STRUCTURAL STUDIES OF METALLIC COMPLEXES

A Thesis submitted for the degree of
Doctor of Philosophy in the
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by

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Summary

This thesis describes the determination of the structures of six compounds using single-crystal X-ray diffraction methods. These comprise four organometallic complexes and two organic compounds. The four complexes were solved by the heavy atom method whilst the organic structures were solved using the symbolic-addition method. Almost all the calculations were carried out using the "X-ray 70" and "X-ray 72" crystallographic computer program systems and the data were measured on a Siemens A.E.D. four-circle diffractometer. All the structures are presented separately. The two organic structures were solved with a view to gaining experience of direct methods and are thus included in Appendices I, II.

Nickel (ethylethylenediamine)$_2(O_2N)^+BF_4^-$, $(C_{12}H_{32}BF_4NiO_2)$, is monoclinic with unit-cell dimensions a = 11.338(1), b = 16.291(1), c = 11.934(1)Å, β = 112.015(8)°, space group $P2_1/c$ and Z = 4. Least-squares refinement, using 2382 independent reflections gave a final R of 0.053. The nitrite group was found to be a chelate although a metal O - N - O bridge was thought might occur from spectral measurements. Steric factors in nitrite co-ordination are discussed.

Cobalt (thiopyrimidine)$_2$ dichloride, $(C_8H_8N_4CoS_2C\ell_2)$ is monoclinic with unit-cell dimensions a = 12.371(1), b = 8.3010(4), c = 14.185(1)A^o, β = 117.180(6)°, space group $C2/c$ and Z = 4. Least-squares refinement, using 1079 observed reflections gave a final R of 0.054. The pyrimidine-2-thiolato ligand is bidentate co-ordinating through both N and S atoms.

Hydridotris-(triphenylphosphine)ruthenium(II) Tetrafluoroborate, $(C_{54}H_{46}BF_4P_3Ru)$ is monoclinic with unit-cell dimensions a = 20.755(2), b = 12.784(1), c = 18.609(3)Å, β = 109.06(2)°, space group $P2_1/c$

and Z = 4. Least-squares refinement, using 4658 observed reflections gave a final R of 0.039. This cation possesses an arene group which is π-bonded to the metal. Although the compound was originally obtained as a methanol solvate only ill-defined traces of the methanol could be located in the interstices of the structure.

Hydridophenoxybis(triphenylphosphine)ruthenium(II) Diphenol is monoclinic with unit-cell dimensions a = 20.221(1), b = 9.561(1), c = 23.744(2)Å, β = 106.24(1)°, space group $P2_1/a$ and Z = 4. Least-squares refinement, using 4226 observed reflections gave a final R of 0.029. The two phenol molecules of solvation are hydrogen bonded to the phenoxy group. This compound also possesses a π-bonded arene to metal and is essentially similar to the ruthenium cation considered above. The two structures have been compared and the structural similarities discussed.

The structure of cambogin, ($C_{38}H_{50}O_6$) a benzophenone derivative isolated from the roots of the plant Garcinia Cambogia has been solved by its dibrosylate derivative ($C_{50}H_{56}O_{10}Br_2S_2$). The crystals are monoclinic, a = 10.140(2), b = 21.269(3), c = 12.378(2)Å, β = 105.84(1)°, space group $P2_1$ and Z = 2. Least-squares refinement, using 2469 observed reflections gave a final R of 0.098. The absolute configuration has been determined. The present structure determination has been compared to the structure of its enantiomer isoxanthochymol isolated from different species of Garcinia. The mechanism of formation of both compounds is discussed.

The ketol bishydropulegone, ($C_{20}H_{34}O_2$) is orthorhombic with unit-cell dimensions a = 10.8378(5), b = 14.3917(9), c = 11.7720(4)Å, space group $P2_12_12_1$ and Z = 4. Least-squares refinement, using 1676 observed reflections gave a final R of 0.047. The structure is compared extensively with the related deshydropulegone and the nor and iso series of the ketols have been compared.

Acknowledgements

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To Mida

CONTENTS

CHAPTER I

General Experimental Procedures.

"*Everything is simpler than you think and at the same time more complex than you imagine*"

... *Goethe.*

GENERAL EXPERIMENTAL METHODS AND PROCEDURES

Structural crystallography is ultimately concerned with the measurement of intensities of reflections from a single-crystal specimen since the intensity of an (hkℓ) reflection is proportional to the square of the corresponding structure amplitude. This may be accomplished by either photographic or counter methods. The latter technique is the more efficient and accurate method. All the data collected for the structures described in this thesis were collected personally using a Siemens four-circle off-line diffractometer. (A.E.D.; Automatische Einkristalle Diffraktometer).

Preliminary Investigation of a Crystal

The crystalline sample was first carefully examined under a polarising microscope. The object of this is to obtain as much information from the sample as possible by studying its directions of uniform extinction under crossed polars to enable one to choose from the sample a single crystal which is well-formed, with no apparent imperfections, and of a suitable size for X-ray photographs and data to be collected. Having selected a suitable specimen, it was first mounted on a glass-fibre with vacuum grease and either oscillation and Weissenberg or precession photographs taken. These initial photographs were taken in order to obtain the unit-cell dimensions and space group of the crystal and to confirm that the specimen is in fact a single crystal.

Diffractometer Data Collection

The A.E.D. is simply a four-circle instrument with a standard Eulerian arrangement of ω, θ, χ and ϕcircles (Figs I ,II) . In normal use as in standard data collections, the instrument is operated as a

Fig. I

The central mechanism of the A.E.D. showing the Eulerian cradle arrangement.

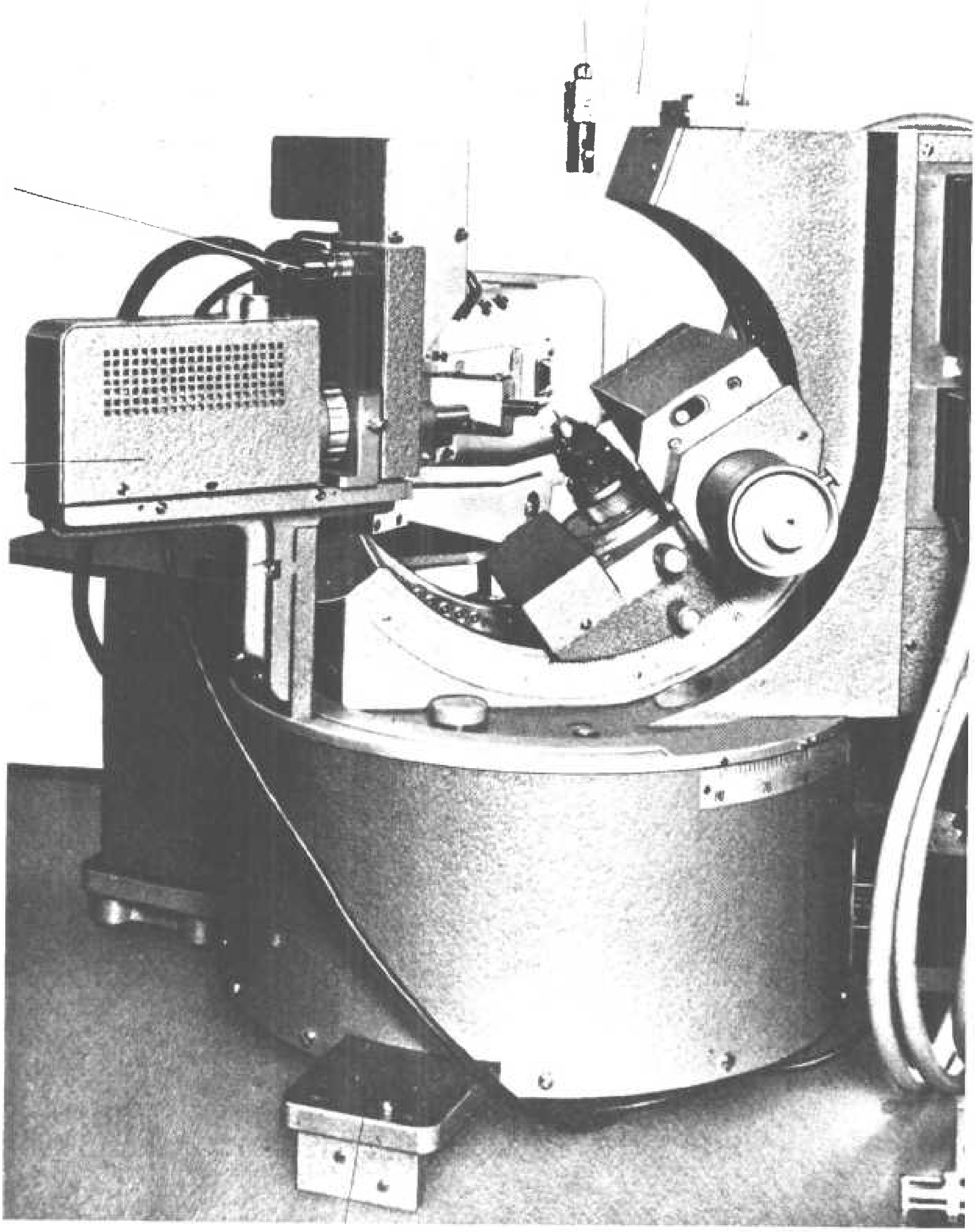
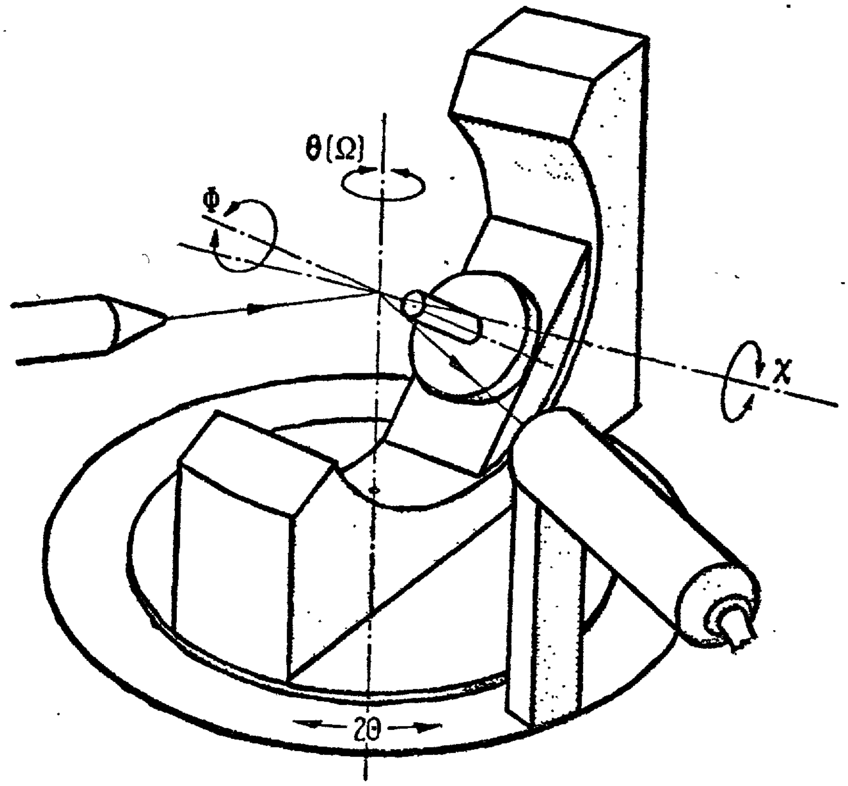


Fig. II

Diagramatic representation of the Eulerian cradle of the A.E.D.



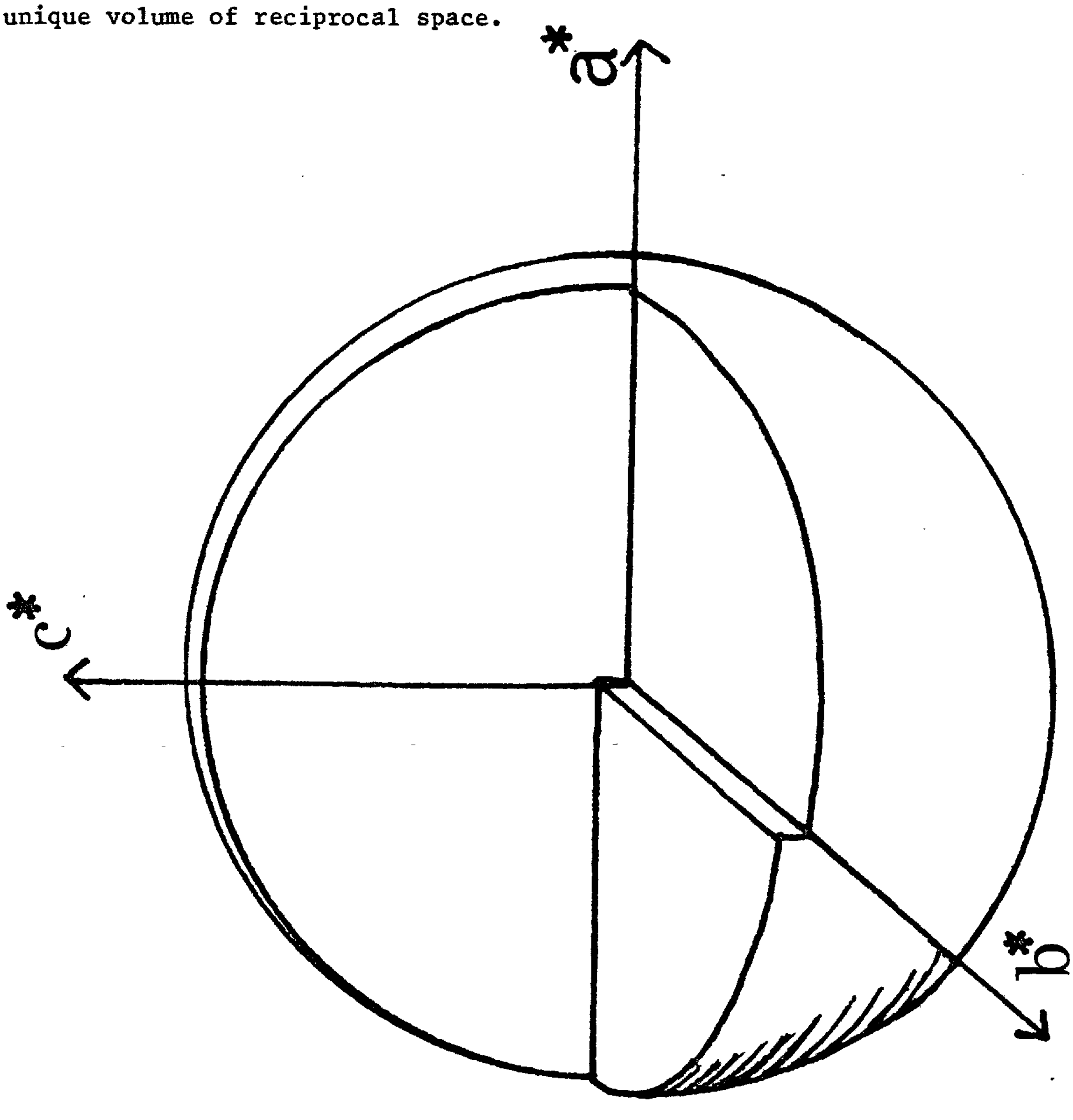
three-circle one with ω coupled to 2θ in a $\theta - 2\theta$ relationship. As a consequence of this mode of operation it utilizes normal-beam equatorial geometry, i.e. the reciprocal lattice vector co-incides with the intersection of the planes of the θ and χ circles when in the reflecting orientation with the plane of the χ circle bisecting the angle between the incident and diffracted beams. The three circles which determine the orientation of the crystal are designated the θ (or ω) circle, the χ-circle which is carried on the θ-circle and whose axis is normal to the θ-axis, and the ϕ circle which is mounted on the χ-circle and carries the goniometer head supporting the crystal.

The instrument is an off-line instrument in that its operation is dependent on computers whilst it is not directly linked to any computer. In the automatic mode of operation, it is driven by a 'steering tape' which is a five-track punched paper tape produced by a computer, and the results are output in a similar way. All the operations of the A.E.D. can also be controlled manually, but this is usually only used for the preliminary setting-up of the crystal and the determination of accurate lattice parameters.

The design of the instrument is such that the ϕ-circle can be set at any angle between 0° and 360°. The range of the θ-circle extends only to 72.5°, such that reflections at a Bragg angle greater than ca. 71° cannot be measured. The χ-circle movement is also limited, its range being -5° to 91°, so that little more than a hemisphere of reciprocal space is accessible (Fig. III). This is not usually a problem since the collection of a hemisphere of reciprocal space is usually adequate even for a triclinic crystal. If for any reason more data are required, a crystal inverter can be used. These restrictions on the amount of data that can easily be collected for any one setting of a crystal, are more than compensated by

Fig. III

The unique volume of the sphere of reflection for a monoclinic crystal. The hkℓ-ranges were chosen so that data was only collected for the unique volume of reciprocal space.



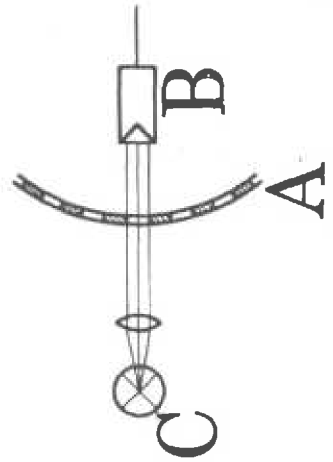
For the monoclinic case it was only necessary to collect one quadrant of the sphere of reflection minus half the zero layer.

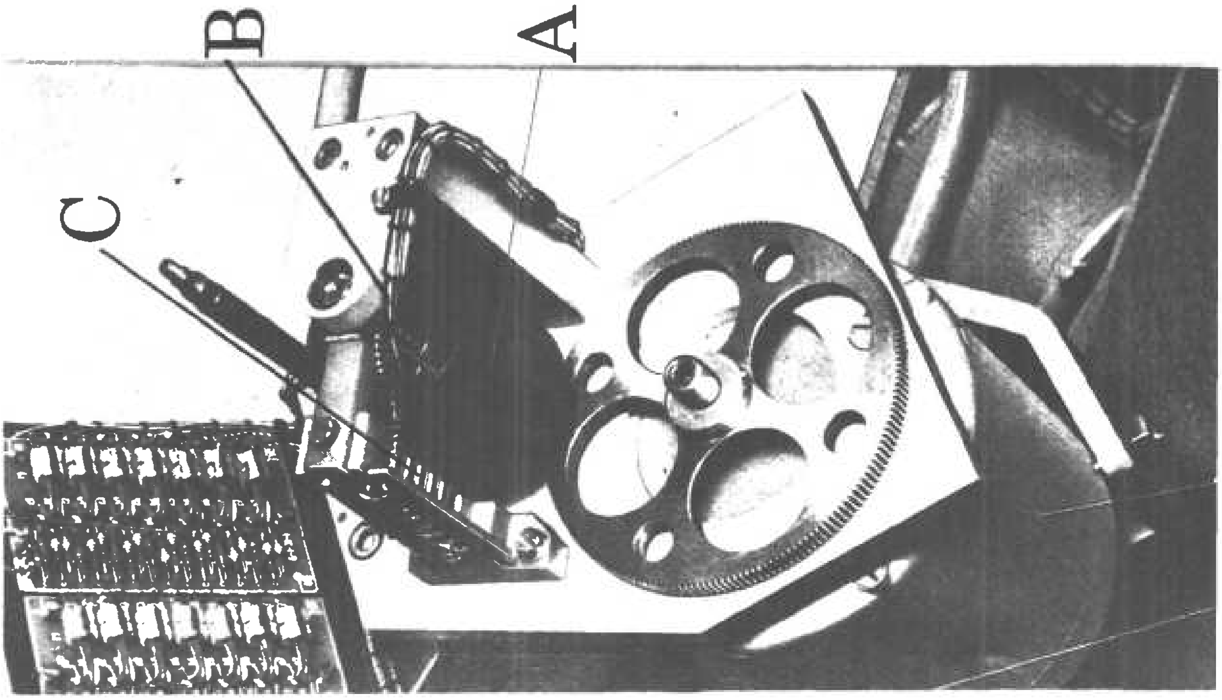
the extra mechanical stability and rigidity of the machine, and by the absence of obscuration or collision problems which otherwise occur.

The three setting circles are each driven by a magnetic impulse motor, one pulse driving a circle through one bit or hundredth of a degree (or 0.02° for 2θ). When moving between reflections it slews at 10° per second. They may be driven either automatically, by paper-tape input or from the control desk which forms part of the paper-tape reader. Additionally, each circle can be de-coupled from its motor drive and set by hand. The three circles can be driven simultaneously thus saving time during data collection. During automatic operation, intensity measurements for each reflection begin and end at the α_1 peak, thus the angular circle increments calculated and specified on the steering tape are those which are required to move from the α_1 peak of one reflection to the next. Manually, each circle can be set accurately to the nearest 0.01°, but when automatic data collection is in operation one must be able to say with some confidence that the circles are in the correct angular positions for a particular reflection. This check is implemented by using a combination of coded digitiser drums and photocells such that 50 distinct positions within a range of 0.5° can be recognised. (Fig. IV; "A" is the metal digitiser drum, "B" is a bank of photocells and "C" is a row of lamps which is flashed when the drum is in the checking position). This means that positions which are exact multiples of half a degree apart cannot be distinguished, but as an error is unlikely to be more than a few bits this ambiguity is not important. If the check is successful and the coded signals from the photocells agree with the data specified on the steering tape, a single character indicating agreement is punched on the output tape. If the check finds that the circle position is incorrect, a search of ± 20 bits is automatically initiated. The circle

Fig. IV

Diagrammatic representation of the photocell arrangement utilised in the A.E.D. mechanism.





stops at the correct position if it lies within that range, otherwise the machine stops. An additional check which is done less often during data collection is to verify the absolute zero-positions of the three circles: this ensures that setting errors of 0.5° or more have not occurred.

All the data collected for structure determination in this thesis was measured with a Na (Tℓ) I scintillation counter and utilised Cu-$\underline{K}\alpha$ radiation at a take-off angle of 6.0° with a nickel β filter. The X-ray generator used with the A.E.D. has its own high voltage stabiliser, the kV being specified to ± 0.1% for ± 10% fluctuations in mains voltage. This stability determines the reliability and rate of accurate data collection. Collimators of diameter 0.4, 0.6, 0.8, or 1.0 mm have been used depending on the crystal size, bearing in mind that the beam has a homogeneous diameter of about 1.4 x the collimator size at the crystal position. This beam should bathe the crystal completely, but not be too wide so as to minimise the signal-to-noise ratio in the detector. The photomultiplier assembly is continuously cooled by water to ensure a constant amplification factor. The counter also has a collimation system, and is normally used with a circular aperture so that while the entire diffracted beam is accepted stray radiation is minimised.

All the intensity measurements have been done by integrating over a reflection peak using a $\theta - 2\theta$ scan. This process is conducted in 0.01° steps in θ (0.02 in 2θ), but before the scan is made, a suitable measuring time per step is chosen by the A.E.D.'s own logic subject to a maximum acceptable time per step which is manually pre-set on a dial. For strong reflections the diffractometer controller logic uses the fastest scan rate and can attenuate the incident X-ray beam by utilising a succession of graded attenuator foils. The result is that, except for the weakest reflections an approximately constant total count is achieved rather than adhere to a constant time. The main advantage of such a system is that it gives nearly constant statistical accuracy throughout the measurements. The advantages of a constant count, as distinct from a constant-time-per-reflection diffractometer experiment, have been discussed by Killean.[1]

The integration procedure used for measurement of reflections throughout this work has been the "five-value" measurement, as illustrated in Fig. V. When the optimum measuring time per step has been selected at the $K\alpha_1$ peak, the reflection is scanned through $\Delta\theta_1$ (decreasing θ) and the count I_1 recorded. The background, I_2, on this low θ side of the peak is then counted, followed by a scan through $\Delta\theta_1 + \Delta\theta_2$ in increasing θ giving the count I_3, representing the entire peak. The background on the high-θ side of the peak, I_4, is then measured and finally the reflection is scanned back through $\Delta\theta_2$ to the $\underline{K\alpha_1}$ peak, giving the count I_5. The $\Delta\theta_1$ and $\Delta\theta_2$ values are chosen so that the scans extend well into the background on either side of the peak. The counting times in this process have the relationship

$$(t_1 + t_5) = t_2 = t_3 = t_4 \qquad \text{where } t_1 \propto \Delta\theta_1 \text{ and } t_5 \propto \Delta\theta_2$$

and the net count is given by:-

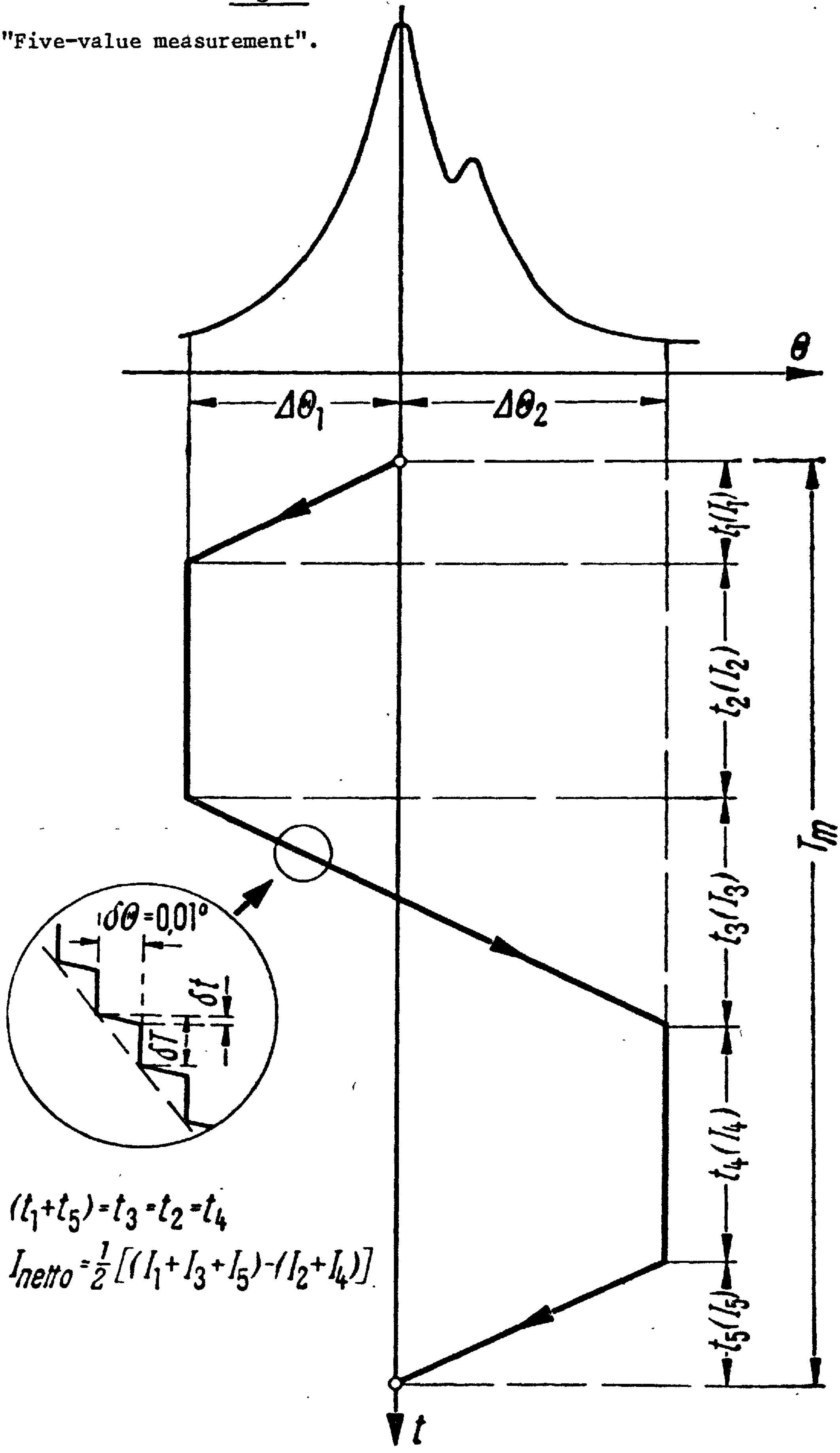
$$I_{net} = \tfrac{1}{2}[\,(I_1 + I_3 + I_5) - (I_2 + I_4)\,]$$

The total time for any complete scan is thus dependent on the selected measuring time per step and the $\Delta\theta_1$ and $\Delta\theta_2$ values chosen.

The five counts are punched onto the output tape, followed by two code digits; one indicating the attenuator used (if any) and the other the measuring time factor. The crystal alignment is checked by means of chosen control reflections every 200 reflections and in order to detect possible deterioration of the crystal or drift in the generator or detector a reference reflection is monitored every 25 or 50 reflections.

Fig. V

"Five-value measurement".



Procedure for setting a crystal on the A.E.D.

When a crystal suitable for data collection has been selected it is mounted on a quartz fibre with some "Araldite" adhesive, the fibre being set in a special brass "pip" with dental wax so that the fibre protrudes to a distance of 0.5 - 1.0 cm. Since the A.E.D. room is maintained at a constant temperature ca. 12^{O}C., the crystal and goniometer head should be allowed to equilibrate in the room for at least twelve hours before any measurements are made.

The crystal must now be set accurately on the A.E.D. in such a way that the ϕ - axis corresponds to a real crystal axis. One needs at this stage to define a standard orientation, to which any crystal setting can be referred. The convention used on the A.E.D. is that the crystal rotates about its c - axis (i.e. $\chi = 0.0^{o}$ for the a*b* plane), the a* vector corresponds to $\phi = 0.0$ and the axes must form a right-handed set. If it is physically more convenient to set a crystal about another axis, the true orientation may be referred to this standard by means of a simple transformation so long as a right-handed set is chosen.

The crystal is first centred and brought to the centre of the three circles of the diffractometer with the aid of the attachable telescope. The a* and b* vectors (assuming standard setting) are initially located by setting the θ circle at angles corresponding to strong low-angle axial reflections and then scanning through ϕ until the reflection is detected. This enables the zero-position of the ϕ -circle to be set coincident with the a* vector. The crystal can then be set accurately by the use of horizontal half-shutters fitted in front of the detector.

The Stoë goniometer head which was used during data collections has the extremely useful facility that the turret carrying the crystal mount can be rotated relative to the arcs, and can also be raised or lowered to permit fine adjustments in centring. The turret was therefore rotated to bring a* and b* approximately parallel to the arcs so that the easily recognisable axial reflections could be utilised for the alignment procedure. The arcs are then adjusted so that the ratios of the half-counts are the same for $h00$ and $\bar{h}00$ and for $0k0$ and $0\bar{k}0$, both being approximately 1:2. If the half-to full-count ratio diverges significantly from this value, this is usually an indication that the crystal is not at the centre of the beam and a vertical height adjustment is necessary.

Once the crystal is set accurately, the accurate data required for the production of steering tapes must be obtained, i.e. accurate lattice parameters and integrating scan widths $\Delta\theta_1$ and $\Delta\theta_2$. For the accurate measurement of lattice parameters, the normal detection collimator (pin-hole type) is replaced by a "slit collimator". This has a vertical slit, approximately 0.2mm wide, which is put close to the scintillator to improve the resolution in θ.

Values of the cell parameters obtained from photographs were used to generate a list of approximate setting angles, using the program SEKO[2], in order to facilitate the task of finding reflections in the initial stages. A suitable $h00$ reflection at a fairly high θ value (ca. 60^{o}+) is selected if available using preliminary photographs and is then located on the A.E.D. . The peak is then scanned so that the reflection profile is obtained and hence accurate values of θ for the $\underline{K}\alpha_1$ and $\underline{K}\alpha_2$ peaks. This process is then repeated for one or two more $h00$ reflections and thus a value of a* is determined. Values of b* and c* are obtained in a similar way. If the crystal symmetry is such that $\gamma^* \neq 90^{o}$, its value can be obtained by scanning suitable axial reflections simultaneously in θ and ϕ. An initial θ-ϕ scan on an $h00$ reflection gives the exact value of ϕ corresponding to a*, which can then be set to 0.00^{o}. A further θ-ϕ on an $0k0$ reflection then gives the optimum ϕ-value corresponding to γ^*.

Unless the crystal symmetry is low or the number of high-angle axial reflections is small, this procedure is sufficient to obtain accurate lattice parameters. Hence for triclinic crystals, or monoclinic mounted about a non-unique axis, θ-values for some off-axial reflections, in addition to axial ones, are refined by least-squares to give the cell parameters. This refinement is usually carried out using the program CEDI as a binary deck for submission to the I.C. 6400 computer via the instant turnaround service. In most cases, a dozen or more accurately measured reflections give rise to cell dimensions with standard deviations ca. 0.002 Å, an accuracy which is quite acceptable for calculating setting angles to the nearest 0.01°.

Estimation of the required integrating scan widths throughout the range of θ necessitates the profiling of certain appropriate reflections. For this purpose, the circular collection collimator is used and reflections are selected, using a preliminary Weissenberg photograph, for which the spread in θ for a given θ is the maximum over the whole range of ϕ (this allows for variations of spot size due to crystal shape). By choosing reflections which lie at fairly regular intervals throughout the range of θ, the integration angles, $\Delta\theta_1$ and $\Delta\theta_2$, can be tabulated as functions of θ.

The steering tapes can now be computed. The approximate number of reflections which will be generated is given by the formula

$$N_{TOTAL} = \frac{4}{3}\pi\left(\frac{2\sin\theta\ \mathrm{max}}{\lambda}\right)^3 .V.f.$$

where θ max is the maximum value of θ to which data is to be collected, λ is the radiation wavelength, V is the volume of the unitcell and f is the fraction of the sphere to be collected. This formula applies to primitive unitcells and does not allow for space-group absences.

Finally reference and control reflections must be chosen and their frequency in the steering tapes specified. The reference reflection monitors the stability of the X-ray tube and counting equipment and checks that the crystal is not suffering X-ray damage or is decomposing. It is also used for scaling the data after collection and so is usually measured every 25 reflections, or every 50 if a high rate of data collection is used. The control reflections are used to check the setting of the crystal, and are usually the same reflections which were originally used to set the goniometer arcs. These controls are measured less frequently usually every 250 - 300 reflections, and both the full counts and those with half-shutters inserted are recorded. Both reference and control reflections should be strong so that they are measured quickly and accurately. The frequency of the zero-checks, that is when the circles are driven to their zero positions and checked, also has to be specified and is usually of the same frequency as the reference reflection.

Once the steering tapes are generated, the only remaining decision before commencing automatic data-collection is the choice of the maximum time per step. The choice is usually a compromise between a time fast enough to give a short period for data collection, and one long enough to give low statistical errors (1%) for all but the weakest reflections. In practice the most commonly used maximum stepping times are 0.24 and 0.6 seconds per step which produce respectively approximately 600 and 260 measurements per day for most crystals.

Once the steering tape has been engaged in the console tape reader and the A.E.D. controls set to the correct settings for automatic operation, the data collection should proceed to completion automatically. Barring machine breakdowns and tape changes, the diffracometer can then be left unattended; nevertheless it is advisable to check the output frequently so that immediate action can be initiated if the crystal orientation has changed.

Finally, before removing the goniometer from the A.E.D. it is necessary to measure the crystal's shape and the orientation of its faces in preparation for an absorption correction. This is usually done by making scaled drawings of the crystal from different directions using the attachable calibrated microscope.

Processing of the A.E.D. Output

During automatic data collection on the A.E.D. all the measured data are output on five-track punched paper tape. Thus, for every reflection including reference and controls, the title $(hk\ell)$, the digitiser checks, the five counts and the measuring time and attenuator code numbers used are all recorded. During the course of the present work, all A.E.D. output tapes obtained have been processed using the computer program SODI which was written by Dr. P.G.M. Troughton in EXCHLF for use on the old ATLAS system and later rewritten by Drs. Fletcher and Stephens[2] in Fortran IV for use on the University of London and Imperial College CDC machines.

This program tests the digitiser checks, evaluates the net intensities, applies scale factors determined by the reference reflections to bring all the data onto a common arbitrary scale, and applies a Lorentz-polarization correction to produce a final list of Fo^2 values and $\sigma(F)$ values. The program also applies certain tests to check that the measurement has proceeded correctly. If the net count has a value less than 2.58 times its own standard deviation (i.e. below the 99% confidence limit, Appendix III;) a reflection is judged to be unobserved. In addition to the printout, the program outputs a computer card for each reflection, containing the Miller indices, the intensity and $\sigma(F)$ written in a format suitable for input to the X-ray system and the other programs used in structure solution and refinement.

References

1. R.C.G. Killean
   Acta Cryst., 1967, 23, 54.

2. S.R. Fletcher and F.A. Stephens,
   SEKO (Fortran version) specification (1971).

CHAPTER II

Crystallographic Computing.

> *"Men have become the tools*
> *of their tools"*
> *... Thoreau.*

CRYSTALLOGRAPHIC COMPUTING

This chapter gives a brief account of the computer programs utilised in the structure determinations described later in this thesis.

Almost all crystallographic calculations deal with large amounts of data and require millions of simple mathematical operations, so many in fact that one man however dedicated could never complete some of the individual least-squares or Fourier calculations by hand in a lifetime.

Thus programs need to be efficient and data handling made as convenient as possible. Program structure for most crystallographers usually requires hiding the difficulties of using the computer for a whole series of programs behind an easily understandable calling sequence. In this laboratory, there are two main divisions in the programs which are available.

The X-ray 70[1] system, which is a suite of programs linked together is available to perform the majority of the necessary calculations of the crystallographer. This system has been superseded by the X-ray 72[2] system which has extended the suite of programs and internal options available. After compilation of the program and its subsequent storage on disc or tape the program is executed simply by informing the operating system of the location of the primary program and providing a single block of data cards. The data cards have a four-level structure. Firstly the start and finish cards, then cards to pass information to the operating system, e.g., CRYLSQ to call a general crystallographic least-squares program, and finally the crystallographic data itself. These data are arranged in a series of data files that are added to and modified during the course of calculations so as to enable a whole series of calculations to be performed in one job.

The advantages of this system are that one firstly has a uniformity of data-card input which makes for greater ease of handling and secondly one may save the data scratch files between runs and thus be able to keep a history of calculations made to date.

Additional programs exist to perform specialist tasks specific to this laboratory, e.g., SEKO and SODI[3] (the diffractometer programs as discussed in Chapter I) and others to provide extra options not readily available within the X-ray program suites. There are often errors and ambiguities in standard packages and special cases are not always covered. There are slightly adapted versions of the standard program with provision for special cases, or special coding to circumvent an ambiguity, or even more simply to effect a different output layout or make adjustment to the size of the calculation. Plotting programs are also free-standing as they depend largely on the computer installation, its operating system and do not fit easily into a standard package. Other specialist programs written or modified within this laboratory are available and provide extra choice in the techniques of structure solution. e.g., NORMAL, MULTAN, ESORT, etc.

The X-ray links used during the present work are:-

DATRDN:- Written by J.M. Stewart, M.A. Jarski, B. Morosin and R.V. Chastain.

Process reflection data to give observed structure amplitudes which are stored on magnetic tape together with scattering factors, cell parameters and symmetry operations.

LOADAT:- Written by J.M. Steward and L. Plastas.

Loads atomic positions in binary data file.

FC:- Written by J.M. Stewart and R. Braun.

Calculates structure factors with or without an anomalous dispersion correction. Can also be used to calculate a fixed atom contribution.

ORFLS:- Written by W.R. Busing, K.O. Martin and H.A. Levy and adapted for the X-ray system by J.M. Stewart *et al.* A full-matrix least-squares refinement program.

BLOKLS:- An adaptation of ORFLS using the block-diagonal matrix approximation.

CRYLSQ:- Written by F.A. Kundell. General crystallographic least-squares program.

FOURR:- Written by D.F. High *et al.*

Uses structure factors from FC or least-squares output to calculate a variety of Patterson, Fourier, or difference Fourier syntheses in all symmetries.

BONDLA:- Written by D.F. High, J.M. Stewart and R.V. Chastain.

Calculates interatomic and intermolecular distances and bond angles with their standard deviations.

BONDAT:- Written by J.M. Stewart *et al.*

Calculates the positions of tetrahedral, trigonal or linearly bonded hydrogen atoms.

LSQPL :- Written by J.M. Stewart *et al.*

Calculates the best least-squares line or plane through a set of atoms and the deviations of these and other atoms from the line or plane.

MODIFY:- Written by J.M. Stewart.

Binary data file editing and generation of pseudo-data e.g. inputing of phase information for E map to solve a direct-method problem.

LISTFC:- Written by J.M. Stewart *et al.*

Outputs final structure factor lists in a format suitable for reproduction in theses and publications.

Other programs used in the laboratory are:-

ICABS:- An absorption/extinction correction program originally written by Coppens *et al*[4] and adapted by Dr. F.A. Stephens.

This program permits corrections to be applied to crystals of any shape provided that the indices of the bounding faces can be determined and the morphology is good enough to permit reliable measurement of the linear dimensions.

An absorption correction has to be applied to account for a reduction in intensity of both the incident and diffracted rays on passage through a crystal. Busing and Levy[5] have suggested a three-dimensional numerical integration technique to evaluate this effect. This is essentially a 3-D numerical equivalent of Albrecht's graphical method. Grid intervals need to be optimised with regard to speed and accuracy of calculation and this is accomplished by means of trial runs on about 25 - 40 reflections chosen to cover the full range of absorption effects.

In this approach the path lengths are derived from the vector analysis method suggested by Coppens *et al*[4]. Other alternative methods of correction have been suggested by Howells[6], Furnas[7], J. de Menlenaer[8] and North[9]. Some have been compared by Coppens *et al*[10].

The transmission factor, A, for hkl reflection is given by:-

$$A(hkl) = \frac{1}{V} \int_V \exp - \left[\mu(r_i + r_d) \right] dv$$

where r_i is the path length of the incident beam before being scattered by the volume element dv, and r_d is the path length after scattering. V is the volume of the crystal. μ is the linear absorption coefficient of the crystal for the wave length given and is defined as:-

$$\mu = \rho \sum_i w_i \, \mu m_i$$

where w_i is the relative weight of the i^{th} element in the crystal and μm is the mass absorption coefficient of the element. ρ is the density of the crystal. The integral is evaluated by a Gaussian integration, which approximates it to the weighted sum of a number of terms. The crystal is described in terms of up to twenty bounding faces and the distance of each face from an arbitrary point usually near to the centre of gravity of the crystal. A grid of regularly spaced sampling points is set up and the components of the incident and diffracted beams for each reflection are then derived according to the vector analysis method of Coppens *et al.*[4] These are used in a three-dimensional Gaussian integration technique where the transmission factor is obtained as the weighted sum over all the other points. The transmission factor becomes:-

$$A(hk\ell) = \sum^{n} W_r \cdot a(r)$$

$1 < N \leqslant 3200$ where W_r is the Gaussian weight of the r^{th} point and $a(r)$ is the transmission factor of the $hk\ell$ reflection at that point.

<u>ORTEP</u>:- A thermal ellipsoid plot program written by C.K. Johnson and described in Oak Ridge National Laboratory Report ORNL - 3794. This program has been adapted by Dr. F.A. Stephens. It can be used to produce any type of crystal-structure illustration, including stereoscopic pairs.

<u>NORMAL</u>:- A program which can calculate E-values and punch out a specified number of the highest E's. (Output suitable for input to MULTAN or PHASEM).

<u>ESORT</u>:- Written by D.J. Williams.

This program sorts the E's into their respective parity groups ready for submission to Σ_2 program to give lists of triple interactions for hand generating of phases.

<u>MULTAN</u>:- Written by Main, Germain and Woolfson.

A general program for generating sets of phases for direct method solution. Chooses possible best starting sets and generates phases.

<u>PHASEM</u>:- Written by Michael Drew, University of California.

A program for investigating phase relationships between reflections in non-centrosymmetric space groups.

All the formulae used in this program are quoted by Karle and Karle[11]. The prerequisites for using the program are a set of |E| values for a crystal.

There are two main sections in the program, the subroutines PHISUM and PHITAN, which use the formulae

$$\phi_{\underline{h}'} \approx \langle \phi_{\underline{h}} + \phi_{\underline{h}-\underline{h}'} \rangle_{\underline{h}'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

and

$$\tan \phi_{\underline{h}} \approx {}^{A}/B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where

$$A = \sum_{\underline{h}'} |E_{\underline{h}'}E_{\underline{h}-\underline{h}'}| \sin (\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$$

$$B = \sum_{\underline{h}'} |E_{\underline{h}'}E_{\underline{h}-\underline{h}'}| \cos (\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$$

PHISUM takes as input a set of reflections whose phases are known either symbolically or numerically. By application of formula (1), the subroutine attempts to find the phases of other reflections from the known $\phi_{\underline{h}'}$, $\phi_{\underline{h}-\underline{h}'}$ values. Before a phase $\phi_{\underline{h}}$ is considered determined, the phase pairs $(\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$ must give the same value for $\phi_{\underline{h}}$ and the α value must be greater than some input value (See Appendix IV).

When formula (1) has been used to the utmost, the subroutine PHITAN is employed using the tangent formula (2). Use of this formula requires numerical values of all phases and the program allows symbols to be given differing values successively. Determination of phases for all $\underline{h}$ can thus be carried out from a small starting set of reflections, all with numerical $\phi_{\underline{h}}$.

The preceding has been a brief summary of the program systems available within the laboratory but has neglected one important problem, namely the handling of large amounts of data for input to these programs and systems. A structure which requires in excess of 4000 reflection data for solution is not uncommon and thus the standard deck for input to the computer may be ca. 4500 cards.

The system which I prefer is to use the UPDATE format of storing source card images on magnetic tape. The update facility allows the storage of source card images on magnetic tape or disc. Blocks of cards can be logically grouped under a deckname and within each deck the cards are numbered. The deck list numbers run down the right-hand side of the listing and are generated by UPDATE on the card images prepared for input to the assembler. Corrections can be made to the card image stored on tape by inserting new card(s) before or after a numbered card or by deleting card images. The 'Update' source deck can then be made available for input to the appropriate compiler or program. Two magnetic tapes are utilised in the process of creating and maintaining this program library and data system.

All computer calculations performed throughout the present work have been carried out on the Imperial College CDC 6400 and the University of London CDC 6400, 6600 and 7600 series computers. The UPDATE system is a CDC feature which provides the useful facility of storing data in a readily accessible manner in a binary format on permanent file or magnetic tape.

Least-Squares Refinement

Before considering the least-squares refinement of the transformation matrix for an arbitrarily-orientated crystal, it is best to discuss the least-squares refinement of cell parameters as this is a simpler illustration of the least-squares principle.

The method of 'Least-squares' was first postulated by Legendre and was placed on a logical foundation by Gauss and Laplace. Least-squares minimizes the sum of squares of the differences between observed and calculated values. The method finds many applications in crystallographic calculations.

Consider the following:

$$\underline{A}\,\underline{x} = \underline{b}$$

where $\underline{A}$ is of the order m . n, $\underline{x}$ is vector of order n and $\underline{b}$ vector of order $\underline{m}$; further m>n. Suppose in this case that $\underline{b}$ represents the intensity data and $\underline{x}$ the positional, thermal and scale parameters of the structure. We can define a residual vector $\underline{r}$ so that:-

$$\underline{r} = \underline{b} - \underline{A}\,\underline{x}$$

If the data set represented by $\underline{b}$ and $\underline{A}$ contained equally precise and independent elements then the criterion that $r^T r$ should be as small as possible will yield the parameters $\underline{x}$. Suppose now that $\underline{B}$ and $\underline{d}$ are of the same order as $\underline{A}$ and $\underline{b}$ but the data set has elements whose errors vary and are not independent, i.e.,

$$\underline{B}\,\underline{x} = \underline{d}$$

Then a matrix $\underline{X}$ can be constructed such that X_{ij} is the expectation value of the product $r_i r_j$ where r_i and r_j are the residuals of the equations i and j. $\underline{X}$ is symmetric and positive definite and a matrix $\underline{W}$ which is lower triangular of order m, can be chosen such that:-

$$\underline{W}\,X\,\underline{W}^T = \underline{I}$$

Now set $\underline{W} \, . \, \underline{B} = \underline{A}$

$$\underline{W} \, . \, \underline{d} = \underline{b}$$

The aim is to derive a set of 'normal equations' whose solution minimises $r^T r$, the sum of squares of residuals.

$$M = \underline{r}^T \cdot \underline{r} = (\underline{b} - \underline{Ax})^T \cdot (\underline{b} - \underline{Ax}) = \underline{b}^T \cdot \underline{b} - 2\underline{b}^T\underline{Ax} + \underline{x}^T\underline{A}^T\underline{Ax}$$

The normal equations:-

$$\frac{\delta M}{\delta x} = -2\underline{b}^T\underline{A} + 2\underline{x}^T\underline{A}^T\underline{A}$$

$\delta M/\delta x = 0$ at the minimum of M with respect to all elements of $\underline{x}$

so:-

$$\underline{A}^T\underline{A}\ \underline{x} = \underline{A}^T\underline{b}$$

From the structure factor equations we get a set of non-linear observational equations.

Given a set of observable data $\phi_1 \ldots\ldots \phi_n$, and an equivalent calculated set of f_i based on the unknowns $\underline{x}$ by the non linear equation:-

$$f_i = f_i\ (x)$$

If the measurements ϕ_i are independent and if each is estimated to be uncertain by $(\sqrt{w_i})^{-1}$, we minimise:-

$$M\ (\underline{x}) = \sum_{i=i}^{m} w_i\ (\phi_i - f_i\ (x)\ )^2$$

This M may have more than one local minimum so the solution may not be unique. Suppose we have an approximate solution $\underline{X}_o$ we want to try and refine, and further this solution lies near to one particular local minimum so that $\underline{X} = \underline{X}_o + \delta\underline{x}$ where every element δx is small compared to $\underline{X}$ then:-

$$M(x) = \sum_{i=1}^{m} w_i \left[\phi_i - \left[f_i\ (x_o) + \sum_{j=i}^{n} \frac{\delta f_i}{\delta x_j}\delta x_j + \tfrac{1}{2} \sum_{j=1}^{n} \sum_{k=1}^{m} \frac{\delta^2 f_i}{\delta x_j \delta x_k}\ \delta x_j \delta x_k + \ldots\right]\right]^2$$

From the assumption that δx is much smaller than x it would seem reasonable to ignore the terms $\delta x_i \cdot \delta x_k$ and all such higher terms so:-

$$M(x) = \sum_{i=1}^{m} w_i \left[\phi_i - f_i\ (x_o) - \sum_{j=1}^{n} \frac{\delta f_i}{\delta x_j}\ \delta x_j\right]^2$$

Ignoring the cross terms this form is equivalent to the linear form and hence a set of normal equations can be generated.

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CHAPTER III

Steric Factors in Nitrite Co-ordination: Crystal Structure of the Complex $[Ni\ (EtNH.CH_2CH_2NHEt)_2(O_2N)]^+BF_4^-$

> *"When a man writes from his own mind, he writes very rapidly. The greater part of a writer's time is spent in reading, in order to write; a man will turn over half a library to make one book."*
>
> *... Samuel Johnson.*

Abstract

The preparations, electronic and infrared spectra are reported for the compounds $NiD_2(NO_2)X$ (X = BF_4 or $C\ell O_4$; D = NN'- and NN-R_2-ethylenediamine, where R = Me or Et). The structure of the NN'-Et_2en complex has been determined from three-dimensional X-ray diffractometer data. The crystals are monoclinic, with unit cell dimensions: a = 11.338(1), b = 16.291(2), c = 11.934(1), $\beta = 112.015(8)^\circ$, space group $\underline{P}2_1/\underline{c}$ and $\underline{Z} = 4$. The structure was refined by least-squares to $\underline{R}$ 0.053 for 2522 independent reflections.

The complex is monomeric with a chelating nitrite forming part of a distorted octahedral environment about nickel. The diethylethylenediamine molecules are arranged in *cis*-positions and there is an approximation to a diad axis in the cation. The steric factors leading to this geometry, as distinct from M-ONO-M bridging, are discussed.

Introduction

Structural studies of metal-nitrite complexes have shown the nitrite ligand to be unusually varied in its mode of co-ordination. This versatility which is perhaps the most interesting feature of this group as a ligand, arises from the number of lone pairs (one on the nitrogen atom and two on each of .the oxygen atoms), which can be utilised in forming donor bonds to metal atoms. Furthermore, π-electrons can be donated or accepted by this ligand, thus assisting in the stability of the complex.

The nitrite ion has frequently been characterised by infrared and electron absorption spectra. I have included a section explaining the spectral criteria normally employed in predicting the mode of co-ordination taking place.

These criteria have been utilised in the later structural section, however, the spectral results do not permit a reliable differentiation to be made between the presence of a type III bridge and a chelating nitrite group.

Absorption Spectra of the Nitrite Group

Infrared Spectra

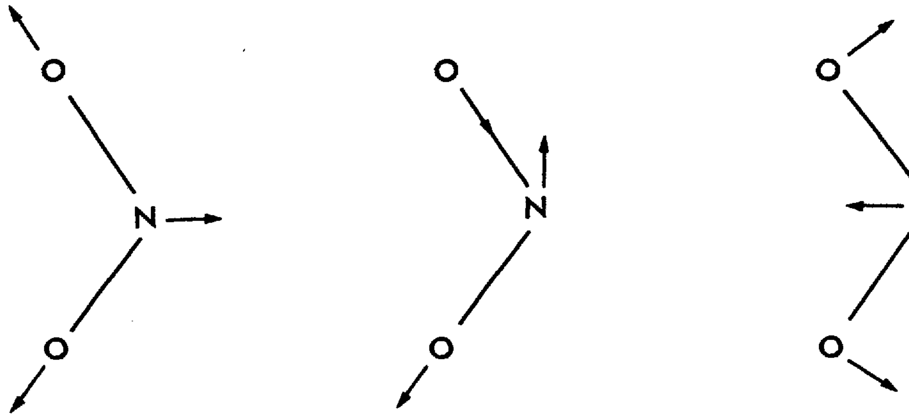
The unco-ordinated nitrite group possesses a point-group symmetry C_{2v}, with three non-degenerate vibrational modes, all of which are infrared active. These are, ν_s, the symmetric nitrogen oxygen stretches; ν_{as}, the antisymmetric nitrogen oxygen stretches; and δ_{NO_2} the NO_2 deformation. (Fig. 1).

1) **Free Nitrite Ion**

The measurement of the infrared and Raman spectra of sodium nitrite, space group Immm, in the solid state and in H_2O and D_2O solution by a number of workers[1,2], led to a general agreement on the observation of three peaks at 823 ± 3 (medium, sharp), 1250 ± 30 (very strong, broad) and 1326 ± 2 cm^{-1} (very weak, sharp). Further conclusion was made that the peak at 828 cm^{-1} was readily. assigned as δ_{NO_2}, the band at 1326 cm^{-1} assigned as ν_s, based on the Raman polarisibility of an aqueous solution, of single crystals, the fluorescence spectrum; and the broad intense absorption centred at ~1250 cm^{-1} as ν_{as} in agreement with the Raman spectra of an aqueous solution and a single crystal of sodium nitrite. The spectra of potassium nitrite[3], silver nitrite[4] and barium nitrite[5] are similar to that of sodium nitrite, the nitrite group is therefore apparently unusual in having ν_s higher than ν_{as}, resembling OF_2 and O_3, which is its isoelectronic compound. However, this can be accounted for by the presence of the two negatively charged oxygen atoms which result in the relatively large interaction constant.

In a metal complex the values of the ν_s and ν_{as} stretching frequencies of the nitrite group are quite characteristically different from their free-ion values depending on a particular type of co-ordination.

Figure 1 (a)



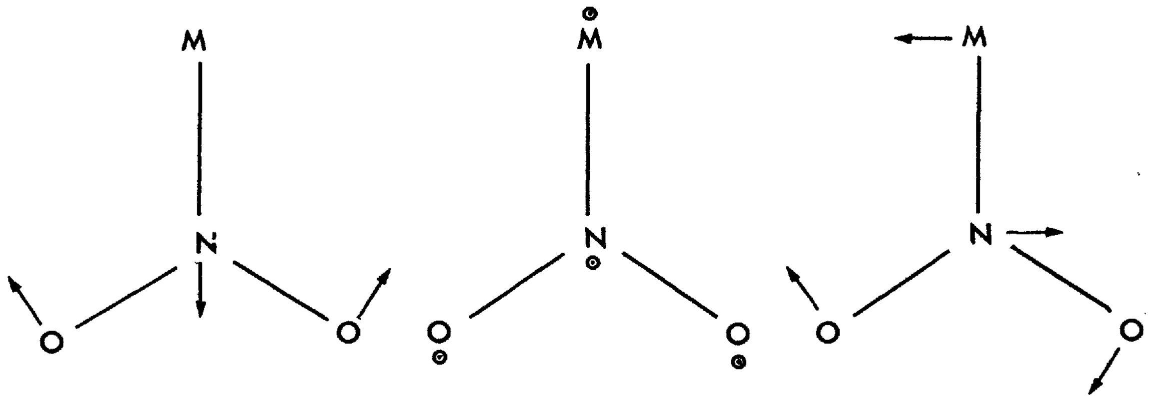
ν_s Symmetric

ν_{as} Antisymmetric

δ_{NO_2} Deformation

The fundamental vibrations of the free nitrite ion,

Figure 1 (b)



ν_{M-N} Stretching

ρ_W Wagging

ρ_r Rocking

The vibrations of the $M-NO_2$

The value of deforming δ_{NO_2} appears, on the other hand, not to change significantly.

2) Nitro Ligand

Co-ordination via nitrogen in a nitrocomplex causes a quite different effect on its vibrational spectrum from oxygen co-ordination. The bonding via nitrogen tends to increase ν_{as} significantly, whereas ν_s is only slightly increased above its free-ion value. Thus, ν_{as} is raised in the nitrocomplexes of Co(III) and Pt(II) to $\sim$1400 cm^{-1} while ν_s remains virtually unaltered from its free-ion value at $\sim$1330 cm^{-1} [6,7]. The effect has been explained by the induction of a positive charge on the nitrogen atom, which causes a decrease in the negative charge on the oxygen atoms, hence the non-bonded interaction term between them, while the double-bond character of the nitrogen-oxygen bonds in increased.

A frequency at $\sim$600 cm^{-1} in many nitrocomplexes of Co(III) [8,9,10,] and at 462 cm^{-1} in $K_2CdNi(NO_2)_6$ has been assigned by Nakamoto *et al*[8] as a wagging vibration ρ_w characteristic of the nitro co-ordination. The corresponding mode of vibration has not been observed in nitrocomplexes and compounds containing bridged nitrite groups.

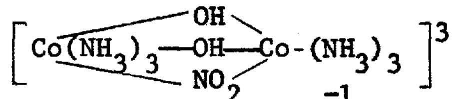
3) Nitrito Ligand

As a monodentate ligand, oxygen co-ordination in nitritocomplexes causes the lowering of one stretching frequency towards that of a nitrogen-oxygen single bond, the other being raised towards that of a nitrogen-oxygen double bond. The ν_{as} frequency is lowered whereas that of ν_s is increased.

4) Chelating Nitrite Ligand

When both oxygen atoms of the nitrite group are employed for chelation, it is expected that there would be only a slight change in the bonding order of the nitrogen-oxygen bonds. A strong band is found at ~1200 cm^{-1} and a medium one at ~1300 cm^{-1} in the chelating nitrite groups in the solid compounds $NiL_2(NO_2)_2$ (where L = pyridine, 2-methylpyridine and quinoline), the bands are assigned as ν_{as} and ν_s respectively, which illustrates that both ν_{as} and ν_s are slightly reduced.

5) Bridging (-$\overset{O}{N}$O-) Ligand

For bidentate co-ordination using nitrogen and oxygen as a bridge, the nitrite group was found to have an appreciable increase in ν_s but only a slight reduction in ν_{as}. The nitrogen-oxygen stretching frequencies occur at ~1240 and ~1430 cm^{-1} in each of the complexes of Ni(ethylenediamine)$(NO_2)_2$, Ni(N-methylethylenediamine)$(NO_2)_2$ and $Ni(NH_3)_2(NO_2)_2$. It was interpreted that nitrogen and oxygen co-ordination in this type of bridging resulted in the slight lowering of ν_{as} from its free ion value, and the raising of the mean of ν_s and ν_{as}.[11] A similar spectral result was found in the compound (Ni(ethylenediamine)$_2$ NO_2)BF_4 which was confirmed by the X-ray crystallographic method to contain the bridging via nitrogen and oxygen of the nitrite group.[12] Compounds of the family  $\left[Co\overset{OH}{\underset{NO_2}{\overline{(NH_3)_3 — OH — }}}Co\text{-}(NH_3)_3\right]^{3+}$ possessing nitrite infrared frequencies at 1200 and 1500 cm^{-1} were therefore deduced to possess this type of bridging.

6) Bridging (-$\overset{NO}{O}$-) Ligand

Bridging via a single oxygen atom by a nitrite ion is expected to affect the infrared spectrum in a similar manner as a monodentate nitrito type of bonding when a single oxygen atom is co-ordinated. A very strong band of ν_{as} at ~1020cm^{-1} and a generally strong peak of ν_s at ~1475 was found by Hitchman[11] to be a characteristic spectrum of a series of compounds $NiL_2(NO_2)_2$ (where L = isoquinoline, 3-methylpyridine, 4-methylpyridine and N,N-diethylethylenediamine) and $NiL_2(NO_2)_2 \cdot 1/3C_6H_6$ (where L = pyridine and 3-methylpyridine). These bands were similar to those found for monodentate oxygen bonding.

As evidence from magnetic moments and electronic spectra suggested that the co-ordination number of each nickel ion in these complexes was six, implying bidentate co-ordination by the nitrite group, it was concluded by Hitchman[11] that the only bidentate nitrite bonding likely to have infrared frequencies similar to those of a monodentate nitrito co-ordination was bridging via a single oxygen atom.

The manner of bridging via a single oxygen atom was furthermore supported by the magnitude of the difference of ν_{as} and ν_s from their free-ion values, as the effect on the nitrite infrared spectrum of two nickel ions attached to a single oxygen atom of a nitrite group should be appreciably more than that produced when one nickel ion was bonded. The values of ν_{as} and ν_s at frequencies of ~1020 and ~1457 cm^{-1} were between those observed for monodentate nitrito groups co-ordinated to Co(III) and Pt(IV).

Electronic Spectra

The analysis of the electronic absorption spectrum of a nitrite complex is relatively more difficult than its infrared spectrum.

The energies of the 'd - d' electronic transitions in a nitrite complex, as measured by the electronic absorption spectra, provides two significant items of information on the nature of the bonding in a nitrite complex.

The first is derived in conjunction with the magnetic susceptibility and often indicates the approximate symmetry of the ligand field, i.e. whether the complex is planar, tetrahedral or octahedral. Stoicheiometric consideration then leads to a conclusion that the nitrite group co-ordinates as a monodentate or bidentate ligand.

The second useful item of information generally provided by the electronic spectrum is whether the nitrite groups are co-ordinated via nitrogen or oxygen. Nitrite groups co-ordinated via oxygen only - nitrito, chelated, and bridged via a single oxygen atom group - are at the weak end of the spectrochemical series, whereas nitrite ions co-ordinated only or partly by nitrogen i.e. nitro and bidentate $-\overset{O}{N}O-$ bridging are at the strong end. For example the oxygen-bonded nitrite groups have an energy of the 'd - d' electronic transition value of ~9,000cm^{-1} when octahedrally co-ordinated to Ni(II), while those bonded via nitrogen have a corresponding value of ~13,000cm^{-1}.

1) <u>Nitro- and Nitrito- Ligands</u>

The nitro- and nitrito- groups can be readily distinguished from a study of the spectrochemical series. Jørgensen[13] listed the following spectrochemical series in order of decreasing field strength:

$CN^- > -NO_2^- >$ o-phenanthroline > ethylene-diamine > NH_3 > pyridine $> -NCS^- > H_2O > -ONO^- > OH^- > Cl^- > Br^- > I^-$.

The nitro- group is therefore a relatively strong ligand, while the nitrito- group is a fairly weak ligand. For transition metal ions, particularly of the first series, the 'd - d' bands in a nitro-complex will generally be of considerably higher energy than the corresponding ones in the analogous nitritocomplex. By comparing the electronic spectrum of a nitrite complex with those of similar compounds containing other ligands, the effective ligand field strength of the nitrito-groups, and hence their mode of co-ordination as a nitro or nitrito bonding can be deduced. For example, the energies of the first spin-allowed electronic transitions for the isomeric forms of $(Co(NH_3)_5\text{-}ONO)Cl_2$, $(Co(NH_3)_5\text{-}NO_2)Cl_2$ and two related compounds, $(Co(NH_3)_5H_2O)Cl_3$ and $Co(NH_3)_6Cl_3$, are 20600, 21900; 20600 and 21000 cm^{-1} respectively[13 14].

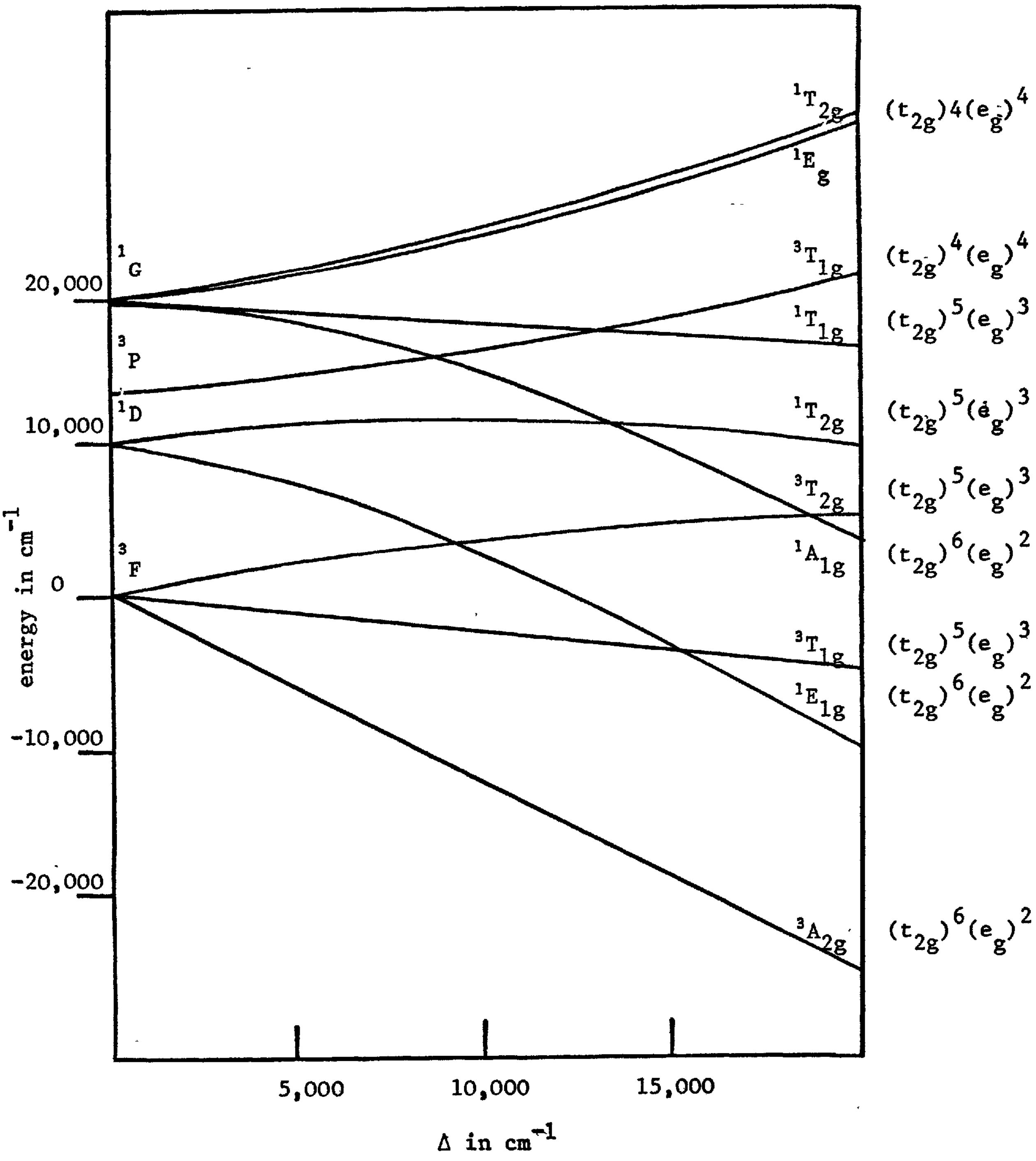
The ligand-field splitting parameter, Δ values, for nitro and nitrito bonding, can be approximately obtained by the 'average environment' treatment as suggested by Jørgensen[13]. In a nickel (II) complex, the partial energy level for the nickel ion, of symmetry d^8, in an octahedral field may be considered. (Fig. 2). The six-co-ordinate nickel ions with spin-triplet ground states exhibit three main bands, for three spin-allowed transitions from the ground state $^3A_{2g}$ to the three triplet states $^3T_{2g}$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ in O_h ligand field symmetry. The first electronic transition $^3A_{2g}$ to $^3T_{2g}$ approximates to Δ value, which is ~12,000 cm^{-1} in a typical nitrocomplex Ni(N-ethylethylenediamine)$_2$(←NO_2)$_2$ and 10,360 cm^{-1} in a typical nitritocomplex Ni(N,N'-diethylethylenediamine)$_2$(←ONO). By taking the Δ value of the diamines as 11,500 cm^{-1} [13], it follows from the values in the two compounds that the Δ values of the nitro- group and of the nitrito-group are ~13,000 and 8,100 cm^{-1} respectively. The corresponding values of NH_3 and H_2O are 10,800 and 8,500 cm^{-1} respectively.

Similar values for the nitro- and nitrito- groups in the isomeric forms of $[Co(NH_3)_5(NO_2)]Cl_2$ were deduced when the difference in oxidation state of the metal ion was taken into account. The difference in ligand-field strength between the nitro- and nitrito- group is usually large enough for correct assignments to be generally made.

2) Chelating Ligand

The electronic spectra of complexes containing chelating nitrite groups indicates a relatively weak ligand nature of the chelating nitrite group. The compounds $NiL_2(NO_2)_2$ (where L = pyridine, 2-methylpyridine and quinoline), Ni(N,N,N',N'-

Figure 2


^1G
^3P
^1D
^3F
20,000
10,000
0
-10,000
-20,000
energy in cm^{-1}
5,000
10,000
15,000
Δ in cm^{-1}
$^1T_{2g}$
$(t_{2g})4(e_g)^4$
^1E_g
$^3T_{1g}$
$(t_{2g})^4(e_g)^4$
$^1T_{1g}$
$(t_{2g})^5(e_g)^3$
$^1T_{2g}$
$(t_{2g})^5(e_g)^3$
$^3T_{2g}$
$(t_{2g})^5(e_g)^3$
$^1A_{1g}$
$(t_{2g})^6(e_g)^2$
$^3T_{1g}$
$(t_{2g})^5(e_g)^3$
$^1E_{1g}$
$(t_{2g})^6(e_g)^2$
$^3A_{2g}$
$(t_{2g})^6(e_g)^2$

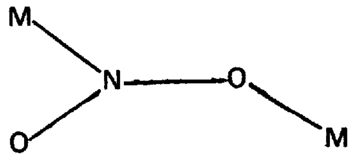
tetramethylethylenediamine)$(NO_2)_2$, and Ni(N,N,N',N'-tetraethylethylenediamine)$(NO_2)_2$, all of which were confirmed by the magnetic moment values of 2.9 - 3.3 B.M. to possess six-co-ordinate, paramagnetic nickel (II) imply the bidentate co-ordination of the nitrite group. The band maxima of these complexes suggest that the nickel (II) in each of them is surrounded by fairly weak ligands.[11]

3) Bridging $(-\overset{\text{O}}{\text{N}}\text{O}-)$ Ligand

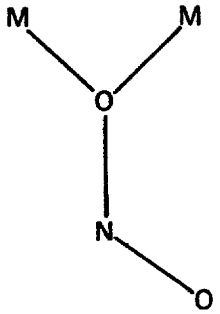
The nitrite bridging via a nitrogen atom and an oxygen atom produces a high ligand field, as the nitrogen atom of the anion is involved in the co-ordination, and thus imposes relatively high energies of the band maxima on the electronic absorption spectrum.

The band maxima of (Ni(ethylenediamine)$_2(NO_2)_2)BF_4$, whose structure has been confirmed by X-rays to contain $-\overset{\text{O}}{\text{N}}\text{O}-$ bridging, are at ~20,200 and ~12,500 - 10,900 cm^{-1}.[11, 12] These band energies are very similar to those found for Ni(ethylenediamine)$_2(NO_2)_2$ and suggests that the Δ value of a $-\overset{\text{O}}{\text{N}}\text{O}-$ bridging nitrite group is close to that produced by a nitro- group and is very high, suggesting a relatively strong ligand field around each nickel ion, whereas Ni(diamine)$(NO_2)_2$, known to contain chelating anions, has a fairly weak ligand field with bands at ~17,000 and 10,000 cm^{-1}.

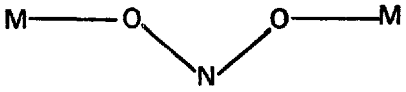
The nitrite ion is an extremely versatile ligand. As a monodentate ligand it can coordinate either via nitrogen forming a nitro-complex, or via oxygen, giving a nitrito complex. Alternatively it can use both oxygen atoms to form a chelate ring, or it can bridge two metal atoms as in I-III.



I



II



III

Although definite examples of bridges of types I and II have been demonstrated by X-ray structural studies[15, 16], there are no proven examples of type III bridges.

Earlier work had shown that with nickel nitrite complexes the mode of nitrite coordination depended on the steric influences of other ligands present. In complexes of the type $NiD_2(NO_2)_2$ (where D = a substituted ethylenediamine), nitrite coordinated via nitrogen for ethylenediamine and N-monoalkyl-ethylenediamines[17] but via one oxygen atom as the extent of substitution on amino and/or methylene hydrogens was increased[18]. Very heavily substituted diamines, such as NNN'N'-tetraalkylethylenediamines gave only $NiD(O_2N)_2$ complexes in which the anions were chelating[12, 19].

These observations suggested that the type I bridge, known to be present in $Nien_2(NO_2)BF_4$[15], would be less favoured as alkyl substitution on the diamine was increased, and that by a suitable choice of diamine, compounds of stoichiometry $NiD_2(NO_2)BF_4$, containing type III bridges might be obtained.

The structural study of $Ni(EtNHCH_2CH_2NH.Et)_2(NO_2)BF_4$ presented here is part of a general study of the compounds $NiD_2(NO_2)$ X (X = BF_4 or $C\ell O_4$; D = NN'- and NN-R_2-en where R = Me or Et), with a view to studying steric factors in nitrite co-ordination.

Experimental

Preparation

All the complexes except Ni(EtNHCH$_2$CH$_2$NHEt)$_2$(NO$_2$)BF$_4$ were prepared by the following method. A methanolic solution of nickel nitrite[19] was refluxed with an equimolar quantity of hydrated nickel perchlorate (or tetrafluoroborate) after the addition of 2,2,-dimethoxypropane. This solution was then added dropwise and with stirring to a methanolic solution of the appropriate amount of the diamine. After concentration and cooling, crystals formed, and these were collected and dried in vacuo.

The compound Ni(EtNHCH$_2$CH$_2$NHEt)$_2$(NO$_2$)(BF$_4$) was obtained by a modification of the above procedure. A concentrated aqueous solution of nickel nitrite and nickel tetrafluoroborate was prepared by adding solid potassium nitrite (0.85g) to an aqueous solution of nickeltetrafluoroboratehexahydrate (3.4g) and filtering off the precipitated potassium tetrafluoroborate. This solution was then added dropwise, with stirring, to a methanolic solution of the diamine. Large green crystals of the complex separated after the solution had been cooled for several hours.

Microanalytical results are given in Table 1 along with relevant spectral data, and ligand abbreviations. Physical measurements were carried out as described previously.[13]

X-Ray Studies

The dark green crystals of Ni(s-dieen)$_2$(NO$_2$)(BF$_4$) were rather irregular in shape. They were stored in their mother liquor as they tended to powder on prolonged exposure to air. Crystals used for X-ray studies were coated with varnish. When examined under polarized light they were opaque so no useful optical information was obtained.

Preliminary photographs gave the Laue symmetry $^2/_m$, monoclinic, with the unique-axis, b, corresponding to one of the shorter dimensions

TABLE 1

Complex [a]	Colour	Characterisation Data Analytical Data (%) [b]			Nitrite i.r. band frequencies (cm^{-1})	Electronic band frequencies (cm^{-1}) [f]
		C	H	N		
Ni(s-dimen)$_2$ (NO$_2$)(CℓO$_4$)	Dark purple	25.45 (25.25)	6.2 (6.4)	18.5 (18.4)	1300m, 1230s, [d]	18,180;~14,900wsh;10,500; ~8300brsh
Ni(s-dimen)$_2$ (NO$_2$)(BF$_4$)	Dark purple	26.3 (26.1)	6.2 (6.6)	19.1 (19.0)	1300m, 1215s, [d]	18,000;10,500 [g]
Ni(a-dimen)$_2$ (NO$_2$)(CℓO$_4$)	Bright green	25.3 (25.25)	6.25 (6.4)	18.45 (18.4)	1295mw,1215vs,857ms	16,800;~12,500wsh;10,050;
Ni(a-dimen)$_2$ (NO$_2$)(BF$_4$)	Bright green	26.5 (26.1)	6.3 (6.6)	19.3 (19.0)	1295mw,1217s,859m	16,650;~12,400wsh;10,000
Ni(s-dieen)$_2$ (NO$_2$)(CℓO$_4$)	Blue green	33.2 (33.0)	7.1 (7.4)	16.3 (16.0)	1315m [e],1210vs,861m, 829w	17,350;~12,500wsh;10,250 [g]
Ni(s-dieen)$_2$ (NO$_2$)(BF$_4$)	Blue green [c]	34.15 (34.0)	7.2 (7.6)	16.6 (16.5)	1295mw [e],1210vs,861m	17,400;~14,700wsh;~12,500wsh; 10,250 [g].

[a] Ligand abbreviations : s-dimen = NN'-dimethylethylenediamine; a-dimen = NN-dimethylethylenediamine;
s-dieen = NN'-diethylethylenediamine.

[b] Required values in parentheses.

[c] When powdered; dark green when crystalline.

[d] Amine bands in region of δ(NO$_2$).

[e] Assignment uncertain because of amine bands.

[f] Reflectance spectra.

[g] Asymmetric to lower energy.

of the crystal.

Preliminary unit-cell dimensions were:-

$a = 11.34\text{Å}$ $D_m = 1.42$

$b = 16.30\text{Å}$ $D_c = 1.41$

$c = 11.94\text{Å}$ $U = 2046\text{Å}^3$

$\beta = 112^\circ$ $Z = 4$

The systematic absences were:-

$hk\ell$	none
$h0\ell$	$\ell = 2n + 1$
$0k0$	$k = 2n + 1$

Thus the space group is unambiguously determined as $P2_1/c$. Intensity data were collected for a crystal of dimensions ca. 0.2 x 0.2 x 0.3 mm^3 mounted about the b axis on a Siemens off-line automatic four-circle diffractometer.

Crystal Data

$C_{12}H_{32}BF_4N_5NiO_2$, $M = 433.9$, Monoclinic $a = 11.338(1)$, $b = 16.291(2)$, $c = 11.934(1)$ Å, $\beta = 112.015(8)^\circ$, $U = 2043.6\text{Å}^3$, D_m (by flotation) $= 1.42$, $D_c = 1.41$, $Z = 4$, $F_{000} = 896$, $\mu = 18.13.\text{cm}^{-1}$ Space group $P2_1/c$ from systematic absences : h01, 1 = 2n + 1, and 0k0, k = 2n + 1.

CuKα radiation at a take-off angle of 6°, a nickel β filter and a Na(Tℓ)I scintillation counter were used. The θ-2θ scan technique was employed, with a 'five-value' measuring procedure[20] to give 2522 independent reflections measured to $\theta = 60^\circ$, of which 140 were judged to be unobserved.[20] The net count of the reference reflection did not vary significantly during the data collection (ca. 6 days). The data were scaled using the reference reflection and the Lorentz and polarisation corrections were applied.

Solution and Refinement of Structure

A three-dimensional Patterson map was computed from which the nickel atom position was readily obtained. Least-squares refinement[21] of this position gave R = 0.495. A difference-Fourier synthesis calculated on the basis of this atom position, with a rejection ratio of 0.5, showed the positions of a further eight meaningful atoms and inclusion in least-squares refinement gave R = 0.38. All the remaining atomic positions were then found inclùding the tetrafluoroborate group, but owing to a large degree of disorder in this group it was excluded from the next refinement in order to redetermine its position (R = 0.277 without BF_4). The tetrafluoroborate group was then more accurately determined from the resultant difference-Fourier. Refinement of all the non-hydrogen atoms with isotropic temperature factors gave R = 0.184. All atoms were then allowed to refine anisotropically to give R = 0.095. At this stage, the data were corrected for absorption effects, according to the method of Busing and Levy[22], using a 10 x 10 x 10 grid, with crystal pathlengths determined by the vector analysis procedure of Coppens *et al*[23]. Further anisotropic refinement brought R to 0.087. An anomolous dispersion correction for nickel was then applied (R = 0.076). Two misprocessed reflections and three reflections suffering from extinction were removed during the refinement procedure. When the hydrogen atoms, located from the latest difference-Fourier were included as a "fixed-atom contribution", R fell to 0.053. (Final R-factor of less thans' = 0.103). The scattering form factors used were those tabulated by Cromer and Weber[24], and the real and imaginary parts of the anomalous dispersion correction were those given by Cromer.[25] A final difference-Fourier was relatively featureless.

Tables 2 and 3 list the final coordinates of the non-hydrogen atoms and the coefficients of their anisotropic temperature factors respectively. The standard deviations have been obtained using the full-matrix least-squares refinement procedure ORFLS of X-ray 70. (See chapter II). The coordinates of the hydrogen atoms are given in Table 4. Structure amplitudes are listed at the end of the chapter.

Discussion

Compounds of the type Ni(diamine)$_2$(NO$_2$)X (X = BF$_4$ or CℓO$_4$) were readily obtained with a-dimen, s-dimen, and s-dieen. The electronic spectra of the solid compounds (Table 1) indicate the absence of type 1 bridges, as the spin-allowed d-d bands are at much lower energies than in the compounds Nien$_2$(NO$_2$)X. For these last, the two lowest energy bands were observed[26] at ca. 20,000 and ca. 12,000 cm^{-1}. Whereas the corresponding bands in the spectra of the compounds described here are at 16,000-18,200 and 10,000-10,500 cm^{-1} respectively. The absence of Type I bridging is supported by the nitrite band frequencies in the infrared (i.r.) spectra (Table 1), particularly by the absence of an N-O stretch in the region 1390-1440 cm^{-1}. These results also show the absence of a single oxygen bridge (typeII).

However, the spectral results do not permit a reliable differentiation to be made between the presence of a type III bridge and a chelating nitrite group. Both types of nitrite coordination would be expected to affect the internal modes of the NO$_2^-$ group in a similar way. Moreover the only significant difference in the electronic spectra would be differences in the splittings of the orbital triplet levels between a trans NiN$_4$O$_2$ system for the chelating nitrite. As such differences are too ill-defined for diagnostic purposes, one of the series of complexes was chosen for X-ray study - the compound Ni(S-dieen)$_2$(NO$_2$)(BF$_4$).

The structural study showed that in this compound the nitrite group acts as a chelate and not a bridging group. The structure of the cation [Ni(s-dieen)$_2$(O$_2$N)]$^+$ is shown in Figure 3, the relevant bond lengths and angles are listed in Tables 5 and 6, and the molecular packing is shown in Figure 4 (drawn using the program ORTEP[27]). Intermolecular contacts are listed in Table 7. The coordination about the nickel atom is distorted octahedral. Within each chelate ring formed by s-dieen both ethyl groups point upward towards the nitrite group. This arrangement allows the s-dieen molecules to occupy cis positions without undue steric strain whilst leaving sufficient room for the nitrite group to chelate. The atoms N_6 and N_{33} lie in the plane containing Ni, O_1, and O_3 (deviations from the plane are 0.02 and 0.009 Å respectively, plane 2, Table 8). As expected, the constraint imposed upon the angle O_1-Ni-O_3 by the "bite" of the nitrite group, permits the angle N_6-Ni-N_{33} to open out from an ideal octahedral angle of 90° to 101.8°. However, the departure from linearity for N_3-Ni-N_{66} is quite small (angle N_3-Ni-N_{66} = 173.6°) and there is almost a diad relationship within the cation. The trans Ni-N bonds (to N_3 and N_{66}) are somewhat longer (2.15 and 2.16 Å) than those to N_{33}(2.13 Å) and N_6(2.10 Å), and all are longer than the Ni-N bonds (2.09 Å) in Ni(tetmen)$(O_2N)_2$[12]. The angles at the nitrite group (O_1-N_2-O_3 and O_1-Ni-O_3) are quite similar to those of the tetmen compound, but the nitrite chelation is more symmetric [Ni-O, 2.10 and 2.12 Å compared with 2.07 and 2.15 Å, and 2.06 and 2.12 Å for the two nitrites in Ni(tetmen)$(O_2N)_2$[12]].

In conclusion, although the steric factors in Ni(s-dieen)$_2$(ONO)$_2$ are sufficient to favour nitrito-coordination[18] as compared with nitro-coordination, they are insufficient in the range of compounds reported here to prevent the cis- chelation of the diamine required for nitrite chelation. In turn, the relatively small steric requirements of the chelating nitrite group facilitate this cis-arrangement of diamine coordination, as they permit any unfavourable diamine-diamine contacts to open out by distortion from octahedral geometry. The present results suggest that the type III bridging nitrite may be rather elusive, as the further increase in steric hindrance required to prevent a cis-arrangement for the diamine would probably result in only one molecule coordinating to the metal ion.

Fig. 3

Structure of the cation Ni(ethylethylenediamine)$_2$(O$_2$N)$^+$.

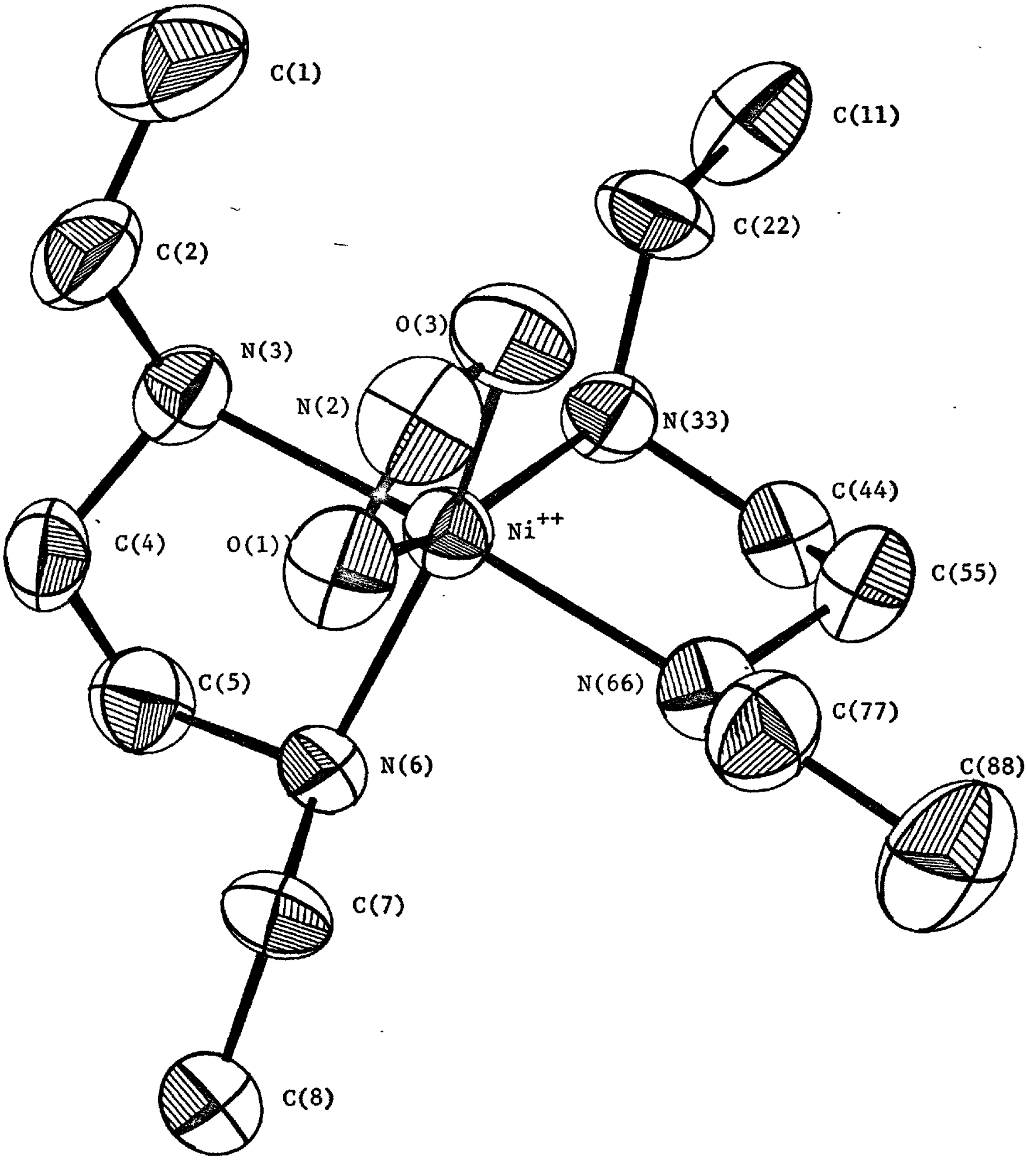


Fig. 3a

Schematic diagrams of the cation.

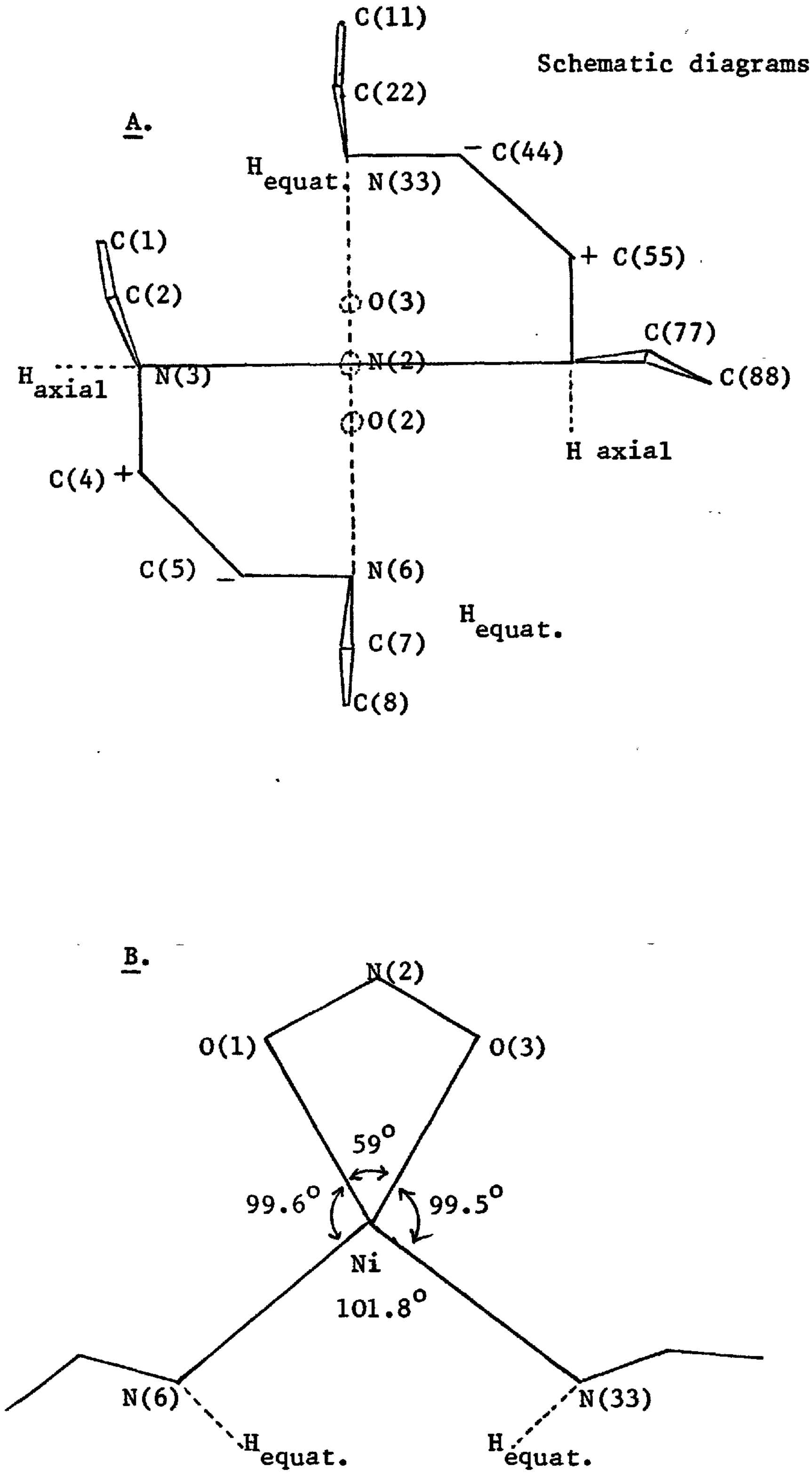


Fig. 4

Stereoscopic packing diagram of the complex

$[Ni(EtNH.CH_2CH_2NHEt)_2(O_2N)]^+BF_4^-$.

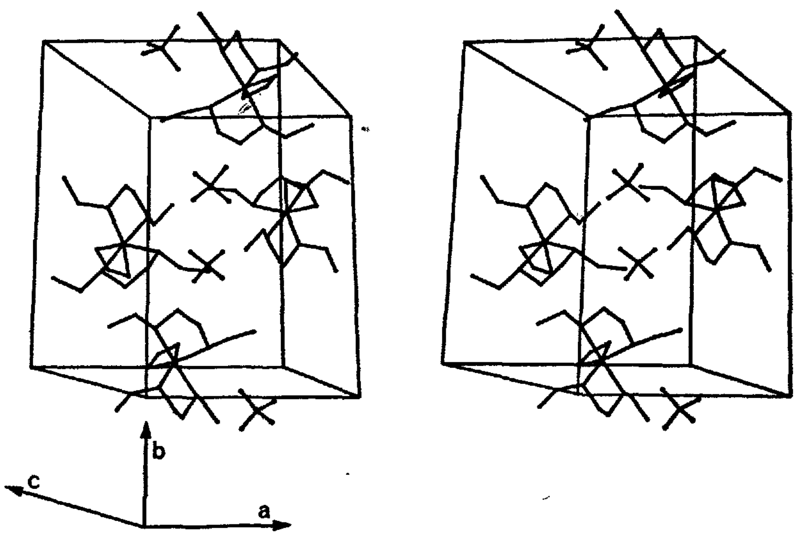


TABLE 2

Non-Hydrogen Atomic Positions

	x	y	z
Ni^{++}	0.23274(6)	0.09381(4)	0.23013(6)
O_1	0.0491(3)	0.0877(2)	0.0961(3)
N_2	0.0694(5)	0.1403(3)	0.0282(4)
O_3	0.1808(3)	0.1686(2)	0.0734(3)
C_1	0.3261(7)	-0.0756(4)	-0.0272(5)
C_2	0.2647(5)	-0.0060(3)	0.0164(4)
N_3	0.2960(3)	-0.0059(2)	0.1485(3)
C_4	0.2513(5)	-0.0806(3)	0.1906(4)
C_5	0.2814(4)	-0.0715(3)	0.3246(4)
N_6	0.2172(3)	0.0018(2)	0.3473(3)
C_7	0.0817(4)	-0.0158(3)	0.3333(5)
C_8	0.0695(5)	-0.0738(3)	0.4271(5)
C_{11}	0.6145(5)	0.1885(4)	0.2854(6)
C_{22}	0.4740(5)	0.1678(3)	0.2317(5)
N_{33}	0.4243(3)	0.1337(2)	0.3206(3)
C_{44}	0.4220(5)	0.1942(3)	0.4122(4)
C_{55}	0.3045(5)	0.2465(3)	0.3630(5)
N_{66}	0.1898(3)	0.1935(2)	0.3282(3)
C_{77}	0.0747(5)	0.2456(3)	0.2737(5)
C_{88}	-0.0430(6)	0.2053(4)	0.2798(6)
B	0.6458(6)	-0.0693(4)	0.3318(5)
F_1	0.5537(4)	-0.1225(3)	0.2706(4)
F_2	0.6912(7)	-0.0313(4)	0.2619(5)
F_3	0.5957(3)	-0.0153(2)	0.3929(3)
F_4	0.7403(3)	-0.1109(2)	0.4148(3)

Table 3

Anisotropic Thermal Parameters

The anisotropic thermal ellipsoid has the form:-

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
Ni^{++}	855(8)	395(3)	823(7)	-5(4)	353(6)	35(4)	x 10^{-5}
O_1	115(4)	68(2)	117(4)	-2(2)	31(3)	2(2)	x 10^{-4}
N_2	138(6)	71(3)	106(5)	7(3)	31(4)	10(3)	x 10^{-4}
O_3	139(4)	60(2)	106(3)	2(2)	51(3)	11(2)	x 10^{-4}
C_1	281(11)	78(4)	138(7)	12(5)	114(7)	-18(4)	x 10^{-4}
C_2	163(7)	59(3)	99(5)	0(3)	60(4)	-8(3)	x 10^{-4}
N_3	108(4)	42(2)	84(4)	-4(2)	47(3)	-4(2)	x 10^{-4}
C_4	128(6)	42(2)	126(5)	-5(3)	58(4)	-4(3)	x 10^{-4}
C_5	117(5)	46(2)	123(5)	6(3)	56(4)	14(3)	x 10^{-4}
N_6	83(4)	42(2)	84(3)	-3(2)	37(3)	3(2)	x 10^{-4}
C_7	96(5)	57(2)	139(6)	-4(3)	61(4)	5(3)	x 10^{-4}
C_8	141(6)	57(3)	180(7)	-16(3)	98(6)	6(3)	x 10^{-4}
C_{11}	131(6)	62(3)	245(9)	-26(3)	114(6)	20(4)	x 10^{-4}
C_{22}	128(6)	48(3)	143(6)	-12(3)	79(5)	-6(3)	x 10^{-4}
N_{33}	89(4)	40(2)	102(4)	-13(2)	45(3)	-3(2)	x 10^{-4}
C_{44}	130(6)	56(2)	107(5)	-20(3)	54(4)	-14(3)	x 10^{-4}
C_{55}	156(6)	44(2)	137(6)	-12(3)	87(5)	-14(3)	x 10^{-4}
N_{66}	109(4)	43(2)	96(4)	9(2)	52(3)	6(2)	x 10^{-4}
C_{77}	163(7)	56(3)	128(6)	32(4)	61(5)	10(3)	x 10^{-4}
C_{88}	131(7)	81(4)	232(9)	25(4)	76(7)	10(5)	x 10^{-4}
B	134(7)	47(3)	93(6)	8(4)	43(5)	4(3)	x 10^{-4}
F_1	162(5)	119(3)	327(7)	3(3)	34(5)	-114(4)	x 10^{-4}
F_2	698(7)	134(4)	327(9)	29(6)	340(11)	87(5)	x 10^{-4}
F_3	157(4)	67(2)	195(4)	27(2)	37(3)	-32(2)	x 10^{-4}
F_4	180(4)	94(2)	157(4)	46(2)	69(3)	17(2)	x 10^{-4}

Table 4

Hydrogen atomic positions; located from difference-Fourier and unrefined. x 10^3

	x	y	z
H_{11}	429	-70	14
H_{12}	300	-135	-1
H_{13}	300	-77	-125
H_{21}	288	53	-14
H_{22}	158	-12	-28
H_{31}	400	-1	191
H_{41}	151	-90	145
H_{42}	301	-135	176
H_{51}	250	-127	358
H_{52}	384	-67	371
H_{61}	269	22	441
H_{71}	38	43	339
H_{72}	34	-41	244
H_{81}	116	-133	424
H_{82}	120	-49	519
H_{83}	-27	-88	418
H_{111}	630	233	357
H_{112}	666	133	322
H_{113}	652	213	221
H_{221}	422	224	195
H_{222}	458	124	161
H_{331}	481	82	365
H_{441}	423	162	491
H_{442}	505	232	435
H_{551}	303	290	431

Table 4 (Continued)

H_{552}	303	280	284
H_{661}	187	163	408
H_{771}	90	303	321
H_{772}	60	256	180
H_{881}	-59	148	232
H_{882}	-28	195	373
H_{883}	-127	244	240

TABLE 5

Bond lengths (Å) with estimated standard deviations in parentheses

$Ni^{++} - O_1$	2.099(3)	$Ni^{++} - N_{33}$	2.132(3)
$Ni^{++} - O_3$	2.123(3)	$Ni^{++} - N_{66}$	2.161(4)
$Ni^{++} - N_3$	2.151(4)	$O_1 - N_2$	1.258(7)
$Ni^{++} - N_6$	2.102(4)	$N_2 - O_3$	1.261(6)

$C_1 - C_2$	1.521(9)	$C_{11} - C_{22}$	1.515(7)
$C_2 - N_3$	1.481(6)	$C_{22} - N_{33}$	1.483(7)
$N_3 - C_4$	1.477(6)	$N_{33} - C_{44}$	1.479(7)
$C_4 - C_5$	1.513(7)	$C_{44} - C_{55}$	1.503(7)
$C_5 - N_6$	1.476(6)	$C_{55} - N_{66}$	1.484(6)
$N_6 - C_7$	1.509(6)	$N_{66} - C_{77}$	1.487(6)
$C_7 - C_8$	1.511(8)	$C_{77} - C_{88}$	1.513(9)

$B - F_1$	1.342(7)
$B - F_2$	1.292(11)
$B - F_3$	1.392(8)
$B - F_4$	1.338(6)

TABLE 6

Selected Bond angles (^{o}) with estimated standard deviations in parentheses

$O_1 - Ni^{++} - O_3$	59.17(15)
$N_6 - Ni^{++} - N_{33}$	101.78(13)
$N_3 - Ni^{++} - N_{66}$	173.61(12)
$O_1 - Ni^{++} - N_3$	91.31(14)
$O_3 - Ni^{++} - N_{66}$	90.09(14)
$O_1 - Ni^{++} - N_6$	99.59(14)
$O_3 - Ni^{++} - N_{33}$	99.46(14)
$O_1 - Ni^{++} - N_{33}$	158.62(15)
$O_3 - Ni^{++} - N_6$	158.60(13)
$O_1 - Ni^{++} - N_{66}$	95.05(14)
$O_3 - Ni^{++} - N_3$	93.66(14)
$N_3 - Ni^{++} - N_6$	83.56(15)
$N_{33} - Ni^{++} - N_{66}$	83.67(14)
$N_3 - Ni^{++} - N_{33}$	90.61(14)
$N_6 - Ni^{++} - N_{66}$	94.79(15)
$O_1 - N_2 - O_3$	111.68(36)

Table 7

Intermolecular distances (A°) with values less than 3.5Å.

				Symmetry operation
$F_4 - N_6$	3.229(5)	$C_5 - F_3$	3.433(6)	(1-x, -y, 1-z)
$F_4 - N_{66}$	3.166(5)	$N_6 - F_3$	3.038(4)	
$C_1 - F_2$	3.240(9)			(1-x, -y, -z)
$C_{55} - F_1$	3.407(8)			(1-x, ½ + y, ½ -z)
$C_{22} - F_1$	3.430(7)			

Table 8

Least-squares planes of selected atoms

The equations of the planes can be expressed in terms of $\underline{P}x + \underline{Q}y + \underline{R}z = \underline{S}$ in direct space.

	P	Q	R	S	Atoms defining plane	Not defining plane
Plane 1	9.03	9.48	-5.39	1.79	Ni -0.040; O(1) -1.032 N(2) 0.007; O(3) 1.036 N(3) 0.052; N(66)-0.023	N(33) 1.569 N(6) -1.683
Plane 2	-6.07	11.35	7.69	1.40	Ni 0.021; O(1) 0.031 N(2) -0.015; O(3) -0.021 N(33) 0.009; N(6) -0.024	N(3) -2.112 N(66) 2.168
Plane 3	-5.89	11.65	7.49	1.44	Ni, O(1), O(3)	N(2) -0.014
Plane 4	8.71	2.93	3.37	3.08	Ni, N(3), N(6)	C(1) -0.548; C(2) -0.781. C(4) -0.478; C(5) 0.279. C(7) -1.280; C(8) -1.227.
Plane 5	2.23	10.19	-9.24	-0.65	Ni, N(33), N(66)	C(11) 1.301; C(22) 1.274. C(44)-0.237; C(55) 0.485. C(77) 0.783; C(88) 0.072.

Angles between planes

1 ^ 2	84.3°
2 ^ 3	1.5°

CHAPTER III

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant _h_ and _k_ and list values of _ℓ_, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

0,0,L

4	382	398
6	335	349
8	77	63
10	65	72

0,1,L

1	116	123
2	9	13
4	616	586
5	452	431
6	227	225
7	185	178
8	189	193
9	310	305
10	97	102
11	178	169

0,2,L

1	882	880
3	415	434
4	140	107
5	583	593
6	164	158
7	162	175
8	139	124
9	132	128
10	57	59
11	15*	5

0,3,L

1	77	80
3	71	78
4	40	35
5	205	181
6	323	328
7	87	78
8	328	336
9	15*	18
10	164	164
11	71	71

0,4,L

0	337	370
2	148	152
3	302	324
5	162	173
6	486	491
7	244	245
8	74	73
9	154	166
10	36	50
11	66	58

0,5,L

1	326	330
2	88	87
3	623	627
4	187	189
5	297	300
6	50	36
7	236	222
8	45	10
9	247	234
10	76	74
11	112	109

0,6,L

0	273	288
1	163	178
2	529	560
3	212	202
4	458	467
5	48	39
6	377	389
7	43	51
8	97	97
9	97	85
10	15*	16
11	14*	9

0,7,L

1	41	36
2	144	144
3	387	375
4	64	63
5	105	101
6	190	179
7	174	163
8	163	160
9	148	141
10	90	89

0,8,L

0	270	269
1	583	597
2	73	52
3	442	456
4	99	96
5	194	202
6	129	126
7	282	272
8	136	158
9	117	110
10	41	52

0,9,L

1	142	134
2	93	109
3	25	22
4	99	78
5	207	203
6	95	85
7	21	17
8	92	91
9	64	55
10	91	92

0,10,L

0	698	713
1	314	305
2	372	366
3	25	7
4	81	85
5	237	246
6	149	143
7	182	184
8	102	107
9	21	18

0,11,L

1	87	94
2	69	73
3	140	133
4	36	26
6	49	50
7	170	166
8	88	83
9	151	145

0,12,L

0	549	560
1	223	222
2	200	168
3	227	222
4	44	38
5	76	73
6	48	43
7	67	51
8	53	54

0,13,L

1	115	119
2	106	116
3	29	12
4	43	47
5	45	57
6	95	96
7	72	71

0,14,L

0	77	55
1	114	105
2	80	95
3	152	158
4	115	117
5	190	193
6	200	196

0,15,L

1	82	78
2	110	115
3	191	189
4	45	43
5	82	80

0,16,L

0	29	20
1	86	69
2	78	81
3	14*	4
4	159	160

0,17,L

1	26	24
2	49	54

1,0,L

−10	195	205
−8	553	554
−6	376	370
−4	85	75
0	299	284
2	110	109
4	66	72
6	446	464
8	365	375
10	194	192

1,1,L

−11	33	38
−10	15*	6
−9	192	214
−8	48	43
−7	27	45
−6	354	351
−5	315	265
−4	473	450
−3	507	493
−2	757	737
−1	1415	1505
1	842	864
2	37	16
3	232	255
4	473	486
5	110	123
6	357	369
7	156	143
8	48	43
9	52	49
10	75	73
11	95	88

1,2,L

−11	207	201
−10	116	126
−9	205	203
−8	181	178
−7	245	241
−6	69	37
−5	55	57
−4	440	445
−3	24	40
−2	716	702
−1	387	405
0	181	127
1	96	96
2	310	316
3	17	24
4	107	109
5	363	360
6	91	65
7	351	342
8	95	74
9	226	226
11	140	135
10	86	79

1,3,L

−10	84	68
−9	159	182
−8	318	319
−7	141	133
−6	819	846
−5	561	558
−4	663	674
−3	74	73
−2	975	975
−1	627	628
1	361	335
2	465	472
3	22	27
4	579	591
5	174	169
6	436	443
7	85	85
8	88	87
9	24	14
10	23	21
11	15*	20

1,4,L

−11	80	76
−10	95	98
−9	170	173
−8	148	152

```
       1,4,L

 -7     75       74
 -6     16       18
 -5    207      212
 -4    422      421
 -3    209      232
 -1    603      607
  0    116      101
  1    164      162
  2    289      296
  3    405      394
  4    144      152
  5    222      202
  6    342      342
  7    245      241
  8    252      254
  9    102       96
 10     56       49
 11     66       61

       1,5,L

-11     34       36
-10     42       36
 -9     19        5
 -8    248      240
 -7    278      290
 -6     39       26
 -5    802      831
 -4    148      130
 -3   1433     1468
 -2    340      333
 -1    533      530
  0    192      194
  1    494      508
  2    472      473
  3    579      597
  4     57       52
  5    216      219
  6    179      171
  7    302      295
  8     75       72
  9     43       33
 10     15*       8

       1,6,L

-11     85       82
-10    114      108
 -9     32       29
 -8    153      157
 -7     43       41
 -6    108      106
 -5     99       85
 -4    416      408
 -3    113       91
 -2    255      250
 -1     96       90
  0    451      443
```

```
  1     35       44
  2    158      167
  3     10*      15
  4    352      346
  5    255      274
  6    396      406
  7     40       46
  8    212      226
  9     70       63
 10     15*       3

       1,7,L

-11     27       32
-10     75       77
 -9    107      102
 -8    185      194
 -7    151      170
 -6    129      149
 -5     42       42
 -4    321      335
 -3    445      453
 -2    613      632
 -1     64       54
  0    461      481
  1    435      449
  2    311      322
  3    217      224
  4    274      277
  5    294      295
  6    230      229
  7    250      238
  8    135      145
  9     67       74
 10     32       32

       1,8,L

-10     15*       2
 -9    207      198
 -8     37       42
 -7    144      139
 -6     41       46
 -5    238      249
 -4    310      314
 -3     40       53
 -2    145      142
 -1    222      230
  0    147      136
  1    117      140
  2     53       51
  3    457      465
  4     25       16
  5    194      203
  6     14*       9
  7    182      188
  8     16        5
  9    169      159
```

```
       1,9,L

-10     75       69
 -9    238      233
 -8    284      284
 -7     64       54
 -6    119      133
 -5     76       60
 -4     26       19
 -3    297      308
 -2    331      318
 -1    312      310
  0    109      108
  1    261      264
  2    138      147
  3    334      342
  4    321      330
  5     14*      15
  6    168      168
  7     16       26
  8    108      110
  9     73       74

       1,10,L

 -9    115      120
 -8    198      198
 -7    221      222
 -6    205      202
 -5    135      147
 -4    181      187
 -3    155      153
 -2     91       67
 -1    239      228
  0     51       37
  1    111      125
  2    278      280
  3     64       63
  4     89       81
  5    170      181
  6     86       70
  7     53       46
  8    135      125
  9     31       29

       1,11,L

 -9    101      102
 -8     27       29
 -7    144      137
 -6     96       95
 -5     21       16
 -4    157      167
 -3    215      223
 -2     38       44
 -1    499      506
  0    157      164
  1    517      528
  2    123      113
  3    259      269
```

```
  4     59       68
  5    241      238
  6     41       30
  7     39       23
  8     15*       8

       1,12,L

 -8    126      128
 -7     33       40
 -6     46       42
 -5    109      101
 -4    111      108
 -3    106       87
 -2    110       92
 -1    107      118
  0    106      109
  1     46       43
  2    118      120
  3     41       32
  4     68       61
  5    103      111
  6    178      177
  7    118      117
  8     44       49

       1,13,L

 -8     78       73
 -7     24       18
 -6    210      201
 -5     32       27
 -4    178      163
 -3     41       38
 -2    238      231
 -1    177      177
  0    297      308
  1    181      196
  2    165      176
  3     14*       2
  4    113      120
  5     18       13
  6    195      192
  7     25       25
  6    195      192
  7     25       25

       1,14,L

 -7     83       84
 -6     96       94
 -5     49       56
 -4     15*       6
 -3    142      146
 -2     36       21
 -1     15*      15
  0     19        5
  1     63       64
  2     66       61
  3     19       17
```

```
  4     38       36
  5     76       78
  6     14*       1

       1,15,L

 -6    101      104
 -5    118      115
 -4     87       90
 -3     95       95
 -2     81       72
 -1     82       76
  0     15*      17
  1     79       68
  2     54       46
  3    161      157
  4     67       65
  5    191      185

       1,16,L

 -4     96      102
 -3     46       36
 -2     68       75
 -1     64       55
  0     68       64
  1     25       34
  2    103      101
  3     25       30
  4     58       54

       1,17,L

 -2     32       30
 -1    105      102
  0     82       79
  1     64       64

       2,0,L

-10    226      212
 -8    227      217
 -6     36       65
 -4    500      462
  0   1215     1261
  2    657      663
  4    557      584
  6    168      149
  8     15*       1
 10     63       69

       2,1,L

-11    118      125
-10     49       47
 -9    197      189
 -8    287      290
 -7     45       73
 -6    245      247
 -5    199      199
```

	2,1,L	
-4	322	288
-3	275	288
-2	207	203
-1	713	650
0	168	147
1	1125	1087
2	11	36
3	115	116
4	128	119
5	576	556
6	199	184
7	249	240
8	172	176
9	168	162
10	58	53
	2,2,L	
-11	33	38
-10	141	133
-9	183	200
-8	219	215
-7	407	422
-6	185	208
-5	443	440
-4	824	837
-2	43	15
-1	1036	1053
1	717	688
3	673	707
4	315	305
5	391	382
6	203	202
7	77	67
8	15*	16
9	108	99
10	15*	6
	2,3,L	
-11	33	23
-10	178	174
-9	17	12
-8	14*	18
-7	364	355
-6	207	212
-5	144	136
-4	451	446
-3	255	258
-2	676	647
-1	61	65
0	164	151
1	399	360
2	159	174
3	168	173
4	324	326
5	191	199
6	246	248
7	90	88
8	178	176
9	30	23
10	95	89
	2,4,L	
-11	15*	8
-10	24	6
-9	190	198
-8	54	50
-7	277	278
-6	620	621
-5	746	742
-4	473	435
-3	784	778
-2	983	986
-1	561	521
0	63	9
1	134	159
2	200	200
3	337	344
4	178	169
5	325	319
6	317	325
7	214	213
8	37	33
9	103	104
10	24	36
	2,5,L	
-11	211	205
-10	154	146
-9	101	100
-8	27	16
-7	119	128
-6	311	309
-5	322	338
-4	222	199
-3	437	410
-2	495	502
-1	332	353
0	196	194
1	379	376
2	20	28
3	355	345
4	301	317
5	654	671
6	140	161
7	240	247
8	38	34
9	133	130
10	46	53
	2,6,L	
-11	28	27
-10	126	112
-9	95	87
-8	83	73
-7	192	192
-6	122	132
-5	566	556
-4	890	862
-3	740	750
-2	1199	1200
-1	344	323
0	488	499
1	265	296
2	274	304
3	418	436
4	192	195
5	13*	0
6	247	244
7	84	95
8	59	60
9	60	53
10	39	44
	2,7,L	
-11	85	91
-10	153	151
-9	134	139
-8	51	51
-7	297	311
-6	94	95
-5	106	135
-4	63	87
-3	184	191
-2	85	92
-1	99	107
0	90	107
1	49	61
2	169	160
3	119	126
4	293	299
5	103	103
6	281	285
7	112	111
8	162	156
9	94	95
	2,8,L	
-11	50	45
-10	15*	3
-9	303	300
-8	54	46
-7	186	199
-6	140	129
-5	332	358
-4	44	42
-3	601	637
-2	411	396
-1	245	264
0	75	67
1	427	465
2	23	9
3	563	588
4	212	224
5	272	261
6	23	16
7	81	77
8	140	144
9	84	76
	2,9,L	
-10	163	165
-9	91	81
-8	70	74
-7	60	69
-6	176	168
-5	308	302
-4	135	129
-3	14	15
-2	90	81
-1	116	111
0	360	361
1	14	9
2	312	311
3	206	209
4	53	53
5	226	228
6	118	117
7	92	98
8	69	64
9	101	99
	2,10,L	
-10	90	86
-9	19	25
-8	219	222
-7	59	52
-6	108	88
-5	70	62
-4	240	239
-3	195	171
-2	178	188
-1	59	71
0	547	543
1	76	78
2	459	457
3	148	143
4	297	295
5	183	175
6	15*	15
7	17	17
8	53	48
	2,11,L	
-9	155	161
-8	90	98
-7	86	94
-6	128	129
-5	161	172
-4	14*	8
-3	52	26
-2	30	26
-1	119	110
0	132	144
1	253	263
2	49	57
3	14	6
4	35	30
5	58	67
6	54	65
7	79	84
8	76	69
	2,12,L	
-9	93	95
-8	53	62
-7	64	59
-6	35	36
-5	20	21
-4	51	34
-3	266	269
-2	185	172
-1	267	266
0	386	389
1	247	253
2	234	234
3	210	213
4	169	159
5	129	130
6	50	48
7	15	3
	2,13,L	
-8	157	162
-7	36	24
-6	124	123
-5	32	40
-4	26	33
-3	94	103
-2	126	134
-1	47	54
0	103	100
1	73	62
2	55	45
3	78	78
4	65	55
5	64	66
6	149	145
	2,14,L	
-7	88	88
-6	58	54
-5	96	100
-4	42	35
-3	136	138

```
       2,14,L

  -2     79      73
  -1    208     214
   0     36      23
   1     70      82
   2     38      36
   3     47      45
   4     54      51
   5    102      91

       2,15,L

  -6     40      39
  -5     20      21
  -4     57      51
  -3     37      38
  -2     14*     13
  -1     33      36
   0     26      12
   1     26      28
   2     65      57
   3     62      63
   4     86      77

       2,16,L

  -4    213     204
  -3     42      37
  -2    179     169
  -1     36      30
   0     65      65
   1     85      82
   2     73      72
   3     37      30

       2,17,L

  -1     14*      6
   0     54      46

        3,0,L

 -10     77      72
  -8    498     501
  -6    313     304
  -4     46      32
  -2     14      27
   2    351     315
   4    376     362
   6    428     445
   8    188     186
  10     98      89

        3,1,L

 -11     56      56
 -10    194     190
  -9    277     308
  -8    331     326
```

```
  -7    459     457
  -6    464     453
  -5     84     101
  -4    244     242
  -3   1054    1048
  -2    373     343
  -1    756     719
   0     20       1
   1    922     933
   2    161     136
   3    566     566
   4     73      75
   5     70      58
   6     88      96
   7     37      48
   8     21      24
   9     75      79
  10     15*      3

        3,2,L

 -11     17      27
 -10    124     117
  -9    200     209
  -8    144     106
  -7    129     142
  -6    367     358
  -5    354     356
  -4    406     382
  -3    274     293
  -2     68      64
  -1    869     816
   0    472     455
   1     99      54
   2    172     143
   3    385     383
   4    357     352
   5    322     336
   6    222     223
   7    144     139
   8     49      40
   9     84      78
  10     69      61

        3,3,L

 -11     97      95
 -10    133     137
  -9     34      24
  -8    313     319
  -7    108     114
  -6    784     796
  -5     84      99
  -4    750     762
  -3    891     903
  -2    231     167
  -1    214     198
   0    159     183
   1    202     168
   2    580     567
```

```
   3    514     535
   4    286     293
   5    139     151
   6    286     289
   7     16      16
   8     67      65
   9     18      35
  10     18      10

        3,4,L

 -11    151     156
 -10     58      52
  -9     83      92
  -8    149     140
  -7     14       1
  -6    157     166
  -5    515     518
  -4     53      52
  -3    260     256
  -2     89      67
  -1    478     429
   0    555     529
   1     35      45
   2    690     687
   3    508     505
   4    227     223
   5    282     287
   6    127     118
   7     60      60
   8    198     185
   9    119     119

        3,5,L

 -11     56      61
 -10    115     111
  -9     27      33
  -8     15      15
  -7     54      48
  -6    227     202
  -5    562     585
  -4    338     334
  -3   1435    1493
  -2    107     101
  -1    270     285
   0    254     240
   1    282     297
   2    196     182
   3    576     600
   4    119     130
   5    167     177
   6     15*     14
   7    180     178
   8     27      28
   9     78      61

        3,6,L

 -11    118     109
```

```
 -10    188     196
  -9     26      27
  -8    214     206
  -7     15      25
  -6    301     294
  -5    431     427
  -4     13      41
  -3    410     402
  -2     71      59
  -1     19      16
   0    350     350
   1    234     247
   2    300     302
   3    315     317
   4    340     361
   5    341     343
   6    260     264
   7     92      93
   8    245     246
   9     23      17

        3,7,L

 -11     37      29
 -10    108      96
  -9     31      39
  -8    125     127
  -7    209     221
  -6    331     313
  -5    271     268
  -4    324     301
  -3    923     930
  -2     14       6
  -1    333     348
   0    238     251
   1    302     305
   2     58      66
   3    261     273
   4     63      61
   5     40      32
   6    199     195
   7     39      33
   8     88      92
   9     15*      2

        3,8,L

 -11    162     164
 -10     16*     25
  -9    163     158
  -8     15      12
  -7    161     161
  -6    132     122
  -5    423     445
  -4     78      90
  -3    109     105
  -2     55      51
  -1     57      43
   0     67      68
   1    144     153
```

```
   2     81      87
   3    193     190
   4    223     224
   5    213     215
   6     40      37
   7     36      42
   8     32      33

        3,9,L

 -10    111     111
  -9    269     261
  -8    228     233
  -7    186     194
  -6    242     257
  -5    166     193
  -4    357     371
  -3    126     147
  -2    128     147
  -1    155     165
   0    476     480
   1    384     379
   2    444     436
   3    259     264
   4    331     332
   5    101      96
   6     60      59
   7     50      43
   8     15*      4

       3,10,L

 -10     58      60
  -9     48      52
  -8     71      70
  -7     23      22
  -6    216     199
  -5     42      47
  -4     14*     21
  -3    115     107
  -2     70      69
  -1    152     148
   0    108     101
   1    150     141
   2    197     203
   3     28      36
   4     57      56
   5     78      86
   6     98      93
   7     15      10

       3,11,L

  -9    167     174
  -8     64      65
  -7    169     156
  -6     14*     15
  -5    192     177
  -4    159     145
```

3,11,L

-3	290	303
-2	206	199
-1	411	422
0	141	145
1	452	456
2	183	203
3	282	284
4	53	57
5	28	22
6	31	41
7	74	81

3,12,L

-9	77	79
-8	81	88
-7	61	82
-6	61	56
-5	97	89
-4	32	49
-3	121	118
-2	72	78
-1	84	76
0	29	22
1	82	86
2	38	35
3	38	43
4	148	153
5	15*	0
6	202	208

3,13,L

-8	14*	13
-7	15*	12
-6	61	58
-5	46	53
-4	171	170
-3	35	30
-2	315	310
-1	102	94
0	234	225
1	89	87
2	118	109
3	52	61
4	92	77
5	66	79
6	14*	6

3,14,L

-7	41	43
-6	18	23
-5	43	33
-4	15*	11
-3	65	63
-2	18	7
-1	95	87
0	108	116
1	46	36
2	40	37
3	76	70
4	22	29
5	104	108

3,15,L

-6	89	91
-5	164	168
-4	123	125
-3	104	106
-2	79	83
-1	109	109
0	15*	10
1	15*	12
2	95	97
3	34	33

3,16,L

-4	87	83
-3	21	17
-2	15*	4
-1	32	36
0	75	76
1	14*	4
2	55	59

4,0,L

-10	230	237
-8	496	491
-6	593	602
-4	402	429
-2	629	609
0	953	930
2	634	602
4	345	342
6	59	38
8	49	51

4,1,L

-11	58	66
-10	128	124
-9	204	215
-8	468	470
-7	151	149
-6	136	121
-5	132	121
-4	51	49
-3	225	199
-2	166	137
-1	140	128
0	696	660
1	287	280
2	499	499
3	486	511
4	180	182
5	266	290
6	169	154
7	109	115
8	67	61
9	115	111

4,2,L

-11	201	213
-10	66	52
-9	340	342
-8	111	72
-7	447	456
-6	165	145
-5	354	348
-4	207	207
-3	363	396
-2	311	268
0	535	474
1	591	599
2	247	208
3	535	549
4	182	178
5	185	194
6	43	49
7	95	93
8	16*	8
9	30	26

4,3,L

-11	16*	23
-10	104	91
-9	173	170
-8	287	286
-7	176	175
-6	228	211
-5	363	365
-4	176	178
-3	567	545
-2	276	256
-1	843	804
0	579	544
1	348	295
2	599	592
3	81	97
4	305	305
5	57	49
6	184	170
7	61	58
8	187	189
9	43	46

4,4,L

-11	83	90
-10	43	48
-9	93	88
-8	131	141
-7	164	153
-6	649	665
-5	596	600
-4	354	371
-3	334	341
-2	382	357
-1	310	309
0	525	544
1	373	389
2	450	477
3	63	69
4	60	60
5	71	75
6	205	217
7	113	112
8	41	34
9	16	16

4,5,L

-11	182	181
-10	53	56
-9	52	46
-8	40	56
-7	252	258
-6	89	107
-5	424	446
-4	54	57
-3	73	102
-2	178	156
-1	77	64
0	312	289
1	203	202
2	379	383
3	358	362
4	14*	16
5	226	201
6	19	17
7	139	140
8	46	52

4,6,L

-11	22	20
-10	115	106
-9	87	83
-8	102	95
-7	122	131
-6	510	532
-4	480	488
-3	379	379
-2	695	669
-1	140	143
0	584	572
1	12*	3
2	192	206
3	117	117
4	39	28
5	162	156
6	128	123
7	15*	8
8	74	62

4,7,L

-11	99	96
-10	54	63
-9	58	75
-8	73	67
-7	242	228
-6	97	80
-5	36	41
-4	437	438
-3	12*	1
-2	16	5
-1	180	160
0	315	301
1	118	126
2	381	383
3	197	209
4	260	255
5	98	95
6	93	84
7	78	71
8	131	123

4,8,L

-11	89	81
-10	42	41
-9	201	183
-8	129	131
-7	113	107
-6	101	113
-5	484	466
-4	74	78
-3	399	415
-2	168	161
-1	268	269
0	117	112
1	297	285
2	50	41
3	246	232
4	66	64
5	31	23
6	22	9
7	62	60
8	38	39

4,9,L

-10	76	76
-9	114	115
-8	86	86
-7	51	51
-6	24	21
-5	91	98
-4	218	207
-3	134	122

```
      4,9,L                -4    166     164           5,0,L                    5,3,L                 1    126     118
                           -3    139     109                                                          2    162     160
  -2     62      52        -2    287     295      -10    424     429      -11     17      26          3     21      23
  -1     76      80        -1    155     143       -8    456     455      -10    112     110          4     55      43
   0    241     243         0    235     233       -6    163     151       -9     39      23          5     90      74
   1     17       5         1    169     157       -4     96      80       -8    433     435          6     81      79
   2    174     180         2     92      78       -2    126     118       -7     33      32          7     26      26
   3     85      78         3    127     123        0    314     280       -6    499     535          8     19      22
   4    146     157         4     79      70        2    433     433       -5    331     316
   5     36      33         5     25      11        4     49      38       -4    441     450             5,6,L
   6    113     118                                 6    329     322       -3     96      92
   7     14*     12            4,13,L               8    145     143       -2    165     159        -11    104     101
                                                                           -1     65      22        -10     34      39
      4,10,L               -8     81      81           5,1,L                0    686     668         -9    128     140
                           -7     20      13                                1    170     202         -8     99     108
 -10    101      99        -6     58      57      -11     71      61        2    282     273         -7     96      74
  -8    124     124        -5     19      27      -10    102     109        3    117     111         -6     46      56
  -9     67      63        -4     15*     13       -9    247     248        4    165     162         -5     86      76
  -7    124     111        -3     37      46       -8    278     276        5    209     212         -4    333     317
  -6    209     195        -2     15*      4       -7    322     315        6    193     170         -3    121     119
  -5    216     214        -1    120     121       -6    250     255        7     58      65         -2     54      48
  -4    225     227         0     83      90       -5    285     282        8     27      15         -1     58      40
  -3    114     119         1     23      17       -4    262     252                                  0    160     133
  -2     47      30         2     15*     19       -3    152     175           5,4,L                  1     66      67
  -1    140     126         3     82      88       -2    203     191                                  2    372     371
   0    399     388         4    111     112       -1    526     512      -11     42      34          3     84      87
   1     41      38         5     39      46        0    662     637      -10     63      67          4    228     238
   2    361     356                                 1    844     858       -9     46      53          5     39      41
   3     50      43            4,14,L               2    308     294       -8    207     197          6     97     100
   4    167     158                                 3    245     248       -7     99      89          7     67      66
   5     16      11        -7    177     165        4    239     230       -6    193     179
   6     14*      2        -6     77      73        5     29      20       -5    136     113             5,7,L
   7     14*     17        -5    236     228        6    160     140       -4    125     129
                           -4     90      90        7    131     143       -3    286     254        -11     72      73
      4,11,L               -3    193     183        8     15*      6       -2     94      83        -10    168     159
                           -2    110     110                               -1    187     191         -9     66      55
  -9    135     133        -1    243     229           5,2,L                0    240     224         -8    170     175
  -8     26      31         0     42      33                                1    204     230         -7     56      57
  -7    137     131         1    147     135      -11     86      86        2    442     456         -6    401     401
  -6    101      88         2     45      42      -10    138     118        3    329     333         -5    303     284
  -5     28      25         3     57      47       -9    337     332        4    161     174         -4    590     583
  -4     51      46         4     14*      7       -8     92      35        5     88      77         -3    313     283
  -3     14*      2                                -7     47      45        6    101     101         -2    392     402
  -2    117     126            4,15,L              -6     57      30        7    124     121         -1    414     413
  -1     26      13                                -5    162     168        8    109     103          0    528     532
   0    166     167        -5     33      28       -4    202     184                                  1    117     115
   1    183     186        -3     14*      1       -3     93      75           5,5,L                  2    171     177
   2    141     139        -2     96      88       -2     72      76                                  3     29      31
   3    171     180        -1     38      31       -1    534     526      -11     79      80          4     15*     16
   4     46      42         0     92      86        0     83      52      -10     93      85          5     35      38
   5    194     200         1     14*      1        1    571     575       -9    110      93          6     69      59
   6     14*     11         2     14*     17        2    148     113       -8    139     130          7     95      98
                                                    3    156     150       -7    151     141
      4,12,L                   4,16,L               4     58      65       -6    163     175             5,8,L
                                                    5    197     192       -5    271     272
  -9     79      77        -3    114      99        6    165     151       -4     88      93        -11     93      97
  -8    104     100        -2    195     191        7     84      78       -3    775     754        -10     31      25
  -7    129     117        -1     98      92        8    152     151       -2     99      72         -9    147     138
  -6    142     132         0    119     116                               -1    737     725         -8     17      15
  -5    190     171                                                         0    161     191         -7     62      55
```

5,8,L

-6	14*	0
-5	43	47
-4	225	222
-3	29	22
-2	36	43
-1	81	81
0	162	162
1	307	306
2	51	35
3	262	255
4	84	99
5	178	175
6	15*	3
7	159	151

5,9,L

-10	93	84
-9	169	159
-8	243	234
-7	180	168
-6	352	353
-5	142	127
-4	212	211
-3	24	17
-2	51	33
-1	28	36
0	81	77
1	182	187
2	144	153
3	112	109
4	46	54
5	15*	21
6	81	82

5,10,L

-10	41	37
-9	106	104
-8	57	53
-7	27	24
-6	49	43
-5	14*	17
-4	16	3
-3	167	159
-2	107	104
-1	61	45
0	308	301
1	121	129
2	268	256
3	51	58
4	119	116
5	82	85
6	141	131

5,11,L

-9	95	94
-8	54	45
-7	278	273
-6	74	72
-5	245	231
-4	102	100
-3	145	133
-2	35	28
0	125	127
-1	254	243
1	300	296
2	56	54
3	152	151
4	15*	12
5	31	24

5,12,L

-8	45	47
-7	57	53
-6	35	28
-5	73	70
-4	20	24
-3	21	13
-2	20	23
-1	188	188
0	23	19
1	55	58
2	15*	10
4	66	69

5,13,L

-7	48	55
-6	191	192
-2	321	325
-1	152	149
0	174	174
1	139	142
2	41	40
3	14*	11
4	63	61

5,14,L

-6	47	39
-5	14*	5
-4	15*	3
-3	15	2
-2	76	76
-1	18	2
0	31	30
1	31	45
2	16	23

5,15,L

-5	139	138
-4	29	33
-3	262	245
-2	29	26
-1	145	126
0	15*	6
1	14*	19

6,0,L

-10	49	27
-8	318	332
-6	477	469
-4	236	229
-2	644	607
0	1036	995
2	215	186
4	208	191
6	36	17

6,1,L

-11	113	104
-10	88	92
-9	201	200
-8	80	62
-7	144	130
-6	15	12
-5	39	45
-4	41	32
-3	232	197
-2	190	172
-1	519	506
0	64	58
1	56	55
2	14*	4
3	53	52
4	44	45
5	332	323
6	32	40
7	126	128

6,2,L

-11	86	89
-10	17	4
-9	372	367
-8	164	150
-7	451	437
-6	152	112
-5	175	170
-4	139	131
-3	500	528
-2	136	53
-1	423	451
0	501	442
1	41	35
2	145	125
3	244	235
4	46	26
5	83	77
6	27	36
7	59	56

6,3,L

-11	64	58
-10	129	131
-9	23	34
-8	288	294
-7	138	131
-6	100	113
-5	53	46
-4	163	165
-3	382	350
-2	31	17
-1	32	61
0	458	449
1	55	52
2	318	321
4	43	40
5	41	40
6	145	141
7	45	44

6,4,L

-11	164	161
-10	105	88
-9	225	227
-8	29	17
-7	284	274
-6	281	288
-5	109	111
-4	343	349
-3	375	370
-2	403	415
-1	192	190
0	247	252
1	108	127
2	40	58
3	179	174
4	76	63
5	64	55
6	23	20
7	20	10

6,5,L

-11	178	174
-10	32	36
-9	94	81
-8	115	111
-7	97	104
-6	34	39
-5	286	287
-4	63	65
-3	71	72
-2	42	60
-1	278	294
0	180	189
1	391	395
2	266	263
3	276	280
4	26	25
5	242	231
6	15*	3
7	207	200

6,6,L

-11	22	17
-10	152	134
-9	58	37
-8	18	21
-7	81	98
-6	469	459
-5	79	62
-4	650	642
-3	201	178
-2	699	693
-1	295	268
0	297	289
1	76	54
2	55	47
3	15*	8
4	17	3
5	40	44
6	131	128

6,7,L

-11	18	29
-10	109	110
-9	45	46
-8	112	116
-7	56	63
-6	94	84
-5	37	27
-4	428	404
-3	409	399
-2	121	110
-1	18	26
0	148	142
1	120	119
2	223	220
3	243	252
4	91	93
5	117	115
6	137	140

6,8,L

-11	116	113
-10	32	35
-9	214	218
-8	15*	14
-7	333	333
-6	138	133
-7	333	333
-6	138	133
-5	217	218
-4	83	68

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        6,8,L

 -3      275      261
 -2       91       95
 -1      289      281
  0      231      225
  1      207      209
  2      128      124
  3      107       95
  4       65       51
  5       87       88
  6       31       41

        6,9,L

-10       48       46
 -9       78       69
 -8       92       95
 -7       74       71
 -6       94      106
 -5       14*       2
 -4      108      115
 -3      289      292
 -2      183      185
 -1      167      162
  0      226      218
  1      142      142
  2      123      117
  3       68       72
  4       91       87
  5       79       82

       6,10,L

 -9       79       86
 -8      335      336
 -7      182      188
 -6      345      341
 -5       87       75
 -4       95       88
 -3       27       22
 -2      118      114
 -1       48       45
  0      285      285
  1       35       35
  2      142      142
  3       50       59
  4       65       62
  5       57       56

       6,11,L

 -9       85       80
 -8       38       37
 -7       58       58
 -6       51       52
 -5      156      154
 -4       78       84
 -3       55       35
 -2      106      101
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```
 -1      113      120
  0       15*       5
  1       55       65
  2       70       64
  3      124      127
  4       16       27

       6,12,L

 -8      123      126
 -7      161      154
 -6       73       67
 -5      198      196
 -4      108       85
 -3      184      182
 -2      211      186
 -1       63       64
  0      104       99
  1       27       24
  2       54       56
  3       54       42

       6,13,L

 -7       23       24
 -6       86       77
 -5       46       41
 -4       29       34
 -3       18       13
 -2       22       25
 -1       32       21
  0      125      118
  1       15       18
  2      137      129

       6,14,L

 -6       58       54
 -5       90       89
 -4       66       66
 -3      159      155
 -2       84       85
 -1       50       49
  0       17       20
  1       14*       5

       6,15,L

 -2       14*       9

        7,0,L

-10       69       71
 -8       16*      18
 -6       23       21
 -4      157      183
 -2      186      205
  0      276      271
  2      260      254
  4      251      249
```

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  6      128      132

        7,1,L

-11       25       25
-10       70       56
 -9      391      393
 -8      159      144
 -7      290      282
 -6      180      172
 -5      293      274
 -4      124      128
 -3      447      468
 -2      198      188
 -1      183      199
  0       68       75
  1      166      145
  2       57       43
  3      322      305
  4       99       97
  5       51       46
  6       16*       9

        7,2,L

-11      166      165
-10       63       52
 -9       17       15
 -8      188      183
 -7      198      193
 -6      149      128
 -5       17       27
 -4       40       15
 -3      182      172
 -2       36       15
 -1      492      490
  0      117       86
  1      196      205
  2       89       84
  3      235      231
  4       70       55
  5      277      274
  6       86       75

        7,3,L

-11       27       18
-10      203      189
 -9       17       18
 -8      275      263
 -7       24       22
 -6      443      435
 -5       35       21
 -4      345      337
 -3      219      216
 -2      332      316
 -1      228      218
  0      219      211
  1      194      212
  2       40       30
```

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  3       29       46
  4       22       24
  5       51       52
  6       29       28

        7,4,L

-11      146      150
-10       33       36
 -9       74       77
 -8       83       77
 -7       42       37
 -6       76       52
 -5       25        2
 -4       40       23
 -3      147      152
 -2       16       10
 -1      175      157
  0      115      105
  1      142      129
  2       53       48
  3       65       56
  4      154      166
  5      121      107
  6      117      119

        7,5,L

-11      131      134
-10       15*      13
 -9      132      131
 -8       19        6
 -7       69       71
 -6       95       99
 -5      437      441
 -4      121      111
 -3      670      666
 -2       81       85
 -1      528      534
  0      105      117
  1      193      186
  2       21       16
  3       63       37
  4       49       54
  5       47       50
  6       71       63

        7,6,L

-11       54       43
-10      127      120
 -9       95       80
 -8       53       47
 -7       14*      18
 -6       51       52
 -5      135      157
 -4       45       37
 -3       42       50
 -2       14*      19
 -1       83       96
```

```
  0      217      214
  1       34       41
  2      163      161
  3       16*       5
  4      150      161
  5       94       90

        7,7,L

-11       62       68
-10      135      128
 -9       72       80
 -8       99       93
 -7       18*      10
 -6      212      208
 -5      140      145
 -4      349      345
 -3      199      201
 -2      262      263
 -1      141      153
  0      221      225
  1      115      116
  2       81       80
  3       15*       7
  4       51       43
  5       53       47

        7,8,L

-10       14*       9
 -9       84       85
 -8       36       37
 -7       54       51
 -6      103      101
 -5       34       25
 -4      217      198
 -3      202      218
 -2       39       45
 -1      167      176
  0       86       94
  1      175      181
  2       15*       9
  3      159      160
  4       57       59
  5      111      109

        7,9,L

-10      151      146
 -9      112      106
 -8      357      354
 -7      185      189
 -6      158      157
 -5      174      175
 -4      100       81
 -3      136      129
 -2      135      130
 -1       90       83
  0       70       53
```

7,9,L

1	134	130
2	40	38
3	120	117
4	128	122

7,10,L

-9	36	38
-8	66	71
-7	31	34
-6	149	146
-5	63	63
-4	50	57
-3	159	151
0	131	132
-1	63	68
-2	108	108
1	65	57
2	178	181
3	77	69

7,11,L

-8	15*	14
-7	176	176
-6	128	116
-5	113	104
-4	36	30
-3	115	110
-2	15*	14
-1	15*	5
0	102	96
1	100	109
2	28	22
3	128	132

7,12,L

-7	24	13
-6	43	51
-5	77	75
-4	24	12
-3	15*	1
-2	94	97
-1	123	127
0	148	153
1	77	80
2	102	91

7,13,L

-6	86	77
-5	56	45
-4	138	124
-3	24	19
-2	118	108
-1	16	8
0	51	38

7,14,L

-3	51	53
-2	50	44

8,0,L

-10	82	67
-8	294	299
-6	390	393
-4	478	496
-2	61	58
0	118	142
2	220	203
4	32	41

8,1,L

-11	16*	8
-10	16*	14
-9	16*	7
-8	47	56
-7	77	66
-6	65	69
-5	68	88
-4	106	110
-3	52	30
-2	211	235
-1	265	253
0	143	151
1	126	142
2	253	247
3	180	182
4	223	214
5	172	170

8,2,L

-11	134	135
-10	16*	2
-9	288	298
-8	146	153
-7	383	387
-6	228	226
-5	303	306
-4	177	165
-3	458	466
-2	94	97
-1	110	116
0	172	169
1	36	20
2	177	167
3	191	177
4	17	18
5	16*	14

8,3,L

-11	35	32
-10	16	4
-9	75	86
-8	29	24
-7	77	87
-6	49	37
-5	91	111
-4	76	85
-3	26	11
-2	301	331
-1	33	54
0	163	171
1	43	36
2	154	152
3	183	180
4	169	161
5	71	79

8,4,L

-11	193	190
-10	191	187
-9	137	131
-8	109	94
-7	213	208
-6	237	213
-5	228	226
-4	319	315
-3	113	101
-2	425	438
-1	149	153
0	101	100
1	139	145
2	27	10
3	45	36
4	119	111
5	22	21

8,5,L

-11	106	115
-10	88	86
-9	35	37
-8	82	74
-7	15*	6
-6	74	57
-5	114	127
-4	15*	3
-3	42	44
-2	66	84
-1	92	88
0	54	53
1	32	11
2	57	52
3	142	148
4	15*	3

8,6,L

-10	100	103
-9	46	47
-8	75	80
-7	109	117
-6	64	44
-5	158	170
-4	280	273
-3	208	211
-2	343	363
-1	78	87
0	200	198
1	57	47
2	19	4
3	42	38
4	51	49

8,7,L

-10	67	70
-9	15*	0
-8	68	70
-7	31	37
-6	15*	14
-5	141	143
-4	98	93
-3	153	155
-2	65	59
-1	15*	14
0	132	129
1	63	61
2	139	144
3	116	122
4	90	91

8,8,L

-10	14*	13
-9	146	146
-8	16*	16
-7	175	182
-6	173	177
-5	203	216
-4	79	85
-3	109	109
-2	244	276
-1	24	16
0	31	33
1	102	90
2	15*	7
3	95	84

8,9,L

-9	37	33
-8	31	29
-7	38	42
-6	73	66
-5	109	112
-4	38	38
-3	17	10
-2	196	208
-1	131	130
0	172	176
1	98	115
2	144	138
3	37	36

8,10,L

-8	199	200
-7	102	95
-6	201	196
-5	98	97
-4	101	93
-3	40	25
-2	19	34
-1	63	58
0	129	117
1	64	68
2	116	113

8,11,L

-7	14*	6
-6	26	25
-5	30	25
-4	84	89
-3	165	163
-2	56	52
-1	160	154
0	26	26
1	123	121

8,12,L

-6	72	73
-5	72	65
-4	158	156
-3	170	168
-2	75	77
-1	110	113
0	64	66

9,0,L

-10	66	84
-8	22	16
-6	163	160
-4	45	37
-2	15*	19
0	25	25
2	344	354
4	214	219

9,1,L

-11	15*	1
-10	165	165
-9	215	205
-8	182	178
-7	395	398

```
        9,1,L

  -6    265    261
  -5    317    310
  -4    299    309
  -3    238    233
  -2     22     18
  -1     26     22
   0     58     66
   1     56     48
   2     47     51
   3     63     67
   4     32     28

        9,2,L

 -11     43     48
 -10     82     85
  -9     68     75
  -8     38     40
  -7     15*     1
  -6     61     41
  -5     46     42
  -4    144    157
  -3     41     32
  -2    179    201
  -1    137    148
   0     64     77
   1     96    105
   2     97     80
   3    162    169
   4     68     53

        9,3,L

 -11     88     93
 -10    203    212
  -9    128    138
  -8    142    144
  -7     19      8
  -6    273    271
  -5     40     45
  -4    164    164
  -3    202    206
  -2     86     79
  -1     26     16
   0    245    239
   1     24      3
   2    126    132
   3     19     18
   4     24     19

        9,4,L

 -10     15*     4
  -9     63     74
  -8     39     30
  -7     15*    14
  -6     26     21
  -5    198    203
  -4    151    148
  -3    282    277
  -2    133    140
  -1    254    259
   0    128    138
   1    124    137
   2    178    181
   3     53     49

        9,5,L

 -10     37     41
  -9     91     93
  -8    109     98
  -7     58     59
  -6     62     12
  -5     86     81
  -4     52     46
  -3    187    176
  -2     51     16
  -1    222    238
   0     53     54
   1    124    127
   2     18     18
   3     28     26

        9,6,L

 -10     33     36
  -9     15*     4
  -8     15*     3
  -7     39     40
  -6     73     76
  -5     61     46
  -4    238    243
  -3     62     69
  -2     21     18
  -1    108    121
   0    132    146
   1     25     40
   2    168    171
   3     70     74

        9,7,L

  -9     47     46
  -8     91     87
  -7     16     11
  -6    226    219
  -5    172    175
  -4     58     59
  -3    167    170
  -2     20      2
  -1    154    155
   0    113    102
   1     21     17
   2     15*     2

        9,8,L

  -9     15     13
  -8     36     44
  -7     24      7
  -6     15*     9
  -5     62     72
  -4     15*    14
  -3    153    144
  -2    114    126
  -1    117    121
   0     44     50
   1    102.   110
   2     33     34

        9,9,L

  -8    137    130
  -7    126    129
  -6    195    196
  -5     67     65
  -4    143    157
  -3     15*     0
  -2     52     64
  -1     14*    10
   0    101     99
   1     14*    10

        9,10,L

  -7     20      8
  -6     19      3
  -5     20     21
  -4    117    119
  -3    102    104
  -2     46     58
  -1     53     51
   0     75     79

        9,11,L

  -5    206    193
  -4     25     20
  -3    160    155
  -2     45     33

        10,0,L

 -10     22     18
  -8    149    160
  -6    266    283
  -4    316    343
  -2     67     59
   0     95     83
   2     59     68

        10,1,L

 -10     40     38
  -9     40     46
  -8     23     10
  -7     78     78
  -6     20     20
  -5     21      9
  -4     15*     1
  -3    123    121
  -2     15*    25
  -1     61     69
   0     70     73
   1    119    142
   2    120    125

        10,2,L

 -10     41     38
  -9    205    203
  -8     89     98
  -7    154    151
  -6    110    120
  -5    140    131
  -4     66     54
  -3     98     92
  -2     59     65
  -1     25     27
   0     42     38
   1     69     79
   2     23     17

        10,3,L

 -10     15*     7
  -9     18     16
  -8     87     84
  -7     19      9
  -6     54     55
  -5     39     37
  -4    172    194
  -3     15*     0
  -2    175    206
  -1     56     63
   0    199    209
   1     16*    17
   2    172    176

        10,4,L

  -9    160    156
  -8    100    101
  -7    190    190
  -6     38     28
  -5     92     86
  -4     27     19
  -3     36     36
  -2     82     90
  -1     81     90
   0    185    194
   1     25     37
   2     56     62

        10,5,L

  -9     15*    18
  -8     15*     0
  -7     16      3
  -6     86     91
  -5     70     79
  -4     24     23
  -3    147    156
  -2     34     40
  -1    156    174
   0     71     72
   1    107    123

        10,6,L

  -9     65     63
  -8    140    136
  -7     48     53
  -6    210    209
  -5     46     42
  -4     45     44
  -3     28     31
  -2    197    215
  -1     26     33
   0    164    179
   1     14*     7

        10,7,L

  -8     32     32
  -7     30     40
  -6     68     78
  -5     71     73
  -4    128    143
  -3     18     16
  -2     54     68
  -1     26     24
   0     76     93

        10,8,L

  -7    172    172
  -6     44     46
  -5    187    192
  -4     39     43
  -3    161    160

        11,1,L

  -4     86     99
  -3    104    111
  -2     21     19
  -1     36     50
   0     67     67

        11,2,L

  -8     51     52
  -7     86     89
  -6     28      1
  -5    119    138
```

```
      11,2,L              -1     47     51      -6     75     79           11,7,L                11,0,L
                           0     65     67      -5     26     23
 -4     18     18                               -4     15*    10      -5     79     91      -8    163    170
 -3    169    192             11,4,L            -3    103    103      -4     99     99      -6    152    158
 -2     35     42                               -2     65     58                            -4     82     86
 -1    173    183         -8     16      4      -1    130    142           10,8,L           -2     93    125
  0     55     57         -7     87     85                                                   0    105    116
                          -6     15*     2           11,6,L           -2     70     71
      11,3,L              -5     46     56                            -1     80     84           11,1,L
                          -4    116    124      -6     86     93
 -8    187    198         -3     55     59      -5     19     30           10,9,L           -9     42     21
 -7     63     61         -2     48     62      -4     36     31                            -8     29     31
 -6     70     71         -1    111    115      -3     49     58      -6    126    123      -7    120    118
 -5     34     27                               -2     14*     1      -5     55     64      -6     73     78
 -4     15*    18             11,5,L                                  -4    129    125      -5    184    185
 -3     15*     1                                                     -3     29     25
 -2     71     83         -7    121    121                            -2     38     33
```

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CHAPTER IV

The crystal and molecular structure of Cobalt (thiopyrimidine)$_2$dichloride.

> "*A long time ago a noted specialist said that his secret of success as a physician was keeping the patient's head cool and his feet warm. And it is just now becoming generally known that 'a hot head' and 'cool feet' are enough to bring disaster to even a well man.*"
>
> ... *O. Byron Cooper.*

COBALT THIOPYRIMIDINE DICHLORIDE

There has recently been considerable interest in the roles played by ambidentate ligands because such molecules may co-ordinate to the metal through either or both possible co-ordinating atoms; those containing nitrogen and sulphur have been of especial interest.[1,2,3]

The complexing behaviour of an ambidentate ligand with a particular metal can often be predicted using either Ahrland, Chatt and Davies idea of class (a) or class (b) behaviour,[4] or Pearson's extension of this idea to hard and soft acids and bases.[5] These theories recognise the large difference between the co-ordination affinities of the first and second elements from Groups Vb, VIb and VIIb of the Periodic Table, i.e. N and P, O and S, F and Cℓ. The class (a) acceptors form their stablest compounds with the first ligand atom of each group, whereas the class (b) acceptors favour the second (or subsequent) ligand atom. Most metals in their common oxidation states show class (a) behaviour while class (b) behaviour is shown by the heavier metals of group VIII.

In Pearson's notation, class (a) metals are 'hard' and class (b) metals 'soft'. Since ligand atoms of the first row such as N, O and F are also classified as 'hard' whereas P, S, and Cℓ are 'soft' the general rule suggested is that 'hard' acids bind strongly to 'hard' bases while 'soft' acids bind strongly to 'soft' bases.

However, it has often been difficult to characterise unambiguously by physical methods the identity of the ligating atoms and to ascertain whether their co-ordination behaviour is determined by their steric or electronic properties e.g. the presence or absence of π-acceptor ligands. Electronic influences are important in such simple ligands as SCN^-, CN^- and NO_2^- and as the identity of the ligating atom can be readily inferred from simple infra-red criteria, these ligands have been extensively studied.

Even with simple ligands such as thiocyanate, where electronic effects are expected to be dominant, steric effects cannot be neglected. In NCS^- the ligand is linear when bonding through nitrogen but bent when co-ordinating through sulphur. The greater steric effect occurring in the latter case is shown in the related complexes $[Pd(dien)(SCN)]^+$ and $[Pd(C_2H_5)_4dien(NCS)]^+$.[6]

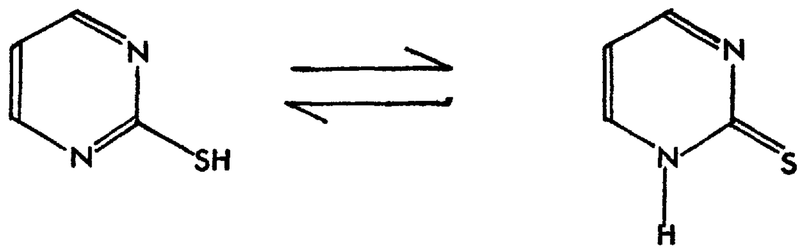
The greater steric hindrance brought about by changing dien to $(C_2H_5)_4$dien results in a change of co-ordinating atom of SCN^- from sulphur to nitrogen in an attempt to relieve the steric strain. Additionally, sulphur co-ordination can be stabilised by the acceptance of electron density from non-bonding d-orbitals on the metal (d_{xz}, d_{xy} and d_{yz}) into empty sulphur d-orbitals.

With more complex ligands, simple criteria such as the change in frequency of a particular vibrational mode are not usually definitive and extremely careful use of spectroscopic techniques is generally necessary.

Metal-sulphur chromophores are of especial interest with a view to predicting how analogous biological molecules will co-ordinate.

The metal-sulphur bond has recently been studied by physical measurements in a group of related pyridine-thiols and in all cases the ligand was shown to be bound to the metal via the sulphur rather than the nitrogen atom.[1] [Bonding through the oxygen atom has also been confirmed for the hydroxy analogues.[1]] However, a recent X-ray study[7] has demonstrated the existence of a chelating pyridine-thiolate anion which is to be expected on account of the loss of the proton.

The present work on the related Cobalt thiopyrimidine and hydroxypyrimidine dichlorides and their Iron analogues was carried out with a view to examine the behaviour of the thiopyrimidine ligand (tautomers I and II).



I II

Metal atoms may be expected to co-ordinate with this ligand through either one of the nitrogen atoms of resonance form I, or through the sulphur atom of form II (less likely in I). There was some experimental evidence (Table I) suggesting that in the Cobalt $(\text{thiopyrimidine})_2\ C\ell_2$ there is a distorted co-ordination and the ligand chelates to produce a four-membered ring. This has been demonstrated in the present structure determination. It was also found that the Cobalt and Iron thiopyrimidine chlorides were isomorphous. The hydroxy analogues of these complexes were prepared as it was hoped to obtain a crystallographic comparison but owing to the inherent disorder in all the crystal specimens prepared, despite having excellent morphologies, not even unit-cell information was obtainable. (The compounds were not isomorphous with their thiopyrimidine analogues).

Experimental

Preparation: A warm solution of Cobalt(II) dichloridehexahydrate (1 mmol) in ethanol ($5cm^3$) was added to a hot solution of 2-pyrimidenethiol (2 mmol) in ethanol ($10cm^3$). The mixture was then heated with stirring for ca 10 minutes after which time the ligand had dissolved and a green crystalline precipitate appeared. The solid was filtered from the hot solution under nitrogen, washed with ethanol ($3 \times 3cm^3$) and ether ($2 \times 3cm^3$)

Table 1

Spectroscopic and Magnetic Data for Co(thiopyrimidine)$_2$Cℓ_2 and Co(hydroxypyrimidine)$_2$Cℓ_2

Co(Pym-2-SH)$_2$Cℓ_2

1. Magnetic moment μeff. = 4.62 B.M.
2. Electronic spectrum

Bands	Assignments
17.36 kk	
15.75 kk	${}^4T_1(P) \leftarrow {}^4A_2$
10.64 kk	
6.62 kk	${}^4T_{1g}(F) \leftarrow {}^4A_2$
5.53 kk	

Implies a distorted co-ordination.

Co(Pym-2-OH)$_2$Cℓ_2

1. Magnetic moment ≈ Unknown for lack of a suitable specimen.
2. Electronic spectrum

Bands	
16.45 kk	${}^4T_1(P) \longleftarrow {}^4A_2$
6.90 kk	${}^4T_{1g}(F) \longleftarrow {}^4A_2$

These bands are consistent with tetrahedral co-ordination,

The spectr~~a~~um of the thiopyrimidine complex is shown in Fig.6 and is compared with the tetrahedral Co(quinoline)$_2$Cℓ_2.

and dried in a vacuum over concentrated sulphuric acid.

The ligand (2-pyrimidine thiol) was obtained commercially and was purified prior to use by recrystallisation from an ethanol-water (1:1) mixture; melting point 228 - 230°C. Gravimetric analysis indicated the formula, $CoC\ell_2(C_4H_4N_2S)_2$

Found %			Calculated %		
C	H	N			
27.11	2.31	15.81	27.11	2.28	15.83

Crystals suitable for X-ray work and with a well developed morphology were grown from ethanol. They were dark green in colour and when examined under polarised light were opaque so no useful optical information was obtained.

The crystal chosen for data collection had the shape outlined in Fig. 1 and approximate dimensions 0.1 x 0.1 x 0.2 mm^3.

Preliminary photographs gave the Laue symmetry as $^2/m$, monoclinic, with c-axis parallel to the elongated direction of the crystal.

Preliminary unit-cell dimensions were as follows:-

$\underline{a}$ = 12.30Å $\underline{D}_m$ = 1.72g cm^{-3}

$\underline{b}$ = 8.25Å $\underline{D}_c$ = 1.80g cm^{-3}

$\underline{c}$ = 14.25Å $\underline{U}$ = 1288$Å^3$

β = 117° $\underline{Z}$ = 4

The systematic absences were:-

hkℓ   h + k = 2n

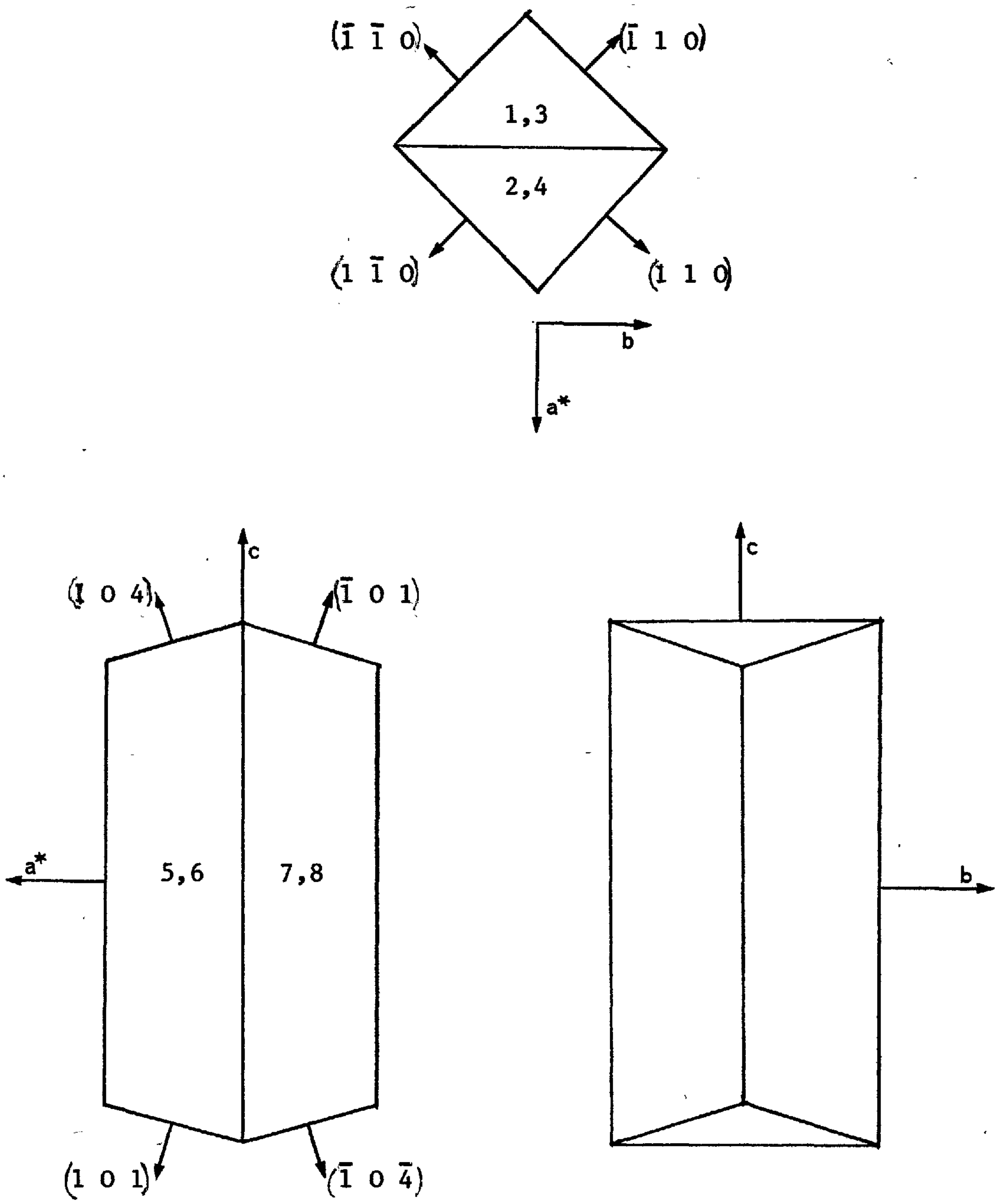
ℓ0ℓ   ℓ = 2n

Thus the space group is either centrosymmetric *C*2/*c* or non-centrosymmetric *Cc*. From visual inspection of the intensity statistics the former is favoured[8] although for *Z* = 4 in this centric space group the molecules must be situated in special positions.

The revised unit-cell dimensions obtained by least squares from

Fig. 1

Morphology of the Cobalt(thiopyrimidine)$_2$dichloride crystal.



θ-scans for 22 reflections are:-

a = 12.371(1)Å β = 117.180(6)°
b = 8.3010(4)Å U =1356.7Å^3
c = 14.851 (1)Å D_c= 1.73g cm^{-3}
μabs = 97.25cm^{-1} for Cu-$K\alpha$ radiation. $\bar{\lambda}$ = 1.5418Å.

Intensity data were collected using filtered Cu-Kα radiation to a θ-value of 70°, and altogether 1206 independent reflections were measured, of which 27 were judged as "unobserved" [$I_{net} < 2.58\ \sigma\ (I)$].

Structural Solution

A three-dimensional Patterson map was computed which indicated that the Cobalt, Chlorine and sulphur atoms lay in positions indicating space group $\underline{C}2/\underline{c}$, the Cobalt atom being situated on a 2-fold axis. Least-squares refinement on these positions gave $\underline{R}$ = 0.313. A difference-Fourier synthesis calculated on the basis of these atomic positions revealed the positions of all the remaining non-hydrogen atoms. Isotropic refinement of these atoms gave $\underline{R}$ = 0.123. All atoms were then allowed to refine anisotropically to give $\underline{R}$ = 0.075. At this stage, the data were corrected for absorption. The correction was made according to the method of Busing and Levy[9] using an 8 x 8 x 12 grid, with crystal pathlengths determined by the vector analysis procedure of Coppens *et al*[10]. Further anisotropic refinement, eliminating four misprocessed reflections and six low-angle reflections which suffered from extinction brought $\underline{R}$ to 0.058. An anomalous dispersion correction for cobalt and sulphur was then applied. When the hydrogen atoms, which were located from the latest difference map, were included as "fixed-atom contributions", $\underline{R}$ fell to 0.054. ($\underline{R}$-factor of less-thans = 0.076). The scattering form-factors used were those tabulated by Cromer and Waber,[11] and the real and imaginary parts of the anomalous dispersion correction were those given by Cromer.[12] The final difference-Fourier was featureless.

Tables 2 and 3 list the final co-ordinates of the non-hydrogen atoms and the coefficients for the anisotropic temperature factors respectively. The standard deviations have been obtained using the full-matrix least-squares refinement procedure ORFLS of X-ray 70. The co-ordinates of the hydrogen atoms are given in Table 4. Comparison of observed and calculated structure amplitudes are listed at the end of the chapter.

Description of the structure and discussion

The complex is monomeric and possesses a diad symmetry axis. The molecular structure is shown in Fig. 2 which is a view down the diad. Fig. 3 shows the molecular packing and indicates the hydrogen bonding present; Fig. 4 is a stereo pair diagram of the unit-cell contents.

The pyrimidine - 2 - thiolato - ligand is bidentate, co-ordinating through both the nitrogen and sulphur atoms. The Co co-ordination is distorted octahedral with the N atoms trans, and the pairs of Cℓ and S atoms cis. The more important bond lengths and angles are shown in Tables 4 and 5 respectively. The Co - Cℓ distance of 2.369Å and Co - N distance of 2.098 are within the expected range of values of octahedral Co - Cℓ and Co - N bonds.[13, 17]

It can be seen that the drive to achieve octahedral co-ordination for Co(II) tolerates a considerable strain in the pyrimidine-2-thiolate, notably at the Co-N-C and N-C-S angles. The values are 111.8(3)° and 116.2(3)° respectively, both being less strained than those in the Ruthenium pyridine-2-thiolato complex.[7] (Fig. 5). The Co-S-C angle is 71.9(2)° (cf. 80° in the Ru-pyridine 2-thiolato analogue) whereas one expects a value of 90° if the sulphur atom utilises pure p orbitals; values of 100 - 110° are more usually found. Like the Ru complex, the angle which departs most from the ideal octahedral co-ordination geometry is the N-Co-S angle of Ca. 59.1(1)° (cf. 67° in Ru analogue). The atom which deviates most from the ideal octahedral co-ordination geometry is thus the S-atom. Table 6 shows the shortest inter-molecular non-bonded interactions. It is notable that the hydrogen of the SH group has moved and become participant in a hydrogen bond between atom N 2 of the pyrimidine ring and the Chlorine atom; this is shown schematically in Fig 3. The intramolecular crowding is considerable and may account for the large degree of distortion from an octahedral environment of cobalt.

The pyrimidine 2-thiolato ligand considered here, the pyrimidine 2-thiolato ligand[7] and the free pyridine 2-thiol molecule as reported by Penfold[18] are compared in Fig. 5. It can be seen that the C-S bond length found here is the same as that in the pyridine-thiol molecule where it was considered due to a degree of double bond character resulting from the contribution of a third tautomeric form of the molecule, that of a α-pyridone. It was also postulated that this accounted for the large variations in bond lengths found within the ring of the pyridine-thiol molecule. In the present study, the bond lengths in the pyrimidine ring do not vary as much and this may be due to the presence of the extra nitrogen within the ring with a consequent more marked tendency toward aromatic delocalisation. It may thus be concluded that the C-S bond in this structure has a larger degree of double bond character than the corresponding pyridine-2 thiolato ligand found in reference 7.

The dihedral angle between the thiopyrimidine four-membered chelate ring and the pyrimidine ligand is 8.2°; the deviations of the atoms from their respective planes are listed in Table 7. The distance between the planes of the pyrimidine rings related through the centres of symmetry is 3.21Å; this feature of the packing may be seen in the stereo-packing diagram (Fig. 4).

Fig. 2

Structure of Cobalt(thiopyrimidine)$_2$dichloride.

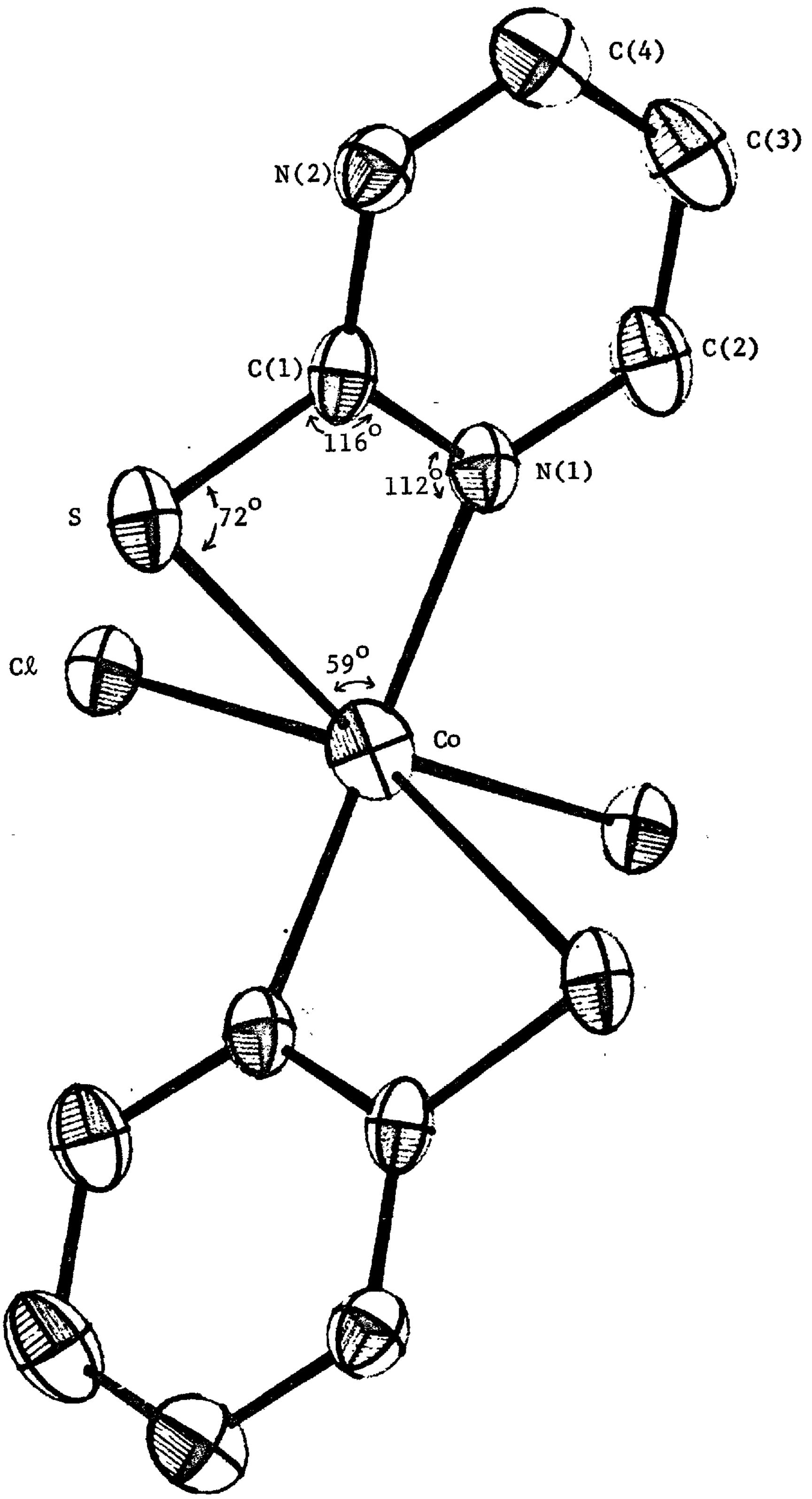


Fig. 3

Molecular packing in Co(thiopyrimidine)$_2$dichloride showing the hydrogen bonding between molecules.

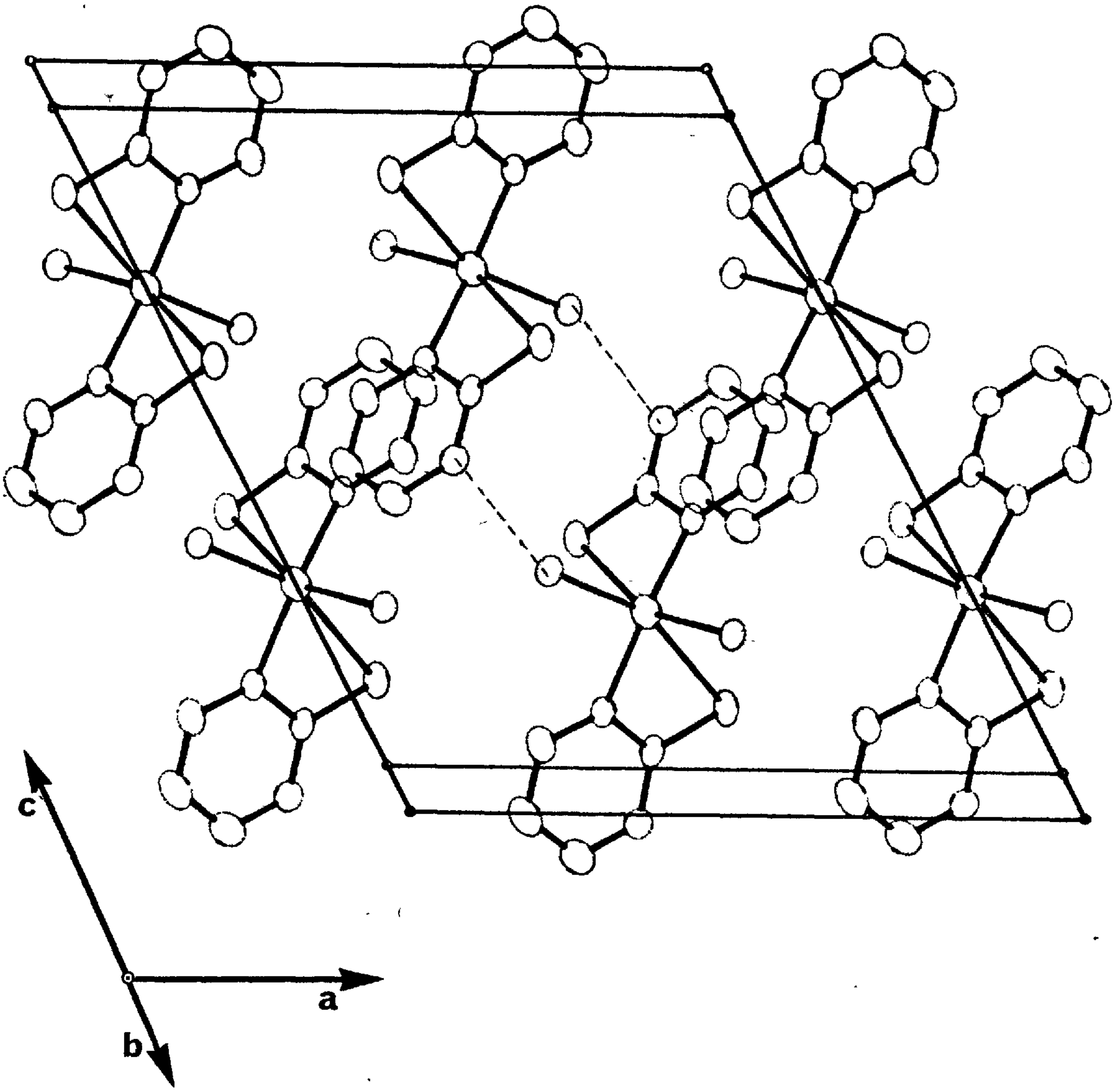


Fig. 4

Stereoscopic packing diagram of the complex of Cobalt(thiopyrimidine)$_2$dichloride.

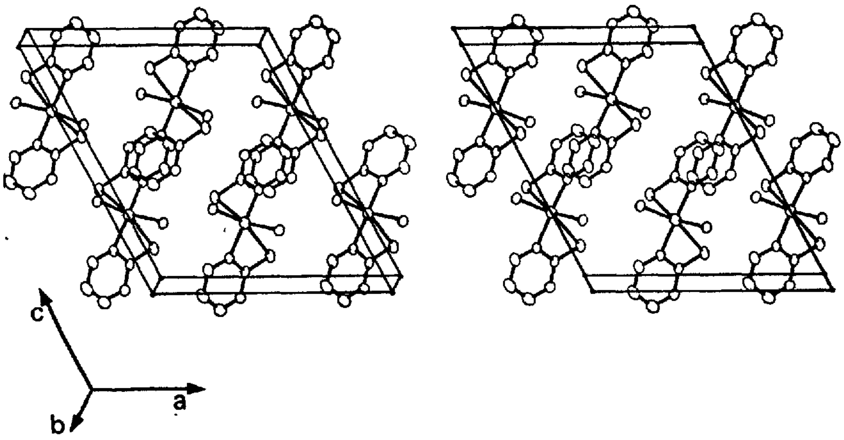
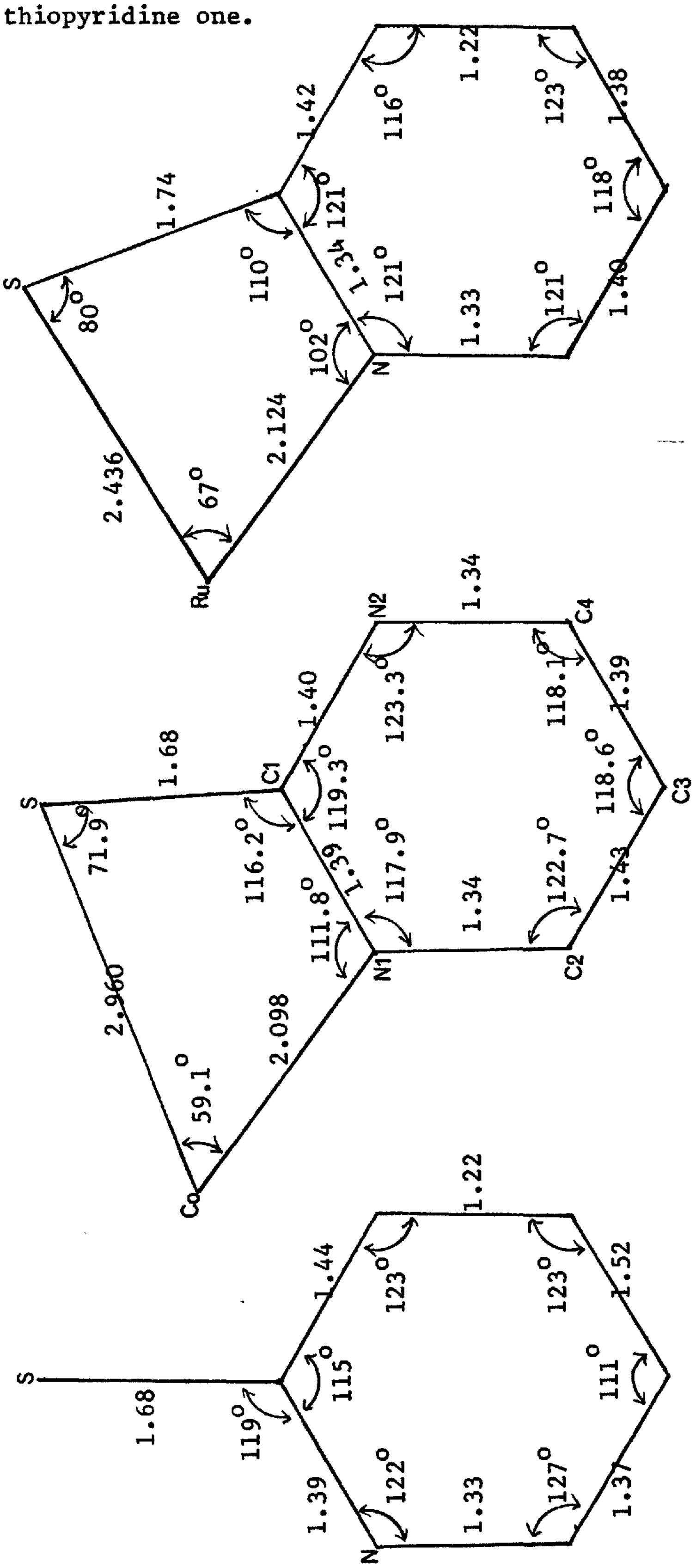


Figure 5

Comparison of the thiopyrimidine complex with the analogous Ru thiopyridine one.



The free thiopyridine is shown for comparative values in the un-complexed state.

Fig. 6

The absorption spectra of the Cobalt thiopyrimidine complex.

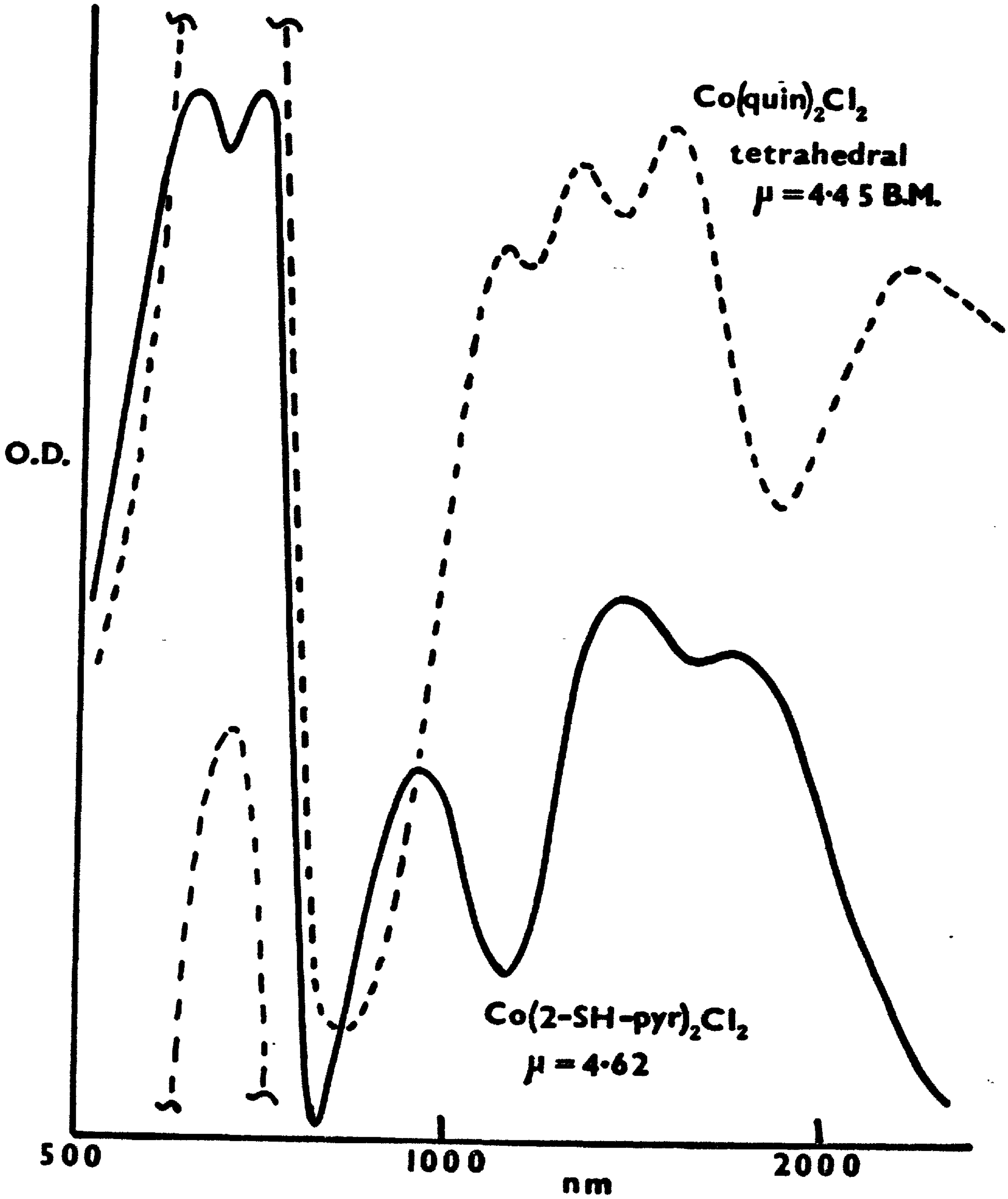


Table 1

Non-hydrogen atomic positions

ATOM	x	y	z
Co^{2+}	0.5	0.60309(15)	0.25
Cℓ	0.61317(10)	0.78926(15)	0.20592(9)
S	0.54799(11)	0.35239(17)	0.13107(11)
C_1	0.4051(4)	0.4173(6)	0.0630(4)
C_2	0.2446(4)	0.5680(6)	0.0617(4)
C_3	0.1664(5)	0.5191(7)	-0.0398(5)
C_4	0.2137(5)	0.4230(7)	-0.0895(4)
N_1	0.3612(4)	0.5215(5)	0.1118(3)
N_2	0.3294(4)	0.3739(5)	-0.0380(3)

Table 2

Anisotropic thermal parameters.

The anisotropic thermal ellipsoid has the form

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)$$

ATOM	$\beta_{11}\mathrm{x}10^5$	$\beta_{22}\mathrm{x}10^5$	$\beta_{33}\mathrm{x}10^5$	$\beta_{12}\mathrm{x}10^5$	$\beta_{13}\mathrm{x}10^5$	$\beta_{23}\mathrm{x}10^5$
Co^{2+}	512(9)	1437(20)	500(7)	—	219(7)	—
Cℓ	474(10)	924(19)	400(7)	-37(10)	254(7)	-12(9)
S	417(10)	1049(21)	562(9)	66(11)	273(8)	-21(10)

	$\beta_{11}\mathrm{x}10^4$	$\beta_{22}\mathrm{x}10^4$	$\beta_{33}\mathrm{x}10^4$	$\beta_{12}\mathrm{x}10^4$	$\beta_{13}\mathrm{x}10^4$	$\beta_{23}\mathrm{x}10^4$
C_1	44(4)	63(7)	46(3)	-9(4)	30(3)	-1(4)
C_2	46(4)	91(8)	58(4)	14(5)	24(3)	5(4)
C_3	50(4)	97(9)	64(4)	12(5)	15(4)	11(5)
C_4	62(5)	90(8)	48(4)	-16(5)	18(3)	11(4)
N_1	40(3)	80(6)	40(3)	4(4)	22(3)	-5(3)
N_2	53(4)	82(6)	40(3)	-13(4)	26(3)	-4(3)

Table 3

Hydrogen atomic positions x 10^3

ATOM	x	y	z
H_2	210	637	98
H_3	78	553	76
H_4	160	397	-164
H_{22}	361	295	-118

Table 4

Bond lengths (Å), with estimated standard deviations in parentheses.

Co - Cℓ	2.369(2)
Co - S	2.960(2)
Co - N_1	2.098(4)
N_1 - C_2	1.343(6)
C_2 - C_3	1.429(8)
C_3 - C_4	1.385(10)
C_4 - N_2	1.341(6)
N_2 - C_1	1.404(6)
C_1 - N_1	1.388(8)
C_1 - S	1.675(4)

Table 5

Selected bond angles (^{o}) with estimated standard deviations in parentheses. Others are shown in Fig. 5

Nomenclature used is that $C\ell^{1}$ is the diad related atom to $C\ell$, S^{1} to S etcetera.

$C\ell - Co - C\ell^{1}$	98.58(7)
$C\ell - Co - S$	89.36(5)
$C\ell - Co - N$	105.26(14)
$C\ell - Co - N^{1}$	99.10(13)
$C\ell - Co - S^{1}$	158.18(3)
$S - Co - S^{1}$	90.65(6)
$S - Co - N^{1}$	93.39(14)
$S - Co - N^{1}$	59.12(13)
$N - Co - N^{1}$	142.32(17)
$S - C_1 - N_1$	116.2(3)
$Co - N_1 - C_1$	111.8(3)
$C_1 - S - Co$	71.9(2)
$S - C_1 - N_2$	124.6(4)
$Co - N_1 - C_2$	129.9(4)

Table 6

Selected Intermolecular non-bonded distances Å

$N_2 - C\ell$	3.191(5)Å	(1-x, 1-y, -z)
$N_2 - S_1$	3.360(5)Å	
$S_1 - H_2$	2,892(9)Å	(½+x, ½+y, z)
$C_1 - C_4$	3.289(8)Å	(½-x, ½-y, -z)
$C\ell_1 - H_4$	3.138(9)Å	(½-x, ³/2-y, -z)
$C\ell_1 - H_3$	2.615(9)Å	

The bond $N_2 - C\ell_1$ is a H-bond with the hydrogen almost symmetrically placed between the two atoms.
Intermolecular $N_2 - H_{22} = 1.5$Å.

Table 7

Deviations (Å) of atoms from plane of pyrimidine ring.

		Deviation Δ (mÅ)
Atoms defining plane	C_1	23
	C_2	0
	C_3	20
	C_4	-18
	N_1	-21
	N_2	-4
	S	103
	Co	-347

Deviations of atoms in distorted four-membered ring

Atoms defining plane	Co	-26
	S	34
	C_1	-67
	N_1	59

The dihedral angle between the normals to the above two planes = 8.24°. This tilt of the pyrimidine ring relative to the chelate ring is due to packing forces, the normal separation between the two rings being 3.26Å.

CHAPTER IV

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant k and ℓ and list values of h, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

H,0,0

2	863	839
4	344	228
6	309	326
8	539	561
10	123	78
12	103	94

H,0,2

−14	367	364
−12	155	156
−10	512	514
−8	658	642
−6	397	287
−4	1059	896
0	433	361
4	1120	1148
6	601	642
8	912	938
10	573	595
12	104	81

H,0,4

−14	239	219
−12	417	419
−10	659	676
−8	1435	1446
−6	1497	1469
−4	571	457
−2	1439	1325
0	137	95
4	473	488
6	182	179
8	355	349
10	747	774

H,0,6

−14	222	214
−12	80	33
−10	125	98
−8	1259	1243
−6	1737	1757
−4	1600	1606
−2	492	393
0	1105	1106
2	698	706
4	106	40
6	501	484
8	80	45
10	421	406

H,0,8

−14	398	416
−12	459	481
−10	560	554
−8	191	182
−6	1536	1537
−4	859	851
−2	961	982
0	322	348
2	999	1009
4	720	718
6	78	35
8	189	197

H,0,10

−14	391	410
−12	532	531
−10	194	182
−8	270	232
−6	251	220
−4	504	499
−2	116	22
0	228	224
2	679	664
4	798	801
6	442	409

H,0,12

−14	664	731
−12	781	825
−10	324	313
−8	93	36
−6	210	145
−4	819	814
−2	82	30
0	456	461
2	81	42
4	426	422

H,0,14

−12	424	450
−10	300	282
−8	89	48
−6	817	789
−4	491	504
−2	304	296
0	59	24
2	184	183

H,0,16

−10	223	219
−8	85	50
−6	207	220
−4	430	447
−2	575	590

H,1,0

3	1027	1067
5	236	260
7	469	470
9	100	77
11	57	35
13	91	67

H,1,1

−13	143	167
−11	259	251
−9	1111	1101
−7	1119	1114
−5	393	404
−3	501	397
−1	429	414
3	454	385
5	971	892
7	383	379
9	556	580
11	458	476

H,1,2

−13	383	383
−11	212	193
−9	332	310
−7	529	437
−5	494	493
−3	843	832
−1	420	433
1	385	416
3	719	753
5	1189	1237
7	860	886
9	105	88
11	98	61

H,1,3

−13	293	324
−11	364	364
−9	608	596
−7	1002	989
−5	513	507
−3	544	550
3	518	512
5	513	485
7	550	545
9	302	318
11	200	210

H,1,4

−13	307	302
−11	687	698
−9	500	509
−7	676	681
−5	353	365
−3	509	499
−1	95	63
1	378	291
3	454	477
5	874	895
7	109	45
9	470	461
11	275	263

H,1,5

−13	67	58
−11	361	372
−9	395	369
−7	650	621
−5	592	580
−3	632	564
−1	381	452
5	285	280
7	69	34
9	83	56

H,1,6

−13	141	133
−11	541	542
−9	399	398
−7	451	458
−5	1236	1200
−3	790	835
−1	509	574
1	586	585
3	95	90
5	454	434
7	471	473
9	166	147

H,1,7

−13	447	461
−11	102	88
−9	232	242
−7	611	587
−5	232	221
−3	547	517
−1	739	734
1	416	439
3	1044	1073
5	299	297
7	108	79
9	189	175

H,1,8

−13	112	99
−11	305	297
−9	265	257
−7	601	574
−5	136	138
−3	767	816
−1	1067	1140
1	425	449
3	105	75
5	423	422
7	134	102

H,1,9

−13	491	512
−11	233	237
−9	107	85
−7	838	819
−5	1010	895
−3	128	135
−1	403	400
1	180	146
3	137	125
5	291	296
7	101	95

H,1,10

−13	110	96
−11	471	464
−9	377	361
−7	229	181
−5	101	58
−3	200	230
−1	360	382
1	504	509
3	360	337
5	300	272

H,1,11

−13	130	123
−11	84	46
−9	193	186
−7	271	274
−5	1101	1119
−3	683	751
−1	81	51
1	119	109
3	304	304
5	137	133

H,1,12

−13	382	394
−11	390	392
−9	330	320
−7	238	217
−5	187	174
−3	62	49
−1	153	139
1	78	32
3	215	201

H,1,13

−13	328	344
−11	72	41

```
       H,1,13

  -9     411     411
  -7     210     204
  -5     249     259
  -3     501     534
  -1     232     227
   1      58      16
   3     265     236

       H,1,14

 -13      75      47
 -11      69      19
  -9     305     298
  -7     646     633
  -5     248     269
  -3     118      92
  -1      75      52
   1     208     208

       H,1,15

 -11     434     444
  -9     105     108
  -7     368     380
  -5      45      38
  -3     248     269
  -1      52      34

       H,1,16

 -11      42      18
  -9     223     213
  -7     113     106
  -5     162     153
  -3     145     139

       H,1,17

  -7      56      64
  -5      31*     23

        H,2,0

   0     368     376
   2     693     656
   4     542     565
   6     479     476
   8      44      37
  10     104     128
  12     324     341

        H,2,1

 -12     354     332
 -10     665     662
  -8     686     677
  -6    1314    1307
  -4    1623    1613
```

```
  -2     369     251
   0     121      29
   2     260     160
   4     346     371
   6     419     432
   8     341     360
  10     175     142
  12     507     526

        H,2,2

 -12     177     176
 -10     147     139
  -8     197     173
  -6     106     116
  -4    1048    1005
  -2    1775    1816
   0    1237    1312
   2     861     849
   4     644     641
   6     497     512
   8     192     200
  10     205     212
  12      71      78

        H,2,3

 -14      65      23
 -12     144     118
 -10     197     180
  -8     265     258
  -6     719     711
  -4    1251    1263
   0     390     451
   2     545     587
   4     349     351
   6     156     146
   8     167     146
  10      73      19

        H,2,4

 -14     142     152
 -12     345     350
 -10     213     221
  -8     605     566
  -6     196     163
  -4    1225    1183
  -2     643     648
   0     218     196
   2     152     135
   4     256     265
   6     430     432
   8      46      16
  10     253     258

        H,2,5

 -14     158     137
 -12     349     333
```

```
 -10     151     113
  -8     395     339
  -6     153      91
  -4    1226    1242
  -2     730     777
   2     596     650
   4     763     797
   6     795     800
   8     263     255
  10     147     145

        H,2,6

 -14      62      48
 -12     408     424
 -10     182     176
  -8     168     160
  -6     657     617
  -4     151     155
  -2     605     635
   0     614     630
   2     404     381
   4      83      82
   6     362     362
   8     292     295

        H,2,7

 -14     374     375
 -12     474     468
 -10     867     865
  -8     412     391
  -6     327     257
  -4     237     186
  -2     213     243
   0     319     348
   2     408     421
   4     530     530
   6     526     518
   8     519     502

        H,2,8

 -14      50      67
 -12      80      66
 -10     677     658
  -8     174     166
  -6     249     231
  -4     349     331
  -2     584     618
   0     177     201
   2     242     226
   4     278     286
   6     305     300
   8     352     341

        H,2,9

 -14      93      58
 -12     550     560
```

```
 -10     846     848
  -8     749     734
  -6     589     582
  -4     117      82
  -2     683     735
   0     230     236
   2     237     215
   4     180     155
   6     229     219

       H,2,10

 -14     338     376
 -12      41*     17
 -10     513     522
  -8     578     563
  -6     275     260
  -4     202     192
  -2     379     404
   0     411     426
   2     130     135
   4     196     196
   6      40       9

       H,2,11

 -14     265     294
 -12     159     156
 -10     290     274
  -8     673     659
  -6     425     420
  -4     815     848
  -2     402     422
   0     491     488
   2     267     257
   4     105      85

       H,2,12

 -14     154     180
 -12     170     177
 -10     173     176
  -8     276     265
  -6      68      54
  -4      42*     11
  -2      97     100
   0     367     360
   2     214     211
   4     126     130

       H,2,13

 -12     150     155
 -10      67      11
  -8     195     180
  -6     171     158
  -4     132     119
  -2     382     390
   0     595     586
   2     383     358
```

```
       H,2,14

 -12     263     285
 -10      68      56
  -8     258     265
  -6     296     287
  -4     342     363
  -2     146     154
   0     295     292

       H,2,15

 -12     186     165
 -10     177     152
  -8     117      81
  -6     119      95
  -4      78      71
  -2      72      66
   0     173     155

       H,2,16

 -10      41      47
  -8     360     363
  -6      71      79
  -4     164     168
  -2      92     118

        H,3,0

   1     637     662
   3     754     769
   5     912     907
   7     249     232
   9     643     646
  11      87      93

        H,3,1

 -13     306     300
 -11     244     227
  -9     342     318
  -7     462     473
  -5    1172    1153
  -3     969     952
  -1     127      15
   1     156      76
   5     682     708
   7     573     565
   9     247     236
  11     325     316

        H,3,2

 -13     382     396
 -11     202     195
  -9     332     321
  -7     609     565
```

H,3,2

-5	144	126
-3	495	487
-1	608	566
1	35	6
3	1158	1174
5	756	787
7	479	475
9	234	230
11	150	161

H,3,3

-13	262	264
-11	371	359
-9	302	285
-7	219	149
-5	727	722
-3	1760	1763
1	131	172
3	223	234
5	725	732
7	132	92
9	177	159
11	58	22

H,3,4

-13	461	473
-11	614	609
-9	381	365
-7	149	161
-5	99	99
-3	224	187
-1	101	68
1	630	638
3	636	593
5	468	463
7	701	699
9	128	120

H,3,5

-13	222	213
-11	587	582
-9	258	232
-7	83	18
-5	664	644
-3	896	936
1	233	261
3	248	280
5	658	672
7	561	573
9	78	26

H,3,6

-13	132	139
-11	408	406
-9	601	599
-7	169	175
-5	354	373
-3	1158	1186
-1	559	599
1	420	423
3	566	562
5	63	5
7	43	41
9	40	17

H,3,7

-13	266	260
-11	447	439
-9	814	816
-7	101	78
-5	298	238
-3	522	539
-1	599	652
1	278	289
3	308	310
5	193	184
7	532	521

H,3,8

-13	259	282
-11	63	49
-9	84	22
-7	266	248
-5	84	79
-3	822	858
-1	770	800
1	356	358
3	169	151
5	109	94
7	34*	9

H,3,9

-13	110	86
-11	583	591
-9	632	628
-7	319	285
-5	88	8
-3	433	455
-1	711	744
1	331	338
3	394	388
5	228	213
7	230	225

H,3,10

-13	102	94
-11	104	93
-9	43*	12
-7	195	188
-5	404	392
-3	368	374
-1	460	470
1	547	560
3	49	36
5	121	98

H,3,11

-13	240	265
-11	158	140
-9	555	531
-7	355	357
-5	287	277
-3	254	263
-1	484	489
1	264	259
3	189	173
5	81	85

H,3,12

-13	32*	16
-11	192	186
-9	675	676
-7	250	242
-5	460	463
-3	184	203
-1	41*	10
1	55	38
3	33*	22

H,3,13

-13	46	12
-11	63	12
-9	333	335
-7	403	388
-5	131	109
-3	53	20
-1	369	364
1	468	451

H,3,14

-11	121	122
-9	340	343
-7	453	452
-5	224	215
-3	77	86
-1	71	70
1	69	68

H,3,15

-11	55	9
-9	180	167
-7	276	273
-5	117	92
-3	59	61
-1	79	45

H,3,16

-9	30*	2
-7	197	204
-5	204	199

H,4,0

2	776	837
4	1091	1125
6	251	252
8	285	285
10	87	84
12	108	101

H,4,1

-12	232	251
-10	146	145
-8	406	403
-6	55	32
-4	492	436
-2	85	77
2	722	770
4	370	379
6	53	33
8	349	362
10	121	110

H,4,2

-12	422	422
-10	148	118
-8	409	394
-6	94	71
-4	561	544
-2	163	151
0	84	63
4	812	850
6	792	808
8	507	525
10	63	31

H,4,3

-12	71	62
-10	336	328
-8	416	391
-6	226	227
-4	919	872
-2	181	183
0	257	286
2	811	845
4	71	12
6	95	84
8	281	262
10	464	483

H,4,4

-12	524	548
-10	465	452
-8	673	671
-6	336	338
-4	181	91
-2	553	555
0	89	33
2	470	426
4	396	394
6	674	694
8	303	288
10	237	224

H,4,5

-12	38	10
-10	62	24
-8	771	766
-6	678	657
-4	643	647
-2	696	688
0	54	34
2	331	347
4	138	147
6	230	240
8	104	90

H,4,6

-12	194	182
-10	758	767
-8	333	327
-6	218	217
-4	1172	1217
-2	773	812
0	311	339
2	166	150
4	236	217
6	161	153
8	210	203

H,4,7

-12	232	242
-10	168	157
-8	374	379
-6	1026	1025
-4	238	242
-2	151	126
0	367	375
2	498	509
4	224	216
6	199	192
8	204	208

H,4,8

-12	67	25

```
        H,4,8

 -10     86      27
  -8    131      99
  -6    174     182
  -4    404     408
   0    597     603
   2    219     197
   4    265     259
   6    104      82

        H,4,9

 -12     38*      2
 -10    294     299
  -8    243     234
  -6    320     318
  -4    283     298
  -2    347     350
   0     67      44
   2    420     407
   4    390     385
   6     81      70

        H,4,10

 -12    196     183
 -10    277     260
  -8     91      47
  -6    156     129
  -4    181     157
  -2    124      98
   0    607     599
   2    484     479
   4    100      48

        H,4,11

 -12    352     353
 -10    201     209
  -8    115     118
  -6     99     101
  -4    517     518
  -2    267     254
   0    239     229
   2    126     105
   4    385     372

        H,4,12

 -12    157     142
 -10    424     413
  -8    580     573
  -6     52      12
  -4    197     196
  -2     91      76
   0    189     181
   2     63      11
```

```
        H,4,13

 -12    330     352
 -10    243     240
  -8     95      99
  -6    227     229
  -4    228     224
  -2     87      91
   0    140     154

        H,4,14

 -10    265     266
  -8    457     443
  -6    424     416
  -4    124      99
  -2    108      78
   0    117     111

        H,4,15

 -10     96      84
  -8     98     101
  -6     69      50
  -4    320     320
  -2    343     326

        H,5,0

   3    143     142
   5    139      96
   7    357     357
   9    385     385
  11    338     348

        H,5,1

 -11    389     391
  -9    138     134
  -7    194     183
  -5    708     665
  -3    321     311
  -1    640     633
   1    376     388
   3    454     473
   5    232     230
   7     74      73
   9    198     191
  11     88      84

        H,5,2

 -11    100      81
  -9    582     566
  -7    509     486
  -5    235     233
  -3    165     174
  -1    352     367
   1    928     971
   3    541     564
```

```
   5    209     140
   7    216     208
   9    538     559

        H,5,3

 -11    243     242
  -9    202     204
  -7    304     306
  -5    399     391
  -3    681     695
  -1    589     607
   1    163     121
   3     38*     33
   5    181     170
   7    196     192
   9    318     329

        H,5,4

 -11     69      32
  -9    402     393
  -7   1029    1013
  -5    389     391
  -3    549     507
  -1    390     399
   1    995    1034
   3    429     431
   5    144     125
   7     69      10
   9    279     274

        H,5,5

 -13     28*     25
 -11    132     139
  -9    159     160
  -7    612     611
  -5    286     266
  -3    164     164
  -1    482     490
   1    480     479
   3    159     160
   5    307     305
   7    142     148
   9    160     161

        H,5,6

 -13    100      66
 -11     62      53
  -9    261     250
  -7    585     581
  -5    469     449
  -3    215     225
  -1    220     240
   1    413     417
   3    615     610
   5    109      53
   7     58      19
```

```
        H,5,7

 -13    153     169
 -11    414     427
  -9     60      51
  -7    369     370
  -5    465     458
  -3     83      90
  -1    211     212
   1    178     177
   3     41*     25
   5    328     316
   7    217     224

        H,5,8

 -13    281     289
 -11    146     157
  -9    108      86
  -7    500     480
  -5    763     773
  -3    347     348
  -1    312     288
   1    275     264
   3    631     612
   5    269     262

        H,5,9

 -11    246     251
  -9    383     375
  -7    395     398
  -5     93      89
  -3    191     194
  -1     43*     36
   1    319     298
   3    156     160
   5    169     167

        H,5,10

 -11    152     132
  -9    159     151
  -7    334     331
  -5    646     653
  -3     96      35
  -1     61      39
   1    268     248
   3    303     292

        H,5,11

 -11    109     111
  -9    214     227
  -7    163     158
  -5    152     153
  -3    272     259
  -1    203     198
   1    253     238
   3    225     216
```

```
        H,5,12

 -11    151     129
  -9     49      19
  -7     72      23
  -5    352     341
  -3    512     496
  -1    114      81
   1    201     195

        H,5,13

 -11    239     245
  -9    143     149
  -7     42      36
  -5    141     145
  -3     60      42
  -1    277     270

        H,5,14

  -9     86      76
  -7     51      13
  -5    306     293
  -3    389     371

        H,6,0

   0    132     131
   2    125     107
   4    277     283
   6     83      51
   8    366     369
  10    402     421

        H,6,1

 -10    393     406
  -8    561     555
  -6    399     400
  -4     60       1
  -2     66       8
   0    456     469
   2    297     292
   4    465     456
   6    167     172
   8    346     356
  10    389     412

        H,6,2

 -10    122     108
  -8    180     162
  -6    833     831
  -4    472     463
  -2    454     468
   0    181     173
   2    108     105
```

```
       H,6,2

  4    236    219
  6     49      7
  8    139    131

       H,6,3

-10    111    106
 -8    634    638
 -6    444    428
 -4    116    109
 -2    185    201
  0    750    768
  2    590    600
  4     66     53
  6    451    464
  8     99     81

       H,6,4

-10    151    153
 -8    289    298
 -6    229    220
 -4    199    194
 -2    495    509
  0    550    556
  2    576    581
  4    243    234
  6     96     79
  8     97     96

       H,6,5

-12    141    169
-10    182    193
 -8    142    121
 -6    483    473
 -4    275    261
 -2     77     70
  0    630    644
  2    700    713
  4    266    257
  6     82     78
  8    101    107

       H,6,6

-12    171    166
-10    115    108
 -8     87     67
 -6    327    329
 -4    172    173
 -2     81     69
  0    446    451
  2    260    247
  4    361    346
  6    247    221
```

```
       H,6,7

-12     69     48
-10     61      9
 -8    259    251
 -6    173    160
 -4    173    171
 -2    314    322
  0    311    291
  2    527    520
  4    509    506
  6     56     47

       H,6,8

-12    230    246
-10    270    260
 -8    113     77
 -6    429    433
 -4     57      9
 -2     43      8
  0    257    245
  2     84     58
  4    206    194

       H,6,9

-10    129    130
 -8    160    140
 -6    750    766
 -4    374    364
 -2    334    327
  0    138    139
  2     94     78
  4    205    193

       H,6,10

-10    177    175
 -8    417    423
 -6    317    308
 -4    283    278
 -2     98     74
  0     96     75
  2    136    122

       H,6,11

-10    102    112
 -8     71     63
 -6    408    402
 -4    516    516
 -2    226    207
  0    121    135
  2    102     95

       H,6,12

-10     85     78
 -8     38     18
```

```
 -6    114    105
 -4    315    294
 -2    290    269
  0    303    276

       H,6,13

 -8    204    220
 -6     68     57
 -4    332    330
 -2    290    266

       H,7,0

  1    605    619
  3    152    156
  5    184    182
  7     93     93
  9     31*    13

       H,7,1

 -9     64     38
 -7     85     46
 -5    403    397
 -3    341    328
 -1     91     26
  1    459    465
  3    434    434
  5    254    246
  7    224    217
  9    105     87

       H,7,2

 -9     88     87
 -7     40*     5
 -5    724    733
 -3    651    654
 -1     40*     8
  1    511    524
  3    293    296
  5    114    125
  7     61     60

       H,7,3

 -9    104     77
 -7    231    216
 -5    121     90
 -3    167    150
 -1    360    368
  1    209    199
  3    176    160
  5    242    224
  7    221    197

       H,7,4

 -9    257    267
```

```
 -7    331    330
 -5    130    142
 -3    563    568
 -1    365    368
  1    184    180
  3     40*    10
  5    224    226
  7     32     28

       H,7,5

 -9    253    244
 -7    167    145
 -5    288    279
 -3    278    280
 -1    271    256
  1     82     61
  3     78     34
  5    197    178

       H,7,6

 -9     55     52
 -7    522    521
 -5    604    622
 -3    177    184
 -1    523    534
  1    223    223
  3     39*    23
  5    274    278

       H,7,7

 -9    219    212
 -7    173    163
 -5    186    173
 -3    385    366
 -1    221    207
  1    197    171
  3    179    166
  5    116     98

       H,7,8

 -9    359    379
 -7    179    202
 -5    154    147
 -3     40*    11
 -1    172    161
  1    101     93
  3    266    277

       H,7,9

 -9     68     31
 -7    131    109
 -5    170    151
 -3    194    175
 -1    282    273
  1    218    200
```

```
  3    140    114

       H,7,10

 -9    413    434
 -7    307    317
 -5    118    129
 -3     37*    13
 -1    302    305
  1     72     68

       H,7,11

 -7    115     92
 -5    135    107
 -3     74     32
 -1    125     96

       H,7,12

 -7     55     70
 -5     65     84
 -3     29*     7

       H,8,0

  0    100     85
  2    198    194
  4     93     77
  6    292    303
  8    139    158

       H,8,1

 -8    271    293
 -6     96     90
 -4    346    337
 -2    202    187
  0     74     53
  2    340    320
  4    775    796
  6    299    298

       H,8,2

 -8     63     48
 -6    254    261
 -4    190    194
 -2     60     42
  0     59     20
  2    110    100
  4    315    318
  6    142    136

       H,8,3

 -8    140    161
 -6    105    108
 -4    112     79
 -2    170    160
```

```
        H,8,3

 0      144       158
 2       72        48
 4      196       172
 6      427       438

        H,8,4

-8       53        59
-6      105        98
-4      120       115
-2      122       112
 0       41*       30
 2      224       226
 4      102        96
 6      179       183

        H,8,5

-8      235       231
-6       85        61
-4      374       377
-2      360       354
 0       71        64
 2      470       486
 4       54        42

        H,8,6

-8       38        22
-6      180       178
-4      179       174
-2      226       222
 0       70        45
 2       48        40
 4      116       118

        H,8,7

-8      126       124
-6       44        23
-4      347       341
-2      575       565
 0      267       257
 2       46        54

        H,8,8

-8      139       145
-6      190       202
-4       90        79
-2      244       233
 0      285       284
 2       32        14

        H,8,9

-6      132       141
-4       45        25
-2      375       371
 0      423       419

        H,8,10

-6       29*       19
-4       69        77
-2       72        67

        H,9,0

 1      111       114
 3      121       104
 5      302       309

        H,9,1

-5      132       137
-3       84        85
-1      112        93
 1      407       421
 3      373       383
 5       30*        4

        H,9,2

-5      265       260
-3      449       456
-1       79        40
 1       98       111
 3       65        36
 5      164       160

        H,9,3

-5      137       139
-3      409       433
-1       36*        0
 1      307       314
 3       44        35

        H,9,4

-5      171       155
-3      391       384
-1      346       335
 1       73        66
 3      124       101

        H,9,5

-5      138       132
-3       34*       26
-1      111       118
 1      182       178

        H,9,6

-5       41        12
-3      215       211
-1      160       147
 1      159       140

        H,9,7

-5      286       296
-3       71        50
-1       55        32

        H,10,0

 0      128       128
 2       37        13

        H,10,1

-2       75        71
 0       99       112

        H,10,2

-2      159       148
 0      216       209
```

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CHAPTER V

The Crystal and Molecular Structure of Hydridotris(triphenylphosphine)ruthenium(II) Tetrafluoroborate.

"*Achievements ordinarily*
follow in due course when
a person, after planning
his work, works his plan."
... *Elsie Bouman.*

Abstract

The crystal structure of the title compound $[RuH(\eta\text{-}PhPPh_2)(PPh_3)_2]^+BF_4^-$ has been determined from three-dimensional X-ray diffractometer data, and refined using least-squares techniques to $\underline{R}$ 0.039 for 5138 independent reflections. Crystals are monoclinic with unit-cell dimensions

$\underline{a}$ = 20.755(2)Å, $\underline{b}$ = 12.784(1)Å, $\underline{c}$ = 18.609(3)Å, β = 109.06(2)°, space group $\underline{P2_1/c}$ and $\underline{Z}$ = 4.

The complex cation is mononuclear and the metal atom has a co-ordination consisting of two σ-bonded triphenylphosphine groups, a hydride hydrogen, and a phenyl ring of the third triphenylphosphine bonded as an arene to the metal. Ru-P bond distances for the two σ-bound triphenylphosphine groups are 2.312Å and 2.331Å respectively and the P-Ru-P angle is 98.7°. The six Ru-C distances are in the range 2.244-2.324Å, and the centroid of the π-bonded ring is 1.777Å from the ruthenium atom. Ru-H is ca 1.67Å.

Although the compound was originally obtained as a methanol solvate only ill-defined traces of the methanol could be located in the interstices of the structure.

Introduction

Owing to the importance of catalysts in homogenous hydrogenation of alkenes, further catalytic studies have been undertaken by Wilkinson and co-workers. Previous work on the protonation of hydridoacetotris(triphenylphosphine)ruthenium(II) by fluoroboric acid[1] has been extended and our present X-ray study complements the chemical work.

The action of fluoroboric or other non-complexing strong acids on several ruthenium phosphine complexes, notably $RuH_2(PPh_3)_4$, $RuH(CO_2Me)(PPh_3)_3$ and $Ru(CO_2Me)_2(PPh_3)_2$, in methanol solution gives labile red solutions that under hydrogen become yellow-orange and catalyse the homogeneous hydrogenation of alkenes.[1] The proper characterisation of these species proved difficult due to the low solubility but it seemed that they were cationic. Sanders[2] has shown that in the interaction of tritylhexafluorophosphate with $RuH_2(PPh_3)_4$ a similar red salt is formed, $[RuH(PPh_3)_4]^+PF_6^-$ which on standing in dichloromethane slowly gave a yellow salt $[RuH(PPh_3)_3]^+PF_6^-$. It was proposed that one of the phenyl rings of one triphenylphosphine group was π-bonded to the metal.

During additional work by Wilkinson and co-workers on the species produced in the protonation,the title π-complex has been made.[3,4]

The initial red species in methanol and acetone is $[RuH(PPh_3)_3S]^+$ where S = solvent. The methanol solution ages in the absence of excess triphenylphosphine to yellow $[RuH(PPh_3)_2(H_2O)_2(MeOH)]^+$ but in the presence of excess PPh_3 forms the stable π-bonded $[RuH(\eta^6-C_6H_5PPh_2)(PPh_3)_2]^+$ which is the subject of the present study. These complexes share a common feature in that they obey the eighteen electron or rare gas rule.

Owing to the great stability of this ionic title complex it is catalytically inactive in the hydrogenation of alkenes. We have determined the X-ray crystal structure of this complex in order to confirm the presence of the π-bonded model in the present system and support the ^{31}P n.m.r. in characterising the complex.

Preliminary details of the title structure have been reported.[5]

Experimental

Pale yellow needles of the salt $[RuH(PPh_3)_3]BF_4$ were crystallised from methanol. On heating a suspension of $RuH(CO_2Me)(PPh_3)_3$ with a large excess of fluoroboric acid in methanol, the compound was obtained on cooling.[3]

Crystal Data

$C_{54}H_{46}BF_4P_3Ru(O_{\frac{1}{2}}?)$, $M = 975.8$, Monoclinic, $a = 20.755(2)$, $b = 12.784(1)$, $c = 18.609(3)$, $\beta = 109.062(8)$, $U = 4666.8 Å^3$, $D_m = 1.40$ (by flotation), $Z = 4$, $D_c = 1.39 gcm^{-3}$, $F(000) = 1952$. Cu-Kα radiation, $\lambda = 1.5418 Å$; $\mu(Cu\text{-}K\alpha) = 42.2 cm^{-1}$. Space group $P2_1/c$ from systematic absences; $h0\ell$, $\ell = 2n+1$; $0k0$, $k = 2n+1$.

The needles are elongated about the c-axis. A crystal of size ca $0.05 \times 0.05 \times 0.18 mm^3$ was selected and mounted about its c axis. X-ray intensity data were collected on a Siemens four-circle diffractometer using Cu-Kα radiation at a take-off angle of 6°, a Ni β-filter and a Na(Tℓ)I scintillation counter. The θ-2θ scan technique was employed, using a 'five-value' measuring procedure. A total of 5138 independent reflections were measured (to θ = 60°) of which 480 were judged to be unobserved. Lorentz and polarisation corrections were applied and at a later stage the data were corrected for absorption. This correction was calculated according to the method of Busing and Levy[6] using a 10 x 10 x 10 grid with crystal pathlengths determined by the vector analysis procedure of Coppens *et al*[7].

Solution and Refinement of the Structure

The structure was solved by Patterson and Fourier methods. The Crystal Structure Calculations System 'X-ray 70' and its updated version of 1972[8] were used for the calculations which were carried out on the Imperial College CDC 6400 and the University of London

CDC 6400, 6600 and 7600 series computers.

A three-dimensional Patterson synthesis gave a quite easy solution for the ruthenium atom and a few cycles of least squares gave the standard agreement factor $\underline{R}$ = 0.548. Subsequently, the three phosphorus atoms were found ($\underline{R}$ = 0.375) and on the next difference Fourier sixteen meaningful carbon positions were found ($\underline{R}$ = 0.356). All the atoms were then located and isotropic refinement gave $\underline{R}$ = 0.183. When all the expected non-hydrogen atoms were allowed to refine anisotropically, there still remained a residual peak in the difference Fourier map and it was suspected that this could be residual methanol solvent (D_m = 1.40, D_c = 1.39). This position was then assigned to be that of an oxygen atom with a partial occupancy of half an atom. Addition of this atom and refinement as previously gave $\underline{R}$ = 0.055. The hydride hydrogen was now clearly visible in a difference Fourier synthesis together with the phenyl hydrogens. Addition of the phenyl hydrogen atoms as a fixed-atom contribution with isotropic temperature factors of their parent carbon atoms reduced $\underline{R}$ to 0.041.

Towards the end of refinement, a weighting scheme of the type suggested by Hughes[8] was utilised where $w = 1$ for $F<F^*$, $\sqrt{w} = F^*/F$ for $F>F$, with $F^* = 39.7$ being the final value. The application of this weighting scheme had little effect on $\underline{R}$ but decreased the estimated standard deviations by ca 15%.

The full procedure for optimising the hydride position was then applied[10] using $\lambda^{-1}\text{Sin}\theta$ cut-offs of 0.25, 0.35, 0.45 and 0.56Å^{-1}. An optimum value of Ru(1) - H(1) of 1.67Å was obtained. The final $\underline{R}$ obtained = 0.039 and the final difference Fourier was relatively featureless with a maximum electron-density peak of 0,6e/Å^3 which was part of a small ripple around the ruthenium atom.

Atomic scattering factors used were those of Cromer and Waber[11] except those for hydrogen which were obtained from Stewart *et al*[12].

The correction for the effects of the real and imaginary parts of the anomalous dispersion correction for ruthenium and phosphorus were made using the tabulated values after Cromer.[13]

Table 1 lists the fractional co-ordinates of the non-hydrogen atoms with their estimated standard deviations (obtained from CRYLSQ of X-ray '70 and are thus a slight underestimate of the true deviations). Table 2 contains the coefficients in the expression for the anisotropic Debye-Waller factor :-

$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}\ell^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*h\ell + 2U_{23}b^*c^*k\ell)\ ].$$

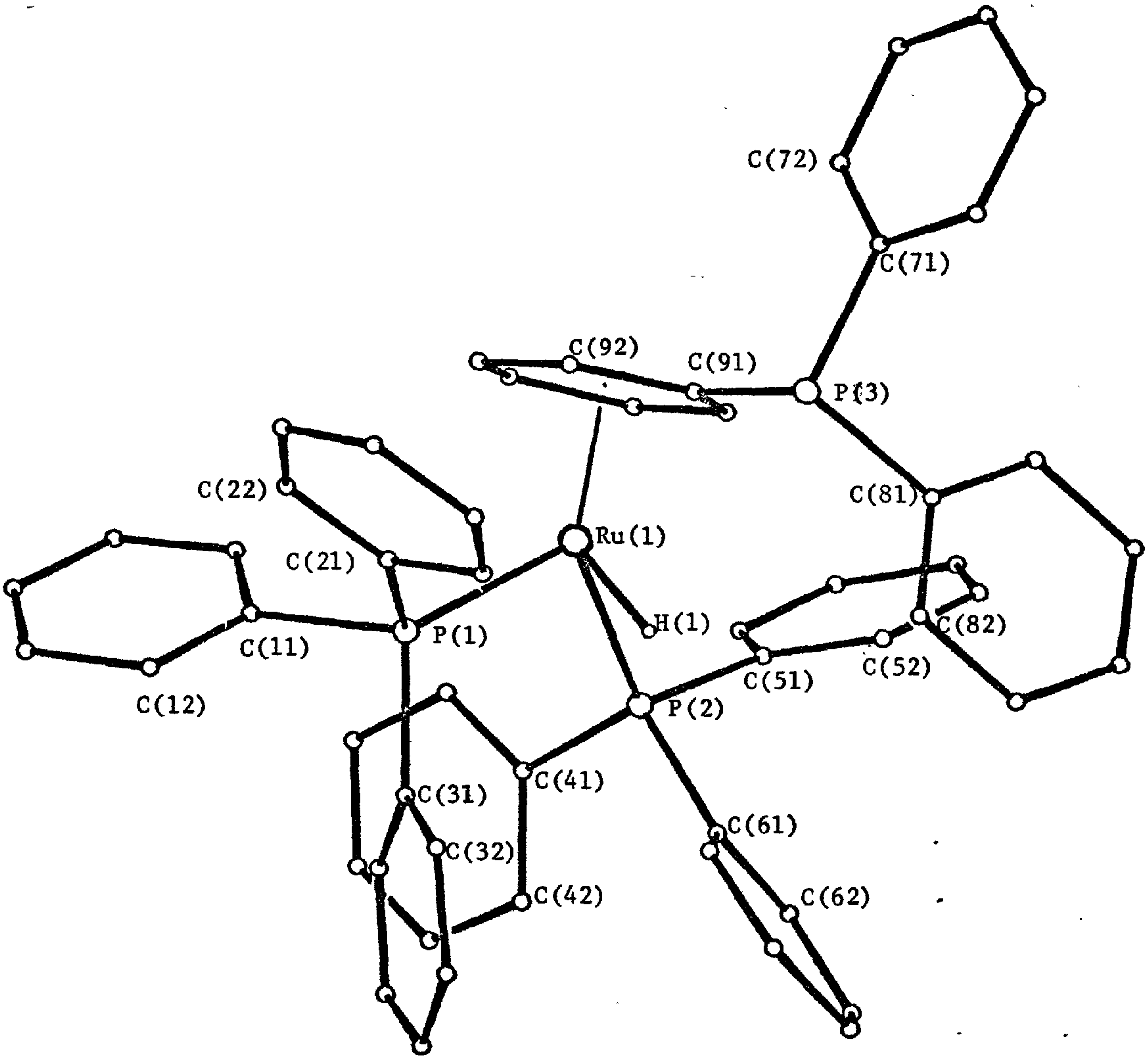
The unrefined co-ordinates of the hydrogen atoms are given in Table 3. Observed and calculated structure amplitudes are listed at the end of the chapter.

Description of the Structure and Discussion

Figure 1 shows the structure of the cation. The central metal atom may be considered to have a distorted tetrahedral co-ordination if the centre of gravity of the η-bonded phenyl ring is considered as a single co-ordination position. The remaining phosphorus atoms of the two σ-bonded triphenylphosphines together with the hydride hydrogen complete the co-ordination about the metal. The more important bond lengths and bond angles are quoted in Tables 4 and 5 respectively.

The two cis Ru-P distances [Ru(1)-P(1) 2.312Å and Ru(1)-P(2) 2.331Å] are similar and of the order expected for normal cis P-bonded triphenylphosphines. The range of literature values for Ru-P bonds vary between 2.2-2.45Å; the long end of the range being usually associated with trans influences and steric effects [a value of 2.425Å is found in $Ru(NPEt_2Ph)C\ell_3(PEt_2Ph)_2$[14] which shows a predominant trans effect] whilst the shorter end may be considered characteristic of the apical third Ru-P bond in five co-ordinate complexes usually associated with two longer Ru-P trans bonds.[15,16,17] The distances to which the present structural values are more directly comparable may be considered to be those of Ru-P (cis to P) which are intermediate in the range; e.g. a mean of 2.326Å in $Ru(pyS)_2(PPh_3)_2$[18] and 2.346Å in $Ru(HCS)_2(PPh_3)_2$.[19] The P(1)-Ru(1)-P(2) angle is 98.68(4)° whilst the P(1)-Ru(1)-H(1) and P(2)-Ru(1)-H(1) are 81° and 76° respectively. The stereochemistry may thus be regarded as quasi-tetrahedral or distorted octahedral whichever one may prefer. This almost symmetrical placement of the hydride hydrogen relative to the two metal-bonded P atoms is expected and the reduction in angle may be explained by the presence of a large flat arene ring close to the Ru atom which pushes the other three ligand atoms together to give less than tetrahedral

Figure 1.



Atoms are numbered in sequence around each ring in the order C(<u>m</u>1) - C(<u>m</u>6), where <u>m</u> is the number of the ring. Atoms C(<u>m</u>3) - C(<u>m</u>6) have been omitted for the sake of clarity.

angles between them. The metal-carbon (arene) bond lengths average 2.269Å whilst the distance of the ruthenium atom to the calculated centre of the arene ring is 1.777Å. These values may be compared to the mean metal-carbon distance of 2.208Å in the structure of $(\pi\text{-}C_5H_5)Ru(BPh_4)$.[20] The distance of the Ru atom from the plane through the six atoms of the arene ring is 1.701Å. In this latter structure, the packing constraints are less severe (no bulky triphenylphosphine groups) thus the ring is more strongly bonded to the metal than in the present case. Additionally the present value of 1.777Å is rather longer than the value of 1.726Å in $(C_6H_6)Cr(CO)_3$[22] confirming this steric effect.

It is also notable that the carbon-carbon bond lengths in the arene (average = 1.411Å) are greater than those in the unbound rings (average = 1.384Å) which indicates the drift of the π-cloud towards the ruthenium atom with a consequential slight decrease in bond order around the ring. The corresponding values in $(\pi\text{-}C_5H_5)Ru(BPh_4)$[20] are 1.408Å and 1.379Å respectively and thus confirm a similar effect present in the structure. The above values compare quite well with that of 1.401Å observed in the planar ring of bis(hexamethylbenzene)ruthenium(0).[23] The arene ring of the present structure is almost planar, the largest deviation from the plane of all six carbons being 0.017Å. The plane of $(\pi\text{-}C_5H_5)Ru(BPh_4)$[20] is also nearly planar (max. deviation is 0.011Å) and compares reasonably well with the present structure. In the case of the complex $Rh[P(OCH_3)_3]B(C_6H_5)_4$, the η-phenyl ring is not planar and may best be described as boat-shaped with two of the carbon atoms tilted out of the plane of the best four atoms away from the Rh atom. (deviations: C(51) 0.093Å and C(54) 0.060Å). There is some considerable variation in the bending at the C(*m*1) carbon atoms of the phenyl rings in that each phosphorus atom lies reasonably close to two of its three rings (max. deviation = 0.098Å) whilst the third ring deviates to nearly twice this distance from the plane (max. deviation = 0.185Å). The deviations shown at P(3) are significantly greater than those of P(1), P(2). This is probably a crystal packing effect. The planarity of the phenyl rings are shown in Table 6 together with the distances of the respective phosphorus atoms from the planes.

The position of the hydride hydrogen has been optimised and the Ru(1)-H(1) bond length of 1.67Å agrees very well with that of 1.68Å in $RuH(CO_2Me)(PPh_3)_3$,[15] 1.68Å in $RuHC\ell(PPh_3)_3$[16] and of 1.67Å in RuH(napthyl) [2-bis(dimethylphosphino)ethane].[24 25]

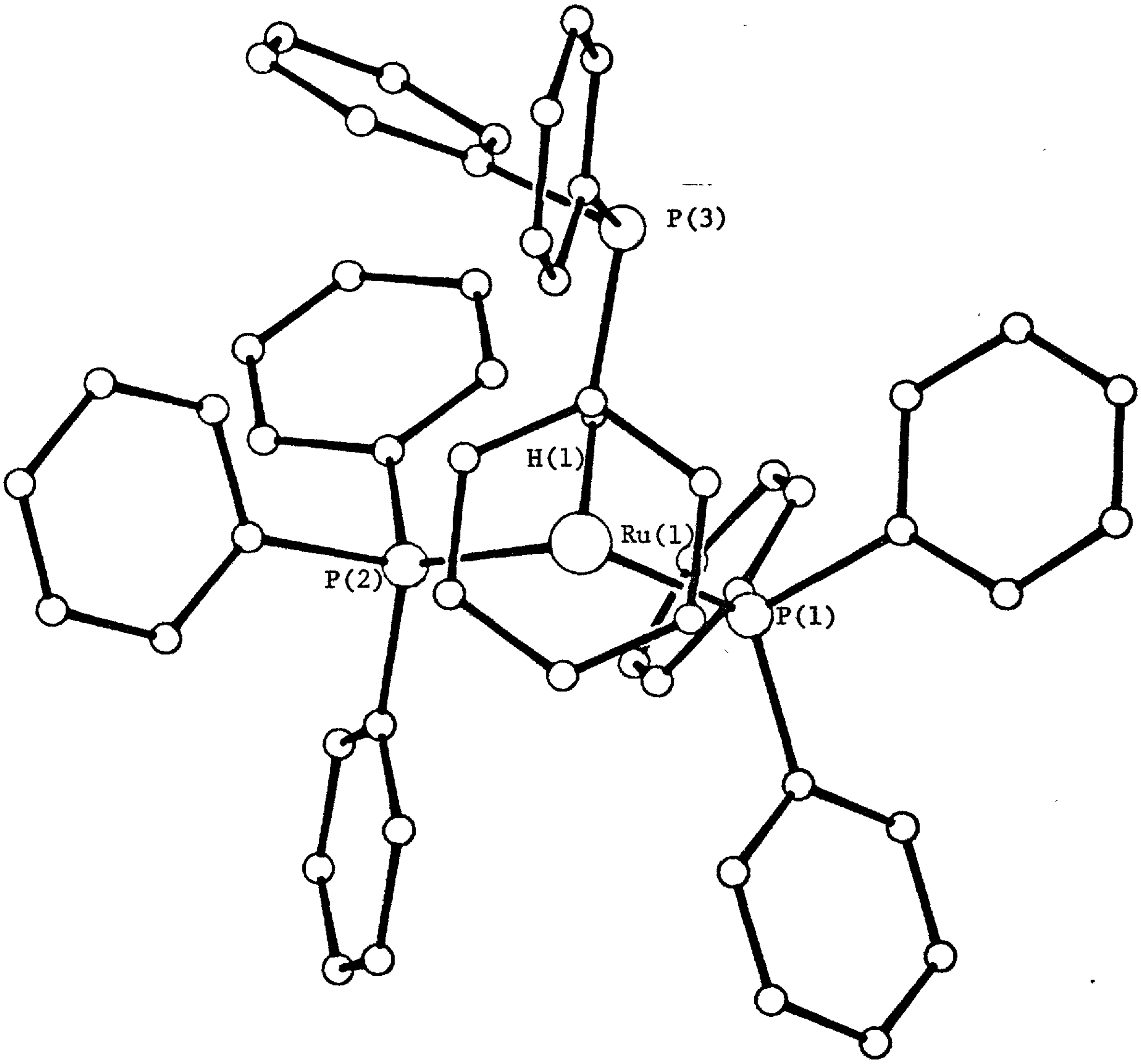
The mean P-C distance of 1.834Å is similar to that found in many transition-metal complexes. However, there are small variations between these bonds, and the bond angles at phosphorus, which may be related to the degree of distortion from ideal tetrahedral geometry at P. This mean value can be compared to the means obtained in $RuH(CO_2Me)(PPh_3)_3$[15] - 1.841Å; $RuHC\ell(PPh_3)_3$ - 1.841Å[16] and in $Ru(PPh_3)_2(pyS)_2$ - 1.845Å[18]. P-C (phenyl) distances are appreciably shorter in a less distorted tetrahedral environment found in the benzyl-triphenylphosphonium ion[26] where the mean P-C (phenyl) distance is 1.790Å. The present structure has mean values of 115.7° for Ru(1)-P-C and of 102.3° for C-P-C valence angles respectively which may be considered as normal for this type of complex. Means of 116.4° and 101.5° are reported in the related structure of $RuH(CO_2Me)(PPh_3)_3$.[15]

Fig. 2 shows a view of the Ru-atom and the arene ring in projection. It is notable that the alignment of the Ru(1)-H(1) is in the same direction as P(3)-C(91).

The molecular packing is shown in the stereoscopic view (Fig. 3) which was drawn using the ORTEP program.[27] Although the present structure has been compared with its most directly related structures, there still remains another structure which deserves mention; the structure of the triclinic complex $Mo(PMe_2Ph)_3(\eta\text{-}PhPMe_2)$[28] is of interest (although it has not been determined very accurately) in that it also displays π-bonding

Fig. 2

A view normal to the plane of the arene ring showing the alignment of the hydride hydrogen with the P(3)-C(91) vector.



of a phenyl ring as an arene to a metal as in the present structure. The metal-carbon (arene) bond lengths average 2.28(2)Å which is considerably shorter than one might have anticipated from a comparison with the value of the mean π-cyclopentadienyl Mo-C bond lengths of 2.37Å in $(\pi\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$.[29] The arene ring in this structure is nearly planar with little variation in C-C bond length (mean value of 1.43Å).

The complex cation in the present structural study is inherently stable thermodynamically owing to its achievement of a rare gas configuration. It seems that the Ru-atom strives to obtain this energetically favourable state and will thus bind with any six electron donor system to form a stable complex.

Fig. 3

A stereoscopic view of the unit-cell showing the packing of the molecules.

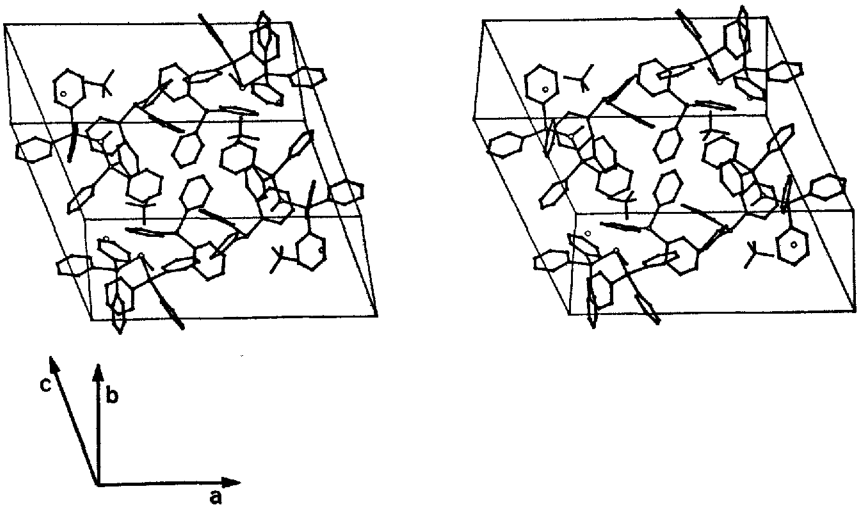


Table 1.

Fractional co-ordinates of non-hydrogen atoms with estimated standard deviations in parentheses.

All ring carbon atoms are numbered C(mn) where m is the ring number and n is the atom number in the ring; n is such that C(m1) is attached to the P atom and other ring atoms are numbered in succession such that C(m4) is *para* to C(m1). The π-bonded phenyl ring is C(9n).

	x	*y*	*z*
Ru(1)	0.24136(2)	0.16770(3)	0.24150(2)
P(1)	0.14874(5)	0.05966(9)	0.22744(6)
P(2)	0.24010(6)	0.16796(10)	0.11580(6)
P(3)	0.40391(6)	0.10245(10)	0.39084(6)
C(11)	0.0641(2)	0.1173(4)	0.2115(2)
C(12)	- 0.0087(2)	0.0529(5)	0.2044(3)
C(13)	- 0.0554(3)	0.0967(7)	0.1924(3)
C(14)	- 0.0641(3)	0.2041(8)	0.1867(3)
C(15)	- 0.0100(3)	0.2668(6)	0.1919(3)
C(16)	0.0542(3)	0.2242(5)	0.2043(3)
C(21)	0.1646(2)	- 0.0106(4)	0.3180(2)
C(22)	0.1263(2)	0.0070(4)	0.3652(3)
C(23)	0.1430(3)	- 0.0442(5)	0.4358(3)
C(24)	0.1966(3)	- 0.1125(5)	0.4578(3)
C(25)	0.2348(3)	- 0.1291(4)	0.4112(3)
C(26)	0.2200(2)	- 0.0779(4)	0.3429(3)
C(31)	0.1265(2)	- 0.0416(4)	0.1539(2)
C(32)	0.0919(2)	- 0.0073(4)	0.0802(2)
C(33)	0.0792(2)	- 0.0788(5)	0.0191(3)
C(34)	0.0999(3)	- 0.1803(5)	0.0323(3)
C(35)	0.1326(3)	- 0.2147(4)	0.1052(3)
C(36)	0.1456(2)	- 0.1467(4)	0.1663(3)
C(41)	0.1613(2)	0.2081(5)	0.0425(3)
C(42)	0.1361(3)	0.1629(6)	- 0.0290(3)
C(43)	0.0757(5)	0.2026(12)	- 0.0806(5)
C(44)	0.0412(5)	0.2814(13)	- 0.0618(8)

/Continued ......

C(45)	0.0641(4)	0.3257(8)	0.0079(6)
C(46)	0.1251(3)	0.2876(6)	0.0602(3)
C(51)	0.3015(2)	0.2643(4)	0.1045(2)
C(52)	0.3701(2)	0.2390(4)	0.1317(2)
C(53)	0.4188(2)	0.3110(4)	0.1299(3)
C(54)	0.3994(2)	0.4101(4)	0.1007(2)
C(55)	0.3321(3)	0.4350(4)	0.0729(3)
C(56)	0.2826(2)	0.3628(4)	0.0740(3)
C(61)	0.2681(3)	0.0522(4)	0.0771(3)
C(62)	0.2872(4)	0.0624(6)	0.0117(4)
C(63)	0.3104(5)	- 0.0247(8)	- 0.0176(5)
C(64)	0.3147(5)	- 0.1188(7)	0.0160(6)
C(65)	0.2959(4)	- 0.1308(5)	0.0809(5)
C(66)	0.2733(3)	- 0.0446(4)	0.1103(3)
C(71)	0.4617(2)	0.1929(4)	0.4581(2)
C(72)	0.4465(3)	0.2953(5)	0.4696(3)
C(73)	0.4916(3)	0.3563(5)	0.5249(3)
C(74)	0.5533(3)	0.3131(6)	0.5704(3)
C(75)	0.5685(3)	0.2128(6)	0.5597(3)
C(76)	0.5231(2)	0.1514(4)	0.5048(3)
C(81)	0.4469(2)	0.0840(4)	0.3190(2)
C(82)	0.4272(3)	- 0.0034(5)	0.2734(3)
C(83)	0.4620(4)	- 0.0276(5)	0.2218(3)
C(84)	0.5149(4)	0.0333(6)	0.2192(4)
C(85)	0.5335(3)	0.1201(6)	0.2637(4)
C(86)	0.4998(3)	0.1465(4)	0.3138(3)
C(91)	0.3334(2)	0.1921(4)	0.3447(2)
C(92)	0.2750(2)	0.1854(4)	0.3684(2)
C(93)	0.2197(2)	0.2529(4)	0.3373(3)
C(94)	0.2219(3)	0.3314(4)	0.2848(3)
C(95)	0.2795(3)	0.3368(4)	0.2606(3)
C(96)	0.3349(2)	0.2678(4)	0.2904(2)
B(1)	0.7291(4)	0.1277(6)	0.2451(4)
F(1)	0.6805(2)	0.0636(3)	0.2011(2)
F(2)	0.7496(3)	0.0917(5)	0.3174(3)
F(3)	0.7856(3)	0.1303(6)	0.2275(4)
F(4)	0.7060(3)	0.2247(4)	0.2433(4)
O(1)*	0.8948(5)	0.0063(7)	0.3444(6)

* Probably a trace of the solvated methanol; the occupancy factor of this atom was fixed at one half.

Table 2

Anisotropic thermal parameters

	$10^4\underline{U}_{11}$	$10^4\underline{U}_{22}$	$10^4\underline{U}_{33}$	$10^4\underline{U}_{12}$	$10^4\underline{U}_{13}$	$10^4\underline{U}_{23}$
Ru(1)	430(2)	534(3)	331(2)	16(2)	132(1)	-4(2)
P(1)	401(6)	602(7)	389(6)	70(5)	135(5)	54(5)
P(2)	532(7)	742(9)	358(6)	-140(6)	142(5)	0(6)
P(3)	526(7)	641(8)	414(6)	53(6)	100(5)	36(6)

	$10^3\underline{U}_{11}$	$10^3\underline{U}_{22}$	$10^3\underline{U}_{33}$	$10^3\underline{U}_{12}$	$10^3\underline{U}_{13}$	$10^3\underline{U}_{23}$
C(11)	50(3)	80(4)	44(2)	16(3)	17(2)	5(2)
C(12)	42(3)	106(4)	69(3)	7(3)	20(2)	4(3)
C(13)	56(3)	165(7)	77(4)	5(4)	26(3)	5(4)
C(14)	66(4)	163(7)	71(4)	48(5)	17(3)	-3(4)
C(15)	78(4)	124(5)	70(4)	49(4)	11(3)	-3(4)
C(16)	64(3)	92(4)	61(3)	30(3)	16(2)	4(3)
C(21)	47(2)	66(3)	42(2)	-1(2)	15(2)	3(2)
C(22)	61(3)	72(3)	49(3)	-6(2)	20(2)	2(2)
C(23)	84(4)	89(4)	49(3)	-15(3)	31(3)	13(3)
C(24)	78(4)	91(4)	52(3)	-13(3)	10(3)	23(3)
C(25)	61(3)	82(4)	65(3)	-12(3)	7(3)	27(3)
C(26)	50(3)	75(3)	54(3)	2(3)	12(2)	15(3)
C(31)	39(2)	62(3)	51(2)	-4(2)	19(2)	-3(2)
C(32)	42(2)	85(3)	41(2)	-6(2)	11(2)	7(2)
C(33)	56(3)	89(4)	51(3)	-4(3)	16(2)	1(3)
C(34)	59(3)	92(4)	65(3)	-7(3)	19(3)	-17(3)
C(35)	67(3)	65(3)	81(4)	-2(3)	25(3)	-10(3)
C(36)	57(3)	68(3)	57(3)	1(2)	17(2)	-1(3)
C(41)	56(3)	130(5)	50(3)	-32(3)	6(2)	28(3)
C(42)	100(5)	179(7)	46(3)	-77(5)	-3(3)	29(4)
C(43)	117(7)	302(16)	59(4)	-138(9)	-21(5)	64(7)
C(44)	64(5)	318(19)	133(10)	-44(7)	-5(5)	132(12)
C(45)	61(4)	219(10)	133(7)	2(5)	17(4)	95(7)
C(46)	52(3)	152(6)	87(4)	-3(3)	14(3)	54(4)
C(51)	56(3)	68(3)	33(2)	-11(2)	13(2)	1(2)
C(52)	58(3)	71(3)	47(2)	-6(3)	22(2)	2(2)
C(53)	52(3)	78(4)	57(3)	-7(3)	21(2)	-6(3)
C(54)	65(3)	74(4)	52(3)	-17(3)	21(2)	-1(3)

Table 2 (Continued)

	$10^3\underline{U}_{11}$	$10^3\underline{U}_{22}$	$10^3\underline{U}_{33}$	$10^3\underline{U}_{12}$	$10^3\underline{U}_{13}$	$10^3\underline{U}_{23}$
C(55)	74(3)	66(3)	64(3)	-8(3)	20(3)	10(3)
C(56)	56(3)	76(4)	54(3)	-4(3)	14(2)	9(3)
C(61)	88(3)	86(4)	59(3)	-36(3)	46(3)	-33(3)
C(62)	177(7)	128(6)	89(4)	-78(5)	93(5)	-57(4)
C(63)	234(10)	148(8)	154(7)	-107(7)	150(8)	-94(7)
C(64)	186(8)	124(7)	221(10)	-88(7)	156(8)	-112(7)
C(65)	113(5)	97(5)	156(6)	-43(4)	91(5)	-68(5)
C(66)	67(3)	81(4)	81(3)	-24(3)	42(3)	-30(3)
C(71)	58(3)	71(4)	44(2)	-3(2)	18(2)	4(2)
C(72)	79(3)	78(4)	48(3)	-7(3)	9(2)	-4(3)
C(73)	108(5)	89(4)	64(3)	-20(4)	25(3)	-10(3)
C(74)	75(4)	137(6)	57(3)	-38(4)	22(3)	-18(4)
C(75)	54(3)	138(6)	58(3)	-14(4)	16(3)	-7(4)
C(76)	50(3)	101(4)	53(3)	0(3)	12(2)	3(3)
C(81)	60(3)	74(3)	41(2)	16(3)	10(2)	3(3)
C(82)	72(3)	88(4)	54(3)	24(3)	10(3)	-1(3)
C(83)	100(5)	103(5)	64(4)	36(4)	19(3)	-9(3)
C(84)	100(5)	119(6)	72(4)	41(4)	38(4)	21(4)
C(85)	90(4)	116(5)	77(4)	20(4)	44(3)	22(4)
C(86)	73(3)	86(4)	61(3)	10(3)	28(3)	13(3)
C(91)	53(2)	59(3)	34(2)	0(2)	8(2)	-6(2)
C(92)	56(3)	72(3)	35(2)	4(3)	16(2)	-1(2)
C(93)	64(3)	78(4)	51(3)	4(3)	24(2)	-17(3)
C(94)	73(3)	68(3)	60(3)	16(3)	14(3)	-6(3)
C(95)	75(3)	61(3)	51(3)	0(3)	12(2)	-7(2)
C(96)	61(3)	53(3)	39(2)	1(2)	11(2)	-1(2)
B(1)	88(5)	78(5)	90(5)	-11(4)	15(4)	2(4)
F(1)	87(2)	93(2)	114(3)	-9(2)	-4(2)	0(2)
F(2)	267(7)	239(7)	97(3)	-138(6)	-13(4)	32(4)
F(3)	120(4)	277(7)	242(7)	-54(4)	93(4)	-69(5)
F(4)	151(4)	97(3)	269(7)	-16(3)	26(4)	-18(4)
O(1)	144(8)	83(6)	122(7)	-7(5)	18(6)	-7(5)

Table 3

Fractional co-ordinates of the hydrogen atoms. Except for H(1), these are numbered according to the carbon atom to which they are attached.

	x	y	z
H(1)	0.276	0.053	0.231
H(12)	0.015	- 0.025	0.208
H(13)	- 0.096	0.050	0.189
H(14)	- 0.110	0.236	0.178
H(15)	- 0.017	0.344	0.186
H(16)	0.094	0.272	0.208
H(22)	0.086	0.057	0.349
H(23)	0.115	- 0.031	0.470
H(24)	0.208	- 0.149	0.508
H(25)	0.275	- 0.180	0.427
H(26)	0.250	- 0.089	0.310
H(32)	0.067	0.037	0.034
H(33)	0.054	- 0.036	- 0.027
H(34)	0.091	- 0.231	- 0.011
H(35)	0.147	- 0.290	0.114
H(36)	0.168	- 0.153	0.222
H(42)	0.161	0.103	- 0.043
H(43)	0.059	0.169	- 0.134
H(44)	- 0.002	0.303	- 0.101
H(45)	0.037	0.385	0.020
H(46)	0.142	0.322	0.112
H(52)	0.384	0.167	0.153
H(53)	0.468	0.292	0.150
H(54)	0.435	0.463	0.100
H(55)	0.318	0.507	0.051
H(56)	0.233	0.382	0.053
H(62)	0.289	0.122	- 0.023
H(63)	0.312	0.034	- 0.052
H(64)	0.322	- 0.195	0.029

/Continued ....

	x	y	z
H(65)	0.304	- 0.207	0.096
H(66)	0.259	- 0.053	0.157
H(72)	0.402	0.327	0.437
H(73)	0.480	0.430	0.534
H(74)	0.586	0.358	0.610
H(75)	0.613	0.183	0.592
H(76)	0.535	0.077	0.498
H(82)	0.389	- 0.050	0.277
H(83)	0.446	- 0.090	0.187
H(84)	0.540	0.012	0.183
H(85)	0.573	0.164	0.260
H(86)	0.514	0.210	0.347
H(92)	0.274	0.132	0.407
H(93)	0.178	0.245	0.352
H(94)	0.183	0.382	0.265
H(95)	0.282	0.390	0.222
H(96)	0.376	0.273	0.273

Table 4

Selected bond lengths (Å), with estimated standard deviations in parentheses.

Ru(1) - P(1)	2.312(1)	Ru(1) - C(91)	2.245(4)
Ru(1) - P(2)	2.331(1)	Ru(1) - C(92)	2.244(4)
Ru(1) - H(1)	1.67	Ru(1) - C(93)	2.256(5)
Ru(1) - C*	1.777	Ru(1) - C(94)	2.324(5)
		Ru(1) - C(95)	2.290(5)
Mean Ru - C	2.269	Ru(1) - C(96)	2.254(4)

.... where C* is the centroid of the η-bonded phenyl ring.

P(1) - C(11)	1.837(5)	P(2) - C(61)	1.822(6)
P(1) - C(21)	1.841(4)	P(3) - C(71)	1.833(4)
P(1) - C(31)	1.830(4)	P(3) - C(81)	1.848(5)
P(2) - C(41)	1.827(4)	P(3) - C(91)	1.836(4)
P(2) - C(51)	1.833(5)	Mean P - C	1.834

Mean phenyl C - C bonds.

Ring		Ring	
C(1<u>n</u>)	1.381	C(5<u>n</u>)	1.379
C(2<u>n</u>)	1.381	C(6<u>n</u>)	1.381
C(3<u>n</u>)	1.389	C(7<u>n</u>)	1.382
C(4<u>n</u>)	1.377	C(8<u>n</u>)	1.380
Overall mean			1.381

η-bonded ring C(9<u>n</u>), individual values.

C(91) - C(92)	1.421(7)	C(94) - C(95)	1.409(9)
C(92) - C(93)	1.401(6)	C(95) - C(96)	1.411(7)
C(93) - C(94)	1.412(8)	C(96) - C(91)	1.408(6)
Overall mean			1.411

Table 5

Selected bond angles ($^{\circ}$), with estimated standard deviations in parentheses.

P(1) - Ru(1) - P(2)	98.68(4)	Ru(1) - P(1) - C(11)	119.62(17)
P(1) - Ru(1) - H(1)	81	Ru(1) - P(1) - C(21)	107.12(13)
P(2) - Ru(1) - H(1)	76	Ru(1) - P(1) - C(31)	120.35(15)
P(1) - Ru(1) - C*	127.92(4)	Ru(1) - P(2) - C(41)	117.60(19)
P(2) - Ru(1) - C*	128.95(4)	Ru(1) - P(2) - C(51)	109.63(13)
H(1) - Ru(1) - C*	125	Ru(1) - P(2) - C(61)	119.69(17)

Ru(1) - C* — P(3) 89.64(2)

Mean Ru - P - C (rings 1 to 6) 115.67

C(11) - P(1) - C(21)	102.7(2)	C(51) - P(2) - C(61)	100.2(3)
C(11) - P(1) - C(31)	99.7(2)	C(71) - P(3) - C(81)	102.2(2)
C(21) - P(1) - C(31)	105.4(2)	C(71) - P(3) - C(91)	99.8(2)
C(41) - P(2) - C(51)	102.2(2)	C(81) - P(3) - C(91)	103.9(2)
C(41) - P(2) - C(61)	104.8(2)		

Mean C - P - C (rings 1 to 9) 102.32

Table 6

Planarity of groups of atoms in the molecule and distances (Å) from calculated least-square planes. Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space.

				Deviations (Å) of atoms from plane	
P	Q	R	S	Atoms defining plane	Not defining plane
-2.95	0.81	18.24	3.75	C(11) 0.010; C(12)-0.008; C(13)-0.001 C(14) 0.008; C(15)-0.006; C(16)-0.004	P(1) 0.005
10.06	9.67	4.78	3.08	C(21)-0.011; C(22)-0.001; C(23) 0.009 C(24)-0.007; C(25)-0.006; C(26) 0.014	P(1) 0.076
20.07	2.97	-7.73	1.21	C(31) 0.014; C(32)-0.008; C(33)-0.003 C(34) 0.008; C(35)-0.002; C(36)-0.009	P(1) 0.194
13.90	8.45	-10.02	3.57	C(14) 0.007; C(42)-0.009; C(43) 0.004 C(44) 0.001; C(45) 0.001; C(46) 0.000	P(1) 0.029
-5.59	4.19	17.56	1.25	C(51) 0.009; C(52)-0.003; C(53)-0.005 C(54) 0.007; C(55) 0.000; C(56)-0.008	P(2) 0.147
16.50	2.63	5.22	4.96	C(61)-0.001; C(62)-0.001; C(63)-0.001 C(64) 0.000; C(65)-0.003; C(66) 0.003	P(2) 0.043
-14.31	-3.79	15.81	-0.09	C(71)-0.008; C(72) 0.003; C(73) 0.000 C(74) 0.001; C(75)-0.005; C(76) 0.009	P(3) 0.098
9.10	-7.11	9.76	6.58	C(81) 0.006; C(82) 0.003; C(83)-0.012 C(84) 0.011; C(85)-0.002; C(86)-0.007	P(3) 0.185
3.86	8.27	11.88	6.96	C(91) 0.006; C(92) 0.006; C(93)-0.017 C(94) 0.016; C(95)-0.003; C(96)-0.007	P(3) 0.085 Ru(1)-1.776

CHAPTER V

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant k and ℓ and list values of h, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

H,0,0

1	35*	90
2	2598	2781
3	1205	1181
4	2238	2404
5	1614	1575
6	2298	2269
7	729	733
8	957	973
9	441	427
10	1262	1285
11	1398	1456
12	773	770

H,0,2

-12	760	746
-11	772	789
-10	945	986
-9	180	195
-8	985	1038
-7	564	570
-6	346	329
-5	1677	1742
-4	1357	1439
-3	571	688
-2	2588	2567
-1	344	332
0	2529	2431
1	1173	1101
2	1287	1428
3	923	1039
4	2954	3110
5	708	751
6	1457	1440
7	1323	1352
8	1351	1384
9	1139	1176
10	1316	1357
11	874	909

H,0,4

-12	633	659
-11	234	252
-10	1076	1120
-9	604	642
-8	700	711
-7	416	418
-6	295	255
-5	1434	1574
-4	3893	4046
-3	1869	1908
-2	909	963
-1	1010	1160
0	2009	2168
1	664	625
2	145	107
3	78	17
4	658	632
5	83	101
6	214	190
7	868	861
8	452	474
9	947	919

H,0,6

-12	860	917
-11	283	248
-10	411	429
-9	100	98
-8	685	730
-7	1398	1430
-6	1996	2044
-5	786	789
-4	657	676
-3	156	110
-2	2926	3043
-1	171	203
0	1810	1871
1	852	824
2	1086	1117
3	93	49
4	1272	1268
5	322	300
6	1361	1380
7	125	140
8	1052	1111

H,0,8

-11	281	254
-10	460	459
-9	764	831
-8	1449	1496
-7	262	250
-6	1135	1245
-5	301	301
-4	1137	1186
-3	631	641
-2	2188	2208
-1	1628	1651
0	893	948
1	192	201
2	1138	1171
3	834	884
4	526	540
5	786	768

H,0,10

-9	43*	52
-8	1141	1146
-7	112	158
-6	873	916
-5	511	552
-4	744	744
-3	893	878
-2	1737	1828
-1	535	569
0	295	294
1	774	783
2	443	442

H,1,0

1	2558	2774
2	391	422
3	791	820
4	154	142
5	1328	1402
6	1028	1056
7	1294	1377
8	56	52
9	1088	1167
10	416	439
11	1078	1113
12	785	780

H,1,1

-12	322	341
-11	441	468
-10	294	284
-9	982	1018
-8	509	504
-7	883	923
-6	253	282
-5	1116	1167
-4	710	735
-3	696	746
-2	556	679
-1	2235	2431
0	328	411
1	897	929
2	1366	1498
3	354	310
4	1686	1655
5	1462	1541
6	165	182
7	774	837
8	571	571
9	1021	1041
10	540	552
11	1014	1035

H,1,2

-12	157	127
-11	953	994
-10	308	299
-9	693	776
-8	794	788
-7	1332	1424
-6	162	136
-5	1364	1427
-4	255	286
-3	1112	1139
-2	380	365
-1	1184	1168
0	645	629
1	913	931
2	306	306
3	1520	1559
4	898	921
5	112	91
6	1142	1133
7	862	922
8	929	939
9	433	447
10	805	826
11	658	674

H,1,3

-12	431	428
-11	1037	1066
-10	137	158
-9	647	708
-8	320	342
-7	92	81
-6	625	618
-5	36*	54
-4	132	180
-3	388	329
-2	217	213
-1	232	233
0	362	289
1	1229	1309
2	126	94
3	280	276
4	801	774
5	219	199
6	305	317
7	333	302
8	39*	18
9	491	502
10	703	705

H,1,4

-12	432	441
-11	975	1054
-10	371	386
-9	1047	1097
-8	318	342
-7	885	860
-6	535	519
-5	583	553
-4	356	352
-3	121	63
-2	2750	2635
-1	1828	1787
0	48	31
1	1064	1043
2	350	371
3	1604	1648
4	277	263
5	399	427
6	492	482
7	202	201
8	78	57
9	1238	1255

H,1,5

-12	171	165
-11	1487	1539
-10	139	154
-9	185	198
-8	114	140
-7	231	202
-6	571	601
-5	623	611
-4	768	779
-3	532	483
-2	707	639
-1	397	384
0	1684	1684
1	248	212
2	482	451
3	482	528
4	359	374
5	461	477
6	56	32
7	608	589
8	69	54
9	399	418

H,1,6

-12	518	565
-11	896	946
-10	209	235
-9	314	320
-8	74	14
-7	975	952
-6	542	546
-5	973	992
-4	468	450
-3	1008	1007
-2	644	605
-1	2349	2314
0	615	602
1	470	478
2	614	585
3	819	836
4	168	149
5	792	767
6	324	342
7	1182	1210
8	52	32

H,1,7

-12	427	445
-11	645	672

	H,1,7	
-10	274	314
-9	597	578
-8	324	372
-7	1480	1428
-6	89	91
-5	660	650
-4	602	555
-3	1138	1090
-2	43	27
-1	1385	1366
0	956	946
1	518	540
2	220	185
3	371	409
4	152	183
5	673	672
6	213	184
	H,1,8	
-11	1191	1215
-10	174	143
-9	1125	1142
-8	406	380
-7	1407	1398
-6	36*	1
-5	1093	1069
-4	209	203
-3	1155	1059
-2	918	932
-1	1745	1760
0	1124	1138
1	1131	1153
2	362	375
3	851	854
4	845	885
5	1117	1130
	H,1,9	
-10	218	238
-9	629	632
-8	215	186
-7	587	590
-6	480	508
-5	205	170
-4	943	898
-3	820	793
-2	845	837
-1	1203	1242
0	1083	1116
1	292	294
2	846	882
3	126	110
4	516	534
	H,1,10	
-9	919	912
-8	266	245
-7	979	982
-6	260	281
-5	785	759
-4	498	529
-3	1051	1039
-2	373	389
-1	811	806
0	470	513
1	522	493
2	750	790
	H,1,11	
-7	197	191
-6	117	122
-5	276	246
-4	196	190
-3	948	936
-2	46*	5
-1	183	156
	H,2,0	
0	1387	1501
1	97	31
2	586	585
3	634	635
4	1366	1481
5	482	441
6	921	990
7	796	826
8	203	216
9	350	398
10	645	671
11	260	290
	H,2,1	
-12	874	910
-11	491	474
-10	1019	1057
-9	700	713
-8	1331	1366
-7	609	605
-6	1635	1644
-5	167	147
-4	3045	3180
-3	1297	1296
-2	1805	1784
-1	38	86
0	2929	2973
1	498	491
2	224	202
3	1580	1652
4	757	794
5	394	426
6	708	743
7	809	781
8	322	359
9	878	886
10	1042	1037
11	850	886
	H,2,2	
-12	843	851
-11	238	221
-10	116	125
-9	162	128
-8	95	105
-7	643	641
-6	777	808
-5	797	778
-4	1841	1777
-3	1797	1716
-2	2291	2300
-1	221	202
0	185	142
1	357	418
2	1950	1894
3	1474	1559
4	448	476
5	746	756
6	765	822
7	975	990
8	665	672
9	144	156
10	249	259
	H,2,3	
-12	435	430
-11	270	242
-10	873	886
-9	204	194
-8	1025	1028
-7	265	275
-6	1493	1447
-5	1161	1197
-4	113	71
-3	488	517
-2	2176	2124
-1	828	792
0	2999	3078
1	833	806
2	872	887
3	1225	1269
4	1371	1393
5	137	142
6	128	87
7	712	727
8	65	41
9	648	663
10	588	626
	H,2,4	
-12	43	20
-11	374	352
-10	213	211
-9	629	637
-8	741	770
-7	579	545
-6	1110	1082
-5	1322	1265
-4	545	558
-3	889	873
-2	400	339
-1	707	625
0	250	185
1	287	219
2	1168	1177
3	322	367
4	288	335
5	877	874
6	785	806
7	65	46
8	284	293
9	54	27
	H,2,5	
-12	513	521
-11	911	882
-10	852	883
-9	177	154
-8	88	21
-7	211	207
-6	108	116
-5	535	516
-4	2027	1995
-3	939	972
-2	129	58
-1	703	657
0	594	579
1	835	825
2	1098	1120
3	690	676
4	378	404
5	420	434
6	533	545
7	449	451
8	1363	1403
	H,2,6	
-12	166	146
-11	161	194
-10	56	46
-9	675	674
-8	122	142
-7	292	269
-6	739	719
-5	36*	8
-4	410	406
-3	559	610
-2	1485	1412
-1	582	569
0	656	659
1	53	69
2	604	662
3	392	357
4	860	882
5	206	184
6	552	598
7	62	81
	H,2,7	
-11	79	76
-10	877	882
-9	421	379
-8	811	810
-7	395	426
-6	1482	1479
-5	873	816
-4	450	486
-3	720	658
-2	2098	2076
-1	282	267
0	1374	1407
1	917	877
2	699	735
3	519	530
4	343	360
5	784	784
6	769	787
	H,2,8	
-11	54	66
-10	704	742
-9	195	174
-8	866	942
-7	84	53
-6	470	488
-5	505	522
-4	775	757
-3	313	267
-2	952	948
-1	242	253
0	626	595
1	65	71
2	1319	1339
3	87	99
4	604	624
5	443	477
	H,2,9	
-10	770	752
-9	850	896
-8	1582	1579
-7	114	69
-6	245	250
-5	314	318
-4	879	863

H,2,9

-3	489	478
-2	1826	1807
-1	796	754
0	649	684
1	374	386
2	603	616
3	689	688

H,2,10

-8	592	601
-7	720	688
-6	939	953
-5	398	377
-4	323	325
-3	97	106
-2	191	172
-1	883	851
0	614	620
1	64	34

H,2,11

-5	101	100
-4	746	726
-3	110	89

H,3,0

1	1349	1288
2	474	474
3	766	797
4	450	440
5	423	436
6	362	365
7	593	569
8	1293	1315
9	130	123
10	84	54
11	112	105

H,3,1

-11	1057	1074
-10	190	187
-9	1335	1414
-8	542	500
-7	1255	1291
-6	1123	1095
-5	1043	1107
-4	514	483
-3	2430	2453
-2	441	511
-1	1426	1360
0	41	47
1	179	169
2	186	155
3	868	920
4	819	756
5	910	926
6	889	877
7	904	967
8	1041	1057
9	538	560
10	1016	1011

H,3,2

-11	310	287
-10	495	477
-9	326	332
-8	391	393
-7	324	317
-6	190	207
-5	504	505
-4	501	462
-3	448	446
-2	430	427
-1	409	386
0	93	71
1	836	831
2	1613	1632
3	512	533
4	342	362
5	243	243
6	845	850
7	825	820
8	600	583
9	163	143
10	71	86

H,3,3

-11	838	881
-10	270	276
-9	640	681
-8	621	599
-7	1800	1815
-6	657	647
-5	1175	1168
-4	441	482
-3	611	577
-2	60	53
-1	1081	1024
0	482	444
1	786	706
2	1327	1321
3	264	309
4	48	37
5	327	337
6	867	863
7	428	431
8	330	331
9	492	498

H,3,4

-11	437	441
-10	252	235
-9	426	414
-8	108	100
-7	38*	55
-6	151	129
-5	179	206
-4	102	105
-3	824	775
-2	139	139
-1	268	254
0	174	112
1	276	260
2	1021	1003
3	1012	1013
4	859	872
5	401	375
6	520	513
7	48	21
8	420	421

H,3,5

-11	565	574
-10	465	477
-9	375	405
-8	657	659
-7	556	573
-6	267	257
-5	1384	1365
-4	469	441
-3	949	882
-2	627	553
-1	759	732
0	520	473
1	211	191
2	899	885
3	921	899
4	82	100
5	455	434
6	1350	1365
7	599	633
8	365	342

H,3,6

-11	507	518
-10	382	404
-9	354	347
-8	203	186
-7	244	199
-6	308	300
-5	370	351
-4	563	539
-3	464	450
-2	321	346
-1	706	659
0	1044	1012
1	1173	1146
2	42	17
3	224	190
4	202	207
5	288	304
6	214	236
7	278	288

H,3,7

-11	1202	1242
-10	359	347
-9	1144	1162
-8	789	777
-7	1829	1813
-6	297	295
-5	1523	1454
-4	70	73
-3	1140	1032
-2	286	274
-1	867	843
0	382	387
1	1139	1116
2	679	683
3	1480	1477
4	659	674
5	701	735

H,3,8

-10	341	338
-9	131	128
-8	804	774
-7	116	90
-6	464	491
-5	740	678
-4	756	694
-3	41	16
-2	439	389
-1	924	846
0	319	316
1	182	191
2	429	451
3	139	136
4	379	366

H,3,9

-9	1345	1326
-8	113	88
-7	1390	1344
-6	535	542
-5	1241	1196
-4	960	920
-3	843	804
-2	721	700
-1	1160	1128
0	491	488
1	891	891
2	1030	1027

H,3,10

-7	810	754
-6	160	137
-5	211	207
-4	640	637
-3	794	783
-2	115	98
-1	108	87
0	88	110

H,4,0

0	885	892
1	859	808
2	1256	1262
3	420	443
4	1755	1726
5	664	676
6	1203	1206
7	699	686
8	569	622
9	275	276
10	170	171

H,4,1

-10	839	832
-9	434	457
-8	1021	1028
-7	726	735
-6	1768	1760
-5	57	62
-4	1769	1762
-3	162	159
-2	860	862
-1	369	327
0	518	523
1	95	76
2	1818	1853
3	139	128
4	1273	1309
5	347	353
6	858	928
7	1148	1191
8	598	613
9	257	283
10	572	580

H,4,2

-11	189	199
-10	682	687
-9	41*	49
-8	331	342
-7	575	552
-6	824	789
-5	39	39
-4	447	447
-3	288	256
-2	964	955

H,4,2

-1	281	284
0	99	116
1	367	400
2	624	575
3	759	757
4	680	691
5	293	285
6	901	939
7	100	89
8	366	380
9	490	479

H,4,3

-11	480	490
-10	157	156
-9	117	118
-8	787	791
-7	38*	6
-6	1721	1708
-5	494	465
-4	443	424
-3	184	171
-2	252	270
-1	351	364
0	216	194
1	47	48
2	730	748
3	37*	22
4	724	779
5	665	679
6	1365	1380
7	486	515
8	219	234

H,4,4

-11	251	253
-10	435	444
-9	179	179
-8	405	414
-7	415	403
-6	152	144
-5	95	62
-4	1027	975
-3	396	399
-2	942	931
-1	118	69
0	968	872
1	1103	1096
2	385	367
3	626	624
4	253	255
5	690	656
6	51	53
7	642	641
8	456	456

H,4,5

-10	695	711
-9	352	311
-8	630	681
-7	956	922
-6	212	228
-5	414	414
-4	734	754
-3	38*	52
-2	93	26
-1	196	195
0	289	339
1	225	217
2	514	567
3	238	233
4	974	956
5	706	690
6	1086	1111
7	74	56

H,4,6

-10	67	72
-9	474	454
-8	334	332
-7	97	92
-6	583	606
-5	553	537
-4	217	234
-3	402	371
-2	288	293
-1	394	377
0	613	624
1	488	446
2	1533	1546
3	391	385
4	642	624
5	733	733
6	622	624

H,4,7

-10	875	857
-9	1288	1226
-8	1348	1367
-7	293	240
-6	1700	1684
-5	343	377
-4	1079	1081
-3	733	730
-2	461	511
-1	366	342
0	823	844
1	219	233
2	1689	1664
3	207	201
4	1417	1422

H,4,8

-9	76	79
-8	427	416
-7	216	186
-6	630	645
-5	427	402
-4	486	485
-3	40*	6
-2	153	167
-1	197	192
0	782	794
1	42*	31
2	253	239
3	280	265

H,4,9

-7	165	196
-6	1134	1131
-5	764	737
-4	1200	1201
-3	767	737
-2	716	714
-1	683	690
0	1028	1015
1	845	842

H,5,0

1	1115	1115
2	194	162
3	1191	1250
4	45	48
5	1460	1499
6	163	153
7	1184	1185
8	411	407
9	507	506

H,5,1

-9	877	869
-8	114	133
-7	598	619
-6	374	407
-5	1031	1023
-4	165	129
-3	1087	1074
-2	38*	16
-1	561	576
0	568	567
1	973	962
2	442	403
3	605	613
4	38*	37
5	75	36
6	613	587
7	140	165
8	469	463
9	630	649

H,5,2

-9	638	658
-8	369	377
-7	1032	1038
-6	695	685
-5	1627	1602
-4	742	769
-3	1851	1787
-2	937	907
-1	1265	1212
0	211	213
1	931	933
2	283	251
3	931	952
4	358	358
5	933	953
6	1007	1033
7	248	248
8	805	837

H,5,3

-9	42*	24
-8	194	187
-7	754	777
-6	284	270
-5	1014	1011
-4	39*	12
-3	246	259
-2	468	460
-1	97	65
0	240	225
1	790	756
2	310	314
3	331	331
4	1050	1041
5	571	610
6	820	844
7	74	75

H,5,4

-9	630	632
-8	496	484
-7	410	438
-6	46	26
-5	873	848
-4	114	111
-3	630	631
-2	854	816
-1	487	474
0	187	194
1	804	798
2	83	76
3	764	757
4	424	405
5	714	717
6	789	792

H,5,5

-9	541	509
-8	185	194
-7	432	423
-6	522	504
-5	567	527
-4	39*	40
-3	211	211
-2	275	274
-1	143	154
0	420	426
1	287	278
2	129	96
3	185	162
4	946	931
5	961	971

H,5,6

-9	597	596
-8	644	624
-7	1581	1549
-6	296	276
-5	1273	1245
-4	139	122
-3	699	652
-2	46	12
-1	231	234
0	693	637
1	1044	1023
2	83	80
3	1091	1090
4	505	488

H,5,7

-8	639	638
-7	727	726
-6	207	189
-5	387	367
-4	137	109
-3	684	632
-2	44	27
-1	416	380
0	590	553
1	556	547
2	425	421
3	660	659

H,5,8

-7	1151	1110
-6	257	252
-5	1316	1235
-4	403	374
-3	915	844
-2	461	455

	H,5,8	
-1	961	904
0	50	34
1	877	851
	H,6,0	
0	1061	991
1	43	70
2	961	925
3	980	953
4	1333	1377
5	277	254
6	1064	1109
7	340	400
	H,6,1	
-8	498	485
-7	272	262
-6	275	268
-5	138	129
-4	287	245
-3	205	160
-2	202	177
-1	328	314
0	117	109
1	325	313
2	683	644
3	150	171
4	99	86
5	238	258
6	456	483
7	54	47
	H,6,2	
-8	963	980
-7	43*	30
-6	1464	1439
-5	42*	43
-4	1254	1210
-3	97	64
-2	1237	1175
-1	383	420
0	573	577
1	164	174
2	1058	1063
3	295	291
4	645	685
5	891	924
6	713	720
	H,6,3	
-8	238	210
-7	505	483
-6	466	407
-5	41*	19
-4	307	301
-3	254	226
-2	59	48
-1	296	271
0	310	305
1	40*	2
2	370	361
3	40*	19
4	893	915
5	207	197
6	406	412
	H,6,4	
-8	910	920
-7	587	568
-6	762	765
-5	446	443
-4	843	809
-3	41*	18
-2	192	192
-1	769	722
0	830	817
1	319	321
2	814	800
3	192	217
4	851	838
5	693	692
	H,6,5	
-7	322	330
-6	177	187
-5	373	352
-4	332	298
-3	187	174
-2	764	739
-1	73	49
0	310	301
1	197	213
2	43*	63
3	291	290
4	80	86
	H,6,6	
-6	1307	1266
-5	527	462
-4	945	927
-3	173	190
-2	939	929
-1	190	148
0	820	807
1	42*	46
2	1187	1168
	H,6,7	
-5	60	40
-4	90	86
-3	169	142
-2	175	179
-1	255	244
0	243	236
	H,7,0	
1	1049	1064
2	372	367
3	1643	1631
4	127	79
5	1007	1025
	H,7,1	
-5	530	524
-4	205	206
-3	328	323
-2	253	237
-1	201	212
0	40*	19
1	720	697
2	203	209
3	513	526
4	151	153
5	249	232
	H,7,2	
-6	177	190
-5	1126	1074
-4	43*	32
-3	1060	1040
-2	42*	12
-1	581	600
0	279	293
1	1170	1157
2	240	242
3	672	700
4	288	296
	H,7,3	
-5	669	637
-4	450	431
-3	364	341
-2	427	422
-1	155	129
0	42*	1
1	391	387
2	41*	11
3	303	300
	H,7,4	
-5	533	502
-4	158	142
-3	671	644
-2	194	204
-1	936	907
0	96	83
1	1001	997
2	159	158
	H,7,5	
-3	503	476
-2	572	533
-1	243	242
0	463	464
	H,0,0	
13	1128	1106
14	73*	40
15	90	97
16	136	139
17	460	477
18	121	108
19	428	412
20	263	248
21	422	409
22	50*	7
	H,0,2	
-22	347	326
-21	347	331
-20	448	423
-19	50*	4
-18	122	114
-17	73	60
-16	558	561
-15	301	284
-14	411	408
-13	662	677
12	659	685
13	726	739
14	165	139
15	411	394
16	84	82
17	643	616
18	66	63
19	280	277
20	85	74
21	360	342
	H,0,4	
-23	363	341
-22	487	454
-21	343	325
-20	336	325
-19	356	332
-18	354	362
-17	166	159
-16	247	256
-15	249	243
-14	261	255
-13	957	972
10	947	951
11	251	259
12	203	213
13	437	458
14	74	64
15	420	409
16	279	285
17	245	257
18	102	102
19	343	333
20	96	103
	H,0,6	
-23	445	423
-22	142	147
-21	346	334
-20	345	332
-19	335	344
-18	602	593
-17	534	537
-16	105	94
-15	661	651
-14	447	463
-13	120	97
9	209	221
10	809	833
11	530	527
12	231	250
13	643	638
14	410	415
15	166	151
16	141	129
17	152	143
18	224	201
	H,0,8	
-23	364	351
-22	410	399
-21	210	211
-20	297	301
-19	215	206
-18	826	816
-17	564	561
-16	141	117
-15	209	188
-14	988	1020
-13	707	681
-12	785	854
6	1386	1434
7	78	47
8	998	1002
9	673	675
10	228	226
11	733	742
12	217	210
13	246	252
14	81	86

H,0,8

15	323	320
16	95	96
17	422	402

H,0,10

−23	163	170
−22	513	500
−21	112	100
−20	140	118
−19	50*	26
−18	419	403
−17	236	244
−16	536	538
−15	274	248
−14	1087	1117
−13	122	136
−12	731	743
−11	993	1042
−10	1158	1153
3	882	884
4	109	130
5	621	618
6	65	32
7	136	112
8	294	302
9	948	947
10	476	472
11	611	614
12	384	382
13	160	151
14	324	324
15	386	379

H,0,12

−22	350	356
−21	64	62
−20	96	85
−19	50*	19
−18	410	412
−17	102	92
−16	147	160
−15	150	163
−14	438	434
−13	49*	49
−12	757	754
−11	302	315
−10	426	441
−9	326	347
−8	307	313
−7	50	49
−6	663	678
−5	239	238
−4	1143	1147
−3	231	242
−2	1066	1053
−1	350	340
0	285	293
1	455	456
2	601	603
3	50*	28
4	238	234
5	152	161
6	471	472
7	408	392
8	501	488
9	504	496
10	159	155
11	288	277
12	107	96
13	321	333

H,0,14

−21	88	81
−9	380	374
−8	442	411
−7	131	109
−6	458	457
−5	329	358
−4	687	684
−3	199	218
−2	922	935
−1	693	718
0	624	643
1	298	320
2	315	295
3	233	247
4	444	447
5	448	460
6	765	752
7	164	153
8	483	461
9	281	271
10	95	108
11	358	357

H,0,16

−20	369	385
−19	50*	1
−18	287	312
−17	75	60
−16	642	644
−15	53*	10
−14	727	736
−13	205	215
−12	816	851
−11	530	547
−10	827	860
−9	845	871
−8	656	690
−7	311	303
−6	462	487
−5	96	68
−4	797	806
−3	867	865
−2	749	757
−1	629	647
0	283	279
1	483	487
2	67	43
3	514	532
4	457	444
5	254	272
6	466	437
7	296	285
8	115	113

H,0,18

−17	49*	4
−16	514	516
−15	120	117
−14	418	434
−13	469	469
−12	426	441
−11	613	623
−10	343	377
−9	297	311
−8	505	535
−7	212	198
−6	447	463
−5	602	582
−4	465	480
−3	733	745
2	59	152
−1	404	397
0	54*	20
1	643	649
2	158	152
3	337	361
4	153	152

H,0,20

−13	340	339
−12	326	334
−11	54	47
−10	200	224
−9	67	67
−8	229	262
−7	134	143
−6	343	363
−5	53*	9
−4	395	411
−3	346	348
−2	49*	24
−1	74	279

H,1,0

13	586	597
14	332	322
15	374	382
16	446	430
17	63	47
18	553	534
19	238	227
20	296	284
21	124	110
22	311	300

H,1,1

−22	219	210
−21	244	219
−20	188	174
−19	232	226
−18	182	166
−17	50*	21
−16	78	90
−15	202	205
12	491	505
13	60	22
14	342	323
15	205	213
16	217	218
17	287	257
18	284	283
19	254	228
20	199	179
21	83	64

H,1,2

−22	193	198
−21	328	312
−20	402	391
−19	154	159
−18	88	87
−17	545	543
−16	52*	5
−15	687	694
−14	478	499
−13	915	934
12	412	433
13	240	231
14	432	421
15	133	139
16	659	669
17	51*	8
18	253	253
20	353	344
21	47*	29

H,1,3

−22	223	215
−21	431	413
−20	127	112
11	486	476
12	85	90
13	157	172
14	383	382
15	226	219
16	255	238
17	128	114
18	166	152
19	138	123
20	148	135

H,1,4

−23	132	127
−22	261	263
−21	236	221
10	432	428
11	685	695
12	344	337
13	213	204
14	473	457
15	393	373
16	211	203
17	71	49
18	303	290
19	155	138
20	304	295

H,1,5

−23	130	118
−22	346	336
−21	218	201
−20	54	25
−19	367	367
−18	60	65
−17	330	334
−16	295	305
−15	310	304
−14	583	581
−13	759	774
10	91	80
11	103	99
12	312	303
13	52*	32
14	274	272
15	299	286
16	80	61
17	143	125
18	46*	4
19	205	184

H,1,6

−23	72	86
−22	235	230
−21	171	178
−20	246	246
−19	291	294
9	975	980
10	224	237
11	266	244
12	677	691
13	530	525
14	148	152

	H,1,6	
15	362	358
16	348	330
17	141	143
18	232	219
	H,1,7	
-23	45*	10
-22	250	242
-21	193	178
-20	73	73
-19	117	130
-18	238	257
-17	138	134
-16	364	376
-15	185	189
-14	229	235
-13	677	691
7	703	708
8	46*	7
9	381	375
10	494	495
11	323	318
12	528	521
13	55	49
14	82	83
15	194	176
16	90	70
17	136	124
18	187	169
	H,1,8	
-23	186	172
-22	328	336
-21	439	432
-20	163	169
-19	430	423
-18	341	353
-17	513	512
-16	296	324
-15	572	586
-14	404	421
-13	943	974
-12	234	270
6	786	788
7	1010	1010
8	268	277
9	159	135
10	835	841
11	417	412
12	447	442
13	104	83
14	448	450
15	88	68
16	421	401
17	175	155
	H,1,9	
-23	282	268
-22	79	77
-21	277	271
-20	159	147
-19	94	85
-18	186	192
-17	50*	27
-16	97	105
-15	524	523
-14	223	225
-13	627	651
-12	255	283
-11	394	427
5	445	459
6	120	86
7	157	153
8	467	469
9	69	83
10	744	733
11	143	139
12	369	368
13	126	132
14	54	27
15	49*	12
16	154	137
	H,1,10	
-22	124	115
-21	245	226
-20	69	54
-19	183	192
-18	92	98
-17	456	464
-16	51*	8
-15	786	801
-14	248	267
-13	742	763
-12	203	201
-11	1027	1032
-10	208	202
3	464	469
4	622	605
5	190	192
6	230	226
7	119	112
8	638	638
9	605	616
10	466	471
11	54*	27
12	426	423
13	50*	34
14	304	292
15	84	87
	H,1,11	
-22	47*	14
-21	133	114
-20	51*	38
-19	175	183
-18	52*	44
-17	194	204
-16	259	264
-15	328	352
-14	184	189
-13	346	382
-12	100	86
-11	635	661
-10	64	56
-9	230	246
-8	296	281
0	642	660
1	354	343
2	552	553
3	47*	11
4	260	259
5	158	163
6	49*	5
7	148	148
8	516	507
9	326	330
10	528	526
11	50*	29
12	267	262
13	271	259
14	163	173
	H,1,12	
-22	126	125
-21	191	202
-20	121	118
-19	266	259
-18	54	10
-17	104	99
-16	74	52
-15	385	401
-14	143	136
-13	416	419
-12	242	253
-11	472	481
-10	82	82
-9	336	348
-8	173	170
-7	286	261
-6	207	210
-5	575	558
-4	48*	46
-3	1137	1134
-2	126	136
-1	71	10
0	523	527
1	316	320
2	365	354
3	183	172
4	201	198
5	117	109
6	489	515
7	457	467
8	432	446
9	58	41
10	304	307
11	50*	28
12	159	157
13	76	85
	H,1,13	
-21	48*	8
-20	79	80
-19	173	182
-18	52*	47
-17	62	48
-16	351	358
-15	89	101
-14	157	172
-13	520	560
-12	51*	6
-11	340	358
-10	57	41
-9	171	179
-8	47*	24
-7	49	4
-6	47*	18
-5	459	468
-4	205	191
-3	696	691
-2	333	327
-1	289	282
0	461	476
1	268	275
2	50	28
3	50*	36
4	52*	16
5	115	101
6	256	247
7	354	356
8	356	349
9	181	178
10	165	155
11	48*	50
12	196	186
	H,1,14	
-21	244	259
-20	108	92
-19	475	490
-18	257	271
-17	273	270
-16	359	362
-15	456	487
-14	232	232
-13	593	601
-12	194	175
-11	418	426
-10	163	149
-9	393	368
-8	230	244
-7	564	568
-6	242	253
-5	677	653
-4	148	120
-3	565	561
-2	618	623
-1	286	299
0	63	44
1	531	552
2	150	148
3	266	254
4	828	812
5	449	453
6	148	157
7	295	282
8	343	343
9	267	254
10	286	296
11	48*	40
	H,1,15	
-20	75	79
-19	161	176
-18	55	41
-17	52*	35
-16	170	155
-15	376	395
-14	237	229
-13	481	514
-12	54*	24
-11	362	391
-10	291	291
-9	185	196
-8	373	372
-7	94	91
-6	320	298
-5	54*	8
-4	194	185
-3	683	666
-2	556	577
-1	413	423
0	321	329
1	52*	10
2	142	136
3	54*	58
4	267	266
5	358	366
6	116	109
7	263	254
8	267	269
9	65	65
	H,1,16	
-19	391	412
-18	52*	13

H,1,16

-17	372	392
-16	56*	62
-15	646	656
-14	55*	38
-13	549	581
-12	344	356
-11	457	476
-10	239	253
-9	625	634
-8	276	278
-7	874	854
-6	157	169
-5	457	447
-4	374	383
-3	614	632
-2	598	626
-1	529	519
0	314	317
1	108	111
2	650	651
3	323	324
4	351	364
5	267	259
6	341	345
7	255	246
8	300	294

H,1,17

-18	50*	17
-17	189	187
-16	120	99
-15	302	303
-14	56	54
-13	307	322
-12	212	213
-11	159	154
-10	377	407
-9	240	236
-8	108	116
-7	317	308
-6	146	159
-5	306	295
-4	399	411
-3	291	305
-2	412	434
-1	56*	64
0	74	58
1	118	106
2	453	455
3	149	144
4	158	163
5	96	86
6	147	134

H,1,18

-17	347	362
-16	66	64
-15	282	301
-14	194	206
-13	236	240
-12	377	390
-11	394	403
-10	454	467
-9	613	610
-8	334	325
-7	201	200
-6	427	432
-5	279	292
-4	214	220
-3	198	207
-2	357	368
-1	70	4
0	466	463
1	136	145
2	341	330
3	57	56
4	240	249

H,1,19

-16	182	174
-15	251	262
-14	125	126
-13	279	283
-12	289	292
-11	77	72
-10	59	41
-9	53*	5
-8	121	107
-7	139	121
-6	140	152
-5	224	229
-4	135	134
-3	190	196
-2	181	181
-1	75	76
0	222	222
1	49*	30
2	81	99

H,1,20

-13	314	324
-12	158	163
-11	335	346
-10	91	103
-9	116	137
-8	161	172
-7	221	232
-6	100	102
-5	348	360
-4	114	122
-3	86	91
-2	305	322

H,2,0

12	51	42
13	161	178
14	220	205
15	429	448
16	387	377
17	459	454
18	55*	35
19	238	243
20	50*	7
21	178	183

H,2,1

-22	199	180
-21	176	184
-20	475	448
-19	290	308
-18	103	99
-17	102	82
-16	592	597
-15	203	205
-14	819	831
-13	578	599
12	727	747
13	609	628
14	220	233
15	287	287
16	126	125
17	539	546
18	303	295
19	204	216
20	223	217
21	303	292

H,2,2

-22	48	15
-21	125	126
-20	51*	11
-19	159	159
-18	205	196
-17	90	70
-16	500	494
-15	50*	34
-14	427	425
-13	52	65
11	99	117
12	74	61
13	65	83
14	141	124
15	252	272
16	183	182
17	418	413
18	52*	30
19	338	334
20	49*	34
21	129	137

H,2,3

-22	292	270
-21	356	347
-20	195	184
-19	160	158
-18	349	333
-17	86	94
-16	493	511
-15	179	193
-14	481	474
-13	437	447
11	743	715
12	234	254
13	539	523
14	395	393
15	332	335
16	180	171
17	158	169
18	105	113
19	164	181
20	75	66

H,2,4

-22	47*	14
-21	68	56
-20	129	113
-19	250	240
-18	197	204
-17	296	306
-16	271	272
-15	208	219
-14	548	561
-13	166	170
10	365	345
11	308	308
12	265	259
13	50*	16
14	290	309
15	236	237
16	50*	1
17	214	217
18	68	50
19	186	193

H,2,5

-23	267	250
-22	120	128
-21	148	148
-20	172	159
-19	52*	1
-18	457	449
-17	406	406
-16	161	152
-15	671	689
-14	48*	20
-13	466	451
9	314	297
10	720	762
11	200	193
12	114	145
13	571	577
14	427	444
15	73	64
16	168	180
17	83	74
18	137	117
19	163	150

H,2,6

-23	45*	24
-22	49*	36
-21	55	37
-20	52*	24
-19	445	437
-18	64	44
-17	524	523
-16	655	661
-15	294	286
-14	167	170
-13	50	37
8	273	263
9	74	99
10	436	417
11	222	224
12	135	140
13	276	285
14	345	335
15	418	428
16	170	170
17	226	227
18	136	125

H,2,7

-23	297	287
-22	277	280
-21	266	263
-20	303	303
-19	221	222
-18	499	504
-17	209	203
-16	92	43
-15	299	290
-14	621	623
-13	486	478
-12	949	947
7	488	465
8	1001	1000
9	545	532
10	355	359
11	889	891
12	310	307
13	441	457
14	204	196
15	82	94
16	97	103

H,2,7

17	318	318
18	201	199

H,2,8

−23	85	83
−22	51*	27
−21	240	248
−20	172	174
−19	159	149
−18	520	501
−17	54*	8
−16	499	499
−15	61	52
−14	262	270
−13	335	316
−12	676	685
6	362	355
7	379	392
8	224	206
9	153	158
10	54*	15
11	72	55
12	183	190
13	278	272
14	274	265
15	464	467
16	48*	26
17	270	264

H,2,9

−22	508	503
−21	210	210
−20	452	443
−19	252	255
−18	399	397
−17	148	145
−16	301	293
−15	226	208
−14	942	929
−13	442	434
−12	756	752
−11	272	290
4	800	785
5	588	555
6	587	593
7	173	172
8	289	297
9	960	954
10	268	259
11	618	619
12	110	119
13	293	289
14	50*	38
15	383	374
16	52*	71

H,2,10

−22	59	56
−21	118	118
−20	196	198
−19	89	83
−18	138	142
−17	182	202
−16	373	358
−15	82	84
−14	337	348
−13	194	201
−12	376	390
−11	246	248
−10	580	609
−9	148	150
2	497	516
3	63	62
4	499	495
5	703	697
6	71	56
7	403	394
8	130	124
9	53*	8
10	59	56
11	74	61
12	211	211
13	282	278
14	157	133
15	257	248

H,2,11

−22	297	299
−21	49*	25
−20	207	210
−19	92	95
−18	397	404
−17	96	106
−16	283	284
−15	120	123
−14	686	691
−13	152	147
−12	794	787
−11	670	683
−10	792	772
−9	270	262
−8	131	123
−7	66	48
−6	554	529
−2	651	656
−1	640	640
0	65	56
1	744	742
2	224	231
3	249	232
4	170	176
5	99	82
6	133	142
7	345	345
8	323	323
9	473	471
10	201	194
11	200	202
12	119	137
13	148	142
14	48*	8

H,2,12

−22	110	123
−21	113	115
−20	151	155
−19	228	223
−18	294	288
−17	58	72
−16	292	314
−15	53*	72
−14	66	47
−13	74	68
−12	59	55
−11	280	283
−10	89	82
−9	117	125
−8	471	455
−7	346	329
−6	427	418
−5	289	284
−4	492	484
−3	154	159
−2	160	154
−1	181	158
0	50*	28
1	111	107
2	196	194
3	188	187
4	273	275
5	337	354
6	64	75
7	330	324
8	53*	22
9	113	120
10	53*	30
11	155	159
12	136	129
13	149	144

H,2,13

−21	108	125
−20	141	142
−19	52*	42
−18	230	242
−17	316	330
−16	251	239
−15	334	345
−14	394	368
−13	215	210
−12	785	791
−11	120	121
−10	276	246
−9	61	42
−8	347	321
−7	301	274
−6	596	556
−5	161	124
−4	836	805
−3	176	188
−2	422	420
−1	746	716
0	381	371
1	121	93
2	490	493
3	54*	52
4	255	244
5	515	515
6	312	309
7	369	383
8	366	367
9	264	264
10	102	92
11	262	257
12	47*	30

H,2,14

−21	100	86
−20	183	188
−19	172	173
−18	346	357
−17	51*	8
−16	340	340
−15	52*	15
−14	164	180
−13	85	75
−12	53*	32
−11	214	196
−10	327	341
−9	289	299
−8	618	616
−7	151	140
−6	337	323
−5	676	667
−4	317	309
−3	86	101
−2	58	56
−1	336	333
0	448	465
1	54*	2
2	493	501
3	511	528
4	223	227
5	209	211
6	53*	32
7	58	25
8	206	204
9	183	179
10	86	77

H,2,15

−20	334	343
−19	259	267
−18	260	284
−17	220	237
−16	423	427
−15	106	119
−14	713	738
−13	277	299
−12	559	549
−11	56*	43
−10	515	516
−9	182	149
−8	691	671
−7	91	101
−6	793	768
−5	157	140
−4	647	634
−3	507	491
−2	654	664
−1	581	608
0	749	759
1	358	367
2	208	201
3	579	576
4	367	371
5	386	392
6	562	561
7	313	314
8	218	210
9	416	406

H,2,16

−19	50*	41
−18	384	386
−17	50*	26
−16	310	321
−15	54*	12
−14	176	190
−13	226	237
−12	168	188
−11	120	111
−10	312	313
−9	115	101
−8	461	454
−7	298	274
−6	411	399
−5	236	231
−4	231	221
−3	171	175
−2	77	65
−1	341	342
0	304	310
1	350	359
2	97	102
3	260	247
4	199	204
5	312	316

H,2,16

6	163	171
7	175	177
8	91	85

H,2,17

−18	164	164
−17	110	116
−16	541	549
−15	52*	17
−14	451	462
−13	293	291
−12	276	293
−11	340	324
−10	392	388
−9	358	345
−8	511	512
−7	216	189
−6	263	268
−5	345	319
−4	516	526
−3	503	497
−2	465	469
−1	411	416
0	161	168

H,2,18

−9	393	392
−8	335	352
−7	322	313
−6	185	186
−5	85	59
−4	175	172

H,3,0

12	107	80
13	233	222
14	49*	4
15	258	256
16	190	214
17	63	66
18	87	70

H,3,1

−19	372	388
−18	445	446
−17	359	356
−16	338	338
−15	982	1005
−14	392	398
−13	1199	1230
−12	518	529
11	532	574
12	772	777
13	571	595
14	542	531
15	377	374
16	707	711
17	357	341
18	396	404

H,3,2

−19	53*	54
−18	148	129
−17	52*	27
−16	58	39
−15	265	285
−14	393	423
−13	164	180
−12	74	84
11	72	57
12	99	119
13	264	284
14	245	259
15	78	86
16	164	167
17	228	231
18	84	84

H,3,3

−19	214	219
−18	237	236
−17	666	677
−16	182	181
−15	648	664
−14	173	175
−13	757	769
−12	356	348
10	647	653
11	337	341
12	153	140
13	58	59
14	360	354
15	267	265
16	368	357
17	120	110

H,3,4

−19	178	191
−18	166	182
−17	53*	24
−16	333	322
−15	184	196
−14	567	574
−13	272	277
−12	318	301
9	247	238
10	189	177
11	187	181
12	171	174
13	506	523
14	189	186
15	175	199
16	53*	52
17	112	107

H,3,5

−20	234	238
−19	131	137
−18	505	503
−17	459	457
−16	828	864
−15	687	721
−14	326	365
−13	537	560
−12	295	293
9	633	640
10	365	348
11	390	386
12	431	436
13	666	671
14	244	254
15	337	320
16	335	339

H,3,6

−20	131	132
−19	101	93
−18	98	118
−17	147	142
−16	54*	26
−15	375	387
−14	96	81
−13	125	115
−12	286	286
8	243	259
9	109	90
10	62	59
11	107	121
12	279	276
13	55*	46
14	71	75
15	52*	8

H,3,7

−20	455	461
−19	259	251
−18	696	710
−17	678	692
−16	468	461
−15	667	671
−14	496	512
−13	657	670
−12	542	547
6	989	1024
7	782	797
8	134	117
9	701	707
10	692	710
11	473	491
12	660	661
13	397	396
14	421	422

H,3,8

−19	169	168
−18	52*	30
−17	421	422
−16	57	78
−15	173	163
−14	73	77
−13	207	204
−12	228	230
−11	162	172
5	77	68
6	210	218
7	307	305
8	93	88
9	98	86
10	505	485
11	67	50
12	474	456
13	53*	24
14	251	257

H,3,9

−19	527	542
−18	190	182
−17	444	441
−16	81	93
−15	704	726
−14	286	282
−13	787	804
−12	52*	41
−11	977	998
−10	357	339
3	972	976
4	777	776
5	566	581
6	925	926
7	174	178
8	753	767
9	55*	14
10	324	327
11	221	202
12	331	322
13	430	422

H,3,10

−19	54*	35
−18	224	214
−17	90	97
−16	87	88
−15	146	145
−14	381	377
−13	51*	18
−12	54*	25
−11	236	260
−10	286	289
−9	116	66
−8	179	200
1	271	278
2	162	138
3	83	76
4	470	467
5	130	120
6	420	412
7	51*	3
8	223	200
9	117	106
10	156	146
11	186	182
12	54*	44

H,3,11

−19	363	364
−18	151	138
−17	446	459
−16	80	69
−15	516	543
−14	82	52
−13	381	372
−12	171	190
−11	818	805
−10	353	326
−9	781	737
−8	423	414
−7	687	667
−6	338	332
−5	439	410
−4	460	439
−3	577	516
−2	636	587
−1	360	340
0	624	580
1	315	325
2	532	527
3	489	484
4	639	631
5	162	175
6	709	731
7	56*	37
8	563	568
9	80	92
10	360	356

H,3,12

−18	90	99
−17	236	247
−16	292	294
−15	60	18
−14	108	110
−13	105	131

H,3,12

-12	506	506
-11	256	292
-10	219	217
-9	305	247
-8	50*	35
-7	330	302
-6	148	149
-5	52	31
-4	61	55
-3	51	21
-2	455	450
-1	158	137
0	507	505
1	51*	36
2	101	87
3	53*	30
4	130	118
5	140	161
6	89	96
7	61	56
8	54*	23
9	161	149

H,3,13

-17	406	433
-16	110	96
-15	379	376
-14	209	197
-13	433	433
-12	328	313
-11	437	435
-10	695	668
-9	699	688
-8	184	170
-7	659	617
-6	313	307
-5	722	652
-4	105	79
-3	274	257
-2	195	172
-1	376	368
0	104	97
1	690	692
2	288	279
3	497	510
4	609	621
5	59	50
6	410	415
7	375	379
8	299	302

H,3,14

-16	155	171
-15	100	105
-14	58	72
-13	205	224
-12	190	191
-11	62	62
-10	76	77
-9	215	200
-8	193	162
-7	55*	52
-6	193	193
-5	124	122
-4	175	150
-3	227	247
-2	311	306
-1	67	51
0	311	340
1	55*	20
2	113	117
3	473	477
4	54*	6
5	168	151
6	132	120

H,3,15

-15	592	612
-14	221	207
-13	406	390
-12	140	146
-11	516	508
-10	159	155
-9	738	708
-8	162	169
-7	772	740
-6	357	340
-5	712	699
-4	270	248
-3	536	540
-2	320	305
-1	697	692
0	519	488
1	613	607
2	494	503
3	303	296
4	634	630

H,3,16

-14	133	130
-13	89	90
-12	71	67
-11	102	90
-10	55*	4
-9	57*	60
-8	201	184
-7	56*	0
-6	151	123
-5	199	188
-4	147	135
-3	318	322
-2	106	114
-1	218	213
0	182	186
1	198	197
2	121	137

H,3,17

-12	220	233
-11	418	401
-10	270	271
-9	603	596
-8	360	350
-7	413	407
-6	400	390
-5	455	449
-4	504	495
-3	419	427
-2	688	684
-1	213	236

H,4,0

11	467	449
12	518	508
13	302	292
14	324	327
15	55*	6
16	60	61
17	290	277
18	145	146

H,4,1

-18	234	232
-17	432	431
-16	500	485
-15	394	406
-14	753	749
-13	142	116
-12	652	650
-11	61	32
11	383	393
12	161	158
13	454	475
14	512	500
15	529	556
16	329	301
17	515	521
18	53*	1

H,4,2

-19	252	260
-18	56*	73
-17	54*	10
-16	266	264
-15	154	167
-14	272	264
-13	244	252
-12	141	133
10	482	510
11	435	427
12	102	117
13	178	164
14	70	74
15	261	248
16	127	113
17	171	154

H,4,3

-19	248	239
-18	474	477
-17	524	531
-16	620	611
-15	85	72
-14	475	469
-13	120	102
-12	372	379
9	312	334
10	50	14
11	113	131
12	270	255
13	115	117
14	361	369
15	610	628
16	222	212
17	427	425

H,4,4

-19	52*	5
-18	141	137
-17	57*	45
-16	246	230
-15	258	267
-14	90	86
-13	206	204
-12	49*	16
9	234	245
10	228	221
11	51*	34
12	162	161
13	363	362
14	54*	36
15	83	85
16	208	210

H,4,5

-19	391	370
-18	278	249
-17	294	285
-16	436	429
-15	150	149
-14	583	581
-13	609	579
-12	389	372
-11	381	364
8	67	29
9	295	313
10	281	280
11	103	111
12	534	537
13	158	159
14	489	503
15	444	458

H,4,6

-19	255	242
-18	71	68
-17	381	395
-16	85	77
-15	180	188
-14	363	366
-13	94	84
-12	293	271
-11	91	102
7	200	197
8	552	579
9	52*	42
10	160	168
11	261	248
12	148	156
13	300	299
14	247	245
15	54*	36

H,4,7

-19	445	449
-18	211	205
-17	458	478
-16	776	769
-15	405	396
-14	523	508
-13	90	69
-12	466	459
-11	69	62
5	656	622
6	615	624
7	284	280
8	277	254
9	411	399
10	370	363
11	259	262
12	340	338
13	436	439
14	398	383

H,4,8

-19	141	148
-18	191	183
-17	77	69
-16	77	90
-15	112	104
-14	463	431
-13	260	261
-12	521	497

H,4,8

-11	64	76
-10	334	316
4	402	392
5	346	353
6	411	386
7	88	91
8	193	178
9	246	246
10	172	159
11	326	343
12	432	432
13	184	185

H,4,9

-19	247	238
-18	510	511
-17	366	368
-16	605	596
-15	136	115
-14	461	454
-13	143	150
-12	823	812
-11	123	99
-10	711	712
-9	49*	1
-8	1417	1371
2	1251	1241
3	482	438
4	829	813
5	913	894
6	196	180
7	739	737
8	69	56
9	516	524
10	143	135
11	223	219
12	123	110

H,4,10

-18	194	204
-17	201	181
-16	255	244
-15	143	129
-14	238	236
-13	189	178
-12	205	203
-11	490	470
-10	542	516
-9	71	47
-8	724	697
-7	167	156
-6	208	176
-5	537	496
-4	405	434
-3	165	155
-2	537	556
-1	225	193
0	65	58
1	273	251
2	366	383
3	53*	23
4	502	505
5	281	271
6	52*	40
7	255	231
8	306	312
9	226	222
10	81	75
11	100	86

H,4,11

-18	425	411
-17	55*	5
-16	525	525
-15	250	258
-14	483	485
-13	145	128
-12	324	321
-11	315	325
-10	352	335
-9	286	284
-8	642	601
-7	432	419
-6	397	387
-5	420	407
-4	183	145
-3	795	785
-2	421	407
-1	324	317
0	828	815
1	157	145
2	368	354
3	535	517
4	187	181
5	591	563
6	57*	41
7	371	356
8	57*	6
9	531	518
10	56*	52

H,4,12

-17	89	97
-16	231	215
-15	95	98
-14	52*	16
-13	96	107
-12	208	187
-11	55*	54
-10	521	487
-9	74	82
-8	206	198
-7	393	356
-6	51*	2
-5	425	412
-4	434	427
-3	53*	4
-2	53*	35
-1	448	431
0	395	395
1	100	73
2	434	423
3	53*	1
4	173	160
5	140	122
6	55*	5
7	88	76
8	352	316
9	91	60

H,4,13

-17	74	52
-16	497	498
-15	58*	41
-14	236	238
-13	82	69
-12	462	468
-11	434	401
-10	323	302
-9	212	194
-8	947	933
-7	136	128
-6	478	474
-5	167	165
-4	271	241
-3	209	188
-2	382	384
-1	130	122
0	357	347
1	57*	5
2	369	370
3	335	307
4	450	452
5	488	480
6	181	167
7	374	353

H,4,14

-16	198	204
-15	117	87
-14	323	314
-13	63	42
-12	524	505
-11	211	218
-10	196	166
-9	64	79
-8	469	456
-7	77	90
-6	575	553
-5	72	71
-4	184	163
-3	108	89
-2	55*	9
-1	301	295
0	600	577
1	58*	13
2	142	145
3	98	102
4	58*	49
5	256	264
6	179	185

H,4,15

-15	102	81
-14	272	262
-13	135	128
-12	343	330
-11	58*	11
-10	584	579
-9	254	246
-8	511	485
-7	473	456
-6	451	432
-5	702	669
-4	733	718
-3	174	165
-2	456	437
-1	184	173
0	500	503
1	475	474
2	582	583
3	481	472
4	319	308

H,4,16

-13	124	113
-12	175	168
-11	227	213
-10	203	192
-9	270	233
-8	438	427
-7	171	166
-6	332	329
-5	399	387
-4	476	466
-3	292	277
-2	315	319
-1	280	253
0	214	221
1	68	58

H,4,17

-10	495	467
-9	256	223
-8	584	579
-7	401	391
-6	408	396
-5	553	551
-4	148	172
-3	398	396
-2	59	57

H,5,0

10	425	431
11	480	485
12	290	283
13	566	567
14	240	234
15	431	430
16	467	467
17	332	321

H,5,1

-18	114	127
-17	201	200
-16	336	353
-15	391	391
-14	55*	12
-13	482	507
-12	87	92
-11	512	521
-10	359	348
10	100	90
11	274	276
12	191	183
13	183	191
14	330	317
15	308	322
16	128	141
17	123	127

H,5,2

-18	375	361
-17	469	456
-16	423	409
-15	616	607
-14	61	42
-13	522	532
-12	207	203
-11	177	169
-10	59	59
9	53	16
10	534	547
11	66	86
12	269	265
13	541	554
14	402	399
15	410	391
16	579	559
17	54*	2

H,5,3

-18	167	184
-17	306	304

H,5,3

-16	177	189
-15	201	218
-14	74	72
-13	545	537
-12	320	306
-11	422	408
-10	193	179
8	337	332
9	62	81
10	316	319
11	52*	6
12	184	166
13	133	134
14	82	81
15	245	239
16	143	153

H,5,4

-18	267	252
-17	340	342
-16	311	319
-15	438	439
-14	203	196
-13	226	228
-12	359	357
-11	281	273
-10	69	66
7	367	376
8	361	370
9	175	156
10	252	247
11	222	229
12	230	214
13	289	290
14	475	474
15	306	307

H,5,5

-18	75	74
-17	55*	2
-16	91	99
-15	268	281
-14	227	233
-13	233	222
-12	477	482
-11	82	72
-10	66	34
6	61	28
7	295	310
8	258	263
9	94	79
10	339	342
11	331	349
12	137	126
13	438	461
14	142	145
15	75	50

H,5,6

-18	330	312
-17	346	343
-16	354	356
-15	327	338
-14	211	187
-13	326	334
-12	276	257
-11	71	47
-10	257	247
5	703	717
6	450	459
7	218	218
8	137	119
9	365	386
10	84	67
11	465	450
12	89	84
13	356	366
14	340	347

H,5,7

-18	172	187
-17	359	384
-16	143	146
-15	270	271
-14	127	132
-13	55	48
-12	155	153
-11	155	118
-10	223	228
-9	605	588
4	338	330
5	887	880
6	196	217
7	186	174
8	605	609
9	353	351
10	207	205
11	227	238
12	133	139
13	56*	34

H,5,8

-18	381	387
-17	390	403
-16	161	151
-15	599	608
-14	134	134
-13	480	495
-12	114	75
-11	718	711
-10	50*	17
-9	890	852
-8	52	76
2	502	480
3	934	932
4	355	368
5	727	743
6	711	713
7	363	380
8	504	498
9	182	183
10	544	539
11	423	435
12	304	288

H,5,9

-18	188	185
-17	386	392
-16	202	187
-15	204	210
-14	246	250
-13	268	259
-12	54*	9
-11	673	650
-10	92	105
-9	627	599
-8	186	175
-7	504	449
-6	235	222
-5	779	725
-4	49	52
-3	422	396
-2	114	77
-1	101	92
0	497	475
1	701	669
2	152	120
3	398	388
4	180	190
5	156	146
6	301	306
7	243	248
8	550	565
9	288	288
10	116	127
11	68	85

H,5,10

-18	241	229
-17	451	449
-16	56*	5
-15	362	367
-14	111	121
-13	259	259
-12	279	273
-11	384	388
-10	55*	17
-9	646	604
-8	230	232
-7	859	802
-6	472	449
-5	645	596
-4	601	569
-3	572	534
-2	415	386
-1	397	366
0	262	248
1	554	552
2	184	196
3	469	469
4	546	540
5	349	357
6	402	385
7	56*	6
8	355	362
9	92	103
10	310	306

H,5,11

-17	244	246
-16	132	128
-15	283	279
-14	241	241
-13	571	532
-12	56*	51
-11	201	180
-10	70	58
-9	54*	21
-8	122	109
-7	564	504
-6	316	312
-5	307	264
-4	325	290
-3	69	7
-2	666	617
-1	478	467
0	105	99
1	230	222
2	55	40
3	56*	32
4	321	326
5	132	140
6	53*	2
7	53*	33
8	77	95
9	75	76

H,5,12

-17	450	463
-16	107	101
-15	434	436
-14	75	92
-13	206	213
-12	54*	9
-11	344	340
-10	426	397
-9	461	453
-8	129	125
-7	572	539
-6	137	103
-5	119	89
-4	431	385
-3	69.	58
-2	67	46
-1	276	255
0	102	79
1	276	249
2	237	218
3	413	406
4	268	257
5	90	61
6	337	346
7	133	141
8	133	130

H,5,13

-16	57*	51
-15	241	236
-14	54*	18
-13	384	379
-12	98	108
-11	103	70
-10	109	107
-9	447	405
-8	56*	8
-7	470	446
-6	116	114
-5	55*	14
-4	349	335
-3	389	377
-2	56*	23
-1	276	270
0	142	132
1	82	73
2	206	216
3	320	320
4	343	340
5	234	231
6	113	131

H,5,14

-15	337	349
-14	55*	21
-13	379	382
-12	81	56
-11	506	493
-10	58*	30
-9	810	776
-8	222	210
-7	778	738
-6	128	120
-5	541	523
-4	300	292
-3	412	397
-2	58*	32
-1	485	471

	H,5,14	
0	179	163
1	451	449
2	142	112
3	380	385
4	377	386
5	200	201
	H,5,15	
-13	117	98
-12	129	131
-11	493	492
-10	63	63
-9	419	388
-8	65	56
-7	59*	24
-6	389	359
-5	420	412
-4	169	142
-3	414	422
-2	57*	29
-1	251	265
0	455	453
1	290	294
2	393	392
3	269	271
	H,5,16	
-11	462	448
-10	58*	27
-9	577	579
-8	417	409
-7	559	546
-6	427	413
-5	426	422
-4	505	480
-3	328	307
-2	365	349
-1	406	403
0	262	247
	H,5,17	
-6	165	142
	H,6,0	
8	1120	1118
9	559	582
10	675	683
11	184	184
12	599	600
13	224	214
14	430	425
15	608	618
16	351	347
17	395	403
	H,6,1	
-17	57	32
-16	56*	27
-15	260	273
-14	55*	45
-13	245	238
-12	103	84
-11	53*	24
-10	156	142
-9	57	37
8	449	422
9	282	269
10	250	249
11	152	157
12	68	66
13	177	186
14	212	204
15	55*	3
16	56*	31
	H,6,2	
-17	384	383
-16	470	443
-15	302	313
-14	451	448
-13	107	111
-12	788	762
-11	208	206
-10	837	775
-9	263	287
7	597	614
8	513	516
9	127	136
10	89	73
11	345	368
12	296	293
13	424	423
14	245	228
15	367	379
16	143	128
	H,6,3	
-18	83	91
-17	55*	2
-16	55*	27
-15	69	49
-14	55*	35
-13	87	85
-12	375	342
-11	460	452
-10	50*	29
-9	181	185
-10	50*	29
-9	181	185
7	423	408
8	153	147
9	54	51
10	51*	7
11	252	251
12	56*	4
13	83	113
14	125	128
15	175	178
	H,6,4	
-18	219	211
-17	315	325
-16	122	111
-15	129	125
-14	461	449
-13	264	255
-12	358	329
-11	425	440
-10	445	435
-9	64	23
6	908	918
7	261	263
8	271	262
9	325	316
10	67	62
11	273	299
12	183	157
13	186	206
14	267	259
15	321	328
	H,6,5	
-18	61	45
-17	57*	37
-16	104	108
-15	54*	55
-14	118	111
-13	268	252
-12	126	137
-11	52*	39
-10	321	295
-9	648	638
-8	99	88
5	200	183
6	50*	9
7	317	320
8	125	120
9	52*	15
10	180	182
11	190	207
12	79	86
13	56*	43
14	172	156
	H,6,6	
-18	179	180
-17	246	248
-16	399	391
-15	263	268
-14	326	314
-13	370	364
-12	109	100
-11	189	169
-10	531	529
-9	707	664
-8	851	843
-7	696	660
3	221	194
4	1630	1620
5	128	135
6	1101	1099
7	296	300
8	278	268
9	593	597
10	481	476
11	58*	19
12	432	432
13	271	287
	H,6,7	
-18	157	137
-17	56*	53
-16	55*	3
-15	502	502
-14	263	255
-13	121	91
-12	52*	14
-11	212	206
-10	112	112
-9	50*	8
-8	128	134
-7	51*	74
-6	247	242
1	462	427
2	129	110
3	257	250
4	137	138
5	254	270
6	69	89
7	75	67
8	506	519
9	180	197
10	86	107
11	66	62
12	54*	17
	H,6,8	
-17	255	261
-16	608	627
-15	56*	1
-14	458	456
-13	200	187
-12	631	611
-11	240	252
-10	1000	965
-9	318	312
-8	858	846
-7	63	22
-6	980	949
-5	146	161
-4	1048	1034
-3	265	272
-2	685	684
-1	72	87
0	951	948
1	406	395
2	1133	1130
3	252	237
4	1200	1182
5	428	410
6	669	659
7	576	557
8	370	369
9	660	682
10	520	520
11	423	438
12	239	237
	H,6,9	
-17	55*	17
-16	122	114
-15	55*	43
-14	76	66
-13	60	36
-12	230	219
-11	103	79
-10	343	342
-9	56*	80
-8	150	149
-7	90	89
-6	53	19
-5	199	194
-4	137	135
-3	181	157
-2	121	112
-1	52*	32
0	113	114
1	231	216
2	106	98
3	133	139
4	264	255
5	223	225
6	342	329
7	134	136
8	89	103
9	92	79
10	142	130
11	54*	27
	H,6,10	
-17	155	184
-16	490	484
-15	364	350

H,6,10

-14	518	515
-13	528	521
-12	535	527
-11	116	94
-10	519	513
-9	91	79
-8	653	642
-7	619	597
-6	1006	969
-5	414	406
-4	487	475
-3	893	873
-2	205	190
-1	386	365
0	820	812
1	156	147
2	619	602
3	231	220
4	158	138
5	441	435
6	189	165
7	279	269
8	55*	26
9	237	245

H,6,11

-16	147	140
-15	56*	13
-14	189	184
-13	58*	67
-12	235	235
-11	281	303
-10	68	69
-9	295	308
-8	57*	73
-7	62	85
-6	230	209
-5	294	288
-4	57	45
-3	159	138
-2	124	144
-1	290	286
0	128	139
1	108	114
2	132	133
3	55*	13
4	56*	6
5	128	129
6	105	130
7	56*	46
8	53*	32

H,6,12

-16	403	425
-15	57*	23
-14	458	448
-13	57*	51
-12	504	495
-11	55*	5
-10	324	317
-9	127	125
-8	608	588
-7	97	103
-6	422	401
-5	272	270
-4	94	89
-3	522	508
-2	420	423
-1	59	50
0	398	394
1	166	174
2	147	141
3	295	297
4	206	202
5	289	271
6	95	87
7	237	248

H,6,13

-15	167	160
-14	57*	39
-13	260	248
-12	57*	32
-11	58	35
-10	79	95
-9	77	69
-8	354	369
-7	55*	5
-6	122	130
-5	59*	25
-4	149	144
-3	261	275
-2	269	273
-1	79	80
0	106	93
1	126	136
2	169	151
3	118	128
4	56*	26
5	66	70

H,6,14

-13	195	185
-12	464	462
-11	128	128
-10	677	663
-9	121	114
-8	733	718
-7	109	89
-6	401	366
-5	372	351
-4	554	553
-3	313	299
-2	698	699
-1	58*	28
0	383	375
1	381	383
2	413	410
3	355	351

H,6,15

-12	60*	56
-11	203	197
-10	137	143
-9	186	180
-8	238	238
-7	179	183
-6	59	32
-5	75	96
-4	90	97
-3	130	152
-2	59*	64
-1	57*	22
0	155	139
1	162	143

H,6,16

-9	241	236
-8	583	566
-7	412	392
-6	602	577
-5	353	331
-4	479	494
-3	243	237

H,7,0

6	175	155
7	565	561
8	305	317
9	810	809
10	384	383
11	592	607
12	187	160
13	237	247
14	444	449
15	200	204
16	244	249

H,7,1

-16	305	295
-15	349	347
-14	57*	3
-13	412	405
-12	118	106
-11	444	444
-10	336	314
-9	210	186
-8	356	333
-7	313	293
-6	132	131
6	162	156
7	200	191
8	382	380
9	125	117
10	175	171
11	123	121
12	302	281
13	300	310
14	239	224
15	264	255

H,7,2

-16	264	269
-15	173	170
-14	167	174
-13	551	554
-12	57*	67
-11	748	708
-10	281	275
-9	717	682
-8	91	120
-7	760	721
5	147	151
6	417	427
7	852	855
8	120	105
9	569	594
10	416	414
11	72	33
12	566	565
13	201	175
14	372	385
15	70	50

H,7,3

-17	146	128
-16	235	245
-15	176	183
-14	52*	8
-13	301	288
-12	54*	32
-11	53*	11
-10	55	41
-9	248	219
-8	67	53
-7	371	333
-6	380	346
4	283	299
5	89	94
6	499	512
7	103	108
8	125	116
9	67	55
10	63	51
11	241	226
12	98	82
13	56*	29
14	78	50

H,7,4

-17	94	90
-16	109	108
-15	263	283
-14	116	129
-13	337	326
-12	229	241
-11	83	61
-10	122	133
-9	576	555
-8	353	319
-7	750	675
-6	117	166
3	221	224
4	435	451
5	398	386
6	129	136
7	499	496
8	64	34
9	130	138
10	220	215
11	210	213
12	411	428
13	79	57
14	216	235

H,7,5

-17	182	178
-16	89	63
-15	254	260
-14	139	122
-13	166	176
-12	156	153
-11	82	85
-10	251	241
-9	153	159
-8	302	303
-7	428	406
-6	57	60
-5	591	559
-4	429	413
1	116	131
2	211	197
3	97	108
4	158	168
5	232	240
6	405	398
7	156	167
8	694	696
9	157	160
10	283	262
11	96	87
12	119	134
13	224	214

H,7,6

-16	152	176
-15	294	303
-14	443	467
-13	296	293
-12	215	206
-11	347	335
-10	55*	42
-9	694	655
-8	222	238
-7	437	413
-6	476	468
-5	227	202
-4	193	180
-3	917	862
-2	48*	29
-1	836	823
0	84	86
1	746	727
2	629	643
3	968	998
4	181	202
5	847	860
6	287	266
7	596	616
8	481	495
9	583	604
10	376	386
11	402	401
12	231	254

H,7,7

-17	326	317
-16	162	154
-15	306	290
-14	128	115
-13	203	204
-12	181	172
-11	103	80
-10	365	358
-9	298	280
-8	146	124
-7	577	558
-8	146	124
-7	577	558
-6	106	109
-5	565	532
-4	90	87
-3	370	355
-2	100	58
-1	354	362
0	65	76
1	263	289
2	136	135
3	341	337
4	65	42
5	602	616
6	373	375
7	122	121
8	383	365
9	56*	32
10	58*	50
11	248	255

H,7,8

-16	218	237
-15	210	225
-16	218	237
-15	210	225
-14	161	161
-13	242	230
-12	97	122
-11	948	930
-10	56*	44
-9	827	807
-8	191	167
-7	422	401
-6	200	154
-5	834	784
-4	122	147
-3	960	912
-2	170	159
-1	717	692
0	569	592
1	840	826
2	475	479
3	487	480
4	61	36
5	443	444
6	102	105
7	424	441
8	585	615
9	283	282
10	353	371
11	236	240

H,7,9

-16	59	34
-15	388	388
-14	217	222
-13	142	136
-12	182	197
-11	68	31
-10	430	438
-9	218	213
-10	430	438
-9	218	213
-8	85	90
-7	609	581
-6	386	380
-5	576	534
-4	168	132
-3	132	150
-2	296	294
-1	116	92
0	146	132
1	56*	4
2	158	162
3	306	328
4	535	549
5	234	238
6	394	373
7	56*	13
8	158	169
9	287	296

H,7,10

-16	57*	52
-15	363	372
-14	237	221
-13	697	696
-12	266	257
-11	771	765
-10	181	148
-9	297	267
-8	413	373
-7	450	431
-6	234	200
-5	751	721
-4	124	94
-3	414	394
-2	631	612
-1	616	600
0	334	338
1	627	611
2	65	28
3	193	190
4	250	263
5	175	180
6	274	280
7	151	142
8	270	287

H,7,11

-15	90	98
-14	56*	20
-13	58*	16
-12	59	50
-11	170	172
-10	65	50
-9	122	116
-8	63	70
-7	520	516
-6	101	91
-5	57*	34
-4	428	424
-3	58*	35
-2	56*	34
-1	56*	6
0	84	73
1	140	137
2	291	307
3	61	63
4	426	421
5	87	86
6	301	301
7	70	55

H,7,12

-14	67	85
-13	398	394
-12	93	104
-11	388	395
-10	301	285
-9	276	280
-8	107	96
-7	379	350
-6	58*	64
-5	253	226
-4	426	421
-3	415	426
-2	292	302
-1	470	470
0	115	118
1	155	157
2	80	77
3	85	78
4	77	72
5	241	248

H,7,13

-13	94	98
-12	118	103
-11	186	197
-10	58*	40
-9	363	370
-8	59*	34
-7	435	434
-6	60	73
-7	435	434
-6	60	73
-5	226	230
-4	57*	29
-3	145	151
-2	61	52
-3	145	151
-2	61	52
-1	288	292
0	57*	1
1	134	129
2	149	142
3	262	267
4	208	200

H,7,14

-11	405	389
-10	145	131
-9	480	471
-8	178	190
-7	267	261
-6	60*	38
-5	467	450
-4	237	232
-3	478	461
-2	97	83
-1	336	328
0	200	229
1	213	203

H,7,15

-9	223	211
-8	127	124
-7	326	330
-6	60*	20
-5	58*	55
-4	220	227
-3	142	157
-2	57*	18

H,8,0

0	749	684
1	102	109
2	591	551
3	155	164
4	354	318
5	51*	62
6	322	298
7	115	112
8	363	376
9	332	349
10	614	635
11	177	188
12	300	308
13	297	299
14	124	113
15	78	78

H,8,1

-15	307	312
-14	179	165
-13	105	97
-12	709	708
-11	296	297
-10	459	438
-9	436	427
-8	580	594
-7	116	123
-6	441	440
-5	54	45
-4	873	856
-3	268	282
-2	576	557
-1	196	178
0	395	396
1	242	260
2	769	737
3	112	109

H,8,1

4	617	634
5	271	254
6	342	346
7	600	605
8	747	765
9	481	511
10	257	249
11	217	222
12	212	193
13	392	407
14	248	231

H,8,2

-15	166	175
-14	56*	23
-13	124	127
-12	362	360
-11	270	263
-10	514	516
-9	93	79
-8	285	254
-7	317	306
-6	335	311
-5	134	134
-4	717	695
-3	52*	40
-2	942	856
-1	84	70
0	387	346
1	330	321
2	531	484
3	167	167
4	68	72
5	190	192
6	96	91
7	200	231
8	498	508
9	248	258
10	57*	30
11	403	422
12	89	76
13	377	411
14	92	103

H,8,3

-15	55*	50
-14	354	365
-13	72	65
-12	474	455
-11	100	105
-10	315	316
-9	258	258
-8	485	495
-7	54*	13
-6	518	510
-5	52*	75
-4	415	427
-3	48*	15
-2	232	234
-1	199	211
0	440	428
1	153	141
2	566	552
3	164	159
4	64	86
5	482	495
6	253	238
7	256	280
8	545	568
9	86	77
10	110	115
11	389	398
12	344	348
13	317	313

H,8,4

-16	67	58
-15	253	274
-14	294	297
-13	354	367
-12	163	144
-11	180	164
-10	317	314
-9	187	178
-8	207	185
-7	51*	22
-6	51*	20
-5	116	95
-4	232	219
-3	253	245
-2	447	428
-1	217	231
0	516	492
1	284	276
2	185	168
3	181	184
4	258	256
5	95	81
6	313	347
7	91	107
8	448	470
9	197	202
10	179	189
11	157	163
12	139	134
13	229	244

H,8,5

-16	303	306
-15	159	162
-14	391	390
-13	291	302
-12	198	198
-11	190	193
-10	253	264
-9	147	157
-8	549	564
-7	307	310
-6	308	341
-5	156	147
-4	219	215
-3	84	85
-2	569	555
-1	71	72
0	565	560
1	190	173
2	200	184
3	328	310
4	391	382
5	239	239
6	477	477
7	57*	29
8	211	184
9	266	262
10	409	403
11	248	253
12	328	331

H,8,6

-15	234	246
-14	266	289
-13	184	184
-12	154	138
-11	114	105
-10	422	407
-9	82	74
-8	373	376
-7	63	36
-6	99	95
-5	491	446
-4	143	123
-3	141	133
-2	587	575
-1	54*	5
0	319	313
1	316	295
2	152	158
3	513	505
4	215	246
5	78	93
6	58*	9
7	58*	4
8	481	497
9	161	171
10	390	403
11	226	253

H,8,7

-15	208	225
-14	350	351
-13	389	402
-12	315	318
-11	246	257
-10	994	1004
-9	59*	74
-8	422	439
-7	163	161
-6	485	467
-5	56*	51
-4	549	537
-3	55*	4
-2	826	807
-1	68	68
0	477	472
1	551	558
2	473	458
3	393	395
4	375	343
5	58*	26
6	348	349
7	365	378
8	426	435
9	360	365
10	433	421

H,8,8

-15	216	219
-14	61*	60
-13	59*	48
-12	421	426
-11	132	139
-10	572	551
-9	456	484
-8	220	201
-7	56*	44
-6	360	352
-5	58*	52
-6	360	352
-5	58*	52
-4	671	664
-3	66	59
-2	425	416
-1	90	94
0	393	394
1	547	525
2	524	538
3	222	211
4	126	149
5	59*	64
6	240	266
7	191	190
8	295	317
9	263	270

H,8,9

-15	252	279
-14	449	441
-13	59*	27
-12	615	616
-11	87	103
-10	663	671
-9	60*	49
-8	182	164
-7	341	331
-6	709	701
-5	166	159
-4	762	777
-3	155	159
-2	425	427
-1	469	481
0	487	477
1	589	588
2	421	409
3	345	346
4	193	185
5	388	401
6	326	320
7	589	604
6	326	320
7	589	604
8	226	218

H,8,10

-14	390	396
-13	57*	34
-14	390	396
-13	57*	34
-12	415	414
-11	107	100
-10	413	382
-9	58*	20
-8	58*	17
-7	233	237
-6	79	67
-5	58*	30
-4	327	308
-3	58*	26
-2	312	318
-1	454	460
0	349	357
1	272	264
2	60*	36
3	67	52
4	58*	17
5	58*	53
6	246	249
7	188	202

H,8,11

-13	57*	47
-12	286	287
-11	59*	15
-10	377	373
-9	181	184
-8	237	253
-7	131	117
-6	566	571

H,8,11

-5	72	73
-4	172	170
-3	431	431
-2	306	304
-1	256	248
0	226	214
1	165	152
2	85	62
3	349	373
4	234	225
5	410	412

H,8,12

-12	277	274
-11	77	84
-10	358	354
-9	127	135
-8	114	102
-7	145	132
-6	57*	22
-5	77	68
-4	103	84
-3	173	172
-2	260	249
-1	150	145
0	100	88
1	143	121
2	57*	22
3	56*	28

H,8,13

-11	57*	15
-10	207	226
-9	63	81
-8	343	343
-7	169	172
-6	314	313
-5	59*	43
-4	301	313
-3	262	265
-2	348	350
-1	58*	31
0	219	228
1	131	141

H,8,14

-8	80	82
-7	70	65
-6	275	274
-5	82	79
-4	307	298
-3	74	82
-2	165	170

H,9,0

1	271	285
2	130	145
3	198	181
4	317	315
5	54*	31
6	179	195
7	75	43
8	124	161
9	137	152
10	72	66
11	55*	24
12	61*	67
13	163	182

H,9,1

-14	258	268
-13	278	258
-12	178	194
-11	618	604
-10	294	291
-9	793	773
-8	68	49
-7	436	421
-6	307	309
-5	664	658
-4	55*	6
-3	983	958
-2	82	70
-1	820	830
0	434	395
1	867	870
2	485	486
3	770	797
4	176	185
5	311	321
6	230	228
7	616	639
8	290	329
9	695	688
10	157	185
11	337	345
12	359	364
13	206	217

H,9,2

-14	93	99
-13	60*	21
-12	62	58
-11	127	154
-10	61*	69
-9	172	172
-8	158	131
-7	66	61
-6	113	91
-5	53*	42
-4	112	101
-3	124	118
-2	87	78
-1	126	121
0	55*	38
1	115	101
2	117	126
3	155	163
4	56*	32
5	57*	16
6	131	133
7	60*	33
8	120	110
9	59*	40
10	57*	29
11	109	106
12	60*	56

H,9,3

-14	129	138
-13	556	554
-12	158	191
-11	495	475
-10	180	201
-9	522	513
-8	215	188
-7	191	170
-6	71	66
-5	256	233
-4	243	238
-3	392	378
-2	157	160
-1	662	689
0	443	456
1	650	668
2	319	321
3	85	88
4	365	361
5	94	105
6	181	185
7	659	657
8	220	227
9	311	305
10	329	346
11	193	186
12	395	425

H,9,4

-14	127	151
-13	60*	29
-12	68	66
-11	59	72
-10	64	37
-9	174	182
-8	56*	18
-7	146	130
-6	91	96
-5	56*	59
-4	56*	42
-3	305	306
-2	71	62
-1	54*	32
0	176	201
1	55*	34
2	66	50
3	53*	12
4	98	108
5	126	141
6	58*	56
7	167	184
8	131	129
9	156	157
10	98	73
11	109	111

H,9,5

-14	355	381
-13	426	424
-12	266	281
-11	271	258
-10	57*	17
-9	688	687
-8	118	123
-7	309	292
-6	306	306
-5	219	211
-4	259	271
-3	600	601
-2	56*	48
-1	811	816
0	63	74
1	322	310
2	239	251
3	177	186
4	108	118
5	311	316
6	209	192
7	475	494
8	123	130
9	272	282
10	236	254

H,9,6

-14	57*	25
-13	85	83
-12	71	75
-11	58*	17
-10	102	70
-9	138	129
-8	72	87
-7	174	174
-6	340	354
-5	134	122
-4	145	154
-3	118	113
-2	82	100
-1	58	25
0	56*	14
1	180	171
2	166	181
3	225	226
4	58*	16
5	60*	61
6	72	89
7	177	181
8	64*	79
9	60*	67
10	59*	42

H,9,7

-14	382	395
-13	449	451
-12	198	203
-11	547	547
-10	60*	1
-9	643	638
-8	57*	22
-7	198	174
-6	60*	45
-5	721	727
-4	169	172
-3	1015	1020
-2	58*	46
-1	595	580
0	284	287
1	692	721
2	427	420
3	640	673
4	313	329
5	285	283
6	148	179
7	338	343
8	311	331
9	373	388

H,9,8

-13	59*	52
-12	58*	43
-11	100	102
-10	128	124
-9	58*	19
-8	57*	17
-7	167	156
-6	63*	79
-5	61*	36
-4	56*	3
-3	58*	0
-2	59*	19
-1	58*	16
0	66	68
1	235	237
2	240	239
3	107	112
4	57*	9
5	246	239

	H,9,8	
6	59*	41
7	88	71
	H,9,9	
-13	622	643
-12	58*	4
-11	665	657
-10	61*	2
-9	389	387
-8	66	55
-7	279	269
-6	292	260
-5	699	701
-4	176	180
-3	516	524
-2	299	314
-1	521	514
0	569	579
1	627	642
2	479	490
3	283	291
4	260	276
5	224	233
6	334	345
	H,9,10	
-12	61*	70
-11	110	110
-10	143	136
-9	103	117
-8	58*	57
-7	237	242
-6	88	87
-5	56*	6
-4	151	137
-3	62*	35
-2	67	47
-1	83	73
0	88	116
1	58*	4
2	130	138
3	56*	21
4	96	97
5	135	145
	H,9,11	
-11	421	432
-10	124	118
-9	418	440
-8	260	253
-7	394	417
-6	58*	9
-5	219	221
-4	57*	14
-3	388	390
-2	165	143
-1	465	455
0	368	384
1	187	192
2	262	276
3	124	130
	H,9,12	
-9	178	165
-8	61	52
-7	59*	52
-6	123	116
-5	109	125
-4	117	113
-3	86	72
-2	128	110
-1	59*	34
0	180	183
1	58*	49
	H,9,13	
-6	57*	31
-5	367	384
-4	122	124
	H,10,0	
0	326	334
1	194	174
2	586	586
3	59*	52
4	448	452
5	215	201
6	163	161
7	79	69
8	411	430
9	61*	70
10	316	317
11	171	167
12	79	83
	H,10,1	
-12	430	443
-11	216	255
-10	573	593
-9	239	227
-8	393	361
-7	158	141
-6	244	218
-5	59*	63
-4	412	386
-3	62*	82
-2	691	657
-1	66	56
0	679	640
1	196	182
2	550	544
3	381	404
4	410	399
5	197	193
6	312	323
7	153	147
8	450	486
9	356	375
10	358	373
11	174	173
	H,10,2	
-12	182	171
-11	61*	75
-10	152	142
-9	69	69
-8	59*	40
-7	139	146
-6	78	55
-5	92	90
-4	140	152
-3	187	177
-2	98	87
-1	243	242
0	466	466
1	416	405
2	441	439
3	123	130
4	58*	34
5	130	138
6	236	229
7	58*	5
8	371	379
9	156	179
10	180	171
11	177	180
	H,10,3	
-12	492	502
-11	203	201
-10	392	386
-9	60*	28
-8	422	428
-7	73	65
-6	211	208
-5	105	100
-4	234	228
-3	77	54
-2	463	446
-1	145	115
0	291	279
1	153	138
2	60*	19
3	192	195
4	105	117
5	362	388
6	130	131
7	225	275
8	193	177
9	276	294
10	185	200
	H,10,4	
-12	281	299
-11	152	143
-10	59*	80
-9	184	174
-8	159	171
-7	143	119
-6	102	102
-5	331	344
-4	78	66
-3	202	205
-2	433	428
-1	68	64
0	432	429
1	59*	35
2	239	232
3	58*	1
4	137	142
5	93	88
6	160	178
7	58*	10
8	220	239
9	141	141
	H,10,5	
-12	248	252
-11	220	214
-10	338	335
-9	60*	22
-8	295	306
-7	58*	22
-6	355	364
-5	216	237
-4	462	459
-3	58*	21
-2	365	364
-1	58*	5
0	417	397
1	62*	22
2	361	365
3	321	311
4	152	153
5	174	190
6	240	256
7	145	143
8	302	306
9	233	262
	H,10,6	
-12	95	101
-11	137	127
-10	346	356
-9	60*	4
-8	147	160
-7	88	102
-6	67	40
-5	146	145
-4	446	457
-3	59*	26
-2	595	586
-1	152	140
0	256	259
1	71	64
2	258	263
3	57*	23
4	95	92
5	58*	18
6	121	134
7	125	123
8	58*	30
	H,10,7	
-12	292	295
-11	255	247
-10	276	292
-9	61*	42
-8	357	361
-7	62*	35
-6	388	394
-5	103	102
-4	466	494
-3	62*	16
-2	520	540
-1	59*	38
0	412	423
1	312	314
2	397	425
3	259	267
4	326	335
5	160	161
6	386	398
	H,10,8	
-11	198	177
-10	323	343
-9	74	69
-8	61*	39
-7	60*	37
-6	206	201
-5	84	97
-4	389	393
-3	63*	36
-2	256	257
-1	59*	47
0	166	186
1	192	210
2	219	224
3	135	169
4	138	136
5	57*	36

H,10,9

-9	177	162
-8	332	343
-7	59*	18
-6	217	220
-5	62*	30
-4	487	490
-3	195	192
-2	348	369
-1	344	351
0	209	216
1	363	385
2	199	216
3	326	338
4	120	115

H,10,10

-9	205	201
-8	124	116
-7	201	174
-6	243	257
-5	113	116
-4	83	74
-3	61*	55
-2	148	154
-1	161	178
0	145	142
1	220	240
2	62*	46

H,10,11

-7	59*	68
-6	324	360
-5	101	106
-4	266	280
-3	82	99
-2	224	248
-1	141	156

H,11,0

1	653	656
2	207	201
3	588	614
4	74	90
5	293	300
6	57*	18
7	347	346
8	93	113
9	446	439

H,11,1

-10	80	86
-9	165	169
-8	169	176
-7	305	293
-6	59*	23
-5	280	273
-4	123	133
-3	355	364
-2	246	260
-1	466	443
0	142	150
1	212	188
2	136	140
3	262	286
4	175	167
5	366	365
6	123	129
7	62	56
8	159	169
9	72	27

H,11,2

-10	58*	14
-9	426	418
-8	101	81
-7	236	247
-6	104	95
-5	343	345
-4	275	276
-3	173	175
-2	58*	8
-1	358	353
0	282	292
1	502	513
2	223	254
3	320	325
4	230	260
5	304	319
6	89	117
7	282	304
8	196	217

H,11,3

-10	85	97
-9	211	206
-8	70	87
-7	305	315
-6	58*	4
-5	256	245
-4	237	248
-3	284	269
-2	106	101
-1	190	178
0	276	277
1	239	256
2	78	69
3	286	298
4	248	270
5	157	172
6	56*	4
7	66	43
8	89	97

H,11,4

-10	81	102
-9	269	257
-8	140	150
-7	233	236
-6	61*	57
-5	239	236
-4	160	159
-3	293	302
-2	75	103
-1	501	529
0	60*	32
1	319	338
2	93	104
3	237	245
4	117	126
5	148	159
6	60*	16
7	247	251

H,11,5

-10	169	182
-9	58*	1
-8	58*	9
-7	200	207
-6	144	145
-5	328	327
-4	59*	9
-3	113	98
-2	76	50
-1	64*	59
0	59*	32
1	246	237
2	57*	13
3	170	185
4	56*	22
5	106	127
6	173	196

H,11,6

-9	429	447
-8	144	145
-7	157	164
-6	61*	78
-5	221	218
-4	59*	39
-3	392	418
-2	113	90
-1	472	476
0	62*	42
1	463	475
2	116	114
3	275	304
4	113	131
5	338	335

H,11,7

-8	113	93
-7	287	291
-6	58*	32
-5	245	247
-4	70	49
-3	257	246
-2	151	144
-1	233	229
0	125	125
1	225	240
2	57*	42
3	177	178

H,11,8

-7	168	167
-6	59*	33
-5	344	355
-4	60*	9
-3	484	508
-2	91	95
-1	400	410
0	245	268
1	256	273
2	241	265

H,11,9

-5	259	252
-4	222	230
-3	263	278
-2	113	123
-1	245	266

H,12,0

0	432	428
1	60*	3
2	436	443
3	62*	55
4	378	381
5	196	212
6	435	448

H,12,1

-6	111	116
-5	73	84
-4	60*	27
-3	250	256
-2	121	135
-1	60*	22
0	59*	23
1	147	140
2	72	61
3	60*	6
4	124	131
5	61*	59
6	78	101

H,12,2

-6	418	422
-5	62*	56
-4	369	376
-3	61*	8
-2	373	386
-1	62*	61
0	414	418
1	58*	25
2	472	481
3	156	153
4	364	365
5	214	230

H,12,3

-6	58*	2
-5	59*	29
-4	78	86
-3	98	101
-2	57*	23
-1	90	80
0	228	234
1	57*	11
2	105	97
3	63*	47
4	130	141

H,12,4

-6	248	258
-5	57*	22
-4	199	213
-3	95	94
-2	252	260
-1	79	90
0	208	218
1	58*	18
2	347	352
3	130	160

H,12,5

-5	78	47
-4	178	181
-3	56*	3
-2	125	142
-1	82	79
0	124	125
1	63	89

H,12,6

-3	58*	49
-2	305	323
-1	58*	19

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CHAPTER VI

The Crystal and Molecular Structure
of Hydridophenoxybis(triphenylphosphine)ruthenium(II) Diphenol
A Complex with a Phenoxy Group Co-ordinated to Ruthenium as a π-Bonded Arene.

Abstract

The crystal structure of the title molecule has been determined from three-dimensional X-ray data by Patterson and Fourier methods, and refined using least-squares techniques to R = 0.029 for 4520 independent reflections. X-ray intensity data were collected on a Siemens four-circle diffractometer using Cu-$K\alpha$ radiation. Crystals are monoclinic with unit-cell dimensions

a = 20.331(1)Å, b = 9.561(1)Å, c = 23.744(2)Å, β = 106.24(1),
Space group $P2_1/a$ and $Z = 4$.

The complex is monomeric and the metal atom has a co-ordination consisting of two σ-bonded triphenylphosphine groups, a hydride hydrogen and a phenoxy ring bonded as an arene to the metal. Ru-P bond distances for the two triphenylphosphine groups are 2.314Å and 2.303Å respectively and the P-Ru-P angle is 97.3°. Five of the six Ru-C distances are in the range 2.246 — 2.301Å, whilst the sixth is considerably longer 2.482Å. The six membered ring is markedly non-planar. The Ru-H distance has been optimised (1.54Å) and is rather shorter than expected.

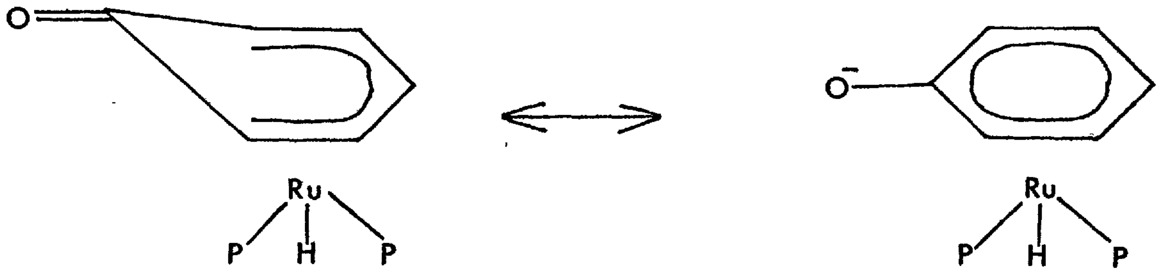
The two phenol molecules of solvation are hydrogen bonded to the phenoxy group.

Introduction

The title compound has been prepared by the action of excess phenol on $RuH_2(PPh_3)_4$ in toluene.[1] This was done as part of an investigation into the catalytic behaviour of Ruthenium complexes by Professor Wilkinson and co-workers.

The infra-red and nuclear magnetic resonance spectra of the complex show certain unusual features which are best accounted for by postulating that the phenoxy group is not bound to the ruthenium through the oxygen atom, but rather as an arene through the π-electron cloud of the phenyl ring.

In a complex of this kind, the phenoxide moiety may be considered as being a resonance hybrid of a uninegative five electron donor containing a carbon-oxygen double bond (I) or as a neutral six electron donor with the negative charge localised on the oxygen atom (II).



I

II

This present X-ray investigation, which complements our previous studies on the cation $[RuH(\eta^6-C_6H_5PPh_2)(PPh_3)_2]^+$ was carried out to confirm that π-bonding of the phenoxide ring, which had not been previously crystallographically characterised, although it may occur in $Rh(PPh_3)_2OPh$[2], is occurring, and to ascertain the contributions of the two canonical forms.

Experimental

Hydridophenoxybis(triphenylphosphine)ruthenium(II) crystallises from the solution obtained by the reaction of excess phenol on $RuH_2(PPh_3)_4$ in toluene as a phenol solvate. Suitable crystals were obtained and the unit-cell dimensions and space group were determined from preliminary Weissenberg and oscillation photographs.

Crystal Data

$C_{54}H_{48}O_3P_2Ru$, $\underline{M}$ = 907.9, Monoclinic
$\underline{a}$ = 20.331(1)Å, $\underline{b}$ = 9.561(1), $\underline{c}$ = 23.744(2)Å, β = 106.24(1)°,
$\underline{U}$ = 4431.3Å, $\underline{D}_m$ = 1.36g.cm^{-3}(by flotation), $\underline{Z}$ = 4, $\underline{D}_c$ = 1.36g.cm^{-3}
$\underline{F}$(000) = 1880. Cu-$\underline{K}\alpha$ radiation, λ = 1.5418Å; μ(Cu-$\underline{K}\alpha$) = 39.94cm^{-1}.
Space group $\underline{P}2_1/\underline{a}$ from systematic absences: h0ℓ, h = 2n + 1;
0k0, k = 2n + 1.

The needles are elongated about the $\underline{b}$ axis. A crystal of size ca. 0.21 X 0.27 x 0.08mm^3. was selected and mounted about the $\underline{b}$ axis on a Siemens off-line automatic four-circle diffractometer using Cu-$\underline{K}\alpha$ radiation at a take-off angle of 6°, a Ni β-filter and a Na(Tℓ)I scintillation counter. The θ-2θ scan technique was employed, using a 'five-value' measuring procedure. A total of 4520 independent reflections were measured (to θ = 50°), of which 294 were judged to be unobserved, i.e. I < 2.58σ(I). The net count of the reference reflection measured at every 50 reflections did not deteriorate significantly during the entire data collection (ca. 13 days). The data were converted to a common arbitrary scale by use of the reference reflection and Lorentz and polarisation corrections were applied. The data were corrected at a later stage for absorption effects and this was done according to the method of Busing and Levy[3] using a 10 x 10 x 10 grid with crystal pathlengths determined by the vector analysis procedure of Coppens *et al.*[4]

Solution and Refinement of the Structure

The structure was solved by Patterson and Fourier methods. All calculations were carried out using the Crystal Structure Calculations Systems "X-ray'70" and its updated version "X-ray '72"[5] using either the Imperial College CDC. 6400 or the University of London CDC. 6400, 6600 and 7600 computers.

A three-dimensional Patterson synthesis gave a straightforward solution for the ruthenium atom, and three cycles of least-squares gave the standard agreement factor $\underline{R}$ 0.45. From subsequent difference-Fourier syntheses all the remaining 59 non-hydrogen atoms were located, and anisotropic refinement gave $\underline{R}$ 0.082. Correction for absorption and refinement as previously gave $\underline{R}$ 0.051. Addition of the phenyl, phenoxy and phenolic hydrogen atoms,obtained from the latest difference-Fourier map, as a fixed-atom contribution with isotropic temperature factors of their respective parent atoms, reduced $\underline{R}$ to 0.035. The hydride hydrogen and one of the two phenol - OH hydrogens were also found; the hydride hydrogen was later optimised using the full procedure of La Placa and Ibers.[6]

At this stage of refinement, after inclusion of all atoms save the one unlocatable hydrogen-bonded-hydrogen a weighting scheme of the type suggested by Hughes[7] was used, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F > F^*$, with $F^* = 85$ being the final value. The application of the weighting scheme reduced $\underline{R}$ to 0.029. The hydride hydrogen was at this stage redetermined and optimised; $\underline{R}$ remained unchanged.

Atomic scattering factors used were those of Cromer and Waber[8] except those for hydrogen which were obtained from Stewart *et al*[9]. The correction for the effects of the real and imaginary parts of the anomalous dispersion correction for ruthenium and phosphorus were made using the tabulated values after Cromer.[10]

Table 1 lists the fractional co-ordinates of the non-hydrogen atoms with their estimated standard deviations. (These are obtained from the CRYSLQ program of X-ray '70 and are thus a slight underestimate of the true deviations). Table 2 contains the coefficients in the expression for the anisotropic Debye-Waller factor:-

$$\exp\,[-2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}\ell^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*h\ell + 2U_{23}b^*c^*k\ell)],$$

while the unrefined co-ordinates of the hydrogen atoms are given in Table 3. The observed and the calculated structure amplitudes are listed at the end of the chapter.

Description of the Structure and Discussion

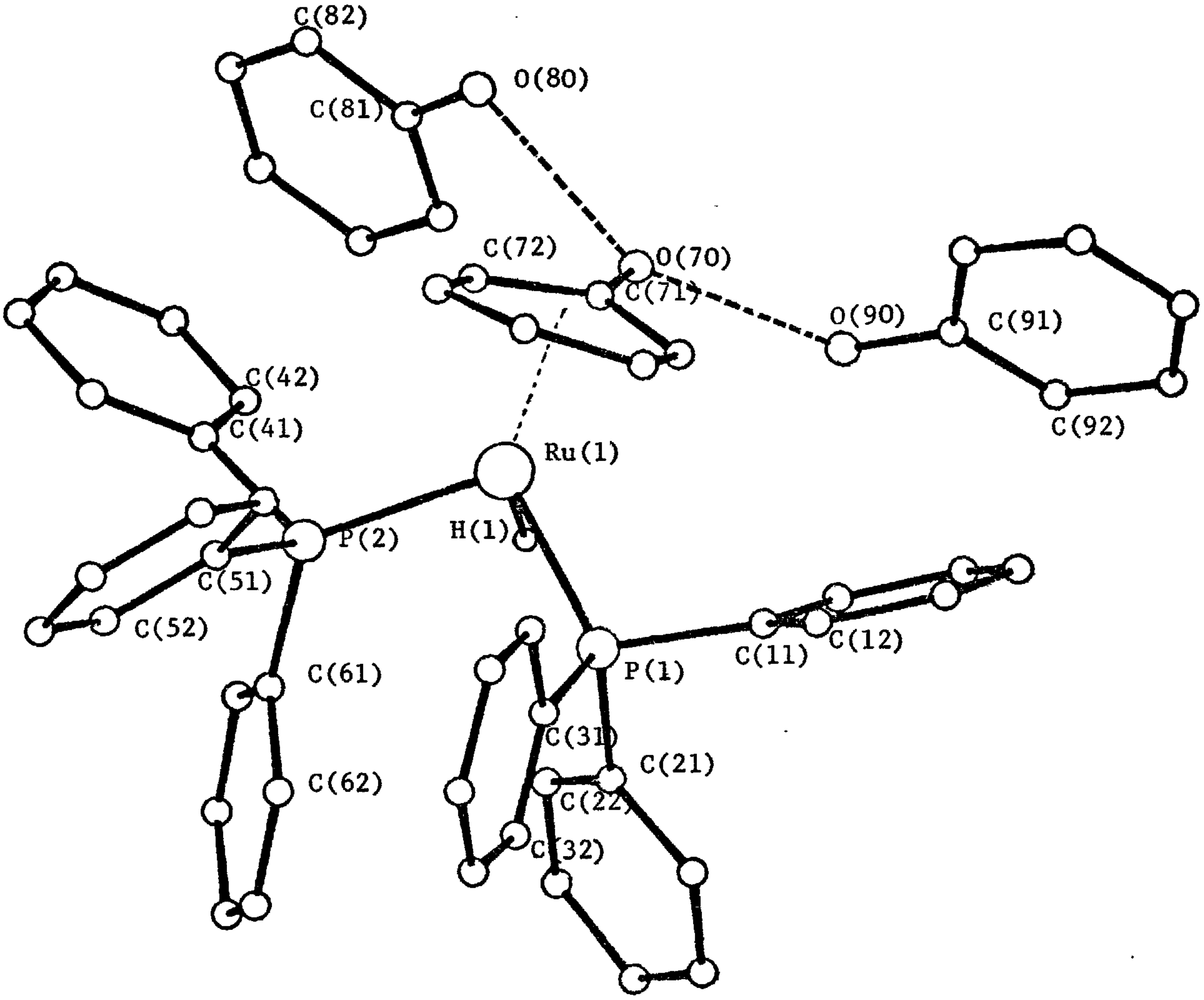
Figure 1 shows the molecular structure of the complex as well as the relative orientation of the two hydrogen-bonded phenol solvate groups. The central metal atom may be considered to have a distorted tetrahedral co-ordination, as in the structure discussed in the previous chapter, if one considers the η-bonded phenoxy ring as a single co-ordination position. The two σ-bound triphenylphosphine groups and the hydride hydrogen complete the co-ordination about the metal. The more important bond lengths and bond angles are quoted in Tables 4 and 5 respectively.

The two cis Ru-P distances [Ru(1)-P(1) 2.314Å and Ru(1)-P(2) 2.303Å] are similar to those in the structure of $RuH(PPh_3)_2(\eta\text{-}Ph,P,Ph_2)^+$, (A), [Ru(1)-P(1) 2.312Å and 2.331Å] discussed in Chapter V, and the previous comparisons made there to the values of 2.336Å in $Ru(PyS)_2(PPh_3)_2$ [11] and 2.346Å in $Ru(HCS)_2(PPh_3)_2$ [12] hold true. The P(1)-Ru(1)-P(2) angle is 97.32° (98.68° in A) and the P(1)-Ru(1)-H(1) and P(2)-Ru(1)-H(2) angles are 77° and 86° respectively.

The metal-carbon (arene) bond lengths average 2.309Å although the Ru(1)-C(71) distance is significantly longer, being 2.482Å. The mean Ru-C distance excluding C(71) and C(74) is 2.268Å which is comparable to the value of 2.269Å in the previous structure determination (A). The arene ring is markedly non-planar (Table 6) and thus two centroids of the ring were calculated, one using all the six atoms and the other using the four atoms C(72), C(73), C(75), and C(76).

The distances of ruthenium to the calculated centroids are 1.829Å and 1.789Å respectively. It is again notable that the carbon-carbon bond lengths in the arene (mean of 1.415Å) are greater than those in the unbound phenyl rings (mean of 1.384Å). These values are equivalent to those found in the previous structure (A) for which the corresponding values are 1.411Å and 1.384Å respectively. This again indicates the

Figure 1



Atoms are numbered in sequence around each ring in the order C(m1)-C(m6), where m is the number of the ring. Atoms C(m3)-C(m6) have been omitted for the sake of clarity.

drift of the π-electron cloud towards the ruthenium atom with a consequential slight decrease in bond order around the ring. The arene ring is not planar and is boat-shaped with atom C(71) being significantly out of plane (0.185A^{o}) from the plane of C(72), C(73), C(75), C(76) whilst C(74) deviates considerably less (0.052Å) from this plane.

The bond distances and bond angles around the arene ring demonstrate this bending of the phenoxy ring. C(71)-C(72) and C(71)-C(76) are longer than the other four C-C bonds within the ring, (1.438Å and 1.431Å respectively as compared to a mean of 1.406Å for the four distances) whilst the valence angles inside the ring are reduced at the apical positions [C(72)-C(71)-C(76) = 114.4°; C(73)-C(74)-C(75) = 117.8°]. The planarity of the phenyl, phenoxy and phenol rings are shown in Table 6 together with the distances of particular atoms from the best planes.

The position of the hydride hydrogen has been determined and the Ru(1)-H(1) bond length of 1.54Å is shorter than the expected value of 1.67-1.68Å as quoted in Chapter V. This hydrogen position was optimised using $\mathrm{Sin}\theta^{-1}\lambda$ cut-off values as previously; a diffraction ripple of ca 0.4e/Å^{3} was situated near the hydrogen peak and may be the cause of this experimentally short value.

The mean P-C distance of 1.839Å is similar to that found in many transition metal complexes and is a very good agreement with the previously determined mean value of 1.834Å in structure A. The angular distortion at P is similar to that encountered in the structure of $\mathrm{RuH(PPh_3)_2}$-$(\eta\text{-Ph.P.Ph}_2)^{+}$, A. Mean values of 116.3° for Ru-P-C and of 101.8° for C-P-C valence angles can be compared with the corresponding values of 115.7° and 102.3° in A. A further comparison of these values with those found in $\mathrm{RuH(CO_2Me)(PPh_3)_3}$[13], of 116.4° and 101.5° respectively demonstrates the similar distortions experienced at the phosphorus atoms in these structures.

Fig. 2 shows a composite view of structure A and the title compound viewed normal to the arene ring. There is a great similarity between the two, and the alignment of P(3)-C(91) in A and C(71)-O(70) in the same direction as Ru-H in the present structure is notable and is suggestive of some weak interaction between these atoms.

The intermolecular packing is shown in the stereoscopic view (fig. 3) which was drawn using the ORTEP program.[14]

A least-squares planes calculation shows that the six phenyl and the two phenol rings are satisfactorily planar; the maximum deviation for all the planes is 0.015Å. The π-bonded phenoxy ring is distinctly non-planar as has been previously discussed. The planarity of this π-bonded arene-ring can be compared to those found in other structures. The structures of $[RuH(PPh_3)_2(\eta\text{-Ph.P.Ph}_2)]^+$, (A), as discussed in Chapter V; $Rh[P(OCH_3)_3]_2\ B(\eta\text{-Ph-BPh}_3)$,[15] (C), and $(\pi\text{-}C_5H_5)Ru(\eta\text{-Ph-BPh}_3)$,[16] (D), are comparable and the results of this are of significant interest.

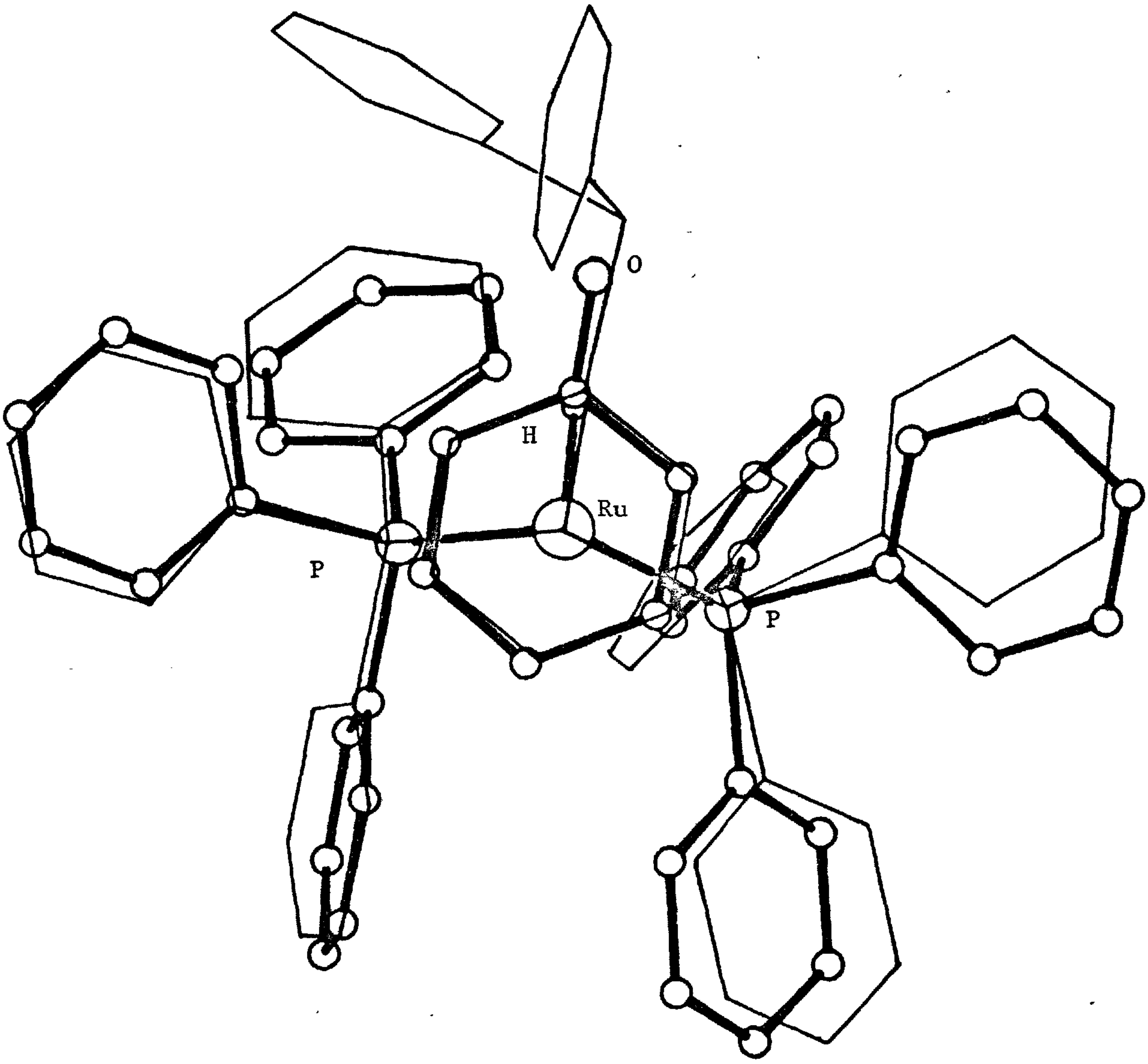
The least-squares planes of both the C(m1)-C(m6) and C(m2), C(m3), C(m5), C(m6) planes have been calculated for all these structures and are tabulated in Table 7. The present structural determination has been identified as (B) in the scheme for ease of reference.

It is notable that the π-bonded arene in structures A and D are almost planar, the maximum deviations being 0.017Å and 0.011Å respectively for the planes calculated on all six atoms. B is the most distorted plane of all while plane C is in an intermediate category.

A further comparison may be drawn between the metal-arene plane distance experienced in the three ruthenium structures A, B and D. The corresponding values based on planes of all six atoms are 1.776Å, 1.826Å and 1.701Å respectively whilst the values based on the four atom plane are 1.771Å, 1.789Å and 1.690Å. The bond order in

Fig. 2

A superimposition diagram of the present structure with that presented in the previous chapter. The orientation is such that the arene ring is in the plane of the paper. The present structure is in bold style.



The mirror image of the present structural co-ordinates were used to plot the above diagram to achieve a suitable comparison with the earlier structural study.

reducing strength of metal-arene bonds is D > A > B. The position of D in this respect may be accounted for if one considers that the steric factors in this structure are at a minimum with no bulky triphenylphosphines to cause intermolecular crowding. The phenoxy group experiences less delocalisation than one would encounter in a phenyl ring owing to the presence of the electron withdrawing oxygen atom and as a consequence the metal-arene bonds in B are the longest.

The two solvate phenol molecules are hydrogen-bonded to the phenoxy group, the O-O H-bond distances being 2.672Å and 2.736Å respectively. The hydrogen atom of the former H-bond (O_{70}- O_{90}) was readily locatable in the difference-Fourier synthesis but the second hydrogen atom could not be located. The fact that it is attached to the solvate molecule rather than to the π-bonded ring is demonstrated by the C-O bond lengths. These are 1.367 and 1.363Å in the phenol molecules compared to 1.277Å in the phenoxy group. The C-O distances in the two phenol molecules are unexceptional and may be compared to 1.36 and 1.35Å in p-Nitrophenol[17] and 1.36, 1.37Å in o-Aminophenol - hydrochloride.[18] On the other hand, C=O double bond lengths found in related aromatic systems are 1.22Å in p-Benzoquinone[19] and 1.23Å in Tetrahydroxy-p-benzoquinone dihydrate.[20]

The distance of 1.277Å found in the phenoxy group in this structure, and the marked non-planarity of the arene ring show that the resonance form I plays an important role in this molecule.

Fig. 3

A stereoscopic view of the unit-cell showing the packing in the molecules.

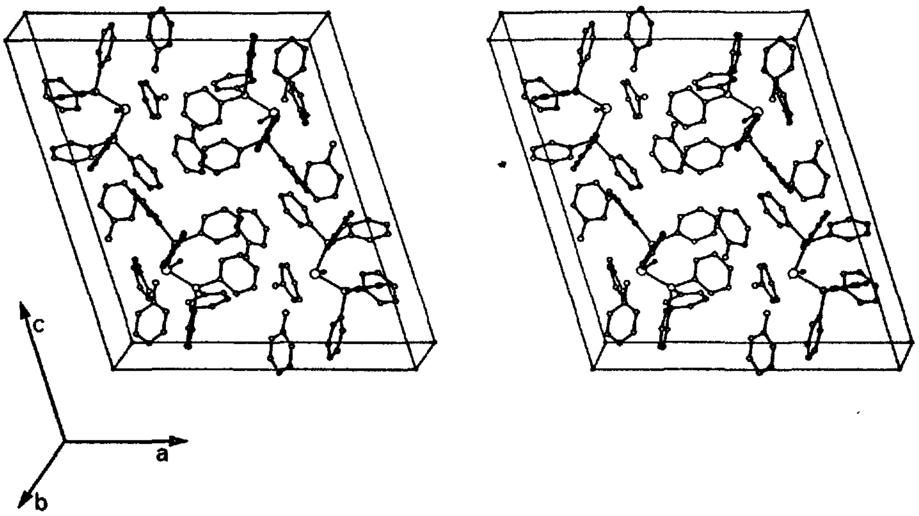


Table 1

Fractional co-ordinates of non-hydrogen atoms with estimated standard deviations in parentheses.

All ring carbon atoms are numbered C(*mn*) where *m* is the ring number and *n* is the atom number in the ring; *n* is such that C(*m*1) is attached to the P or O atoms, and other ring atoms are numbered in succession such that C(*m*4) is *para* to C(*m*1). The π-bonded phenyl ring is C(7*n*).

	x	y	z
Ru(1)	0.20697(1)	0.18435(3)	0.23376(1)
P(1)	0.28697(5)	0.19437(10)	0.18112(4)
P(2)	0.27458(5)	0.27876(10)	0.31978(4)
C(11)	0.2473(2)	0.1411(4)	0.1045(2)
C(12)	0.2312(2)	0.2322(4)	0.0574(2)
C(13)	0.1975(3)	0.1819(6)	0.0016(2)
C(14)	0.1800(2)	0.0437(5)	-0.0072(2)
C(15)	0.1962(2)	-0.0475(5)	0.0391(2)
C(16)	0.2303(2)	0.0001(4)	0.0948(2)
C(21)	0.3630(2)	0.0824(4)	0.1967(2)
C(22)	0.3829(2)	0.0005(4)	0.2470(2)
C(23)	0.4412(2)	-0.0821(5)	0.2579(2)
C(24)	0.4796(2)	-0.0844(5)	0.2180(2)
C(25)	0.4593(2)	-0.0073(5)	0.1673(2)
C(26)	0.4014(2)	0.0755(5)	0.1562(2)
C(31)	0.3201(2)	0.3694(4)	0.1736(2)
C(32)	0.3885(2)	0.4041(5)	0.1815(2)
C(33)	0.4071(3)	0.5426(6)	0.1751(2)
C(34)	0.3587(3)	0.6454(5)	0.1613(2)
C(35)	0.2908(3)	0.6139(5)	0.1530(2)
C(36)	0.2720(2)	0.4766(4)	0.1603(2)
C(41)	0.2384(2)	0.2372(4)	0.3811(2)
C(42)	0.2201(2)	0.1001(4)	0.3888(2)
C(43)	0.1919(2)	0.0646(5)	0.4337(2)
C(44)	0.1811(3)	0.1663(6)	0.4708(2)
C(45)	0.1981(3)	0.3019(6)	0.4639(2)

C(46)	0.2271(2)	0.3384(5)	0.4193(2)
C(51)	0.2850(2)	0.4699(4)	0.3260(2)
C(52)	0.3354(2)	0.5312(4)	0.3717(2)
C(53)	0.3425(2)	0.6759(5)	0.3751(2)
C(54)	0.2995(3)	0.7588(5)	0.3330(2)
C(55)	0.2494(3)	0.7009(5)	0.2885(2)
C(56)	0.2426(2)	0.5573(4)	0.2849(2)
C(61)	0.3642(2)	0.2229(4)	0.3489(2)
C(62)	0.4151(2)	0.2889(5)	0.3301(2)
C(63)	0.4826(2)	0.2468(6)	0.3496(2)
C(64)	0.5002(2)	0.1344(7)	0.3873(3)
C(65)	0.4510(3)	0.0672(5)	0.4062(2)
C(66)	0.3830(2)	0.1109(5)	0.3873(2)
O(70)	0.0897(1)	−0.0938(3)	0.2219(1)
C(71)	0.1035(2)	0.0342(5)	0.2149(2)
C(72)	0.1101(2)	0.1366(5)	0.2605(2)
C(73)	0.1128(2)	0.2807(4)	0.2493(2)
C(74)	0.1155(2)	0.3297(5)	0.1943(2)
C(75)	0.1209(2)	0.2309(5)	0.1524(2)
C(76)	0.1185(2)	0.0858(4)	0.1633(2)
O(80)	0.0211(2)	−0.0933(5)	0.3060(2)
C(81)	0.0544(2)	−0.1620(5)	0.3564(2)
C(82)	0.0295(3)	−0.1373(7)	0.4043(3)
C(83)	0.0616(3)	−0.2051(8)	0.4565(3)
C(84)	0.1157(4)	−0.2898(7)	0.4596(3)
C(85)	0.1378(4)	−0.3094(6)	0.4101(3)
C(86)	0.1074(3)	−0.2456(6)	0.3580(3)
O(90)	0.1120(2)	−0.3024(3)	0.1547(1)
C(91)	0.0819(2)	−0.2964(5)	0.0957(2)
C(92)	0.1046(3)	−0.3889(5)	0.0604(2)
C(93)	0.0771(3)	−0.3862(6)	0.0007(2)
C(94)	0.0275(3)	−0.2922(7)	−0.0251(2)
C(95)	0.0036(3)	−0.2008(6)	0.0096(3)
C(96)	0.0302(2)	−0.2029(5)	0.0706(2)

Table 2

Anisotropic thermal parameters.

ATOM	$\underline{U}_{11}\mathrm{x}10^4$	$\underline{U}_{22}\mathrm{x}10^4$	$\underline{U}_{33}\mathrm{x}10^4$	$\underline{U}_{12}\mathrm{x}10^4$	$\underline{U}_{13}\mathrm{x}10^4$	$\underline{U}_{23}\mathrm{x}10^4$
Ru(1)	248(2)	296(2)	293(2)	2(1)	93(1)	12(1)
P(1)	296(5)	304(6)	302(5)	9(4)	101(4)	30(4)
P(2)	335(6)	298(6)	327(6)	-12(4)	120(4)	-9(4)
	$\underline{U}_{11}\mathrm{x}10^3$	$\underline{U}_{22}\mathrm{x}10^3$	$\underline{U}_{33}\mathrm{x}10^3$	$\underline{U}_{12}\mathrm{x}10^3$	$\underline{U}_{13}\mathrm{x}10^3$	$\underline{U}_{23}\mathrm{x}10^3$
C(11)	33(2)	36(2)	27(2)	-3(2)	12(2)	-5(2)
C(12)	52(3)	43(3)	33(3)	-3(2)	11(2)	5(2)
C(13)	77(3)	69(4)	31(3)	-7(3)	9(2)	7(3)
C(14)	64(3)	72(4)	37(3)	-16(3)	14(2)	-16(2)
C(15)	62(3)	46(3)	55(3)	-11(2)	25(2)	-15(2)
C(16)	49(3)	38(2)	40(3)	-1(2)	18(2)	-3(2)
C(21)	29(2)	32(2)	35(2)	0(2)	11(2)	-2(2)
C(22)	42(2)	34(2)	38(2)	4(2)	11(2)	-2(2)
C(23)	49(3)	43(3)	45(3)	15(2)	5(2)	2(2)
C(24)	33(2)	46(3)	69(3)	8(2)	10(2)	-10(3)
C(25)	37(2)	55(3)	58(3)	5(2)	24(2)	-3(3)
C(26)	39(2)	53(3)	46(3)	3(2)	21(2)	6(2)
C(31)	39(2)	34(2)	27(2)	-5(2)	11(2)	1(2)
C(32)	41(3)	55(3)	41(3)	-13(2)	7(2)	6(2)
C(33)	54(3)	73(4)	47(3)	-35(3)	3(2)	5(3)
C(34)	83(4)	43(3)	43(3)	-21(3)	11(3)	1(2)
C(35)	76(4)	35(3)	58(3)	-4(3)	25(3)	1(2)
C(36)	52(3)	33(3)	50(3)	-5(2)	23(2)	1(2)
C(41)	29(2)	39(2)	31(2)	-1(2)	10(2)	3(2)
C(42)	45(2)	41(3)	36(2)	-5(2)	11(2)	2(2)
C(43)	53(3)	54(3)	45(3)	-16(2)	9(2)	9(3)
C(44)	60(3)	89(4)	43(3)	-17(3)	25(2)	4(3)
C(45)	71(3)	74(4)	52(3)	-9(3)	37(3)	-13(3)
C(46)	53(3)	48(3)	47(3)	-4(2)	24(2)	-6(2)
C(51)	39(2)	30(2)	41(2)	-5(2)	17(2)	-4(2)
C(52)	50(3)	39(3)	51(3)	-5(2)	13(2)	-5(2)
C(53)	63(3)	43(3)	61(3)	-15(2)	27(3)	-15(3)
C(54)	85(4)	29(2)	63(3)	-2(3)	39(3)	2(3)

C(55)	78(3)	35(3)	56(3)	4(3)	19(3)	5(2)
C(56)	58(3)	36(2)	45(3)	0(2)	12(2)	2(2)
C(61)	34(2)	37(2)	28(2)	-3(2)	8(2)	-8(2)
C(62)	41(3)	52(3)	51(3)	-3(2)	18(2)	-7(2)
C(63)	39(3)	80(4)	76(4)	-5(3)	24(3)	-11(3)
C(64)	37(3)	93(4)	84(4)	13(3)	7(3)	-18(4)
C(65)	55(3)	62(3)	57(3)	17(3)	1(3)	-1(3)
C(66)	41(3)	48(3)	41(2)	3(2)	4(2)	-6(2)
O(70)	48(2)	50(2)	47(2)	-18(1)	15(1)	-1(1)
C(71)	22(2)	51(3)	35(2)	-8(2)	8(2)	1(2)
C(72)	25(2)	58(3)	39(2)	-3(2)	16(2)	2(2)
C(73)	26(2)	49(3)	57(3)	7(2)	18(2)	-4(2)
C(74)	29(2)	45(3)	62(3)	11(2)	9(2)	10(3)
C(75)	23(2)	60(3)	36(2)	3(2)	2(2)	12(2)
C(76)	27(2)	50(3)	35(2)	-6(2)	6(2)	-2(2)
O(80)	80(3)	109(3)	96(3)	-7(2)	23(2)	11(3)
C(81)	56(3)	74(3)	42(3)	-29(3)	-5(3)	26(3)
C(82)	58(3)	106(5)	89(5)	-12(3)	23(3)	17(4)
C(83)	103(5)	150(6)	65(4)	-56(5)	29(4)	0(4)
C(84)	122(6)	102(5)	75(4)	-35(4)	-7(4)	39(4)
C(85)	108(5)	66(4)	106(5)	17(4)	4(4)	13(4)
C(86)	66(3)	54(3)	88(4)	8(3)	0(3)	4(3)
O(90)	85(2)	59(2)	48(2)	4(2)	15(2)	3(2)
C(91)	51(3)	48(3)	49(3)	-11(2)	14(2)	2(2)
C(92)	68(3)	52(3)	58(3)	6(3)	16(3)	1(3)
C(93)	75(4)	79(4)	57(4)	6(3)	14(3)	-10(3)
C(94)	75(4)	99(5)	53(3)	10(4)	-1(3)	-8(3)
C(95)	58(3)	88(4)	74(4)	14(3)	-9(3)	-2(3)
C(96)	46(3)	63(3)	67(3)	-2(3)	14(3)	-11(3)

Table 3

Fractional co-ordinates of the hydrogen atoms. Except for H(1), H(900), these are numbered according to the carbon atom to which they are attached.

	x	y	z
H(1)	0.249	0.049	0.252
H(900)	0.100	-0.200	0.174
H(12)	0.245	0.337	0.064
H(13)	0.185	0.249	-0.033
H(14)	0.155	0.008	-0.049
H(15)	0.183	-0.151	0.032
H(16)	0.242	-0.070	0.130
H(22)	0.354	0.002	0.276
H(23)	0.456	-0.143	0.296
H(24)	0.524	-0.144	0.227
H(25)	0.487	-0.013	0.137
H(26)	0.387	0.135	0.118
H(32)	0.425	0.326	0.192
H(32)	0.458	0.570	0.181
H(34)	0.373	0.747	0.157
H(35)	0.255	0.692	0.142
H(36)	0.221	0.453	0.156
H(42)	0.228	0.022	0.361
H(43)	0.179	-0.038	0.439
H(44)	0.159	0.140	0.504
H(45)	0.191	0.377	0.493
H(46)	0.239	0.442	0.414
H(52)	0.368	0.469	0.403
H(53)	0.380	0.721	0.409
H(54)	0.305	0.866	0.335
H(55)	0.217	0.766	0.258
H(56)	0.205	0.515	0.251
H(62)	0.402	0.371	0.301
H(63)	0.520	0.299	0.336
H(64)	0.551	0.102	0.402
H(65)	0.464	-0.018	0.435
H(66)	0.346	0.059	0.402
H(72)	0.113	0.105	0.303
H(73)	0.113	0.351	0.282

H(74)	0.114	0.436	0.186
H(75)	0.126	0.264	0.113
H(76)	0.128	0.015	0.133
H(82)	-0.013	-0.071	0.400
H(83)	0.042	-0.181	0.493
H(84)	0.139	-0.346	0.498
H(85)	0.183	-0.373	0.416
H(86)	0.123	-0.259	0.319
H(92)	0.144	-0.461	0.080
H(93)	0.096	-0.452	-0.028
H(94)	0.006	-0.290	-0.070
H(95)	-0.035	-0.126	-0.011
H(96)	0.012	-0.132	0.098

Table 4

Selected bond lengths (Å) with estimated standard deviations in parentheses.

Ru(1) - P(1)	2.314(1)	Ru(1) - C(71)	2.482(4)
Ru(1) - P(2)	2.303(1)	Ru(1) - C(72)	2.279(4)
Ru(1) - H(1)	1.54	Ru(1) - C(73)	2.246(4)
Ru(1) - $C_{C^*_{71-76}}$	1.829(4)	Ru(1) - C(74)	2.301(4)
Ru(1) - $C_{C^*_1}$	1.789(4)	Ru(1) - C(75)	2.258(3)
		Ru(1) - C(76)	2.289(3)
Mean Ru(1) - C	2.309(4) .. excluding C(71), C(74)		2.268(4)

...where $C_{C^*_{71-76}}$ is the centre of gravity of the π-bonded phenyl ring and $C_{C^*_1}$ is the centre of gravity of atoms C(72), C(73), C(75) and C(76) only.

P(1) - C(11)	1.844(4)	P(2) - C(41)	1.849(4)
P(1) - C(21)	1.832(4)	P(2) - C(51)	1.841(4)
P(1) - C(31)	1.831(4)	P(2) - C(61)	1.837(4)

Mean P - C .... 1.839(4)

Mean phenyl C - C bonds :-

Ring		Ring	
C(1$\underline{n}$)	1.383	C(4$\underline{n}$)	1.382
C(2$\underline{n}$)	1.386	C(5$\underline{n}$)	1.383
C(3$\underline{n}$)	1.384	C(6$\underline{n}$)	1.383

Mean C - C 1.384

Mean phenol and phenoxy C - C bonds :-

Ring		
C(7$\underline{n}$)	1.415	
C(8$\underline{n}$)	1.385	} mean 1.382
C(9$\underline{n}$)	1.379	

π-bonded ring C(7$\underline{n}$), individual values :-

C(71) - C(72)	1.438(6)	C(74) - C(75)	1.398(6)
C(72) - C(73)	1.407(6)	C(75) - C(76)	1.414(6)
C(73) - C(74)	1.403(7)	C(76) - C(71)	1.431(6)

Table 4 (continued)

Phenol and phenoxy C - O bonds :-

C(71) - O(70)	1.277(5)
C(81) - O(80)	1.367(6)
C(91) - O(90)	1.363(5)

Hydrogen bonds :-

O(70) ...H(900) - O(90)	2.672(5)
O(70) ...H(800) - O(80)	2.736(4)

Table 5

Selected bond angles (°), with estimated standard deviations in parentheses. (Atom nomenclature as for table 4).

P(1) - Ru(1) - P(2)	97.32(4)	Ru(1) - P(1) - C(11)	110.01(13)
P(1) - Ru(1) - H(1)	77.	Ru(1) - P(1) - C(21)	123.22(14)
P(2) - Ru(1) - H(1)	86.	Ru(1) - P(1) - C(31)	115.09(14)
P(1) - Ru(1) - $C_{C^{*}_{71-76}}$	128.3(1)	Ru(1) - P(2) - C(41)	110.12(11)
P(1) - Ru(1) - $C_{C^{*}_{1}}$	128.3(1)	Ru(1) - P(2) - C(51)	119.16(12)
P(2) - Ru(1) - $C_{C^{*}_{71-76}}$	128.8(1)	Ru(1) - P(2) - C(61)	120.17(13)
H(1) - Ru(1) - $C_{C^{*}_{71-76}}$	122.	Mean Ru(1) - P - C [rings (1n) - (6n)]	116.30(13)
H(1) - Ru(1) - $C_{C^{*}_{1}}$	122.		

C(11) - P(1) - C(21)	98.6(2)
C(11) - P(1) - C(31)	103.1(2)
C(21) - P(1) - C(31)	104.0(2)
C(41) - P(2) - C(51)	102.2(2)
C(41) - P(2) - C(61)	102.2(2)
C(51) - P(2) - C(61)	100.3(2)
Mean C - P - C [rings (1n)-(6n)]	101.8(2)

π-bonded ring (7n):-

O(70) - C(71) - C(72)	122.2	C(72) - C(73) - C(74)	121.2(4)
O(70) - C(71) - C(76)	123.4(4)	C(73) - C(74) - C(75)	117.8(4)
C(72) - C(71) - C(76)	114.4(4)	C(74) - C(75) - C(76)	121.4(4)
C(71) - C(72) - C(73)	121.6(4)	C(75) - C(76) - C(71)	121.4(4)

Table 6

Planarity of groups of atoms in the molecule and distances (Å) from calculated least-squares planes. Equations of the planes are expressed as Px + Qy + Rz = S in direct space.

				Deviations (Å) of atoms from plane	
P	Q	R	S	Atoms defining plane	Not defining plane
18.98	-0.50	1.88	2.45	C(71)-0.099; C(72) 0.060; C(73) 0.018 C(74)-0.058; C(75) 0.016; C(76) 0.063	O(70)-0.283 Ru(1) 1.826
19.05	-0.21	1.73	2.52	C(72)-0.001; C(73) 0.001 C(75)-0.001; C(76) 0.001	C(71)-0.185 O(70)-0.409 C(74)-0.052 Ru(1) 1.789
19.67	-1.77	-10.34	3.54	C(11)-0.008; C(12) 0.002; C(13) 0.004 C(14)-0.004; C(15)-0.002; C(16) 0.008	P(1)-0.115
8.97	7.30	7.83	5.38	C(21) 0.015; C(22)-0.010; C(23)-0.004 C(24) 0.011; C(25)-0.005; C(26)-0.008	P(1) 0.027
-3.37	1.54	23.28	3.54	C(31)-0.007; C(32) 0.001; C(33)-0.009 C(34) 0.002; C(35) 0.002; C(36) 0.012	P(1) 0.011
15.74	-1.56	8.81	6.73	C(41) 0.002; C(42)-0.005; C(43) 0.003 C(44) 0.001; C(45)-0.004; C(46) 0.002	P(2)-0.034
-16.87	0.39	18.19	1.31	C(51)-0.003; C(52) 0.003; C(53) 0.002 C(54)-0.006; C(55) 0.006; C(56)-0.001	P(2)-0.016
-1.26	5.99	18.12	7.20	C(61) 0.002; C(62)-0.007; C(63) 0.008 C(64)-0.004; C(65)-0.002; C(66) 0.003	P(2)-0.078
11.62	7.41	2.32	0.26	C(81)-0.001; C(82) 0.004; C(83)-0.005 C(84) 0.003; C(85)-0.000; C(86)-0.001	O(80) 0.004
15.12	6.36	-6.57	-1.29	C(91) 0.012; C(92)-0.002; C(93)-0.009 C(94) 0.009; C(95) 0.001; C(96)-0.011	O(90) 0.041

Table 7

Planarity of the π-bonded arene six-membered rings of related named structures and distances (Å) from calculated least-squares planes. Equations of the planes are expressed as <u>P</u>x + <u>Q</u>y + <u>R</u>z = <u>S</u>.

A Structure of $[RuH(PPh_3)_2(\eta\text{-}PhPPh_2)]^+$
B Structure of $[RuH(PPh_3)_2(\eta\text{-}PhO)].(PhOH)_2$
C Structure of $Rh[P(OCH_3)_3]_2\ (\eta\text{-}Ph\text{-}BPh_3)$
D Structure of $(\pi\text{-}C_5H_5)Ru(\eta\text{-}Ph\text{-}BPh_3)$

					Deviations (Å) of atoms from plane	
	<u>P</u>	<u>Q</u>	<u>R</u>	<u>S</u>	Atoms defining plane	Not defining plane
A(i)	3.86	8.27	11.88	6.96	C(91) 0.006; C(92) 0.006; C(93)-0.017 C(94) 0.016; C(95)-0.003; C(96)-0.007	P(3) 0.085 Ru(1)-1.776
A(ii)	3.76	8.32	11.86	6.94	C(92) 0.007; C(93)-0.007 C(95) 0.007; C(96)-0.007	C(91) 0.002 C(94) 0.031 P(3) 0.068 Ru(1)-1.771
B(i)	18.98	-0.50	1.88	2.45	C(71)-0.099; C(72) 0.060; C(73) 0.018 C(74)-0.058; C(75) 0.016; C(76) 0.063	O(70)-0.283 Ru(1) 1.826
B(ii)	19.05	-0.21	1.73	2.52	C(72)-0.001; C(73) 0.001 C(75)-0.001; C(76) 0.001	C(71)-0.185 O(70)-0.409 C(74)-0.052 Ru(1) 1.789
C(i)	11.57	5.83	-0.03	12.37	C(51) 0.056; C(52)-0.039; C(53)-0.013 C(54) 0.046; C(55)-0.027; C(56)-0.023	Rh(1)-1.867 B(1) 0.372
C(ii)	11.52	5.91	-0.03	12.32	C(52)-0.007; C(53) 0.007 C(55)-0.007; C(56) 0.007	C(51) 0.093 C(54) 0.060 B(1) 0.422 Rh(1)-1.841
D(i)	2.03	-4.56	13.08	6.60	C(41) 0.010; C(42)-0.011; C(43) 0.001 C(44) 0.010; C(45)-0.010; C(46) 0.000	Ru(1)-1.701 B(1) 0.135
D(ii)	2.03	-4.85	13.08	6.59	C(42)-0.005; C(43) 0.005 C(45)-0.005; C(46) 0.005	C(41) 0.017 C(44) 0.015 Ru(1)-1.69 B(1) 0.141

Angles between planes;

A(i) - A(ii)	0.4°
B(i) - B(ii)	1.81°
C(i) - C(ii)	0.45°
D(i) - D(ii)	0.0°

CHAPTER VI

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant k and ℓ and list values of h, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

H,0,-23

2	636	619
4	285	280
6	325	317
8	110	123

H,0,-22

2	364	333
4	98	99
6	408	441
8	922	922
10	758	750
12	451	425

H,0,-21

2	1047	1021
4	519	505
6	73	102
8	454	436
10	825	810
12	559	554

H,0,-20

2	593	570
4	188	174
6	957	944
8	799	785
10	555	550
12	495	469
14	249	259

H,0,-19

2	203	224
4	487	469
6	310	315
8	464	437
10	565	560
12	750	748
14	771	779
16	403	423

H,0,-18

2	238	240
4	364	375
6	694	678
8	555	540
10	595	604
12	244	227
14	63*	46
16	317	324

H,0,-17

2	938	935
4	686	668
6	218	137
8	299	298
10	715	678
12	598	599
14	464	464
16	182	184

H,0,-16

2	814	788
4	1051	1029
6	983	961
8	853	844
10	309	311
12	59*	33
14	488	521
16	740	757
18	837	853

H,0,-15

2	1460	1444
4	601	601
6	128	116
8	305	323
10	428	403
12	346	353
14	295	289
16	124	124
18	63*	26

H,0,-14

2	1391	1338
4	934	943
6	1255	1245
8	819	803
10	55*	45
12	638	626
14	1030	1017
16	1213	1203
18	890	912

H,0,-13

2	1444	1412
4	297	316
6	538	496
8	331	327
10	908	853
12	491	494
14	349	326
16	68*	46
18	120	135

H,0,-12

2	1506	1465
4	998	983
6	1297	1305
8	207	227
10	230	216
12	1378	1385
14	943	936
16	1260	1254
18	953	953

H,0,-11

2	600	602
4	661	657
6	372	375
8	183	245
10	1164	1143
12	685	688
14	225	228
16	473	468
18	297	295

H,0,-10

2	1209	1216
4	292	332
6	690	716
8	94	107
10	943	936
12	1188	1176
14	674	681
16	777	790
18	1019	1030

H,0,-9

2	228	219
4	272	242
6	1035	1020
8	2749	2792
10	1434	1462
12	380	397
14	138	138
16	110	103
18	941	941
20	627	640

H,0,-8

2	1246	1234
4	120	189
6	802	794
8	619	594
10	728	722
12	224	243
14	568	580
18	737	734
20	212	231

H,0,-7

2	955	905
4	1612	1628
6	2467	2410
8	2541	2575
10	1946	1982
12	965	986
14	916	936
16	110	123
18	899	886
20	529	528

H,0,-6

2	199	225
4	1205	1142
6	1390	1340
8	1374	1389
10	312	289
12	167	188
14	242	264
16	98	142
18	297	287
20	365	372

H,0,-5

2	3199	3194
4	3361	3552
6	3279	3355
8	2476	2523
10	1882	1893
12	756	767
14	358	337
16	529	530
18	752	752
20	651	630

H,0,-4

2	1081	1095
4	1463	1418
6	111	141
8	692	656
10	1462	1481
12	735	769
14	680	676
16	189	212
18	218	226
20	289	293

H,0,-3

2	577	615
4	2703	2727
6	683	693
8	665	674
10	797	805
12	368	356
14	580	595
16	564	566
18	824	836

H,0,-2

2	2033	1965
4	342	290
6	670	599
8	962	950
10	1242	1254
12	1438	1420
14	686	689
16	613	601
18	141	154

H,0,-1

2	679	647
4	334	334
6	462	452
8	1200	1173
10	1063	1053
12	722	721
14	749	751
16	303	293
18	579	567

H,0,0

2	2786	2856
4	845	850
6	1401	1344
8	791	747
10	2178	2153
12	1778	1757
14	475	471
16	533	506
18	300	306

H,0,1

0	467	404
2	597	529
4	107	185
6	729	733
8	1493	1456
10	230	203
12	840	817
14	572	558
16	430	412
18	317	304

H,0,2

0	3127	3341
2	1055	951
4	283	197
6	2145	2028
8	173	213
10	1393	1388
12	1415	1375

	H,0,2	
14	652	643
16	566	558
18	307	314
	H,0,3	
0	335	298
2	522	569
4	1080	1101
6	554	596
8	471	457
10	703	703
12	1276	1251
14	485	482
16	613	603
18	725	705
	H,0,4	
0	163	220
2	121	170
4	454	467
6	403	403
8	1929	1951
10	1347	1317
12	695	679
14	192	189
16	57*	57
18	198	196
	H,0,5	
0	3166	3121
2	2669	2646
4	1720	1714
6	1334	1359
8	1299	1283
10	367	373
12	868	855
14	405	395
16	731	733
	H,0,6	
0	936	885
2	717	672
4	448	410
6	636	644
8	1560	1531
10	295	330
12	475	454
14	52*	57
16	156	146
	H,0,7	
0	502	485
2	1356	1370
4	1508	1494
6	1805	1773
8	1332	1302
10	383	379
12	80	108
14	243	244
16	842	843
	H,0,8	
0	296	264
2	1096	1064
4	327	368
6	1518	1477
8	1058	1051
10	135	180
12	73	101
14	163	168
16	523	498
	H,0,9	
0	254	309
2	1206	1238
4	1607	1631
6	694	689
8	255	258
10	389	392
12	226	234
14	1034	1011
	H,0,10	
0	673	686
2	514	370
4	1615	1621
6	609	613
8	861	842
10	432	447
12	462	451
14	365	352
	H,0,11	
0	357	397
2	842	870
4	950	975
6	71	102
8	191	203
10	395	362
12	810	799
14	769	743
	H,0,12	
0	1462	1495
2	498	479
4	746	727
6	576	575
8	735	721
10	846	851
12	277	288
	H,0,13	
0	1812	1835
2	174	247
4	579	583
6	341	333
8	687	682
10	955	926
12	573	553
	H,0,14	
0	869	884
2	167	174
4	209	210
6	531	532
8	781	772
10	574	550
12	376	371
	H,0,15	
0	886	923
2	320	342
4	244	258
6	79	79
8	777	779
10	662	640
	H,0,16	
0	78*	60
2	104	88
4	524	510
6	848	860
8	625	640
10	365	339
	H,0,17	
0	856	906
2	280	294
4	114	116
6	278	249
8	822	821
	H,0,18	
0	549	592
2	526	540
4	707	706
6	854	863
8	260	263
	H,0,19	
0	202	234
2	501	519
4	281	288
6	219	217
	H,0,20	
0	335	342
2	574	587
4	946	981
	H,0,21	
0	576	596
2	814	847
	H,0,22	
0	496	498
	H,1,-23	
2	426	402
3	302	320
4	47*	37
5	110	114
6	312	301
7	233	227
8	453	429
9	68	79
	H,1,-22	
1	134	145
2	339	350
3	344	339
4	452	426
5	73	82
6	164	162
7	67	60
8	373	367
9	51*	49
10	436	418
11	88	90
12	692	692
	H,1,-21	
1	57	38
2	239	246
3	49*	19
4	68	77
5	404	409
6	679	672
7	476	459
8	705	685
9	190	188
10	770	762
11	218	209
12	410	412
13	97	84
	H,1,-20	
1	594	609
2	347	335
3	755	767
4	133	138
5	287	311
6	111	125
7	64	75
8	466	467
9	251	237
10	748	715
11	432	418
12	741	718
13	473	469
14	686	694
	H,1,-19	
1	59	68
2	289	328
3	122	133
4	86	91
5	51*	59
6	255	260
7	239	244
8	868	852
9	161	156
10	367	341
11	161	155
12	237	231
13	52*	28
14	149	145
15	102	103
	H,1,-18	
1	315	304
2	649	630
3	721	730
4	399	404
5	152	157
6	62	29
7	80	92
8	719	721
9	73	111
10	548	534
11	172	166
12	698	688
13	511	508
14	797	815
15	526	534
16	517	516
	H,1,-17	
1	48*	22
2	352	321

H,1,-17

3	178	178
4	687	658
5	87	90
6	1087	1065
7	53*	92
8	861	849
9	90	93
10	187	177
11	193	186
12	54*	67
13	383	404
14	240	228
15	312	302
16	487	476
17	52*	63

H,1,-16

1	379	376
2	699	690
3	538	540
4	964	973
5	47*	32
6	178	180
7	96	104
8	339	334
9	77	73
10	404	426
11	321	305
12	644	638
13	368	361
14	631	642
15	325	324
16	300	291
17	51*	23

H,1,-15

1	513	503
2	1082	1061
3	1030	995
4	1036	1004
5	400	393
6	1121	1098
7	312	316
8	718	712
9	358	357
10	149	161
11	74	84
12	48*	61
13	302	292
14	420	415
15	269	273
16	807	807
17	75	79
18	798	789

H,1,-14

1	396	380
2	886	888
3	96	93
4	1091	1055
5	197	198
6	383	383
7	69	71
8	221	199
9	475	456
10	449	451
11	673	666
12	481	476
13	363	352
14	192	193
15	265	260
16	98	69
17	53*	72
18	96	107

H,1,-13

1	320	331
2	1232	1241
3	784	774
4	1843	1829
5	964	953
6	1543	1515
7	471	471
8	432	453
9	615	613
10	45*	40
11	415	409
12	384	368
13	48*	48
14	726	728
15	79	72
16	1187	1206
17	360	356
18	870	895
19	150	152

H,1,-12

1	298	297
2	1016	989
3	549	533
4	626	593
5	418	392
6	387	352
7	42*	66
8	870	843
9	763	772
10	651	654
11	512	497
12	235	248
13	142	156
14	80	94
15	59	48
16	55*	51
17	50*	38
18	55	64
19	50*	56

H,1,-11

1	72	80
2	868	885
3	111	138
4	956	966
5	293	315
6	1105	1082
7	450	468
8	771	788
9	312	325
10	42*	14
11	180	192
12	185	196
13	170	159
14	905	914
15	165	171
16	1010	1033
17	574	582
18	611	622
19	143	158

H,1,-10

1	693	675
2	69	109
3	586	562
4	305	318
5	536	496
6	379	409
7	318	318
8	983	969
9	384	362
10	505	529
11	520	492
12	632	652
13	232	228
14	266	256
15	314	308
16	52*	65
17	294	305
18	406	406
19	325	331

H,1,-9

1	794	789
2	204	163
3	58	101
4	1568	1564
5	471	471
6	683	656
7	1242	1250
8	352	356
9	85	60
10	304	300
11	346	320
12	1056	1059
13	325	337
14	749	763
15	47*	80
16	567	584
17	264	262
18	274	279
19	372	359

H,1,-8

1	1252	1223
2	136	140
3	131	109
4	824	796
5	430	407
6	1873	1881
7	269	259
8	1248	1259
9	118	147
10	1127	1179
11	250	231
12	665	692
13	44*	33
14	375	380
15	111	105
16	261	257
17	386	388
18	800	803
19	334	323
20	741	737

H,1,-7

1	1552	1409
2	194	201
3	166	236
4	1122	1097
5	334	287
6	963	939
7	1649	1620
8	555	506
9	304	300
10	358	373
11	282	274
12	459	456
13	46	79
14	192	209
15	118	131
16	60	116
17	370	373
18	235	216
19	371	371
20	321	316

H,1,-6

1	1384	1312
2	449	425
3	679	654
4	71	146
5	329	343
6	1029	1076
7	211	202
8	1533	1528
9	401	424
10	1391	1414
11	498	502
12	966	967
13	327	320
14	558	566
15	160	172
16	314	317
17	502	506
18	519	517
19	317	317
20	734	736

H,1,-5

1	1347	1277
2	1784	1696
3	1304	1295
4	754	770
5	67	56
6	386	393
7	35*	7
8	194	195
9	825	833
10	376	393
11	991	987
12	614	612
13	414	410
14	132	161
15	276	268
16	243	242
17	190	186
18	49*	20
19	108	102
20	449	432

H,1,-4

1	391	412
2	551	544
3	354	317
4	547	507
5	79	93
6	1388	1425
7	364	360
8	1751	1785
9	513	531
10	1389	1392
11	259	277
12	191	187
13	171	171
14	531	528
15	109	110

H,1,-4

16	612	614
17	180	182
18	600	590
19	421	416

H,1,-3

1	363	292
2	1151	1159
3	541	483
4	1362	1372
5	1480	1508
6	33*	89
7	325	313
8	807	827
9	271	301
10	541	570
11	652	657
12	1269	1283
13	269	271
14	603	602
15	484	473
16	606	616
17	48*	28
18	69	64
19	68	67

H,1,-2

1	125	75
2	518	524
3	408	450
4	114	156
5	612	578
6	480	506
7	501	458
8	564	586
9	515	563
10	425	428
11	239	243
12	42*	10
13	58	83
14	816	822
15	147	162
16	657	652
17	269	263
18	540	519
19	374	369

H,1,-1

1	647	653
2	2701	2810
3	480	505
4	459	477
5	1003	1001
6	114	86
7	336	357
8	81	118
9	161	160
10	997	1014
11	822	837
12	1101	1109
13	425	421
14	1048	1040
15	228	229
16	328	322
17	149	145
18	230	228
19	167	158

H,1,0

1	385	376
2	426	395
3	1777	1774
4	3005	3040
5	1688	1676
6	953	923
7	1109	1069
8	726	725
9	454	458
10	50	37
11	306	294
12	206	213
13	45*	41
14	871	864
15	48*	68
16	392	373
17	273	259
18	431	411
19	145	151

H,1,1

0	2710	2688
1	848	809
2	2263	2283
3	1370	1320
4	1203	1141
5	327	295
6	834	817
7	382	377
8	119	147
9	322	336
10	1765	1755
11	878	880
12	1536	1532
13	304	299
14	660	654
15	49	48
16	400	394
17	155	167
18	349	357
19	116	107

H,1,2

0	159	160
1	652	700
2	1461	1414
3	939	890
4	868	817
5	475	414
6	175	194
7	937	913
8	64	96
9	738	737
10	339	332
11	57	72
12	847	853
13	46*	51
14	636	632
15	228	229
16	494	466
17	374	366
18	540	536

H,1,3

0	1708	1641
1	541	583
2	346	337
3	883	889
4	598	586
5	253	298
6	372	388
7	116	118
8	680	677
9	585	564
10	1665	1647
11	235	238
12	1048	1060
13	238	230
14	595	568
15	266	278
16	318	293
17	179	179
18	153	162

H,1,4

0	1289	1194
1	570	551
2	2456	2432
3	68	108
4	1022	1051
5	443	442
6	656	655
7	268	290
8	306	309
9	41*	22
10	333	323
11	628	617
12	971	979
13	506	497
14	683	678
15	395	385
16	427	421
17	410	388
18	515	520

H,1,5

0	496	512
1	1535	1463
2	1082	1063
3	634	615
4	370	358
5	75	57
6	963	945
7	665	656
8	1371	1353
9	467	470
10	1035	1026
11	88	99
12	775	782
13	49*	53
14	340	330
15	174	183
16	51	25
17	75	79

H,1,6

0	1368	1339
1	170	193
2	1659	1632
3	305	333
4	1573	1583
5	755	767
6	1543	1540
7	558	562
8	1504	1488
9	46*	51
10	444	436
11	387	383
12	346	338
13	395	383
14	480	465
15	374	366
16	388	391
17	435	420

H,1,7

0	181	181
1	948	941
2	339	308
3	127	121
4	650	647
5	560	542
6	801	813
7	144	161
8	476	489
9	218	228
10	601	593
11	369	362
12	338	328
13	258	257
14	52*	4
15	51*	77
16	425	413

H,1,8

0	918	928
1	625	623
2	2331	2337
3	1086	1104
4	1698	1701
5	639	647
6	872	885
7	456	477
8	769	764
9	100	95
10	268	266
11	140	159
12	259	233
13	55	72
14	519	514
15	250	242
16	394	381

H,1,9

0	293	279
1	100	84
2	283	299
3	341	325
4	942	935
5	260	263
6	1330	1350
7	283	292
8	533	552
9	564	559
10	520	511
11	216	207
12	211	223
13	57	39
14	521	516
15	198	194

H,1,10

0	851	868
1	628	624
2	935	950
3	274	281
4	1054	1076
5	183	188
6	890	894
7	133	103
8	164	160
9	281	266
10	135	145
11	54	57

	H,1,10	
12	353	339
13	115	147
14	508	493
15	320	308
	H,1,11	
0	402	394
1	158	156
2	116	139
3	294	287
4	442	460
5	429	420
6	815	822
7	695	691
8	709	714
9	485	482
10	597	585
11	181	182
12	114	103
13	118	118
14	207	197
	H,1,12	
0	695	729
1	88	131
2	1012	1064
3	42*	63
4	680	680
5	314	302
6	177	190
7	98	91
8	362	350
9	56	64
10	394	399
11	293	281
12	520	497
13	54*	59
	H,1,13	
0	1100	1138
1	88	94
2	52	24
3	324	326
4	817	802
5	417	418
6	607	597
7	356	369
8	459	477
9	63	77
10	544	540
11	233	234
12	287	282
	H,1,14	
0	386	436
1	225	217
2	715	744
3	167	188
4	178	179
5	293	309
6	376	372
7	172	183
8	672	664
9	84	81
10	692	684
11	356	350
12	678	680
	H,1,15	
0	927	956
1	197	204
2	231	254
3	77	71
4	143	150
5	168	155
6	186	190
7	230	228
8	249	255
9	81	73
10	497	502
11	51*	35
	H,1,16	
0	636	672
1	300	308
2	741	770
3	223	254
4	49*	51
5	319	322
6	480	489
7	283	278
8	668	648
9	379	385
10	658	666
	H,1,17	
0	171	179
1	235	257
2	80	95
3	49*	56
4	628	657
5	129	118
6	476	477
7	83	68
8	456	450
9	56	67
	H,1,18	
0	585	596
1	90	99
2	453	473
3	60	42
4	110	106
5	73	76
6	500	532
7	345	348
8	486	500
	H,1,19	
0	443	451
1	61	89
2	418	418
3	49*	55
4	566	584
5	77	87
6	537	566
	H,1,20	
0	635	664
1	149	143
2	165	161
3	175	185
4	96	96
5	66	67
	H,1,21	
0	482	504
1	49*	55
2	779	795
3	241	242
	H,1,22	
0	473	475
1	152	164
	H,2,-23	
4	215	207
5	230	220
6	177	189
7	74	66
	H,2,-22	
1	50*	49
2	82	90
3	130	131
4	165	155
5	169	177
6	117	103
7	631	629
8	515	522
9	529	515
10	569	565
11	253	254
	H,2,-21	
1	651	628
2	256	221
3	541	545
4	267	230
5	495	486
6	151	171
7	327	336
8	457	457
9	219	229
10	627	629
11	256	258
12	448	454
	H,2,-20	
1	51*	70
2	439	438
3	51*	31
4	247	252
5	490	478
6	136	102
7	750	744
8	453	446
9	212	210
10	347	340
11	270	258
12	287	250
13	222	218
14	205	197
	H,2,-19	
1	575	557
2	61	106
3	882	866
4	500	470
5	782	779
6	156	162
7	56	47
8	564	558
9	140	131
10	366	370
11	307	300
12	460	472
13	850	865
14	308	290
15	684	675
	H,2,-18	
1	428	428
2	77	65
3	338	338
4	284	299
5	244	227
6	689	663
7	64	110
8	488	478
9	145	154
10	153	145
11	113	110
12	54*	32
13	51*	29
14	51*	28
15	387	397
16	234	234
	H,2,-17	
1	727	713
2	598	593
3	760	778
4	461	429
5	585	572
6	157	140
7	200	217
8	273	258
9	352	353
10	485	476
11	305	289
12	471	482
13	593	599
14	491	500
15	439	425
16	279	265
	H,2,-16	
1	129	110
2	659	654
3	496	500
4	956	964
5	534	545
6	1010	991
7	70	126
8	777	750
9	70	104
10	195	198
11	106	115
12	52*	17
13	439	431
14	196	176
15	654	677
16	513	542
17	320	321
	H,2,-15	
1	614	605
2	354	348
3	559	552
4	434	449
5	305	297
6	426	407
7	361	355
8	61	57
9	321	319

H,2,-15

10	200	196
11	604	596
12	284	276
13	655	651
14	381	381
15	543	545
16	148	139
17	115	106
18	79	76

H,2,-14

1	57	68
2	1129	1090
3	637	618
4	772	776
5	934	924
6	803	801
7	781	771
8	439	404
9	610	615
10	169	164
11	275	286
12	282	264
13	431	403
14	561	555
15	674	678
16	740	747
17	502	500
18	558	557

H,2,-13

1	906	880
2	441	422
3	144	142
4	602	604
5	68	87
6	344	328
7	305	301
8	272	250
9	651	645
10	207	193
11	648	648
12	127	132
13	611	605
14	64	61
15	54*	53
16	56	64
17	193	182
18	243	245

H,2,-12

1	385	372
2	750	719
3	597	620
4	956	941
5	837	861
6	788	771
7	682	673
8	398	403
9	198	209
10	66	58
11	68	65
12	433	424
13	399	391
14	825	815
15	617	612
16	812	808
17	385	398
18	393	386
19	302	282

H,2,-11

1	633	597
2	595	590
3	268	243
4	606	604
5	338	331
6	177	173
7	324	346
8	645	660
9	771	776
10	604	606
11	373	393
12	315	317
13	267	275
14	167	171
15	451	439
16	365	377
17	51	60
18	242	247
19	350	368

H,2,-10

1	423	454
2	362	364
3	479	526
4	655	650
5	777	792
6	358	359
7	748	754
8	300	291
9	398	400
10	164	80
11	560	546
12	290	290
13	87	123
14	602	616
15	763	764
16	618	621
17	798	830
18	410	421
19	538	532

H,2,-9

1	263	267
2	581	563
3	561	576
4	481	475
5	418	435
6	612	605
7	1295	1286
8	1735	1748
9	1036	1063
10	890	911
11	555	546
12	485	494
13	76	82
14	264	278
15	294	292
16	205	230
19	534	539
17	586	585
18	321	316

H,2,-8

1	1672	1651
2	333	319
3	757	743
4	649	612
5	1553	1591
6	480	469
7	484	475
8	102	96
9	197	213
10	588	605
11	520	530
12	464	475
13	163	188
14	482	503
15	444	442
16	404	422
17	625	639
18	81	74
19	334	330

H,2,-7

1	76	77
2	209	213
3	412	384
4	226	178
5	1008	1001
6	1112	1137
7	1318	1339
8	1283	1334
9	548	582
10	881	920
11	584	599
12	538	542
13	385	373
14	123	105
15	205	208
16	325	313
17	588	578
18	466	467
19	490	480

H,2,-6

1	101	168
2	217	241
3	801	788
4	851	810
5	922	942
6	574	553
7	523	503
8	285	262
9	212	207
10	178	187
11	397	401
12	68	95
13	455	467
14	77	101
15	270	259
16	173	167
17	437	448
18	162	181
19	99	98

H,2,-5

1	394	374
3	640	615
4	486	396
5	800	792
6	1472	1496
7	1193	1242
8	544	538
9	833	858
10	919	949
11	799	799
12	704	708
13	653	647
14	165	176
15	49*	48
16	526	543
17	336	334
18	281	277
19	566	568

H,2,-4

1	250	312
2	2072	2035
3	1028	988
4	1118	1117
5	1146	1156
6	172	160
7	1148	1145
8	445	420
9	1020	1015
10	147	87
11	908	917
12	594	611
13	943	966
14	398	398
15	474	474
16	260	257
17	91	87
18	50*	21
19	199	190

H,2,-3

1	362	321
2	655	612
3	325	301
4	1712	1654
5	1371	1341
6	936	959
7	711	747
8	1162	1138
9	531	517
10	654	657
11	890	895
12	127	145
13	232	232
14	379	390
15	47*	58
16	624	630
17	221	230
18	354	347
19	546	544

H,2,-2

1	1550	1518
2	2295	2342
3	985	982
4	168	207
5	46	70
6	120	131
7	490	486
8	419	404
9	551	558
10	448	444
11	927	912
12	953	951
13	1127	1113
14	489	470
15	403	389
16	378	366
17	81	97
18	52	14
19	227	221

H,2,-1

1	763	779
2	1864	1806

H,2,-1

3	1093	1132
4	648	621
5	113	170
6	427	428
7	873	903
8	411	408
9	781	784
10	444	417
11	190	215
12	238	226
13	179	185
14	550	552
15	108	110
16	165	166
17	169	170
18	364	345
19	331	322

H,2,0

0	2873	2776
1	2807	2821
2	1315	1287
3	824	832
4	773	801
5	843	824
6	233	213
7	684	644
8	185	138
9	584	608
10	891	890
11	758	772
12	863	885
13	761	773
14	779	776
15	274	266
16	269	266
17	93	88
18	55	46

H,2,1

0	794	741
1	383	369
2	1002	962
3	780	789
4	364	330
5	1580	1570
6	333	302
7	1366	1355
8	279	252
9	380	364
10	212	184
11	139	121
12	509	504
13	421	431
14	720	706
15	468	465
16	216	215
17	269	255
18	342	322

H,2,2

1	93	176
2	1345	1368
3	2116	2148
4	521	545
5	220	198
6	237	137
7	457	446
8	765	798
9	154	199
10	1044	1026
11	643	631
12	639	650
13	585	581
14	714	709
15	367	359
16	136	133
17	305	317
18	158	142

H,2,3

0	944	870
1	1683	1694
2	882	832
3	340	387
4	520	513
5	1578	1571
6	135	147
7	677	686
8	234	221
9	205	203
10	73	19
11	227	239
12	624	615
13	745	751
14	705	690
15	664	660
16	401	387
17	449	434
18	367	363

H,2,4

0	317	341
1	552	560
2	255	257
3	1102	1128
4	872	865
5	234	233
6	604	628
7	208	186
8	846	854
9	391	400
10	1045	1050
11	261	262
12	615	601
13	65	87
14	376	372
15	50*	42
16	221	218
17	52*	30

H,2,5

1	1571	1624
2	1310	1250
3	1040	1079
4	1617	1580
5	638	682
6	659	651
7	92	125
8	563	558
9	41*	28
10	221	230
11	407	410
12	223	200
13	844	858
14	593	573
15	848	830
16	511	494
17	594	586

H,2,6

0	396	377
1	1183	1177
2	385	341
3	819	822
4	286	317
5	431	417
6	499	514
7	550	557
8	633	625
9	597	585
10	516	519
11	380	377
12	361	356
13	143	145
14	73	71
15	116	121
16	100	105

H,2,7

0	1047	1057
1	177	240
2	1106	1096
3	1290	1290
4	1409	1404
5	767	794
6	968	946
7	492	505
8	218	191
9	182	185
10	268	268
11	64	74
12	240	230
13	468	460
14	338	334
15	742	725
16	434	411

H,2,8

0	238	234
1	759	761
2	155	106
3	236	204
4	713	740
5	984	979
6	990	980
7	708	703
8	322	311
9	676	666
10	352	350
11	456	443
12	54	55
13	78	58
14	293	303
15	102	99

H,2,9

0	982	1020
1	214	273
2	974	1019
3	748	766
4	971	986
5	497	517
6	593	609
7	300	288
8	548	550
9	68	79
10	54	24
11	52	83
12	307	303
13	457	424
14	462	458
15	273	252

H,2,10

0	773	785
1	43*	35
2	347	327
3	557	581
4	990	990
5	1145	1132
6	485	485
7	484	487
8	237	236
9	562	568
10	337	340
11	827	821
12	329	315
13	54*	27
14	344	326

H,2,11

0	397	416
1	617	639
2	1170	1200
3	399	410
4	247	255
5	47*	78
6	345	342
7	245	251
8	249	242
9	81	82
10	201	217
11	460	447
12	358	343
13	590	589
14	301	294

H,2,12

0	441	426
1	117	118
2	193	174
3	930	932
4	758	748
5	760	771
6	898	868
7	741	726
8	369	345
9	821	816
10	747	739
11	644	634
12	79	80
13	114	132

H,2,13

0	672	671
1	1000	1035
2	844	892
3	525	522
4	94	99
5	93	123
6	245	243
7	121	122
8	315	285
9	529	544
10	527	523
11	448	449
12	607	590

H,2,14

0	411	423
1	77	51

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    H,2,14

 2     63     78
 3    404    410
 4    187    182
 5    419    443
 6    297    298
 7    536    536
 8    621    615
 9    300    299
10    317    306
11    354    345

    H,2,15

 0    220    220
 1    661    692
 2    361    350
 3    491    499
 4    176    157
 5    168    179
 6    391    387
 7    110    118
 8    420    414
 9    316    308
10    363    346

    H,2,16

 0    163    152
 1    168    166
 2    119    149
 3    277    268
 4    175    209
 5    458    466
 6    196    193
 7    309    297
 8    371    364
 9    347    346

    H,2,17

 0    610    637
 1    483    514
 2    602    603
 3    445    465
 4    177    177
 5     53     63
 6    471    460
 7    153    154
 8    411    406

    H,2,18

 0     56     38
 1    284    300
 2    401    425
 3    452    464
 4    494    474
 5    406    425
```

```
 6    424    430
 7    295    288

    H,2,19

 0    435    460
 1    286    290
 2    412    413
 3    382    391
 4     55     20
 5     49*    49
 6    334    337

    H,2,20

 0    283    285
 1     65     98
 2    408    432
 3    328    340
 4    534    537

    H,2,21

 0    400    421
 1    400    432
 2    329    333

    H,2,22

 0    398    399

    H,3,-22

 2    305    323
 3    512    506
 4     50*    47
 5    302    291
 6    126    115
 7     73     81
 8    241    232

    H,3,-21

 1    260    259
 2     51*    39
 3    250    262
 4    122    129
 5    432    415
 6     93    101
 7    437    418
 8    229    212
 9    653    643
10    464    480
11    421    417

    H,3,-20

 1    671    666
 2     58     76
 3    699    692
```

```
 4     54     44
 5    236    223
 6     52     48
 7     51*    34
 8     58     70
 9    379    374
10    373    364
11    706    699
12    218    207
13    692    686

    H,3,-19

 1    319    317
 2     70     62
 3     52*    50
 4    212    202
 5    283    263
 6    221    221
 7    386    353
 8    176    169
 9    495    489
10     66     67
11    355    374
12    151    172
13     88     84
14     50*    20

    H,3,-18

 1    964    965
 2    250    225
 3    714    702
 4     52*    49
 5    667    661
 6     79     73
 7     93     72
 8    134    121
 9    467    468
10    431    447
11    607    617
12    169    172
13    743    748
14     97     85
15    745    737

    H,3,-17

 1    186    194
 2    302    302
 3    155    141
 4    244    237
 5    574    570
 6    676    689
 7    293    289
 8    380    367
 9    130    138
10     87     77
11     62    101
12     53*    17
```

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13    374    369
14     65     92
15    464    456
16     52*    42

    H,3,-16

 1    795    792
 2     66     58
 3    648    633
 4    362    350
 5    391    384
 6    275    286
 7     50*    33
 8    135    128
 9    781    782
10    465    472
11    711    712
12    256    274
13    785    780
14    315    293
15    694    686
16     97    104

    H,3,-15

 1    382    369
 2    312    312
 3    864    851
 4    459    419
 5    765    759
 6    723    715
 7    683    677
 8    184    204
 9    213    203
10     49*    21
11     52*    13
12     87     93
13    570    566
14     54*    56
15    798    803
16    329    317
17    661    662

    H,3,-14

 1    634    628
 2    256    266
 3    449    427
 4     48     50
 5    439    445
 6     67     48
 7    163    153
 8    293    298
 9    509    514
10     50*    49
11    620    625
12    227    229
13    576    568
14    109    115
```

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15    564    572
16     50*    14
17    194    200

    H,3,-13

 1    625    611
 2    412    432
 3   1386   1324
 4     81    104
 5   1350   1332
 6    253    249
 7    914    912
 8    108    105
 9    367    359
10     49     52
11     49*    24
12    383    376
13    380    383
14    262    269
15    738    750
16    457    460
17    714    736
18    289    274

    H,3,-12

 1    178    211
 2    638    639
 3    432    416
 4    259    234
 5    132    138
 6    198    203
 7    394    403
 8    141    107
 9    769    758
10    152    143
11    529    533
12    178    170
13     76    122
14     52*    31
15     80     73
16     50*    28
17    223    227
18    223    213

    H,3,-11

 1    427    456
 2    584    575
 3   1216   1209
 4    179    189
 5   1150   1143
 6    501    486
 7   1183   1182
 8    451    441
 9    546    545
10     47     21
11     47*    41
```

H,3,-11

12	492	498
13	429	426
14	619	636
15	791	789
16	322	319
17	762	753
18	445	428

H,3,-10

1	76	104
2	119	119
3	116	118
4	713	689
5	388	397
6	305	315
7	1104	1103
8	487	477
9	732	741
10	410	418
11	708	713
12	161	167
13	283	281
14	137	149
15	145	144
16	231	244
17	396	391
18	198	181

H,3,-9

1	1039	1000
2	119	110
3	869	869
4	57	71
5	1160	1170
6	41*	36
7	848	841
8	41*	27
9	482	477
10	50	45
11	160	151
12	276	277
13	351	338
14	426	436
15	691	687
16	176	186
17	542	536
18	248	246
19	531	527

H,3,-8

1	608	627
2	215	184
3	602	574
4	265	284
5	966	964
6	385	400
7	1556	1565
8	512	532
9	1279	1265
10	600	602
11	600	624
12	272	289
13	245	266
14	129	145
15	489	484
16	67	70
17	619	621
18	87	85
19	930	923

H,3,-7

1	854	836
2	151	127
3	905	926
4	39*	55
5	711	719
6	81	83
7	732	714
8	378	358
9	231	229
10	175	170
11	488	492
12	47	57
13	369	388
14	143	143
15	355	360
16	207	220
17	389	385
18	54	43
19	54	79

H,3,-6

1	949	932
2	328	307
3	51	55
4	147	184
5	381	410
6	92	102
7	1201	1210
8	851	870
9	1161	1183
10	845	864
11	870	871
12	89	90
13	168	190
14	74	80
15	48*	52
16	55	60
17	572	583
18	368	388
19	684	674

H,3,-5

1	552	581
2	777	741
3	510	548
4	594	546
5	692	685
6	110	113
7	245	278
8	172	179
9	669	650
10	655	654
11	579	619
12	45*	55
13	615	620
14	62	73
15	720	720
16	72	70
17	438	432
18	46*	7
19	87	90

H,3,-4

1	94	76
2	506	464
3	179	168
4	231	257
5	495	527
6	427	425
7	789	789
8	1228	1263
9	1853	1859
10	379	363
11	285	307
12	141	130
13	293	294
14	180	169
15	51*	65
16	279	284
17	293	310
18	405	426
19	506	505

H,3,-3

1	1325	1345
2	67	91
3	1288	1293
4	377	386
5	537	516
6	56*	45
7	602	587
8	414	394
9	1724	1718
10	295	308
11	1057	1083
12	180	155
13	1202	1219
14	110	96
15	948	930
16	56	38
17	253	251
18	62	52

H,3,-2

1	205	195
2	210	194
3	140	155
4	401	396
5	549	607
6	111	123
7	870	913
8	385	369
9	764	791
10	308	312
11	232	245
12	133	114
13	45*	4
14	47*	39
15	121	94
16	251	258
17	465	457
18	93	91

H,3,-1

1	809	834
2	766	753
3	1646	1632
4	1511	1502
5	1161	1129
6	241	246
7	1192	1194
8	206	230
9	728	756
10	229	241
11	957	980
12	103	116
13	1056	1047
14	435	425
15	882	875
16	352	358
17	135	127
18	94	108

H,3,0

1	456	464
2	35*	42
3	119	180
4	358	339
5	1285	1305
6	75	76
7	770	793
8	234	237
9	136	159
10	145	132
11	251	234
12	237	243
13	346	337
14	326	311
15	380	373
16	140	113
17	496	480
18	161	164

H,3,1

0	983	1002
1	1080	1122
2	355	341
3	1296	1303
4	1006	1018
5	277	264
6	267	266
7	308	319
8	780	756
9	1036	1043
10	123	163
11	874	889
12	349	339
13	803	789
14	524	525
15	399	406
16	360	348
17	51*	24
18	49*	13

H,3,2

0	165	126
1	839	853
2	453	442
3	2179	2189
4	276	243
5	1213	1193
6	46	38
7	1049	1046
8	473	458
9	399	393
10	451	444
11	54	42
12	613	603
13	497	502
14	359	347
15	801	803
16	235	215
17	546	528

H,3,3

0	1354	1326
1	1415	1403
2	364	344
3	904	950
4	228	197
5	207	205
6	563	540

H,3,3

7	83	89
8	302	318
9	528	533
10	411	423
11	600	600
12	411	411
13	563	560
14	436	412
15	352	369
16	192	181
17	49*	39

H,3,4

0	1077	1056
1	798	836
2	504	509
3	1994	2037
4	803	784
5	1515	1538
6	153	135
7	928	928
8	165	162
9	324	313
10	94	89
11	203	200
12	46*	37
13	553	547
14	180	167
15	1017	1008
16	432	442
17	581	559

H,3,5

0	685	651
1	771	775
2	266	229
3	275	326
4	104	39
5	290	276
6	300	282
7	856	855
8	482	487
9	350	359
10	416	416
11	501	496
12	405	402
13	166	172
14	110	114
15	53*	19
16	52*	28

H,3,6

0	559	506
1	1178	1180
2	716	708
3	1328	1387
4	462	472
5	1136	1161
6	368	381
7	614	625
8	237	235
9	284	276
10	272	269
11	367	360
12	140	143
13	886	864
14	53*	54
15	831	812
16	141	140

H,3,7

0	234	261
1	669	671
2	304	301
3	98	81
4	1073	1072
5	524	527
6	281	286
7	765	770
8	534	528
9	515	513
10	96	89
11	610	603
12	134	133
13	135	125
14	305	300
15	209	225

H,3,8

0	593	579
1	1185	1176
2	126	140
3	1351	1380
4	166	205
5	709	735
6	344	355
7	356	356
8	622	606
9	378	380
10	52	19
11	196	188
12	52*	32
13	766	739
14	136	136
15	527	512

H,3,9

0	529	483
1	654	641
2	186	180
3	174	184
4	412	402
5	574	595
6	469	477
7	915	913
8	400	394
9	957	944
10	183	192
11	296	284
12	206	190
13	216	213
14	249	223

H,3,10

0	691	720
1	772	799
2	278	279
3	751	745
4	500	513
5	169	187
6	431	412
7	105	110
8	519	497
9	83	71
10	249	247
11	322	306
12	162	162
13	472	444
14	52*	53

H,3,11

0	233	241
1	46*	43
2	432	451
3	414	417
4	176	161
5	724	730
6	147	151
7	1033	1042
8	72	74
9	973	967
10	56*	36
11	488	461
12	50*	17
13	288	280

H,3,12

0	554	554
1	803	808
2	268	275
3	627	631
4	139	147
5	215	212
6	139	165
7	337	339
8	61	52
9	330	321
10	351	328
11	531	537
12	229	231

H,3,13

0	45*	50
1	67	58
2	101	84
3	444	441
4	77	84
5	966	979
6	147	152
7	801	798
8	363	361
9	740	750
10	173	114

H,3,19

0	179	181
1	417	444
2	259	251
3	436	465
4	203	209
5	333	336

H,3,20

0	76	78
1	509	506
2	122	119
3	208	208

H,3,21

0	297	318
1	265	279

H,4,-21

2	48*	25
3	517	509
4	93	98
5	385	381
6	155	149
7	75	75
8	224	233

H,4,-20

1	90	76
2	66	66
3	57	62
4	282	298
5	323	316
6	113	111
7	579	565
8	54*	56
9	398	410
10	50*	10
11	337	338

H,4,-19

1	689	688
2	274	277
3	756	734
4	169	160
5	311	298
6	175	183
7	212	208
8	329	335
9	478	479
10	53*	29
11	737	731
12	53*	35

H,4,-18

1	205	205
2	138	126
3	100	99
4	147	142
5	417	408
6	49*	28
7	323	312
8	176	198
9	95	107
10	198	190
11	54*	50
12	89	102
13	52*	35

H,4,-17

1	1147	1149
2	166	156
3	958	930
4	131	128
5	153	156
6	183	199
7	155	166
8	144	146
9	413	391
10	89	90
11	917	920
12	53*	24
13	882	865
14	53*	22

H,4,-16

1	74	63
2	223	232
3	401	386
4	413	440
5	868	844
6	87	74
7	510	506
8	155	155

H,4,-16

9	135	130
10	57	11
11	181	165
12	53*	7
13	449	459
14	72	58
15	484	481

H,4,-15

1	982	972
2	162	147
3	697	684
4	51*	17
5	251	251
6	231	201
7	94	88
8	351	352
9	494	478
10	311	309
11	870	856
12	73	86
13	839	837
14	157	158
15	703	691
16	50*	38

H,4,-14

1	530	515
2	348	344
3	863	869
4	221	228
5	732	730
6	161	172
7	709	708
8	91	102
9	474	472
10	50*	30
11	177	171
12	204	228
13	474	475
14	292	277
15	437	450
16	275	296

H,4,-13

1	488	481
2	268	268
3	257	266
4	163	180
5	50*	37
6	594	592
7	377	372
8	472	480
9	425	427
10	718	730
11	399	402
12	183	197
13	471	482
14	317	324
15	328	338
16	119	116
17	132	136

H,4,-12

1	899	897
2	101	87
3	1091	1097
4	53*	19
5	971	969
6	207	205
7	1071	1064
8	180	193
9	644	630
10	115	108
11	48*	36
12	302	324
13	771	789
14	269	273
15	649	661
16	137	150
17	536	533

H,4,-11

1	490	450
2	395	401
3	81	66
4	243	208
5	302	313
6	47*	46
7	799	813
8	237	217
9	974	979
10	269	260
11	475	476
12	49*	36
13	240	271
14	48*	18
15	53	36
16	183	164
17	565	563

H,4,-10

1	1026	1023
2	608	627
3	1173	1155
4	354	354
5	1032	1040
6	360	344
7	1182	1180
8	46*	49
9	690	681
10	254	272
11	132	118
12	248	260
13	557	558
14	252	86
15	648	641
16	92	89
17	701	703

H,4,-9

1	455	452
2	44*	2
3	726	717
4	376	365
5	601	586
6	392	377
7	952	981
8	266	269
9	1099	1116
10	593	594
11	514	543
12	331	334
13	195	207
14	181	190
15	52*	57
16	49*	50
17	528	526
18	233	237

H,4,-8

1	884	852
2	512	505
3	839	843
4	1044	1001
5	1144	1115
6	334	349
7	834	837
8	128	124
9	135	132
10	118	104
11	164	170
12	132	121
13	213	227
14	513	522
15	524	526
16	380	403
17	435	432
18	82	64

H,4,-7

1	534	529
2	116	70
3	177	165
4	118	95
5	650	649
6	450	449
7	1201	1198
8	205	208
9	1207	1240
10	317	326
11	704	696
12	230	235
13	65	73
14	243	248
15	217	219
16	150	151
17	628	621
18	67	62

H,4,-6

1	453	471
2	284	273
3	745	764
4	401	411
5	798	802
6	220	201
7	708	709
8	92	78
9	857	857
10	353	365
11	255	258
12	191	184
13	494	503
14	281	277
15	815	824
16	422	427
17	328	311
18	197	205

H,4,-5

1	776	767
2	107	58
3	146	165
4	77	95
5	822	837
6	948	949
7	1001	1032
8	42*	6
9	891	905
10	52	40
11	921	928
12	189	201
13	430	434
14	78	81
15	145	151
16	187	213
17	465	468
18	80	79

H,4,-4

1	1153	1131
2	538	519
3	579	609
4	247	245
5	243	245
6	412	412
7	1012	1001
8	178	188
9	1175	1156
10	144	170
11	1030	1024
12	145	139
13	889	892
14	159	148
15	665	662
16	118	137
17	347	347
18	49*	20

H,4,-3

1	679	657
2	639	615
3	61	71
4	65	29
5	895	930
6	62	59
7	902	911
8	354	355
9	867	885
10	329	316
11	399	408
12	47*	19
13	221	215
14	50	54
15	162	161
16	61	67
17	440	456
18	49*	15

H,4,-2

1	1145	1136
2	889	872
3	1169	1168
4	605	587
5	524	505
6	759	765
7	520	520
8	198	184
9	875	895
10	339	359
11	1174	1184
12	102	97
13	914	906
14	98	110
15	825	811
16	117	145
17	206	206
18	46*	17

H,4,-1

1	391	368

H,4,-1

2	94	69
3	201	236
4	459	461
5	177	205
6	324	323
7	1068	1090
8	186	192
9	860	846
10	358	366
11	82	94
12	45*	19
13	246	252
14	181	191
15	249	245
16	79	70
17	517	531

H,4,0

0	401	368
1	1349	1361
2	730	731
3	1159	1174
4	408	386
5	161	160
6	349	346
7	442	465
8	237	227
9	627	660
10	152	141
11	986	975
12	84	78
13	875	887
14	133	122
15	694	678
16	164	170
17	69	63

H,4,1

0	66	61
1	994	996
2	393	408
3	1369	1353
4	351	319
5	1314	1331
6	875	888
7	804	798
8	255	271
9	124	160
10	266	264
11	349	355
12	228	229
13	396	391
14	131	140
15	509	498
16	72	61
17	671	653

H,4,2

0	122	77
1	1115	1156
2	293	217
3	536	562
4	406	399
5	734	738
6	173	173
7	961	974
8	135	117
9	656	665
10	234	246
11	639	643
12	187	185
13	739	741
14	151	158
15	345	333
16	49*	18
17	60	60

H,4,3

0	892	843
1	1018	1034
2	1129	1134
3	1173	1190
4	224	207
5	1693	1724
6	283	267
7	900	905
8	503	514
9	232	219
10	102	107
11	134	142
12	91	92
13	491	501
14	55	41
15	812	803
16	49*	20

H,4,4

0	311	303
1	795	842
2	463	481
3	622	618
4	125	132
5	838	866
6	66	38
7	356	343
8	115	88
9	508	521
10	158	182
11	663	665
12	48*	12
13	376	377
14	74	74
15	143	138
16	112	116

H,4,5

0	821	801
1	661	679
2	457	456
3	1828	1868
4	82	104
5	1266	1289
6	461	453
7	534	555
8	115	118
9	62	66
10	237	233
11	298	281
12	453	464
13	696	686
14	376	397
15	1060	1051

H,4,6

0	699	675
1	849	867
2	126	54
3	402	397
4	564	593
5	334	328
6	153	144
7	589	578
8	123	125
9	556	539
10	49*	16
11	228	239
12	104	112
13	165	162
14	54*	39
15	108	113

H,4,7

0	294	282
1	922	965
2	136	120
3	1235	1271
4	52	26
5	1025	1056
6	432	414
7	463	460
8	209	211
9	142	122
10	241	229
11	225	212
12	249	253
13	636	614
14	174	164

H,4,8

0	322	321
1	741	756
2	68	39
3	315	313
4	220	225
5	637	658
6	310	322
7	827	835
8	256	259
9	767	758
10	61	47
11	454	452
12	103	115
13	379	359
14	163	166

H,4,9

0	457	472
1	364	376
2	51	36
3	908	937
4	208	203
5	792	790
6	52	30
7	406	415
8	380	386
9	182	196
10	105	119
11	565	576
12	53*	41
13	554	538

H,4,10

0	577	568
1	143	133
2	68	69
3	549	559
4	137	110
5	961	974
6	176	179
7	1028	1038
8	570	580
9	692	677
10	182	186
11	658	676
12	72	60
13	284	266

H,4,11

0	46*	3
1	529	532
2	60	73
3	330	348
4	48*	6
5	161	167
6	178	192
7	56*	54
8	59	70
9	54*	59
10	59	71
11	509	509
12	58	44

H,4,12

0	246	254
1	242	262
2	47*	19
3	531	534
4	230	219
5	927	918
6	202	217
7	966	980
8	343	356
9	883	862
10	79	82
11	502	508

H,4,13

0	95	94
1	788	812
2	56	92
3	422	426
4	61	32
5	57	78
6	50*	34
7	51*	25
8	108	109
9	383	399
10	73	90

H,4,14

0	169	166
1	49	17
2	50*	29
3	405	414
4	146	147
5	470	467
6	361	375
7	908	932
8	152	178
9	647	637

H,4,15

0	63	64
1	799	826
2	222	234
3	262	273
4	225	228
5	332	336
6	48*	37
7	300	297
8	142	141

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     H,4,16

0      54*     42
1     244     258
2     243     262
3     138     143
4      74      65
5     435     456
6      49*     31
7     488     487

     H,4,17

0     233     233
1     706     714
2     244     273
3     627     653
4     212     222
5     114      90
6      72      94

     H,4,18

0     135     132
1     157     182
2      53      49
3     424     441
4     193     203
5     401     423

     H,4,19

0      92      67
1     686     704
2      69      83
3     407     418

     H,4,20

0      88      70
1     323     365

     H,5,-20

4     257     247
5     329     305
6     269     258

     H,5,-19

1     129     121
2     136     169
3      78      48
4      87      75
5     170     175
6     248     235
7     335     331
8     128     124
9     168     160

     H,5,-18

 1   1048    1056
 2    432     415
 3    451     452
 4    227     196
 5    368     357
 6    236     212
 7     50*     34
 8    125     124
 9    165     175
10    395     382
11    685     677

     H,5,-17

 1     94      68
 2    131     118
 3     50*     77
 4     51*     57
 5    408     406
 6    133     133
 7    573     559
 8    194     178
 9     78      93
10     81      83
11    323     339
12    150     135

     H,5,-16

 1    787     774
 2    700     705
 3    504     474
 4    389     375
 5    281     277
 6    290     296
 7     72      50
 8     93      95
 9    396     392
10    386     356
11    727     725
12    205     205
13    874     882

     H,5,-15

 1    207     214
 2    242     257
 3    466     456
 4     53*     60
 5    718     716
 6    243     226
 7    545     540
 8    183     172
 9    141     165
10     52*     35
11     53*     24
12     95      75
13     80      93
14     56      52

     H,5,-14

 1    640     639
 2     53*     68
 3    569     539
 4     93      89
 5    203     205
 6    298     304
 7    448     446
 8    404     394
 9    294     283
10    263     251
11    586     595
12    226     226
13    957     960
14    247     250
15    263     249

     H,5,-13

 1    464     456
 2    187     173
 3    909     908
 4    374     374
 5    828     817
 6    538     532
 7    411     397
 8    131     135
 9    464     479
10    157     166
11     48*     17
12     59      63
13    209     204
14     67      69
15    357     363

     H,5,-12

 1    208     209
 2     87      78
 3    323     325
 4     51*     11
 5    538     533
 6    597     601
 7    873     878
 8    606     596
 9    587     574
10    601     602
11    238     242
12    509     507
13    509     508
14    516     523
15    126     131
16     49*     32

     H,5,-11

 1    755     742
 2    278     277
 3    986     976
 4    554     544
 5    928     937
 6    805     804
 7    734     725
 8    181     184
 9    873     871
10     50*     39
11     51*     33
12     51*     63
13    570     592
14    192     178
15    529     517
16    324     320

     H,5,-10

 1    211     215
 2    147     124
 3    105     119
 4     49*     19
 5    688     715
 6    222     216
 7    819     814
 8    283     287
 9    419     431
10    103     126
11    315     335
12     59      59
13    452     457
14    325     324
15    150     157
16    280     274

     H,5,-9

 1    816     801
 2    551     549
 3    871     897
 4    382     371
 5   1287    1281
 6    320     329
 7    778     787
 8     94      96
 9    656     658
10     48*     27
11     85     115
12     97      95
13    489     504
14    185     165
15    634     639
16    220     219

     H,5,-8

 1    258     246
 2    186     173
 3    165     155
 4    247     256
 5    829     839
 6    211     210
 7    491     499
 8    345     345
 9    326     323
10     79     114
11    308     303
12     60      52
13     88     100
14    103     105
15    489     508
16    291     286
17    362     343

     H,5,-7

 1    836     824
 2    709     687
 3   1161    1133
 4    610     585
 5    811     799
 6    293     295
 7    426     411
 8    239     237
 9     74      79
10    148     156
11    189     177
12    487     489
13    614     632
14    676     693
15    428     418
16    496     514
17    282     281

     H,5,-6

 1    607     589
 2    143     145
 3    223     217
 4    219     222
 5    449     464
 6    590     584
 7    449     478
 8    502     511
 9    708     731
10    345     332
11    917     920
12    193     202
13    196     213
14     51*      6
15    246     256
16     51*     55
17    412     411

     H,5,-5

 1    957     949
 2    430     432
 3    433     463
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	H,5,-5	
4	390	383
5	344	346
6	70	65
7	228	202
8	76	73
9	575	573
10	181	177
11	840	855
12	373	370
13	494	489
14	716	721
15	769	773
16	376	367
17	413	411
	H,5,-4	
1	347	338
2	41*	39
3	375	366
4	115	126
5	593	600
6	361	357
7	1098	1089
8	540	515
9	778	815
10	338	331
11	420	414
12	50*	45
13	270	283
14	61	41
15	278	282
16	74	83
17	318	316
	H,5,-3	
1	436	459
2	172	190
3	266	287
4	415	427
5	297	268
6	80	65
7	702	723
8	370	360
9	1087	1096
10	450	447
11	783	786
12	401	399
13	792	791
14	369	361
15	500	511
16	150	148
17	291	289
	H,5,-2	
1	1182	1177
2	154	153
3	228	231
4	50	71
5	654	663
6	283	309
7	1032	1051
8	742	735
9	320	339
10	215	226
11	770	783
12	237	232
13	375	376
14	50*	42
15	129	133
16	162	165
	H,5,-1	
1	477	518
2	131	166
3	1088	1095
4	311	327
5	239	234
6	41*	20
7	711	725
8	522	524
9	587	609
10	548	542
11	889	901
12	154	172
13	893	882
14	257	243
15	359	361
16	75	74
	H,5,0	
1	136	127
2	392	384
3	332	349
4	629	633
5	1055	1053
6	480	485
7	874	882
8	562	573
9	177	199
10	459	459
11	200	194
12	249	247
13	279	290
14	56	62
15	231	249
16	362	348
	H,5,1	
0	315	314
1	526	572
2	536	529
3	949	964
4	183	193
5	180	156
6	172	179
7	555	537
8	336	333
9	797	799
10	444	445
11	767	777
12	100	117
13	781	784
14	76	94
15	158	168
16	119	135
	H,5,2	
0	353	340
1	809	823
2	452	450
3	1081	1116
4	1020	1003
5	1308	1304
6	419	432
7	504	501
8	199	187
9	166	168
10	509	512
11	203	199
12	52*	65
13	288	278
14	132	139
15	626	633
	H,5,3	
0	731	717
1	1388	1386
2	323	310
3	1079	1082
4	102	103
5	209	213
6	44*	18
7	190	181
8	144	149
9	320	307
10	68	85
11	596	603
12	462	459
13	558	550
14	58	79
15	124	129
	H,5,4	
0	247	242
1	767	804
2	421	436
3	1280	1301
4	849	841
5	1456	1488
6	509	501
7	577	567
8	187	177
9	135	147
10	98	116
11	211	187
12	197	202
13	599	596
14	507	511
15	872	865
	H,5,5	
0	942	944
1	606	622
2	614	604
3	500	502
4	187	179
5	81	50
6	106	112
7	226	243
8	66	77
9	170	188
10	159	154
11	153	177
12	418	407
13	100	111
14	54*	56
	H,5,6	
0	177	191
1	1058	1067
2	327	334
3	970	981
4	242	248
5	1259	1251
6	111	117
7	473	497
8	106	116
9	49*	15
10	625	635
11	275	264
12	378	382
13	779	763
14	464	452
	H,5,7	
0	498	507
1	96	132
2	194	179
3	218	203
4	59	63
5	472	482
6	145	154
7	142	156
8	113	144
9	532	530
10	148	157
11	482	493
12	104	99
13	53*	60
	H,5,8	
0	372	379
1	854	866
2	314	323
3	785	811
4	226	229
5	742	763
6	161	161
7	436	443
8	82	80
9	53*	41
10	199	192
11	422	404
12	457	452
13	595	595
	H,5,9	
0	281	281
1	207	214
2	53	42
3	331	326
4	235	236
5	798	807
6	482	472
7	902	899
8	664	660
9	646	642
10	503	498
11	494	487
12	291	289
	H,5,10	
0	50*	69
1	176	205
2	383	379
3	224	241
4	347	345
5	138	136
6	54*	28
7	343	341
8	69	32
9	235	237
10	83	69
11	304	271
	H,5,11	
0	239	267
1	192	204
2	224	224
3	495	496
4	359	366

H,5,11

5	717	725
6	665	678
7	920	927
8	554	565
9	718	725
10	104	111
11	573	535

H,5,12

0	139	171
1	127	149
2	52*	87
3	159	178
4	169	167
5	255	255
6	166	172
7	192	198
8	96	125
9	266	270
10	52*	45

H,5,13

0	125	137
1	87	90
2	56	39
3	324	319
4	362	371
5	829	844
6	519	527
7	854	832
8	381	398
9	578	593

H,5,14

0	255	259
1	281	294
2	227	231
3	397	407
4	296	284
5	162	160
6	52*	35
7	206	206
8	125	139

H,5,15

0	70	70
1	189	206
2	301	299
3	423	421
4	418	445
5	502	499
6	366	365
7	379	362

H,5,16

0	474	475
1	901	961
2	366	369
3	460	468
4	182	181
5	67	53
6	47*	5

H,5,17

0	50*	19
1	52*	49
2	214	208
3	254	255
4	340	344

H,5,18

0	466	475
1	687	717
2	537	548
3	280	267

H,5,19

0	97	104

H,6,-18

2	213	207
3	105	98
4	262	265
5	163	161
6	431	420
7	52*	68

H,6,-17

1	981	975
2	608	599
3	696	693
4	500	497
5	200	186
6	121	121
7	69	68
8	373	364
9	114	106

H,6,-16

1	54*	19
2	139	171
3	339	347
4	203	194
5	215	215
6	361	343
7	144	183
8	318	319
9	222	223
10	93	93
11	53*	41

H,6,-15

1	675	665
2	652	624
3	368	363
4	505	498
5	96	74
6	250	258
7	52*	33
8	258	249
9	383	368
10	90	132
11	594	593
12	475	455

H,6,-14

1	119	107
2	56*	83
3	284	291
4	499	476
5	243	240
6	522	500
7	181	174
8	555	538
9	293	290
10	55	66
11	120	128
12	99	102
13	258	274

H,6,-13

1	184	190
2	253	240
3	51*	34
4	65	62
5	238	224
6	578	580
7	170	169
8	638	643
9	303	307
10	294	293
11	420	409
12	495	503
13	215	219

H,6,-12

1	427	422
2	460	453
3	727	724
4	977	944
5	474	461
6	829	834
7	287	277
8	494	477
9	378	376
10	49*	27
12	315	308
12	315	308
13	209	215
14	461	444

H,6,-11

1	201	193
2	258	247
3	492	476
4	225	209
5	557	545
6	532	535
7	530	515
8	425	413
9	189	197
10	328	319
11	415	413
12	465	482
13	154	160
14	272	288

H,6,-10

1	410	399
2	535	509
3	912	878
4	941	919
5	565	586
6	717	702
7	916	912
8	342	331
9	600	608
10	459	480
11	51*	19
12	60	69
13	201	208
14	279	298
15	180	192

H,6,-9

1	77	63
2	510	514
3	299	287
4	90	90
5	565	552
6	478	475
7	559	558
8	296	289
9	459	464
10	272	271
11	574	569
12	284	302
13	72	66
14	134	135
15	226	207

H,6,-8

1	512	506
2	801	777
3	627	605
4	772	789
5	459	459
6	526	526
7	402	397
8	173	153
9	143	140
10	100	101
11	277	288
12	220	220
13	278	254
14	405	417
15	307	301

H,6,-7

1	65	73
2	205	195
3	48*	15
4	136	142
5	456	453
6	781	782
7	420	417
8	697	696
9	396	396
10	521	512
11	63	106
12	381	393
13	54	51
14	61	75
15	124	134

H,6,-6

1	324	324
2	709	705
3	471	449
4	174	196
5	452	447
6	256	251
7	47*	26
8	64	65
9	282	277
10	269	263
11	223	211
12	664	652
13	568	568
14	589	602
15	608	614

H,6,-5

1	977	965
2	126	131

	H,6,-5	
3	46*	10
4	312	310
5	270	264
6	897	890
7	463	475
8	526	517
9	357	334
10	571	578
11	381	382
12	479	479
13	230	210
14	77	70
15	50*	32
	H,6,-4	
1	700	696
2	878	861
3	726	714
4	201	210
5	131	125
6	188	179
7	538	533
8	166	161
9	390	383
10	660	651
11	549	539
12	928	923
13	694	689
14	415	400
15	430	421
	H,6,-3	
1	464	476
2	231	213
3	308	296
4	144	166
5	514	499
6	491	501
7	259	263
8	524	550
9	657	671
10	361	361
11	593	595
12	231	248
13	183	178
14	98	85
15	149	133
	H,6,-2	
1	517	518
2	680	688
3	411	421
4	355	358
5	98	110
6	161	156
7	360	360
8	315	307
9	758	747
10	608	614
11	510	496
12	763	769
13	366	362
14	318	307
15	363	372
	H,6,-1	
1	48	23
2	151	173
3	207	208
4	139	173
5	471	476
6	596	623
7	524	536
8	424	435
9	859	866
10	398	409
11	456	459
12	52*	52
13	186	203
14	287	277
15	51*	52
	H,6,0	
0	479	481
1	736	725
2	882	889
3	185	206
4	453	430
5	109	109
6	278	284
7	300	297
8	519	520
9	347	361
10	377	373
11	376	375
12	529	542
13	226	214
14	425	413
15	181	178
	H,6,1	
0	273	269
1	420	427
2	587	601
3	450	467
4	870	841
5	582	599
6	798	790
7	675	684
8	451	433
9	224	231
10	224	220
11	69	68
12	165	165
13	53*	62
14	388	374
	H,6,2	
0	381	402
1	728	723
2	705	703
3	244	265
4	105	115
5	469	463
6	167	162
7	114	106
8	474	473
9	145	162
10	420	424
11	354	369
12	416	420
13	206	213
14	401	394
	H,6,3	
0	660	653
1	636	659
2	824	835
3	347	384
4	1209	1185
5	810	805
6	701	698
7	792	781
8	344	333
9	343	364
10	57	54
11	396	402
12	240	255
13	337	323
14	438	427
	H,6,4	
0	678	669
1	433	416
2	511	505
3	758	750
4	87	97
5	523	521
6	59	60
7	413	428
8	193	194
9	150	163
10	777	777
11	218	221
12	403	405
13	77	86
	H,6,5	
0	393	388
1	730	729
2	717	713
3	769	768
4	921	900
5	576	568
6	504	513
7	141	149
8	52*	64
9	239	241
10	61	63
11	430	440
12	272	282
13	278	276
	H,6,6	
0	654	648
1	553	584
2	379	385
3	570	574
4	57	51
5	396	407
6	144	138
7	164	169
8	196	231
9	303	281
10	663	641
11	53*	67
12	191	195
	H,6,7	
0	284	286
1	542	532
2	515	510
3	451	451
4	419	435
5	446	449
6	610	626
7	210	220
8	74	51
9	126	127
10	56*	63
11	360	352
12	306	282
	H,6,8	
0	579	580
1	156	163
2	51*	52
3	51*	30
4	534	533
5	225	217
6	773	781
7	792	783
8	358	360
9	362	352
10	668	657
11	55	86
	H,6,9	
0	405	412
1	78	90
2	504	518
3	71	93
4	452	468
5	81	87
6	763	782
7	96	89
8	78	78
9	102	89
10	417	428
	H,6,10	
0	204	197
1	243	248
2	241	238
3	486	494
4	541	546
5	586	588
6	769	760
7	686	652
8	573	580
9	467	462
10	458	441
	H,6,11	
0	100	116
1	195	199
2	237	236
3	107	101
4	120	127
5	397	395
6	323	311
7	219	196
8	81	82
9	54*	28
	H,6,12	
0	316	311
1	333	349
2	133	162
3	529	543
4	281	305
5	679	678
6	542	542
7	679	688
8	380	369
	H,6,13	
0	401	424
1	168	171

H,6,13		
2	505	483
3	112	113
4	250	264
5	53*	31
6	86	109
7	52*	22
H,6,14		
0	136	158
1	421	447
2	79	101
3	405	426
4	436	436
5	266	260
6	532	551
H,6,15		
0	607	647
1	455	447
2	441	421
3	53*	82
4	204	218
5	224	232
H,6,16		
0	53*	17
1	53*	30
2	158	180
3	239	257
H,6,17		
0	593	625
1	512	530
H,7,-15		
1	50*	12
2	224	209
3	286	288
4	515	500
5	156	140
6	544	522
7	190	173
8	297	278
H,7,-14		
1	87	78
2	487	490
3	58	52
4	464	463
5	53*	49
6	76	75
7	59*	31
8	123	131
9	288	300
H,7,-13		
1	54*	41
2	763	735
3	172	191
4	963	941
5	199	196
6	661	640
7	53*	62
8	294	298
9	106	100
10	52*	31
H,7,-12		
1	52*	7
2	407	401
3	72	57
4	56*	15
5	56*	38
6	418	409
7	86	87
8	470	470
9	87	76
10	486	477
11	52*	45
H,7,-11		
1	419	423
2	743	714
3	685	684
4	788	759
5	452	454
6	720	708
7	503	506
8	489	483
9	348	353
10	201	197
11	289	284
12	142	135
H,7,-10		
1	140	118
2	414	405
3	173	167
4	196	178
5	188	185
6	345	320
7	299	295
8	378	370
9	102	90
10	475	475
11	207	203
12	356	342
H,7,-9		
1	286	270
2	751	728
3	522	531
4	834	813
5	446	443
6	802	802
7	485	498
8	545	547
9	175	167
10	157	170
11	156	163
12	160	161
13	98	93
H,7,-8		
1	98	96
2	149	140
3	247	236
4	696	693
5	264	275
6	604	590
7	94	97
8	552	539
9	51*	49
10	720	727
11	50*	44
12	380	366
13	54	33
H,7,-7		
1	57*	51
2	694	668
3	257	235
4	441	443
5	170	186
6	86	110
7	52*	61
8	149	154
9	51*	30
10	50	55
11	52*	32
12	422	420
13	115	117
H,7,-6		
1	662	670
2	54*	24
3	53*	18
4	594	598
5	49*	45
6	452	469
7	91	101
8	814	807
9	51*	43
10	834	863
11	52*	42
12	378	376
13	52	46
H,7,-5		
1	85	76
2	744	743
3	160	167
4	203	203
5	292	289
6	60	66
7	227	245
8	51*	36
9	145	138
10	495	504
11	229	222
12	534	531
13	175	161
H,7,-4		
1	569	590
2	148	135
3	156	162
4	169	178
5	144	141
6	691	693
7	71	68
8	1020	1037
9	134	127
10	538	546
11	50*	34
12	275	277
13	209	205
H,7,-3		
1	100	114
2	555	579
3	205	222
4	316	330
5	252	245
6	59	66
7	467	482
8	224	222
9	560	568
10	714	706
11	123	120
12	683	672
13	454	448
H,7,-2		
1	337	331
2	48*	36
3	71	81
4	194	200
5	49*	28
6	453	452
7	141	169
8	414	422
9	183	189
10	319	303
11	244	261
12	53*	49
13	124	116
H,7,-1		
1	214	215
2	690	703
3	63	59
4	435	441
5	260	257
6	48*	9
7	612	616
8	532	521
9	387	401
10	1011	1011
11	262	256
12	740	734
13	533	527
H,7,0		
1	101	89
2	611	601
3	48*	57
4	456	459
5	242	232
6	276	292
7	265	257
8	344	344
9	281	272
10	52*	63
11	52*	32
12	332	338
13	52*	55
H,7,1		
0	808	786
1	166	164
2	738	749
3	137	141
4	612	620
5	63	61
6	69	69
7	173	185
8	627	635
9	52*	42
10	716	716
11	207	196
12	732	736
H,7,2		
0	429	419

H,7,2

1	312	316
2	751	741
3	214	206
4	675	666
5	128	116
6	469	462
7	231	232
8	432	425
9	68	60
10	227	218
11	110	124
12	259	255

H,7,3

0	1093	1082
1	185	178
2	562	558
3	315	318
4	250	238
5	374	375
6	189	174
7	87	86
8	426	436
9	132	130
10	420	416
11	50*	32
12	435	424

H,7,4

0	560	562
1	777	782
2	1038	1024
3	608	625
4	1146	1149
5	409	405
6	869	849
7	364	356
8	555	557
9	87	88
10	50*	11
11	50*	29

H,7,5

0	823	812
1	59*	62
2	154	188
3	163	161
4	158	175
5	547	541
6	88	103
7	254	253
8	471	451
9	151	147
10	317	316
11	216	219

H,7,6

0	337	347
1	554	559
2	531	518
3	617	643
4	779	772
5	492	498
6	902	899
7	216	208
8	515	527
9	134	133
10	62	67

H,7,7

0	268	275
1	76	86
2	331	355
3	107	113
4	210	207
5	257	263
6	101	120
7	265	268
8	609	592
9	139	162
10	488	480

H,7,8

0	762	793
1	249	263
2	718	744
3	101	90
4	649	634
5	65	64
6	600	608
7	111	121
8	172	181
9	52*	64

H,7,9

0	232	223
1	53*	23
2	105	106
3	55*	54
4	436	443
5	54*	37
6	613	619
7	226	234
8	822	800

H,7,10

0	775	791
1	158	149
2	346	357
3	61	73
4	401	401
5	100	128
6	342	335
7	53*	7

H,7,11

0	393	395
1	113	107
2	373	386
3	144	149
4	103	134
5	259	251
6	536	563

H,7,12

0	535	541
1	52*	15
2	217	222
3	77	88
4	290	284
5	147	160

H,7,13

0	180	202
1	276	294
2	51*	43
3	50*	35
4	265	249

H,7,14

0	376	374
1	48*	40
2	286	299

H,7,15

0	62	73

H,8,-12

1	115	101
2	459	434
3	53*	18
4	714	684
5	54*	23
6	660	645

H,8,-11

1	259	245
2	55*	64
3	62	57
4	195	179
5	57*	24
6	399	383
7	55*	36

H,8,-10

1	54*	37
2	584	560
3	58*	53
4	847	823
5	249	257
6	670	647
7	185	193
8	435	420

H,8,-9

1	431	443
2	58*	40
3	179	165
4	330	315
5	267	264
6	676	659
7	53*	49
8	682	671
9	339	332

H,8,-8

1	204	204
2	474	468
3	211	207
4	514	500
5	245	249
6	363	360
7	103	103
8	52*	48
9	51*	22
10	89	74

H,8,-7

1	84	74
2	56*	22
3	183	178
4	308	281
5	210	236
6	478	462
7	70	63
8	875	855
9	397	383
10	546	534

H,8,-6

1	95	98
2	415	392
3	74	96
4	444	431
5	163	175
6	67	80
7	62	51
8	270	266
9	134	136
10	215	198

H,8,-5

1	400	400
2	189	158
3	354	364
4	423	430
5	152	148
6	614	619
7	135	120
8	717	703
9	300	298
10	570	556

H,8,-4

1	314	311
2	877	865
3	104	117
4	738	742
5	301	329
6	69	71
7	504	519
8	161	148
9	52*	22
10	443	443

H,8,-3

1	346	350
2	55*	23
3	420	412
4	477	478
5	97	67
6	441	442
7	227	222
8	512	529
9	170	161
10	663	666

H,8,-2

1	264	252
2	706	705
3	51*	46
4	344	351
5	557	582
6	208	221
7	457	457
8	314	305
9	49*	34
10	548	530

H,8,-1

1	116	99
2	413	399

H,8,-1

3	70	69
4	509	505
5	57	47
6	572	573
7	50*	24
8	389	376
9	53*	60
10	430	429

H,8,0

0	871	842
1	65	70
2	654	641
3	49*	33
4	350	344
5	70	63
6	72	77
7	83	72
8	507	525
9	157	153
10	544	547

H,8,1

0	132	113
1	134	142
2	379	369
3	48*	33
4	621	607
5	50*	40
6	489	482
7	51*	9
8	381	383
9	163	150
10	78	96

H,8,2

0	669	666
1	241	227
2	570	570
3	150	167
4	480	495
5	130	154
6	175	183
7	202	202
8	159	162
9	159	169

H,8,3

0	452	446
1	88	91
2	529	513
3	94	92
4	546	536
5	51*	7
6	662	658
7	72	72
8	435	442
9	124	122

H,8,4

0	821	828
1	247	240
2	495	484
3	270	274
4	426	430
5	59	86
6	89	77
7	347	341
8	307	310
9	218	224

H,8,5

0	577	573
1	88	89
2	764	761
3	126	121
4	743	746
5	234	249
6	475	460
7	52*	35
8	308	310

H,8,6

0	434	413
1	56	16
2	269	256
3	221	230
4	101	103
5	66	53
6	316	309
7	102	90

H,8,7

0	251	248
1	189	201
2	418	421
3	134	131
4	485	498
5	91	100
6	227	227
7	83	83

H,8,8

0	140	136
1	54*	42
2	55*	19
3	234	237
4	152	140
5	104	110
6	601	622

H,8,9

0	404	414
1	417	432
2	467	466
3	317	299
4	509	510
5	268	278

H,8,10

0	131	121
1	114	133
2	132	121
3	74	58
4	396	398

H,8,11

0	301	306
1	130	142
2	421	419

H,8,12

0	95	101

H,9,-7

1	55*	51
2	313	303
3	128	131
4	362	360

H,9,-6

1	125	143
2	82	108
3	235	220
4	269	255
5	153	151

H,9,-5

1	270	283
2	389	383
3	185	187
4	373	368
5	119	118

H,9,-4

1	114	106
2	52*	26
3	225	207
4	197	196
5	424	406
6	422	415

H,9,-3

1	336	334
2	384	382
3	350	337
4	364	366
5	337	328
6	130	133

H,9,-2

1	56*	62
2	57	68
3	111	98
4	235	240
5	351	334
6	510	500

H,9,-1

1	341	337
2	474	461
3	341	331
4	203	196
5	253	260
6	134	120

H,9,0

1	158	159
2	64	70
3	218	229
4	412	405
5	93	117
6	488	483

H,9,1

0	500	492
1	320	304
2	628	609
3	380	364
4	79	91
5	141	149

H,9,2

0	145	145
1	95	92
2	261	258
3	118	120
4	380	366
5	55	67

H,9,3

0	463	440
1	421	409
2	622	610
3	352	361
4	149	158
5	98	89

H,9,4

0	457	460
1	121	118
2	579	578
3	381	371
4	601	587

H,9,5

0	191	179
1	114	119
2	406	391
3	129	136

H,9,6

0	432	418
1	84	78
2	623	624

H,9,7

0	54*	72

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APPENDICES

APPENDIX I, II

The following two structural investigations were undertaken as exercises to gain practical experience of "direct methods" as a technique of structure determination. This was done in order to implement in a practical way the theory studied during my M.Sc degree in Crystallography and the dissertation on "Phase Probability and Image-Seeking Methods", which was undertaken as part of that degree and thus to broaden my experience of crystallographic techniques.

The first compound studied was Cambogin ($C_{38}H_{50}O_6$) extracted from the roots of the plant Garcinia Cambogia Desr (Guttiferae). Both Cambogin and its dibrosylate were crystallised from methanol with material supplied by Professor Govindachari. Preliminary photographs were taken on both substances to ascertain in each case the probable difficulty of structural solution. It was decided to use the dibrosylate ($C_{50}H_{56}O_{10}B_{12}S_2$) to determine the absolute configuration of the molecule by utilising the anomalous dispersion contribution of the bromine and sulphur atoms and this has been successfully achieved. Concordant structure solutions were obtained by both heavy-atom and direct-method techniques; the Patterson map was readily solved and its solution was later confirmed by the direct-method solution.

The structure of the ketol ($C_{20}H_{34}O_2$) supplied by Professor Pascual Vila was also solved by direct methods using the powerful phase-expansion procedure of the program MULTAN.

APPENDIX I

The crystal and molecular structure of Cambogin dibrosylate.

> *"Nothing is really work unless*
> *you would rather be doing*
> *something else."*
> *... Sir James Barrie.*

Appendix I

Introduction

A large number of xanthones[1] and complex xanthone derivatives e.g. morellin[2], and 3,8-linked biflavonoids, e.g. morelloflavone (fukugetin),[3,4] have been isolated from Garcinia (Guttiferae).

Xanthochymol (I), isoxanthochymol (IIa) and its presently confirmed enantiomer, Cambogin (IIb), are all derivatives of maclurin (III) modified in the A ring by the substitution of five prenyl groups.

The mass spectra of both isoxanthochymol and cambogin demonstrate the presence of a dihydroxybenzoyl group, two C_5H_9 groups and one $C_{10}H_{17}$ group. Using these results and U.V. and N.M.R. data, and making the assumption that the biogenetic precursor of these compounds is maclurin (III) in which the catechol group is unchanged and the phloroglucinol unit has become the target of attack by five "active isoprene" groups, Karanjgoakar *et al*[5] proposed the part structure IV for isoxanthochymol[5]. This was confirmed and completed (IIa) by an X-ray study of its dibrosylate.[5]

Scheinman *et al*[6] had earlier demonstrated the significance of maclurin in xanthone biosynthesis by a statistical analysis of xanthones in higher plants. It is now clear that prenylation of both rings A and B of maclurin is involved in the biosynthesis of morellin, whereas prenylation of ring A alone is involved in the biosynthesis of xanthochymol, isoxanthochymol and cambogin.

General

The structure of cambogin, a benzophenone derivative isolated from the roots of the plant Garcinia Cambogia has been solved via its dibrosylate derivative. Cambogin was isolated by Drs. Pai and Rao of the Chemistry Department of Presidency College, Madras. Preliminary studies by these workers based solely on spectroscopic data for lack of material suggested that either of the two structures (V or VI) were likely, though some variant of the isoxanthochymol skeleton was also possible.[7]

Since it proved difficult to differentiate between these structures by chemical means, samples of cambogin and its di-p-bromobenzene-sulphonate were sent to this laboratory for further study through the kind intermediacy of Professor Govindachari.

The gem-dimethyl group close to the dihydroxybenzoyl group is more hindered in structure VI than in V, but inspection of models shows that it does not seem to be overcrowded even in VI. In the nuclear magnetic resonance spectrum of cambogin (Fig. 1), it appears that none of the four tertiary methyl groups present in the molecule is significantly shielded. This evidence which is negative would also not dismiss any variant of isoxanthochymol, since the dihydroxybenzoyl group is not rigidly attached and its shielding effect on the methyl groups may be small. Additionally, the evidence for the presence of a geranyl side chain on the chromane ring and the position of the γ-γ- dimethylallyl group was derived solely from mass spectral data and a supposed biogenetic route.[5] The proposed structures were therefore far from certain.

After the structure of cambogin had been determined from three-dimensional data (see later experimental section) it proved to have the same structural skeleton as isoxanthochymol whose stereochemistry, though found by X-rays, was not fully defined in ref. 5. This seemed rather strange in the light of the melting point and optical rotary measurements (Table I);

Table I

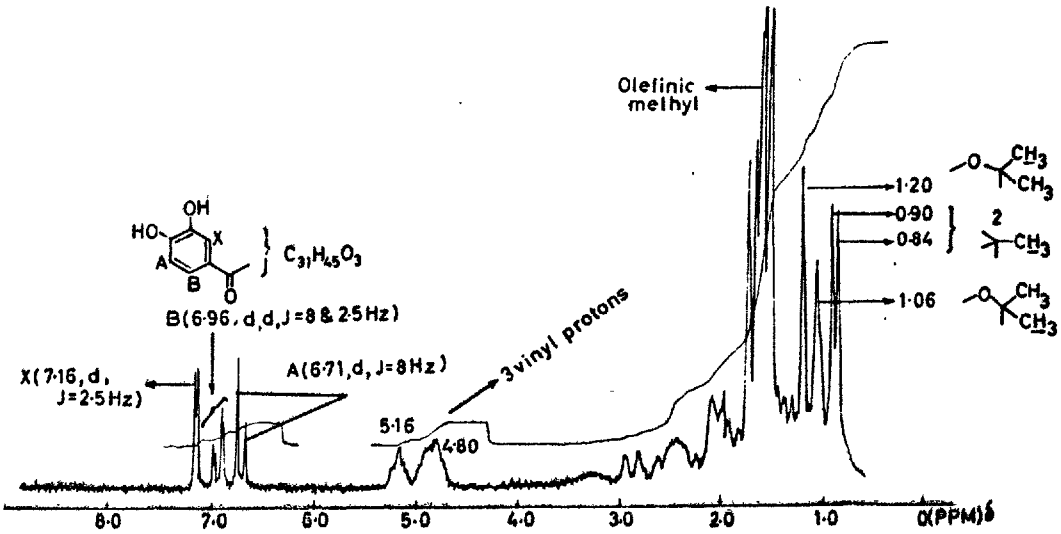
Comparative Data for Cambogin and Isoxanthochymol

	mpt.	$[\alpha]_D^{25}$ (1% in EtOH)
isoxanthochymol	218 - 225° *	+179.2
cambogin	242 - 244°	-212.6°

* depressed by at least 5° on admixture with cambogin

Fig. 1

Nuclear Magnetic Resonance Spectrum of Cambogin.



100MHz NMR SPECTRUM OF CAMBOGIN

the $[\alpha]_D^{25}$'s are opposite in sign but not equal, whilst the mpt's are quite different. This suggested that the compounds were epimers rather than enantiomers. The two starred centres (*) in IIa indicate the two possible epimeric positions which were not defined in ref. 5.

A direct comparison between the two structures was not immediately possible as no crystallographic data or co-ordinates had been published for isoxanthochymol.[5] Reference to Dr. Palmer, who did the X-ray work, elicited the surprising result that the two compounds had the same space group, almost identical cell parameters and closely corresponding atomic co-ordinates. In view of the opposite signs of $[\alpha]_D$ for these substances, (see Table I) it appeared that the two compounds must be enantiomeric, but from the lack of agreement of the numerical values of the mpt's and optical rotations it seems likely that the specimen of isoxanthochymol, while probably chemically pure, is not so optically homogenous as that of cambogin.

It thus remained to determine the absolute configuration of the two species. The absolute configuration of cambogin has been confirmed (see experimental section) and fortuitously it had the same configuration as the arbitrary heavy-atom and direct methods solution. Quite by chance, too, isoxanthochymol had been solved in the enantiomeric configuration, thus both sets of co-ordinates quoted represent the true chiralities. Dr. Palmer considered that his data, which were collected from three crystals, despite being refined to $\underline{R}$ 0.09 suggest but are not strong enough to prove that isoxanthochymol has the enantiomeric configuration. The specimens which he studied had decomposed, so the m.pt., $[\alpha]_D^{25}$ and chirality could not be checked.

Experimental

Preliminary data for cambogin and its dibrosylate are compared in Table 2. The crystals of the dibrosylate were colourless rectangular blocks.

Table 2

Comparative table of preliminary results of cambogin and its dibrosylate.

<u>Cambogin</u>: $C_{38} H_{50} O_6$; $\underline{M} = 602$
Orthorhombic; a = 11.1Å, b = 14.52Å, c = 20.7Å
Space group $\underline{P}2_12_12_1$; $\underline{Z} = 4$; $\underline{Dc} = 1.2\text{g cm}^{-3}$

Intensity data for a 24-hour Weissenberg were discernible to $\theta \simeq 50^\circ$, though larger crystals than the specimen examined were available. There would probably be enough data for a direct-method solution, but the presence of 44 non-hydrogen atoms would make the possibility of success unsure.

<u>Cambogin dibrosylate</u>: $C_{50} H_{56} O_{10} Br_2 S_2$; $\underline{M} = 12.4$Å
Monoclinic; $\underline{a} = 10.64$Å, $\underline{b} = 21.0$Å, $\underline{c} = 12.4$Å, $\beta = 105^\circ$
Space group $\underline{P}2_1$; $\underline{Z} = 2$; $\underline{Dc} = 1.29\text{g cm}^{-3}$

Intensity data for a 24-hour Weissenberg ran to $\theta \simeq 45^\circ$. Nevertheless this compound was thought preferable as it poses a straight heavy-atom solution and also the presence of bromine and sulphur atoms enables the determination of the absolute configuration which is required. This compound was recrystallised in this laboratory from methanol owing to the deterioration of the crystal samples in transit. The specimens used were coated with picture varnish.

Crystal data

$C_{50} H_{56} O_{10} Br_2 S_2$, mpt. 104°, $[\alpha]_D = -107.75°$
(C = 0.8 in EtOH) $\underline{M} = 1040.9$, monoclinic,

$\underline{a} = 10.140(2)$, $\underline{b} = 21.269(3)$, $\underline{c} = 12.378(2)$,

$\beta = 105.84(1)°$, $\underline{U} = 2568.2$ Å^3, $\underline{D}_m$ (by flotation)=1.36g cm^{-3},

$\underline{Z} = 2$, $\underline{D}_c = 1.34$g cm^{-3}, $\underline{F}(000) = 1136$.

Optical activity and systematic absences uniquely indicated space group $\underline{P}2_1$ (NO. 4). Cu-Kα radiation ($\bar{\lambda} = 1.5418$Å); μ(Cu - Kα) = 38.7cm^{-1}.

The crystal chosen for intensity measurements was a rectangular block ca 0.25 x 0.25 x 0.50 mm^3 mounted about $\underline{b}$. Intensities were measured on a Siemens off-line automatic four-circle diffractometer with filtered Cu -Kα radiation (See Chapter I). A total of 3268 independent reflections (to $\theta = 55°$) were measured by means of the $\theta - 2\theta$ scan technique with the five-value measuring procedure. Of these, 799 reflections were judged to be unobserved, i.e. $I < 2.58\sigma(\underline{I})$. The net count of the reference reflection measured as a reference every 50 reflections deteriorated by approximately 20% during the data collection (ca. 8 days). The data were converted to a common arbitrary scale by use of the reference reflection and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure

The structure was solved by both direct methods and the heavy-atom method.

Initially, the largest four-hundred $|E|$ values were calculated using the free standing program NORMAL. All $|E|$'s greater than 1.7 were then sorted into their various parity groups for input to the program SIGMA which gave lists of all Σ2 interactions of each reflection encountered amongst the input reflection data. The program listed the interacting reflections, the $E_1 x E_2 x E_3$ value and the probability of the relationship. Three origin and one enantiomorph defining reflections were chosen using the criteria explained in Appendix IV.

	h	k	ℓ	E	Phase
	2	0	1	2.71	0
	1	0	4	2.75	0
	0	1	2	3.28	$\pi/2$
a	1	6	1	2.69	
b	1	5	2	2.43	
c	3	3	$\bar{1}$	2.69	

The starting set input to the PHISUM subroutine was identical to that of the hand calculation and it was successful in assigning 124 consistent relationships from the 179 starting terms with $|E| > 1.7$. The symbolic phases a,b,c were each given values ranging in steps of 250 millicycles from 125 to 875mc, the enantiomorph fixing reflection 161 being restricted to values between 0 to π. Owing to this enantiomorph restriction only 2 x 4 x 4 combinations were required to be computed.

The sum with the lowest R_{Karle} (0.205) and the highest $\langle t_{\underline{h}} \rangle$ (0.921) and $\langle \alpha \rangle$ (109.3) was from starting values of a = 125mc, b = 125, c = 125. The corresponding E-map computed from these numerical phases clearly showed the positions of the bromine and sulphur atoms and some forty other meaningful atomic positions. Isotropic refinement in CRYLSQ, using phases based on these positions gave $\underline{R} = 0.29$. Comparison of these atomic positions with the heavy-atom solution confirmed the results of this exercise. Looking back at this direct-method solution with the heavy-atom solution as a model, it would have been possible to find an additional six atoms from the E-map although their relative peak heights were much lower than that which one would expect for a carbon atom.

A three-dimensional, origin-removed Patterson was calculated whilst the above direct-methods calculations were still taking place. One bromine was easily located with the aid of the Harker section $V = \frac{1}{2}$ of the map, but, owing to the overlap of some Harker peaks and the occurrence of a number of strong non-Harker peaks on the Harker section, the second bromine was more difficult to find. The x and z co-ordinates of the first Br atom were found and its y co-ordinate was arbitrarily fixed at 0.25. The second Br's y co-ordinate was calculated using the Br(1) - Br(2) intervectors with the fixed y-value for Br(1). Their y co-ordinates differed substantially, (Ca. $0.32b \equiv 6.8$Å). It is notable that the presence of this second bromine atom at such a height separation is convenient insofar as it breaks the pseudo-plane of symmetry normally encountered in $P2_1$ when only one heavy atom is present.

After assignment of the bromines, tentative assignments of the sulphurs were made. Three cycles of isotropic least-squares refinement of Br and S atoms gave $\underline{R} = 0.41$. The remaining non-hydrogen atoms were located from successive difference syntheses, and three cycles of isotropic refinement of all these atoms gave $\underline{R} = 0.147$. Some six misprocessed reflections and three low-angle reflections suffering from extinction were removed. Anisotropic refinement on all atoms brought $\underline{R}$ to 0.106. Some twenty-four hydrogen atoms were then found from the corresponding difference-synthesis and allowance for these as a fixed atom contribution brought $\underline{R}$ to 0.098. (No further H-atoms were located).

At this stage, an absorption correction was applied according to the method of Busing and Levy[8], with crystal path lengths determined by the procedure of Coppens *et al.*[9] Further anisotropic refinement increased $\underline{R}$ to 0.102 and despite checks on the measurements of the crystal and assignment of the crystal faces no error could be found. It was decided to ignore this correction as no significant improvement could be seen in the standard deviations of the atoms.

Absolute Configuration

The method used was that suggested by Ibers and Hamilton,[10] the commonly named "R-factor-ratio test". Two sets of structure factors were computed using the latest positional co-ordinates with $\Delta f''$ for both bromine and sulphur being +ve and -ve respectively. The results gave R = 0.093 and 0.099 respectively for all data, but when the centric $h0\ell$ data were excluded, the respective R values were 0.0895 and 0.0952. The ratio $R-/R+ = \mathcal{R}$ is thus 1.064 which, by reference to Hamilton's Tables,[10] indicates very strongly that the absolute stereochemistry is depicted by Fig. 3.

The refinement was carried out for 3268 reflections and 577 parameters. Hence there were 2691 degrees of freedom.

The statement, "The second absolute configuration is correct" is a one-dimensional hypothesis since it involves changing only the signs of all the y co-ordinates. To extrapolate to 2691 degrees of freedom, the Hamilton formula can be used:

$$\mathcal{R}_{1,2691,0.005} \approx 1 + \frac{120}{2691}\left(\mathcal{R}_{1,120,0.005} - 1\right)$$

The value of $\mathcal{R}_{1,120,0.005}$ obtained from Hamiltons tables for the 0.005 level of significance (the lowest listed) is 1.034.

Hence:

$$\mathcal{R}_{1,2691,0.005} \simeq 1 + 0.0445 \times (1.034 - 1) \simeq 1.0015$$

whence

$$\mathcal{R}_{1,2691,0.005} - 1 \simeq 0.0015$$

As this value is very much smaller than $(\frac{R-}{R+} - 1) = 0.064$ it follows that the probability that the structure corresponds to the mirror image of the structure whose co-ordinates are given in Table 3 is << 0.005 and so can be strongly rejected. All the diagrams of

Cambogin shown in this chapter depict the correct absolute configuration.

Description of the Structure and Discussion

The molecular structure is shown in Fig. 3 and the corresponding packing diagram in Fig. 4. Tables 3 and 4 list the final co-ordinates of the non-hydrogen atoms and the coefficients for the anisotropic temperature factors. The standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. Tables 5 and 6 list the final co-ordinates of the enantiomer and the coefficients for the anisotropic temperature factors supplied by Dr. Palmer. Table 7 lists the co-ordinates of the 24 hydrogen atoms in cambogin obtained from the latest difference-Fourier: these are unrefined.

Fig. 5a, 5b compares the numbering schemes used by us for cambogin and by Dr. Palmer for isoxanthochymol. Fig. 6, 7, and 8, 9 show the bond lengths and angles for the two structures with estimated standard deviations. Least-squares planes and dihedral angles for both molecules have been calculated; least-squares planes are tabulated in Tables 8 and 9 whilst dihedral angles are shown in Figs. 10 and 11.

Detailed discussion of the differences between these two structures will be deferred to a full paper later, but first impressions suggest that they may be due in part to lack of homogeneity in the isoxanthochymol specimen. The much greater susceptibility of isoxanthochymol to X-ray damage reported by Dr. Palmer may also point in the same direction. The matter cannot be pressed very far, however, in view of the limited accuracy of both determinations - again due in part to radiation damage. However despite this limitation it has been possible successfully to determine the absolute configuration of cambogin.

Comparison of observed and calculated structure amplitudes are listed at the end of the chapter.

Steric Considerations and the possible Mechanism of formation of Cambogin and Isoxanthochymol.

Previously, the two asymmetric positions marked with stars in IIa were only considered with respect to whether cambogin and isoxanthochymol were enantiomers or epimers. If one considers the stereochemistry at these two centres one can gain insight into the possible biogenesis of these compounds.

In cambogin (VII) Prenyl σ is in the equatorial position with respect to a boat-shaped ring C. This ring is doubtless constrained in this conformation by the need to arrange σ equatorially (principally to relieve congestion between prenyls ν and σ). The presence of the ether oxygen (instead of methylene) has also helped by removing the hydrogen-methyl steric interaction which would otherwise have resisted the boat configuration. However, had prenyl σ been β-oriented in VII (or α in VIII) it would have gone equatorial and thus allowed ring C to become a chair, which is energetically slightly more favourable.

Prenyl τ is axial to a chair-shaped ring D. In this case the efforts of τ to become equatorial by flipping the ring to a boat are strongly resisted by the eclipsed interactions between both methyls and the adjacent two substituent C-C bonds. It is thus evident that a marked reduction in strain could result from changing τ to the β-orientation in VII(α in VIII). So one is tempted to look at these steric factors in relation to the possible biogenesis of these compounds.

Karanjgoakar *et al*[5] suggested that isoxanthochymol is formed via some intermediate akin to Compound X. The analogous precursor of cambogin is, therefore, IX. These part-structures have only one dissymmetric centre (starred) at which the prenyl λ can be α or β.

At the other side of the ring there are two identical prenyls. IX and X are therefore enantiomers. When prenyl λ is β as in IX it will orient itself equatorially and so tilt the carbonyl bridge to the β-side of the plane of the remainder of ring B. It then follows that the β-oriented prenyl μ will bridge to the hydroxyl to form ring C, and the α-oriented prenyl ν bridges the hexenone ring B to form ring D, thus forming the nucleus of cambogin.

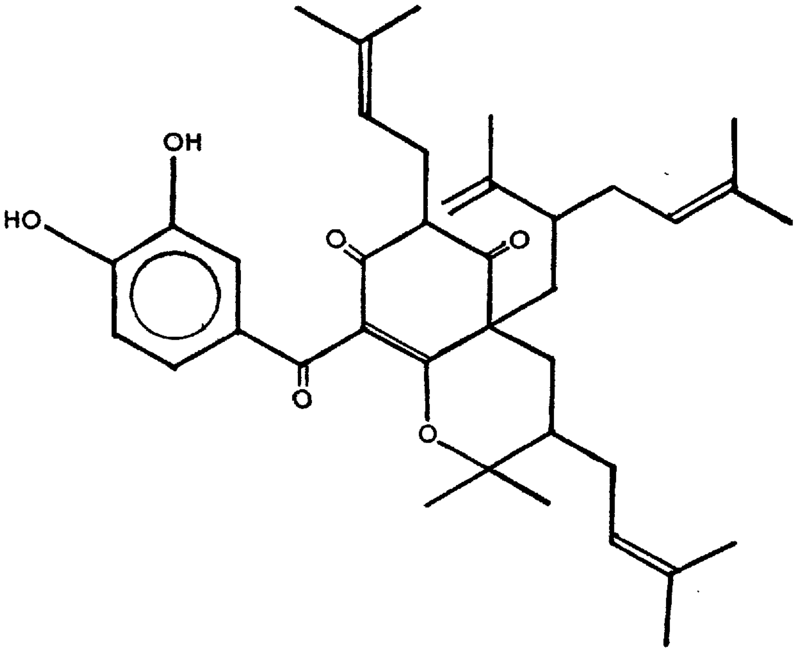
However, when prenyl λ is α-oriented as in X it deflects the carbonyl α, so this time it is the β-oriented prenyl μ which cyclises across ring B and the α-prenyl ν which bridges to the hydroxyl to form the nucleus of isoxanthochymol. As the addition of the remaining prenyls σ and τ was thought to be performed simultaneously with these closures (and the geometry of their attachment is consistent with this assumption), it would give rise to versions of VII and VIII that were exact enantiomers. Thus the existence of these two enantiomers seems to substantiate the proposed mechanism of Karanjgoakar *et al*[5] and traces them back to the simpler enantiomers IX and X. It is rather easier to understand that different members of the Garcinia might produce these stereo-selectively, though it should be borne in mind that in the present state of our knowledge we cannot be sure that they do so homogeneously. The query mentioned earlier as to the homogeneity of the isoxanthochymol specimen is relevant here, and we cannot at present rule out the possibility that the work up procedures may have interfered with the chirality ratio and helped to produce crystals of the major constituent through spontaneous resolution.

<u>Fig. 2</u>

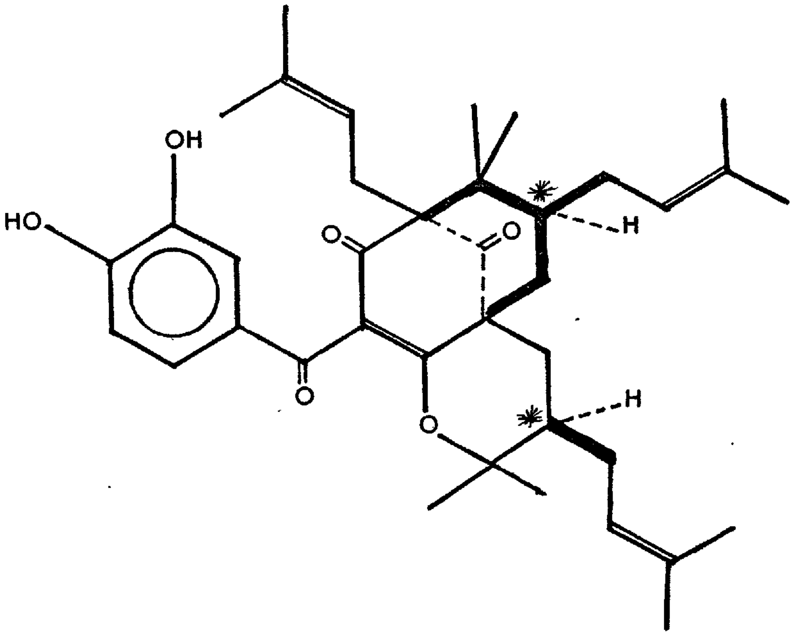
Schematic Diagrams

of molecular formulae referred to in text.

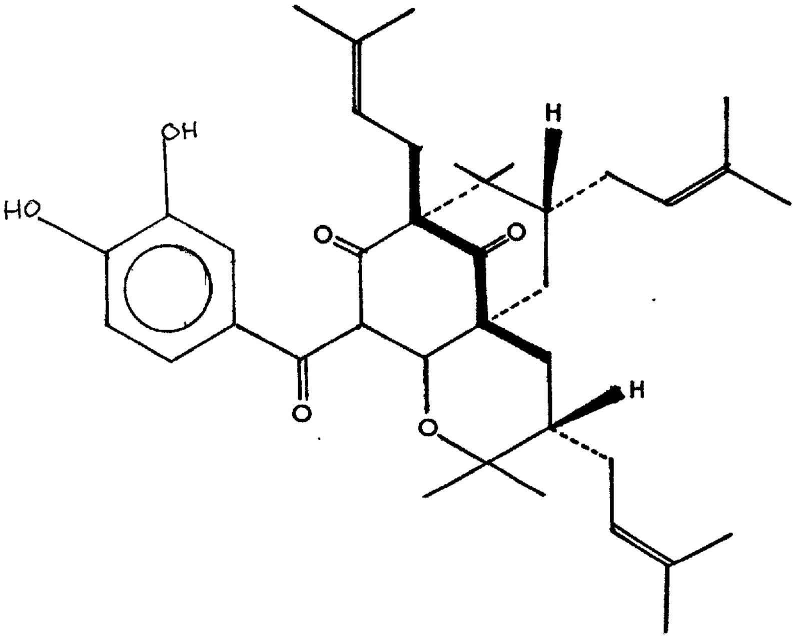
I - X



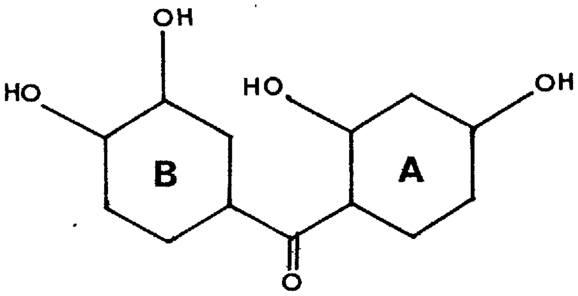
I



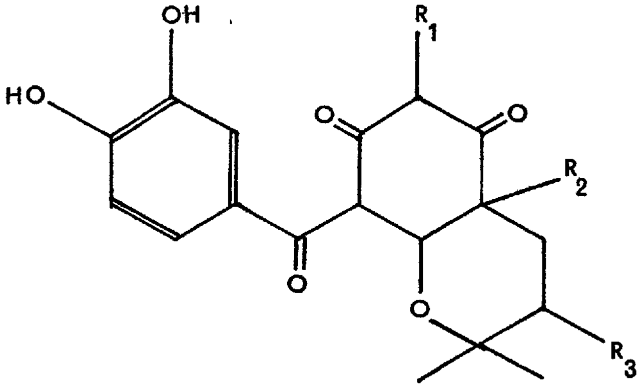
IIa



IIb

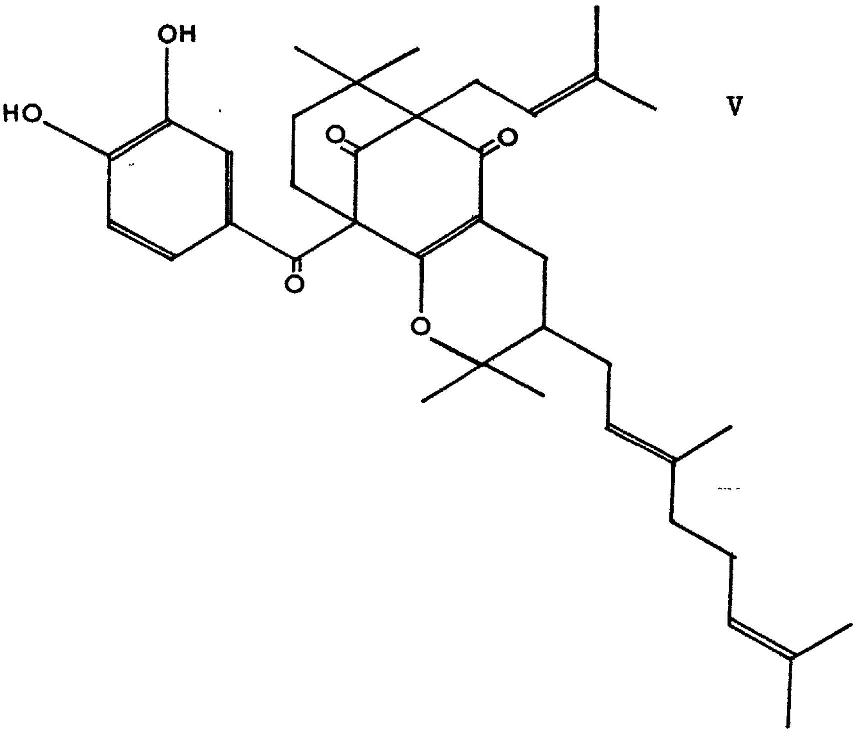


III

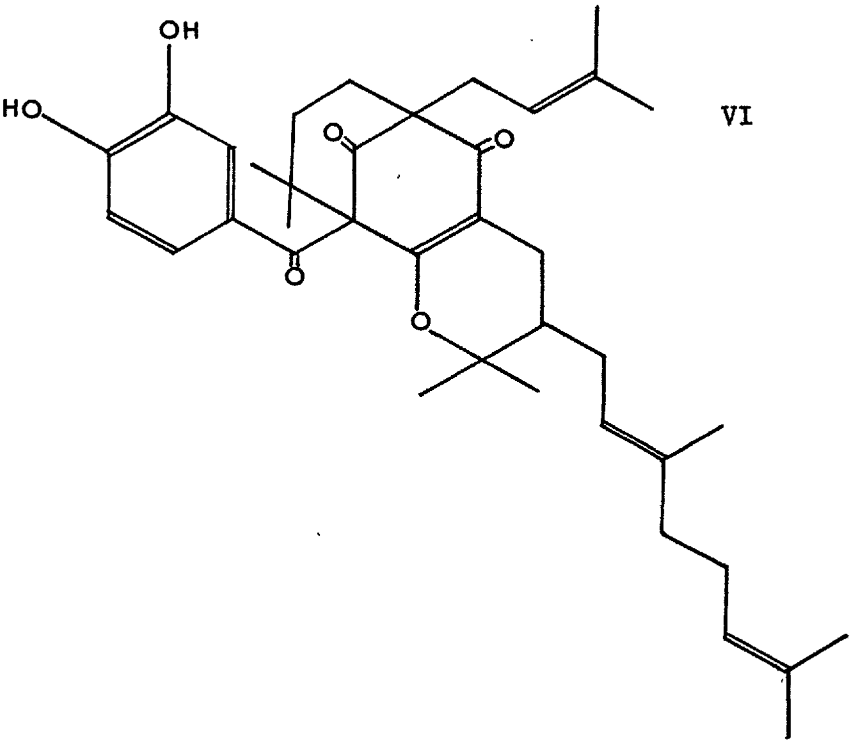


IV

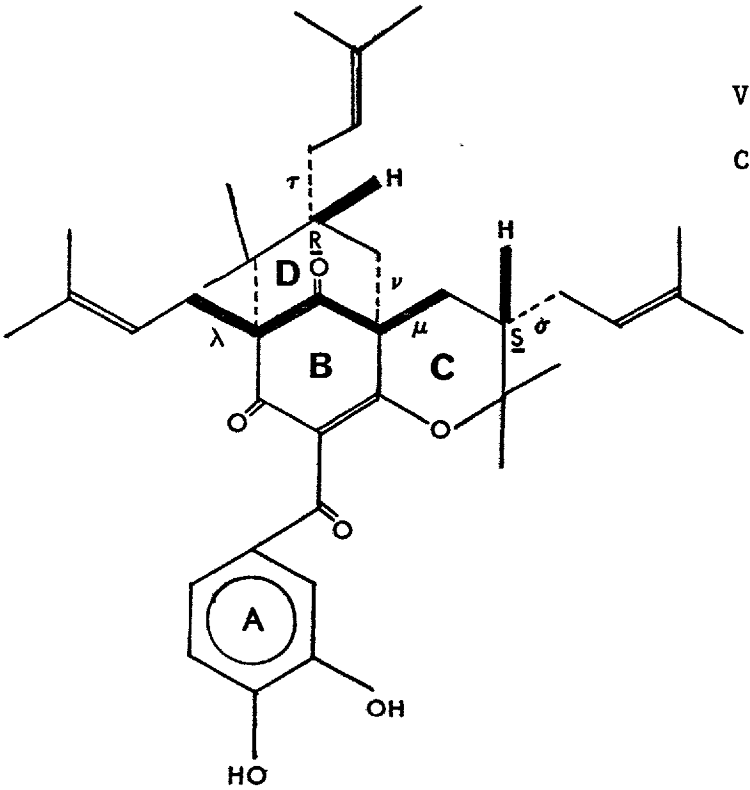
R_1
R_2
R_3
Position of attachment of isoprene units



V

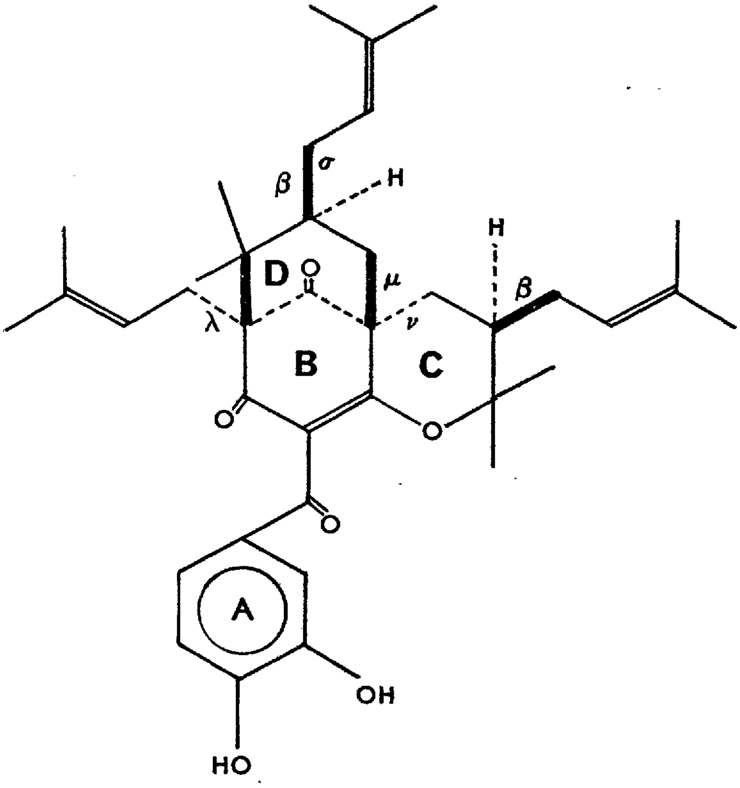


VI

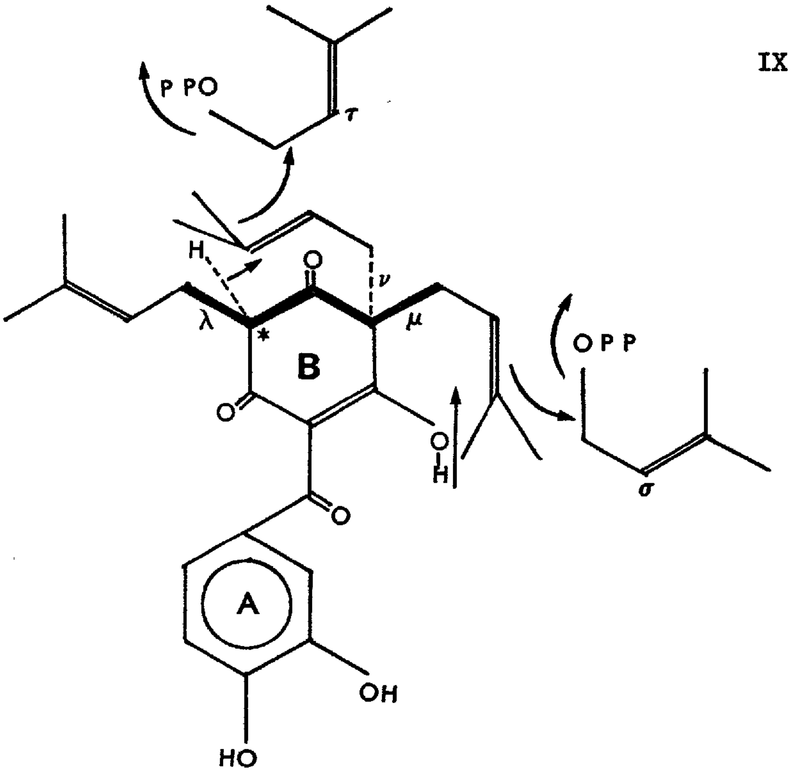


VII

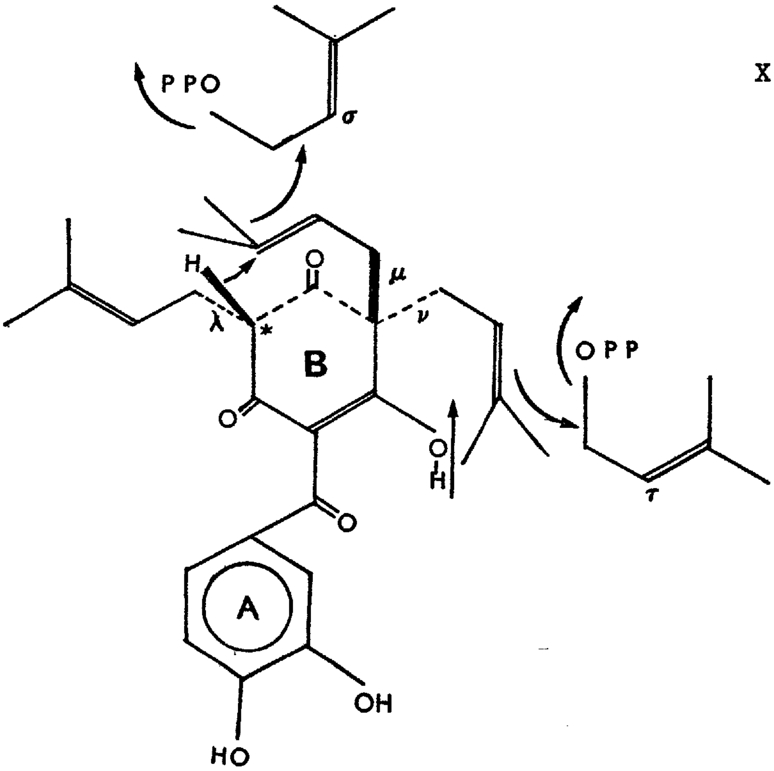
Cambogin C = boat
D = chair



VIII Isoxanthochymol



IX



X

Fig. 3

Molecular Structure of Cambogin Dibrosylate.

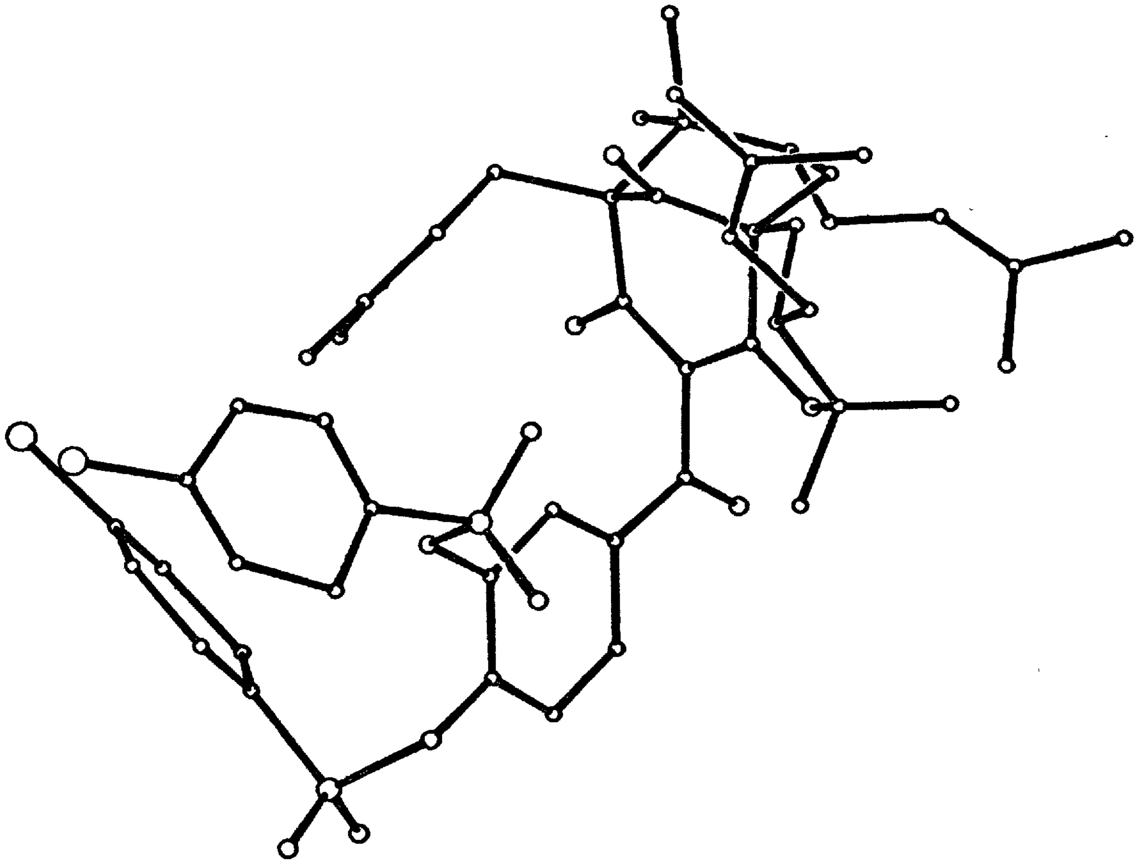


Fig. 4

Stereoscopic packing diagram of Cambogin Dibrosylate.

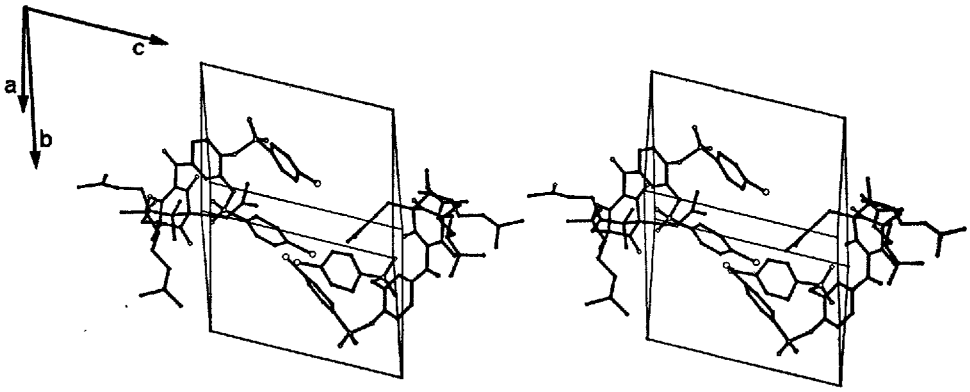


Fig. 5a

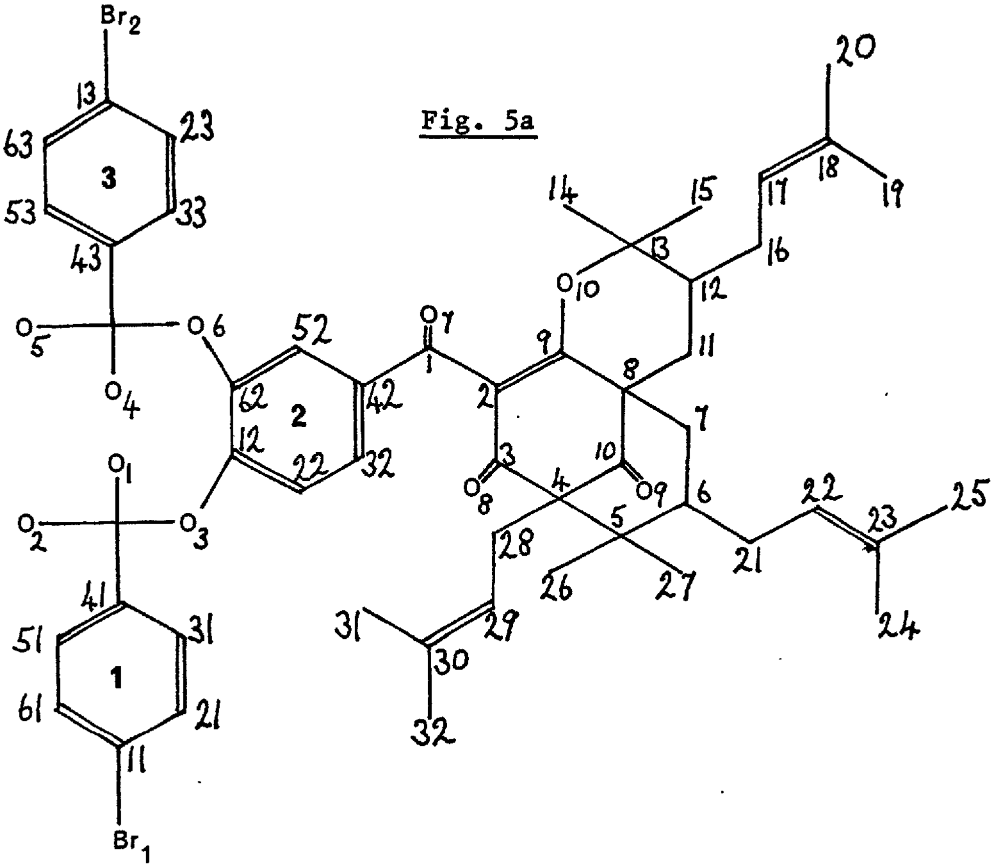
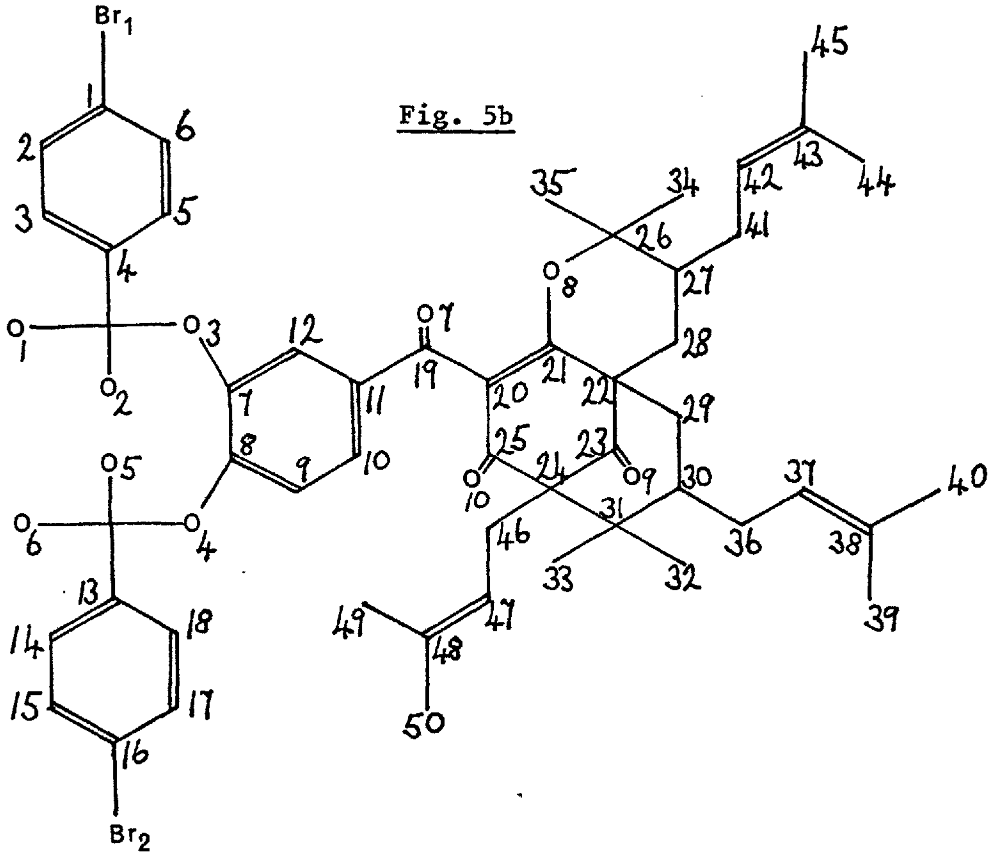


Fig. 5b



Comparison of the numbering in Cambogin and Isoxanthochymol.

FIGURE 6

Cambogin dibrosylate

Bond lengths (Å) with estimated standard deviations in parentheses.

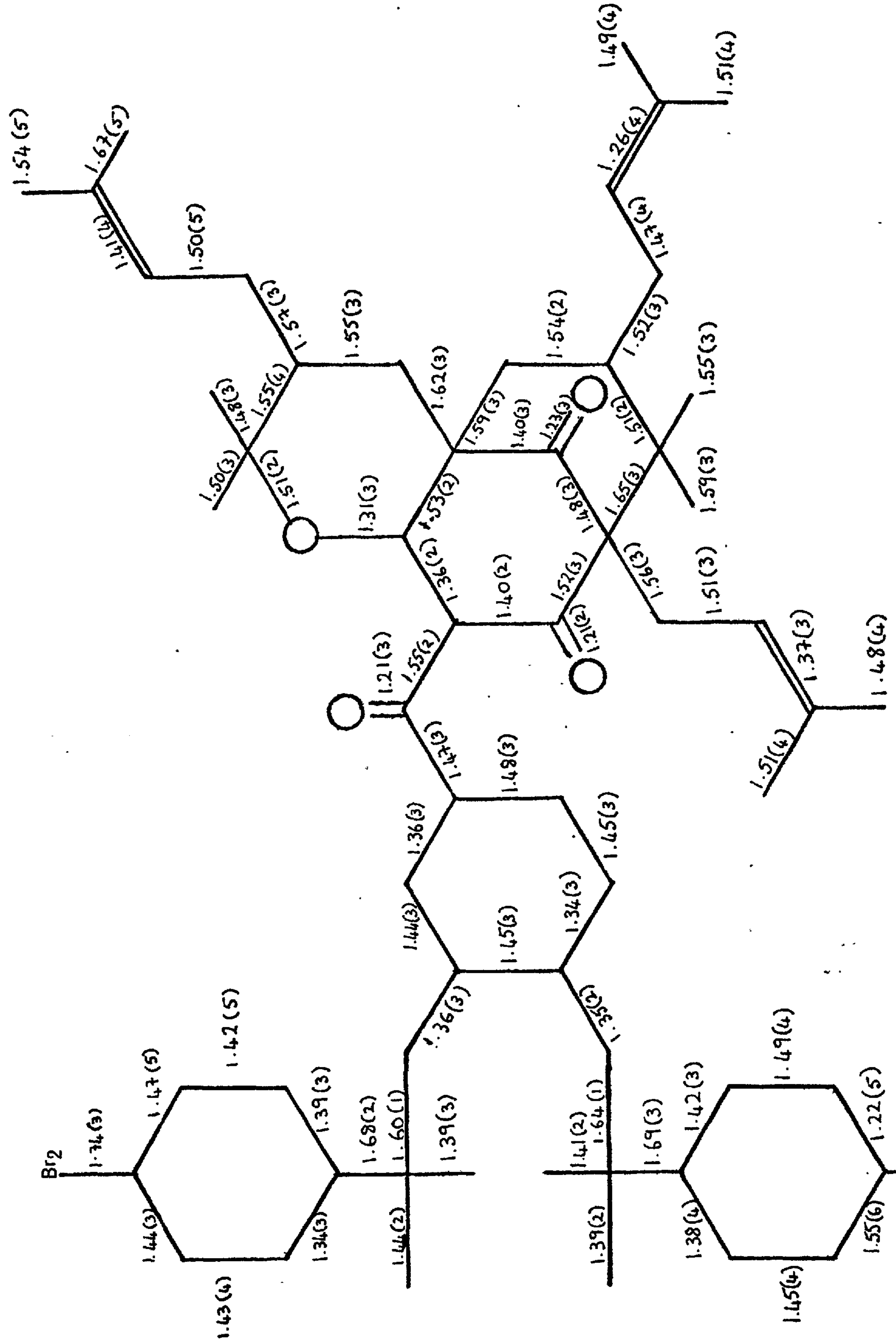


FIGURE 7

Cambogin dibrosylate

Valence angles (^{o}) with estimated standard deviations in parentheses.

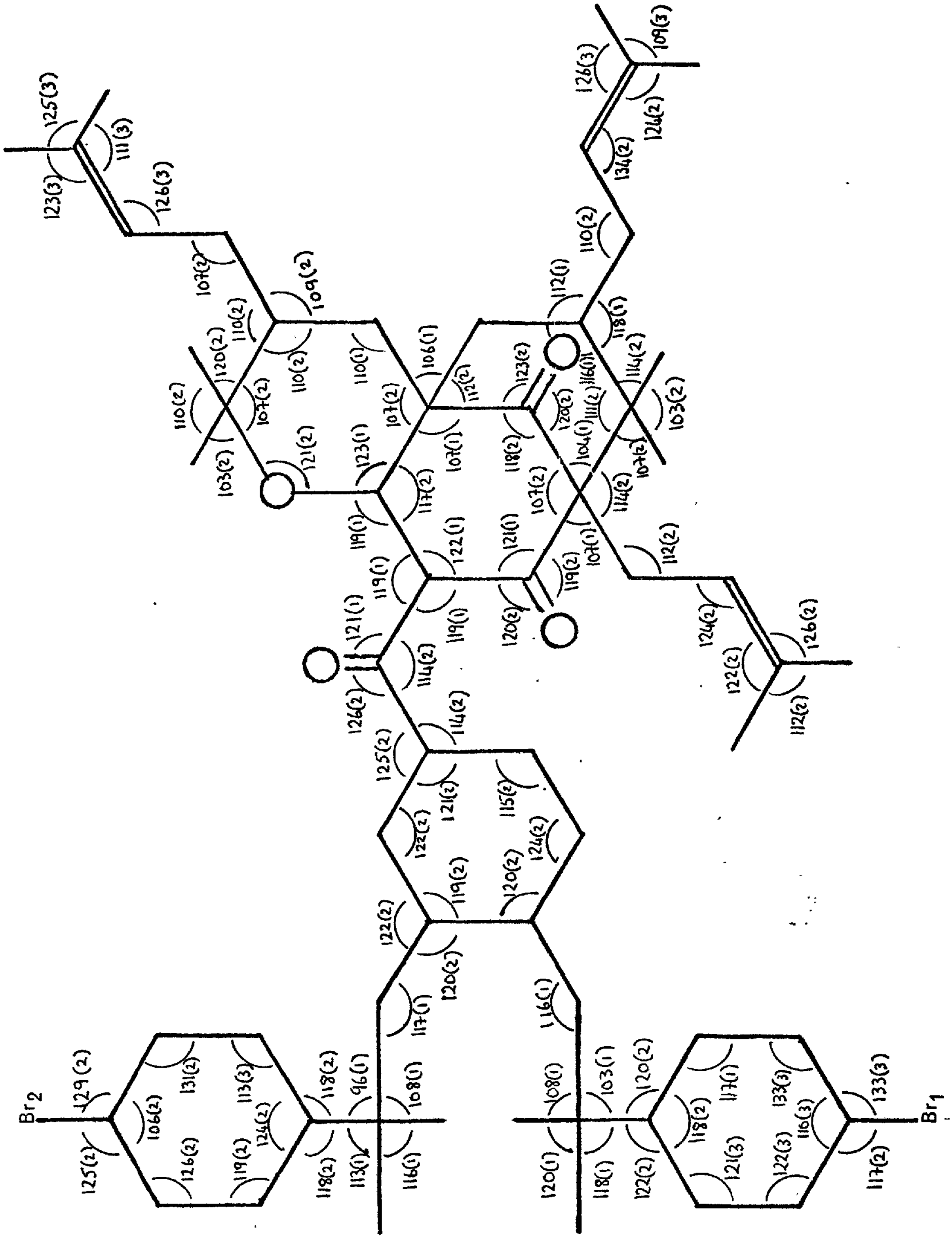


FIGURE 8

Isoxanthochymol dibrosylate

Bond lengths (Å) with estimated standard deviations in parentheses

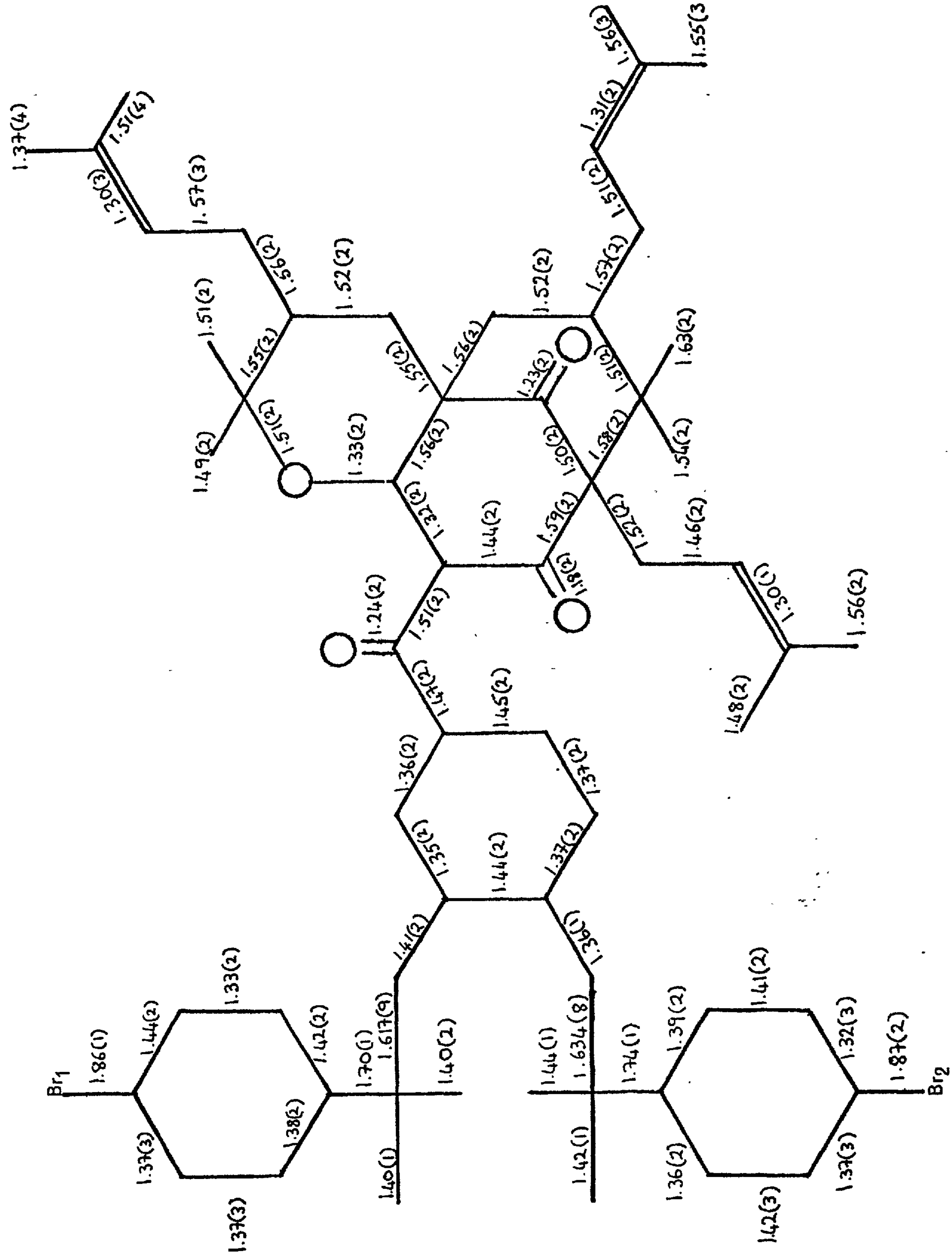


FIGURE 9

Isoxanthochymol dibrosylate

Valence angles (°) with estimated standard deviations in parentheses

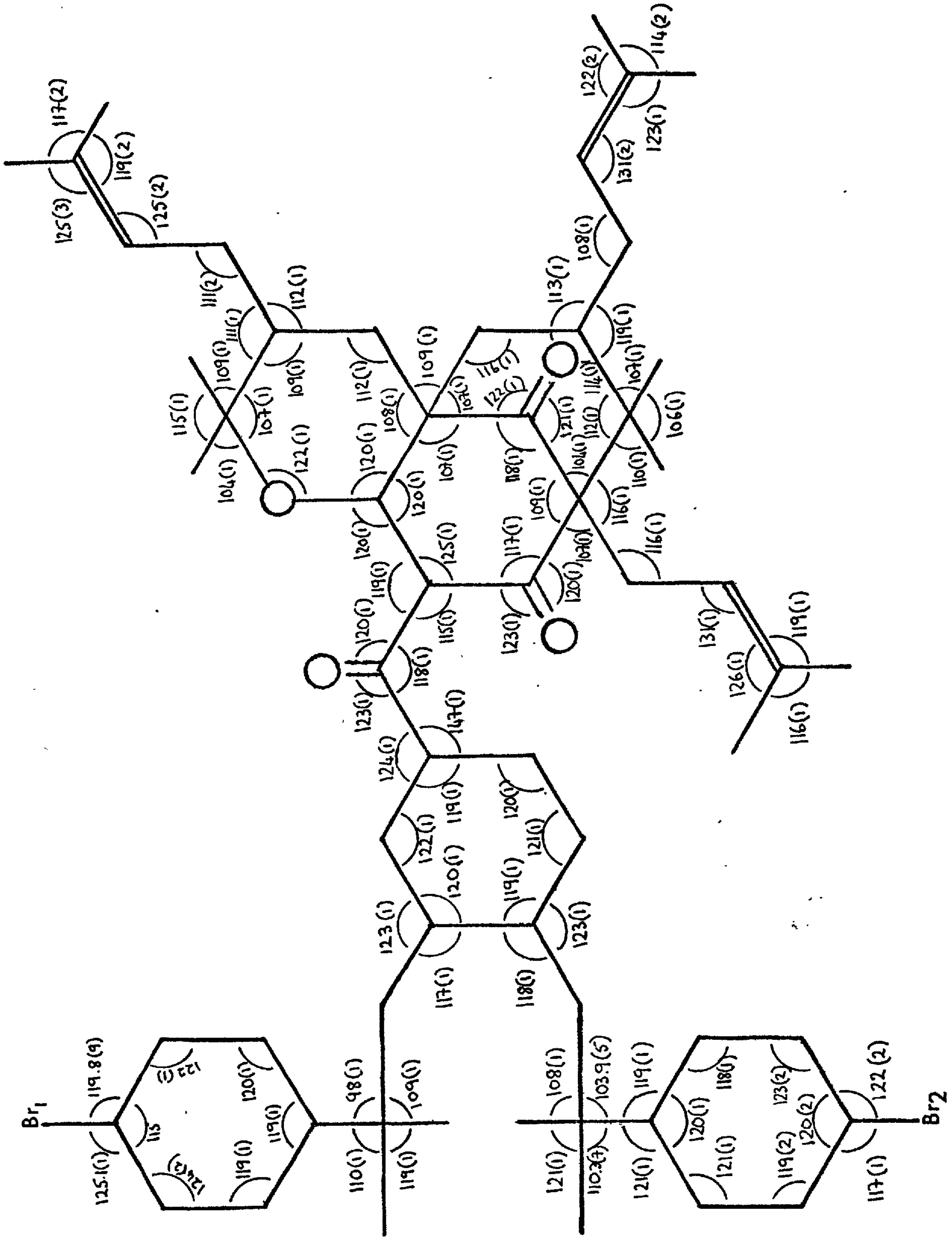


Figure 10

Cambogin dibrosylate

Dihedral angles (°)

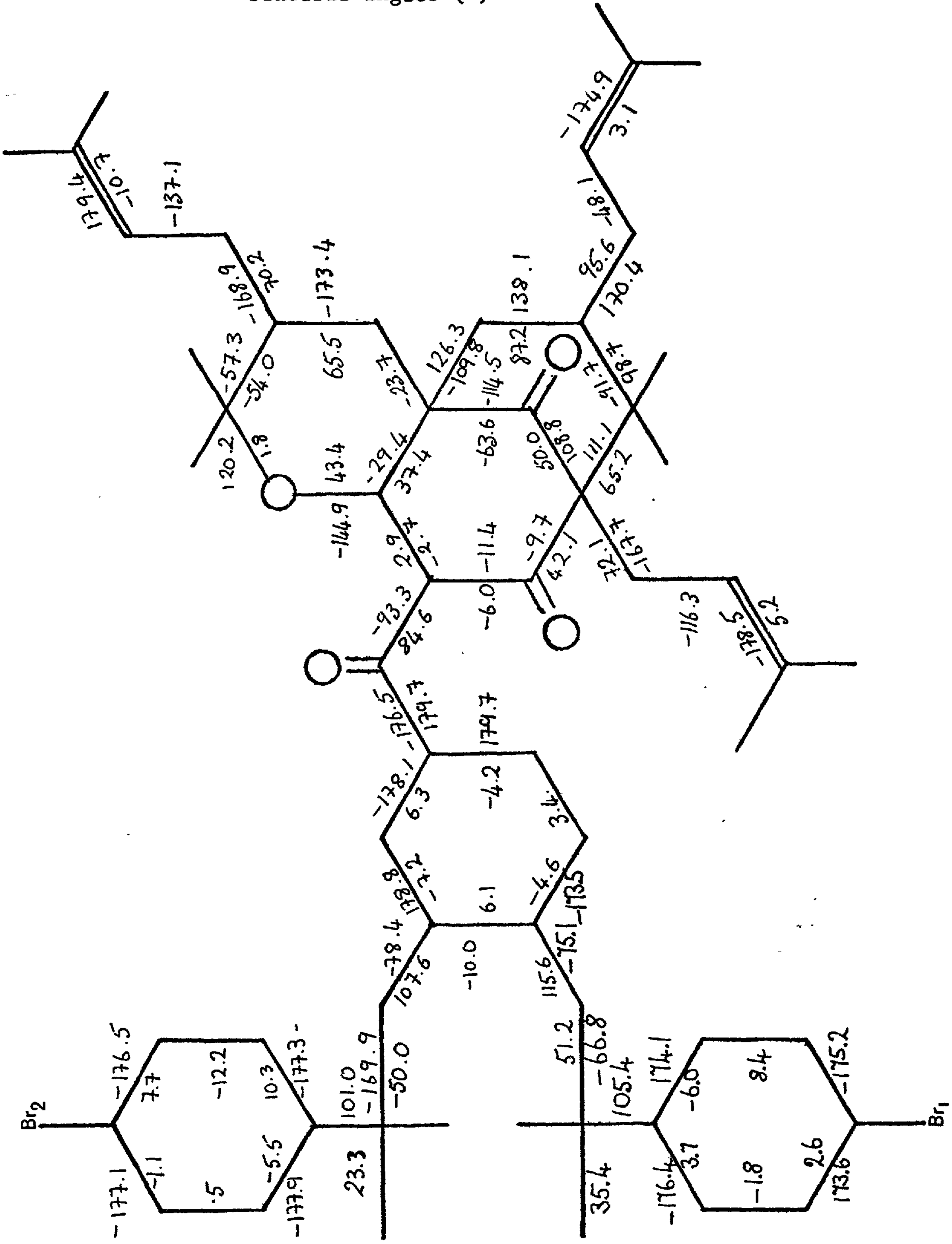


Figure 11

Isoxanthychymol Enantiomer

Dihedral angles (°)

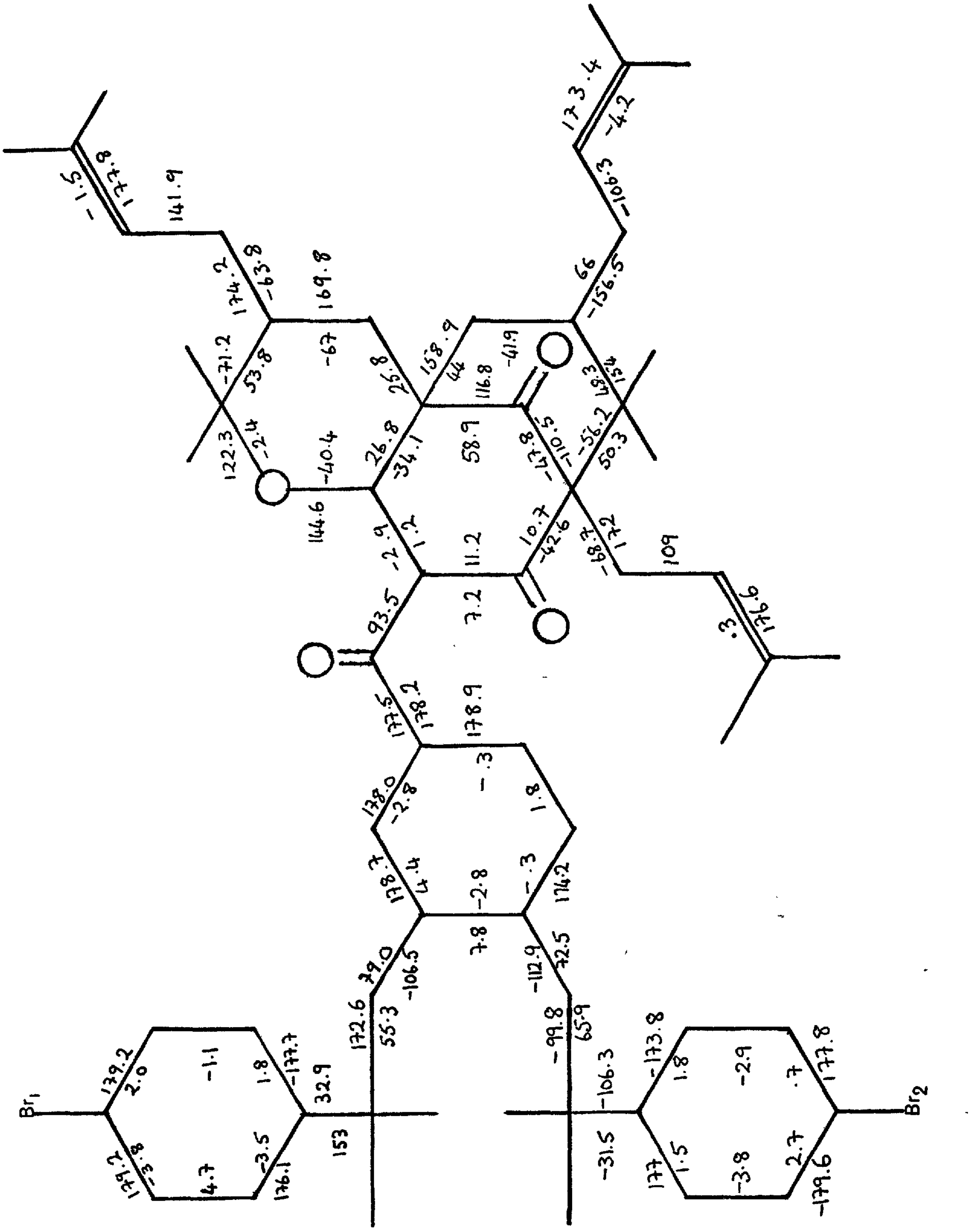


Table 3

Cambogin enantiomer.

Fractional co-ordinates of non-hydrogen atoms

Estimated standard deviations in parentheses.

ATOM	x	y	z
Br(1)	0.4063(3)	0.25	0.4252(3)
Br(2)	0.4483(3)	-0.0670(2)	0.6571(4)
S(1)	0.7302(5)	0.1170(3)	0.1203(5)
S(2)	0.9027(6)	0.0534(3)	0.6015(7)
C(11 1)	0.505(2)	0.221(2)	0.353(3)
C(21 1)	0.559(2)	0.244(1)	0.282(2)
C(31 1)	0.640(2)	0.218(1)	0.211(2)
C(41 1)	0.650(2)	0.152(1)	0.211(2)
C(51 1)	0.594(2)	0.117(1)	0.286(2)
C(61 1)	0.521(2)	0.148(2)	0.356(2)
O(1)	0.763(1)	0.1604(9)	0.034(1)
O(2)	0.681(1)	0.0604(7)	0.067(1)
O(3)	0.843(1)	0.0951(6)	0.240(1)
C(12 1)	0.908(2)	0.142(1)	0.307(2)
C(22 1)	0.976(2)	0.177(1)	0.254(2)
C(32 1)	1.054(2)	0.223(1)	0.331(2)
C(42 1)	1.060(2)	0.228(1)	0.479(2)
C(52 1)	0.990(2)	0.193(1)	0.532(2)
C(62 1)	0.916(2)	0.1466(9)	0.452(2)
C(13 1)	0.574(2)	-0.036(1)	0.642(2)
C(23 1)	0.636(3)	-0.052(1)	0.541(3)
C(33 1)	0.741(3)	-0.030(1)	0.528(3)
C(43 1)	0.782(2)	0.021(1)	0.612(2)
C(53 1)	0.737(2)	0.042(1)	0.709(2)
C(63 1)	0.635(3)	0.014(1)	0.723(2)
O(4)	0.964(2)	0.018(1)	0.532(3)
O(5)	0.966(2)	0.081(1)	0.728(2)
O(6)	0.847(1)	0.1113(6)	0.506(1)
O(7)	1.199(1)	0.3078(8)	0.505(1)
O(8)	1.030(2)	0.3643(7)	0.668(1)
O(9)	1.069(1)	0.2361(8)	1.029(1)
O(10)	1.279(1)	0.2011(7)	0.753(1)
C(1)	1.140(2)	0.275(1)	0.554(2)
C(2)	1.145(2)	0.280(1)	0.707(2)

C(3)	1.082(2)	0.3256(9)	0.750(2)
C(4)	1.070(2)	0.3259(8)	0.895(2)
C(5)	1.154(2)	0.380(1)	0.984(2)
C(6)	1.275(2)	0.369(1)	-0.016(2)
C(7)	1.318(2)	0.301(1)	1.017(2)
C(8)	1.226(2)	0.2498(9)	0.950(2)
C(9)	1.215(1)	0.2402(9)	0.798(2)
C(10)	1.119(2)	0.2663(9)	0.960(1)
C(11)	1.271(2)	0.184(1)	1.027(2)
C(12)	1.241(2)	0.129(1)	0.924(2)
C(13)	1.306(2)	0.1362(9)	0.813(2)
C(14)	1.260(3)	0.094(1)	0.691(2)
C(15)	1.429(2)	0.134(1)	0.852(3)
C(16)	1.273(2)	0.065(1)	1.003(2)
C(17)	1.191(3)	0.056(1)	1.087(3)
C(18)	1.217(3)	0.035(1)	1.224(3)
C(19)	1.349(3)	0.008(2)	1.275(3)
C(20)	1.129(3)	0.027(1)	1.304(3)
C(21)	1.316(2)	0.398(1)	0.871(3)
C(22)	1.439(2)	0.404(1)	0.913(2)
C(23)	1.518(2)	0.373(1)	0.884(3)
C(24)	1.501(3)	0.320(2)	0.784(3)
C(25)	1.640(2)	0.383(2)	0.947(4)
C(26)	1.146(2)	0.375(1)	1.138(2)
C(27)	1.108(3)	0.446(1)	01927(2)
C(28)	0.944(2)	0.337(2)	0.885(2)
C(29)	0.874(2)	0.280(1)	0.830(2)
C(30)	0.791(2)	0.279(1)	0.7L9(3)
C(31)	0.722(2)	0.221(1)	0.661(3)
C(32)	0.763(3)	0.331(2)	0.608(4)

Table 4

Cambogin enantiomer.

Anisotropic thermal parameters

	$\underline{U}_{11}x10^3$	$\underline{U}_{22}x10^3$	$\underline{U}_{33}x10^3$	$\underline{U}_{12}x10^3$	$U_{13}x10^3$	$U_{23}x10^3$
Br(1)	125(3)	256(5)	98(2)	44(3)	6(2)	-59(3)
Br(2)	136(3)	132(3)	127(3)	-40(2)	13(2)	23(2)
S(1)	97(4)	82(4)	61(3)	4(3)	3(3)	-13(3)
S(2)	107(5)	101(5)	107(5)	6(4)	15(4)	50(4)
	$\underline{U}_{11}x10^2$	$\underline{U}_{22}x10^2$	$\underline{U}_{33}x10^2$	$\underline{U}_{12}x10^2$	$\underline{U}_{13}x10^2$	$\underline{U}_{23}x10^2$
C(11 1)	6(2)	38(6)	14(3)	2(30	3(2)	6(3)
C(21 1)	9(2)	12(2)	10(2)	6(2)	-3(1)	-7(2)
C(31 1)	9(2)	9(2)	10(2)	-1(1)	-3(1)	-1(1)
C(41 1)	10(2)	8(1)	6(1)	0(1)	-1(1)	0(1)
C(51 1)	16(2)	9(2)	7(1)	-5(2)	3(2)	0(1)
C(61 1)	8(2)	31(4)	4(1)	-2(2)	0(1)	-1(2)
O(1)	15(1)	14(1)	5(1)	-2(1)	2(1)	3(1)
O(2)	14(1)	8(1)	8(1)	-1(1)	-1(1)	-3(1)
O(3)	8(1)	7(1)	9(1)	1(1)	-1(1)	-1(1)
C(12 1)	7(1)	9(2)	6(1)	-3(1)	1(1)	1(1)
C(22 1)	17(2)	11(2)	3(1)	-4(2)	0(1)	1(1)
C(32 1)	12(2)	12(2)	6(1)	-1(2)	4(1)	1(1)
C(42 1)	8(1)	9(1)	3(1)	-1(1)	2(1)	1(1)
C(52 1)	7(1)	9(1)	4(1)	1(1)	1(1)	1(1)
C(62 1)	7(1)	6(1)	7(1)	-1(1)	2(1)	-1(1)
C(13 1)	15(2)	6(1)	5(1)	0(1)	-2(1)	-1(1)
C(23 1)	22(4)	7(2)	7(2)	-1(2)	-6(2)	0(1)
C(33 1)	14(2)	10(2)	8(2)	-4(2)	4(2)	1(2)
C(43 1)	9(1)	9(2)	5(1)	-1(1)	2(1)	1(1)
C(53 1)	10(2)	6(1)	9(2)	-3(1)	1(1)	1(1)
C(63 1)	21(3)	6(2)	7(1)	4(2)	2(2)	2(1)
O(4)	20(2)	13(2)	25(3)	11(2)	14(2)	10(2)
O(5)	16(2)	22(2)	8(1)	-8(2)	-5(1)	5(1)
O(6)	10(1)	7(1)	7(1)	-1(1)	2(1)	2(1)
O(7)	14(1)	13(1)	5(1)	-5(1)	2(1)	2(1)
O(8)	18(2)	6(1)	7(1)	4(1)	2(1)	1(1)
O(9)	11(1)	12(1)	5(1)	-1(1)	0(1)	1(1)
O(10)	9(1)	10(1)	6(1)	0(1)	2(1)	0(1)

C(1)	7(1)	11(2)	5(1)	-1(1)	0(1)	1(1)
C(2)	6(1)	9(1)	5(1)	0(1)	1(1)	-1(1)
C(3)	9(1)	5(1)	7(1)	2(1)	1(1)	1(1)
C(4)	12(2)	4(1)	4(1)	-2(1)	2(1)	-1(1)
C(5)	11(2)	7(1)	7(1)	0(1)	3(1)	0(1)
C(6)	7(1)	9(1)	7(1)	0(1)	3(1)	-2(1)
C(7)	12(2)	9(2)	4(1)	-1(1)	-1(1)	-1(1)
C(8)	8(1)	7(1)	4(1)	-2(1)	1(1)	0(1)
C(9)	6(1)	8(1)	7(1)	0(1)	2(1)	0(1)
C(10)	8(1)	8(1)	4(1)	-3(1)	2(1)	-1(1)
C(11)	12(2)	7(1)	6(1)	2(1)	2(1)	1(1)
C(12)	13(2)	7(1)	6(1)	0(1)	0(1)	0(1)
C(13)	9(2)	5(1)	6(1)	1(1)	1(1)	-1(1)
C(14)	23(3)	9(1)	6(1)	1(2)	4(2)	-1(1)
C(15)	8(2)	11(2)	14(2)	0(2)	0(1)	2(2)
C(16)	14(2)	9(2)	9(2)	2(2)	1(2)	4(1)
C(17)	16(3)	9(2)	13(2)	0(2)	2(2)	8(2)
C(18)	16(3)	9(2)	13(2)	-3(2)	1(2)	-3(2)
C(19)	16(3)	21(4)	11(2)	-6(3)	-5(2)	6(2)
C(20)	17(3)	15(3)	9(2)	-2(2)	6(2)	-2(2)
C(21)	11(2)	10(2)	11(2)	-4(2)	3(1)	2(1)
C(22)	9(2)	8(2)	10(2)	-2(1)	5(1)	0(1)
C(23)	9(2)	12(2)	10(2)	-3(2)	4(1)	-3(2)
C(24)	22(3)	13(3)	12(2)	-2(2)	5(2)	-2(2)
C(25)	15(3)	16(3)	17(3)	-2(2)	1(2)	1(3)
C(26)	14(2)	13(2)	5(1)	-5(2)	4(1)	-4(1)
C(27)	21(3)	6(2)	8(2)	-2(2)	2(2)	0(1)
C(28)	7(1)	9(2)	9(1)	0(1)	1(1)	-1(1)
C(29)	7(1)	9(2)	11(2)	-2(1)	1(1)	-1(1)
c(30)	11(2)	9(2)	10(2)	1(1)	0(1)	-1(1)
C(31)	11(2)	10(2)	18(3)	-2(1)	-3(1)	-3(1)
C(32)	17(3)	11(2)	16(3)	-2(2)	-2(2)	5(2)

Table 5

Isoxanthochymol enantiomer.

Fractional co-ordinates of non-hydrogen atoms

Estimated standard deviations in parentheses.

ATOM	x	y	z
BR(1)	0.6618(2)	-0.1149	-0.0538(2)
BR(2)	0.4252(2)	0.2013(2)	-0.0968(2)
S(1)	0.6020(4)	0.0045(2)	0.4031(3)
S(2)	0.1238(3)	0.0689(2)	0.2318(3)
O(1)	0.727(1)	0.0300(8)	0.464(1)
O(2)	0.582(2)	-0.0330(6)	0.459(1)
O(3)	0.5074(8)	0.0634(4)	0.3463(7)
O(4)	0.2414(8)	0.0471(4)	0.3443(7)
O(5)	0.038(1)	0.1145(6)	0.2651(9)
O(6)	0.070(1)	0.0107(5)	0.1828(9)
O(7)	0.5078(8)	0.2597(5)	0.6968(8)
O(8)	0.7560(8)	0.1541(4)	0.7780(7)
O(9)	1.0371(8)	0.1906(5)	0.5649(7)
O(10)	0.664(1)	0.3167(5)	0.5237(9)
C(1)	0.643(1)	-0.0830(7)	0.081(1)
C(2)	0.546(2)	-0.1019(8)	0.133(2)
C(3)	0.535(1)	-0.0783(8)	0.233(1)
C(4)	0.619(1)	-0.0294(7)	0.283(1)
C(5)	0.720(1)	-0.0073(6)	0.232(1)
C(6)	0.730(1)	-0.0325(7)	0.136(1)
C(7)	0.456(1)	0.1001(6)	0.420(1)
C(8)	0.312(1)	0.0934(6)	0.412(1)
C(9)	0.256(1)	0.1300(7)	0.479(1)
C(10)	0.335(1)	0.1722(7)	0.553(1)
C(11)	0.479(1)	0.1794(6)	0.558(1)
C(12)	0.532(1)	0.1437(6)	0.4891(9)
C(13)	0.216(1)	0.1056(6)	0.150(1)
C(14)	0.284(2)	0.0713(7)	0.090(1)
C(15)	0.354(2)	0.101(1)	0.019(1)
C(16)	0.345(2)	0.165(1)	0.007(1)
C(17)	0.277(2)	0.1983(9)	0.064(1)
C(18)	0.212(1)	0.1708(8)	0.140(1)

C(19)	0.559(1)	0.2260(6)	0.6371(9)
C(20)	0.710(1)	0.2320(6)	0.6446(9)
C(21)	0.799(1)	0.1946(6)	0.7130(9)
C(22)	0.955(1)	0.2021(6)	0.724(1)
C(23)	0.967(1)	0.2208(6)	0.6138(9)
C(24)	0.897(1)	0.2804(6)	0.564(1)
C(25)	0.744(1)	0.2801(6)	0.0575(1)
C(26)	0.820(1)	0.0899(6)	0.805(1)
C(27)	0.930(1)	0.0838(7)	0.740(1)
C(28)	1.027(1)	0.1395(7)	0.769(1)
C(29)	1.018(1)	0.2561(8)	0.807(1)
C(30)	0.979(1)	0.3225(7)	0.766(1)
C(31)	0.978(1)	0.3334(7)	0.645(1)
C(32)	1.136(1)	0.330(1)	0.639(1)
C(33)	0.925(2)	0.3988(7)	0.601(1)
C(34)	0.703(2)	0.0459(8)	0.755(2)
C(35)	0.868(2)	0.0891(8)	0.930(1)
C(36)	0.859(2)	0.3505(8)	0.809(1)
C(37)	0.911(2)	0.3577(8)	0.935(1)
C(38)	0.885(2)	0.3254(8)	1.017(1)
C(39)	0.779(2)	0.271(1)	0.998(2)
C(40)	0.963(3)	0.337(1)	1.143(2)
C(41)	1.007(2)	0.0197(8)	0.766(2)
C(42)	1.108(2)	0.0103(8)	0.691(1)
C(43)	1.229(2)	-0.0154(9)	0.724(2)
C(44)	1.311(2)	-0.023(1)	0.640(2)
C(45)	1.288(3)	-0.037(2)	0.830(3)
C(46)	0.887(1)	0.2890(7)	0.440(1)
C(47)	0.829(1)	0.2361(7)	0.3678(9)
C(48)	0.711(1)	0.2306(7)	0.293(1)
C(49)	0.604(2)	0.280(1)	0.263(2)
C(50)	0.680(2)	0.1688(9)	0.223(1)

Table 6

Isoxanthochymol enantiomer.

Anisotropic temperature factors.

ATOM	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
BR(1)	7.1(1)	8.3(1)	7.0(1)	1.26(9)	1.60(8)	-2.48(9)
BR(2)	6.08(9)	17.0(2)	6.8(1)	-4.9(1)	0.77(7)	3.1(1)
S(1)	6.0(2)	6.7(2)	5.2(2)	3.3(2)	1.3(2)	-0.0(2)
S(2)	2.8(1)	5.0(2)	5.3(2)	-0.9(1)	0.3(1)	0.4(1)
O(1)	6.8(7)	13.8(11)	9.1(8)	5.5(8)	-2.5(6)	-6.3(8)
O(2)	15.9(12)	7.6(7)	9.2(8)	6.5(8)	8.5(8)	4.6(6)
O(3)	3.7(3)	4.2(4)	4.9(4)	1.0(3)	1.9(3)	-0.3(3)
O(4)	3.8(4)	4.2(4)	4.5(4)	-0.8(3)	1.0(3)	0.0(3)
O(5)	3.7(4)	7.7(6)	7.6(6)	1.6(4)	1.9(4)	-0.6(5)
O(6)	5.4(5)	5.1(5)	6.8(5)	-2.5(4)	-0.4(4)	-0.3(4)
O(7)	2.6(3)	6.8(5)	6.8(5)	0.0(4)	2.1(3)	-2.1(4)
O(8)	3.2(3)	5.2(4)	5.1(4)	0.3(3)	1.6(3)	0.7(4)
O(9)	3.2(3)	6.7(5)	5.4(4)	1.4(4)	1.1(3)	-0.9(4)
O(10)	3.3(4)	5.0(5)	8.5(6)	1.0(4)	2.5(4)	1.9(5)
C(1)	3.4(6)	5.6(7)	7.9(9)	0.7(6)	0.5(6)	1.1(7)
C(2)	4.8(7)	5.7(8)	9.3(10)	-1.1(6)	2.2(7)	-2.0(8)
C(3)	4.5(7)	6.2(8)	7.8(9)	-0.2(6)	2.8(6)	-0.6(8)
C(4)	3.5(6)	5.0(7)	5.9(7)	2.1(5)	0.7(5)	-0.0(6)
C(5)	3.8(6)	4.3(6)	6.1(7)	-0.4(5)	1.9(5)	-1.1(5)
C(6)	3.3(6)	6.1(8)	5.8(8)	-0.2(6)	0.7(5)	0.6(6)
C(7)	2.0(4)	4.7(6)	4.4(5)	0.3(4)	0.6(4)	-0.5(5)
C(8)	2.9(5)	4.7(6)	3.9(5)	-0.8(5)	0.7(4)	-0.4(5)
C(9)	1.3(4)	5.7(7)	7.4(7)	-0.1(5)	1.6(5)	-1.2(6)
C(10)	1.8(5)	5.7(7)	6.7(7)	0.0(5)	1.5(5)	-0.5(6)
C(11)	2.1(4)	4.2(6)	4.7(6)	-0.3(4)	0.8(4)	-0.2(5)
C(12)	1.6(4)	4.1(6)	4.4(5)	-0.2(4)	1.2(4)	-0.1(5)
C(13)	2.9(5)	4.5(6)	4.5(6)	-0.9(5)	0.7(4)	-0.3(5)
C(14)	6.1(8)	4.6(7)	7.9(9)	-0.2(6)	2.9(7)	0.0(7)
C(15)	5.8(9)	10.5(14)	5.7(8)	0.2(9)	1.9(7)	-0.7(9)
C(16)	4.4(7)	9.8(13)	4.5(7)	-2.3(8)	-0.6(6)	2.0(8)
C(17)	6.7(9)	6.2(9)	6.4(8)	-2.3(8)	-0.7(7)	1.5(8)
C(18)	5.4(7)	6.2(9)	4.3(6)	-2½6(6)	-1.0(5)	0.7(6)

C(19)	1.9(4)	4.9(6)	3.8(5)	0.0(4)	0.8(4)	0.6(5)
C(20)	1.5(4)	4.2(5)	4.2(5)	0.0(4)	0.5(4)	-0.2(5)
C(21)	2.2(4)	5.1(6)	4.1(5)	-0.5(5)	0.7(4)	-0.8(5)
C(22)	1.4(4)	4.5(6)	5.9(6)	-0.1(4)	0.2(4)	-1.0(5)
C(23)	2.0(4)	4.5(6)	3.7(5)	-0.8(4)	0.5(4)	-0.9(5)
C(24)	2.5(5)	3.8(6)	5.3(6)	-0.7(4)	1.7(4)	-0.4(5)
C(25)	2.1(5)	4.9(6)	3.9(5)	-0.2(5)	0.9(4)	-0.4(5)
C(26)	4.0(6)	3.8(6)	4.6(6)	-0.2(5)	0.3(5)	0.6(5)
C(27)	4.1(6)	4.5(7)	8.2(9)	0.8(5)	2.4(6)	0.4(6)
C(28)	3.8(6)	5.6(7)	5.6(7)	1.2(6)	0.7(5)	0.4(6)
C(29)	2.0(5)	6.8(9)	6.1(7)	-0.7(5)	0.4(5)	-1.7(6)
C(30)	3.9(6)	4.8(6)	6.0(7)	-0.4(5)	1.9(5)	-1.2(6)
C(31)	3.6(5)	4.9(6)	4.2(6)	-1.1(5)	1.7(4)	-0.4(5)
C(32)	3.1(6)	11.8(12)	6.7(8)	-4.5(7)	2.7(6)	-2.9(8)
C(33)	7.0(9)	3.9(7)	7.3(8)	-0.5(6)	1.6(7)	0.1(6)
C(34)	6.4(9)	5.8(8)	9.6(11)	-1.3(7)	3.2(8)	0.3(8)
C(35)	7.7(10)	6.7(9)	6.9(9)	2.5(8)	2.7(8)	2.4(7)
C(36)	6.2(8)	5.7(7)	6.3(8)	-0.3(6)	3.3(7)	-2.0(6)
C(37)	5.9(8)	6.5(8)	5.0(7)	-1.2(7)	2.1(6)	-1.3(6)
C(38)	7.1(9)	6.2(8)	6.9(9)	-0.9(7)	3.2(7)	-1.8(7)
C(39)	8.4(11)	9.0(12)	10.1(12)	-4.4(10)	5.2(10)	-1.7(10)
C(40)	14.6(19)	9.3(13)	6.4(10)	-1.5(13)	3.3(11)	-2.0(9)
C(41)	7.0(9)	5.0(8)	9.2(11)	2.8(7)	2.2(8)	1.7(8)
C(42)	8.8(11)	6.1(9)	5.6(7)	3.2(8)	1.4(7)	-0.3(7)
C(43)	5.7(9)	5.8(9)	9.3(11)	-0.5(7)	1.8(9)	-0.9(8)
C(44)	9.2(12)	8.9(12)	11.2(13)	-1.9(11)	6.1(11)	-1.8(11)
C(45)	7.1(12)	15.0(23)	14.7(22)	3.8(14)	3.8(14)	-4.3(19)
C(46)	4.5(6)	5.2(7)	5.0(6)	-1.0(5)	2.5(5)	-0.3(5)
C(47)	4.1(6)	5.6(7)	3.0(5)	0.1(5)	0.3(4)	0.1(5)
C(48)	5.4(7)	5.4(7)	5.1(7)	-1.0(6)	1.7(6)	0.9(6)
C(49)	6.6(10)	8.8(12)	9.8(12)	3.1(9)	0.1(9)	-0.5(10)
C(50)	9.9(12)	7.9(11)	4.7(7)	-4.1(10)	0.8(7)	-1.6(7)

Table 7

Fractional co-ordinates of hydrogen atoms ($x10^3$) obtained from the latest difference-Fourier.

ATOM		x	y	z
H21	1	546	292	268
H31	1	685	247	165
H51	1	603	70	292
H61	1	478	122	408
H22	1	972	170	153
H32	1	1102	251	287
H52	1	989	200	632
H23	1	596	-83	468
H33	1	783	-51	465
H53	1	774	78	773
H63	1	603	32	798
H61		1360	357	5
H71		1367	286	1120
H17		1133	98	1030
H112		1250	179	1120
H141		1267	48	715
H143		1293	110	620
H162		1350	71	1050
H203		1147	12	1405
H251		1653	417	900
H262		1150	333	1175
H271		1100	452	825
H282		933	381	850

Table 8

Cambogin molecule

Mean planes through various groups of atoms of the cambogin structure.

The displacements (Å) of atoms from their planes.

Atoms which do not define the plane are grouped below the atoms defining the plane.

A		B	
C(13 1)	-0.009	C(11 1)	0.012
C(23 1)	0.046	C(21 1)	-0.030
C(33 1)	-0.056	C(31 1)	0.032
C(43 1)	0.034	C(41 1)	-0.020
C(53 1)	0.001	C(51 1)	0.002
C(63 1)	-0.156	C(61 1)	0.005
Br(2)	0.042	Br(1)	-0.163
S(1)	-0.000	S(1)	-0.108
O(6)	1.575	O(3)	1.408

C		D	
C(12 1)	0.020	C(22 1)	0.010
C(22 1)	-0.010	C(32 1)	-0.010
C(32 1)	0.008	C(52 1)	0.010
C(42 1)	-0.019	C(62 1)	-0.010
C(52 1)	0.029		
C(62 1)	-0.028	C(12 1)	0.057
		C(42 1)	-0.055
O(3)	-0.124	O(3)	-0.052
O(6)	-0.004	O(6)	0.031
C(1)	-0.005	C(1)	-0.080
O(7)	0.012	O(7)	-0.079
C(2)	-0.025	C(2)	-0.119

Table 8 (continued)

E

C(2)	-0.054
C(10)	0.013
O(9)	0.025
C(6)	0.016
C(13)	1.172
C(4)	1.288
C(5)	1.339
C(9)	-1.227
C(8)	-1.167
C(7)	-1.239

F

C(2)	-0.019
C(3)	0.096
C(4)	-0.084
C(8)	0.075
C(9)	-0.067
C(10)	-0.601
O(9)	-1.525
C(7)	1.600
C(16)	2.867
C(5)	1.397

G

C(2)	-0.104
C(3)	0.092
C(4)	0.113
C(10)	-0.331
C(8)	0.287
C(9)	-0.054
O(9)	-1.139
C(7)	1.860
C(6)	1.741
C(5)	1.675

H

C(9)	-0.081
C(8)	0.079
C(3)	0.082
C(4)	-0.080
C(2)	-0.041
C(10)	-0.591
C(7)	1.610
C(5)	1.409

I

C(8)	0.063
C(7)	-0.060
C(4)	-0.061
C(5)	0.058
C(10)	0.631
C(9)	-1.303
C(2)	-2.019
C(3)	-1.522

J

O(10)	0.056
C(13)	-0.055
C(8)	-0.052
C(11)	0.051
C(9)	-0.346
C(12)	-0.731
C(16)	-0.762
C(14)	-0.935
C(15)	1.318

Table 8 (continued)

(i) Equations of the planes may be expressed in direct space as $\underline{P}x + \underline{Q}y + \underline{R}z = \underline{S}$

Plane	$\underline{P}$	$\underline{Q}$	$\underline{R}$	$\underline{S}$
A	-4.47	14.02	-5.43	-6.56
B	6.99	1.85	6.44	6.2
C	-8.33	15.00	-0.31	-5.55
D	-8.49	14.63	-0.42	-5.81
E	-8.83	14.33	0.09	-5.98
F	8.61	15.02	-0.61	13.65
G	8.18	14.94	0.75	14.18
H	8.57	15.03	-0.48	13.72
I	-5.28	-5.43	9.64	1.27
J	10.99	6.87	0.74	15.94

(ii) Selected angles between planes (^{o})

Plane C	Plane D	1.49	Plane D	Plane G	88.12
C	F	89.98	D	H	88.65
C	G	89.51	H	I	69.60
C	H	89.97	H	J	27.00
D	F	88.68	I	J	79.8

Table 9

Isoxanthochymol molecule

Mean planes through various groups of atoms of the isoxanthochymol structure.

The displacements (Å) of atoms from their planes.

Atoms which do not define the plane are grouped below the atoms defining the plane.

A	
C(1)	-0.010
C(6)	0.001
C(5)	-0.001
C(4)	0.008
C(3)	-0.018
C(2)	0.019
Br(1)	0.017
S(1)	0.064
O(3)	1.662

B	
C(16)	-0.006
C(17)	-0.014
C(18)	0.018
C(13)	-0.003
C(14)	-0.017
C(15)	0.022
Br(2)	-0.109
S(2)	-0.128
O(4)	1.372

C	
C(8)	0.005
C(9)	0.011
C(10)	-0.012
C(11)	-0.004
C(12)	0.020
C(7)	-0.020
C(4)	-0.866
O(3)	0.030
C(19)	-0.004
O(7)	0.018
C(20)	-0.038

D	
C(9)	0.016
C(10)	-0.016
C(12)	0.016
C(7)	-0.016
C(8)	0.014
C(11)	-0.012
O(4)	-0.072
O(3)	0.039
C(19)	-0.022
O(7)	-0.003
C(20)	-0.061

Table 9 (continued)

E	
C(20)	-0.000
C(23)	0.001
O(9)	-0.001
C(30)	0.000
C(25)	1.261
C(24)	1.290
C(31)	1.238
C(21)	-1.166
C(22)	-1.239
C(29)	-1.287

F	
C(20)	-0.026
C(25)	0.092
C(24)	-0.057
C(22)	0.068
C(21)	-0.057
C(23)	-0.593
O(9)	-1.503
C(29)	1.560
C(30)	2.237
C(31)	1.372

G	
C(20)	-0.108
C(25)	0.084
C(24)	0.122
C(23)	-0.321
C(22)	0.275
C(21)	-0.051
O(9)	-1.116
C(29)	1.811
C(30)	2.452
C(31)	1.640

H	
C(21)	-0.076
C(22)	0.073
C(25)	0.074
C(24)	-0.072
C(20)	-0.054
C(23)	-0.580
C(29)	1.571
C(31)	1.387

I	
C(22)	0.048
C(29)	-0.048
C(24)	-0.047
C(31)	0.047
C(23)	0.659
C(21)	-1.370
C(20)	-2.053
C(25)	-1.589

J	
O(8)	0.054
C(26)	-0.054
C(22)	-0.053
C(28)	0.053
C(21)	-0.341
C(27)	-0.728
C(41)	-0.837
C(35)	1.345
C(34)	-0.998

Table 9 (continued)

(i) Equations of the planes may be expressed in direct space as $\underline{P}x + \underline{Q}y + \underline{R}z = \underline{S}$

Plane	P	Q	R	S
A	-5.41	14.27	-4.33	-5.00
B	6.63	1.77	6.74	2.63
C	-0.40	14.88	-8.36	-2.19
D	-0.43	14.79	-8.40	-2.23
E	-0.48	13.53	-9.01	-3.01
F	-0.53	15.15	8.51	8.65
G	0.80	15.11	8.07	9.38
H	-0.37	15.17	8.46	8.76
I	9.70	-4.91	-5.33	4.37
J	0.74	7.04	10.96	10.11

(ii) Selected angles between planes (^{o})

Plane	Plane	Angle	Plane	Plane	Angle
C	D	0.36	D	G	89.35
C	F	89.97	D	H	89.71
C	G	89.69	H	I	71.17
C	H	89.96	H	J	26.88
D	F	89.71	I	J	80.10

APPENDIX I

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant h and ℓ and list values of k, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

```
     1,K,-10

1     50     56
2     59     56
3     61     64
4     54     71
5     39*    25
6     41     43
7     39*    17

     2,K,-10

0    152    141
1     83     76
2    104     71
3     57     57
4     40*    29
5    139    124
6     62     58
7     39*    28
8     48     35

     3,K,-10

0     44     73
1     78     61
2     40*    36
3     40*    38
4     40*     8
5     39*    36
6     55     79
7     79     55
8    101    110

     4,K,-10

0     60     67
1     56     38
2     70     59
3     60     57
4     40*    40
5     40*    15
6     39*    24
7     60     64
8     46     29

     5,K,-10

0     40*    39
1     40*    16
2     43     68
3     41*    90
4     39*    48
5     39*    63
6     39*    27
7     38*    23

     6,K,-10

0     40*     3
```

```
 1     40*    59
 2     40*    41
 3     39*    34
 4     40*    35
 5     39*    20
 6     39*    65
 5     39*    20
 6     89     65

      7,K,-10

 0     39*     8
 1     39*    14
 2     48     33
 3     39*     5
 4     68     58
 5     46*    28

      8,K,-10

 0     37*    21
 1     38*    25

      1,K,-9

 0    145    116
 1     58     58
 2     40*    25
 3    110    127
 4     44     59
 5     41*    53
 6    121    111
 7    110    104
 8     51     52
 9     74     78
10     39*    42
11     40*    22

      2,K,-9

 0    103    119
 1     74     72
 2    175    175
 3     84     97
 4    103    109
 5    123    127
 6     54     45
 7     60     43
 8     42*    31
 9     40*    20
10     73     60
11     79     76
12     52     65

      3,K,-9

 0     41*    70
 1    119    110
 2     66     79
 3     41*    24
```

```
 4     93     69
 5     42*    19
 6     66     62
 7    140    119
 8     85     83
 9     41*    45
10     94     66
11     51     51
12     99     78

      4,K,-9

 0    170    149
 1    164    155
 2     53     36
 3    125    137
 4     43*    58
 5     70     46
 6    100     89
 7    178    161
 8     43*    28
 9    156    139
10     41*    23
11     57     28
12     40*    33

      5,K,-9

 0     66     81
 1     97     74
 2     70     29
 3    121     95
 4    109    116
 5     45     40
 6    156    153
 7     74     69
 8     94    100
 9     54     30
10     42*    54
11     41*    27

      6,K,-9

 0     42*    33
 1     41*    29
 2     42*    14
 3    168    128
 4     43*    30
 5    102     79
 6    105     95
 7     43*    28
 8     41*    28
 9    123     88
10     41*    15
11     56     43

      7,K,-9

 0    102    101
 1     43*    54
```

```
 2     46     24
 3     88     93
 4     88     85
 5     42*    31
 6     75     58
 7     70     56
 8     62     63
 9     45     46
10     40*    26

      8,K,-9

 0     57     42
 1     97     86
 2     41*    28
 3     84     53
 4     42*    31
 5     90     68
 6     44*    45
 7     75     59
 8     41*    14

      9,K,-9

 0     43*    67
 1     42*    26
 2     71     40
 3     41*    28
 4     42*    17
 5     42*    34
 6     41*    26

      1,K,-8

 0    217    208
 1     51     53
 2     67     68
 3    223    232
 4    126    112
 5     43*    14
 6     70     58
 7    101    110
 8     68     72
 9    263    253
10     56     86
11     43*    28
12     82     82
13     79     86
14     43*    38

      2,K,-8

 0    185    165
 1     43*    48
 2     97     94
 3    133    160
 4     83     73
 5     97     89
 6    111    100
 7     76     70
```

```
 8    110    105
 9     49     67
10     53     80
11    134    141
12    102    100
13     76     62
14     42*    37
15     51     56

      3,K,-8

 0    156    132
 1    154    153
 2     78     83
 3    189    161
 4    115     96
 5    224    224
 6     78     83
 7     75     53
 8    130    127
 9    165    160
10    133    118
11    148    148
12     87     79
13     52     51
14     43*    25
15     41*     9

      4,K,-8

 0    118    144
 1     43*    58
 2    186    180
 3    109     75
 4     70     54
 5    128    144
 6    133     82
 7    137    115
 8     85     72
 9     74     86
10     45*    64
11     81     97
12     95     77
13     89     71
14     59     40

      5,K,-8

 0     43*    57
 1    165    145
 2    151    144
 3     43*    41
 4     68     62
 5     43*    40
 6    139    144
 7    156    157
 8    188    186
 9    159    120
10     44*     5
```

```
      5,K,-8

11      44*      35
12      75       66
13      63       52
14      61       44

      6,K,-8

 0      43*      11
 1      44*      38
 2     138      113
 3      44*      23
 4      44*      44
 5     164      161
 6      59       32
 7     173      172
 8     214      182
 9      67       58
10      82       64
11      44*       5
12      76       49
13      68       57

      7,K,-8

 C      44*      10
 1     106       74
 2      57       42
 3      45*      46
 4     218      195
 5     145      117
 6      57       54
 7      60       49
 8      62       49
 9      87       53
10      49       35
11      57       34
12      43*      24
13      41*      37

      8,K,-8

 0      88       92
 1      60       50
 2      52       40
 3     125      103
 4      44*      51
 5      49       48
 6      44*      32
 7      64       47
 8      54       49
 9      76       74
10      71       66
11      42*       4

      9,K,-8

 0     131      135
 1      53       54

 2      43*      62
 3      61       36
 4      44*      13
 5     107       78
 6      45*      20
 7      43*      11
 8      42*      32
 9      42*      23
10      42*      29

      10,K,-8

 0      55       41
 1      90       75
 2      99       76
 3      82       62
 4      43*      29
 5      60       54
 6      42*      18
 7      42*       4

      11,K,-8

 0      42*      37
 1      41*      12
 2      83       47

      1,K,-7

 0      48       29
 1     209      226
 2     134      145
 3      82       65
 4     262      256
 5     217      220
 6     107       99
 7      50       71
 8     215      224
 9     147      147
10     165      166
11     262      256
12     128      118
13      46*      32
14      69       65
15      64       80
16      69       65
17      63       50

      2,K,-7

 0     136      125
 1     340      322
 2     145      157
 3      40*      17
 4     198      203
 5     257      257
 6      58       49
 7     151      153
 8     101       97
 9     202      207

10      78       81
11     344      328
12      86       67
13     121       94
14      77       75
15      92       88
16      43*      29
17      42*      28

      3,K,-7

 0      51       84
 1     153      131
 2      48       67
 3      86       67
 4      56       73
 5      66       63
 6      63       76
 7     207      187
 8     122      126
 9     141      120
10     238      246
11      58       46
12     201      187
13     114       91
14     174      169
15      78       69
16      59       36
17      68       55

      4,K,-7

 0      39       38
 1     182      169
 2      49       49
 3      89       96
 4     109       71
 5     115      109
 6      55       44
 7     181      166
 8     222      197
 9      43*      19
10      90       98
11     138      147
12      62       56
13     108       98
14      49       55
16      43*      23

      5,K,-7

 0      46       19
 1      74       70
 2     283      257
 3      80       45
 4     198      194
 5     109      112
 6      92       91
 7     184      190
 8     142      113

 9     123      153
10      49       41
11     167      178
12     100       88
13      43*      21
14     106       82
15      44       27
16      43*      53

      6,K,-7

 0     136      131
 1      87       92
 2     267      238
 3     118      146
 4     173      130
 5      92       89
 6      42*      53
 7     174      163
 8     126      119
 9      52       54
10      48       78
11      85       92
12      46       39
13      54       64
14     130       95
15      53       57

      7,K,-7

 0     209      221
 1     196      185
 2     237      216
 3     176      161
 4     199      176
 5     126      136
 6     104       95
 7     103      127
 8     151      128
 9      66       49
10      76       91
11      80       73
12      52       50
13      78       69
14      55       26
15      41*      13

      8,K,-7

 0     278      235
 1     257      237
 2     154      151
 3     131      145
 4      85       58
 5     103       95
 6      56       48
 7     119      110
 8      72       45
 9      62       71
10      79       77

11      49       20
12      44*      23
13      42*      11

      9,K,-7

 0      68       75
 1      71       64
 2     118      14
 3     123      124
 4      44*      19
 5      47       29
 6      77       91
 7      68       38
 8      48       31
 9      44*      34
10      44*      14
11      43*      10
12      44       49

      10,K,-7

 0      43*      27
 1      55       26
 2      43*      60
 3      44*      32
 4      45*      74
 5      44       25
 6      44*      31
 7      77       38
 8      56       25
 9      43*      22
10      43*      15

      11,K,-7

 0      50       40
 1      49       37
 2      94       62
 3      57       18
 4      44*      26
 5      45*      49
 6      87       45
 7      56       34

      1,K,-6

 0      54       53
 1      87       75
 2     332      343
 3     427      419
 4     275      273
 5     135      110
 6      56       64
 7     150      134
 8     378      361
 9     220      228
10     184      201
11      56       45
```

1,K,-6

12	74	65
13	147	167
14	130	97
15	57	52
16	44*	31
17	52	61
18	96	82

2,K,-6

0	163	133
1	150	152
2	182	183
3	243	259
4	345	354
5	342	337
6	118	111
7	78	82
8	144	125
9	170	179
10	230	247
11	181	167
12	44*	32
13	48	68
14	257	226
15	108	109
16	45*	32
17	100	69
18	43*	13

3,K,-6

0	182	168
1	305	291
2	85	79
3	209	221
4	137	153
5	204	201
6	77	82
7	139	137
8	91	62
9	41*	48
10	276	286
11	195	189
12	195	196
13	116	123
14	46*	51
15	87	68
16	61	31
17	116	101
18	43*	41

4,K,-6

0	349	372
1	197	209
2	165	154
3	105	85
4	77	66
5	280	262
6	276	273
7	216	231
8	41*	19
9	161	162
10	126	115
11	71	45
12	125	126
13	134	123
14	46*	11
15	46*	53
16	111	105
17	76	83
18	43*	26

5,K,-6

0	37*	82
1	60	56
2	257	232
3	249	255
4	229	247
5	40*	65
6	187	202
7	297	291
8	175	170
9	43*	77
10	137	116
11	46*	24
12	136	139
13	93	106
14	46*	48
15	56	72
16	46	62
17	115	104
18	55	41

6,K,-6

0	83	68
1	253	275
2	170	177
3	39*	24
4	118	130
5	102	124
6	46	65
7	178	175
8	124	127
9	200	227
10	63	44
11	79	84
12	45*	25
13	46*	38
14	109	115
15	122	103
16	45*	50
17	80	65

7,K,-6

0	41*	39
1	164	158
2	196	207
3	181	162
4	59	56
5	121	154
6	56	81
7	169	158
8	47	44
9	119	129
10	79	60
11	46*	31
12	46*	42
13	96	95
14	79	81
15	53	32
16	44*	12

8,K,-6

0	77	40
1	153	143
2	113	85
3	204	203
4	95	62
5	108	104
6	66	96
7	44*	20
8	78	67
9	102	72
10	92	97
11	45*	21
12	67	95
13	45*	12
14	111	87
15	44*	8

9,K,-6

0	64	103
1	44*	39
2	97	83
3	117	132
4	64	74
5	62	66
6	140	139
7	59	34
8	45*	68
9	61	79
10	45*	15
11	106	99
12	111	70
13	54	53
14	42*	26

10,K,-6

0	136	126
1	96	75
2	59	68
3	45*	5
4	66	62
5	45*	23
6	128	80
7	46*	57
8	45*	30
9	45*	11
10	107	88
11	83	49
12	44*	39

11,K,-6

0	46*	34
1	45*	12
2	58	55
3	97	80
4	46*	15
5	96	90
6	46*	10
7	77	54
8	44*	21
9	44*	25

12,K,-6

0	44*	5
1	79	16
2	65	49
3	53	19
4	65	52
5	45	48

1,K,-5

0	310	314
1	378	420
2	603	628
3	400	433
4	171	173
5	197	219
6	202	189
7	460	455
8	38*	22
9	297	290
10	196	186
11	103	139
12	129	118
13	124	106
14	65	77
15	209	192
16	160	154
17	47*	53
18	69	72
19	44*	36
20	48	37

2,K,-5

0	732	773
1	415	453
2	402	411
3	531	541
4	306	312
5	340	310
6	66	68
7	264	283
8	38	48
9	315	319
10	133	158
11	40*	14
12	207	212
13	109	103
14	233	227
15	201	195
16	141	146
17	95	90
18	46*	24
19	44*	46
20	73	68

3,K,-5

0	327	325
1	320	309
2	295	292
3	211	233
4	373	402
5	236	216
6	249	226
7	111	97
8	37*	42
9	113	106
10	260	241
11	214	208
12	46	34
13	215	199
14	206	191
15	77	82
16	84	77
17	96	80
18	55	59
19	56	69

4,K,-5

0	269	311
1	341	340
2	133	109
3	171	162
4	213	207
5	87	94
6	262	271
7	49	76
8	192	202
9	243	260
10	238	219
11	187	193

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      4,K,-5

12      44*     33
13      45*     44
14     162     146
15      47*     60
16      65      86
17      99     102
18     110      71
19      47      42

      5,K,-5

 0     275     334
 1      70      66
 2      70      83
 3      91      94
 4     151     138
 5     120      97
 6     345     369
 7     118     117
 8     199     194
 9      70      81
10     124     126
11      64      78
12     194     207
13     113     105
14      46*     49
15      46*     53
16      46*     24
17      46*     41
18      69      71
19      72      61

      6,K,-5

 0      44      22
 1      87      70
 2     102      98
 3     324     320
 4      64      39
 5     191     206
 6      62      87
 7     111     109
 8     190     197
 9     171     163
10     107      71
11     102      91
12      72     112
13     153     136
14      55      64
15     109      86
16     106     101
17      46*     25
18      44*      5

      7,K,-5

 0      43      60
 1      75      41
```

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 2     251     253
 3     257     246
 4      41*     60
 5     100     111
 6      99      80
 7     208     192
 8     139     133
 9      83      51
10      83      72
11      49      53
12      64      50
13     170     149
14     137     115
15      47*     18
16      92      73
17      45*     35

      8,K,-5

 0     147     113
 1     307     323
 2     100     120
 3      55      68
 4      93      85
 5      75      73
 6      43*      4
 7     122     102
 8      45*     61
 9     133     133
10     110     106
11      92      86
12     104     124
13      54      60
14      47*     35
15     140     115
16      64      38

      9,K,-5

 0      43*     30
 1      74      78
 2     173     157
 3     101      93
 4     113     102
 5     134     125
 6     100      84
 7      49      63
 8      61      56
 9      95      85
10     105     104
11      65      55
12      45*     15
13      46*     46
14      54      50
15      83      59

      10,K,-5

 0     101     100
 1      65      52
```

```
 2      45*     24
 3     108     131
 4      51      52
 5      65      59
 6      47*     44
 7      82      91
 8      47*     35
 9      66      38
10      52      40
11      47*     25
12      46*     27
13      45*     45

      11,K,-5

 0      46*     16
 1      95      79
 2      47*     25
 3      46*     21
 4      57      46
 5      47*     40
 6     115      84
 7      47*     26
 8      49      28
 9      46*     30
10      46*     29
11      45*     12

      12,K,-5

 0      47*     16
 1      46*     23
 2      78      28
 3      46*      9
 4      46*     29
 5      57      33
 6      45*     18
 7      50      38

      1,K,-4

 0     115     170
 1     473     450
 2     206     173
 3     461     512
 4     396     418
 5     174     162
 6     139     154
 7     434     406
 8     107     126
 9     377     366
10     271     269
11      40*     57
12     110     100
13     274     261
14      85      77
15     101     114
16      93      98
17     110     102
18      48*     51
```

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19     109      90
20      51      55

      2,K,-4

 0     372     365
 1     147     188
 2     429     401
 3     708     727
 4     350     314
 5     102     121
 6     427     415
 7     114     151
 8     349     385
 9     530     529
10     245     241
11     178     164
12     207     196
13     186     163
14     168     157
15     224     198
16      89      56
17      68      65
18     138     126
19      48*     14
20      47*     10

      3,K,-4

 0     299     344
 1     373     405
 2     478     501
 3      73     122
 4     297     336
 5     393     411
 6     564     580
 7     180     158
 8     148     144
 9      79      74
10     172     190
11     448     489
12     150     143
13     188     154
14     182     179
15     166     156
16      76      51
17      96      72
18      97      94
19      65      71
20      68      52

      4,K,-4

 0     384     403
 1     441     459
 2     280     334
 3     215     219
 4     494     538
 5     479     515
 6     185     192
```

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 7     351     356
 8     244     270
 9     231     208
10     266     281
11     192     183
12     128     137
13     142     127
14      53      66
15     114     108
16      80      80
17     168     158
18      49*     65
19      66      54
20      68      68

      5,K,-4

 0     264     280
 1     517     548
 2     195     231
 3     127     132
 4     204     233
 5     205     244
 6     125     120
 7     240     270
 8      65      45
 9     163     178
10     132     106
11     133     134
12     161     140
13      95     108
14     101      92
15      49*     67
16      73      78
17      48*     79
18      87      74
19      47*     26

      6,K,-4

 0     322     367
 1     361     395
 2     149     160
 3      72      60
 4     100     124
 5     190     175
 6     369     402
 7      67      89
 8     162     184
 9      42*     72
10      43*     48
11      80      54
12     102      92
13     100     121
14      57      53
15      77      65
16      53      42
17      78      73
18     130     100
```

6,K,-4

19	47*	61

7,K,-4

0	134	143
1	155	168
2	265	288
3	213	237
4	164	185
5	74	71
6	148	147
7	79	107
8	85	112
9	57	52
10	116	152
11	104	112
12	65	42
13	70	63
14	113	97
15	59	86
16	48*	27
17	47*	14
18	45*	18

8,K,-4

0	41*	3
1	88	84
2	277	266
3	142	160
4	146	125
5	73	51
6	43*	20
7	44*	51
8	279	266
9	129	139
10	54	27
11	46*	23
12	47*	61
13	128	116
14	67	64
15	48*	32
16	47*	33
17	46*	24

9,K,-4

0	94	79
1	99	86
2	140	127
3	46	40
4	98	120
5	119	104
6	46*	38
7	144	163
8	97	80
9	66	60
10	61	54
11	49*	43
12	48*	22
13	61	55
14	94	67
15	97	91

10,K,-4

0	117	110
1	110	114
2	72	73
3	105	121
4	78	108
5	161	142
6	108	85
7	98	79
8	78	60
9	69	40
10	91	87
11	102	96
12	48*	18
13	46*	16
14	46*	34

11,K,-4

0	48*	6
1	61	54
2	79	80
3	48*	49
4	48*	22
5	98	70
6	49*	61
7	48*	4
8	48*	22
9	47*	31
10	48*	33
11	94	58

12,K,-4

0	47*	6
1	48*	21
2	49*	12
3	52	44
4	47*	9
5	75	32
6	47*	6
7	60	31
8	46*	8

13,K,-4

0	46*	6
1	46*	26
2	46*	11

1,K,-3

0	87	81
1	707	713
2	820	802
3	258	247
4	316	403
5	451	449
6	675	628
7	33*	61
8	411	404
9	48	73
10	351	314
11	289	259
12	314	306
13	337	311
14	50	51
15	148	154
16	68	79
17	48*	39
18	53	56
19	76	68
20	58	48

2,K,-3

0	83	102
1	472	529
3	586	628
4	535	537
5	319	346
6	238	249
7	80	92
8	287	315
9	95	83
10	359	344
11	155	161
12	135	109
13	290	274
14	122	129
15	137	138
16	213	207
17	53	54
18	84	73
19	70	74
20	47*	40

3,K,-3

0	520	578
1	232	231
3	692	738
5	402	490
6	259	269
7	323	333
8	422	439
9	305	324
10	219	233
11	160	175
12	196	193
13	178	155
14	228	210
15	190	194
16	195	211
17	114	124
18	50*	62
19	61	60
20	59	76

4,K,-3

0	143	149
2	175	169
3	377	463
4	426	509
5	402	414
6	273	333
7	288	287
8	301	318
9	299	324
10	115	106
11	211	217
12	48	57
13	45*	58
14	178	155
15	199	184
16	128	108
17	172	151
18	66	78
19	68	66
20	55	44

5,K,-3

0	246	262
2	314	349
3	60	64
4	247	275
6	181	232
7	261	322
8	128	129
9	133	112
10	138	154
11	309	297
12	131	141
13	96	97
14	59	64
15	80	86
16	99	101
17	98	77
18	58	26
19	49*	35
20	47*	8

6,K,-3

0	35*	30
2	122	170
3	389	379
4	108	85
5	286	344
6	65	76
7	129	156
8	175	200
9	178	150
10	147	155
11	147	154
12	55	71
13	47*	43
14	49*	31
15	79	73
16	49*	51
17	88	79
18	51	43
19	48*	20

7,K,-3

0	44	25
1	174	172
2	212	232
3	104	93
4	85	92
5	138	123
6	195	200
7	120	141
8	113	112
9	45*	61
10	62	61
11	69	53
12	122	100
13	150	143
14	162	152
15	51*	47
16	50*	38
17	49*	45
18	49*	18

8,K,-3

0	121	112
1	171	182
2	235	269
3	137	155
4	71	90
5	62	60
6	85	67
7	67	78
8	170	154
9	58	48
10	88	71
11	50*	57
12	128	130
13	99	97
14	57	40
15	50*	55
16	87	71
17	48*	42

9,K,-3

0	46*	0

9,K,-3

1	304	318
2	177	165
3	46*	63
4	157	142
5	68	85
6	111	114
7	86	74
8	99	94
9	107	108
10	50*	71
11	65	80
12	78	61
13	49*	27
14	72	48
15	101	77
16	47*	17

10,K,-3

0	80	55
1	103	102
2	99	105
3	72	49
4	104	99
5	57	50
6	100	105
7	97	112
8	124	89
9	96	98
10	50*	10
11	50*	27
12	49*	26
13	50*	57
14	58	34

11,K,-3

0	89	72
1	52*	46
2	50*	63
3	71	54
4	51*	55
5	91	83
6	81	80
7	51*	31
8	50*	26
9	70	57
10	69	49
11	99	53
12	47*	14

12,K,-3

0	57	35
1	68	32
2	50*	34
3	50*	44
4	50*	33
5	71	47
6	73	45
7	50	37
8	63	36
9	48*	21

13,K,-3

0	48*	19
1	47*	3
3	46*	16

1,K,-2

0	822	730
1	185	176
2	499	483
3	872	875
5	534	592
6	295	282
7	177	157
8	346	379
9	114	102
10	150	139
11	130	132
12	144	163
13	260	238
14	268	229
15	46*	50
16	47*	14
17	62	78
18	100	109
19	62	40
20	75	59

2,K,-2

0	174	111
1	788	760
3	475	416
4	580	629
5	255	251
6	430	366
7	222	244
8	825	852
9	315	332
10	77	103
11	37*	56
12	40*	75
13	94	102
14	132	100
15	45*	26
16	289	292
17	82	69
18	71	67
19	93	90
20	51*	59

3,K,-2

0	450	444
1	243	240
2	453	418
4	470	488
5	316	309
6	338	365
7	371	399
8	45	58
9	140	131
10	304	303
11	139	109
12	226	238
13	147	154
14	180	170
15	53	51
16	86	96
17	117	96
18	51*	48
19	77	81
20	150	119

4,K,-2

0	490	551
1	498	539
2	350	370
3	175	162
4	155	166
5	168	236
6	579	658
7	223	283
8	504	500
9	258	241
10	287	306
11	160	158
12	164	106
13	141	123
14	77	84
15	136	111
16	174	169
17	105	110
18	206	178
19	50*	15
20	49*	17

5,K,-2

0	40	15
1	174	200
2	257	296
3	202	171
4	396	441
5	724	762
6	47	72
7	329	340
8	256	260
9	141	144
10	228	265
11	186	167
12	140	152
13	121	122
14	150	128
15	268	251
16	65	68
17	164	187
18	128	117
19	51*	38
20	87	54

6,K,-2

0	457	440
1	473	488
2	340	385
3	84	82
4	510	546
5	155	187
6	165	186
7	185	245
8	91	112
9	161	157
10	156	147
11	265	250
12	253	260
13	48*	31
14	205	225
15	49*	23
16	51*	62
17	120	100
18	50*	38
19	49*	15
20	50	53

7,K,-2

0	412	411
1	167	192
2	128	122
3	155	169
4	49	63
5	230	214
6	141	155
7	257	262
8	66	63
9	169	189
10	139	133
11	137	136
12	88	93
13	50*	35
14	107	90
15	92	64
16	117	120
17	51*	48
18	50*	32
19	48*	14

8,K,-2

0	136	118
1	152	158
2	131	100
3	184	185
4	64	41
5	67	48
6	45*	77
7	257	257
8	103	108
9	191	175
10	160	157
11	49*	56
12	51*	54
13	138	127
14	51*	39
15	60	44
16	60	59
17	50*	25

9,K,-2

0	83	100
1	74	61
2	88	84
3	278	245
4	125	112
5	47*	3
6	108	97
7	145	145
8	103	132
9	74	50
10	138	126
11	50*	32
12	50*	20
13	73	52
14	114	81
15	50*	13
16	50	27

10,K,-2

0	48*	14
1	89	75
2	48*	24
3	191	186
4	66	67
5	98	103
6	66	50
7	158	148
8	119	102
9	53	71
10	50*	15
11	65	50
12	68	63
13	70	33
14	49*	22

11,K,-2

0	76	47
1	134	113

11,K,-2

2	49*	26
3	59	36
4	142	111
5	51*	60
6	86	60
7	132	97
8	51	25
9	76	62
10	82	66
11	49*	36
12	56	40

12,K,-2

0	49*	2
1	49*	2
2	50*	29
3	49*	8
4	120	93
5	49*	44
6	67	31
7	50*	37
8	48*	16
9	47*	39

13,K,-2

0	49	13
1	47*	24
2	66	47

1,K,-1

0	375	255
3	686	763
4	1716	1604
5	745	776
6	286	314
7	156	146
8	115	121
9	136	148
10	409	443
11	385	396
12	259	282
13	312	316
14	124	137
15	107	133
16	56	39
17	122	93
18	51*	34
19	89	68
20	58	55

2,K,-1

3	874	859
4	292	262
6	112	95
8	335	337
9	509	531
10	230	251
11	38*	32
12	152	161
13	133	124
14	44*	29
15	301	297
16	125	143
17	98	87
18	65	77
19	114	113
20	50*	15

3,K,-1

0	205	274
1	229	311
4	554	579
5	216	191
6	272	294
7	339	400
8	129	166
9	378	423
10	246	260
11	106	112
12	128	123
13	141	128
14	190	180
15	104	76
16	90	109
17	84	85
18	96	118
19	77	63
20	99	88

4,K,-1

0	515	471
1	607	654
2	475	494
3	656	738
4	121	135
5	101	120
6	621	667
7	291	313
8	120	105
9	228	228
10	322	320
11	52	50
12	127	133
13	274	277
14	46*	23
15	49*	62
16	223	201
17	122	105
18	70	89
19	182	177
20	53	45

5,K,-1

0	868	936
1	133	158
2	464	527
3	155	110
4	284	298
5	330	381
6	327	342
7	281	285
8	78	57
9	60	72
10	187	218
11	166	185
12	273	262
13	47*	11
14	112	83
15	160	160
16	301	264
17	131	128
18	62	75
19	64	63
20	50*	62

6,K,-1

0	641	678
1	282	283
2	271	278
3	274	257
4	275	249
5	239	238
6	382	408
7	228	266
8	108	110
9	279	253
10	163	148
11	201	227
12	47*	31
13	57	80
14	111	123
15	84	74
16	64	60
17	52*	51
18	75	47
19	51*	65
20	53	48

7,K,-1

0	337	338
1	93	103
2	221	226
3	351	351
4	330	331
5	224	215
6	246	265
7	167	182
8	103	116
9	50	59
10	206	184
11	123	141
12	179	141
13	51*	33
14	53*	33
15	152	138
16	52*	33
17	52*	29
18	72	58
19	59	39

8,K,-1

0	87	83
1	201	225
2	130	176
3	166	142
4	277	237
5	64	78
6	159	151
7	136	146
8	73	74
9	112	93
10	157	145
11	163	170
12	82	105
13	113	90
14	116	106
15	91	60
16	52*	55
17	64	36

9,K,-1

0	65	72
1	117	106
2	63	82
3	151	139
4	97	80
5	61	72
6	49*	30
7	213	191
8	123	124
9	61	31
10	52*	36
11	52*	44
12	100	99
13	119	111
14	75	35
15	53	27
16	88	69

10,K,-1

0	53	50
1	53	29
2	87	67
3	168	118
4	51*	20
5	56	72
6	127	105
7	51*	13
8	71	43
9	142	119
10	128	107
11	51*	24
12	75	79
13	51	18
14	50*	29

11,K,-1

0	88	64
1	84	61
2	53*	35
3	75	65
4	67	46
5	55	48
6	75	61
7	116	104
8	80	67
9	78	56
10	49*	29
11	49*	21
12	50	47

12,K,-1

0	71	66
1	51*	32
2	53	46
3	50*	35
4	52*	33
5	118	69
6	50*	19
7	74	60
8	50*	38

0,K,0

2	1044	1110
4	268	253
6	993	975
8	245	239
10	727	756
12	270	294
14	51	53
16	223	227
18	136	116
20	52	43

1,K,0

0	53	129
5	555	547
7	192	219
8	146	144
9	242	244
10	265	304

	1,K,0	
11	100	88
12	96	91
13	194	215
14	87	101
15	123	129
16	109	108
17	160	152
18	87	58
19	130	139
20	51*	13

	2,K,0	
0	220	110
3	359	304
4	742	783
5	393	480
6	177	214
7	125	172
8	245	257
9	222	252
10	290	320
11	91	90
12	295	316
13	150	136
14	192	196
15	169	156
16	54	49
17	100	97
18	75	74
19	172	162
20	52*	32

	3,K,0	
0	226	165
1	308	365
2	558	514
4	220	250
5	135	167
6	696	743
7	338	444
8	273	297
9	320	361
10	38*	37
11	114	144
12	178	172
13	229	226
14	45*	25
15	72	61
16	51*	48
17	150	149
18	132	125
19	57	66
20	53*	39

	4,K,0	
0	129	108
1	651	659
2	288	299
3	256	295
4	502	564
5	186	224
6	437	459
7	161	165
8	257	264
9	570	595
10	207	220
11	124	124
12	67	76
13	108	58
14	53	75
15	211	199
16	110	135
17	95	110
18	134	143
19	92	61
20	53*	65

	5,K,0	
0	157	134
1	186	223
2	229	239
3	344	386
4	478	490
5	133	162
6	143	161
7	495	518
8	190	187
9	56	88
10	88	88
11	142	143
12	247	219
13	204	205
14	178	182
15	58	55
16	53*	9
17	94	70
18	80	88
19	94	80
20	50*	15

	6,K,0	
0	555	626
1	208	206
2	273	207
3	129	151
4	297	294
5	377	399
6	244	271
7	143	165
8	126	112
9	276	267
10	391	390
11	311	319
12	51*	43
13	104	111
14	101	108
15	230	224
16	94	78
17	87	75
18	52*	35
19	52*	48

	7,K,0	
0	243	238
1	250	253
2	45*	71
3	131	133
4	166	140
5	329	301
6	356	354
7	82	93
8	48*	8
9	136	144
10	140	138
11	243	207
12	309	285
13	105	98
14	87	98
15	53*	55
16	83	55
17	83	79
18	50*	8

	8,K,0	
0	45*	30
1	291	261
2	187	193
3	56	47
4	49	43
5	226	217
6	143	135
7	48*	31
8	124	106
9	203	211
10	139	133
11	123	135
12	94	104
13	101	109
14	55	58
15	86	91
16	51*	52
17	62	57

	9,K,0	
0	48*	10
1	214	193
2	216	176
3	80	49
4	74	89
5	49*	17
6	82	81
7	65	61
8	283	256
9	90	93
10	134	127
11	73	70
12	53*	27
13	106	85
14	79	41
15	50*	33

	10,K,0	
0	51*	43
1	86	90
2	115	104
3	52*	45
4	153	110
5	52*	53
6	77	61
7	178	164
8	52*	39
9	76	64
10	75	59
11	53*	47
12	88	75
13	50*	28

	11,K,0	
0	52*	17
1	52*	9
2	150	116
3	54*	36
4	148	131
5	53*	28
6	53*	47
7	51*	16
8	118	83
9	70	57
10	52*	45
11	48*	21

	12,K,0	
0	51*	17
1	109	78
2	76	51
3	52*	48
4	51*	40
5	101	75
6	50*	30
7	49*	29

	0,K,1	
0	507	474
1	93	83
2	266	223
3	1474	1362
4	1399	1428
5	704	558
6	330	374
7	570	539
8	242	246
9	357	394
10	345	354
11	216	239
12	248	240
13	43*	14
14	102	125
15	250	245
16	89	125
17	51*	41
18	98	83
19	53*	31
20	52*	37

	1,K,1	
0	670	587
2	841	830
3	633	429
4	1302	1220
5	1112	1088
6	1363	1441
7	249	299
8	507	506
9	260	279
10	350	344
11	358	365
12	300	297
13	149	147
14	44*	70
15	45*	34
16	137	138
17	59	65
18	82	75
19	111	97
20	65	63

	2,K,1	
0	1660	1774
1	1178	1205
2	1072	985
3	731	768
4	712	743
5	1203	1220
6	654	684
7	350	370
8	360	372
9	430	434
10	351	394
11	213	268
12	233	241
13	44*	40
14	248	267
15	118	122

	2,K,1	
16	269	285
17	69	41
18	63	50
19	54*	3
20	54*	13
	3,K,1	
0	445	406
1	338	284
2	473	456
3	390	418
4	503	444
5	492	471
6	539	576
7	544	563
8	616	633
9	135	118
10	309	327
11	93	118
12	72	59
13	118	109
14	141	115
15	81	109
16	52*	34
17	142	122
18	87	95
19	89	100
20	68	58
	4,K,1	
0	152	166
1	105	93
2	637	698
3	551	529
4	318	359
5	200	189
6	280	297
7	355	380
8	402	415
9	327	301
10	231	198
11	52	15
12	160	179
13	53	46
14	250	233
15	100	90
16	54*	64
17	55*	66
18	55*	55
19	54*	31
20	89	63
	5,K,1	
0	291	245
1	330	336
2	516	515
3	76	108
4	512	564
5	479	493
6	135	119
7	267	264
8	197	195
9	107	117
10	216	231
11	241	225
12	48*	47
13	55	62
14	126	126
15	55*	72
16	113	135
17	103	91
18	54*	23
19	53*	33
20	51*	17
	6,K,1	
0	342	295
1	547	563
2	162	180
3	178	179
4	335	337
5	154	197
6	270	277
7	248	252
8	46*	23
9	95	84
10	310	333
11	91	82
12	225	242
13	137	141
14	71	73
15	88	85
16	56*	22
17	55*	35
18	54*	35
19	52*	31
	7,K,1	
0	137	137
1	297	297
2	180	178
3	84	101
4	107	90
5	205	201
6	99	117
7	269	269
8	187	175
9	231	213
10	52*	23
11	136	115
12	56*	60
13	177	166
14	63	75
15	116	111
16	54*	39
17	55*	51
18	51*	13
	8,K,1	
0	47*	20
1	240	207
2	122	135
3	68	81
4	123	114
5	435	403
6	102	105
7	118	129
8	64	63
9	91	76
10	103	109
11	162	135
12	199	184
13	88	82
14	54*	8
15	53*	19
16	67	50
	9,K,1	
0	54	30
1	126	136
2	183	190
3	51*	27
4	161	151
5	130	114
6	142	146
7	71	74
8	105	86
9	62	58
10	56*	42
11	55*	65
12	56*	61
13	55*	30
14	52*	13
15	52*	34
	10,K,1	
0	157	123
1	56*	31
2	148	114
3	55*	45
4	64	61
5	72	62
6	54*	42
7	56*	21
8	56*	27
9	59	43
10	54*	29
11	68	59
12	54*	27
	11,K,1	
0	56*	42
1	55*	35
2	99	57
3	55*	30
4	55*	23
5	53*	22
6	55*	27
7	74	77
8	119	69
9	53*	6
	12,K,1	
0	52*	4
1	77	60
2	52*	24
3	64	47
4	64	55
	0,K,2	
0	196	176
1	2036	1731
2	631	589
3	663	594
4	325	182
5	600	541
6	140	202
7	926	893
8	168	204
9	469	458
10	291	274
11	382	353
12	241	230
13	115	135
14	147	153
15	65	46
16	188	180
17	239	205
18	77	78
19	86	97
20	73	59
	1,K,2	
0	1549	1484
1	1948	1793
2	897	690
3	398	340
4	557	484
5	1184	1192
6	179	117
7	379	381
8	396	356
9	178	157
10	661	675
11	287	278
12	178	196
13	174	174
14	141	167
15	179	188
16	96	114
17	154	112
18	92	99
19	56*	22
20	86	53
	2,K,2	
0	841	734
1	1299	1244
2	575	560
3	423	380
4	484	451
5	368	410
6	414	455
7	521	501
8	308	276
9	525	561
10	351	348
11	191	217
12	200	193
13	202	177
14	49*	28
15	99	124
16	61	84
17	56*	50
18	57*	81
19	127	121
20	82	77
	3,K,2	
0	198	207
1	848	790
2	166	177
3	680	702
4	837	853
5	550	550
6	399	435
7	404	413
8	323	294
9	304	349
10	269	283
11	226	231
12	178	190
13	64	40
14	114	80
15	137	142
16	70	71
17	99	72
18	65	47
19	55*	39
20	54*	54

4,K,2

1	201	246
2	582	630
3	234	265
4	260	294
5	184	206
6	142	166
7	42*	54
8	377	385
9	219	217
10	159	161
11	160	186
12	80	78
13	124	97
14	168	140
15	65	64
16	86	79
17	57	72
18	103	74
19	73	62
20	53*	41

5,K,2

0	108	103
1	173	202
2	529	548
3	165	166
4	178	200
5	228	228
6	120	126
7	94	118
8	235	253
9	55	66
10	183	167
11	50*	21
12	133	127
13	59	46
14	201	207
15	64	70
16	87	89
17	56*	32
18	56*	46
19	55*	34

6,K,2

0	43*	15
1	266	258
2	283	260
3	309	302
4	184	195
5	208	228
6	136	123
7	48*	40
8	165	177
9	132	130
10	139	116
11	96	88
12	144	147
13	55*	45
14	88	79
15	55*	56
16	56*	60
17	54*	29
18	55*	41

7,K,2

0	368	378
1	57	70
2	77	48
3	72	70
4	101	74
5	294	290
6	211	189
7	104	116
8	84	92
9	171	155
10	219	202
11	94	83
12	56*	42
13	56*	50
14	55*	35
15	60	49
16	132	106
17	54*	29

8,K,2

0	166	172
1	177	148
2	52*	61
3	119	153
4	251	243
5	54*	48
6	217	191
7	54*	17
8	111	105
9	62	62
10	83	84
11	70	67
12	57*	66
13	55*	40
14	56*	30
15	54*	46

9,K,2

0	169	169
1	98	99
2	158	141
3	78	63
4	86	73
5	56*	50
6	126	107
7	206	178
8	72	83
9	85	65
10	89	86
11	57	62
12	55*	46
13	54*	40

10,K,2

0	97	93
1	66	73
2	55*	19
3	77	75
4	93	56
5	57*	48
6	58*	45
7	63	73
8	65	58
9	73	57
10	58	30
11	55*	44

11,K,2

0	55*	34
1	117	78
2	56*	38
3	65	51
4	55*	15
5	65	53
6	54*	19
7	54*	37

0,K,3

0	961	760
1	472	404
2	546	452
3	683	648
4	292	301
5	488	487
6	511	478
7	185	213
8	389	414
9	69	72
10	346	360
11	100	117
12	143	167
13	49	60
14	260	248
15	52*	14
16	66	84
17	73	103
18	67	50
19	56*	35
20	56*	22

1,K,3

0	699	708
1	698	513
2	285	254
3	112	123
4	526	502
5	681	711
6	177	198
7	585	589
8	542	531
9	85	111
10	127	114
11	333	352
12	224	220
13	87	61
14	71	82
15	75	66
16	55*	19
17	87	63
18	58*	49
19	56*	32
20	73	60

2,K,3

0	495	524
1	412	424
2	626	619
3	137	76
4	715	728
5	430	445
6	879	900
7	580	597
8	279	279
9	389	391
10	259	273
11	140	149
12	112	129
13	75	76
14	53*	82
15	134	128
16	62	44
17	158	137
18	64	50
19	56*	23
20	55*	13

3,K,3

0	804	808
1	296	304
2	372	399
3	408	419
4	414	388
5	285	250
6	374	384
7	167	194
8	268	292
9	269	271
10	401	424
11	192	190
12	51*	52
13	146	106
14	147	155
15	85	71
16	65	63
17	57*	60
18	78	59
19	67	71
20	54*	31

4,K,3

0	382	424
1	424	453
2	218	188
3	393	428
4	87	96
5	96	73
6	242	299
7	215	204
8	175	176
9	254	235
10	124	130
11	54	47
12	112	109
13	201	194
14	79	76
15	136	126
16	56*	54
17	55*	19
18	56*	31
19	58	56

5,K,3

0	75	85
1	89	81
2	279	294
3	353	372
4	460	473
5	139	132
6	314	331
7	312	309
8	166	167
9	280	275
10	52*	59
11	126	124
12	98	113
13	71	94
14	56*	22
15	125	101
16	57*	51
17	56*	56
18	55*	55

6,K,3

0	314	321
1	272	274
2	62	35
3	300	281
4	159	175

6,K,3

5	176	181
6	120	120
7	187	193
8	52*	48
9	57	48
10	144	114
11	223	251
12	55*	25
13	148	142
14	56*	42
15	57*	51
16	56*	34
17	54*	53

7,K,3

0	138	136
1	96	99
2	226	226
3	121	113
4	177	185
5	52*	32
6	184	179
7	126	132
8	189	191
9	112	100
10	143	144
11	74	81
12	78	81
13	56*	30
14	57*	42
15	56*	51
16	54*	9

8,K,3

0	137	137
1	55*	57
2	132	122
3	153	157
4	231	214
5	70	68
6	187	182
7	57*	51
8	57*	28
9	61	56
10	56*	44
11	57*	33
12	121	105
13	56*	53
14	54*	46

9,K,3

0	201	162
1	56*	49
2	56*	35
3	61	46
4	71	72
5	111	102
6	164	145
7	56*	17
8	63	30
9	56*	34
10	101	104
11	56	36
12	65	38

10,K,3

0	58	12
1	65	68
2	57*	43
3	130	115
4	57*	50
5	54*	23
6	55*	34
7	55*	25
8	55*	41
9	53*	7

11,K,3

0	54*	24
1	72	48
2	60	45
3	54*	34

0,K,4

0	287	210
1	351	348
2	695	620
3	445	467
4	423	350
5	118	84
6	298	297
7	484	539
8	130	121
9	215	223
10	321	319
11	160	187
12	85	64
13	171	156
14	224	221
15	56*	63
16	76	73
17	82	83
18	82	81
19	58*	56
20	56*	48

1,K,4

0	1052	1000
1	576	533
2	101	79
3	646	609
4	332	355
5	437	410
6	661	695
7	214	211
8	112	99
9	132	159
10	130	127
11	212	234
12	214	191
13	63	76
14	69	86
15	107	101
16	91	83
17	112	95
18	58*	39
19	56*	18
20	56*	41

2,K,4

0	638	665
1	164	221
2	334	366
3	256	243
4	383	388
5	423	431
6	440	460
7	55	85
8	246	253
9	201	192
10	249	250
11	140	141
12	145	139
13	54*	39
14	91	89
15	57*	44
16	60*	42
17	59*	60
18	122	72
19	57*	1
20	56*	46

3,K,4

0	676	678
1	415	432
2	214	219
3	127	127
4	515	533
5	82	81
6	294	287
7	100	97
8	309	302
9	264	264
10	196	206
11	155	188
12	79	85
13	93	84
14	126	117
15	58*	33
16	113	103
17	59*	35
18	57*	10
19	56*	17

4,K,4

0	475	479
1	397	441
2	171	158
3	404	390
4	295	282
5	112	83
6	338	361
7	193	190
8	299	322
9	99	95
10	354	358
11	57*	39
12	136	136
13	66	65
14	85	76
15	76	73
16	58*	21
17	58*	51
18	57*	18

5,K,4

0	369	384
1	111	109
2	176	154
3	358	371
4	192	206
5	153	157
6	77	79
7	54*	54
8	67	86
9	302	303
10	93	118
11	58*	81
12	57*	7
13	59*	38
14	58*	23
15	84	90
16	58*	61
17	56*	13

6,K,4

0	64	81
1	52*	62
2	132	132
3	290	291
4	131	141
5	63	72
6	138	126
7	92	69
8	99	80
9	59	52
10	78	46
11	71	66
12	59*	71
13	137	137
14	63	77
15	57*	17
16	56*	25

7,K,4

0	177	192
1	190	177
2	114	128
3	56*	55
4	88	104
5	68	53
6	197	203
7	221	208
8	168	145
9	60*	58
10	124	121
11	57*	19
12	58*	57
13	57*	54
14	56*	24

8,K,4

0	71	56
1	88	78
2	88	96
3	113	111
4	99	87
5	189	181
6	58*	8
7	57*	5
8	59*	34
9	64	50
10	68	59
11	90	84
12	67	44

9,K,4

0	58*	44
1	70	88
2	60*	77
3	57*	17
4	58	55
5	62	58
6	90	90
7	67	65
8	58*	53
9	56*	45
10	54*	27

10,K,4

0	55*	17

10,K,4

1	85	77
2	77	56
3	60	44
4	55*	23
5	55*	11

0,K,5

0	265	238
1	322	343
2	305	319
3	316	303
4	330	336
5	69	90
6	237	240
7	275	293
8	145	159
9	225	225
10	295	292
11	116	131
12	168	175
13	217	209
14	57*	26
15	65	65
16	59*	33
17	79	87
18	85	78
19	74	63

1,K,5

0	248	244
1	161	182
2	214	200
3	375	385
4	87	104
5	91	88
6	213	238
7	163	154
8	132	134
9	178	155
10	169	192
11	80	80
12	66	50
13	152	145
14	73	59
15	103	85
16	60*	21
17	85	112
18	58*	39
19	56*	23

2,K,5

0	499	503
1	174	209
2	84	97
3	263	281
4	138	148
5	431	470
6	529	536
7	348	384
8	145	150
9	170	167
10	55*	28
11	108	99
12	130	124
13	59*	55
14	77	69
15	59*	23
16	60*	44
17	58*	19
18	95	73

3,K,5

0	246	252
1	443	448
2	63	71
3	179	191
4	249	254
5	125	127
6	316	316
7	239	255
8	69	61
9	110	131
10	193	206
11	231	234
12	99	100
13	61*	70
14	61*	66
15	59*	44
16	79	64
17	86	67
18	56*	18

4,K,5

0	99	105
1	241	240
2	173	163
3	206	207
4	187	191
5	290	306
6	88	95
7	219	222
8	226	216
9	129	140
10	116	132
11	104	101
12	102	101
13	60*	16
14	108	93
15	60*	67
16	60*	61
17	57*	14

5,K,5

0	176	173
1	270	274
2	137	120
3	109	118
4	129	130
5	64	79
6	153	164
7	65	98
8	191	166
9	116	125
10	60*	66
11	59*	15
12	104	75
13	107	106
14	105	96
15	57*	54
16	57*	58

6,K,5

0	73	89
1	138	149
2	114	120
3	146	149
4	329	326
5	102	108
6	243	253
7	60*	52
8	60*	24
9	60*	79
10	209	209
11	59*	56
12	58*	14
13	58*	38
14	56*	6

7,K,5

0	90	97
1	60*	66
2	96	85
3	67	73
4	111	105
5	61	57
6	60*	35
7	61*	66
8	60*	57
9	59*	66
10	59*	68
11	57*	52
12	56*	18

8,K,5

0	58*	12
1	59*	29
2	104	92
3	96	93
4	60*	40
5	60*	36
6	61*	60
7	59*	57
8	106	77
9	57*	46
10	56*	8

9,K,5

0	58*	52
1	96	101
2	73	68
3	101	87
4	58*	60
5	84	80
6	56*	19

0,K,6

0	50*	15
1	63	69
2	252	243
3	83	81
4	417	377
5	53	48
6	139	135
7	247	254
8	94	110
9	290	306
10	98	62
11	85	97
12	134	115
13	61*	63
14	256	227
15	115	132
16	66	66
17	71	67
18	57*	35

1,K,6

0	111	92
1	106	108
2	399	397
3	213	204
4	329	325
5	163	166
6	279	305
7	203	226
8	366	390
9	60	43
10	163	148
11	104	107
12	90	94
13	78	68
14	82	104
15	60*	85
16	60*	19
17	59*	35
18	70	58

2,K,6

0	112	99
1	294	308
2	152	153
3	52*	34
4	207	220
5	234	252
6	55*	53
7	218	217
8	94	102
9	211	210
10	107	92
11	61*	32
12	158	162
13	65	55
14	60*	34
15	107	86
16	59*	24
17	59*	49

3,K,6

0	87	90
1	279	284
2	65	47
3	54*	12
4	60	64
5	175	184
6	59*	75
7	322	332
8	110	127
9	93	104
10	144	147
11	95	83
12	100	118
13	70	77
14	60*	33
15	59*	28
16	58*	32

4,K,6

0	62	83
1	184	208
2	60	69
3	117	131
4	173	181
5	297	296
6	67	74
7	60*	28
8	60	67
9	144	145
10	73	79
11	135	158
12	62	23
13	93	94
14	60*	24

```
        4,K,6

15       57*     57

        5,K,6

 0      159     183
 1      126     148
 2      166     176
 3       75      61
 4       59*     46
 5      131     138
 6       83      89
 7       60*     24
 8      182     194
 9       69      72
10       60*     47
11       61*     66
12       59*     34
13       67      63
14       56*     39

        6,K,6

 0      202     216
 1      162     192
 2      212     223
 3       98     103
 4       93      92
 5       60*     38
 6       67      64
 7       80      82
 8       76      65
 9       72      65
10       58*     47
11       58*     18
12       57*     21

        7,K,6

 0      103      92
 1       79      62
 2      148     158
 3       98      86
 4      165     157
 5       69      78
 6       63      64
 7       58*      5
 8       59*     61
 9       58*     34

        8,K,6

 0       58*     67
 1       58*     37
 2       56*     22
 3       73      58
 4       65      73
 5      102      81
```

```
        0,K,7

 0       85      91
 1       72      64
 2      180     168
 3       73      88
 4      241     236
 5      181     195
 6       78      90
 7      330     321
 8      252     249
 9      172     152
10      115     107
11      206     212
12       69      57
13      125     133
14       62*     50
15       60*     44
16       58*      9

        1,K,7

 0       55*     51
 1      122     124
 2      229     232
 3      132     142
 4       56*     81
 5       63      64
 6       59*     50
 7      131     137
 8      269     267
 9       61*     41
10      194     191
11      130     130
12       62*     48
13       64      64
14       99      99
15       59*     62
16       58*     60

        2,K,7

 0       57*      3
 1       72      98
 2      139     140
 3      201     198
 4      106     114
 5      200     185
 6       68     100
 7      179     196
 8       90      94
 9      172     157
10       99     110
11       85     106
12      117     107
13       60*      3
14       60*     53
15       58*     38
```

```
        3,K,7

 0      203     202
 1      210     225
 2      176     168
 3      164     168
 4      100      98
 5      224     229
 6      189     192
 7      204     201
 8       60*     44
 9       72      42
10       60*     40
11       59*     29
12       87      99
13       59*     27
14       67      70

        4,K,7

 0      229     269
 1       97      91
 2      242     249
 3      144     140
 4      246     249
 5       60*      9
 6       61*     24
 7       61*     57
 8       61*     73
 9      130     130
10       70      86
11       60*     54
12       58*     39

        5,K,7

 0       60*     11
 1      212     218
 2       62*     45
 3       62*     35
 4       62*     21
 5       61*     38
 6       89      81
 7       85      89
 8       60*     12
 9       70      53
10       83      72
11       57*     31

        6,K,7

 0       80      93
 1      108     107
 2       66      93
 3       61*     53
 4       60*     27
 5       60*     18
 6       63      56
 7       81      76
 8       57*     12
```

```
        7,K,7

 0       59*     79
 1      112     116
 2       59*     75
 3       90      74
 4       57*     17

        0,K,8

 0       79      60
 1       60*     47
 2      119     103
 3      215     206
 4      274     251
 5      184     188
 6      132     121
 7       63*     63
 8      123     120
 9       61*     25
10      161     176
11       62*     47
12       62*     23
13      116     103
14       69      53

        1,K,8

 0       62*     38
 1      255     234
 2       61*     42
 3       78      81
 4       61*     36
 5      242     244
 6       83      75
 7      289     282
 8      139     137
 9      125     114
10       63*     36
11       61*     18
12       63      86
13       90     101

        2,K,8

 0       62*     18
 1       63*     68
 2       90      81
 3      157     156
 4      117     108
 5       65      56
 6       62*     22
 7       68      67
 8       80     105
 9      134     132
10       62*     51
11       61*     65
12       94     101
```

```
        3,K,8

 0      109     112
 1       62*     26
 2       81      85
 3       93      78
 4       61*     42
 5      102      94
 6       78      92
 7       94      99
 8       62*     19
 9       62*     57
10       88      80
11       58*     51

        4,K,8

 0      122     110
 1       82      97
 2       83      83
 3       62*     78
 4       98      99
 5       61*     62
 6       93      88
 7       59*     36
 8       58*     40
 9       58*     33

        5,K,8

 0       90      93
 1       59*     19
 2       68      56
 3       58*     52
 4       57*     11
 5       58*     45
 6       94     113

        0,K,9

 0      105      89
 1       62*     49
 2       62*     68
 3      137     143
 4      157     161
 5       62*     22
 6       62*     15
 7       61*     64
 8       68      86
 9       61*     55
10       81      78
11       58*     29

        1,K,9

 0       61*     53
 1       76      73
 2       62*     33
 3      153     125
 4       73      78
```

```
      1,K,9                     2,K,9                 8     86        97        6     57*       38        6     58*       28

  5    131       144        0     60*       21              3,K,9                     0,K,10                    1,K,10
  6     61*       79        1     67        55
  7     92       119        2     83        93        0     60*       46        0     59*        7        0     59*       61
  8     62*       76        3     61*       64        1     59        50        1    152       134        1     58*       39
  9    102        84        4     60*       22        2     79        91        2     59*       30        2    112       112
 10     58*       28        5    106        86        3     58*       22        3     59*       67        3     58*       52
                            6     83       103        4     72        70        4    125       148
                            7     60*       62        5     60        65        5     58*       45
```

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APPENDIX II

Crystal and molecular structure of the ketol bishydropulegone.

"We learn wisdom from failure much more than from success. We discover what will do by finding out what will not do; and he who never made a mistake never made a discovery."

... Samuel Smiles.

Introduction

The structure determination of the ketol bishydropulègone ($C_{20}H_{34}O_2$) was undertaken as part of a larger research study within this laboratory of reductive dimerization products of R(+)-pulegone.

The ketol chosen for the structural study was one of four sent here for preliminary investigation. All the ketols are orthorhombic $\underline{P}2_12_12_1$ and their respective unit-cell dimensions are given in Table 1. Bishydropulegone (m.p.102°, $[\alpha]_D$ + 85°) was chosen because it had quite short unit-cell lengths and the intensity data on an overnight Weissenberg photograph were visible to $\theta = 55°$. The measured density was $1.1 g.cm^{-3}$ ($\underline{D}_c$ = 1.11 for $\underline{Z}$ = 4), thus it posed a straightforward non-centrosymmetric $\underline{P}2_12_12_1$ direct method problem.

The structure of the related deshydrobispulegone ($C_{20}H_{28}O$) has been determined by a colleague, Dr. A. Quick, in this laboratory and thus it has been compared quite extensively with the present structure. These two structures, together with two earlier X-ray studies[14,15] of related compounds (one of which[15] has been shown to be incorrectly named) and the published chemical and physico-chemical data of the five ketol dimers, have permitted a Scheme to be drawn up which defines the absolute stereochemistries of all the key compounds in the family. In particular, in the nor (normal) and iso series of isomers the methyl group at C12 is cis and trans respectively relative to the hexanone ring and the gem-dimethyl groups; this is a reversal of the earlier arbitrary assumption made by Pascual *et al*[3]. It is notable that one of the bonds in the five-membered ring is abnormally long in all four structures due to severe steric interactions.

Professor Rogers is to be thanked for the contribution re. chemical comments on the interconversions of the ketols and provision of background information.

Table 1

Preliminary Comparative data for Four Ketols.

All crystals were orthorhombic, space group $P2_12_12_1$.

Bishydropulegone (nor): m.p. 102°C; $[\alpha]_D$ + 850°;
prismatic needle-shaped crystals
Intramolecular H-bonding occurs.

a = 10.84Å — Intensity to $\theta \simeq 55^\circ$ (on one day
b = 14.40Å — Weissenberg photograph).
c = 11.78Å

Ketol IV (iso): m.p. 115°C; $[\alpha]_D$= -99.3;
Needle-shaped crystals
Intramolecular H-bonding occurs.

a = 11.86Å
b = 8.57Å — $\theta \simeq 45^\circ$
c = 17.13Å

Harries-Roeder Ketol (nor): m.p. 118°C; $[\alpha]_D$ + 59.9°;
Needle-shaped crystals.

a = 6.85Å — $\theta \simeq 45^\circ$
b = 8.29Å
c = 34.26Å

Isobishydropulegone (iso): m.p. 138°C; $[\alpha]_D$ + 61°

a = 12.34Å — $\theta \simeq 45^\circ$
b = 18.14Å
c = 29.4Å

The reductive dimerization of (+)R-pulegone (I) carried out under various conditions has produced a number of compounds. The first, reported by Harries and Roeder[11] (1899), was for long regarded as a diol, and the existence of others in impure forms was indicated by the work of Law[12] (1912) and Müller[13] (1921), but the matter was not pursued.

Recently Pascual and his co-workers have extensively explored the chemistry of the immediate products and numerous derivatives and have reported them in a series of papers.[1-10] They recognized the Harries-Roeder compound as a ketol and have isolated and characterized four others which occupy a key position in these studies. Comparative data are given in Table 2. They have shown through an elaborate series of chemical correlations that the five ketols and their derivatives fall into two isomeric series called nor(mal) and iso, whose absolute stereochemistries can be represented by IIa or IIb. In paper III[3] Pascual, for the purposes of argument, arbitrarily assigned these two stereochemistries to the iso- and nor- series respectively, but in his latest paper(X)[10] he has produced n.m.r. evidence for reversing the assignment. Meanwhile two X-ray studies were undertaken on bromoderivatives in order to make the assignment unambiguously.

The first[14] was of dibromodehydrobispulegone (mpt. 188-9°, $[\alpha]_D = -92.9^{\circ}$) whose structure (IV)(C in the Scheme given later), therefore, identifies IIa with the nor series. (Unfortunately this X-ray result was presented without either drawing this conclusion or inferring the absolute configuration from the R configuration at C(12).) The second[15] was published while the present study was in progress. It described the structure of a compound that was identified by name only as monobromodehydrobispulegone. However, its structure (V, D in the Scheme) - again reported without drawing the distinction - indicated that it was in the other series and a check with Prof. Pascual, who supplied the compounds, confirmed that it was wrongly named: it was

Table 2

The five $C_{20}H_{34}O_2$ Ketols

Name	Series	mpt.	$[\alpha]_D$	Intramolecular hydrogen bond?	References	
Harries-Roeder ketol	nor	118°	+57.9°	Yes	11 (14/II)*	H
Bishydropulegone	nor	102°	+85°	Yes	1 (5/1)	F
Isobishydropulegone	iso	138°	+61°	No	1 (6/1)	K
4th ketol	iso	115°	-99.3°	Yes	6 (1/VI)	L
5th ketol	nor	147°	+70.3°	No	7 (1/VII)	G

* This indicates the first or most significant reference to the Compound in Pascual's series of papers. Thus this compound is designated 14 in paper II of the series and was first characterised in reference 11. Its stereochemistry is depicted as H in the Scheme.

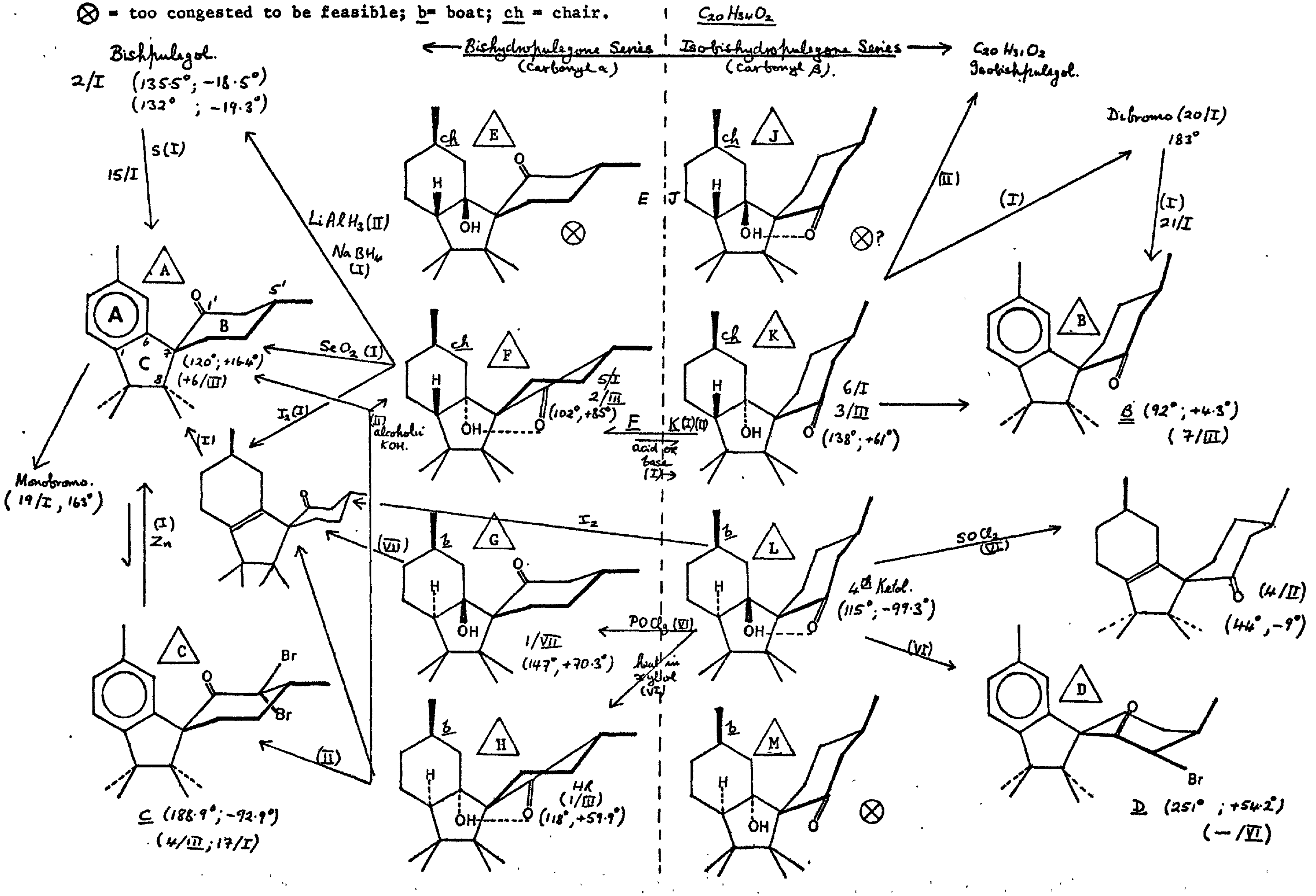
in fact monobromodeshydroisobispulegone (mpt.251° dec.;$[\alpha]_D$ =+54.2). Brief details of this correction have been submitted to Acta Crystallographica.

In the present study, the structure of the ketol bishydropulegone ($C_{20}H_{34}O_2$) has been determined [the second ketol in Table 2 (VII , F in the scheme)] and is compared with the structure of deshydrobispulegone ($C_{20}H_{28}O$, mpt. 120°, $[\alpha]_D = +16.4^\circ$; VI, A in the Scheme) which was determined by Dr. A. Quick. To facilitate comparison with the earlier X-ray structures we have adopted the same numbering scheme as was used in IV though this differs from that used by Pascual *et al* (see III). The two new structures were known to be in the nor-series, so the stereochemistries found provide further evidence for identifying IIa with the nor-series. As Pascual *et al* have isolated the achiral compounds, VIIIa and VIIIb,[8,10] it is clear that the distinction between the two series is best drawn, not by defining the chirality at C(9) (our numbering), but by noting the relative orientation of the methyl group at C(12) (C(5') in Pascual's numbering) and the gem-dimethyls with reference to the 6-membered spiro-ring B: they are cis in the nor-series and trans in the iso-series.

It is now possible to combine the chemical and physico-chemical results with those of the X-ray studies to produce a comprehensive and consistent stereochemical Scheme(see adjoining page), which agrees with but goes beyond Pascual's latest assignments. Models of the eight possible ketol isomers shown in the Scheme suggest that three (E, M and probably J) are almost certainly too overcrowded to exist. This restriction, taken with the data in Table 2 relating to the relevant series and the presence or absence of intramolecular hydrogen bonding, identifies stereoformulae G, K, L in the Scheme with the compounds shown in Table 2. The remaining two hydrogen-bonded ketols (F, H,) in the nor-series are distinguished by the X-ray results of the structure presented here.(F).

SCHEME OF THE KETOLS

⊗ = too congested to be feasible; b = boat; ch = chair.



To avoid further confusion substances are identified in this Scheme by their mpt. and $[\alpha]_D$ and by both letters and numeric references as explained at the foot of Table 2. The arrows indicate some of the more significant known reactions and relationships, and Roman numerals beside an arrow indicate in which of Pascual's papers the reaction is reported. It is believed that in all the interconversions between the ketols (at least) the bond C(5) - C(9) ruptures to give a keto-enol, but is later rejoined. Some of the conversions deserve comment.

1) The acid or base catalysed equilibrium between isomers F and K is strongly biassed toward F. In this case the keto-enol preserves the configuration at C4 and rings A and B. The bias in favour of F is undoubtedly due to the presence of the hydrogen bond which will inhibit rupture of C(5) - C(9) and may well tend to form in the keto-enol even before these atoms rejoin. Of the four possible ways they may rejoin E and J can be ruled out as being too crowded.

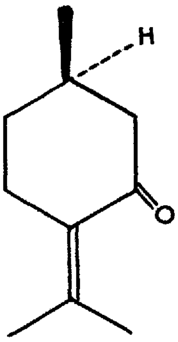
2) The transition from L to G in the presence of $POC\ell_3$ at low temperatures follows a similar path and again the major component of the equilibrium is the hydrogen-bonded L. M is too sterically hindered to be formed.

3) The transition from L to H by refluxing in xylol suggests that the latter is the thermodynamically more stable isomer. Examination of models of the two isomers shows no obvious reason for this difference: both contain ring A in a boat form and similar amounts of congestion. However, models of the keto-enol intermediate just prior to fusion to form either L or H reveal interesting steric factors in favour of H, in whose precursor the ketone π-orbital is angled downward to make a good overlap with the π-orbital on C(9), whereas in the precursor of L it is angled upward and the overlap is poor. It is also much less easy to proximate these atoms to produce L because of collisions between the oxygens and between the methyl-carrying ends of rings A and B, and also

due to the intervention of the hydrogen on C(4) between the rings in the precursor of L.

4) The 100% conversion from H to F in alcoholic KOH involves epimerization at C(4) - possibly via a di-enol, which would entail loss of distinction between rings A and B. The driving force in this case seems to be the conversion of ring A from boat to chair and the release of some congestion. The conclusion seems to be that F (bishydropulegone) is the thermodynamically most stable of the ketols, though the energy differences are probably quite small.

Individual features of the present crystal structure will be discussed later and compared with the three related structures, but it is evident that, even in the ketol F where congestion is greatest, the length of C(5) - C(9) is not abnormal, so it does not appear to be under strain. However, C(8) - C(9) is in all four structures exceptionally long (A 1.615, F 1.603, C 1.69, D 1.69Å) and C(7) - C(8) is also somewhat long. The five-membered ring is, therefore, under considerable strain which provides the driving force, but rupture when it does occur takes place under electronic influences along the path between the two oxygen atoms.



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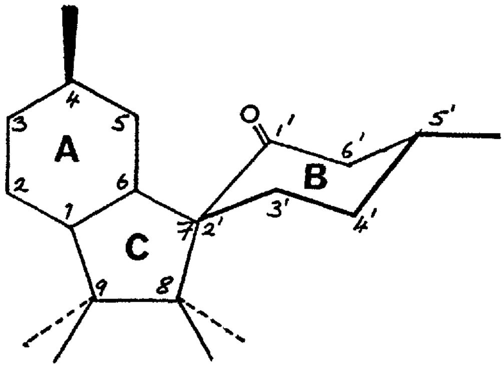

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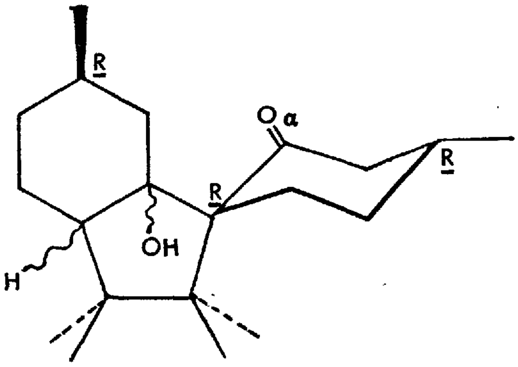
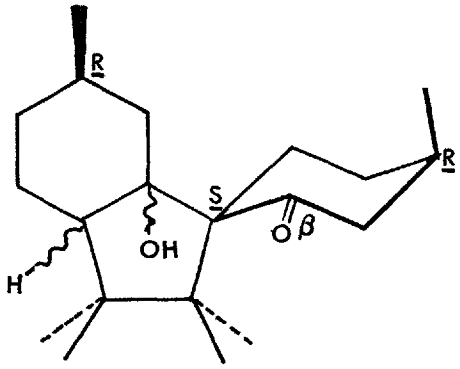
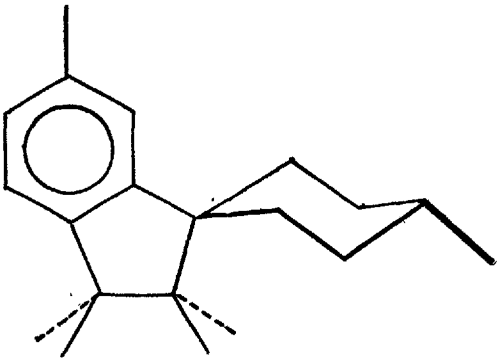


IIa

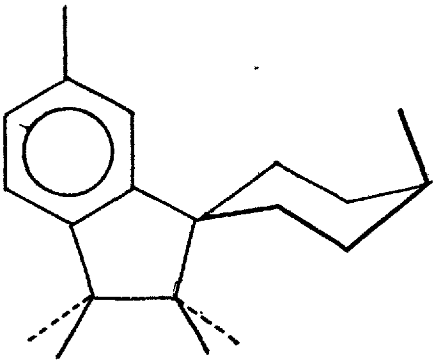


IIb

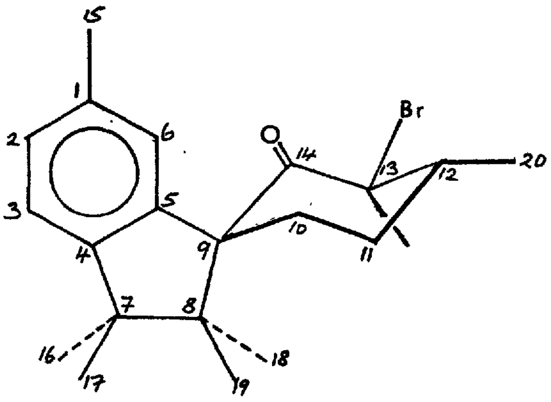
∿ indicates that either stereochemistry (α or β) is possible .



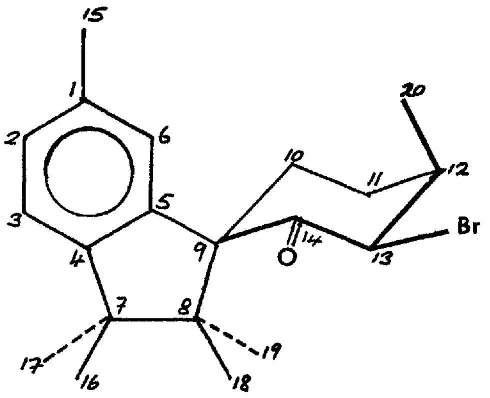
VIIIa



VIIIb


15
1
2
6
3
5
O
14
Br
13
12
20
10
4
9
11
7
8
16
17
18
19

IV


15
1
2
6
20
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12
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14
O
13
Br
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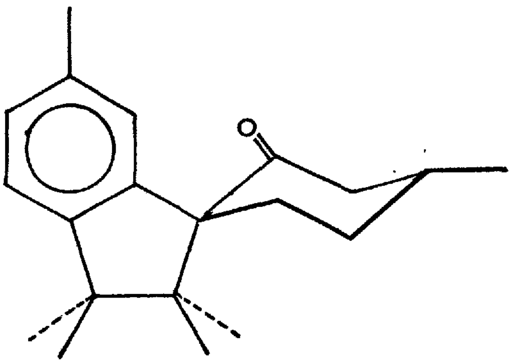
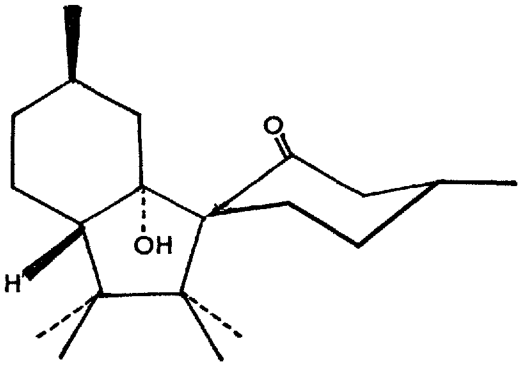
19
18

V


O

VI


O
OH
H

VII

Experimental

The crystals were colourless blocks.

Crystal Data

$C_{20}H_{34}O_2$, $\underline{M}$ = 306.5, orthorhombic,
$\underline{a}$ = 10.8378(5), $\underline{b}$ = 14.3917(9), $\underline{c}$ = 11.7720(4)Å,
$\underline{U}$ = 1836.1Å^3, $\underline{D}_m$ = 1.11 g.cm^{-3}(by flotation), $\underline{Z}$ = 4,
$\underline{D}_c$ = 1.108 g.cm^{-3}, $\underline{F}$(000) = 680.
Space group $P2_12_12_1$(no. 19) uniquely from systematic absences.
Cu-$\underline{K}\alpha$ radiation ($\bar{\lambda}$ = 1.5418Å). μ(Cu-$\underline{K}\alpha$) = 5.38cm^{-1}.

A crystal ca. 0.35 x 0.4 x 0.4mm^3 was mounted along its $\underline{a}$-axial direction and data were measured on a Siemens off-line automatic four-circle diffractometer, with filtered Cu-$\underline{K}\alpha$ radiation. A total of 1783 independent reflections (to θ = 65°) were measured by use of the θ-2θ scan technique and the 'five-value'measuring procedure.[16] Of these, 107 reflections were judged to be unobserved, i.e. $I < 2.58\ \sigma(I)$. The net count of the reference reflection measured after every 50 reflections, did not alter significantly during the data collection (ca. 3 days). The data were scaled by use of this reference and Lorentz and polarisation corrections were applied. No absorption corrections were applied.

Solution and Refinement of the Structure

The structure was solved by direct methods using two distinct routes. Initially, hand iteration was utilised but difficulty was experienced in the phase expansion procedure due to the fact that, though several starting sets were tried, the best had not been chosen. The program MULTAN,[17] which chooses the most likely starting set, was then applied to a list of 202 reflections having normalised structure factors $|E| \geqslant 1.48$. Phases were computed from a starting set of seven reflections three of which determined the origin (0 4 7, 5 11 0, and 7 6 0) and one the enantiomorph (1 11 3).

Table A

Starting set of reflections from MULTAN

Values in brackets are those phases assigned during tangent-formula run with highest overall figure of merit (FOM).

h	k	ℓ	E	Phase	
5	11	0	3.11	90°	Origin
0	4	7	2.22	360°	defining
7	6	0	2.09	90°	reflections
1	11	3	3.21	(29°)	Enantiomorph fixing reflection * (See Appendix IV).
0	12	2	2.39	360°	Fixed value.
4	12	0	3.89	(360°)	
6	1	9	3.02	(129°)	

Absolute figure of merit = 0.7462

Combined figure of merit = 2.0524

RESID = 25.99.

* Inconsistent with parities of origin defining reflections.

The E map, calculated from the phase solution with the highest combined figure of merit (2.0524), gave plausible positions for some sixteen of the non-hydrogen atoms in the structure. The remaining six atoms were obtained from the difference-Fourier map calculated on the basis of the known atomic positions. The solution refined with isotropic temperature factors to $R = 0.135$, $R = \Sigma| F_o - F_c |/\Sigma F_o$, and a difference-Fourier map computed at this stage showed no major unassigned peaks. The structure was then refined anisotropically, reducing R to 0.102, and from the corresponding difference-Fourier all the 34 hydrogen positions were found. These were assigned temperature factors that were isotropic equivalents of their parent atoms. When all these atoms were included in the full-matrix least-squares procedure of ORFLS, R dropped to 0.078. Two misprocessed reflections were removed. Subsequent refinement reduced R to a final value of 0.047. It was not found necessary to use other than unit weights throughout the refinement procedures. A final difference map showed no significant peaks. Atomic scattering factors were taken from Cromer and Waber,[18] except those for hydrogen which were taken from Stewart, Davidson, Simpson.[19] Fig. 1 shows the atom numbering used. Tables 3 and 4 list the final co-ordinates of the non-hydrogen atoms and their anisotropic temperature factors. The co-ordinates of the hydrogen atoms are given in Table 5 and the observed and calculated structure factors are listed at the end of the chapter.

The bond lengths in all four X-ray structures are compared in Table 6, the angles in Table 7, and some of the intramolecular distances in Table 8. The torsion angles are shown in fig. 2, supplemented by Table 9. Table 10 gives the details of the best planes and deviations of atoms from these planes and mutual inclinations of the planes for the structures bishydropulegone and deshydrobispulegone.

Throughout the tables, the numbering shown in V has been adopted for structure D.[15] It differs from the published numbering in that C_{16}, C_{17}, and C_{18}, C_{19} have been interchanged. This has been done so as to keep C_{16}, C_{18} on the same side of the plane of rings A and C as the carbonyl and to permit torsion angles to be compared.

Discussion

The conformation of the bishydropulegone(F)molecule is shown in Fig. 3. It differs from deshydrobispulegone(A) chiefly from the character of the ring A which is aromatic in A and saturated in F although the addition of the hydroxyl group in F has greatly increased the overcrowding. Both the present structure F and the structure determination by Dr. A. Quick of A have been refined to similar fairly high levels of accuracy. It is thus possible to compare and discuss the differences with some confidence. The other related structures C and D[14,15] were not determined very accurately, consequently it is not possible to compare these so effectively. (For C, 329 visually estimated intensities, no absorption correction or allowance for hydrogen atoms, refined to R = 0.161; for D, 692 photometer estimated intensities, no absorption correction or allowance for hydrogen atoms, refined to R = 0.107). Compound C differs from A only in that it possesses a gem-dibromo group, thus comparisons between A and C are limited by the accuracy of the C structure determination.

As expected the aromatic ring (A) in deshydrobispulegone (A, VI) has a mean bond length of 1.388Å, mean bond angle of 120.0° and mean deviation of its atoms from the best plane of 0.007Å (See Table 10a, Plane A). Its immediate substituent atoms also lie close to this plane. In this compound ring C has an envelope conformation with C(8) lying 0.449Å out of plane on the β side. This deviation has the effect of slewing both the gem-dimethyl at C(7) and ring B away from the gem-dimethyl on C(8) toward the α side. Newman diagrams for these twists are shown in Fig. 4. Ring B has a shape and dimensions typical of a cyclohexanone ring. (See later).

In bishydropulegone (F, VII) a distinctly different geometry is obtained. Ring A is a typical slightly flattened chair-shaped cyclohexane ring with mean bond length 1.523Å, bond angle 111.0°, and torsion angle 56.0°. Fusion with a five-membered ring has not distorted it much, though the common bond, C(4)-C(5) 1.495Å, is distinctly and significantly short. The substituent atoms, C(15), C(7), C(9) are all equatorial, whereas O(22) is axial. Ring C again has an envelope conformation, but this time it is C(5) which deviates (0.634Å) to the α side. The consequences are that the two gem-dimethyl groups are nearly exactly eclipsed (the torsion angle C(4)[C(7)-C(8)]C(9) is only 4.0°, and see the Newman diagram Fig. 4). It also deflects ring B to the β side of the molecule, thus making room for the hydroxyl group (which is intramolecularly hydrogen-bonded to O(21) at 2.643Å). The four atoms in ring C are very closely coplanar ($\bar{\Delta}$ = 0.006Å, Plane C, Table 10b) and their plane is nearly parallel (5°) to the plane of C(2), C(3), C(5), C(6) in ring A (Plane B, Table 10b).

There is little difference between the details of ring B in the two compounds. Mean values of the Csp^3-Csp^3 bond lengths, bond and torsion angles are:-

A	1.535Å;	110.5°;	53.0°
F	1.534 ;	110.6 ;	52.3

The mean of the Csp^3-Csp^2 bond lengths do, however, differ (A 1.547, F 1.510Å), and so do the C = O bonds (A 1,210Å, F 1.227Å) but the latter is to be expected as a result of the hydrogen bonding.

These general conformational differences can be traced in Table 8 which gives a selection of the intramolecular nonbonded contacts, and this Table gives some idea of the general overcrowding and particularly the multiple contacts made by O(22).

There are certain features of ring C that require some attention. First, bond C(5)-C(9), which in the ketols is believed to rupture to form the keto-enol, has in A, VI a value 1.520(5)Å typical of Csp^3-Csp$^2_{ar}$, whereas in the ketol it is 1.564(4)Å. This is slightly, but just significantly longer than a normal Csp^3-Csp^3 bond and is to be expected in view of the general overcrowding in the ketol. The lengths of C(4)-C(7) show a similar difference, but they are not significantly different from standard values doubtless due to the presence of one hydrogen among the six terminating atoms. On the other hand, the lengths of the other two bonds, C(7)-C(8) and C(8)-C(9) (especially) are elongated. Thus

	F	A	C	D
C(7)-C(8)	1.577(5)Å	1.587(5)Å	1.68Å	1.63(3)Å
C(8)-C(9)	1.603(4)Å	1.615(5)Å	1.69Å	1.69(3)Å

The latter is consistently and severely stretched in all four structures, though no great significance should be attached to the lengths in C, D, because of the low accuracy of those studies. The bond length C(7)-C(8) can be regarded as slightly but significantly stretched in the two more accurate structures. The greater stretching for both bonds occurs in A and this is almost certainly a consequence of the strained sp^2 angles at C(4) and C(5) and the relative shortness of the three bonds flanking those angles compared with the less strained sp^3 angles in F.

An examination of the Newman diagrams about C(7)-C(8) (Fig. 4) shows that the longer bond (in A) is associated unexpectedly with the less eclipsed orientation. Likewise the difference between the two values of C(8)-C(9) does not correlate with the non-eclipsed angles in fig. 5. One is inclined, therefore, to attribute these large stretches mainly to the multiple contacts between C(8)-C(9) on the one hand and the ring B atoms C(10), C(11), C(13), C(14), on the other (see Table 8). In F there is additional contact between C(18) and O(21) because of the slewing of ring B. This is also revealed in a more marked flattening of ring B in F near the spiro junction (one of two torsion angles flanking C(9) = 45.5° in A, 42.3° in F). It is also noteworthy that the nonbonded distance C(7)-C(9) is the same in both structures (2.527 in A, 2.525Å in F,) so, as the bond angle at C(8) is limited by the ring constraints, the bonds C(7)-C(8) and C(8)-C(9) are necessarily long. A comparison of bond lengths, and valence angles for ring B is shown in Fig. 6.

A further interesting effect is that certain sp^3 angles are consistently small that might well have been expected to be splayed.

Thus:

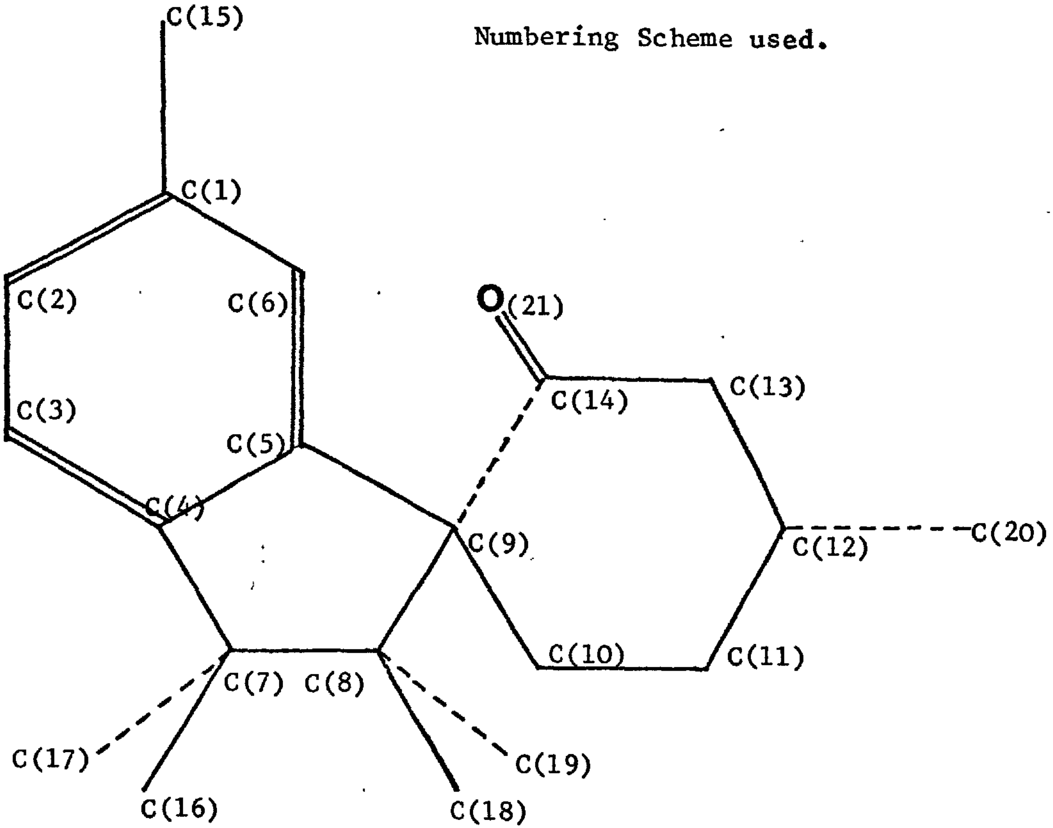
	A	F
C(16)-C(7)-C(17)	106.4°	105.5°
C(4)-C(7)-C(8)	102.3°	105.2°
C(18)-C(8)-C(19)	106.1°	103.4°
C(7)-C(8)-C(9)	104.2°	105.2°
C(10)-C(9)-C(14)	106.7°	107.3°
C(14)-C(9)-C(8)	101.6°	101.3°

i.e., in each case the angles included between, say, the gem-dimethyls and the angle between the other two bonds are small, whereas the other four angles at the same sp^3 atom show no such trend. The same trends were detected though less reliably in the two earlier studies.

A stereoscopic packing diagram of the bishydropulegone structure is shown in Fig. 7, drawn using the structure illustration program ORTEP (as referred to previously). Only Van der Waals contacts occur in the structure.

Fig. 1

Numbering Scheme used.



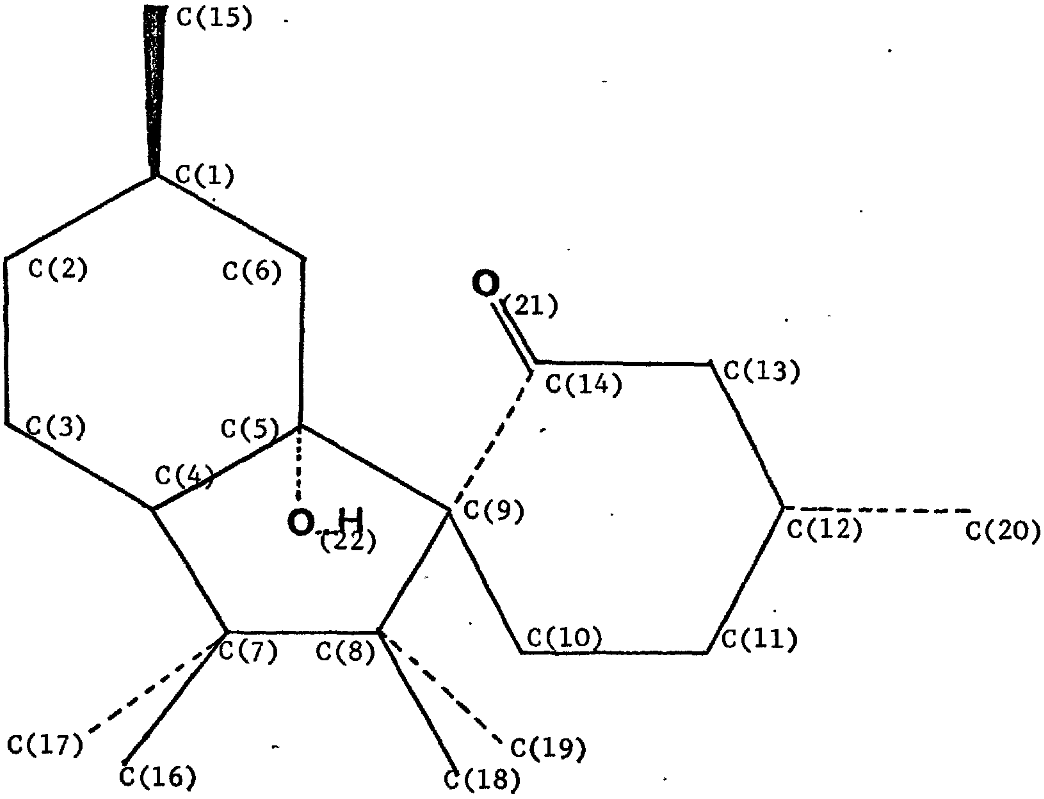
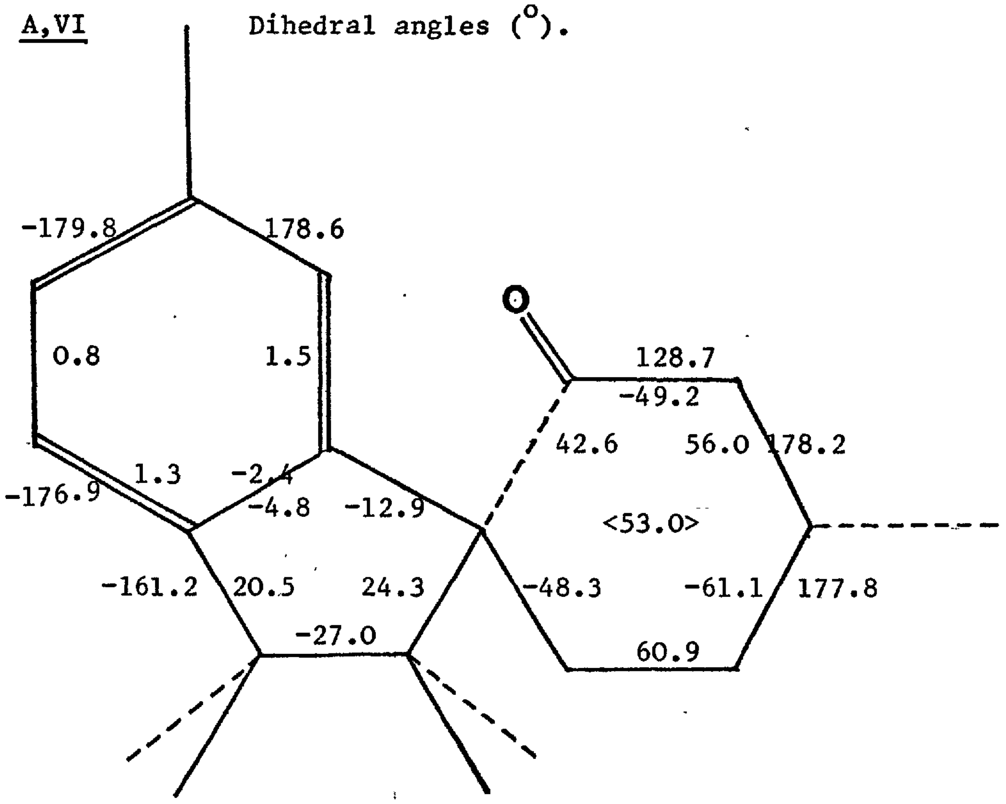


Fig. 2

Dihedral angles (°).

A,VI



F,VII

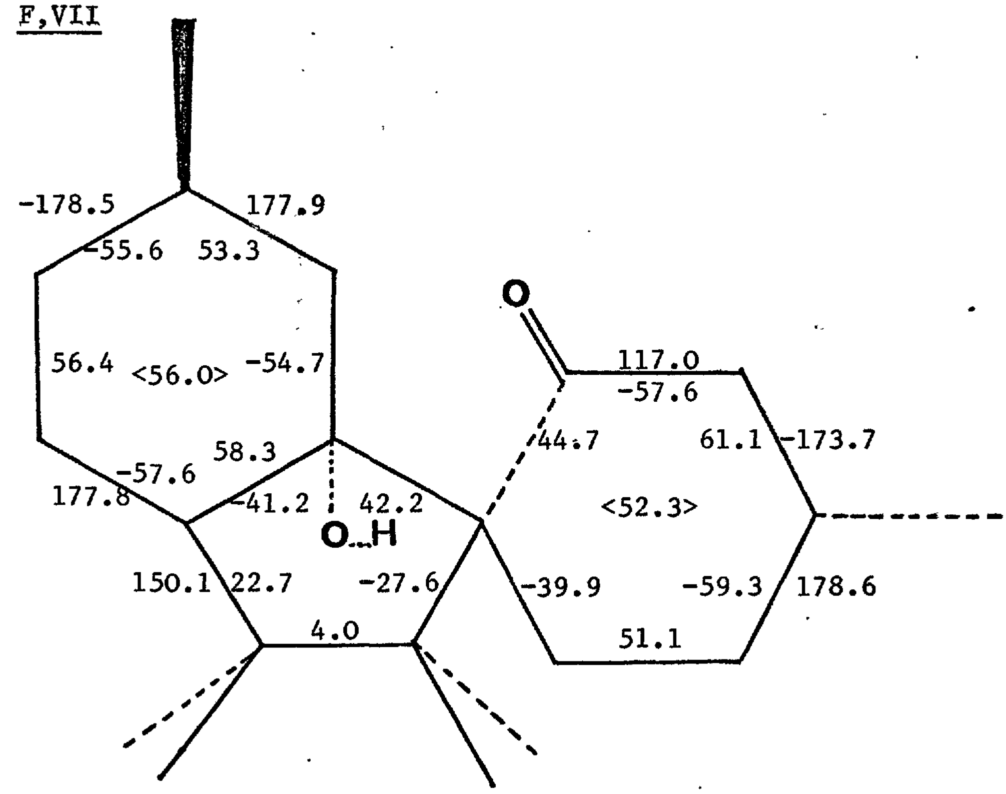


Fig. 3

Molecular Structure of the ketol bishydropulegone.

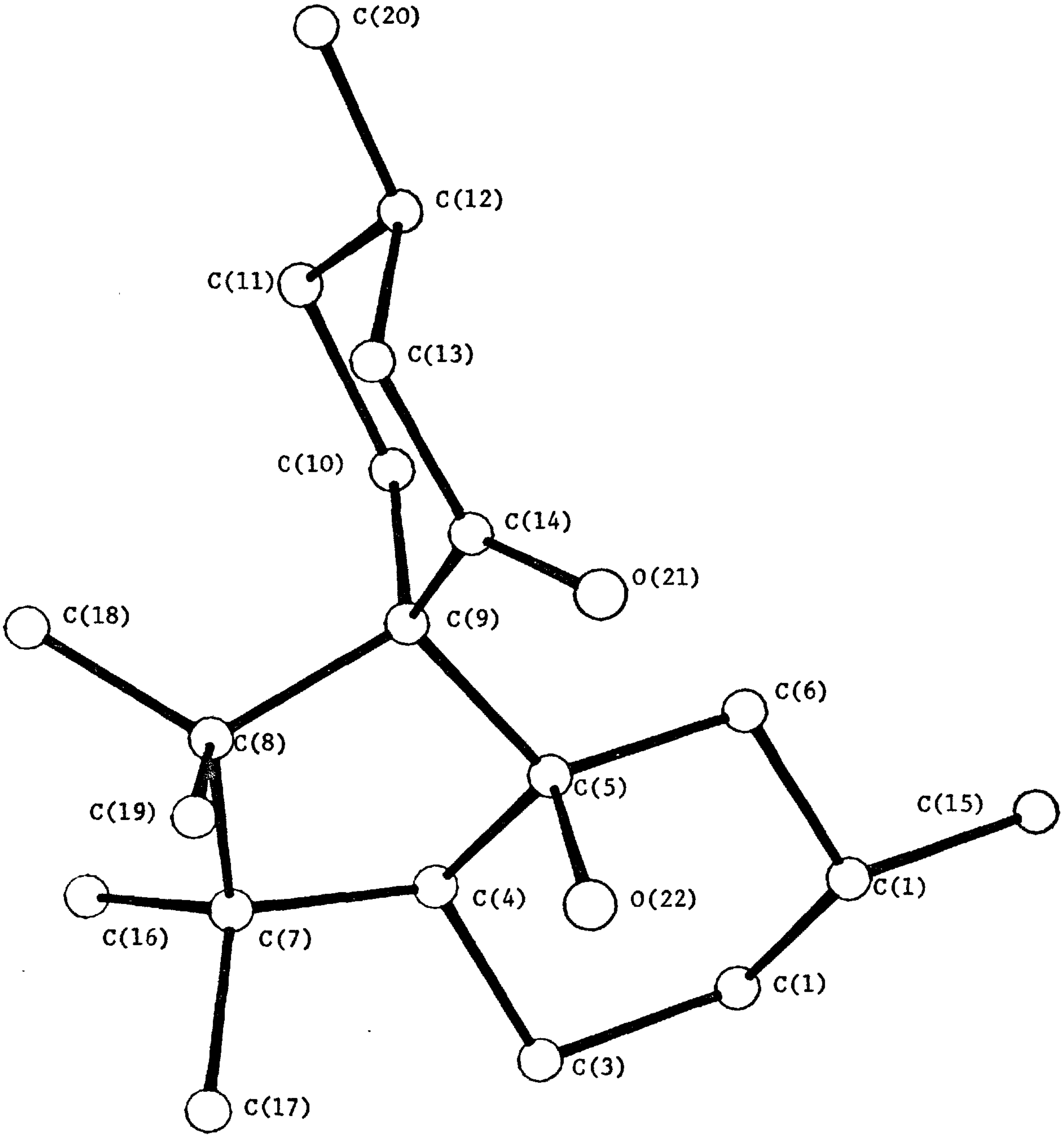
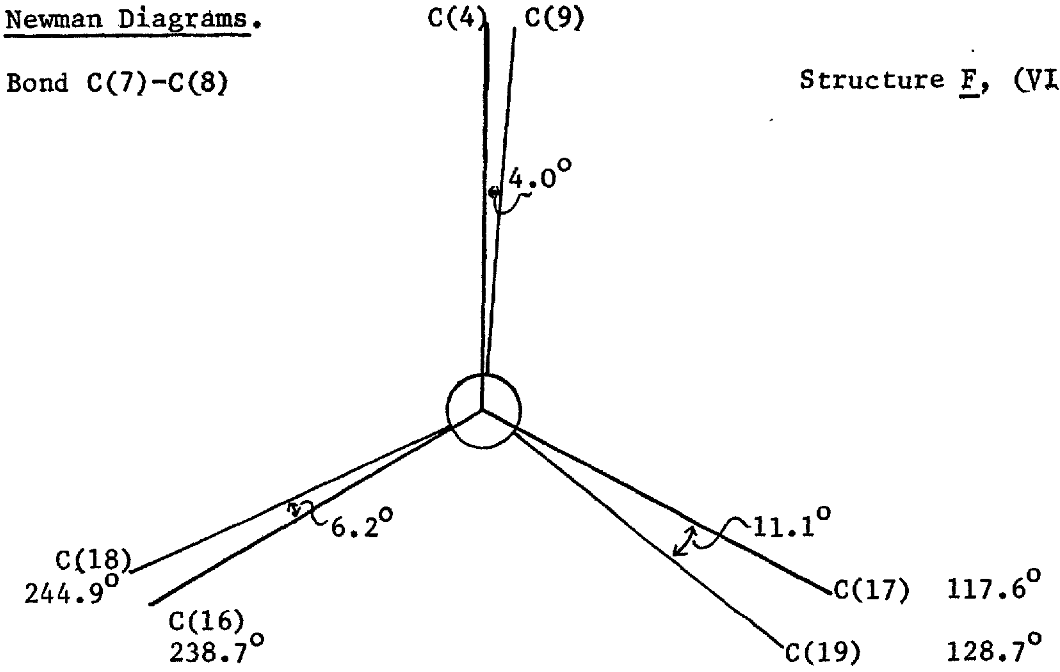


Fig. 4

Newman Diagrams.

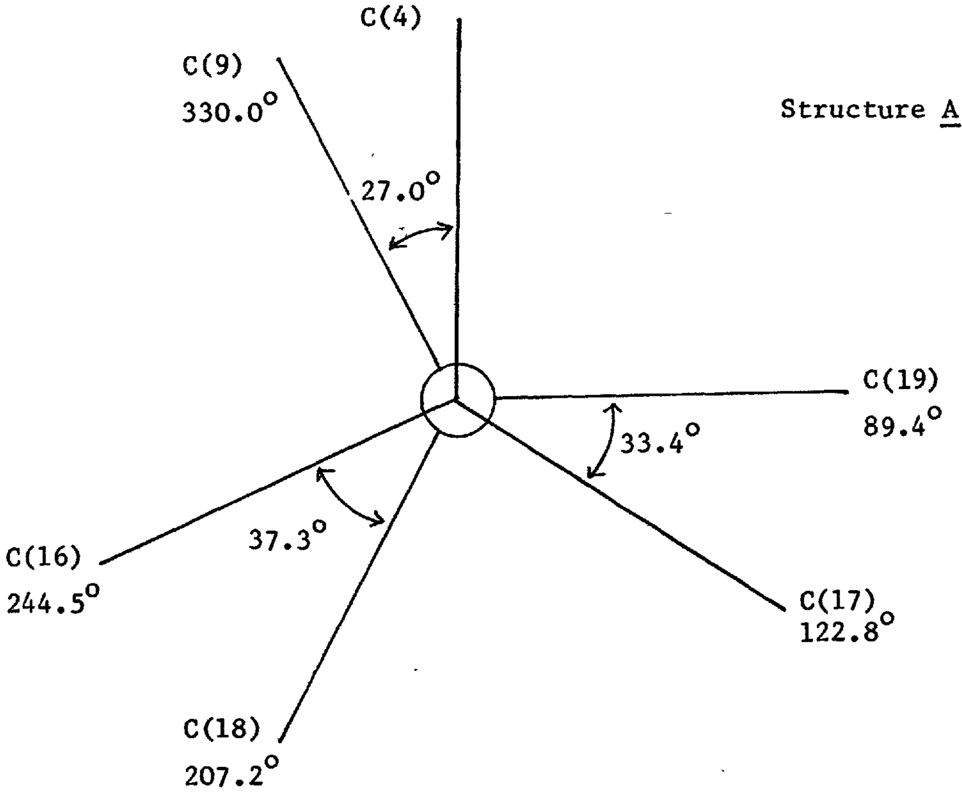
Bond C(7)-C(8)

Structure F, (VII)



Δ = <+7.1°>

Structure A, (VI)

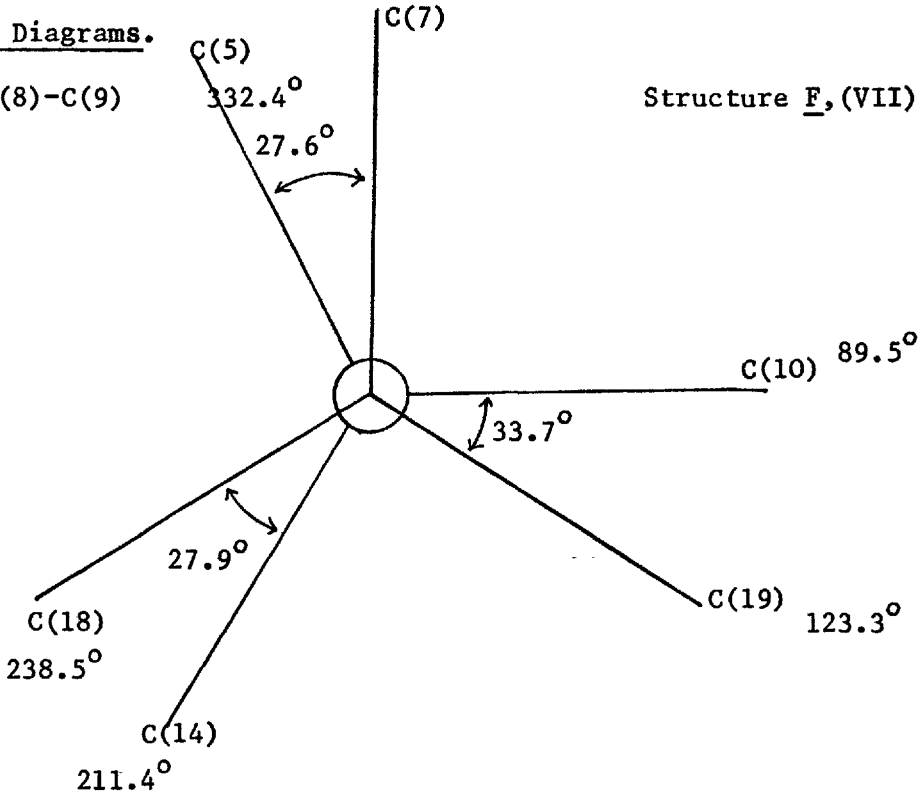


Δ = <39.7°>

Fig. 5

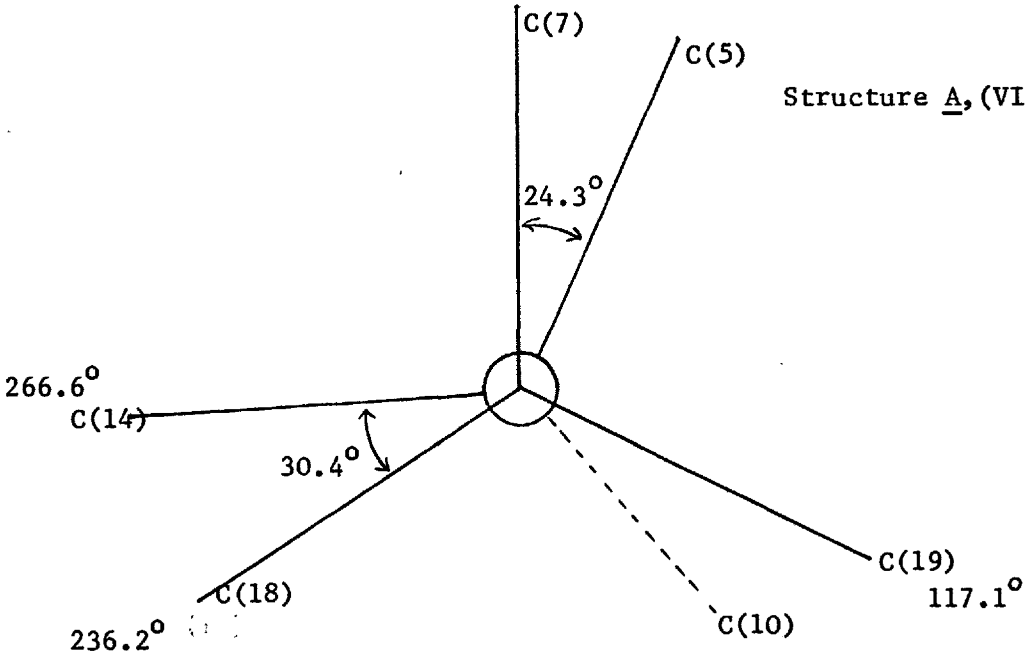
Newman Diagrams.

Bond C(8)-C(9)



Structure F,(VII)

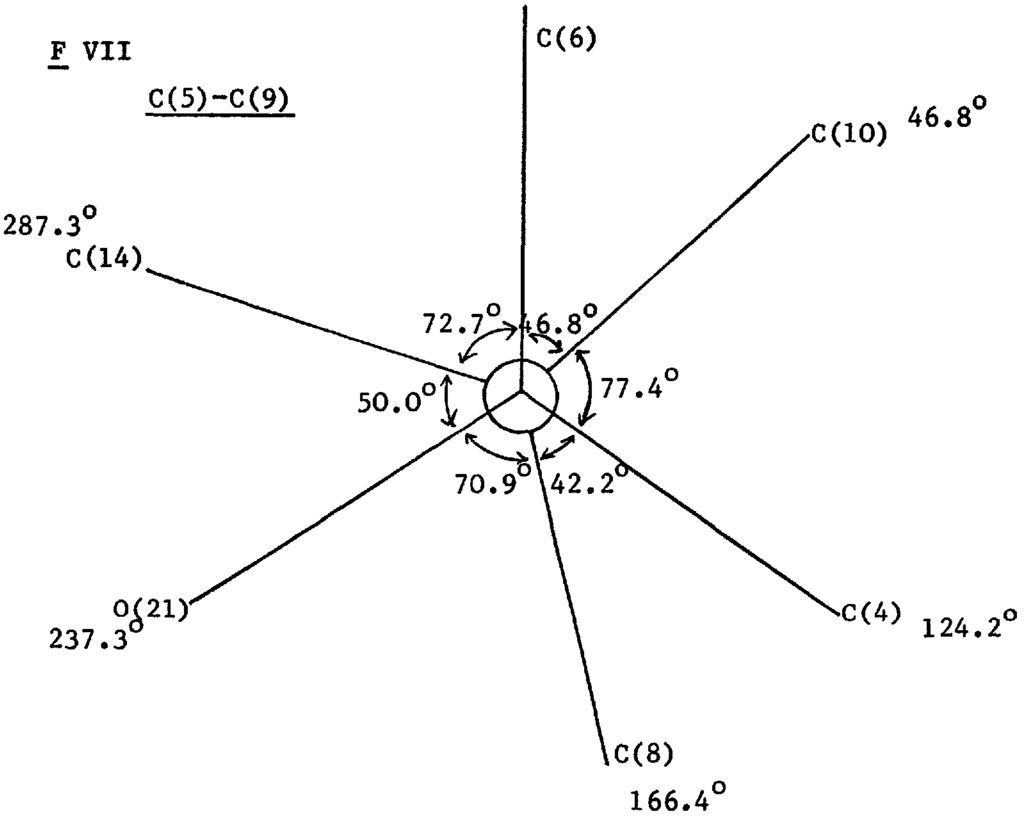
Δ = <-29.4>



Structure A,(VI)

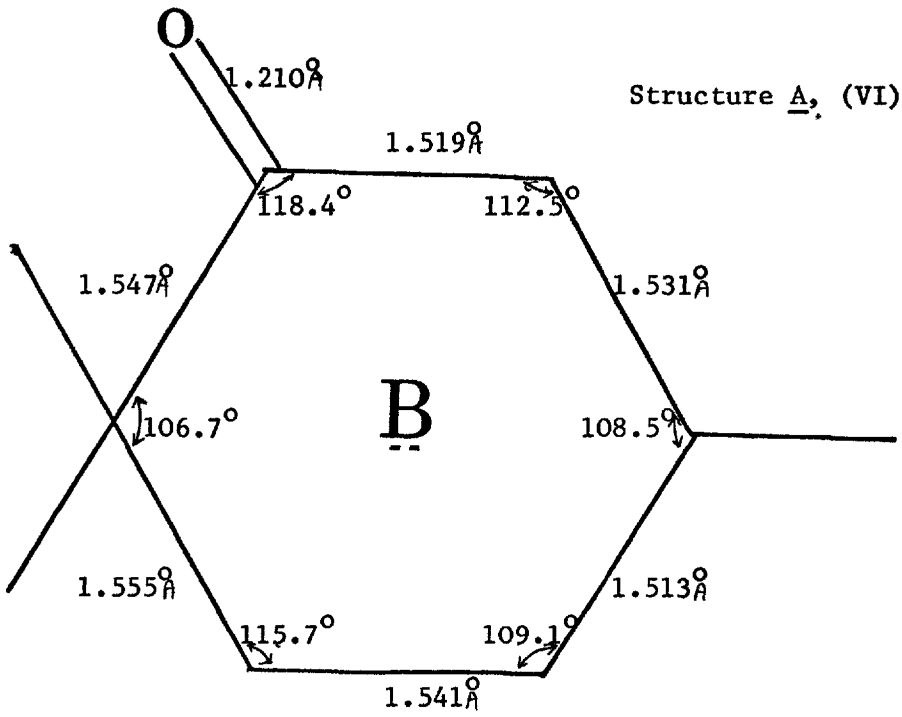
Incomplete data available

Fig. 5

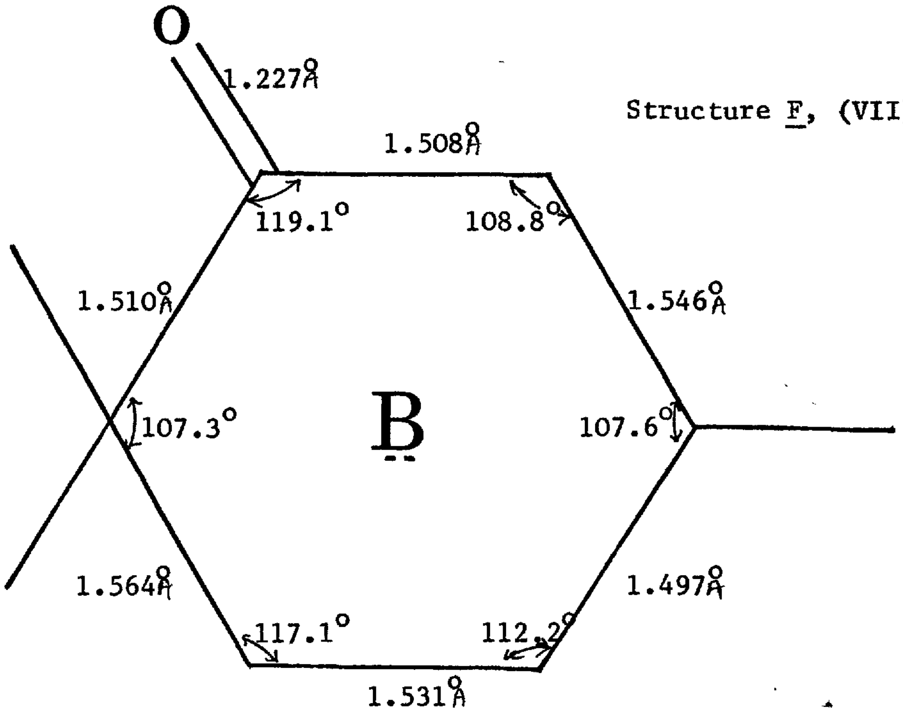


Average departure from eclipsed orientation = 46.3°

Fig. 6



Structure A, (VI)



Structure F, (VII)

Comparison of the bond lengths (Å) and valence angles (°) in ring B for both deshydropulegone and bishydropulegone.

Fig. 7

Stereoscopic packing diagram of the ketol bishydropulegone.

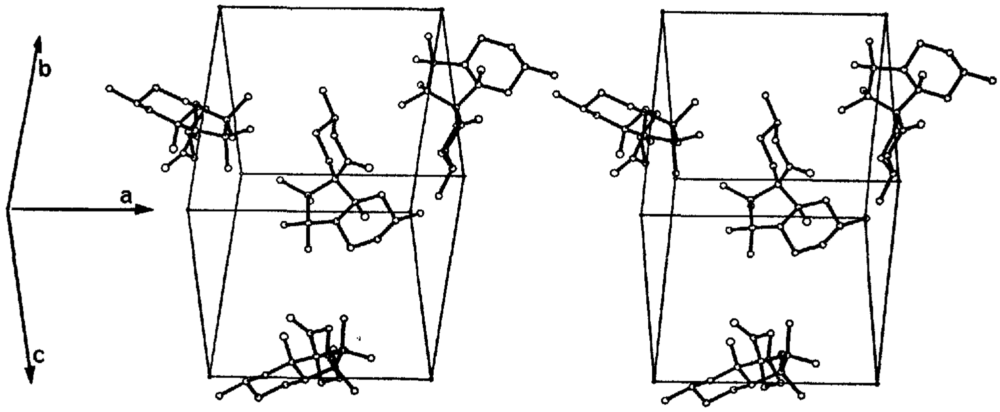


Table 3

Atomic co-ordinates of non-hydrogen positions with estimated standard deviations in parentheses.

ATOM			
C_1	0.8196(3)	0.5760(3)	0.4312(3)
C_2	0.7448(4)	0.6636(3)	0.4222(4)
C_3	0.6213(4)	0.6485(2)	0.3592(3)
C_4	0.5499(3)	0.5722(2)	0.4203(3)
C_5	0.6218(3)	0.4837(2)	0.4264(2)
C_6	0.7464(3)	0.4979(3)	0.4877(3)
C_7	0.4191(3)	0.5447(2)	0.2778(3)
C_8	0.4047(3)	0.4387(2)	0.4088(3)
C_9	0.5278(3)	0.4125(2)	0.4772(2)
C_{10}	0.5157(3)	0.4284(2)	0.6081(2)
C_{11}	0.4587(3)	0.3497(3)	0.6781(3)
C_{12}	0.5189(3)	0.2581(3)	0.6548(3)
C_{13}	0.5033(3)	0.2373(2)	0.5267(3)
C_{14}	0.5666(3)	0.3128(2)	0.4596(3)
C_{15}	0.9407(4)	0.5910(4)	0.4967(4)
C_{16}	0.4050(4)	0.5644(3)	0.2484(3)
C_{17}	0.3257(4)	0.6098(3)	0.4373(4)
C_{18}	0.3936(4)	0.3750(3)	0.3021(3)
C_{19}	0.2847(3)	0.4194(3)	0.4741(3)
C_{20}	0.4676(4)	0.1762(4)	0.7247(4)
O_{21}	0.6541(3)	0.2905(2)	0.3993(2)
O_{22}	0.6511(2)	0.4587(2)	0.3091(2)

Table 4.

Anisotropic thermal parameters

ATOM	$U_{11}x10^3$	$U_{22}x10^3$	$U_{33}x10^3$	$U_{12}x10^3$	$U_{13}x10^3$	$U_{23}x10^3$
C_1	61(2)	83(3)	50(2)	-29(2)	-2(2)	4(2)
C_2	92(3)	64(2)	72(3)	-34(2)	5(3)	3(2)
C_3	85(3)	48(2)	70(2)	-3(2)	-1(2)	11(2)
C_4	62(2)	46(2)	43(2)	1(2)	2(2)	-2(2)
C_5	47(3)	50(2)	33(2)	-2(2)	3(1)	-2(1)
C_6	49(2)	69(2)	45(2)	-11(2)	-2(2)	7(2)
C_7	55(2)	59(2)	50(2)	12(2)	-5(2)	1(2)
C_8	38(2)	61(2)	44(2)	4(2)	-2(1)	-5(2)
C_9	41(2)	50(2)	34(2)	-1(1)	3(1)	-1(1)
C_{10}	59(2)	63(2)	35(2)	-9(2)	1(2)	0(2)
C_{11}	57(2)	88(3)	42(2)	-16(2)	1(2)	10(2)
C_{12}	53(2)	80(3)	70(2)	-17(2)	-12(2)	34(2)
C_{13}	59(2)	49(2)	76(3)	-6(2)	1(2)	9(2)
C_{14}	46(2)	51(2)	56(2)	-1(2)	-2(2)	3(2)
C_{15}	69(3)	140(4)	72(3)	-49(3)	-7(2)	8(3)
C_{16}	94(3)	87(3)	63(2)	9(3)	-22(2)	22(2)
C_{17}	68(3)	77(3)	109(4)	30(2)	8(3)	-4(3)
C_{18}	63(2)	70(2)	57(2)	-8(2)	-9(2)	-14(2)
C_{19}	40(2)	86(3)	73(2)	6(2)	3(2)	9(2)
C_{20}	93(3)	113(4)	89(3)	-35(3)	-14(3)	54(3)
O_{21}	73(2)	60(1)	91(2)	15(1)	30(2)	2(1)
O_{22}	58(1)	62(1)	37(1)	0(1)	9(1)	-2(1)

Table 5

Fractional co-ordinates ($x10^3$) for the hydrogen atoms in the ketol, bishydropulegone (F,VII) with standard deviations in parentheses.

ATOM	x	y	z
H(11)	852(3)	548(2)	353(3)
H(21)	787(3)	718(2)	385(3)
H(22)	711(5)	695(3)	500(5)
H(31)	645(3)	621(2)	209(3)
H(32)	575(3)	700(3)	351(3)
H(42)	540(3)	595(2)	499(3)
H(61)	791(3)	427(2)	492(3)
H(62)	727(3)	522(2)	566(3)
H(101)	600(3)	439(2)	636(2)
H(102)	480(2)	491(2)	619(2)
H(111)	464(4)	368(3)	751(3)
H(112)	366(3)	336(2)	659(2)
H(12)	607(3)	256(2)	666(3)
H(131)	537(3)	173(2)	508(3)
H(132)	407(3)	234(2)	508(3)
H(151)	1004(4)	642(3)	456(4)
H(152)	917(4)	618(3)	562(3)
H(153)	1000(5)	531(4)	495(4)
H(161)	475(3)	533(2)	203(3)
H(162)	310(4)	525(3)	229(4)
H(163)	415(4)	636(2)	234(3)
H(171)	343(3)	689(2)	405(3)
H(172)	241(4)	597(3)	404(4)
H(173)	340(5)	589(4)	510(5)
H(181)	467(3)	388(2)	259(3)
H(182)	386(3)	306(2)	325(2)
H(183)	316(4)	368(3)	269(4)
H(191)	273(3)	345(2)	485(3)
H(192)	292(3)	469(2)	545(3)
H(193)	215(3)	448(2)	429(3)
H(201)	497(7)	80(5)	700(5)
H(202)	469(4)	199(3)	791(3)
H(203)	387(5)	161(3)	726(4)
H(221)	660(4)	396(3)	325(3)

Table 6

Comparison of bondlengths (Å) in the four structures.

		F	A	C	D
C(1)-C(2)		1.502(6)	1.375(5)	1.42	1.35(3)
C(2)-C(3)		1.546(6)	1.389(6)	1.39	1.38(3)
C(3)-C(4)	Ring A	1.523(5)	1.393(5)	1.40	1.42(3)
C(5)-C(6)		1.545(5)	1.396(5)	1.39	1.34(3)
C(6)-C(1)		1.528(5)	1.393(5)	1.40	1.44(3)
C(4)-C(5)		1.495(4)	1.380(5)	1.41	1.33(3)
C(4)-C(7)		1.555(5)	1.517(5)	1.46	1.42(3)
C(7)-C(8)	Ring C	1.577(5)	1.587(5)	1.68	1.63(3)
C(8)-C(9)		1.603(4)	1.615(5)	1.69	1.69(3)
C(9)-C(5)		1.564(4)	1.522(5)	1.48	1.51(3)
C(9)-C(10)		1.564(4)	1.555(5)	1.62	1.58(3)
C(10)1C(11)		1.531(5)	1.541(6)	1.68	0.61(3)
C(11)-C(12)	Ring B	1.497(6)	1.513(6)	1.59	1.53(3)
C(12)-C13)		1.546(5)	1.531(5)	1.60	1.52(4)
C(13)-C(14)		1.508(5)	1.519(5)	1.46	1.53(4)
C(14)-C(9)		1.510(5)	1.547(5)	1.48	1.45(3)
C(1)-C(15)		1.537(6)	1.503(6)	1.44	1.62(3)
C(7)-C(16)		1.557(5)	1.557(6)	1.60	1.57(4)
C(7)-C(17)		1.547(6)	1.531(6)	1.62	1.504(3)
C(8)-C(18)		1.560(5)	1.537(6)	1.67	1.62(3)
C(8)-C(19)		1.537(5)	1.546(6)	1.60	1.56(3)
C(12)-C(20)		1.541(7)	1.546(6)	1.52	1.50(4)
C(14)-O(21)		1.227(4)	1.210(4)	1.27	1.19(3)
C(5)-O(22)		1.462(4)			

Table 7

Comparison of bond angles (°) in the four structures.

Angle	F	A	C	D
C(2)-C(1)-C(15)	112.2(4)	120.4(3)	126	121(2)
C(6)-C(1)-C(15)	109.1(3)	120.3(3)	122	119(2)
C(2)-C(1)-C(6)	111.6(3)	119.3(3)	112	120(2)
C(1)-C(2)-C(3)	112.5(3)	121.6(4)	120	122(2)
C(2)-C(3)-C(4)	108.3(3)	118.7(3)	126	118(2)
C(3)-C(4)-C(5)	111.8(3)	120.4(3)	111	119(2)
C(3)-C(4)-C(7)	119.7(3)	127.8(3)	121	
C(5)-C(4)-C(7)	105.9(3)	111.7(3)	113	116(2)
C(4)-C(5)-C(6)	111.5(3)	120.1(3)	122	125(2)
C(4)-C(5)-C(9)	103.7(3)	112.6(3)	111	114(2)
C(6)-C(5)-C(9)	118.5(3)	127.3(3)	127	
C(1)-C(6)-C(5)	110.3(3)	119.7(3)	126	117(2)
C(4)-C(7)-C(8)	105.2(3)	102.3(3)	106	102(2)
C(4)-C(7)-C(16)	111.0(3)	108.0(3)		
C(4)-C(7)-C(17)	107.3(3)	113.0(3)		
C(8)-C(7)-C(16)	113.2(3)	111.9(3)		
C(8)-C(7)-C(17)	114.7(3)	115.1(8)		
C(16)-C(7)-C(17)	105.5(3)	106.4(3)	109	104(2)
C(7)-C(8)-C(9)	105.2(3)	104.2(3)	109	102(2)
C(7)-C(8)-C(18)	112.9(3)	112.4(3)		
C(7)-C(8)-C(19)	112.0(3)	109.8(3)		
C(9)-C(8)-C(18)	109.3(3)	115.5(3)		
C(9)-C(8)-C(19)	114.3(3)	108.8(3)		
C(18)-C(8)-C(19)	103.4(3)	106.1(3)	103	111(2)
C(5)-C(9)-C(8)	101.3(2)	101.6(3)	98	99(2)
C(5)-C(9)-C(10)	109.6(3)	109.0(3)		
C(5)-C(9)-C(14)	112.9(3)	110.2(3)		
C(8)-C(9)-C(10)	113.1(3)	116.9(3)	117	
C(8)-C(9)-C(14)	112.8(3)	112.3(3)	104	
C(10)-C(9)-C(14)	107.3(3)	106.7(3)	112	

Table 7 (Continued)

	F	A	C	D
C(9)-C(10)-C(11)	117.1(3)	115.7(3)	109	113(2)
C(10-C(11)-C(12)	112.2(3)	109.1(3)	109	110(2)
C(11)-C(12)-C(13)	107.6(3)	108.5(3)	111	108(2)
C(11)-C(12)-C(20)	114.7(3)	111.5(3)	109	114(2)
C(13)-C(12)-C(20)	109.5(3)	109.8(3)	120	113(2)
C(12)-C(13)-C(14)	108.8(3)	112.5(3)	111	108(2)
C(9)-C(14)-C(13)	119.1(3)	118.4(3)	129	117(2)
C(9)-C(14)-C(21)	122.9(3)	122.2(3)	117	124(2)
C(13)-C(14)-O(21)	117.9(3)	119.3(3)	113	119(2)
C(4)-C(5)-O(22)	106.1(2)			
C(6)-C(5)-O(22)	106.5(2)			
C(9)-C(5)-C(22)	109.9(2)			

Table 8

Selected intramolecular distances (Å)

C(3)-C(16)	2.94	3.32
C(3)-C(17)	3.38	3.09
C(16)-C(18)	2.80	2.90
C(17)-C(19)	2.81	2.88
C(18)-C(14)	2.79	2.96
C(19)-C(10)	2.96	2.89
C(15)-C(13)	> 3.50	3.27
C(19)-C(11)	3.21	3.50
C(19)-C(14)	3.42	
C(16)-C(14)	> 3.50	3.48
C(18)-C(10)	> 3.50	
C(6)-C(10)	3.04	3.04
C(6)-C(14)	3.32	3.30
C(6)-C(21)	3.32	3.34
C(18)-C(21)	3.28	3.32
O(22)-O(21)	2.64 (H-Bond)	
O(22)-C(1)	2.87	
O(22)-C(3)	2.81	
O(22)-C(7)	2.92	
O(22)-C(8)	2.93	
C(22)-C(14)	2.90	
O(22)-C(16)	3.15	
O(22)-C(18)	3.04	

Table 9

Comparison of torsion angles (^{o}) other than those shown in Fig. 2

	F	A
C(2)[C(3)-C(4)]C(7)	177.8	-176.9
C(7)[C(4)-C(5)]C(6)	-169.8	
C(3)[C(4)-C(5)]C(9)	-173.1	
C(3)[C(4)-C(7)]C(8)	150.1	-161.2
C(3)[C(4)-C(7)]C(16)	27.4	
C(3)[C(4)-C(7)]C(17)	-87.4	
C(5)[C(4)-C(7)]C(16)	-100.0	-97.8
C(5)[C(4)-C(7)]C(17)	145.2	144.5
C(4)[C(7)-C(8)]C(18)	-115.1	-152.8
C(4)[C(7)-C(8)]C(19)	128.7	89.4
C(16)[C(7)-C(8)]C(9)	125.3	89.5
C(16)[C(7)-C(8)]C(18)	6.2	-37.3
C(16)[C(7)-C(8)]C(19)	-110.0	-155.1
C(17)[C(7)-C(8)]C(9)	-113.6	-149.8
C(17)[C(7)-C(8)]C(18)	127.3	84.4
C(17)[C(7)-C(8)]C(19)	11.1	-33.4
C(7)[C(8)-C(9)]C(10)	89.5	
C(7)[C(8)-C(9)]C(14)	-148.6	-93.4
C(18)[C(8)-C(9)]C(5)	93.9	148.1
C(18)[C(8)-C(9)]C(10)	-149.0	
C(18)[C(8)-C(9)]C(14)	-27.0	30.3
C(19)[C(8)-C(9)]C(5)	-150.9	-92.8
C(19)[C(8)-C(9)]C(10)	-33.7	
C(19)[C(8)-C(9)]C(14)	88.2	149.5
C(4)[C(5)-C(9)]C(10)	-77.4	
C(4)[C(5)-C(9)]C(14)	163.1	
C(6)[C(5)-C(9)]C(8)	166.4	
C(6)[C(5)-C(9)]C(10)	46.8	42.2
C(6)[C(5)-C(9)]C(14)	-72.2	
C(5)[C(9)-C(10)]C(11)	-162.8	-167.3
C(8)[C(9)-C(10)]C(11)	85.1	
C(5)[C(9)-C(14)]C(13)	165.5	
C(8)[C(9)-C(14)]C(13)	-80.4	-86.7

Table 9 (Continued).

	F	A
C(5)[C(9)-C(14)]O(21)	-8.8	
C(8)[C(9)-C(14)]O(21)	105.2	
C(10)[C(9)-C(14)]O(21)	-129.7	-135.1
C(1)[C(6)-C(5)]O(21)	60.6	
C(3)[C(4)-C(5)] O(21)	-57.3	
C( )[C(4)-C(5)] O(21)	74.7	
C(8)[C(9)-C(5)] O(21)	-70.9	
C(10)[C(9)-C(5)] O(21)	169.5	
C(14)[C(9)-C(5)] O(21)	50.0	

Table 10a

Mean planes through various groups of atoms of the deshydrobispulegone (A) structure.
The displacements (Å) of atoms from their planes.
Atoms which do not define the plane are marked by an asterisk(*)

Plane A		B		C	
C(1)	-0,008	C(4)	0,082	C(4)	0.025
C(2)	0,009	C(5)	0.034	C(5)	-0,025
C(3)	0,000	C(7)	-0.160	C(7)	-0,013
C(4)	-0,011	C(8)	0.173	C(9)	0.014
C(5)	0,012	C(9)	-0.130	C(8)*	0.449
C(6)	-0,002				

D		E		F	
C(1)	0,032	C(9)	0.160	C(9)	0.314
C(2)	0,079	C(10)	-0,231	C(10)	-0.285
C(3)	0,029	C(11)	0.290	C(11)	0.133
C(4)	-0,055	C(12)	-0;272	C(12)	-0.324
C(5)	-0,061	C(13)	0.211	C(13)	0.358
C(6)	-0,034	C(14)	-0.157	C(14)	0.096
C(7)	-0.183			C(20)	0,021
C(8)	0.271			C(21)	-0.312
C(9)	-0.078				

G	
C(10)	-0.038
C(11)	0.038
C(13)	-0.039
C(14)	0.039
C(9)*	0.589
C(12)*	-0.710

Table 10b

Mean planes through various groups of atoms of bishydropulegone (F) structure.

The displacements (Å) of atoms from their planes.

Atoms which do not define the plane are marked by an asterisk(*)

A

C(1)	-0.223
C(2)	0.234
C(3)	-0.241
C(4)	0.251
C(5)	-0.236
C(6)	0.216
C(15)*	0.285
C(7)*	-0.039
C(9)*	0.217
O(21)*	-1.695
O(22)*	-1.459

B

C(2)	0.006
C(3)	-0.006
C(5)	0.006
C(6)	-0.006
C(1)*	-0.645
C(4)*	0.674
C(15)*	-0.595
C(7)*	0.852
C(9)*	0.726
O(21)*	-1.390
O(22)*	-1.180

C

C(4)	-0.0163
C(7)	0.025
C(8)	-0.024
C(9)	0.016
C(5)*	-0.634
C(3)*	-0.649
C(6)*	-0.509
C(10)*	1.469
C(14)*	-0.741
C(16)*	-1.152
C(17)*	1.313
C(18)*	-1.321
C(19)*	1.101

D

C(9)	-0.131
C(10)	0.154
C(11)	-0.242
C(12)	0.294
C(13)	-0.272
C(14)	0.198
O(21)*	0.645
O(22)*	0.919
C(20)*	-0.043
C(5)*	0.710
C(8)*	-1.624

Table 10b (continued).

E	
C(10)	-0.021
C(11)	0.021
C(13)	-0.021
C(14)	0.021
C(9)*	0.730
C(5)*	-0.109
C(12)*	0.836
O(21)*	-0.366
O(22)*	0.602

F	
C(9)	0.009
C(14)	-0.029
C(13)	0.009
C(21)	0.011
O(22)*	-0.553
C(5)*	0.325
H(221)*	-0.377

G	
C(15)	
C(1)	
C(4)	
C(2)*	1.250
C(3)*	1.242
C(15)*	-1.253
C(6)*	-1.253
C(7)*	-0.243
O(22)*	-1.244

H	
C(5)	
C(6)	
O(22)	
C(4)*	1.257
C(9)*	-1.134
C(7)*	1.016
C(8)*	-0.551
O(21)*	-2.611
C(16)*	1.679
C(17)*	1.754
C(18)*	-1.117
C(19)*	-1.004

I	
C(9)	
C(12)	
C(20)	
C(13)*	-1.134
C(14)*	-1.220
C(11)*	1.277
C(10)*	1.224
C(4)*	0.943
C(5)*	-0.122
C(7)*	0.888
C(8)*	0.208
O(21)*	-2.256
O(22)*	-1.394

Table 10b (continued).

(i) Equations of the planes may be expressed in direct space where $Px + Qy + Rz = S$.

Plane	P	Q	R	S
A	-2.26	4.42	10.93	5.63
B	-5.34	3.88	9.74	2.71
C	-4.47	4.05	10.20	4.16
D	10.45	0.23	3.11	7.23
E	9.50	-2.82	5.17	6.86
F	7.00	1.54	8.90	8.57
G	-0.07	13.90	-3.06	6.63
H	-0.11	13.92	-3.00	5.39
I	-4.07	9.26	7.85	5.42

(ii) Angles between planes ($^{\circ}$)

Plane A	plane B	17.46	plane C	plane E	87.91
A	C	12.35	D	E	16.57
A	G	86.77	D	I	79.86
B	C	5.12	E	F	28.70
B	F	70.32	E	I	80.63
B	G	87.23			
B	H	86.85			

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APPENDIX II

Comparison of observed and calculated structure amplitudes

The data are listed in groups of constant _h_ and _k_ and list values of _ℓ_, $10|F_o|$ and $10|F_c|$. Reflections marked "*" were classified as unobserved.

0,0,L

4	177	177
6	82	78
8	61	54
10	141	149
12	69	82

0,1,L

3	305	296
4	568	568
5	457	464
6	435	435
7	17	23
8	35	38
9	28	25
10	33	36
11	25	27
12	35	36
13	72	76

0,2,L

1	274	264
2	352	342
3	472	469
4	148	149
5	205	194
6	174	159
7	278	268
8	34	25
9	19	17
10	139	145
11	151	162
12	44	46
13	16	19

0,3,L

1	456	480
2	269	260
3	271	268
4	212	208
5	318	313
6	9*	12
7	79	80
8	47	39
9	70	83
10	127	126
11	68	73
12	52	53
13	87	95

0,4,L

0	247	250
1	257	260
2	155	163
3	156	154
4	195	177
5	238	239
6	43	31
7	327	327
8	59	64
9	86	84
10	11*	3
11	21	18
12	17	13
13	37	38

0,5,L

1	490	508
2	119	116
3	13	8
4	79	80
5	85	91
6	142	148
7	42	40
8	59	64
9	28	17
10	33	31
11	25	25
12	10*	15
13	9*	3

0,6,L

0	356	365
1	172	173
2	332	336
3	232	229
4	47	48
5	116	119
6	68	53
7	110	102
8	94	89
9	69	71
10	16	17
11	11*	10
12	13	15

0,7,L

1	74	84
2	222	217
3	15	12
4	241	240
5	82	73
6	82	80
7	184	189
8	16	6
9	34	31
10	17	19
11	42	42
12	36	36

0,8,L

0	296	295
1	53	55
2	70	70
3	114	120
4	86	92
5	52	56
6	240	236
7	27	18
8	31	29
9	155	148
10	22	27
11	50	50
12	9*	6

0,9,L

1	9*	13
2	78	72
3	102	106
4	41	34
5	119	129
6	30	24
7	120	125
8	47	40
9	85	86
10	40	38
11	64	65

0,10,L

0	88	104
1	127	133
2	221	233
3	115	119
4	179	175
5	38	36
6	38	47
7	77	75
8	24	27
9	106	114
10	10*	2
11	25	28

0,11,L

1	35	36
2	38	46
3	41	26
4	123	124
5	84	83
6	125	126
7	102	108
8	51	49
9	21	26
10	10	10

0,12,L

0	108	103
1	158	148
2	197	198
3	33	40
4	72	78
5	21	22
6	10*	11
7	10*	1
8	24	30
9	9*	10

0,13,L

1	24	31
2	19	21
3	29	44
4	121	122
5	35	40
6	10*	17
7	34	34
8	11	14

0,14,L

0	79	71
1	47	49
2	50	44
3	11*	4
4	50	48
5	42	47
6	48	42
7	9*	7

0,15,L

1	20	11
2	16	13
3	38	34
4	20	13
5	30	25
6	9*	6

0,16,L

0	36	26
1	10*	13
2	17	11
3	53	33
4	22	17

1,0,L

1	412	442
2	541	581
3	453	452
4	81	72
5	350	338
6	134	118
7	78	70
8	35	41
9	74	71
10	84	95
11	21	19
12	10*	6
13	10*	1

1,1,L

2	450	467
3	471	465
4	255	249
5	270	264
6	169	158
7	109	111
8	125	128
9	20	12
10	56	58
11	79	84
12	50	57
13	48	54

1,2,L

2	420	412
3	120	110
4	236	223
5	137	133
6	328	321
7	105	103
8	118	121
9	31	30
10	127	134
11	42	39
12	10*	7
13	46	53

1,3,L

0	9*	6
1	58	59
2	57	56
3	384	381
4	306	289
5	180	173
6	394	377
7	108	107
8	203	196
9	98	106
10	59	64
11	17	14
12	31	32
13	22	23

1,4,L

0	273	280
1	160	162
2	213	214
3	310	303
4	158	152
5	150	156

1,4,L

7	110	115
8	59	62
9	142	147
10	104	108
11	21	16
12	44	45
13	27	31

1,5,L

0	625	671
1	264	280
2	218	227
3	132	123
4	197	178
5	100	98
6	161	151
7	21	21
8	48	52
9	83	85
10	83	83
11	24	23
12	11	11
13	17	14

1,6,L

0	70	70
1	173	177
2	310	317
3	334	323
4	246	242
5	153	150
6	62	63
7	35	31
8	91	87
9	49	47
10	31	31
11	22	24
12	14	13

1,7,L

0	28	14
1	271	280
2	151	152
3	98	101
4	135	129
5	182	180
6	90	91
7	88	83
8	90	88
9	78	77
10	66	64
11	36	38
12	18	21

1,8,L

0	100	102
1	109	114
2	101	97
3	155	158
4	45	50
5	123	125
6	73	75
7	57	60
8	133	135
9	49	48
10	41	42
11	13	10
12	41	40

1,9,L

0	14	19
1	108	113
2	118	121
3	52	46
4	52	54
5	80	89
6	14	16
7	74	78
8	197	200
9	58	55
10	69	68
11	27	28

1,10,L

0	11	7
1	173	179
2	188	198
3	97	95
4	93	93
5	112	109
6	74	79
7	126	126
8	70	72
9	32	32
10	26	27
11	33	34

1,11,L

0	52	53
1	117	123
2	205	209
3	299	309
4	42	46
5	63	68
6	31	32
7	22	17
8	25	25
9	44	42
10	10	11

1,12,L

0	64	66
1	171	175
2	74	81
3	14	10
4	76	89
5	75	76
6	11*	5
7	40	37
8	14	10
9	28	27

1,13,L

0	52	60
1	11*	5
2	52	57
3	35	40
4	49	52
5	52	54
6	27	27
7	29	26
8	28	26

1,14,L

0	10*	3
1	42	36
2	45	46
3	27	18
4	41	40
5	21	20
6	32	30
7	32	24

1,15,L

0	10*	5
1	76	60
2	46	38
3	18	15
4	48	44
5	26	25
6	11	5

1,16,L

0	79	49
1	10*	6
2	80	61
3	22	20
4	17	15

2,0,L

1	26	34
2	377	368
3	231	225
4	29	31
5	97	99
6	129	127
7	25	23
8	133	136
9	46	53
10	18	2
11	13	6
12	17	17
13	9*	2

2,1,L

0	258	265
2	526	524
3	143	142
4	65	41
5	180	172
6	133	131
7	215	221
8	22	24
9	106	107
10	36	39
11	16	23
12	34	38
13	10	9

2,2,L

0	362	381
1	334	334
2	114	108
3	125	117
4	441	424
5	402	388
6	334	328
7	160	153
8	99	91
9	70	70
10	76	76
11	57	56
12	10*	17
13	31	35

2,3,L

0	196	207
1	249	246
2	203	188
3	361	354
4	260	253
5	304	286
6	149	137
7	194	197
8	73	64
9	166	167
10	133	131
11	20	22
12	19	19
13	29	31

2,4,L

0	58	67
1	479	492
2	100	89
3	133	139
4	366	344
5	196	190
6	117	116
7	224	222
8	51	58
9	49	47
10	94	96
11	83	81
12	25	27
13	9*	8

2,5,L

1	307	308
2	450	457
3	340	333
4	145	137
5	194	191
6	121	115
7	117	116
8	32	19
9	73	77
10	21	19
11	39	39
12	39	44
13	10	10

2,6,L

1	294	314
2	468	467
3	206	211
4	100	93
5	97	88
6	39	39
7	68	69
8	126	127
9	46	45
10	67	62
11	24	22
12	45	50

2,7,L

0	170	168
1	158	150
2	125	124
3	62	67
4	79	70
5	23	18
6	71	70
7	93	91
8	97	92
9	46	44

```
        2,7,L

  10      28       33
  11      60       62
  12      36       42

        2,8,L

   0      93       99
   1      26       34
   2      65       58
   3      30       34
   4      88       88
   5     121      114
   6     106      104
   7     102       99
   8      70       72
   9      60       54
  10      67       65
  11      25       27
  12      21       21

        2,9,L

   0      59       62
   1      32       32
   2      45       47
   3     120      118
   4      26       28
   5      53       55
   6      50       45
   7     140      142
   8      38       45
   9      28       30
  10      26       24
  11     - 25      28

       2,10,L

   0     140      144
   1      82       78
   2     125      130
   3      52       55
   4     102      108
   5     105      111
   6      51       51
   7      48       52
   8      77       73
   9      19       15
  10      34       34

       2,11,L

   0     173      168
   1      88       88
   2     114      114
   3      82       89
   4     119      124
   5      49       47
   6      59       62
```

```
   7      25       26
   8      40       39
   9      20       17
  10      26       27

       2,12,L

   0      73       65
   1      74       75
   2     102      105
   3      28       19
   4      83       80
   5      38       41
   6      19       17
   7      25       19
   8      10*       1
   9       9*       7

       2,13,L

   0      41       41
   1      95       83
   2      54       52
   3      27       34
   4      13        6
   5      36       36
   6      23       23
   7      31       31
   8      44       41

       2,14,L

   0      11        2
   1      27       26
   2      31       30
   3      38       36
   4      44       46
   5      60       64
   6      52       47
   7      24       21

       2,15,L

   0      25       18
   1      33       25
   2      23       17
   3      36       35
   4      11       11
   5       9*       6
   6      49       45

       2,16,L

   0      53       41
   1      34       23
   2      16       11
   3      60       45

        3,0,L
```

```
   2      31       33
   3     105      110
   4      38       36
   5     110      109
   6     227      224
   7      28       28
   8     111      114
   9      81       88
  10      11*      13
  11      52       56
  12      24       26
  13      31       34

        3,1,L

   0       8*       9
   1     234      230
   2     602      616
   3     133      128
   4      97      101
   5     362      371
   6      66       65
   7      88       86
   8      89       98
   9      47       51
  10      52       51
  11      21       20
  12      35       38
  13      19       18

        3,2,L

   0      15       15
   1     125      131
   2     206      192
   3     357      339
   4      47       31
   5      83       92
   6     152      146
   7      16       13
   8     129      128
   9      87       87
  10     111      113
  11      78       83
  12      37       41
  13      29       34

        3,3,L

   0     184      184
   1     169      167
   2     211      207
   3     205      196
   4     142      139
   5     191      193
   6      89       83
   7      84       89
   8     278      281
   9     145      149
  10     113      115
```

```
  11      51       51
  12      42       45
  13      12       15

        3,4,L

   0      33       34
   1     140      141
   2     124      121
   3     282      264
   4     106      104
   5     103      103
   6      80       86
   7     154      150
   8     278      280
   9      18       17
  10      82       83
  11      31       27
  12      37       42
  13      43       50

        3,5,L

   0      65       67
   1     275      291
   2     610      601
   3     194      188
   4     180      166
   5     173      170
   6     168      168
   7      71       72
   8     102      101
   9     104      104
  10      59       62
  11      48       53
  12      24       25

        3,6,L

   1     231      240
   2     146      136
   3     149      138
   4     160      146
   5     111       96
   6      88       84
   7      29       20
   8      78       77
   9      63       64
  10      39       36
  11      43       45
  12      40       42

        3,7,L

   0     237      240
   1     249      255
   2     178      178
   3      35       28
   4     137      126
   5      86       79
```

```
   6     144      149
   7      47       45
   8      73       74
   9      40       36
  10      63       64
  11      16       12
  12      21       22

        3,8,L

   0      12        4
   1      63       62
   2      55       62
   3     124      125
   4      91       98
   5      82       82
   6     161      165
   7     128      136
   8      92       85
   9      18       22
  10      58       55
  11      50       48

        3,9,L

   0      71       68
   1     140      142
   2      21       19
   3      92       97
   4     132      137
   5     122      128
   6     157      159
   7      76       82
   8      83       84
   9     112      108
  10      11       12
  11      26       24

       3,10,L

   0      87       83
   1      73       68
   2      87       91
   3      57       68
   4     123      126
   5     125      122
   6      43       46
   7      92       96
   8      31       28
   9      33       35
  10      44       45

       3,11,L

   0     122      125
   1      83       88
   2      45       54
   3     114      116
   4      51       51
```

```
      3,11,L

  5     38     42
  6     34     39
  7     43     42
  8     14     14
  9     20     21
 10     10      6

      3,12,L

  0     13     18
  1     94     93
  2    112    106
  3     13     14
  4     39     45
  5     36     35
  6     12     14
  7     49     48
  8     11      9
  9     48     50

      3,13,L

  0     11*    11
  1     61     54
  2     37     37
  3     85     90
  4     67     66
  5     45     40
  6     11      7
  7     57     52
  8     26     25

      3,14,L

  0     25     20
  1     33     32
  2     48     49
  3     10*    11
  4     22     24
  5     39     35
  6     56     51
  7     66     59

      3,15,L

  0     14      8
  1     48     35
  2     32     27
  3     10*     9
  4     75     66
  5     11     11

      3,16,L

  0      9*     1
  1     17     11
  2     40     27
  3     41     31

      4,0,L

  0     58     61
  1    269    275
  2    574    571
  3    463    456
  4    379    372
  5     98    103
  6    208    202
  7     26     24
  8    129    130
  9    103    105
 10     11*     2
 11     89     93
 12     12      9
 13     33     34

      4,1,L

  0    150    161
  1    236    235
  2    544    544
  3    298    294
  4    262    257
  5    265    261
  6    180    183
  7    222    230
  8    214    217
  9     21     18
 10    112    117
 11     80     81
 12     37     41
 13      9*     1

      4,2,L

  0    201    205
  1    146    145
  2    409    379
  3    234    213
  4    109    100
  5    108    109
  6     76     76
  7    113    109
  8    262    261
  9    225    227
 10    104    108
 11     14     15
 12     50     53
 13     34     43

      4,3,L

  0     50     51
  1    136    133
  2    110    107
  3    166    162
  4    261    245
  5    130    116
  6    123    125
  7    151    154
  8    293    294
  9     81     82
 10     61     54
 11     48     46
 12     33     37

      4,4,L

  0     33     35
  1    194    192
  2    206    198
  3    152    142
  4    148    143
  5    144    143
  6    232    227
  7     57     55
  8     99     98
  9    111    106
 10    134    134
 11     21     22
 12     17     17

      4,5,L

  0     88     92
  1    131    119
  2    171    176
  3    219    225
  4     96     86
  5    116    102
  6    127    125
  7     75     73
  8    118    118
  9     44     47
 10     40     41
 11     39     39
 12     30     30

      4,6,L

  0    133    132
  1    240    240
  2    174    168
  3    173    167
  4    110    106
  5     48     50
  6     68     61
  7     64     59
  8     69     69
  9     77     74
 10     76     75
 11     13     14
 12     36     36

      4,7,L

  0     15     25
  1    236    243
  2    126    123
  3     82     86
  4     39     31
  5    114    109
  6    117    114
  7    103    104
  8    100     96
  9     45     47
 10     36     39
 11     28     23

      4,8,L

  0     43     44
  1     64     65
  2    119    121
  3    112    110
  4     85     86
  5    141    148
  6     95     97
  7    126    121
  8     67     65
  9     43     42
 10     54     50
 11     10      7

      4,9,L

  0     42     38
  1     58     58
  2     19     20
  3     44     49
  4    132    135
  5     57     56
  6    127    132
  7     86     86
  8     50     48
  9     16     17
 10     50     45

      4,10,L

  0     36     38
  1    101    103
  2     33     35
  3     79     82
  4     53     50
  5     33     29
  6     81     81
  7     46     50
  8     82     86
  9     32     29
 10     33     30

      4,11,L

  0     31     29
  1    119    114
  2    111    115
  3    106    106
  4     46     49
  5     37     45
  6     28     33
  7     40     41
  8     54     55
  9     13     12

      4,12,L

  0    266    250
  1    112    114
  2     66     69
  3     27     24
  4     68     66
  5     32     32
  6     40     36
  7     17     19
  8     11     11

      4,13,L

  0     80     81
  1     63     63
  2     48     52
  3     16     21
  4     23     24
  5     38     38
  6     78     76
  7     24     23

      4,14,L

  0     10*     1
  1     12     14
  2     21     18
  3     15     18
  4     40     30
  5      9*    10
  6     35     29

      4,15,L

  0     35     21
  1     10*     6
  2     40     35
  3     11     19
  4     65     52

      4,16,L

  0      9*     3
  1     18     14

      5,0,L

  1    588    583
  2    215    202
  3    235    221
  4    139    135
```

5,0,L

5	12*	4
6	213	214
7	114	114
8	80	79
9	45	47
10	23	24
11	12	18
12	12	10

5,1,L

0	9*	10
1	68	65
2	440	430
3	354	343
4	236	220
5	137	129
6	66	73
7	161	160
8	117	116
9	77	78
10	23	21
11	10*	10
12	32	32

5,2,L

0	109	114
1	250	239
2	112	101
3	152	149
4	82	78
5	70	70
6	103	105
7	235	237
8	104	107
9	120	119
10	83	81
11	94	98
12	9*	4

5,3,L

0	164	166
1	65	54
2	41	41
3	64	59
4	36	37
5	162	160
6	127	125
7	59	62
8	230	232
9	86	86
10	72	70
11	42	44
12	26	33

5,4,L

0	209	216
1	18	22
2	269	264
3	196	194
4	136	130
5	210	216
6	68	69
7	73	72
8	90	90
9	66	72
10	82	79
11	11	7
12	35	41

5,5,L

0	123	118
1	289	303
2	129	136
3	169	156
4	162	160
5	89	79
6	98	94
7	102	97
8	20	19
9	72	70
10	58	63
11	22	24
12	16	14

5,6,L

0	41	40
1	64	66
2	128	134
3	135	125
4	28	29
5	25	17
6	24	27
7	117	114
8	28	27
9	35	35
10	22	25
11	42	46

5,7,L

0	10*	11
1	40	43
2	57	53
3	37	47
4	82	82
5	48	47
6	64	66
7	23	17
8	34	32
9	88	86
10	28	30
11	9*	8

5,8,L

0	31	31
1	25	27
2	41	39
3	47	45
4	67	59
5	79	86
6	51	50
7	125	123
8	45	45
9	55	51
10	13	9

5,9,L

0	46	41
1	54	56
2	22	20
3	40	49
4	55	60
5	78	83
6	163	164
7	57	63
8	31	32
9	18	18
10	9*	13

5,10,L

0	113	113
1	118	117
2	63	67
3	77	76
4	63	61
5	11*	7
6	25	27
7	30	29
8	62	61
9	33	32

5,11,L

0	225	216
1	105	99
2	45	42
3	18	10
4	35	35
5	24	16
6	60	61
7	40	41
8	21	22
9	35	37

5,12,L

0	94	87
1	11*	13
2	77	73
3	27	29
4	11*	9
5	33	32
6	33	33
7	24	23
8	13	16

5,13,L

0	46	37
1	10*	6
2	24	22
3	14	17
4	20	23
5	30	28
6	11	6
7	22	22

5,14,L

0	22	19
1	38	34
2	14	10
3	27	26
4	43	38
5	29	21

5,15,L

0	11	9
1	10	6
2	29	24
3	48	37

6,0,L

0	35	41
1	57	65
2	87	86
3	89	83
4	101	98
5	61	61
6	32	33
7	11*	0
8	105	105
9	26	24
10	11*	3
11	10*	4
12	18	20

6,1,L

0	27	28
1	178	164
2	153	148
3	94	93
4	105	114
5	38	34
6	147	149
7	60	61
8	47	45
9	44	43
10	58	58
11	29	28
12	34	36

6,2,L

0	186	192
1	104	105
2	139	137
3	139	136
4	60	51
5	96	101
6	33	39
7	35	35
8	156	156
9	75	74
10	13	16
11	10*	7
12	32	40

6,3,L

0	9*	9
1	116	111
2	56	62
3	50	51
4	119	119
5	81	79
6	102	104
7	137	143
8	69	72
9	95	94
10	63	65
11	10*	6

6,4,L

0	84	98
1	13	22
2	118	118
3	231	225
4	44	41
5	70	75
6	59	56
7	152	146
8	46	46
9	79	79
10	32	34
11	26	24

6,5,L

0	65	68
1	143	142
2	18	8
3	103	100
4	61	55

6,5,L

5	89	84
6	86	87
7	64	67
8	104	103
9	52	51
10	10	9
11	9*	6

6,6,L

0	197	203
1	131	131
2	243	244
3	147	147
4	77	74
5	57	54
6	63	60
7	41	38
8	42	41
9	16	14
10	33	33
11	24	29

6,7,L

0	185	191
1	24	27
2	35	37
3	151	154
4	29	31
5	74	70
6	66	63
7	67	69
8	42	43
9	10*	5
10	22	21

6,8,L

0	35	35
1	95	102
2	36	39
3	29	24
4	35	43
5	114	112
6	94	99
7	69	60
8	20	18
9	39	39
10	62	62

6,9,L

0	54	54
1	47	46
2	124	127
3	83	82
4	139	143
5	45	46
6	51	54
7	32	30
8	46	49
9	51	50

6,10,L

0	11*	2
1	17	8
2	12	12
3	78	74
4	90	100
5	81	79
6	90	97
7	26	27
8	31	32
9	14	12

6,11,L

0	51	42
1	30	33
2	23	24
3	22	20
4	60	56
5	28	29
6	60	60
7	21	19
8	43	37

6,12,L

0	11*	13
1	26	15
2	31	31
3	19	14
4	22	25
5	48	49
6	22	20
7	34	30

6,13,L

0	10*	4
1	13	14
2	32	33
3	25	28
4	28	22
5	25	24
6	24	22

6,14,L

0	18	15
1	10	16
2	31	21
3	35	26
4	36	32

7,0,L

1	28	21
2	138	129
3	119	120
4	59	60
5	84	82
6	123	119
7	22	20
8	52	48
9	92	94
10	28	31
11	21	22

7,1,L

0	167	172
1	136	140
2	33	35
3	93	90
4	41	42
5	57	65
6	99	103
7	63	64
8	79	80
9	42	41
10	55	55
11	36	34

7,2,L

0	25	7
1	133	133
2	159	157
3	73	85
4	129	125
5	50	53
6	79	72
7	176	181
8	12	12
9	45	41
10	26	29
11	15	19

7,3,L

0	19	11
1	21	25
2	66	54
3	40	40
4	133	131
5	123	121
6	71	67
7	143	141
8	65	67
9	44	44
10	35	32
11	43	43

7,4,L

0	148	150
1	64	70
2	58	57
3	14	17
4	41	42
5	79	78
6	98	98
7	80	71
8	46	45
9	63	63
10	10*	4
11	19	22

7,5,L

0	169	189
1	176	182
2	159	165
3	126	131
4	60	62
5	63	63
6	22	23
7	52	43
8	26	26
9	16	13
10	47	44

7,6,L

0	221	237
1	97	96
2	84	88
3	89	85
4	182	192
5	11*	7
6	51	53
7	28	24
8	18	19
9	10*	3
10	38	39

7,7,L

0	341	353
1	63	70
2	171	170
3	66	70
4	34	28
5	52	55
6	71	70
7	21	19
8	10*	2
9	39	38
10	27	26

7,8,L

0	47	42
1	62	61
2	128	131
3	106	107
4	126	129
5	55	55
6	44	40
7	39	36
8	16	18
9	17	12

7,9,L

0	105	102
1	83	88
2	58	63
3	31	28
4	18	20
5	77	76
6	67	64
7	12	11
8	15	18

7,10,L

0	34	32
1	31	36
2	11	10
3	63	59
4	11*	4
5	33	31
6	24	28
7	57	53
8	26	23

7,11,L

0	11*	8
1	26	24
2	69	67
3	21	19
4	18	18
5	30	27
6	14	12
7	29	26

7,12,L

1	58	50
2	40	38
3	29	29
4	19	15
5	38	37
6	34	29

7,13,L

0	10*	16
1	17	16
2	43	33
3	27	23

7,13,L

4	10	7

7,14,L

0	9*	5
1	14	13

8,0,L

0	89	88
1	248	247
2	51	54
3	40	39
4	44	42
5	11*	13
6	46	49
7	11*	13
8	23	27
9	66	67
10	38	35

8,1,L

0	162	173
1	188	190
2	133	126
3	16	20
4	95	96
5	16	20
6	55	58
7	46	47
8	11*	12
9	23	22
10	27	32

8,2,L

0	15	8
1	70	73
2	129	133
3	41	30
4	62	57
5	47	49
6	99	103
7	44	44
8	44	45
9	55	53
10	25	23

8,3,L

0	111	115
1	134	133
2	104	107
3	45	45
4	115	118
5	70	65
6	97	95
7	78	81
8	32	37
9	15	11
10	53	52

8,4,L

0	154	166
1	87	86
2	131	135
3	169	169
4	71	68
5	97	101
6	125	126
7	29	33
8	43	42
9	41	37
10	17	18

8,5,L

0	174	180
1	200	204
2	74	70
3	44	41
4	102	104
5	101	98
6	66	62
7	50	51
8	44	48
9	31	31

8,6,L

0	98	104
1	174	176
2	83	91
3	42	39
4	14	12
5	27	18
6	44	46
7	37	34
8	33	34
9	23	18

8,7,L

0	55	53
1	105	112
2	143	149
3	101	107
4	72	70
5	73	73
6	24	26
7	23	24
8	39	35
9	23	24

8,8,L

0	156	154
1	63	68
2	92	93
3	47	55
4	89	94
5	60	61
6	11	11
7	11	12
8	25	21

8,9,L

0	46	48
1	27	30
2	97	95
3	21	21
4	38	39
5	35	37
6	10*	7
7	11	12

8,10,L

0	69	61
1	30	27
2	25	24
3	42	42
4	32	32
5	28	29
6	19	14
7	12	14

8,11,L

0	10*	4
1	67	60
2	56	53
3	14	15
4	20	16
5	22	19

8,12,L

0	32	30
1	14	12
2	33	28
3	64	59
4	9*	5

8,13,L

0	12	11
1	33	24

9,0,L

1	12*	3
2	151	157
3	63	60
4	11*	12
5	11*	7
6	48	45
7	11*	8
8	26	23
9	9*	7

9,1,L

0	256	271
1	91	88
2	76	70
3	59	60
4	39	37
5	16*	20
6	19	21
7	10*	12
8	48	46
9	49	46

9,2,L

0	15	16
1	58	58
2	98	96
3	96	95
4	32	35
5	87	91
6	67	67
7	22	25
8	43	44
9	46	47

9,3,L

0	119	120
1	88	93
2	111	110
3	72	72
4	91	92
5	63	64
6	66	68
7	105	111
8	15	16
9	13	10

9,4,L

0	115	116
1	130	131
2	112	110
3	50	51
4	68	70
5	55	56
6	63	65
7	74	71
8	32	34
9	15	21

9,5,L

0	11*	1
1	56	58
2	39	37
3	54	58
4	72	69
5	69	72
6	45	42
7	31	28
8	18	17

9,6,L

0	52	50
1	41	46
2	60	61
3	75	67
4	60	64
5	35	38
6	21	18
7	42	39
8	31	33

9,7,L

0	67	66
1	48	47
2	38	37
3	35	38
4	26	33
5	36	37
6	32	32
7	14	13

9,8,L

0	37	39
1	70	72
2	51	53
3	10*	6
4	28	25
5	38	41
6	38	34
7	48	45

9,9,L

0	35	37
1	30	25
2	27	22
3	32	36
4	31	28
5	49	46
6	34	37

9,10,L

0	10*	0
1	10*	4
2	38	36

9,10,L

3	20	20
4	18	18
5	9*	10

9,11,L

0	10*	14
1	41	35
2	46	40
3	33	27

10,0,L

0	34	34
1	132	126
2	15	12
3	11*	1
4	29	30
5	90	87
6	46	49
7	25	22
8	26	22

10,1,L

0	74	82
1	59	53
2	22	23
3	83	82
4	26	29
5	28	29
6	27	27
7	16	11
8	32	32

10,2,L

0	11*	3
1	91	86
2	81	80
3	45	42
4	80	81
5	49	44
6	99	99
7	51	53
8	19	18

10,3,L

0	68	71
1	69	69
2	11*	9
3	52	46
4	78	81
5	89	85
6	56	52
7	25	23
8	24	23

10,4,L

0	11*	2
1	16	16
2	25	24
3	80	81
4	23	24
5	25	29
6	47	43
7	28	28

10,5,L

0	83	85
1	65	67
2	45	46
3	37	39
4	17	16
5	46	43
6	38	37
7	30	33

10,6,L

0	102	101
1	105	105
2	35	37
3	31	32
4	23	24
5	24	21
6	10	10
7	24	23

10,7,L

0	51	48
1	42	38
2	37	40
3	27	22
4	46	52
5	63	63
6	31	32

10,8,L

0	11*	16
1	37	34
2	21	21
3	36	33
4	28	26
5	34	34

10,9,L

0	39	33
1	17	15
2	29	25
3	17	16
4	9	11

10,10,L

0	39	35
1	11	11
2	52	44

11,0,L

1	11*	9
2	72	70
3	59	50
4	10*	3
5	33	33
6	28	29
7	39	39

11,1,L

0	46	48
1	65	62
2	11*	6
3	56	54
4	59	57
5	45	48
6	40	40

11,2,L

0	14	17
1	18	19
2	28	31
3	36	37
4	61	58
5	26	21
6	59	57

11,3,L

0	17	20
1	16	22
2	37	36
3	28	25
4	32	30
5	33	28
6	39	35

11,4,L

0	11*	4
1	61	59
2	27	26
3	39	36
4	58	55
5	21	21
6	38	36

11,5,L

0	48	49
1	36	40
2	60	57
3	10*	5
4	45	47
5	37	36

11,6,L

0	10*	6
1	37	37
2	47	46
3	19	18
4	24	24
5	14	13

11,7,L

0	19	14
1	13	15
2	13	14
3	27	26
4	28	27

11,8,L

0	9*	3
1	10	10
2	48	47

12,0,L

0	26	25
1	10	13
2	23	20
3	33	30
4	15	17

12,1,L

0	10*	3
1	62	59
2	19	20
3	19	17
4	22	17

12,2,L

0	10*	3
1	10*	6
2	53	50
3	37	34
4	44	44

12,3,L

0	19	20
1	58	50
2	56	54
3	39	41

12,4,L

0	52	50
1	24	20
2	12	13
3	45	41

12,5,L

0	41	39
1	16	20
2	19	17

APPENDIX III

Statistical tests used in processing A.E.D. output.

APPENDIX III

Statistical tests used in processing A.E.D. output

It may be shown that, when counting X-ray quanta from a fully stabilised, smoothed-output tube, using a proportional or scintillation counter, the counting rate values follow a Poissonian distribution if the number of counts is large, and the standard deviation for a counting rate of n p/s is $\sqrt{n}$.

From a well known statistical theorem the variances of the sum or difference of several quantities are both equal to the sum of the variances of the separate quantities. Hence for a five-value measurement on the A.E.D., the standard deviation of $\left[I_1+I_3+I_5-(I_2+I_4)\right]$ may be taken as $(I_1+I_2+I_3+I_4+I_5)^{\frac{1}{2}}$.

Now $I_{net} = \frac{1}{2}\left[I_1+I_3+I_5-(I_2+I_4)\right]$ and hence its standard deviation may be taken as

$$\sigma\,(I_{net}) = \tfrac{1}{2}(I_1+I_2+I_3+I_4+I_5)^{\frac{1}{2}}$$

Similarly

$$\sigma\,(I_1+I_5-I_3) = (I_1+I_3+I_5)^{\frac{1}{2}}$$

It may be shown that, for quantities obeying a Gaussian law, there is a 99% probability that a value will lie within ± 2.58 standard deviations of the mean value, a 90% probability for ± 1.64 standard deviations, a 50% probability for ± 0.67 standard deviation. Thus if the overall peak count, I_3, obtained by the five-value measuring routine is acceptably near equality with the sum of the two half-peak counts, (I_1+I_5) we should have

$$|\,I_1+I_5-I_3\,| < Q(I_1+I_3+I_5)^{\frac{1}{2}}$$

where Q takes one of the values given above. Similarly, if the reflection count is significantly above background, we should have

$$I_{net} > Q\,\sigma\,(I_{net})$$

Experience has shown a value of 2.58 for Q to be satisfactory for both tests.

The test for approximate equality of the two half-peak counts

$$\frac{I_1^2 + I_5^2}{I_1 I_5} < 4$$

is not very stringent, as it allows I_5 to vary between about $0.27I_1$ and $3.7I_1$. This fairly generous latitude is necessary, however, since in some cases a peak may be genuinely asymmetrical, e.g. due to absorption in irregularly shaped crystals.

Intensity scaling, and Lorentz-Polarisation correction for A.E.D. output.

In the expression

$$F_o^2 = K.(Lp)^{-1}.I_o$$

the scale factor K is calculated as follows. Let R_1 and R_2 be the I_o values for the reference reflection at the beginning and end of the block of data containing the reflection for which K is required, and let R be the arbitrary value set for the I_o of the reference reflection during SODI input. The values R_1 and R_2 may be converted to R by means of scale factors K_1 and K_2 such that

$$K_1R_1 = K_2R_2 = R$$

The value of K to be used for all reflections in the block between R_1 and R_2 is the arithmetic mean of K_1 and K_2.

The Lorentz factor, L, for a diffractometer used in normal-beam equatorial mode is

$$L = (\sin 2\theta)^{-1}$$

and for unpolarised radiation, the correction factor, p, is

$$p = \tfrac{1}{2}(1 + \cos^2 2\theta)$$

hence,

$$Lp = \tfrac{1}{2}\frac{(1 + \cos^2 2\theta)}{(\sin 2\theta)}$$

APPENDIX IV

Phase determination for non-centrosymmetric structures.

"Some people never learn anything because they understand everything too soon."

... Alexander Pope.

APPENDIX IV

Phase Determination for Non-centrosymmetric Structures

In general, phases can be anywhere between 0 and 2π radians. The rules for selecting the initial phases for non-centrosymmetric space groups are that three phases, the parities of which are linearly independent, may be chosen arbitrarily and one other may be designated in the range 0 to π to fix the enantiomorph.

The Σ2-type formula,

$$\langle\phi_{\underline{h}}\rangle = \langle\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'}\rangle_{\underline{h}'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

must be used with care since ambiguities can sometimes arise in the averaging e.g. if two estimates of a phase are respectively $^{\pi}/10$ and $^{-2\pi}/10$ (which is ≡ $^{18\pi}/10$), the average $\langle\phi\rangle$ is $^{-\pi}/20$ (or $^{19\pi}/20$) which is π apart. This ambiguity, which would produce misleading results, can be overcome by only accepting concurrent phase indications; the average of all the contributors is then the same as that of a single contributor. If these contributors vary in value, the phase can be considered as undetermined.

The program PHASEM includes provision for calculation of the reliability index $\underline{R}_k$,

$$R_k = \frac{\sum_{h'} |E_{\underline{h}}|_o - |E_{\underline{h}}|_c}{\sum_{h'} |E_{\underline{h}}|_o}$$

and output of tangent-refined phases in a form suitable for direct calculation of E-maps using the X-ray 70 system. The value of R_k has been found to give a good indication of the consistency, and hence the correctness of a particular set. (The set of normalised structure factors greater than 1.7 being usually used.) The tangent formula is capable of refining phases which are found approximately, using the Σ2 formula and extending the list of known phases once the phases of a number of them are approximately known numerically. A rough guide is that if a phase is initially within about $\pi/4$ radians from its value, then the tangent formula is capable of refining it.

The usual difficulty in direct methods is the problem of defining a unique origin and the choice made is fundamental to the entire procedure.

Non-centrosymmetric structures can exist in two enantiomorphic forms, which both give the same intensity distribution. There is thus an ambiguity of $\pm\pi/2$ radians in the origin set, and so it becomes necessary 'to fix' the enantiomorph. This procedure is simple for space group $P2_12_12_1$ because when an origin is chosen, it is uniquely defined, whereas in $P2_1$ there is no such restriction. A series of rules have been derived which are useful in specifying the origin and enantiomorph-defining reflections for both primitive[1,2] and centred[3] space groups.

In the space group $P2_12_12_1$, any one or two dimensional reflection has a phase of 0 or π, or $\pm\pi/2$, depending on its parity. This occurs because all three projections are centrosymmetric. It is thus a relatively simple matter to choose three zonal reflections which are linearly independent analogous to the centrosymmetric case. The sign of each phase (0 or π, or $\pi/2$), can be arbitrarily fixed. Hence, for ketol bishydropulegone

h	k	ℓ	E	ϕ	Parity
5	11	0	3.11	$\pi/2$	uu0
0	4	7	2.22	0	0gu
7	6	0	2.09	$\pi/2$	ug0

where g and u denote even and odd parities respectively. The phases of reflections of type gu0, uuu, and ugu are linearly dependent on these three and are formed by combining them in pairs. The three zonal parity groups 0ug, 0uu, and uu0 are not linearly dependent on these three starting origin-defining reflections and can all be assigned an arbitrary phase of $\pm\pi/2$. This ambiguity may be resolved by the choice of a suitable fourth reflection which can combine with any of the others in the starting set to give linearly dependent phases with no ambiguities. The fourth reflection chosen by MULTAN in the case of the ketol was the 1 11 3(E = 3.21), for which a phase of $\pm\pi/2$ was recommended.*

For space group $P2_1$, the enantiomorph may not be defined in this manner although restriction of a symbolic phase between 0 and π radians is all that is necessary to fix it. The origin set must be of the type $h_1 0 \ell_1$ and $h_2 0 \ell_2$ and $h_3 1 \ell_3$, where $h_1 0 \ell_1$ and $h_2 0 \ell_2$ are two different terms from the parities g0u, u0g and u0u.

The basic set of starting phases, together with the symbolic phases used should be associated with large E values and capable of entering into a large number of Σ2-type relationships, so that the phase expansion process goes well with a large propagation of phases. This problem of obtaining the best starting set comprising reflections which interact well with the reflection data is sometimes difficult and elusive. It was for this reason that the computer program MULTAN was used to obtain the best starting set using the powerful CONVERGENCE routine[4].

General Procedure for Phase determination

The program PHASEM written by M.G.B. Drew[5] was used. A set of normalised structure factors greater than 1.7 is used as input data. The first part of the program calculates the phases of these input reflections throughout the sphere of reflection, since all the reflections in the sphere must be used in the phase determining formulae.

* Prof. Rogers has subsequently shown that the MULTAN choice is wrong: in this case it should have been 0 or π.

A simple set of algorithms is used for this purpose :-

$$\phi_{hk\bar{\ell}} = \pi/2\ [1 + (-1)^{rh+sk+t\ell+1}] - \phi_{hk\ell}$$

$$\phi_{h\bar{k}\ell} = \pi/2\ [1 + (-1)^{uh+vk+w\ell+1}] - \phi_{hk\ell}$$

$\phi_{\bar{h}k\ell}$ is then fixed by these two algorithms. Examples of generating integers illustrate the technique.

	r	s	t	u	v	w
$P2_12_12_1$	1	0	1	0	1	1

When h is reversed, $\phi_{\bar{h}\bar{k}\bar{\ell}}$ is set equal to $-\phi_{hk\ell}$: As a consequence, phases of $-\phi_{hk\ell}$ and $\pi + \phi_{hk\ell}$ can occur in the $\bar{h}$ region.

All combinations of $\underline{h}'$ and $\underline{h}-\underline{h}'$ for a given $\underline{h}$ are now listed; these are computed using the Σ2-type relationship. A choice of origin and enantiomorph defining reflections can now be made, together with three symbolic phases. Employment of the Σ2 formula 1 in a symbolic addition process then enables the phases of a number of reflections in the list to be uniquely determined in terms of symbols. Occasionally a phase will be determined absolutely. An α value may be defined :

$$\alpha_{Drew} = \frac{\alpha}{2\sigma_3\sigma_2{}^{-3}/2}$$

where

$$\alpha = \frac{2\sigma_3}{\sigma^{3/2}} |E_{\underline{h}}| (A^2 + B^2)^{\frac{1}{2}} \text{ and } \sigma_n = \sum_{j=1}^{N} Z_j^n$$

Z_j = Atomic Number of the jth atom in unit cell containing N atoms.

with $$A = \sum_{\underline{h}'} |E_{\underline{h}'} E_{\underline{h}-\underline{h}'}| \sin (\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$$

and $$B = \sum_{\underline{h}'} |E_{\underline{h}'} E_{\underline{h}-\underline{h}'}| \cos (\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$$

For equal atom structures, α_{Drew} reduces to $\alpha\sqrt{N}_{/2}$. Phase indications are only accepted if their variance is less than about 0.5 square radians. (Variance is the square of the standard deviation). It has been experimentally determined that this limiting value usually corresponds to an α limit of about 2.5[6]. If this lower limit is taken for α, then α_{Drew} becomes $1.25N^{\frac{1}{2}}$(as an approximate guide). Thus, during the process of symbolic addition, if a triple product $E_{\underline{h}}E_{\underline{h}'}E_{\underline{h}-\underline{h}'}$ has a value less than this, the phase indication will be rejected.

The tangent formula,

$$\tan \phi_{\underline{h}} \simeq {}^{A}/B$$

is now utilised to find the best set of phases corresponding to numerical values of the symbols. e.g. if a symbol can range between 0 and 1000 millicycles, four different sets in steps of 250 millicycles from 125 mc. are tried: (125, 375, 625, 875 mc.) Thus for three symbols, there are numerous solutions corresponding to the combinations of symbols tried.

During the procedure of tangent refinement, each phase must satisfy two conditions to be introduced into the set. Firstly, its α value must be greater than the preset minimum, and additionally its consistency index $t_{\underline{h}}$, defined as

$$t_{\underline{h}} = \frac{(A^2 + B^2)^{\frac{1}{2}}}{\sum_{h'} |E_{\underline{h}'}E_{\underline{h}-\underline{h}'}|}$$

must be greater than its preset value. This value is a measure of how well the sum of the contributing phases $(\phi_{\underline{h}'} + \phi_{\underline{h}-\underline{h}'})$ agree with each other. The value usually chosen is within the range $0<t<1.0$ although preset values of between 0.25 and 0.40 have been experimentally found to be satisfactory[7]. The number of terms introduced in each cycle can also be varied (this enables a small number of consistent phases to be added at each cycle).

The best set of phases thus obtained is the one with the lowest R_k index and the highest $<\alpha>$ and $<t_{\underline{h}}>$ values. An additional measure of consistency was introduced into this program by Drew[5] and is provided by the R_{Drew} which is defined as

$$R_{Drew} = \frac{\sum_{\underline{h}} |E_{\underline{h}}|(1 - t_{\underline{h}})}{\sum_{\underline{h}} |E_{\underline{h}}|}$$

The program calculates R_D, α and $t_{\underline{h}}$ values and thus the set of phases with the lowest $\underline{R}$ value and the highest $\langle\alpha\rangle$ and $\langle t_{\underline{h}}\rangle$ values is probably, though not necessarily, the correct solution.

Cards can then be punched and an E map calculated using these phases.

MULTAN

In the paper by Germain, Main and Woolfson, details are given of the "CONVERGENCE" method for obtaining the best possible starting set of phases. It does this by testing the effectiveness of using particular sets of origin and enantiomorph-fixing selections and by selecting additional reflections.

A modified tangent formula was introduced which included a weighting scheme.

$$\tan \phi_{\underline{h}} = \frac{\sum_{\underline{h}'} W_{\underline{h}} W_{\underline{h}-\underline{h}'} \mid E_{\underline{h}} E_{\underline{h}-\underline{h}'} \mid \sin(\phi_{\underline{h}} + \phi_{\underline{h}-\underline{h}'})}{\sum_{\underline{h}'} W_{\underline{h}} W_{\underline{h}-\underline{h}'} \mid E_{\underline{h}} E_{\underline{h}-\underline{h}'} \mid \cos(\phi_{\underline{h}} + \phi_{\underline{h}-\underline{h}'})}$$

$$= \frac{T_{\underline{h}}}{B_{\underline{h}}}$$

where $W_{\underline{h}}$ is the weight associated with the phase $\phi_{\underline{h}}$.

Each weight is computed from

$$W_{\underline{h}} = \tanh \ \sigma_3\sigma_2^{-3/2} \mid E_{\underline{h}} \mid \ (T_{\underline{h}}2 + B_{\underline{h}}2)^{\frac{1}{2}}$$

$$= \tanh\ (\alpha_{\underline{h}/2})$$

where $\alpha_{\underline{h}} = 2\sigma_3\sigma_2 \ |E_{\underline{h}}\ |(T_{\underline{h}}2 + B_{\underline{h}}2)^{\frac{1}{2}}$

In the CONVERGENCE routine of MULTAN, the values of $\langle\alpha_{\underline{h}}2\rangle^{\frac{1}{2}}$ are evaluated for each reflection (from a consideration of the number of interactions each reflection is involved in with regard to the entire reflection data). The lowest value of $\langle\alpha_{\underline{h}}2\rangle^{\frac{1}{2}}$ is then sought. The reflections corresponding to these values are then removed from the data and their computer program code numbers and the values of $\langle\alpha_{\underline{h}}2\rangle^{\frac{1}{2}}$ are listed. This process is continued with the proviso that the origin and enantiomorph fixing reflections are never removed from the system. Ultimately, the process 'converges' on the four starting reflections.

As a guide to the best phase sets MULTAN calculates the "absolute figure of merit (FOM) for each phase set. It is defined by

$$\mathrm{FOM} = \frac{\sum_{h} \alpha_{\underline{h}} - \Sigma\alpha_{\underline{r}}}{\Sigma\alpha_{\underline{e}} - \Sigma\alpha_{\underline{r}}}$$

where $\Sigma\alpha_{\underline{h}}$ is the sum of the calculated α's, $\Sigma\alpha_{\underline{r}}$ is the value of $\Sigma\alpha_{\underline{h}}$ assuming random phases and $\Sigma\alpha_{\underline{e}}$ is the sum of the estimated α's. The value of FOM for a correct set of phases is expected to be about 1.2 .

MULTAN additionally calculates a quantity termed the RESID which is equal to R_{Karle} when all the $\Sigma2$-type relationships are used. RESID should be a minimum for the correct phase set.

In the structure determination of bishydropulegone, the MULTAN program was used to determine the best starting set of origin-defining and enantiomorph-fixing reflections. The choice of enantiomorph-fixing reflection is restricted to those parity groups which are independent of the starting set and not defined by them.

The origin-defining set was the 5 11 0, 0 4 7 and 7 6 0 reflections which were assigned phases of $\pi/2$, 0 and $\pi/2$ respectively ;

Thus;-

$\pi/2$ 5 11 0 uu0

> uuu

0 0 4 7 0gu > gug

> ugu

$\pi/2$ 7 6 0 ug0

$\overline{\text{guu}}$

It may thus be seen that one must seek a suitable term among u0u, 0ug and 0uu parities which will give $\Delta\phi$ sums of $\pm\ \pi/2$. Thus either 0ug or 0uu parities of reflection may be used for this purpose.

The routine FASTAN within the MULTAN program chooses an enantiomorph-fixing reflection from the input data in a manner which will constrain the choice to these two parity groups, but if it cannot find a suitable reflection within these parity groups it will then release this restriction and choose a general reflection. In the bishydropulegone structure determination, the 1 11 3 reflection of parity uuu was chosen in the starting set with the highest FOM and lowest RESID values. One could thus say that the constraining of this particular reflection with a value of $\pi/2$ was incorrect,* although if it had been of quite a different value, the RESID value would have been much higher and the absolute FOM much lower. The result of this would have been that this particular starting set would not have been chosen.

* See footnote to p. 322.

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"So *little* done, *so* much *to* do."
... C.J. Rhodes.