	131	42
9	17	10	304
8	54	55	98
7	176	174	237
6	177	181	50
5	46	52	120
4	172	163	179
3	165	161	347
2	178	193	60
1	394	383	89
0	122	114	341
-1	214	198	153
-4	70	70	148
-5	205	204	234
-6	386	378	36
-7	294	295	200
-8	216	200	18
-9	234	241	196
-10	128	133	341
-11	65	66	30
-12	110	104	235
-13	61	53	346
-14	60	58	181
-15	55	56	355
-16	63	71	177

5,3,L

12	46	45	17
10	63	68	174
9	95	99	77
8	87	87	347
7	113	126	174
6	161	159	200
5	284	256	12
4	86	72	125
3	93	78	265
2	235	237	199
1	157	137	283
0	283	271	340
-1	303	304	232
-2	432	417	158
-3	296	290	261
-4	247	244	330
-5	140	135	166
-6	86	81	348
-7	117	116	231
-8	74	65	351
-9	104	102	152
-10	122	125	204
-11	56	57	57
-12	167	170	252
-13	51	54	69
-14	62	59	252
-15	27	25	344
-16	41	38	38

5,2,L

14	31	32	45
13	66	69	183
12	43	49	267
11	42	47	206
10	106	112	122
9	59	61	54
8	165	170	211
7	238	238	344
6	201	196	148
5	108	99	324
4	240	226	180
3	98	90	319
2	241	239	75
1	231	224	196
0	316	291	69
-1	546	528	272
-2	222	231	15
-3	245	230	197
-4	97	73	69
-5	196	187	16
-6	682	683	143
-7	168	157	0
-8	184	180	129
-9	130	134	330
-10	117	115	39
-11	119	119	124

5,2,L

-12	98	94	304

5,1,L

14	27	31	211
12	96	97	201
11	50	51	3
10	137	144	248
9	167	176	71
8	27	23	148
7	151	150	271
6	116	120	92
5	335	305	65
4	101	96	77
3	294	288	206
2	309	287	31
1	127	122	331
0	105	109	140
-1	373	360	277
-2	340	322	184
-3	344	356	84
-4	682	678	241
-5	109	96	26
-6	173	161	114
-7	129	131	326
-8	118	110	30
-9	438	419	228
-10	216	211	28
-11	78	76	163
-12	97	104	309
-13	135	132	227
-14	81	84	356
-15	75	80	40
-17	60	71	265

5,0,L

14	59	55	180
11	68	65	180
10	33	25	180
6	106	113	180
5	56	33	0
4	127	127	180
3	170	185	180
2	93	94	180
1	447	435	0
0	149	130	0
-1	227	236	180
-2	120	139	180
-3	489	473	0
-4	32	30	180
-5	108	73	180
-6	649	645	180
-7	267	235	180
-8	369	372	0
-9	66	68	180
-10	187	184	180
-11	22	17	0
-12	135	136	0
-14	108	124	180
-15	22	31	0

4,9,L

1	61	63	154
-2	36	30	164
-3	56	53	331
-4	55	54	146
-5	61	63	339
-6	43	43	170

4,8,L

8	33	31	340
7	50	55	203
6	62	61	29
5	76	74	234
4	98	96	66
3	75	80	280
1	71	71	9
0	165	162	222
-1	83	81	37
-2	72	74	223
-3	37	43	299
-5	29	28	277
-7	42	43	256
-8	100	101	62
-9	68	66	226
-10	39	46	343

4,7,L

10	36	48	57
9	35	43	232
8	44	45	170
7	53	54	14
6	32	33	173
5	76	76	309
4	58	63	103
2	105	113	296
1	141	136	154
0	96	84	317
-1	48	45	87
-2	33	26	98
-3	40	45	317
-4	32	27	17
-5	37	38	17
-7	60	60	207
-8	57	50	38
-9	55	57	124
-10	38	37	356

4,6,L

9	51	54	32
8	63	60	180
7	73	80	331
6	111	99	105
5	97	106	306
4	34	36	146
3	42	48	58
2	174	174	354
1	65	68	48
0	143	139	311
-1	221	215	159
-2	223	214	344
-3	43	43	132
-5	99	95	311
-6	98	95	151
-7	113	101	343
-8	144	143	150
-9	61	59	289
-10	37	41	309
-11	43	40	335
-12	69	65	160

4,5,L

13	48	55	292
12	43	40	284
11	51	55	63
10	46	43	158
9	91	96	3
8	137	144	210
7	150	146	53
6	71	64	311
5	106	105	226
4	172	157	30
3	262	252	211
2	249	235	32
1	371	372	226
0	98	95	54
-1	110	91	124
-2	169	156	205
-3	201	193	3
-4	163	156	202

4,5,L

-5	215	217	24
-6	243	234	203
-7	87	80	31
-8	56	55	100
-9	98	98	184
-10	91	96	91
-11	84	86	228
-12	56	54	24
-13	52	53	205
-14	50	53	62
-15	38	33	254

4,4,L

12	60	58	186
11	37	43	72
10	57	57	322
9	103	99	81
7	115	116	232
6	162	158	87
5	207	210	313
4	217	214	139
3	100	95	239
2	149	143	72
1	343	332	44
0	195	163	230
-1	303	287	184
-2	104	88	224
-3	279	262	51
-4	203	189	245
-5	138	125	118
-6	33	33	16
-7	116	118	335
-8	99	101	150
-9	194	203	314
-10	78	80	15
-12	51	44	260
-14	22	24	325

4,3,L

13	36	36	324
12	90	91	11
11	97	91	173
9	48	42	198
8	124	132	327
7	64	61	53
6	141	146	183
5	291	279	335
4	131	127	155
3	287	265	299
2	127	120	242
1	337	341	274
0	93	79	310
-1	239	243	125
-2	287	269	264
-3	181	184	112
-4	282	268	21
-5	113	104	177
-6	52	59	227
-7	81	82	0
-8	70	62	53
-9	87	88	190
-10	141	130	173
-11	71	77	274
-13	80	75	297
-14	49	54	144
-15	38	36	353
-16	44	47	223

4,2,L

14	34	40	101
13	64	64	216
12	62	59	353
11	33	32	206
10	85	74	357
9	119	125	88
8	102	96	243
7	122	129	8
6	233	228	168
5	176	162	53
4	257	249	281
3	32	34	224
2	153	142	63
1	206	200	131
0	36	54	305
-1	888	901	202
-2	392	373	38
-3	426	401	178
-4	357	341	277
-5	77	69	32
-6	287	278	125
-7	208	211	1
-8	181	180	249
-9	166	168	60
-10	71	68	2
-11	101	103	86
-12	79	74	276
-13	28	28	236
-14	79	80	12
-15	49	51	152
-16	47	53	316

4,1,L

15	38	40	196
12	32	32	69
11	91	82	222
10	77	81	209
9	128	124	48
8	145	139	208
7	44	38	33
6	107	110	352
5	350	331	77
4	189	194	1
3	587	577	256
2	154	141	54
1	511	511	350
0	352	332	179
-1	526	526	242
-2	608	584	298
-3	653	643	37
-4	155	152	104
-5	352	346	264
-6	218	230	263
-7	393	392	67
-8	88	98	255
-9	108	101	199
-10	58	60	235
-11	75	76	315
-12	88	86	36
-13	65	58	239
-14	38	40	170
-15	138	136	58
-16	96	89	228
-17	27	23	298

4,0,L

15	44	47	0
14	109	106	180
13	86	87	0
12	45	40	0
8	222	218	0
7	190	166	180
6	97	76	180
5	201	202	0
4	347	330	0
3	291	301	0
2	532	522	180
1	308	286	0
0	597	582	0
-1	109	76	180
-2	598	551	180
-3	130	105	0

4,0,L

-4	543	537	0
-5	663	662	180
-6	388	359	180
-7	50	35	0
-8	62	54	0
-9	25	4	0
-10	141	133	180
-11	102	104	180
-12	108	116	0
-13	67	68	180
-14	51	49	180
-15	31	30	0
-16	23	24	0

3,10,L

0	46	46	24

3,9,L

6	46	47	156
1	88	92	181
0	68	63	321
-1	64	66	149
-2	91	88	335
-3	47	44	132
-4	24	24	224
-5	36	42	12
-6	57	60	174
-7	51	50	335
-8	43	49	156

3,8,L

7	46	50	93
6	41	40	314
5	50	47	190
4	110	107	28
3	97	104	221
2	56	54	357
1	119	120	253
0	62	65	108
-1	42	42	349
-2	116	112	224
-3	96	96	18
-7	46	49	260
-8	97	88	46
-9	64	61	226
-10	48	53	15

3,7,L

10	43	39	357
9	64	68	195
8	62	60	333
7	42	40	302
6	60	56	139
5	28	28	299
4	66	63	235
3	153	156	25
2	142	129	181
1	82	91	300
0	42	46	147
-1	55	50	4
-2	46	52	29
-3	60	58	177
-6	57	50	100
-7	61	63	259
-10	71	70	334
-11	21	12	155

3,6,L

12	25	20	77
10	37	41	20
6	86	77	241
5	97	102	42
4	157	156	155
3	260	269	330
2	138	133	109
1	193	195	297
0	132	118	123
-1	74	75	143
-2	253	261	318
-3	107	103	92
-4	76	71	91
-5	65	69	353
-6	38	42	7
-8	46	46	129
-9	84	80	309
-10	47	46	118
-11	52	55	353
-12	39	37	149
-14	47	48	337

3,5,L

11	29	34	98
10	49	57	97
9	116	120	317
8	83	89	246
7	113	115	50
6	118	116	213
5	46	48	49
4	115	114	226
3	103	98	96
2	111	97	245
1	172	158	194
0	384	373	2
-1	304	285	170
-2	256	247	25
-3	37	25	274
-4	160	161	169
-5	222	228	56
-6	147	137	226
-7	218	213	323
-8	146	144	142
-10	80	82	29
-11	129	134	231
-12	93	94	8
-13	101	100	149
-15	27	30	216

3,4,L

13	37	37	344
12	65	71	198
11	61	65	340
10	55	55	226
9	100	102	64
8	129	126	285
7	135	125	162
6	99	95	354
5	166	152	162
4	183	173	328
2	274	255	68
1	48	49	291
0	384	390	151
-1	77	87	25
-2	160	140	168
-3	419	402	51
-4	281	276	250
-5	266	268	71
-6	82	71	272
-7	177	168	347
-8	61	56	93
-9	77	80	254
-10	103	101	48
-12	27	19	344

3,3,L

13	46	48	3
11	111	112	138
10	146	145	62
9	65	58	233

3,3,L

8	229	234	6
7	157	153	180
6	79	75	65
5	86	79	319
4	276	267	256
3	279	261	34
2	345	341	196
1	181	176	0
0	471	454	38
-1	151	139	309
-2	150	143	93
-3	141	126	148
-4	296	270	287
-5	237	235	125
-6	42	43	318
-7	164	144	9
-8	44	47	137
-9	89	85	333
-10	147	136	158
-11	238	235	314
-12	49	46	165
-13	42	31	203
-16	19	19	174

3,2,L

14	31	31	147
12	57	51	322
11	58	57	314
9	176	172	148
8	143	141	301
7	73	71	308
6	36	23	186
5	32	37	47
4	444	438	264
3	410	408	5
2	445	423	162
1	71	70	231
0	426	400	256
-1	582	571	217
-2	357	350	325
-3	458	448	95
-4	484	473	325
-5	379	358	153
-6	113	105	337
-7	385	376	41
-8	60	60	108
-9	226	217	349
-10	297	291	149
-11	103	102	40
-12	43	42	30
-13	107	107	158
-14	60	55	35
-15	61	60	191
-16	74	78	349
-17	27	36	174

3,1,L

15	91	95	238
14	45	43	24
13	36	34	157
11	118	114	228
10	129	127	114
9	205	207	1
8	152	140	90
7	144	153	226
6	126	115	17
5	288	292	71
4	417	402	268
3	350	349	98
2	351	345	38
1	198	182	132
0	1465	1521	50
-1	455	471	184
-2	646	623	105
-3	32	24	165
-4	271	277	200
-5	75	68	84
-6	134	134	179
-7	649	639	62
-8	70	67	81
-9	75	82	237
-10	82	77	288
-11	105	92	98
-12	151	138	4
-13	140	137	220
-14	64	63	13
-15	38	46	40

3,0,L

15	23	15	0
14	51	56	180
12	64	59	0
11	183	177	0
10	139	138	180
9	236	246	180
8	334	334	0
7	192	194	180
6	127	119	180
5	74	77	180
4	833	829	0
3	221	208	180
2	121	115	180
1	46	58	180
0	436	417	180
-1	454	428	0
-2	682	707	180
-3	115	75	0
-4	1168	1372	0
-5	839	875	180
-6	325	325	0
-7	78	61	0
-8	189	185	0
-9	24	25	180
-10	211	219	180
-11	119	124	180
-12	145	158	0
-14	164	160	180
-15	88	85	0

2,10,L

-1	31	31	271
-2	55	49	78

2,9,L

3	55	57	290
2	43	44	162
0	34	34	76
-1	51	49	201
-2	57	61	9
-3	54	55	166
-5	21	21	124
-6	27	28	218
-8	39	39	182

2,8,L

3	27	29	87
2	48	48	189
1	68	63	221
0	42	36	54
-1	40	39	178
-2	61	67	295
-3	102	105	61
-4	103	109	239
-5	82	79	29
-6	74	78	229
-7	46	48	62

2,7,L

10	29	35	318

2,7,L

9	86	87	195
8	53	52	335
7	43	43	184
6	36	38	352
5	53	49	138
4	60	64	317
0	72	73	251
-1	86	88	35
-2	41	34	92
-3	57	61	228
-4	63	65	64
-5	89	86	277
-7	33	30	190
-9	95	89	1

2,6,L

11	63	58	204
10	75	80	358
9	45	45	216
8	50	53	126
7	109	115	119
6	160	160	336
5	61	64	125
4	100	103	209
3	171	168	23
2	106	109	230
1	36	36	52
0	123	120	134
-1	74	79	286
-2	263	253	28
-4	46	39	19
-5	89	91	145
-6	237	238	309
-7	185	178	129
-8	36	35	237
-11	57	52	329
-12	75	74	147
-13	18	20	337

2,5,L

12	55	56	66
11	30	35	17
10	32	32	46
9	75	84	277
8	57	59	341
7	72	65	101
6	55	62	225
5	167	158	339
4	147	145	187
3	121	122	29
2	122	114	98
1	173	167	300
0	118	106	308
-1	72	64	121
-2	146	143	86
-3	199	181	244
-4	149	149	321
-5	113	110	145
-6	52	43	291
-7	120	120	14
-8	180	170	220
-9	175	170	42
-10	138	142	204
-11	50	48	310
-13	77	76	134
-14	34	33	29
-15	40	45	190

2,4,L

14	28	29	82
13	29	34	353
12	69	63	195
11	47	53	287
10	65	64	87
9	60	65	12
8	119	121	204
7	51	53	117
6	129	133	19
5	79	77	190
4	90	70	334
3	220	204	142
2	36	30	86
1	242	254	199
0	273	267	159
-1	167	159	239
-2	524	504	51
-3	191	177	172
-4	78	64	97
-5	59	56	349
-6	47	24	309
-7	132	119	116
-8	182	169	300
-9	152	157	204
-10	179	176	51
-11	40	36	174
-12	31	36	72

2,3,L

14	50	51	170
13	73	81	60
12	54	56	101
11	60	62	95
10	19	23	108
8	113	115	358
7	153	135	225
6	60	67	51
5	110	116	179
4	257	257	310
3	160	143	280
2	192	184	120
1	633	628	15
0	345	340	299
-2	276	290	129
-3	80	67	250
-4	276	261	24
-5	252	234	210
-6	426	425	4
-7	208	197	119
-8	204	194	318
-9	76	79	138
-10	153	154	265
-11	42	38	7
-12	34	40	296
-13	42	41	141
-15	39	41	319

2,2,L

12	101	104	307
11	93	102	280
10	120	120	89
9	32	33	142
8	87	81	20
7	144	142	189
6	77	81	69
5	264	229	350
4	157	153	133
3	263	243	320
2	352	356	199
1	565	525	199
0	395	400	189
-1	111	81	339
-2	752	743	120
-3	475	487	257
-4	285	273	83
-5	64	53	32
-6	312	299	343
-7	380	369	161
-8	132	129	304
-9	125	111	332
-10	347	347	143
-11	85	89	22

2,2,L

-12	126	128	173
-13	90	91	340
-14	71	70	156
-15	25	25	299
-16	25	31	345

2,1,L

15	51	54	200
14	34	34	321
13	72	71	117
12	70	64	116
10	138	145	157
9	122	122	53
8	92	98	237
7	92	98	256
6	115	112	137
5	288	260	29
4	42	38	47
3	301	296	284
2	65	46	172
1	1534	1653	78
0	350	338	352
-1	928	940	262
-2	272	279	47
-3	353	350	323
-4	229	234	87
-5	509	511	270
-6	500	494	79
-7	321	325	24
-8	219	226	199
-9	97	97	0
-10	126	135	300
-11	92	89	54
-12	67	64	12
-13	72	75	189
-14	134	127	54
-15	55	54	198
-16	62	61	14
-17	52	53	190

2,0,L

15	45	44	180
13	75	85	0
11	102	110	0
10	188	194	180
9	28	25	0
8	125	116	0
6	79	75	180
5	242	193	0
4	544	571	0
3	16	17	0
2	339	347	180
1	484	476	0
0	80	83	180
-1	947	942	0
-2	690	689	180
-3	264	272	0
-4	208	180	180
-5	365	383	0
-6	365	371	180
-7	268	240	180
-8	387	410	0
-9	369	356	180
-10	126	131	180
-11	251	243	180
-12	40	50	180
-14	101	96	180
-16	33	39	0

1,10,L

2	59	67	219
-3	35	32	196

1,9,L

6	65	64	286
5	52	49	93
4	47	48	281
1	54	54	235
0	84	82	94
-1	85	82	274
-2	34	37	98
-3	32	43	196
-7	46	52	111
-8	64	70	256

1,8,L

6	58	59	202
5	46	46	61
2	45	42	233
0	58	56	105
-2	59	66	293
-3	47	50	196
-7	43	41	58
-9	39	36	54

1,7,L

9	56	62	267
7	70	66	176
6	129	130	341
5	123	120	181
4	108	107	24
3	61	53	317
2	100	104	128
1	55	63	303
0	137	126	185
-1	164	159	21
-2	114	111	234
-3	85	80	192
-7	69	69	178
-10	33	38	6
-11	28	30	193

1,6,L

11	49	47	222
10	71	71	31
9	57	54	231
8	78	78	85
7	71	65	217
6	71	74	270
5	63	59	53
4	66	66	191
3	162	156	123
2	246	241	282
1	157	146	74
0	110	116	199
-1	60	58	7
-2	161	164	20
-3	179	181	247
-4	118	104	50
-5	127	124	192
-8	104	107	179
-9	59	61	81
-10	75	79	305
-11	54	51	86
-12	62	61	217

1,5,L

14	47	48	24
11	38	39	96
9	132	128	281
8	59	58	325
7	48	58	153
6	49	50	64
5	84	89	235
4	56	50	12
3	159	158	123
2	91	85	193
1	191	195	299

1,5,L

0	104	99	155
-1	48	58	68
-2	102	101	349
-3	150	146	217
-4	62	64	13
-7	24	26	186
-8	104	103	260
-10	51	46	195
-11	58	52	340
-12	62	55	152

1,4,L

15	44	43	163
14	38	41	356
12	62	59	256
11	43	38	274
10	100	91	125
9	169	173	342
8	185	188	167
7	126	128	287
6	67	60	344
5	154	143	171
4	152	152	345
3	414	406	187
2	54	54	152
1	288	274	104
0	21	33	120
-1	115	120	224
-2	242	234	79
-3	187	180	337
-4	202	199	169
-5	119	123	332
-6	73	75	175
-7	33	27	3
-8	169	160	227
-9	36	36	95
-10	100	103	14
-13	37	34	286
-14	64	63	28

1,3,L

15	23	19	358
14	65	66	155
13	107	102	25
12	81	79	182
11	92	99	51
10	243	235	204
9	190	186	348
8	107	108	58
7	157	159	205
6	188	191	353
5	178	165	224
4	258	257	68
3	216	199	212
2	210	228	193
1	458	447	357
0	340	320	167
-1	332	314	350
-2	238	232	223
-3	138	130	2
-4	29	29	295
-5	43	43	205
-6	66	61	55
-7	203	211	206
-8	119	116	339
-9	137	142	250
-10	84	77	273
-11	61	59	47
-12	23	22	266
-13	35	29	34
-14	58	52	217
-15	36	33	336

1,2,L

13	38	30	115
12	128	128	323
11	99	99	172
10	109	114	103
9	60	59	262
8	48	52	340
7	222	211	324
6	295	270	136
5	469	447	295
4	273	261	182
3	292	285	215
2	485	490	237
1	400	384	177
0	412	408	276
-1	932	911	308
-2	261	263	26
-3	334	329	194
-4	417	389	320
-5	606	589	166
-6	329	319	8
-7	61	57	210
-8	131	118	286
-9	88	87	112
-10	116	117	86
-11	67	62	50
-12	75	74	236
-13	80	84	13
-14	107	100	122
-15	73	73	322
-16	45	35	153

1,1,L

16	19	19	344
15	71	71	200
14	37	36	315
13	82	82	113
12	65	58	241
11	72	83	216
10	391	380	264
9	218	217	51
8	107	96	162
7	291	271	300
6	172	191	163
5	355	363	342
4	257	269	185
3	515	503	223
2	857	841	11
1	170	145	122
0	359	340	6

2,1,L

-1	993	940	262

1,1,L

-1	752	757	188
-2	439	424	26
-3	612	617	105
-4	197	209	254
-5	319	313	242
-6	321	300	127
-7	278	270	20
-8	115	111	216
-9	117	113	286
-10	178	177	219
-11	412	420	55
-12	67	67	149
-13	34	37	283
-14	66	69	0
-15	42	40	123
-16	50	44	352

1,0,L

16	94	103	0
15	82	78	180
12	197	203	0

1,0,L

10	336	356	180
9	368	370	0
8	213	206	180
7	269	262	0
6	404	401	180
5	45	59	0
4	620	664	0
3	757	795	180
2	181	133	180
1	256	224	180
0	357	356	0
-1	559	505	0
-2	84	96	180
-3	620	627	0
-4	175	157	180
-5	150	142	0
-6	500	502	180
-7	87	81	0
-8	320	303	0
-9	203	209	180
-10	195	193	180
-11	23	39	0
-12	206	203	0
-13	28	32	180
-14	46	43	180
-15	30	33	0

0,10,L

2	32	33	230
1	61	68	73

0,9,L

7	44	46	311
3	33	39	112
2	47	45	324
1	42	42	136

0,8,L

10	52	51	231
9	25	13	51
8	39	40	149
5	21	21	295
4	59	55	74
3	84	83	235
2	47	49	8
1	107	104	183
0	100	101	12

0,7,L

12	37	36	242
11	51	52	28
10	53	63	207
8	91	94	179
7	85	91	22
6	66	65	94
5	113	123	263
4	129	136	78
3	114	119	172
2	137	131	355
1	88	84	191

0,6,L

13	39	36	7
12	59	65	202
11	39	42	53
10	73	70	282
9	54	46	197
8	68	72	133
7	98	103	268
6	139	139	96
5	124	127	265
4	65	64	107
3	57	66	15
2	50	40	285
1	189	196	357
0	198	179	170

0,5,L

13	19	25	249
12	44	46	334
11	66	67	148
10	59	59	334
9	50	56	295
8	103	104	179
7	172	177	47
6	62	55	184
5	92	85	25
4	128	119	203
3	207	201	112
2	71	61	28
1	96	97	287

0,4,L

14	51	51	13
13	47	45	159
12	50	48	325
11	21	23	179
10	34	44	300
9	60	58	15
8	106	116	230
7	148	150	319
6	144	195	178
5	172	171	346
4	305	299	144
3	41	49	30
2	126	121	298
1	283	276	111
0	648	620	301

0,3,L

15	39	40	144
14	33	32	113
12	42	36	206
11	45	49	179
10	142	151	197
9	203	202	11
8	103	134	225
7	184	244	112
6	118	134	22
5	415	537	192
4	530	528	359
3	571	566	182
2	378	538	11
1	479	480	223

0,2,L

16	41	48	226
15	56	53	19
14	43	48	172
13	24	30	2
12	46	53	227
11	62	55	324
10	88	105	10
9	103	97	163
8	236	225	337
7	123	165	263
6	99	121	104
5	42	50	345
4	85	107	228
3	48	57	74
2	194	244	222
1	358	498	45
0	1693	1759	301

0,1,L

16	25	30	201

0,1,L

15	23	23	235
14	38	38	125
12	97	86	287
11	340	339	212
10	97	128	330
9	229	226	95
8	76	85	227
7	155	137	232
6	316	433	101
5	242	304	314
4	342	476	105
3	543	770	262
2	847	874	121
1	357	480	352

0,0,L

16	48	44	0
15	52	51	180
14	48	38	0
13	127	124	180
12	94	85	0
11	50	6	180
10	223	198	180
9	240	240	0
8	152	142	0
7	259	224	0
6	548	535	180
5	441	419	0
4	164	156	0
3	98	70	0
2	326	322	0
1	878	1010	180