A Thesis

Entitled

The Structure of Yohimbine
and other Organic Molecules
by X-Ray Crystal Analysis

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SUMMARY

This thesis describes work carried out under the supervision of Professor J.M. Robertson since October 1962.   It is divided into two sections.

Section I describes two structures solved by the heavy-atom method.   In both cases, it is the actual structure of the molecule in the chemical sense and the stereochemistry that is of interest, and for this reason refinement was terminated at a fairly early stage.

Part I of this section reviews certain aspects of heavy-atom and Patterson methods.

Part II is concerned with the structure of the methiodide of the 7-acetoxy-7-H-yohimbine.   The configuration of the acetoxy group is the point of major interest here. The results of this analysis have been used by N. Finch and W.I. Taylor of the C.I.B.A. Pharmaceutical Company to establish the stereochemistries of a number of related compounds.   This work is also an independent proof of the structure of yohimbine.

Part III is an investigation of the stereochemistry of the monoximes of benzil through the crystal structure analysis of the para-bromobenzoate of the α-oxime. There is some evidence in the literature that suggests that Meisenheimer's original assignment should be reversed.

but the present work confirms his assignment.

Section II describes an accurate determination of bond lengths in 1,1'-binaphthyl and in perylene. Both molecules can be described as composed of two naphthalenic residues joined by long bond(s). The perylene molecule is planar but the binaphthyl molecule is not. Valence bond theory predicts that the aromatic character of the perylene molecule is localised in the naphthalenic residues and that the linking bonds are pure single bonds with no π-bond character. If this is so, the dimensions of the molecule should be very similar to those of 1,1'-binaphthyl where the dihedral angle between the planes of the naphthalenic residues is 68° - large enough to preclude any interaction between the two aromatic systems.

The refinements of the two structures are described, and the dimensions of the two molecules are compared with other molecules of similar bond type.

Appendix I is a short note concerning the choice of unit cell in a triclinic lattice.

INDEX

Part II Section I cont.

Part III

The Crystal and Molecular Structure of

The Para-Bromobenzoate of Benzilmonoxime

SECTION I

Two Heavy-Atom Structures

INTRODUCTION

This section of the thesis describes the structural
analysis of 7-acetoxy-3H-yohimbine and the para-
bromobenzoate of benzil monoxine. It is divided
into three parts.

Part one discusses some aspects of the theory of heavy-
atom and Patterson methods in the context of the problem
to which they were applied. The structures in point
illustrate different aspects of the cooperative use of
the two methods. This is not intended to be a general
discussion of the theory or application of either method.

Part two is concerned with the structure of the methiodide
of the acetoxy-indolenine of yohimbine. This is an
independent proof of the structure and stereochemistry of
yohimbine and is in agreement with the previous assignment
by chemical means. The feature of interest in this
analysis is the stereochemistry at C(7), the junction
between the indolenine moiety and the aliphatic ring system.
This feature is discussed in terms of the work that has
been done on oxidative transformations of indole alkaloids
at CIBA in Summit, New Jersey.

Part three describes the analysis and refinement of the
structure of the para-bromobenzoate of benzil monoxine.

Certain phenomena suggest that the accepted configuration
of the α and β isomers should be reversed. The structure
was solved by the use of a "minimum function" derived
from a sharpened Patterson synthesis. The configuration
of the molecule agrees with that currently accepted in
the literature. Since the molecule crystallizes in
the triclinic system, the choice of unit cell is not
dictated by symmetry considerations. The cell chosen
is the Bravais reduced cell. A short discussion of the
problem of choosing the unique cell in the triclinic
system is included in Appendix 1.

PART I

1.1 The Phase Problem

It is well known that the ideal diffraction pattern can be calculated for a structure containing N atoms. The structure factor expression gives the amplitude and phase of the scattered wave and has the form

$$(1) \quad F(\underline{H}) = \sum_{j=1}^{N} f_j(\underline{H}) \exp(2\pi i\, \underline{H}.\underline{r}_j) = |F(\underline{H})| \exp(i\, \varphi(\underline{H}))$$

where $F(\underline{H})$ is the structure factor associated with the plane of Miller index $\underline{H} = (h, k, \ell)$; $\underline{r}_j = (x_j, y_j, z_j)$, the fractional coordinates of the jth atom; $\varphi(\underline{H})$ is the phase angle associated with $F(\underline{H})$ and $f_j(\underline{H})$ is the scattering factor of the jth atom. The intensities of the diffraction maxima in the ideal pattern are obtained from $|F(\underline{H})|^2$, the square of the scattering amplitude. The positions of the maxima can be calculated from a knowledge of the size and geometry of the unit cell.

The problem facing the crystallographer is the reverse of the one stated above; given the diffraction pattern, calculate the distribution of the atoms in the unit cell. If we regard the electron density function in the unit cell as the sum of N atomic densities, then

$$(2) \quad \rho(\underline{r}) = \sum_{j=1}^{N} \rho(\underline{r}-\underline{r}_j) = \sum_{j=1}^{N} \rho_j(\underline{r}_j') \quad ,$$

where $\rho(\underline{r})$ is the density function; $\underline{r}$ is the vector (x,y,z); and $\underline{r}_j' = (\underline{r}-\underline{r}_j)$. The function $\rho_j(\underline{r}_j')$ is the atomic density function of the jth atom defined with the atomic centre $\underline{r}(j)$ as origin.

The scattering factor, $f_j(\underline{H})$, is the Fourier transform of the atomic density function of the jth atom. Let $(\underline{r}-\underline{r}_j) = \underline{r}_j'$. Then, by definition,

$$(3) \quad f_j(\underline{H}) = \int_{-\infty}^{\infty} \rho_j(\underline{r}_j') \exp(2\pi i\, \underline{H}.\underline{r}_j')\, dV_{\underline{r}_j'}.$$

Again, $\rho_j(\underline{r}_j')$ is the atomic density function referred to $\underline{r}_j$ as origin. By substituting this expression into equation (1), it can be shown that the structure factor expression is the Fourier transform of the unit cell contents.

$$(4) \quad F(\underline{H}) = \int_0^1 \rho(\underline{r}) \exp(2\pi i\, \underline{H}.\underline{r})\, dV_{\underline{r}}.$$

By the properties of Fourier series, $F(\underline{H})$ is exactly equal to the value of the appropriate Fourier coefficient of $\rho(\underline{r})$, so that

$$(5) \quad \rho(\underline{r}) = \frac{1}{V} \sum_{\underline{H}}^{+\infty}{}_{-\infty} F(\underline{H}) \exp(-2\pi i\, \underline{H}.\underline{r}).$$

The maxima in this function represent the positions of atoms in the unit cell. If the Fourier series could be calculated directly from the experimental data, solution of crystal structures would be trivial. However, the observed intensities yield only the structure amplitudes,

$|F(\underline{H})|$. The phases are not observed. This is the
"phase problem" of crystallography.

Referring back to equation (1), the scattering factors
and structure amplitudes can be regarded as known since
the former are available in tables and the latter can
be obtained from the experiment. This means that the
structure factor expression can be formulated in terms
of two types of unknowns, the atomic positions or the
phases. If either is known, the other can be calculated.
This suggests two possible approaches to the phase
problem. "Direct" methods as developed by Sayre,
Zachariasen, Karle and Hauptman and others, attempt
to find the phases directly by finding relationships
among the structure amplitudes. "Indirect" methods
seek to solve the phase problem through the atomic
positions.

1.2. METHODS INVOLVING HEAVY ATOMS

The heavy-atom method and isomorphous replacement
are distinct techniques, but both methods have developed
from Robertson's work on the phthalocyanines.

"Free" phthalocyanine and its nickel derivative
are isomorphous; they have the same unit cell dimensions
and the same distribution of light atoms in the crystal.
In the metal derivative, the metal atom is situated at

the centre of the molecule.   Since the phthalocyanines
crystallize in space group $P2_1/a$ with two molecules in
the unit cell, the molecular centres must lie on special
positions.   Thus the metal atom lies on a centre of
symmetry and makes a positive contribution to all
reflections.   By comparing the structure amplitudes of
"free" phthalocyanine and its nickel isomorph, Robertson
(1935,1936) was able to determine the phases of nearly
all of the observed reflections from phthalocyanine.
This is the earliest example of the solution of a
crystal structure without recourse to chemical information.

The first direct application of the heavy-atom
method was the solution of the structure of platinum
phthalocyanine by Robertson and Woodward (1940).   The
platinum compound is not isomorphous with the two
phthalocyanines described above, although it has the
same space group.   A Fourier synthesis using the observed
structure amplitudes and the phase of the heavy atom alone
revealed the positions of all of the light atoms other
than hydrogen.

If the scattering power of one atom is very much
larger than that of the other atoms in the structure and
if the position of the heavy atom is known, the structure
factor expression can be factored into light atom and
heavy atom components;

$$(6) \qquad F(\underline{H}) = f_h(\underline{H}) \exp (2\pi i\ \underline{H}.\underline{x}_h) + \sum_{j=1}^{N-1} f_j(\underline{H}) \exp (2\pi i\ \underline{H}.\underline{x}_j).$$

With a suitable choice of heavy atom, it will so
dominate the scattering that for most planes the phase
angle calculated from the first term in the series is
a suitable approximation to the true phase.   If a
Fourier synthesis is calculated with the observed
structure amplitudes as coefficients and with phases
calculated from the heavy atom position, it will reveal
more atomic positions.   These can be used in subsequent
phasing calculations to give a better approximation to
the true phases.   The process is continued until the
positions of all atoms are known.

Lipson and Cochran (1957) suggest that the method
is most effective when the scattering power of the
heavy atom is about equal to that of the light atoms
in the structure.   If a very heavy atom is used, the
contribution of the light atoms to the total scattering
is so small that experimental errors and diffraction
effects become important.   Under these conditions it
is difficult to obtain accurate parameters for the
light atoms.   If the heavy atom is too light, the
phase of the heavy atom is not a good approximation to
the true phase and the Fourier map may reveal no new
atomic positions.   Sim (1957,1959) has calculated

the proportion of structure factors correctly phased
by a heavy atom or a group of heavy atoms in space group
P$\bar{1}$, and has developed formulae for the distribution of
phase angles around the phase of the heavy atom in
space group P1.   His tables provide a good guide in the
selection of a derivative suitable for X-Ray analysis.

1.3.   THE PATTERSON FUNCTION

In 1935 Patterson defined the function

$$(7) \quad P(\underline{r}') = V_0 \int \rho(\underline{r})\rho(\underline{r}+\underline{r}') \, dV_{\underline{r}} .$$

Substituting equation 5 in equation 7 we get

$$(8) \quad P(\underline{r}') = \frac{1}{V_0} \int_{-\infty}^{+\infty} \sum_{\underline{H}} \sum_{\underline{H}'} F(\underline{H})\exp(-2\pi i \underline{H}.\underline{r}) \times F(\underline{H}')\exp(-2\pi i \underline{H}'.\underline{r})$$

$$\times \exp(-2\pi i \underline{H}'.\underline{r}') \, dV_{\underline{r}} .$$

This function is zero except when $\underline{H} = -\underline{H}'$; when this
condition applies

$$(9) \quad P(\underline{r}') = \frac{1}{V} \sum_{\underline{H}}^{+\infty} F(\underline{H}) \, F(-H) \, \exp(-2\pi i \underline{H}'.\underline{r}')$$

$$= \frac{1}{V} \sum_{\underline{H}}^{+\infty} |F(\underline{H})|^2 \, \exp(2\pi i \underline{H}.\underline{r}') .$$

Thus a Patterson function is a Fourier series with the
square of the structure amplitudes as coefficients. As
defined in equation 7, it is the self-convolution of the
electron density.   The maxima of this function represent
interatomic vectors.   If there are N atoms in the unit
cell, there will be N^2 peaks in the Patterson

map with N of these superimposed at the origin and
one half of the remaining $N(N-1)$ related to the other
half by a centre of symmetry at the origin. The
weight of the jth atom is its atomic number Z_j, and
the weight of the ij^{th} Patterson peak is $Z_i Z_j$. Both
the atomic functions $\rho(r_j)$ and the interatomic function
$P(r'_{ij})$, are Gaussian, but the half-width of a Patterson
peak is the root mean square of the half-widths of the
atomic functions of the corresponding atoms. This
leads to chance overlap of vector peaks and tends to
complicate the interpretation of the Patterson function.
However, inversion centers and translations in the
crystal give rise to anti-parallel and parallel vectors
respectively. This results in exact superposition
of certain maxima, thus increasing their weights
relative to background, and is often useful in
interpreting a vector map. If there are a small
number of heavy atoms in the structure, the outstanding
vectors in the Patterson map will be the heavy atom -
heavy atom vectors and the heavy atom-light atom vectors.
Peaks representing interactions between light atoms form
a fluctuating background of vector density for a structure
of moderate complexity. If an atom is heavy enough
to be distinguished in the Patterson map, its position
in the unit cell can be determined from a knowledge of

Table 1

Patterson Vectors for the Space Group $P2_12_12_1$

General Positions

1) $x, \quad y, \quad z$

2) $\frac{1}{2}-x, \quad -y, \quad \frac{1}{2}+z$

3) $\frac{1}{2}+x, \quad \frac{1}{2}-y, \quad -z$

4) $-x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z$

Vector Positions

2-1) $\frac{1}{2}-2x, \quad -2y, \quad \frac{1}{2}$ (1-2) $\frac{1}{2}+2x, \quad 2y, \quad \frac{1}{2}$

3-1) $\frac{1}{2}, \quad \frac{1}{2}-2y, \quad -2z$ (1-3) $\frac{1}{2}, \quad \frac{1}{2}+2y, \quad 2z$

4-1) $-2x, \quad \frac{1}{2}, \quad \frac{1}{2}-2z$ (1-4) $2x, \quad \frac{1}{2}, \quad \frac{1}{2}+2z$

4-2) $\frac{1}{2}, \quad \frac{1}{2}+2y, \quad -2z$ (2-3) $-2x, \quad \frac{1}{2}, \quad \frac{1}{2}+2z$

4-3) $\frac{1}{2}-2x, \quad 2y, \quad \frac{1}{2}$ (2-4) $\frac{1}{2}, \quad \frac{1}{2}-2y, \quad 2z$

3-2) $2x, \quad \frac{1}{2}, \quad \frac{1}{2}-2z$ (3-4) $\frac{1}{2}+2x, \quad -2y, \quad \frac{1}{2}$

Projection on (010)

position	weight
$\frac{1}{2}-2x, \quad \frac{1}{2}$	2
$\frac{1}{2}, \quad -2z$	2
$-2x, \quad \frac{1}{2}-2z$	1
$2x, \quad \frac{1}{2}-2z$	1
$\frac{1}{2}+2x, \quad \frac{1}{2}$	2
$\frac{1}{2}, \quad 2z$	2
$2x, \quad \frac{1}{2}+2z$	1
$-2x, \quad \frac{1}{2}+2z$	1

the equivalent positions of the space group. For
instance, the methiodide of 7-acetoxy-7-H-yohimbine
crystallizes in the orthorhombic system with space
group $P2_12_12_1$. There are four equivalent positions
in the space group and four molecules in the unit cell.
This should give 16 heavy atom heavy atom interactions
with four superimposed at the origin and the other 12
distributed through the cell (Table 1). The symmetry
elements present cause eight of these to coincide in
pairs when viewed in projection, thus giving four double-
weight and four single-weight peaks. In the unique
area of the projection on (010) there are two double-
and one single-weight peak:

$$\tfrac{1}{2}, 2z; \quad \tfrac{1}{2}-2x, \tfrac{1}{2}; \quad 2x, \tfrac{1}{2}-2z;$$

where x, and z are the fractional coordinates of the atom
in the unit cell.

1.4. DECONVOLUTION OF THE PATTERSON FUNCTION

Several methods are described in the literature
for deconvoluting the Patterson function to derive the
crystal structure. These are reviewed briefly by
Lipson and Cochran (1957) and by McLachlan (1957), and
very comprehensively by Buerger (1959). These techniques
are most easily understood as attempts to recover the
fundamental set from the vector set by superimposing
one vector map on the other so that the origin of the

first map lies on a peak in the second. The coincidences
are marked and this gives a "reduced vector set". This
is illustrated for a fundamental set of points and a
vector set of points in figure 1.

If a single weight peak is chosen as the origin for
superposition, and if the fundamental set contains a
centre of symmetry, that set can be recovered by a single
superposition. If the fundamental set is not centro-
symmetric, the "reduced vector set" contains the
fundamental set and its mirror image. The penalty
incurred for placing the origin of one vector map on an
"n"-fold multiple peak in the second is to recover the
fundamental set and its congruent image repeated "n"
times in different positions. However, successive
superpositions will reveal a single solution if sufficient
single weight peaks are found.

This need for single weight peaks limits the
applicability of the method. A Patterson peak
representing a vector between like atoms will have a
half-width $\sqrt{2}$ greater than that of the corresponding
atomic peak. If there are N resolved peaks in the
Fourier synthesis, the N^2 Patterson peaks are unlikely
to be resolved in the same volume. In a structure of
reasonable complexity with atoms of similar scattering
power, the single weight peaks will be among the smallest

"Fundamental set" containing a heavy atom, and
the heavy atom interactions of the "vector set"

Fundamental set

Vector set

"Fundamental set" containing a heavy atom, and
the heavy atom interactions of the "vector set".
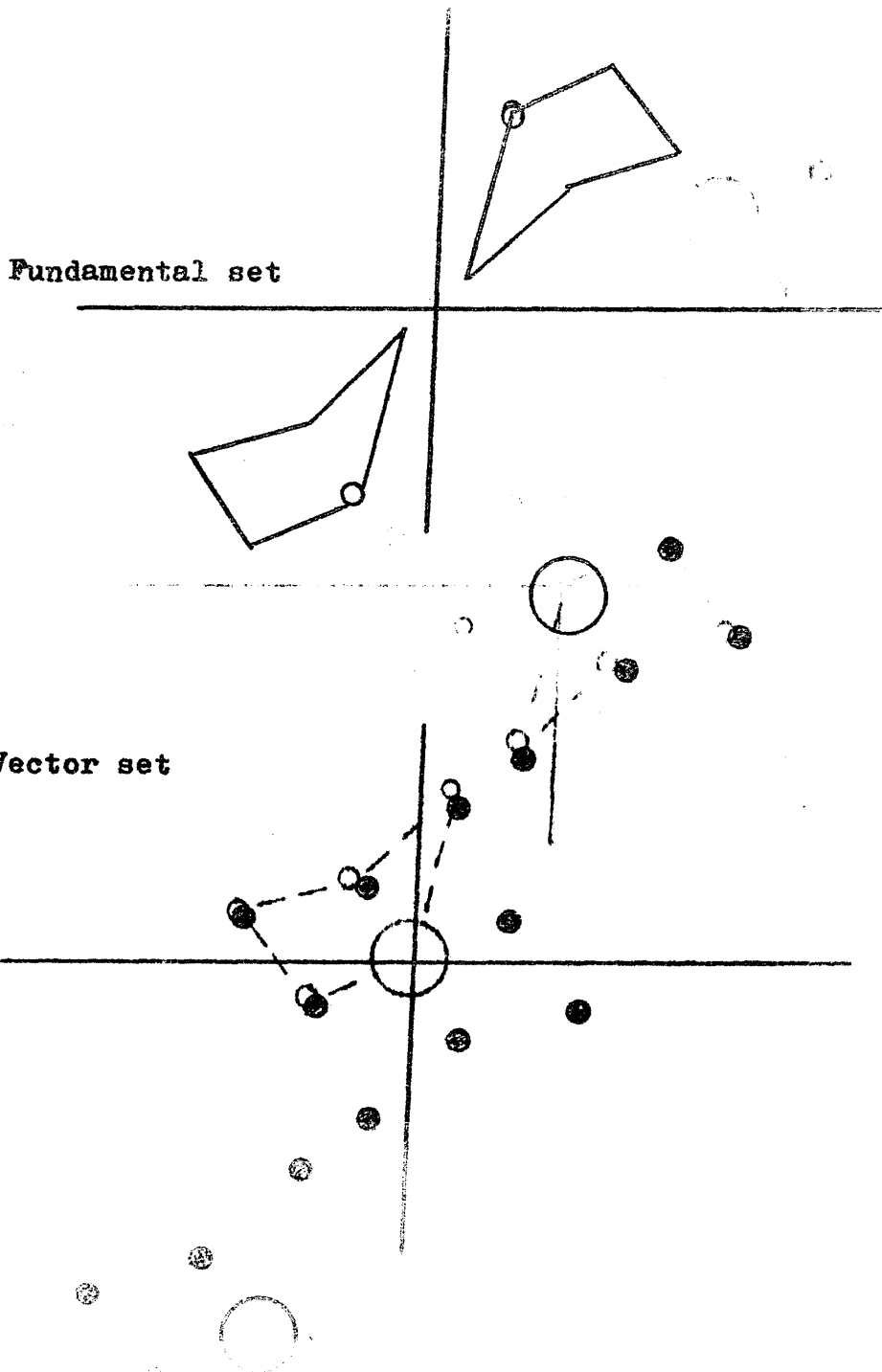
Fundamental set

Vector set
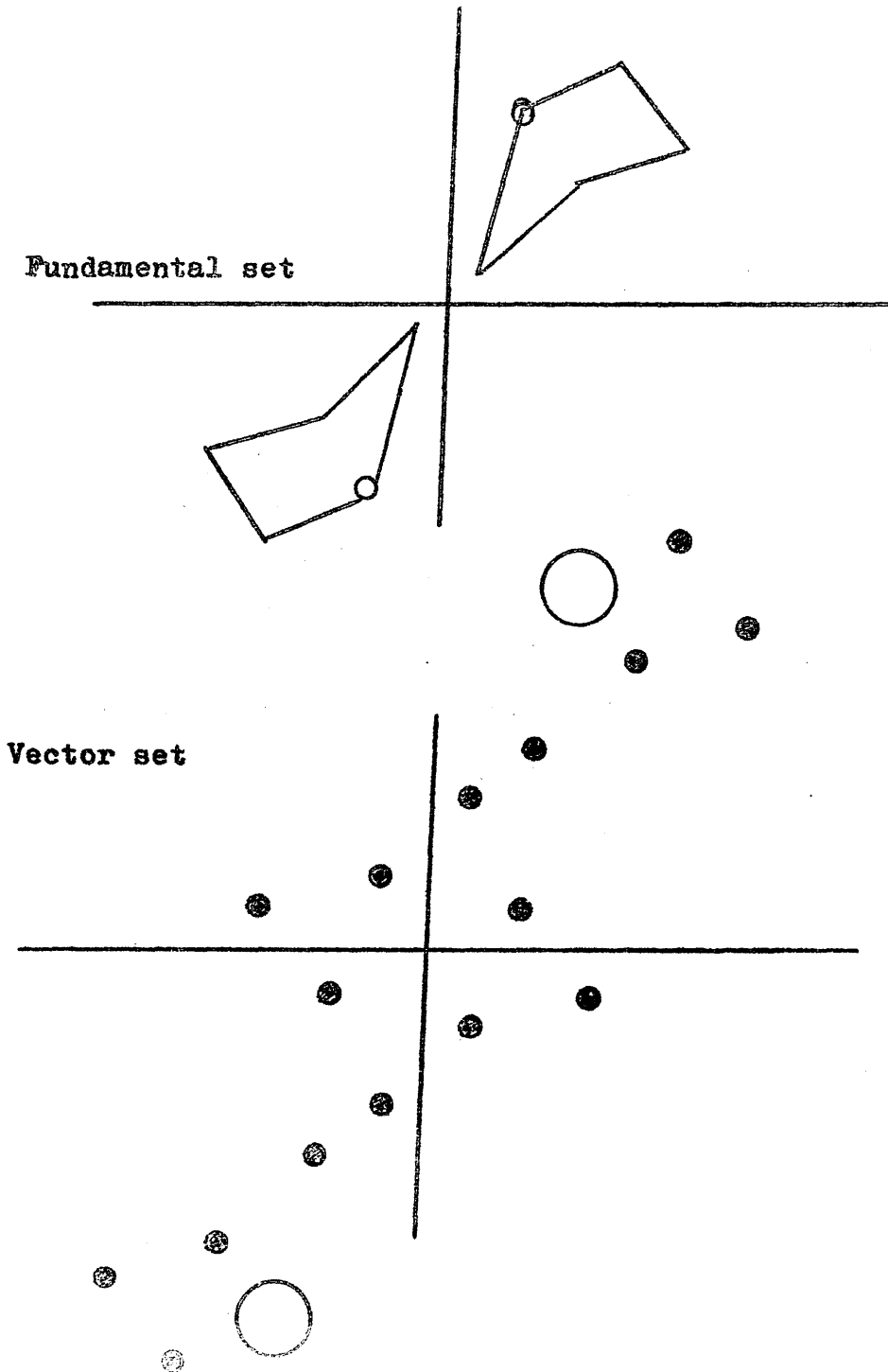
in the map and may be lost in a background of vector density. This lack of resolution causes a further difficulty when we attempt to recover the density function by superposition methods. If we record only the sites where the two functions overlap when superposed, chance coincidences will produce false atomic positions. McLachlan suggests that the resolution of a superposition function can be improved if the vector density is summed or multiplied at each point in the cell. This method does enhance the correct peaks but it does not eliminate "ghost" peaks caused by chance coincidences. Buerger claims that the best resolution is obtained when the minimum value is recorded at each point. The resulting minimum function has a value only when both functions have a positive value and is zero elsewhere.

One of the simplest applications of the method is in the solution of structures with space group $P\bar{1}$. The parabromobenzoate of benzil monoxime will serve as an example. In a centrosymmetric space group, vectors between atoms not related by the inversion centre are constrained to overlap in pairs to give peaks of weight $2Z_iZ_j$ at $r_i - r_j$. Atoms related by the centre of symmetry give rise to vectors of weight Z_j^2 at $2r_j$. Thus the heavy atom-heavy atom interaction produces a single weight peak. Once this has been identified, the electron

density can be recovered in a single superposition.
These conditions apply in the case of the benzil monoxime
derivative. Two copies were made of a sharpened, three-
dimensional Patterson map. The origin of one map was
placed on the centre of the Br-Br vector peak of the
second, and the various sections were paired to maintain
this displacement. A "minimum function" was derived
by tracing minimum contours where peaks in the two maps
overlapped. The origin of coordinates in the "minimum
function" was defined at the mid-point of the displacement;
half-way along the bromine-bromine vector.

1.5. SUMMARY

The Patterson function is a very powerful tool
in the early stages of structure analysis. It can
be used with both centered and non-centered structures,
for molecules with atoms of similar scattering power
or for molecules with one or more heavy atoms. When
combined with the heavy-atom method, it provides a very
elegant means of circumventing the phase problem.

Part II

The Structure of Yohimbine:

The Crystal Structure of the

Methiodide of 7-Acetoxy-7-H-Yohimbine

2.1. INTRODUCTION

Yohimbine is an indole alkaloid isolated from yohimbehe bark and used as an aphrodisiac in veterinary medicine. The structure of yohimbine, I, was first established by chemical means. The final link in the long chain of evidence leading to the complete structure was provided by Swan (1950), when he determined the position of the hydroxyl group. The work of Witkop (1949) and others established the stereochemistry of the molecule. This work is well documented in "The Alkaloids" (Manske, vols. II and VII).
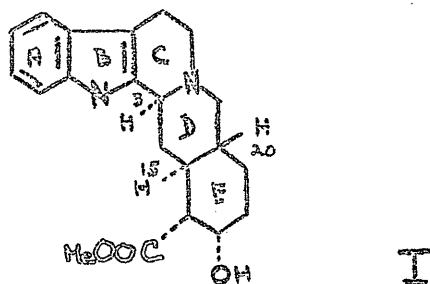
The molecule is characterized by five asymmetric centres. Hydrogen atoms at C(3), C(15) and C(20) are in axial positions; those at C(3) and C(15) are in the α configuration. Rings D and E are _trans_ – fused.

The present structure analysis of the methiodide of 7-acetoxy-7-H-yohimbine confirms both the gross

structure and the stereochemistry of yohimbine itself.
However, its importance lies in its connection with
research on oxidative transformations of indole alkaloids
by N. Finch and W.I. Taylor of the CIBA Pharmaceutical
Company.   By correlating the results of this X-ray
analysis with their own optical rotatory dispersion data,
Finch and Taylor have been able to draw some fairly
definite conclusions about the mechanisms of certain
reactions of indole alkaloids, and to establish the
stereochemistry of several alkaloids of this class.

2.2. OXIDATIVE TRANSFORMATIONS OF YOHIMBINE AND RELATED ALKALOIDS

In 1962, Finch and Taylor reported that yohimbinoid
alkaloids with trans-fused DE ring systems could be
converted to their oxindole equivalents by methanolysis
of the 7-chloro derivatives (II) to give the imino-ester
(III).   When the ester is refluxed with aqueous acetic
acid, the reaction product is a mixture of oxindoles A
and B (IV).

II

III

IV

oxindole A   oxindole B
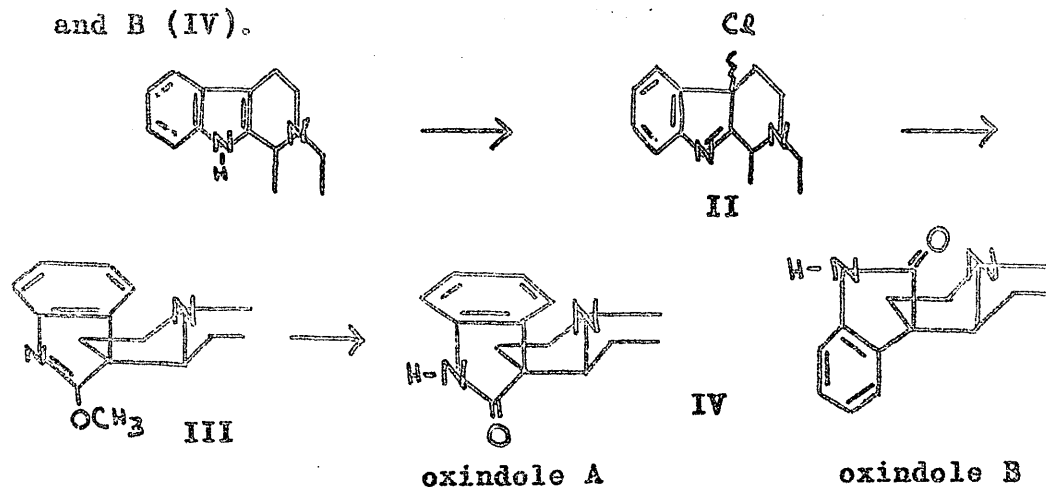
When this series of reactions was attempted using an
alkaloid with cis fused DE rings, the results were markedly
different. Instead of a 50:50 mixture of epimers of
the chloro-derivative, there was a marked preponderance
of the Cl-axial epimer. This resulted in a reduction
from 40% to 4% in the yield of the methanolysis product,
the imino-ester. Thus the method is of practical utility
in synthesising only those oxindole alkaloids that have
trans DE stereochemistry. (Finch and Taylor, 1962a; 1962b).

A later paper (Finch et al., 1963) explored the
reactions of Pb^{IV} salts of carboxylic acids with alkaloids
of the yohimbine type. In all cases, the reactions of
the parent alkaloid in methylene chloride with one molar
equivalent of the lead salt yielded the corresponding acyloxy-
indolenine (V). When treated with acetic acid, the
indolenines eliminated the acyloxy residue to give the
dehydro-compound (VI). However, if the indolenines are
refluxed with methanol and a few drops of acetic acid, those
with trans-fused DE ring systems do not react but those
with cis-fused systems rearrange to give the corresponding
oxindole (IV).

parent alkaloid   indolenine, V   dehydro compound

V   VI

IV
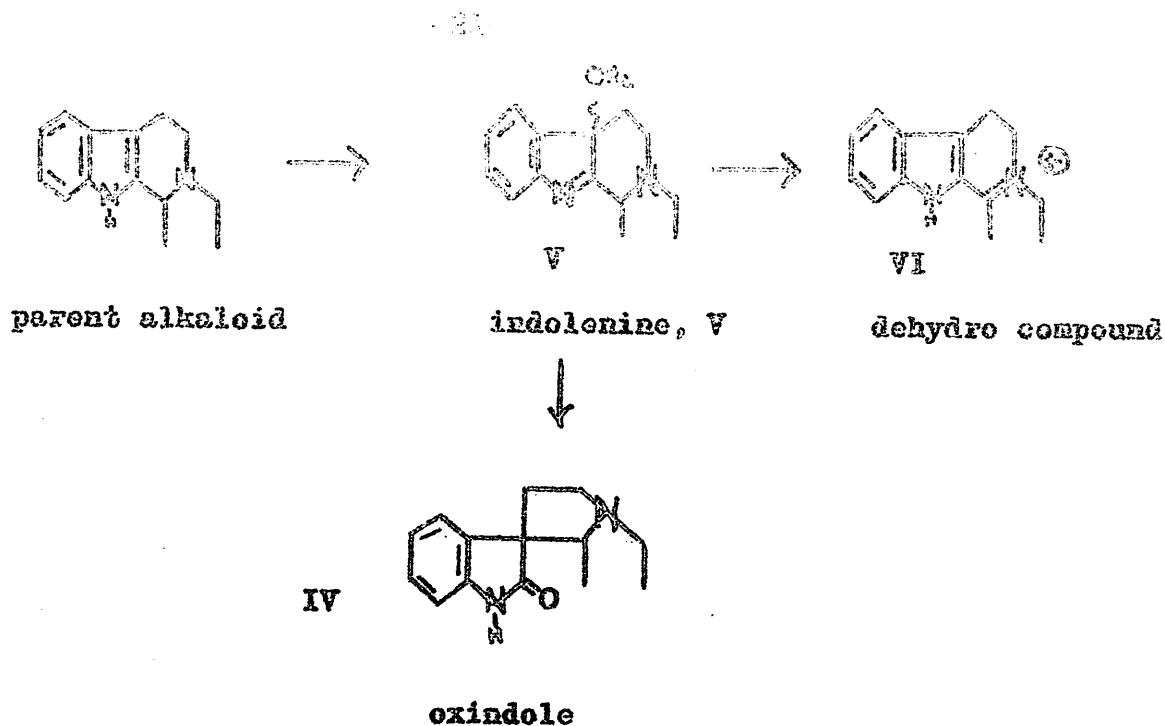
oxindole

Oxindole B is the major product of the rearrangement
regardless of the stereochemistry at C(3). The reaction
mechanism proposed depends on the protonation of the
indolenine nitrogen and rearrangement of the resulting
carbonium ion with neighbouring-group participation by
the acetoxy moiety. This mechanism would explain why
trans-fused systems do not rearrange under the conditions
of the reaction. The bridge-head nitrogen is more basic
than the indolenine nitrogen, therefore protonation cannot
occur at the latter site. However, in acyloxy indolenines
with cis BE stereochemistry there is a fairly large 1:3-
diaxial interaction with the lone pair of the bridge-
head nitrogen. This decreases the basicity of this
nitrogen relative to the indolenine nitrogen and allows
protonation of the latter site. (Finch et al., 1963).

At this stage, it was uncertain whether the $Pb(OAc)_3$ group is displaced with retention or inversion of configuration in the formation of the indolenine. On the basis of chemical evidence, it was not possible to determine whether the rearrangement at C(3) occurs before or after the formation of the oxindole. It was hoped that a detailed knowledge of the stereochemistry of at least one of the acyloxy indolenines would be helpful in interpreting these reactions. The compound chosen for X-ray analysis was the acetoxy-indolenine of yohimbine.

2.2.1. X-RAY ANALYSIS OF 7-ACETOXY-7-H-YOHIMBINE

The methiodide of 7-acetoxy-7-H-yohimbine was prepared by Dr. Taylor and his colleagues by dissolving 7-acetoxy-7-H-yohimbine in methyl iodide and recrystallising the resulting salt from methanol. This gave colourless, well-formed needles, suitable for X-ray crystallography, m.p. 225-227°C. The crystal structure of the methiodide was determined by the heavy atom method. Approximate locations of all light atoms, other than hydrogen, were found from a series of three-dimensional electron −

Figure 2

Stereochemistry of the Methiodide of 7-Acetoxy
7-H-Yohimbine.
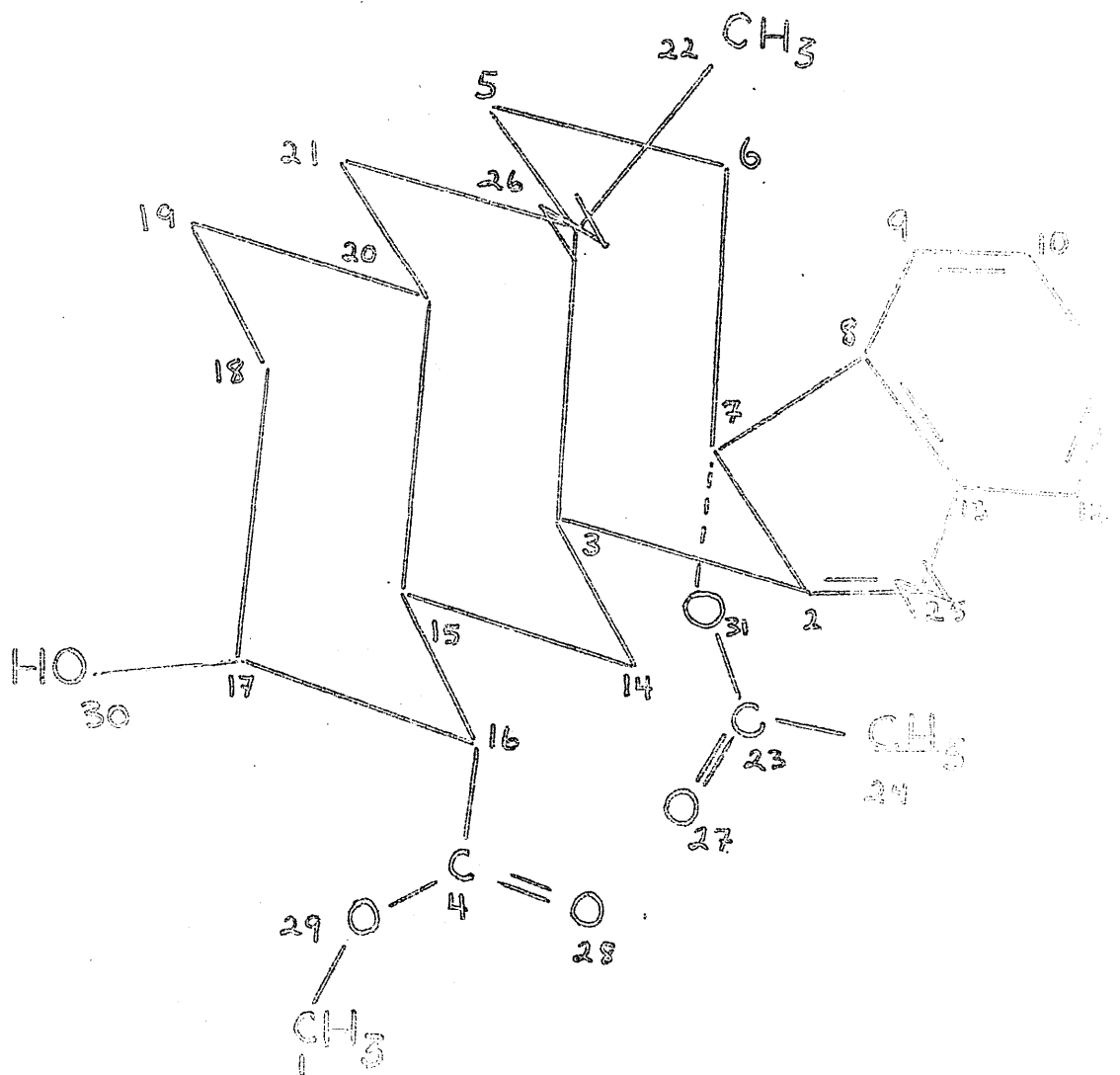
density syntheses.   Refinement of positional and thermal
parameters by the method of least squares gave a final
R-value of 14·60% over 1059 independent reflections.

Molecular dimensions are given in sub-section 2.4
after a description of the experimental work.   The
stereochemistry of the methiodide of 7-acetoxy-7-H-
yohimbine is shown in Figure 2.   The molecule has a
trans-fused DE ring system.   The hydrogen at C(3) is
in the α position as is the acetoxy group at C(7).   This
corresponds to the structural formula VII for the acetoxy
indolenine tentatively proposed by N. Finch at the
I.U.P.A.C. Symposium on the Chemistry of NaturalProducts
Prague, 1962.

VII
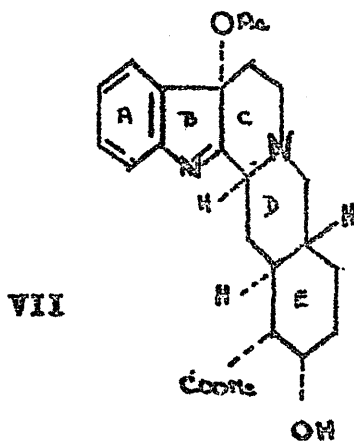
acetoxy indolenine of yohimbine

2.2.2. CORRELATION OF X-RAY RESULTS WITH O.R.D. DATA

Optical rotatory dispersion curves are available
for 7-acetoxy-7-H-yohimbine, VII; two epimeric 7-chloro-
7-H-yohimbans, VIII; methyl-7-hydroxy-7-H-reserpate, IX;
and the acetoxy indolenines of pseudoyohimbine, X, and
aracine, XI. The formula of these compounds are shown
in Figure 3; their O.R.D. curves are shown in Figures
4 and 5. These curves have been drawn from diagrams
published by Finch et al. (1965).

The optical rotatory dispersion curves of the two
chloro-yohimbans bear a mirror image relationship to one
another (Figure 4). This indicates that the C(7)
substituent makes the largest contribution to the Cotton
effect. The two curves have nearly identical amplitude
but opposite sign because the CD ring fusion constrains
the C(7)-C(8) bond to be equatorial or pseudo-equatorial
in the two epimers. This means that the substituent
at C(7) is either axial or pseudo-axial and will have a
large interaction with the chromophore group in either the
α or the β configuration. Any contribution to the
dispersion curve from the hydrogen at C(3) would be expected
to be small.

Figure 3
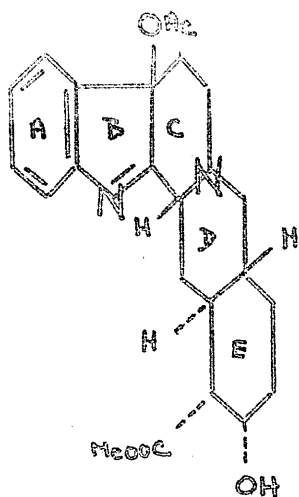
X, 7-β-acetoxy-7-H-
pseudoyohimbine
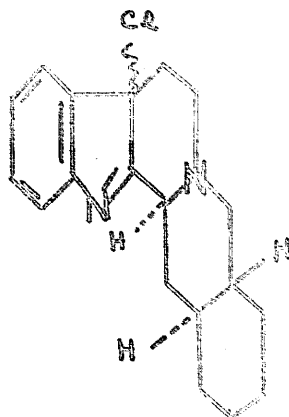
VIII, 7-chloro-7-H-
yohimban
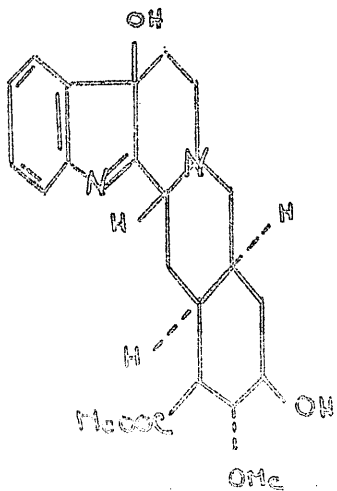
IX, methyl-7-β-hydroxy-
7-H-reserpate
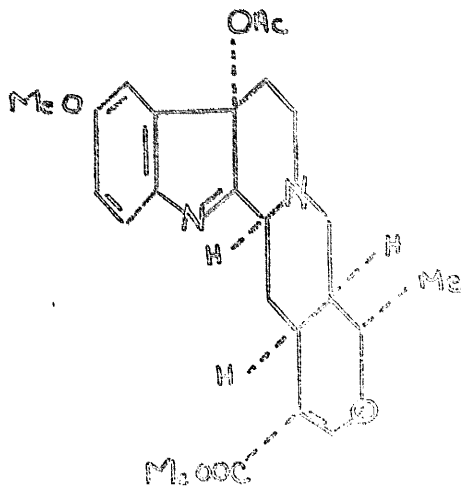
XI, 7-α-acetoxy-7-H-
aricine
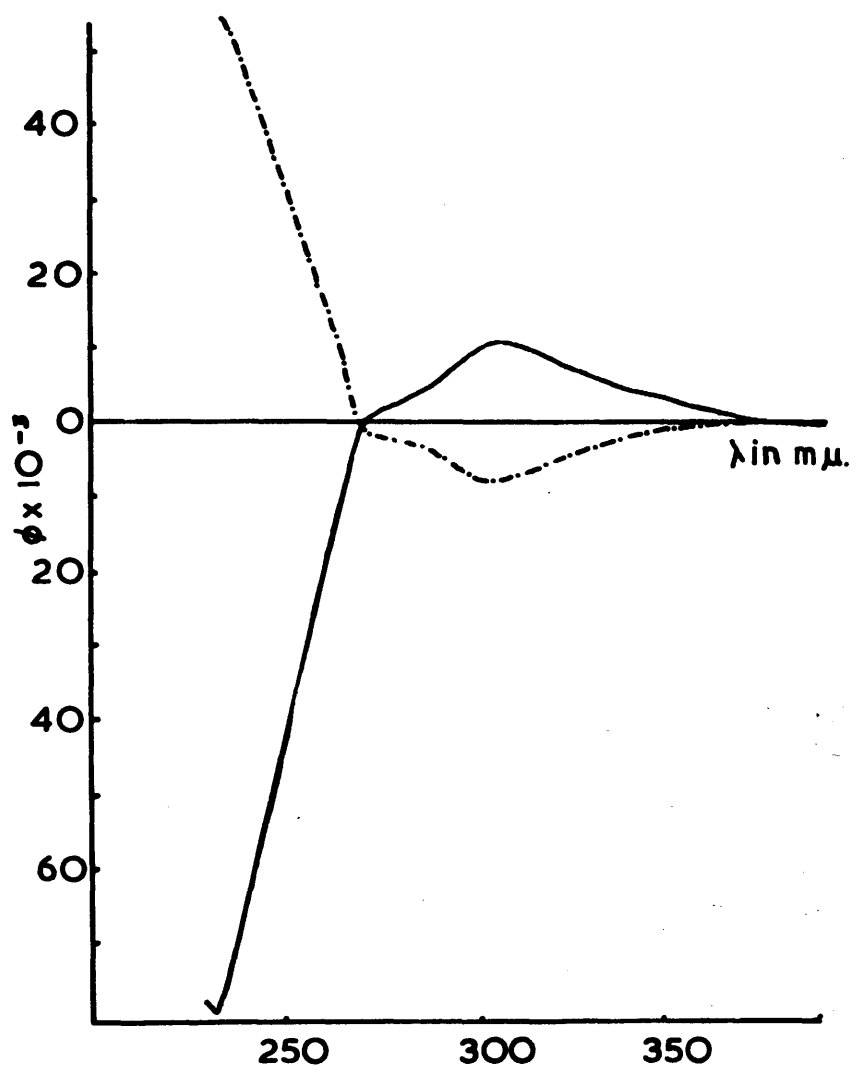
Figure 4

O.R.D. curves for epimeric 7-chloro-7-H-yohimbans

Figure 5

O.R.D. Curves

aricine ——————
7α-acetoxy-7H-aricine ——————

yohimbine ——————
7α-acetoxy-7H-yohimbine ——————
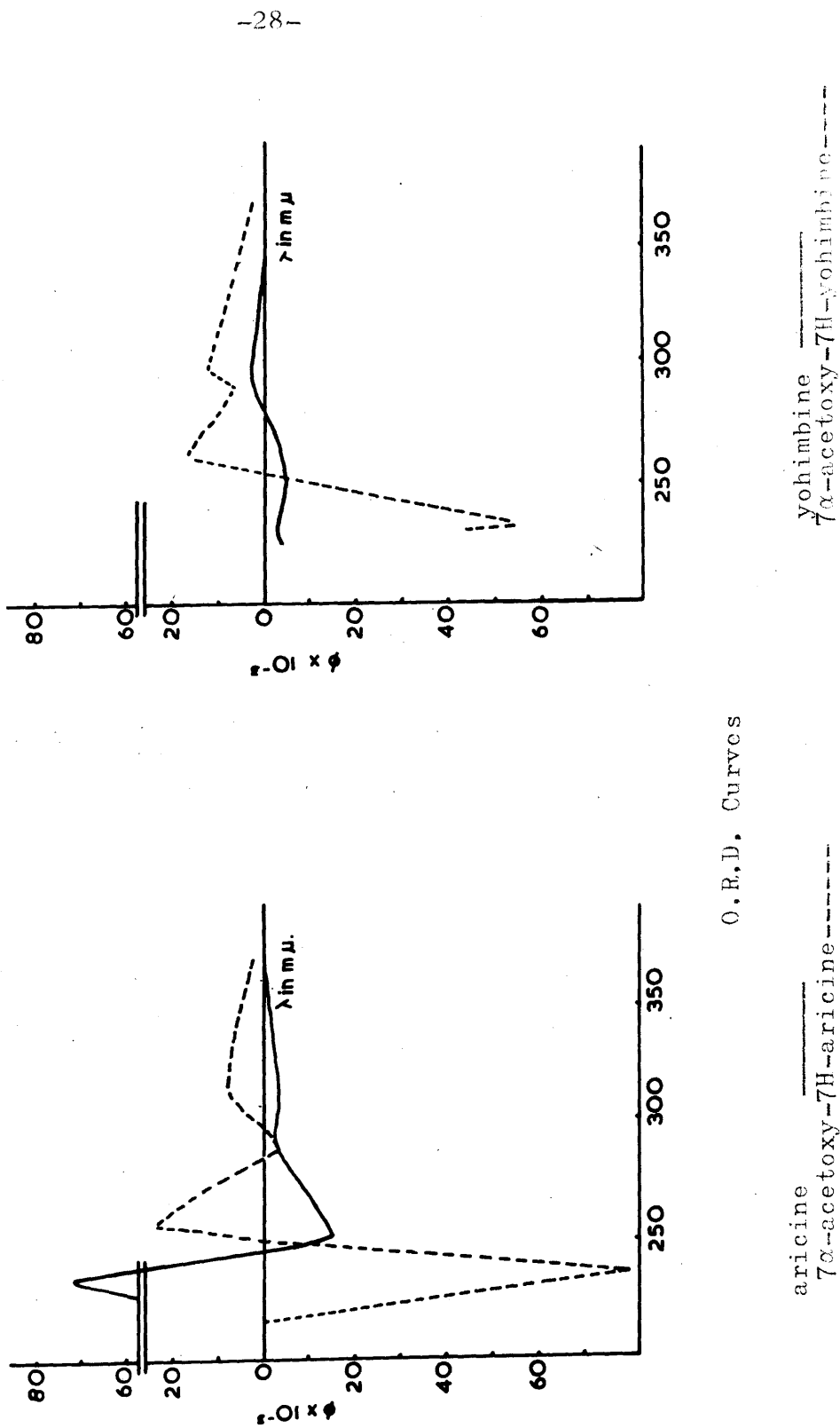
The dispersion curves of the yohimbine and aricine
derivatives (Figure 5) have the same sign and similar
shape in spite of different configurations at the DE
ring junction.   On the assumption that the C(7)
contribution dominates the dispersion curve, the α
configuration was assigned to the acetoxy group in the
aricine derivative.   The curves of the other two compounds
have the sign expected of indolenines with a C(7) substituent
in the β position. (Finch et al., 1965).

These results threw some light on the mechanism of
the reactions of lead salts of carboxylic acids to give
acyloxy indolenines.   The configuration of the C(7)
substituent can be predicted if the position of the
hydrogen at C(3) is known.   If that hydrogen has an α
configuration, the C(7) substituent will do likewise.
This observation is compatible with the reaction mechanism
proposed in an earlier paper (Finch et al., 1963).
Although the stereochemistry of this reaction is now
established, there is still no information about the
subsequent rearrangement of the indolenines to oxindoles.
The fact that the observed product is the one expected
to be most stable in the reaction mixture would seem to
support the thesis that epimerization at C(3) occurs after
rearrangement.

2.3. EXPERIMENTAL

The sample provided by Dr. Taylor consisted of small white needle-like crystals that showed sharp extinction along the needle direction. Rotation, Weissenberg and precession photographs were taken with the crystal mounted so that the needle axis was perpendicular to the X-ray beam. These photographs were used to determine cell dimensions and space group.

2.3.1. CRYSTAL DATA

Formula	$C_{24}H_{31}N_2O_5I$ F.W. 554.43 gm
System	orthorhombic
Lattice constants	$a = 13.16$ Å
	$b = 26.82$ Å
	$c = 7.33$ Å
Absent Spectra	h00 with $h = 2n + 1$
	0k0 with $k = 2n + 1$
	00l with $l = 2n + 1$
Space Group	$P2_12_12_1$
Volume	2587 Å^3
Density (obs.)	1.44 gm./cc
Molecules/cell	4
Density (calc)	1.42 gm./c.c.
F(000)	1128
μ(CuKα)	110 cm^{-1}

2.3.2. INTENSITY DATA

The 0kℓ zone was photographed by the precession
method. Since the crystal-to-film distance is critical
in this method (Buerger, 1944), only one film can be
placed in the casette at a time. A timed series of
six photographs was taken using a stabilised power supply.
Exposure times ranged from 11 minutes to 45 hours. Mo Kα
radiation was used. The precession angle was set at
30°. Lorentz-polarisation corrections were applied to
these data by means of a template. (Buerger 1960, p 188).

Reflection data for the six reciprocal lattice
nets hk0 to hk5 were collected using an equi-inclination
Weissenberg camera and multiple film packs (Robertson,
1943). The intensities of these reflections were estimated
visually by comparison with a calibrated intensity scale.
The film factor between successive photographs of a series
was 3·3 for the zero layer. This was modified for upper
layers to allow for the increase in path length through
the film with increasing inclination angle (Rossmann, 1956).
These data were collected with CuKα radiation. They
were corrected for Lorentz and polarization factors
according to the formula

$$I(hk\ell) = \frac{1}{\sin 2\theta} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot |F(hk\ell)|^2$$

The form of the Lorentz factor shown here applies only
to zero layer photographs of rotating crystals.   For
upper layers, this must be modified by a factor $1/D$, where

$$D = (\cos^2\mu - \cos^2\theta)^{\frac{1}{2}} / \sin\theta$$

the rotation factor defined by Tunnell (1939) for the
equi-inclination case.   The symbols μ and θ are the
equi-inclination angle and the Bragg angle, respectively.
No absorption corrections were applied.

    The structure amplitudes, $|F_{obs}|$, were given
the same relative scale by comparison of axial reflections
from Weissenberg photographs with common reflections
from precession photographs of the $Ok\ell$ zone.

2.3.3. ANALYSIS OF THE STRUCTURE

    Patterson coefficients, $|F|^2$, were modified by a
tabulated function of $\sin^2\theta$
and used to compute sharpened
Patterson projections, $P(VW)$
and $P(UV)$.   The form of the
modification function is shown
in the figure on the left.
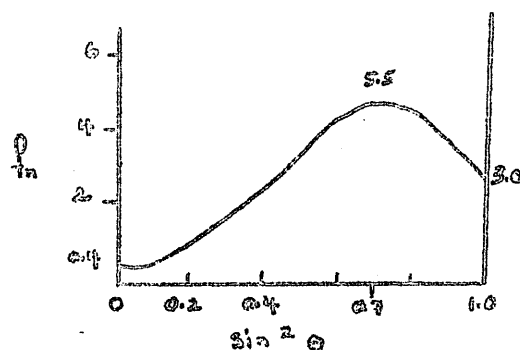
The I-I vectors were easily recognised in the Patterson
maps.   Fractional coordinates of the iodide ion were:

$$x = 0\cdot1772, \quad y = 0\cdot1026, \quad z = 0\cdot1453.$$

Structure factors were calculated with phases determined
by the heavy atom alone. These were placed on absolute
scale by comparison of the sums of the observed and
calculated structure amplitudes.

$$k\Sigma|F_o| = \Sigma |F_c|$$

The R-value, $\Sigma\Delta/k\Sigma|F_o|$, was 37%

The iodide ion is very "heavy" in comparison with
the light atoms in the structure. Using Sim's (1957)
method, it is possible to predict how well the phase
of the heavy atom approximates to the true phase. Sim
has calculated the fraction, $N(\alpha)$, of structure factors
whose phase is within $\pm\alpha$ of the phase of the heavy atom
for various values of r, where r is defined by

$$r = \left(\Sigma f^2_H / \Sigma f^2_L\right)^{\frac{1}{2}}$$

In general, the probable phase-angle error decreases
as r increases. For this compound, the value of r
is 1·46. Interpolation on Sim's graph shows that only
about 20% of the structure factors will have phase errors
greater than $\pm 35°$ in a calculation based on the position
of the heavy atom alone. This estimate is probably a
pessimistic one, as it is strictly valid only for space
group P1. The space group $P2_1 2_1 2_1$ has three centrosymmetric
projections. About 88% of the data from these zones can
be expected to have the correct sign. Since nearly all

of the data were considered to be reliably phased by
the heavy atom, only those planes with very small values
$|F_{obs}|$ were excluded from the first Fourier calculation.
The resulting map revealed the positions of all of the
atoms in the skeleton of the molecule. When these
were included in the next structure-factor calculation
with scattering factors appropriate to carbon atoms,
the R-value dropped to 29.6%. After the second Fourier
synthesis all 31 light atoms, excluding hydrogen, had
been located and identified. They were included in the
next cycle of Fourier refinement with scattering curves
corresponding to their chemical types.

After a third cycle, the coordinates were corrected
for termination of series errors by a modification of
Booth's (1946, 1947) method. This involves calculating
two Fourier syntheses with the same coordinates. Observed
structure amplitudes are used as coefficients in one map,
and calculated structure amplitudes for the other. If
a peak appears at a position, x_{p_j}, in the penultimate
Fourier map, it should appear in the same position in an
F_c map calculated from those coordinates. Termination of
series errors cause these two sets of coordinates to
differ by $\Delta x_j = x_{p_j} - x_{c_j}$ for the jth atom. If x_{o_j} is
the position of this atom in the final Fourier map, its
correct position is given by $x_{o_j} - \Delta x_j$.

If atom peaks appear at different heights in the F_o
and F_c syntheses, the temperature factor is in error by
an amount that can be estimated from the difference in
peak height.   In the two maps calculated here, peaks
in the F_o synthesis were systematically lower than those
in the F_c synthesis, indicating that the temperature factor
$\alpha = 2^{-B}$, had been underestimated.   When α was increased
from 2·8 to 3·0 ($B = 4·94 \, \text{Å}^2$), structure factors calculated
with corrected coordinates showed an R-value of 21%.

2.3.4.   REFINEMENT OF THE STRUCTURE

The computer program used for least-squares
refinement on DEUCE was written by J.S. Rollett and is
described elsewhere.   (Rollett, 1961).   The program uses
a three by three matrix for the atomic positions and a
six by six matrix for the atomic vibrations.   In order
to prevent overflow of the least-squares totals, it was
necessary to reduce the scale of the scattering curves
and of the structure amplitudes to 1/10 of the normal
value.   The weighting scheme used gives maximum value
to the "average" structure amplitude:

if $|F_o| < F^* \quad \sqrt{w} = F_o/F^*$.

$\quad |F_o| > F^* \quad \sqrt{w} = F^*/F_o$,

where $\quad F^* = 8 \, F \, \min = 4·64$.

There is no facility for isotropic refinement in this program. Anisotropic temperature parameters are defined by the equation

$$\exp(-B \sin^2\theta / \lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{13}h\ell)}.$$

After each cycle the b_{ii} terms from the diagonal of the vibration matrix were used to calculate the thermal parameters parallel to each of the principal axes using the following formulae:—

$$B_{11} = b_{11}/1.4427,$$

and $\quad B_X = 4B_{11}/a^{*2}.$

(Rollett, 1961; Rossmann, Jacobson, Hirshfeld and Lipscomb, 1959; Cruickshank, 1956).

The components of B_6 in the three axial directions were averaged to give an isotropic temperature factor for each atom. These individual temperature factors were averaged over all members of each chemical type. After two cycles of least squares, the R-value was 19.9%. The average B_6 values for the different chemical types were

$$I = 4.79 \, \text{Å}^2 \quad C = 4.53 \, \text{Å}^2 \quad N = 3.74 \, \text{Å}^2 \quad O = 5.49 \, \text{Å}^2$$

No further calculations were done on DEUCE. The parameters obtained from the second cycle were used when refinement was continued on KDF9 eight months later.

When the Glasgow SFLS program became available, two
rounds of isotropic least squares were calculated with unit
weights. The R-value was 17·8%. Cruickshank's (1961)
weighting scheme has been recommended for film data and
seemed appropriate for this case. It has the form

$$w = 1/ (p_1 + |F| + p_2|F|^2 + p_3|F|^3).$$

The initial values given to these parameters were as follows:

$$p_1 = 17 \quad p_2 = 8·9 \times 10^{-3} \quad p_3 = 9·9 \times 10^{-5}$$

After a further three cycles of isotropic block-diagonal
least squares, the R-value was 15·4% but the weighting
analysis showed that some adjustment in the weighting
parameters was required. One more cycle with the constants
in the weighting function changed to 8, $1·04 \times 10^{2}$, and
$1·34 \times 10^{-4}$, respectively improved the weighting analysis
but had little effect on the R-value. Reflection data
for the short and median axes were sorted from the full,
scaled, three-dimensional data that had been used for the
least-squares refinement. These data were used in a
"minimum residual" refinement by the method of Bhuiya and
Stanley (1963). Three cycles of refinement reduced the
R-value in the short-axis projection from 19·5 to 17·5%.
A single refinement cycle in the median -axis projection
produced an improvement of about 1% to give a final R-value
of 17·9%. When the new positions were used for a three-

dimensional structure-factor calculation, the R-value
was 16·5% but this dropped to 14·6% after three further
cycles of block-diagonal least squares.   Refinement
was terminated at this point.   Unobserved reflections
were not included in the analysis.

2.4. MOLECULAR DIMENSIONS AND DESCRIPTION OF THE STRUCTURE

Table 2 shows the final atomic coordinates and the
isotropic temperature factor for light atoms other than
hydrogen.   The coordinates and anisotropic thermal
parameters of the iodide ion are listed separately at
the foot of the table.   In all cases, the coordinates
are expressed as fractions of the crystallographic axes.
Their estimated standard deviations have been calculated
from the least squares residuals and are shown in parentheses
to the same number of places of decimal as the coordinates
with which they are associated.   Both the coordinates and
their standard deviations are listed with one figure that is
not significant to permit derived quantities to be calculated
without loss of accuracy.

The isotropic temperature factor used here is the
mean square vibration amplitude, U_{iso}, where

$$U_{iso} = \bar{u}^2 = B/8\pi^2$$

and B is the Debye factor.   Both U and B have the units
of $\AA^2$.   Anisotropic vibrational parameters are defined
by the equation

$$\exp\left(-B\sin^2\theta/\lambda^2\right) = \exp\left[-2\pi^2\left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2}\right.\right.$$
$$\left.\left. + 2U_{12}hka^*b^* + 2U_{23}k\ell b^*c^* + 2U_{13}h\ell a^*c^*\right)\right]$$

Bond lengths and angles with their estimated standard deviations are listed in Tables 3 and 4, respectively. Figure 6 is a schematic diagram showing bond lengths and the numbering used in the Tables. From Table 3, it can be seen that the average standard deviation of bond lengths in this structure is 0·05 to 0·06 Å. In the benzene ring, the average carbon-carbon bond length is 1·39 Å. The $C(sp_3)-C(sp_3)$ single bonds in the CDE ring system have an average length of 1·55 Å as do the $C(sp_2)-C(sp_3)$ bonds at the junction of that ring system with the indolenine moiety. These lengths do not differ significantly from the expected values of 1·397, 1·525 Å, respectively quoted by Sutton et al. (1958).

The carbon-nitrogen bonds fall into three categories. The C=N bond is 1·24±0·04 Å long, not appreciably different from the value of 1·27 Å found in dimethyl-glyoxime. The $C(sp_2)-N$ bond length of 1·36±0·05 Å is in agreement with the value of 1·371 Å reported in para-nitroaniline (Trueblood, Goldish and Donohue, 1961); 1·38 Å in 2-chloro-4-nitro-aniline (McPhail and Sim, 1963); 1·39 and 1·40 Å in ibogain hydrobromide (Arai, Coppola and Jeffrey, 1960). The value of 1·54 Å for the average $C(sp_3)-N$ bond length is somewhat longer than the value given by Sutton et al., but the long

bonds of this type are frequently reported in alkaloids.
In the structure of echitamine (Hamilton, Hamor, Robertson
and Sim, 1962) there are three bonds of this type with
a length of 1·54 Å and a fourth with a length of 1·56 Å.
After comparing the results of several analyses of different
alkaloids, these authors suggest that 1·52 Å is perhaps
a better estimate of the length of such a bond.

Positional standard deviations and thermal parameters
are greater for atoms in the side chains of this molecule.
The bond lengths show broad agreement with the expected values.
The carbon–oxygen single bond lengths can be placed in two
groups; those adjacent to a carbonyl group are shorter than
those removed from the carbonyl. Average lengths are
1·33 and 1·44 Å respectively.

The equation of the weighted mean plane through the
benzene ring is;

$$0.0195X + 0.1207Y - 0.9925Z = 0.1275$$

Each atom was given a weight inversely proportional to the
estimated variance of the atomic position. Deviations from
this "best" plane are shown diagramatically in Figure 7. The
units are Å x 10^3. The only atom in the indolenine moiety
that deviates significantly from the plane through the benzene
ring is C(7). This is not a surprising result since
resonance interaction between the benzene ring and the
double bond would tend to keep the C=N group in the plane

of the benzene ring. C(7) would be expected to deviate
from this plane because it is fully substituted and
cannot take part in resonance interactions.

Intermolecular contacts under 3·6 Å are listed in
Table 5 and are shown in the packing diagram (Figure 8).
For clarity, these have been divided into two groups and
are shown as contacts from molecules I and I'; i.e. the
molecule whose coordinates are given in Table 2, and the
same molecule in the next cell in the positive x-direction.
The only contact of particular interest is that between
N(25) and O(30).   This is a hydrogen bond of the O-H---N
type between the hydroxyl group at C(17) and the indolenine
nitrogen of a symmetry-related molecule.   The O...N
distance (2·90±0·03 Å) is more reliable than many of the
bond distances in the structure.   The C-O...N angle
is 103·8±1·7°.

Table 6 and Figure 9 show the environment of the iodide
ion.   The ion has more than a dozen contacts closer than
the quaternary nitrogen with which it is formally associated.
The N^{+}...I^{-} contacts are quite long and some of the contacts
between the iodide ion and the atoms of the acetoxy group
seem quite short.

The iodide ion is almost midway between the quaternary
nitrogen of one molecule and that of the same molecule
in the next cell in the negative x-direction.   The N^{+}...I

distances are 4·59 and 4·63 Å respectively. However, the iodide ion does not lie on a direct line between the two nitrogens but is displaced towards the acetoxy group. Its closest contacts are with C(23), C(24) and O(31) of that group. Expected van der Waals separations are shown in the table. These were calculated in the following way. Pauling's figures for the ionic radius of iodide (2·16 Å), oxygen (1·40 Å), and a methyl group (2·00 Å), predict a minimum separation of 4·15 Å between iodide and C(24), and 3·66 Å between the ion and O(31). The van der Waals radius of a carbon with no hydrogen would probably be about half the inter-layer spacing in graphite, or 1·70 Å. Thus C(23) would not be expected to be closer than about 3·86 Å. Several of the observed contacts are very near the expected van der Waals distances. The contact with C(24) is very short. In view of the high standard deviation in the experiment and the uncertainties in the van der Waals distances very little significance can be placed on any individual observation.

Both the long $N^+ \ldots I^-$ distances and the short contacts between iodide and carbon and iodide and oxygen seem to be observed frequently in compounds of this type. Silvers and Tulinsky (1963) report $N^+ \ldots I^-$ distances of 4·6 and 5·1 Å in alumindidine; and in carcurine-II dimethiodide, McPhail (1963) reports four distances between 4·42 and 4·16 Å.

Short contacts of iodide with carbon and oxygen have been
observed by Przybylska (1961 a, 1961 b), Jellinek (1957),
McPhail, Robertson and Sim, (1963) and others. This is
probably a steric effect. It is possible that with an
ion the size of an iodide ion, packing consideration and
van der Waals forces play a greater role in determining
the environment of the ion than do forces of Coulombic
attraction.

TABLE

Molecular of 2-(methoxy)-N-(methyl)...

Final atomic coordinates and temperature factors.
Standard deviations are given as units in the last place.

Atom	x		y		z		U_iso
C(1)	0.0006	(28)	0.1995	(15)	-0.3878	(73)	0.070
C(2)	0.0182	(21)	0.3957	(12)	0.1502	(55)	0.065
C(3)	-0.0674	(19)	0.3253	(11)	0.1526	(58)	0.057
C(4)	-0.0641	(18)	0.2134	(10)	-0.1496	(58)	0.061
C(5)	-0.1664	(23)	0.4134	(13)	0.3586		
C(6)	-0.0745	(25)	0.4562	(20)	0.3749	(91)	
C(7)	-0.0162	(19)	0.4268	(10)	0.2083	(54)	
C(8)	0.0850	(28)	0.4765	(16)	0.1955	(70)	
C(9)	0.1248	(25)	0.3930	(13)	0.2179	(69)	
C(10)	0.2131	(37)	0.5350	(21)	0.2594	(91)	
C(11)	0.2873	(25)	0.5061	(20)	0.2840	(88)	
C(12)	0.2619	(23)	0.4059	(11)	0.1833	(59)	0.057
C(13)	0.1601	(25)	0.3951	(15)	0.1899	(68)	0.065
C(14)	-0.0323	(21)	0.3045	(11)	0.0963	(57)	0.051
C(15)	-0.1851	(19)	0.2706	(09)	0.1021	(54)	0.065
C(16)	-0.1010	(29)	0.2133	(16)	0.0385	(76)	0.066
C(17)	-0.1996	(20)	0.1820	(11)	0.0541		0.057
C(18)	-0.2549	(28)	0.1547	(15)	0.2505		
C(19)	-0.2257	(22)	0.2290	(16)	0.2360		
C(20)	-0.1770	(23)	0.2701	(11)	0.3580		
C(21)	-0.2101	(22)	0.3270	(12)	0.3318		
C(22)	-0.0022	(33)	0.3770	(21)	0.5103		
C(23)	-0.0731	(25)	0.4735	(14)	-0.1107		
N(24)	-0.1804	(31)	0.2061	(17)	-0.1037		0.072
N(25)	0.1115	(17)	0.3099	(09)	0.1650		0.052
O(26)	-0.1174	(16)	0.3507	(10)	0.2465		0.055
O(27)	-0.0102	(23)	0.4464	(13)	-0.1679		0.067
O(28)	-0.0516	(21)	0.2499	(12)	-0.2503		0.066
O(29)	-0.0382	(19)	0.1676	(11)	-0.2079		0.077
N(30)	-0.2565	(15)	0.1949	(09)	-0.1073		0.051
C(31)	-0.0793	(16)	0.4733	(09)	0.0655		0.058
Z(32)	-0.35006	(21)	0.39653	(10)	-0.14516		

ANISOTROPIC TEMPERATURE PARAMETERS OF THE ...

U	U	U	2U_23	2U_31	2U_12
0.0418	0.0459	0.0735	0.0185	-0.0191	-0.0045

Table 3

Methiodide of 7-Acetoxy-7-H-Yohimbine:
Bond Lengths (Å). Estimated standard
deviations are given as units in the
last place.

N(25)	C(2)	1.242(36)
C(2)	C(3)	1.737(40)
C(3)	N(26)	1.504(52)
N(26)	C(22)	1.602(62)
N(26)	C(5)	1.524(42)
C(5)	C(6)	1.507(59)
C(6)	C(7)	1.443(71)
C(7)	C(8)	1.501(46)
C(8)	C(9)	1.414(55)
C(9)	C(10)	1.201(59)
C(10)	C(11)	1.360(73)
C(11)	C(12)	1.471(62)
C(12)	C(13)	1.376(47)
C(13)	C(8)	1.508(56)
C(13)	N(25)	1.361(46)
C(3)	C(14)	1.558(40)
C(14)	C(15)	1.524(36)
C(15)	C(20)	1.393(54)
C(15)	C(16)	1.573(51)
C(16)	C(17)	1.592(48)
C(17)	C(18)	1.613(62)
C(18)	C(19)	1.455(58)
C(19)	C(20)	1.618(49)
C(20)	C(21)	1.651(45)
C(22)	N(26)	1.602(62)
C(7)	C(2)	1.603(42)
C(7)	O(31)	1.461(43)
O(31)	C(23)	1.300(60)
C(23)	C(24)	1.312(61)
C(23)	O(27)	1.233(50)
C(16)	C(4)	1.463(65)
C(4)	O(28)	1.266(49)
C(4)	O(29)	1.360(41)
O(29)	C(1)	1.415(61)
C(17)	O(30)	1.435(45)

TABLE 4

Methiodide of 7-Acetoxy-7-H-Yohimbine

Bond angles and their standard deviations

			(°)	e.s.d.
C(2)	C(3)	N(26)	109.2	2.8
C(3)	N(26)	C(22)	114.4	2.6
C(22)	N(26)	C(5)	118.2	3.3
N(26)	C(5)	C(6)	109.5	2.9
C(5)	C(6)	C(7)	112.4	4.5
C(6)	C(7)	C(8)	121.9	3.7
C(6)	C(7)	C(12)	124.9	2.8
C(7)	C(8)	C(9)	138.2	3.4
C(7)	C(8)	C(13)	103.7	3.1
C(8)	C(13)	N(25)	110.6	3.1
C(13)	N(25)	C(2)	111.5	2.7
N(25)	C(2)	C(7)	111.8	2.6
C(8)	C(9)	C(10)	123.5	4.1
C(9)	C(10)	C(11)	123.7	5.2
C(10)	C(11)	C(12)	120.6	4.2
C(11)	C(12)	C(13)	115.7	3.3
C(3)	C(14)	C(15)	107.0	2.2
C(14)	C(15)	C(20)	115.0	3.0
C(14)	C(15)	C(16)	112.8	2.4
C(15)	C(16)	C(17)	110.3	2.8
C(16)	C(17)	C(18)	113.8	3.2
C(17)	C(18)	C(19)	95.0	3.3
C(18)	C(19)	C(20)	107.1	3.2
C(19)	C(20)	C(21)	107.1	2.5
C(19)	C(20)	C(15)	107.1	3.2
C(15)	C(20)	C(21)	111.4	2.7
C(20)	C(21)	N(26)	111.0	2.3
C(7)	O(31)	C(23)	133.5	2.7
O(31)	C(23)	O(27)	111.5	3.7
O(31)	C(23)	C(24)	116.3	3.9
C(24)	C(23)	O(27)	131.5	5.1
C(16)	C(4)	O(28)	127.8	3.2
C(16)	C(4)	O(29)	115.7	3.2
C(4)	O(29)	C(1)	122.8	3.3
O(28)	C(4)	O(29)	116.3	3.6
C(18)	C(17)	O(30)	119.8	2.5
C(16)	C(17)	O(30)	102.7	2.9

Figure 6

Bond lengths in the Methiodide of 7-Acetoxy-7-H-Yohimbine.

Figure 7
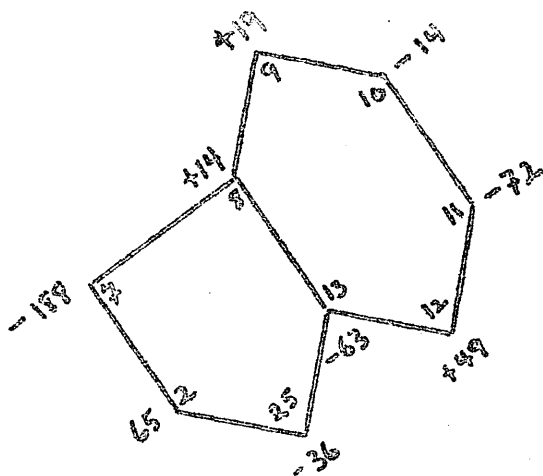
Methiodide of 7-Acetoxy-7-H-Yohimbine:
Weighted Mean Plane.

Deviations from the plane through the benzene
ring are shown in units of angstroms x 10^{-3}.
The equation of the plane is:

$$0.0195 \, X + 0.1207 \, Y - 0.9925 \, Z = 0.1275 \, .$$
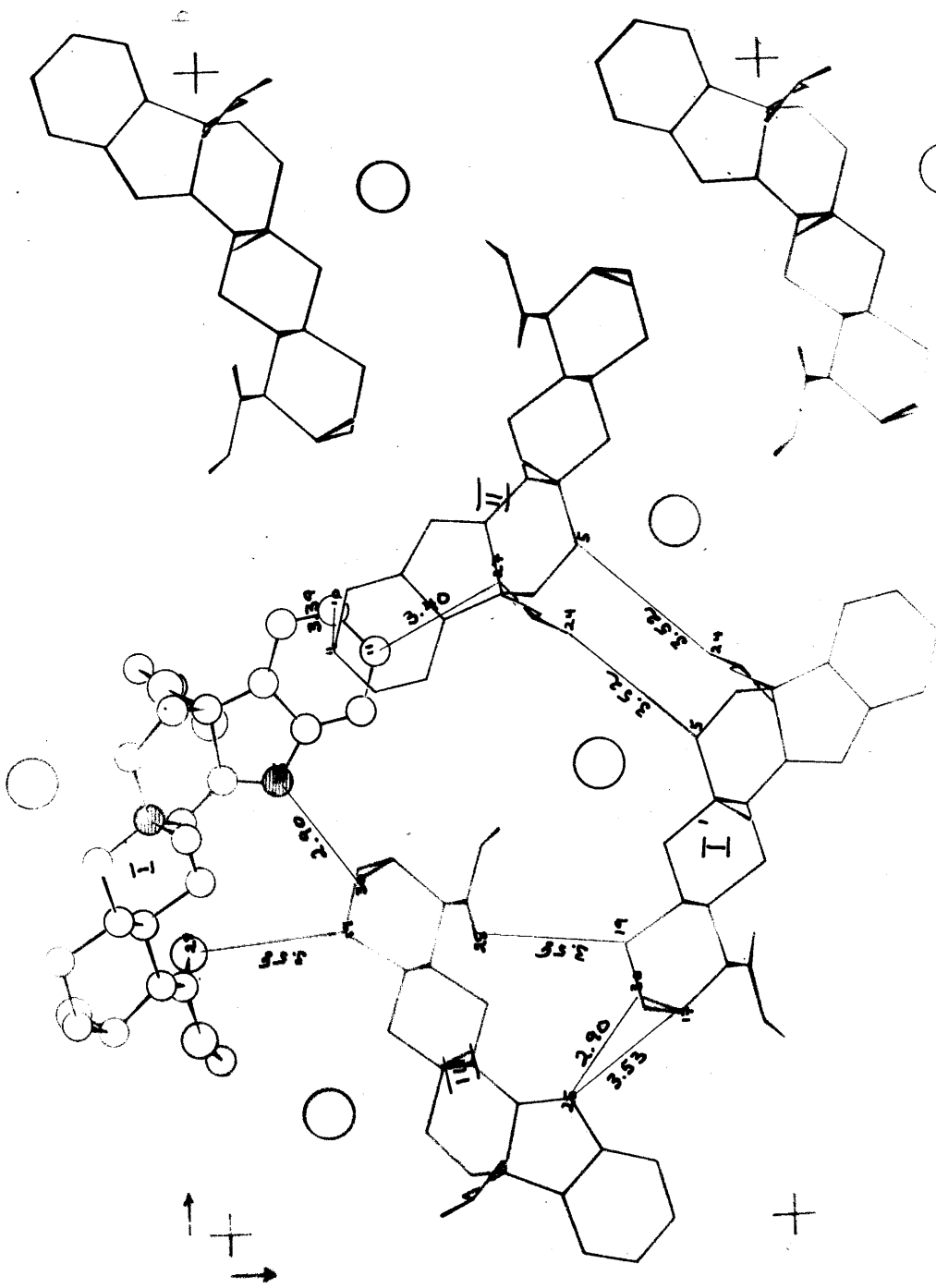
Inter-molecular contacts. Roman numerals refer to equivalent position numbers.

Figure 8
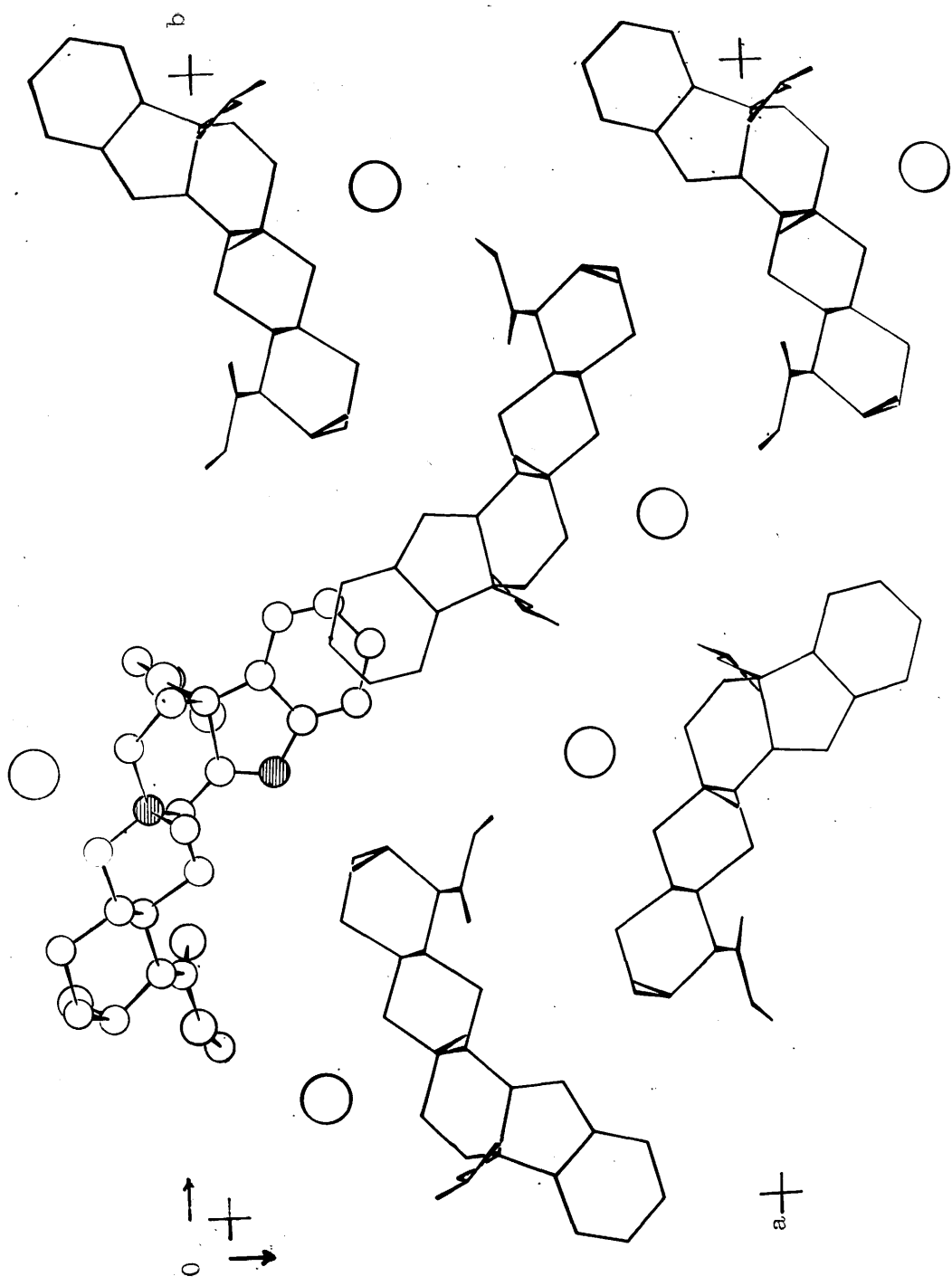
Crystal Structure of the methiodide of 7α-acetoxy-7H-yohimbine
viewed in projection along the c-axis.

Table 5

Methiodide of 7-Acetoxy-7-H-Yohimbine:

Inter-molecular Non-bonded Distances (Å)

Contacts are between the molecule in equivalent
position 1 and a molecule related to it by the
symmetry operation indicated by the equivalent poition
number. The three numbers in brackets refer to the
unit cell translations. The equivalent positions
are given.

1. $x, y, z,$
2. $1/2-x, -y, 1/2+z$
3. $1/2+x, 1/2-y, -z$
4. $-x, 1/2+y, 1/2-z$

Contacts from equivalent position 1, cell $(0,0,0)$.

		e.p.	cell	
C(10)	C(11)	2	(0,1,0)	3.39 A
C(11)	O(27)	2	(0,1,0)	3.40
N(25)	O(30)	3	(0,0,0)	2.90
O(28)	C(19)	3	(0,0,0)	3.58

Contacts from equivalent position 1, cell $(1,0,0)$.

C(5)	C(24)	2	(0,1,0)	3.52 A
C(17)	N(25)	3	(0,0,0)	3.53
C(19)	O(28)	3	(0,0,0)	3.58
C(24)	C(5)	2	(0,1,-1)	3.52
O(30)	N(25)	3	(0,0,0)	2.90

Figure 9
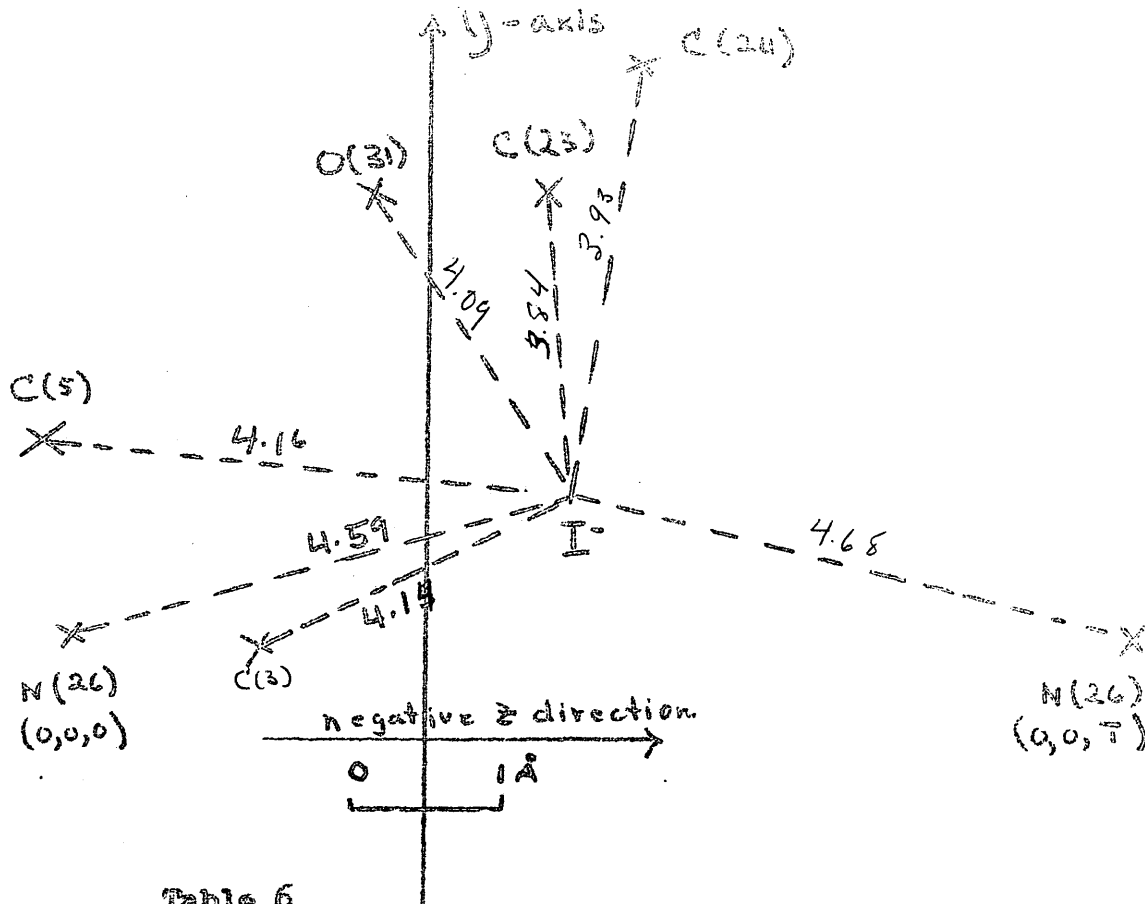
Table 6

Environment of the Iodide Ion:

Contacts with atoms in equivalent
position 1.

C(23)	3.84 A
C(24)	3.93
O(31)	4.09
C(3)	4.14
C(5)	4.16

Closest contacts with quaternary nitrogen

N(26)	1	(0,0,0)	4.59
N(26)	1	(0,0,-1)	4.68

Table 7

The methiodide of 7-acetoxy-7-yohimbine

H	K	L	|Fo|	|Fc|
2	27	0	10.3	13.8
2	28	0	11.2	9.0
2	30	0	10.0	11.9
2	31	0	18.2	16.8
2	33	0	7.9	10.5
3	1	0	71.8	75.6
3	2	0	124.6	145.9
3	3	0	25.6	33.1
3	4	0	113.1	150.3
3	5	0	83.6	110.4
3	6	0	54.6	54.5
3	7	0	21.8	28.8
3	8	0	75.2	75.8
3	9	0	70.6	74.7
3	10	0	51.4	42.0
3	11	0	48.2	47.9
3	12	0	115.1	149.0
3	14	0	18.2	19.3
3	15	0	50.1	48.8
3	16	0	58.4	60.0
3	18	0	50.0	63.6
3	19	0	41.2	38.3
3	20	0	22.8	26.7
3	21	0	33.8	29.6
3	22	0	71.9	57.3
3	23	0	9.6	7.1
3	24	0	13.6	8.4
3	25	0	12.1	11.7
3	26	0	21.0	28.4
3	28	0	8.7	9.5
3	29	0	10.5	12.4
3	30	0	7.7	11.2
3	32	0	9.8	9.0
4	0	0	22.6	16.8
4	1	0	162.2	163.7
4	2	0	41.8	55.0
4	3	0	100.0	119.8
4	4	0	10.3	11.7
4	5	0	22.2	18.2
4	6	0	58.7	44.9
4	7	0	87.9	96.3
4	8	0	118.4	118.9
4	9	0	17.8	8.5
4	10	0	36.9	39.2
4	11	0	49.7	63.5
4	12	0	25.5	23.3
4	13	0	42.8	53.7
4	14	0	19.0	16.3
4	15	0	21.5	14.9
4	16	0	42.8	33.4
4	17	0	56.0	60.9
4	19	0	29.1	27.8
4	20	0	48.3	26.8
4	21	0	62.2	56.9
4	22	0	6.8	12.9
4	23	0	12.2	15.8
4	24	0	19.2	16.5
4	27	0	28.8	30.1
4	28	0	12.0	13.8
5	1	0	60.8	62.4
5	2	0	124.6	127.0
5	3	0	69.5	76.9
5	4	0	54.9	58.8
5	5	0	31.0	39.9
5	6	0	105.4	100.0
5	7	0	53.0	33.4
5	8	0	14.5	17.8
5	9	0	122.9	100.3
5	10	0	31.6	30.9
5	11	0	35.6	47.4
5	12	0	79.2	89.4
5	13	0	15.4	19.5
5	14	0	41.6	42.3
5	15	0	54.4	39.8
5	16	0	39.8	33.5
5	17	0	36.6	24.7
5	18	0	66.6	36.9
5	19	0	48.2	30.7
5	21	0	19.1	16.7
5	22	0	40.1	28.9
5	23	0	10.7	10.5
5	26	0	42.1	29.3
5	28	0	13.0	12.5
5	29	0	10.8	7.6
6	0	0	74.8	51.0
6	1	0	29.1	15.1
6	2	0	18.1	30.7
6	4	0	111.5	125.9
6	6	0	102.9	104.2
6	7	0	93.9	99.9
6	8	0	32.9	29.7
6	9	0	16.2	21.5
6	10	0	70.7	65.9
6	11	0	32.1	35.2
6	13	0	22.2	19.5
6	14	0	43.8	50.3
6	15	0	21.7	26.2
6	16	0	15.7	19.2
6	17	0	20.3	21.7
6	18	0	68.5	57.5
6	19	0	27.1	21.5
6	20	0	39.8	35.8
6	24	0	16.5	19.8
6	25	0	18.1	9.3
6	27	0	10.5	10.0
6	29	0	10.1	13.4
6	30	0	16.0	11.9
7	1	0	83.2	99.6
7	2	0	8.8	9.3
7	3	0	38.5	43.7
7	4	0	29.6	26.3
7	5	0	68.5	71.6
7	6	0	49.4	51.4
7	7	0	56.4	63.9
7	8	0	83.3	73.1
7	9	0	29.1	22.6
7	10	0	42.8	45.4
7	11	0	16.8	18.2
7	12	0	73.1	60.9
7	13	0	22.2	14.6
7	14	0	52.9	47.4
7	15	0	11.6	8.7
7	16	0	15.0	17.1
7	18	0	39.8	42.8
7	19	0	24.0	22.7
7	21	0	26.7	28.3
7	23	0	16.0	21.3
7	24	0	15.4	12.9
7	25	0	53.4	56.5
8	0	0	12.1	2.9
8	1	0	10.9	8.6
8	2	0	40.3	43.4
8	3	0	40.7	43.2
8	4	0	41.7	48.0
8	6	0	18.2	11.9
8	7	0	40.9	34.9
8	8	0	10.6	7.7
8	9	0	50.2	48.2
8	10	0	31.7	33.6
8	11	0	22.3	19.7
8	12	0	43.1	41.9
8	14	0	9.4	8.0
8	15	0	39.5	37.9
8	16	0	21.4	16.4
8	17	0	12.2	8.2
8	18	0	21.3	15.9
8	20	0	8.9	1.8
8	23	0	8.6	12.2
8	24	0	8.1	11.1
8	25	0	17.1	15.4
8	26	0	17.7	17.9
8	27	0	12.8	17.7
8	28	0	7.8	8.8
8	29	0	43.5	47.8
9	1	0	48.9	49.0
9	2	0	14.9	18.0
9	3	0	12.0	7.4
9	4	0	44.6	43.4
9	5	0	40.3	43.4
9	6	0	51.7	49.9
9	8	0	20.0	16.3
9	9	0	22.8	19.7
9	10	0	33.4	31.1
9	11	0	38.9	35.6
9	12	0	27.0	19.6
9	13	0	40.0	37.9
9	15	0	40.1	40.8
9	16	0	10.7	10.2
9	17	0	13.5	11.1
9	18	0	14.9	13.8
9	19	0	13.1	16.2
9	20	0	11.1	8.8
9	21	0	17.5	16.7
9	22	0	10.6	13.8
9	23	0	16.7	16.2
9	25	0	17.9	17.3
10	0	0	22.5	25.9
10	1	0	20.0	20.2
10	2	0	47.0	45.8
10	3	0	12.8	13.7
10	4	0	5.4	7.3
10	5	0	11.2	7.9
10	6	0	23.2	21.8
10	7	0	10.4	10.6
10	8	0	21.0	14.9
10	9	0	15.0	11.9
10	10	0	13.5	15.9
10	11	0	19.2	16.2
10	13	0	18.0	15.8
10	14	0	21.4	20.9
10	15	0	19.0	19.2
10	16	0	23.7	24.4
10	17	0	11.7	7.9
10	18	0	12.0	14.5
10	21	0	9.6	12.3
10	23	0	9.4	10.3
11	1	0	34.2	35.9
11	2	0	6.7	8.9
11	4	0	15.0	19.0
11	5	0	34.6	34.8
11	6	0	21.4	23.4
11	7	0	34.8	41.9
11	8	0	19.2	18.3
11	9	0	26.1	23.8
11	12	0	11.9	7.1
11	14	0	11.6	17.3
11	16	0	13.8	14.5
11	18	0	14.3	15.6
11	22	0	13.6	15.8
12	0	0	10.7	13.0
12	1	0	19.2	18.5
12	2	0	34.9	35.2
12	3	0	12.2	13.6
12	4	0	9.6	2.3
12	5	0	12.1	15.3
12	6	0	27.5	32.2
12	7	0	18.7	18.3
12	11	0	10.3	14.5
12	12	0	22.9	20.6
12	13	0	11.3	8.6
12	14	0	18.3	20.7
12	17	0	8.9	8.1
12	20	0	8.4	9.7
12	22	0	8.4	11.6
13	1	0	13.3	13.1
13	2	0	13.2	15.8
13	4	0	14.7	15.3
13	5	0	12.8	16.2
13	9	0	9.9	5.9
13	10	0	15.2	18.3
13	12	0	9.3	11.1
13	13	0	10.2	12.5
13	14	0	80.5	86.5
0	3	1	93.8	100.2
0	4	1	40.4	65.6
0	5	1	92.6	96.9
0	6	1	57.6	61.2
0	7	1	91.9	99.7
0	8	1	66.6	60.9
0	9	1	31.1	21.2
0	10	1	132.0	132.9
0	11	1	94.7	116.8
0	12	1	41.2	48.0
0	13	1	16.6	17.3
0	14	1	31.7	29.2
0	15	1	53.6	51.9
0	16	1	44.6	43.6
0	17	1	28.6	34.1
0	18	1	35.5	32.8
0	21	1	21.1	24.2
0	22	1	22.9	26.9
0	23	1	10.3	8.2
0	24	1	24.5	26.3
0	25	1	39.5	27.0
0	26	1	38.6	21.9
0	27	1	12.0	13.5
0	28	1	8.8	5.5
0	32	1	112.6	126.3
1	0	1	55.1	30.6
1	1	1	80.7	83.0
1	2	1	181.6	177.5
1	3	1	143.9	135.9
1	4	1	54.2	51.1
1	5	1	123.6	100.5
1	6	1	146.6	130.1
1	7	1	56.4	65.7
1	8	1	71.1	82.1
1	9	1	80.9	80.6
1	10	1	67.9	78.4
1	11	1	71.7	77.1
1	12	1	29.0	39.3
1	13	1	55.3	55.9
1	14	1	45.9	38.5
1	15	1	53.9	46.2
1	16	1	59.3	60.3
1	17	1	34.0	33.8
1	18	1	37.7	27.3
1	19	1	17.0	18.2
1	20	1	51.5	63.7
1	21	1	28.3	24.8
1	22	1	12.8	17.1
1	23	1	37.3	35.8
1	24	1	8.1	12.7
1	25	1	11.4	10.9
1	26	1	17.5	20.1
1	27	1	13.5	12.9
1	28	1	13.9	15.5
1	32	1	48.4	59.2
2	0	1	60.8	76.2
2	1	1	152.5	149.4
2	2	1	161.6	140.3
2	3	1	172.5	146.0
2	4	1	85.8	102.0
2	5	1	91.6	97.9
2	6	1	60.3	57.4
2	7	1	41.8	48.7
2	8	1	79.4	79.3
2	9	1	66.4	55.2
2	10	1	13.0	12.1
2	11	1	34.1	33.9
2	13	1	59.9	62.0
2	14	1	52.5	55.9
2	15	1	46.4	44.4
2	16	1	25.1	25.1
2	17	1	42.3	46.5
2	18	1	35.7	36.2
2	19	1	45.2	36.0
2	20	1	40.4	37.7
2	21	1	22.7	24.4
2	22	1	20.4	16.7
2	23	1	14.6	12.7
2	24	1	12.8	16.1
2	25	1	13.2	13.1
2	30	1	8.1	11.5
2	33	1	151.3	230.3
3	0	1	99.3	117.7
3	1	1	34.0	25.0
3	2	1	99.3	96.4
3	3	1	108.9	117.2
3	4	1	96.2	91.7
3	5	1	113.3	111.5
3	6	1	14.6	20.8
3	7	1	57.4	55.5
3	8	1	52.6	52.9
3	9	1	38.5	52.7
3	10	1	66.3	57.7
3	11	1	26.1	21.0
3	12	1	63.4	56.6
3	13	1	75.9	75.6
3	14	1	37.8	48.1
3	15	1	44.8	46.8
3	16	1	54.0	45.4
3	18	1	35.3	41.4
3	19	1	19.5	23.2
3	20	1	29.6	29.7
3	23	1	33.2	32.9
3	24	1	21.4	19.8
3	25	1	12.5	9.0
3	26	1	108.5	131.4
4	0	1	88.9	87.8
4	1	1	31.3	32.1
4	2	1	25.1	18.9
4	3	1	57.1	48.0
4	4	1	96.4	113.3
4	5	1	61.0	60.5
4	6	1	43.0	35.4
4	7	1	29.5	30.1
4	8	1	125.2	124.1
4	9	1	83.8	75.2
4	10	1	61.3	69.7
4	11	1	31.0	35.4
4	12	1	36.1	31.6
4	13	1	43.1	39.4
4	14	1	63.3	77.7
4	15	1	51.9	47.4
4	16	1	29.5	29.7
4	17	1	26.6	22.2
4	18	1	44.7	41.6
4	19	1	22.4	29.5
4	20	1	14.4	17.6
4	21	1	26.5	25.8
4	23	1	20.4	19.8
4	24	1	25.3	20.9
4	25	1	15.6	10.5
4	26	1	35.2	41.9
5	0	1	61.5	65.5
5	1	1	51.1	46.6
5	2	1	62.9	76.8
5	3	1	75.2	61.6
5	4	1	54.1	58.6
5	5	1	67.4	69.8
5	6	1	39.9	43.8
5	7	1	36.8	41.2
5	8	1	53.8	58.0
5	9	1	76.6	86.0
5	10	1	65.4	62.8
5	11	1	32.9	25.6
5	12	1	24.0	26.7
5	13	1	56.8	51.6
5	14	1	58.7	63.5
5	15	1	48.2	46.1
5	16	1	27.3	25.1
5	17	1	28.0	25.5
5	18	1	32.7	33.5
5	20	1	14.5	20.5
5	21	1	16.3	14.4
5	22	1	23.0	14.2
5	23	1	12.7	12.5
5	24	1	22.3	25.1
5	25	1	19.5	18.2
6	0	1	56.8	72.8
6	1	1	69.5	74.3
6	2	1	57.8	61.0
6	3	1	46.0	45.7
6	4	1	20.5	15.2
6	5	1	61.0	60.0
6	6	1	62.5	64.5
6	7	1	44.8	43.0
6	8	1	41.2	39.9
6	9	1	37.7	40.2
6	10	1	36.0	37.5
6	11	1	56.3	56.9
6	12	1	25.4	22.0
6	13	1	14.4	18.6
6	14	1	48.9	45.8
6	15	1	39.0	34.1
6	16	1	37.4	31.9
6	17	1	30.5	33.5
6	18	1	29.3	23.8
6	19	1	16.3	23.6
6	20	1	26.5	21.6
6	21	1	24.5	25.3
6	22	1	20.2	16.4
6	23	1	21.7	12.7
7	0	1	55.7	56.3
7	2	1	56.0	63.2
7	3	1	56.5	63.6
7	4	1	31.5	27.4
7	5	1	15.6	15.8
7	6	1	55.2	46.7
7	7	1	67.2	67.9
7	8	1	61.4	53.8
7	9	1	12.0	10.4
7	10	1	19.5	15.4
7	11	1	28.6	27.7
7	12	1	41.5	41.8
7	13	1	51.6	50.7
7	14	1	19.0	14.0
7	16	1	15.7	18.3
7	17	1	29.1	34.1
7	18	1	26.2	27.1
7	19	1	16.3	15.5
7	20	1	10.3	9.3
7	21	1	23.0	22.1
7	22	1	35.0	27.1
7	23	1	15.7	13.3
7	27	1	28.2	23.7
8	0	1	21.2	23.9
8	1	1	26.7	27.3
8	2	1	61.5	60.1
8	3	1	46.6	47.7
8	4	1	39.5	33.7
8	5	1	17.0	20.6
8	6	1	64.1	51.4
8	7	1	31.8	26.0
8	8	1	49.5	48.6
8	9	1	23.4	23.3
8	10	1	13.1	13.5
8	11	1	30.4	28.7
8	12	1	56.2	43.6
8	13	1	37.3	41.9
8	15	1	32.5	21.5
8	16	1	31.1	32.4
8	18	1	33.2	25.7
8	22	1	22.0	28.7
8	27	1	22.8	19.4
9	0	1	27.2	26.5
9	1	1	29.0	27.5
9	2	1	36.8	35.2
9	3	1	34.6	30.1
9	4	1	41.7	39.8
9	5	1	33.4	29.0
9	6	1	35.5	35.2
9	7	1	28.8	26.9
9	8	1	15.1	15.7
9	9	1	27.8	28.5
9	10	1	17.4	20.3
9	11	1	35.9	32.4
9	12	1	30.7	27.0
9	13	1	32.7	24.9
9	14	1	21.4	17.3
9	15	1	23.5	25.2
9	18	1	25.6	23.7
9	19	1	22.6	21.7
9	20	1	14.0	14.9
9	22	1	13.1	11.5
9	23	1	18.6	13.8
9	24	1	13.3	12.7
10	0	1	24.9	23.3
10	1	1	31.1	32.9
10	2	1	15.3	12.1
10	3	1	19.3	18.3
10	4	1	17.3	18.9
10	5	1	51.4	42.4
10	6	1	28.5	29.7
10	7	1	15.8	13.8
10	8	1	14.2	17.3
10	9	1	46.0	47.7
10	10	1	18.0	20.5
10	11	1	21.5	19.0
10	13	1	24.5	25.1
10	14	1	17.3	14.5
10	15	1	24.4	23.3
10	17	1	15.9	11.1
10	18	1	19.6	19.9
10	19	1	19.2	21.0
10	20	1	11.7	13.5
11	0	1	41.3	42.9
11	1	1	10.2	16.9
11	2	1	16.1	9.2
11	3	1	18.0	15.0
11	4	1	18.0	14.0
11	5	1	21.4	20.6
11	6	1	29.5	32.1
11	7	1	16.3	17.7
11	8	1	21.6	21.0
11	9	1	29.0	27.2
11	10	1	29.0	22.6
11	11	1	12.9	15.4
11	14	1	11.3	21.0
11	15	1	20.8	12.4
12	0	1	14.6	15.0
12	1	1	12.9	10.5
12	2	1	16.3	15.8
12	3	1	14.6	14.4
12	4	1	18.2	17.5
12	5	1	16.3	12.2
12	6	1	18.2	24.4
12	8	1	18.1	18.7
12	10	1	16.0	16.0
12	11	1	17.7	16.1
13	0	1	15.9	16.3
13	1	1	14.2	16.6
13	3	1	21.0	21.4
13	5	1	13.2	9.4
14	1	1	13.2	12.4
14	3	1	13.1	9.4
0	4	2	54.2	23.8
0	5	2	142.6	176.2
0	6	2	61.8	46.1

Table 7

The methiodide of 7-acetoxy-7-H-yohimbine Ctd.

H	K	L	|Fo|	|Fc|
0	7	2	12.5	8.4
0	8	2	57.5	48.9
0	9	2	61.6	66.2
0	10	2	28.2	15.0
0	11	2	78.4	74.2
0	12	2	20.0	15.3
0	13	2	14.3	17.5
0	14	2	45.1	40.9
0	15	2	68.7	79.1
0	16	2	16.8	13.0
0	18	2	26.2	25.7
0	19	2	43.1	48.1
0	20	2	13.8	20.3
0	21	2	25.8	23.6
0	25	2	22.9	26.7
1	0	2	192.5	250.8
1	1	2	85.2	80.0
1	2	2	96.2	82.8
1	3	2	97.7	85.2
1	4	2	111.3	130.5
1	5	2	59.3	53.4
1	6	2	63.9	85.1
1	7	2	65.0	78.7
1	8	2	36.2	35.3
1	9	2	56.0	38.2
1	10	2	116.6	117.8
1	11	2	79.6	62.1
1	12	2	33.5	39.0
1	13	2	43.2	53.8
1	14	2	82.5	81.3
1	15	2	26.2	15.7
1	16	2	34.6	31.6
1	17	2	28.5	29.5
1	18	2	33.2	35.4
1	19	2	16.8	16.8
1	20	2	46.8	52.4
1	21	2	36.3	31.2
1	23	2	14.6	15.6
1	24	2	20.5	29.5
1	25	2	20.3	25.7
1	26	2	17.7	15.5
2	0	2	50.7	45.4
2	1	2	68.4	75.5
2	2	2	51.2	66.0
2	3	2	69.7	90.3
2	4	2	18.2	21.2
2	5	2	81.0	91.1
2	6	2	58.1	47.9
2	7	2	31.9	17.0
2	8	2	69.2	78.1
2	9	2	103.6	98.6
2	10	2	48.1	47.9
2	11	2	92.1	81.6
2	12	2	39.2	35.3
2	13	2	27.7	31.0
2	15	2	78.0	71.9
2	16	2	40.5	43.7
2	17	2	25.6	15.0
2	18	2	36.5	35.3
2	19	2	29.3	29.9
2	20	2	17.0	19.4
2	21	2	17.3	19.3
2	22	2	24.9	31.8
2	25	2	24.8	26.1
2	26	2	17.1	17.2
3	0	2	43.8	32.3
3	1	2	60.6	67.6
3	2	2	38.4	32.9
3	3	2	99.0	106.9
3	4	2	62.7	81.2
3	5	2	15.0	18.6
3	6	2	24.9	24.4
3	7	2	77.5	108.9
3	8	2	35.3	19.2
3	9	2	46.5	48.7
3	10	2	55.0	38.6
3	11	2	82.7	75.5
3	12	2	42.6	32.7
3	13	2	63.0	57.1
3	15	2	54.1	44.3
3	16	2	13.6	11.0
3	17	2	58.3	62.2
3	18	2	25.8	23.4
3	19	2	16.8	13.1
3	20	2	21.6	21.6
3	21	2	45.0	41.8
3	22	2	19.8	18.1
3	23	2	25.1	25.1
3	27	2	18.2	22.0
4	0	2	17.1	24.8
4	1	2	50.1	47.4
4	2	2	92.1	87.8
4	3	2	32.3	27.6
4	4	2	129.4	116.4
4	5	2	21.0	13.2
4	6	2	116.8	87.6
4	7	2	66.8	47.1
4	8	2	87.2	91.9
4	9	2	35.5	28.5
4	10	2	54.8	51.4
4	11	2	38.5	26.3
4	12	2	91.1	83.3
4	13	2	40.6	32.1
4	14	2	20.7	21.3
4	15	2	43.7	32.1
4	16	2	73.4	60.7
4	18	2	55.1	44.1
4	19	2	17.1	15.9
4	20	2	17.4	22.2
4	21	2	19.7	21.5
4	22	2	36.0	42.9
5	0	2	50.2	52.6
5	1	2	64.8	65.9
5	2	2	36.0	36.5
5	3	2	74.2	85.0
5	4	2	95.6	77.9
5	5	2	38.1	32.8
5	6	2	71.0	58.6
5	7	2	81.8	68.5
5	8	2	75.4	59.6
5	9	2	53.9	48.8
5	10	2	55.7	42.8
5	11	2	51.3	48.1
5	12	2	18.3	17.3
5	13	2	49.1	42.1
5	14	2	35.0	29.3
5	15	2	36.1	24.8
5	17	2	42.9	38.1
5	18	2	19.1	19.7
5	19	2	39.7	29.3
5	20	2	24.9	22.6
5	21	2	25.1	28.0
5	23	2	22.0	20.7
5	24	2	19.3	17.2
6	0	2	31.1	32.1
6	1	2	81.4	91.2
6	2	2	57.0	66.2
6	3	2	45.6	47.7
6	4	2	25.4	25.5
6	5	2	76.4	64.2
6	6	2	48.0	48.0
6	8	2	35.1	37.4
6	9	2	65.5	63.0
6	10	2	14.6	14.0
6	11	2	42.5	39.9
6	12	2	21.5	24.3
6	13	2	35.7	34.6
6	14	2	14.4	9.5
6	15	2	42.4	40.2
6	16	2	15.1	13.1
6	17	2	13.6	7.4
6	18	2	39.8	40.4
6	19	2	34.1	34.2
6	21	2	14.0	10.6
6	22	2	15.7	17.1
6	23	2	17.2	21.5
6	25	2	16.2	16.0
7	0	2	34.5	62.1
7	1	2	30.7	31.6
7	2	2	24.5	20.5
7	3	2	17.1	17.3
7	4	2	50.9	65.0
7	5	2	17.5	19.0
7	6	2	58.9	75.8
7	7	2	12.9	10.9
7	8	2	37.9	36.9
7	9	2	13.5	18.7
7	10	2	56.9	54.5
7	12	2	25.5	21.7
7	13	2	23.3	23.2
7	14	2	43.2	42.3
7	15	2	27.1	25.9
7	16	2	44.6	42.0
7	17	2	22.0	18.5
7	18	2	36.0	39.7
7	19	2	25.1	23.0
7	20	2	19.8	16.2
8	1	2	42.4	53.3
8	2	2	38.0	41.0
8	3	2	21.1	29.7
8	4	2	23.7	21.1
8	5	2	49.0	59.0
8	6	2	27.9	29.0
8	7	2	31.7	36.5
8	8	2	22.4	20.1
8	9	2	51.9	50.5
8	10	2	11.6	14.1
8	11	2	42.8	44.4
8	12	2	26.7	28.4
8	13	2	39.1	38.5
8	14	2	15.6	11.5
8	15	2	56.7	49.6
9	16	2	22.2	20.7
8	17	2	12.5	14.2
8	19	2	17.6	21.2
8	20	2	13.7	12.4
8	21	2	19.0	20.7
9	0	2	22.5	23.7
9	1	2	8.0	12.7
9	2	2	17.9	24.5
9	3	2	42.9	51.3
9	5	2	16.3	14.2
9	6	2	29.0	35.3
9	7	2	16.6	24.2
9	8	2	13.3	15.7
9	10	2	15.4	27.5
9	14	2	17.7	19.3
9	15	2	15.9	19.3
9	16	2	22.2	25.9
10	1	2	13.4	17.8
10	2	2	34.6	46.6
10	3	2	30.3	38.9
10	6	2	32.9	47.7
10	7	2	19.5	20.1
10	8	2	22.0	31.5
10	10	2	14.0	11.1
10	12	2	22.3	32.4
11	1	2	12.5	20.9
11	3	2	27.9	38.2
11	4	2	8.8	16.3
11	5	2	8.9	11.9
11	6	2	8.9	18.1
11	7	2	15.4	24.7
0	1	3	185.5	110.6
0	2	3	19.8	19.1
0	3	3	144.9	148.7
1	0	3	55.2	65.7
0	4	3	48.6	42.0
0	5	3	21.1	6.8
0	6	3	66.1	51.1
0	7	3	89.7	98.7
0	8	3	41.0	33.7
0	9	3	62.3	49.2
0	10	3	12.0	10.2
0	11	3	79.2	70.3
0	12	3	16.8	12.6
0	13	3	44.3	40.5
0	14	3	16.6	16.5
0	15	3	38.4	41.1
0	16	3	27.0	32.9
0	17	3	58.8	74.1
0	18	3	15.5	14.8
0	20	3	18.3	20.4
0	21	3	49.1	59.2
1	0	3	41.4	65.7
1	1	3	29.3	41.0
1	2	3	51.7	66.2
1	3	3	45.6	41.3
1	4	3	55.8	38.2
1	5	3	41.3	39.4
1	6	3	84.7	79.0
1	7	3	26.3	30.4
1	8	3	70.9	74.3
1	9	3	44.7	40.0
1	10	3	34.1	36.9
1	11	3	56.5	47.8
1	12	3	79.4	72.9
1	13	3	33.6	32.9
1	14	3	22.4	31.3
1	15	3	19.6	21.2
1	16	3	27.2	41.9
1	17	3	16.8	16.3
1	18	3	32.6	37.8
1	19	3	20.0	17.7
1	20	3	18.3	14.5
1	22	3	18.7	25.9
2	0	3	133.3	131.2
2	1	3	86.1	62.2
2	2	3	37.3	45.7
2	3	3	65.9	48.4
2	4	3	103.9	95.6
2	5	3	40.6	34.5
2	6	3	81.2	86.3
2	7	3	77.3	79.4
2	8	3	44.0	49.8
2	9	3	29.5	37.3
2	10	3	62.3	68.9
2	11	3	37.2	37.8
2	12	3	17.4	17.1
2	13	3	27.2	28.7
2	14	3	59.6	67.9
2	15	3	19.9	23.6
2	16	3	14.7	22.9
2	17	3	21.4	24.4
2	18	3	15.7	25.5
2	19	3	14.3	13.6
3	0	3	65.7	50.2
3	1	3	190.6	125.5
3	2	3	34.3	32.8
3	3	3	59.3	52.7
3	4	3	61.8	51.3
3	5	3	107.8	119.3
3	6	3	28.9	38.4
3	7	3	9.1	12.3
3	8	3	28.2	31.8
3	9	3	55.4	59.1
3	10	3	35.0	38.6
3	11	3	34.3	37.4
3	12	3	30.3	35.8
3	13	3	31.6	42.0
3	14	3	22.2	20.0
3	15	3	38.3	54.6
3	16	3	15.1	16.6
3	18	3	14.1	21.0
3	19	3	34.2	48.4
3	20	3	16.6	19.4
3	21	3	23.5	27.4
4	0	3	169.8	134.1
4	1	3	17.7	26.6
4	2	3	9.6	13.6
4	3	3	5.5	11.8
4	4	3	104.8	98.8
4	5	3	85.4	74.8
4	6	3	37.8	45.6
4	7	3	41.6	40.2
4	8	3	10.3	17.6
4	9	3	19.1	16.9
4	10	3	55.1	61.0
4	11	3	30.6	30.3
4	12	3	20.1	22.5
4	13	3	19.8	23.4
4	14	3	34.1	47.9
4	15	3	31.5	27.7
4	16	3	34.4	32.3
4	18	3	20.3	27.7
4	19	3	23.2	28.4
14	20	3	33.0	29.2
5	0	3	53.4	55.0
5	1	3	48.1	42.2
5	2	3	32.9	26.7
5	3	3	37.5	33.3
5	4	3	50.8	50.4
5	5	3	27.9	15.7
5	6	3	13.7	14.8
5	7	3	33.2	42.7
5	8	3	80.6	71.0
5	9	3	45.6	49.9
5	10	3	54.3	49.0
5	11	3	62.7	51.5
5	12	3	23.3	23.5
5	13	3	21.3	27.3
5	14	3	40.9	49.5
5	15	3	35.3	37.4
5	16	3	10.7	4.1
6	0	3	12.7	29.3
6	1	3	36.3	35.0
6	2	3	90.8	69.8
6	3	3	12.2	9.3
6	4	3	37.8	33.5
6	5	3	38.6	30.9
6	6	3	55.2	57.8
6	7	3	19.1	18.3
6	8	3	14.0	21.9
6	9	3	37.6	38.6
6	10	3	30.8	34.4
6	11	3	35.3	31.2
6	12	3	28.9	32.7
6	13	3	26.5	31.5
6	14	3	28.5	29.2
6	15	3	16.4	19.8
6	16	3	32.9	41.1
6	17	3	25.1	28.0
7	0	3	21.3	19.5
7	1	3	83.7	73.3
7	2	3	35.7	33.2
7	3	3	32.2	36.5
7	4	3	9.8	12.8
7	5	3	46.8	43.4
7	6	3	53.4	48.3
7	7	3	23.2	31.9
7	8	3	13.2	9.9
7	9	3	13.5	16.6
7	10	3	13.7	13.0
7	11	3	43.8	47.2
7	12	3	24.7	29.0
7	16	3	33.3	33.4
7	17	3	16.8	22.1
7	18	3	16.7	16.3
7	19	3	30.6	27.7
8	1	3	30.8	38.1
8	2	3	39.9	37.7
8	3	3	26.4	24.6
8	4	3	23.8	23.0
8	5	3	21.3	30.9
8	6	3	45.6	39.9
8	7	3	32.6	29.4
8	8	3	24.0	29.9
8	11	3	16.4	20.8
8	12	3	16.6	23.4
8	13	3	14.7	16.8
8	14	3	26.5	22.2
8	15	3	38.8	34.6
9	1	3	38.8	38.9
9	2	3	25.1	19.7
9	4	3	22.4	27.7
9	5	3	28.5	26.8
9	6	3	22.7	35.2
9	7	3	32.4	25.0
9	8	3	14.8	21.4
9	12	3	16.8	24.5
9	13	3	18.7	16.7
9	14	3	108.8	116.3
1	0	4	57.7	29.9
0	1	4	13.8	13.9
0	3	4	110.1	115.4
0	4	4	32.9	32.7
0	5	4	55.0	60.1
0	7	4	17.2	13.9
0	8	4	36.9	45.9
0	9	4	83.8	85.7
0	10	4	34.0	34.8
0	14	4	29.3	35.8
0	16	4	69.9	91.6
1	1	4	22.0	29.2
1	2	4	35.1	46.7
1	3	4	21.5	21.2
1	4	4	57.9	63.5
1	5	4	33.6	29.6
1	6	4	43.7	48.3
1	7	4	31.3	30.0
1	8	4	42.1	49.7
1	9	4	25.1	31.8
1	10	4	42.0	39.4
1	11	4	23.2	20.0
1	13	4	43.2	31.9
1	14	4	27.3	30.7
1	18	4	27.1	26.0
2	0	4	30.9	34.6
2	1	4	27.3	23.5
2	2	4	49.5	63.5
2	3	4	47.7	50.2
2	4	4	21.4	25.1
2	5	4	39.0	42.4
2	6	4	46.6	60.1
2	7	4	23.3	24.3
2	8	4	31.0	36.8
2	9	4	29.1	38.3
2	10	4	34.4	38.2
2	11	4	28.7	28.1
2	12	4	37.5	45.3
2	13	4	27.8	31.3
2	14	4	32.2	36.1
2	15	4	21.0	18.1
2	16	4	27.0	35.4
2	17	4	29.3	30.2
3	0	4	64.5	58.0
3	2	4	56.0	47.7
3	3	4	43.8	41.0
3	4	4	34.2	32.2
3	5	4	48.1	45.0
3	6	4	29.8	33.4
3	7	4	74.9	66.9
3	8	4	25.5	36.3
3	11	4	47.0	53.4
3	12	4	24.6	20.5
4	0	4	52.7	42.3
4	1	4	39.8	33.3
4	2	4	77.1	65.1
4	3	4	37.1	33.1
4	4	4	28.0	24.3
4	6	4	46.1	43.3
4	7	4	21.3	30.8
4	9	4	17.7	21.4
4	11	4	53.3	57.7
4	12	4	49.1	51.5
4	13	4	20.2	21.3
5	0	4	39.8	25.9
5	1	4	28.2	27.1
5	2	4	80.5	57.1
5	3	4	40.8	28.8
5	4	4	46.6	36.0
5	5	4	47.6	39.9
5	6	4	38.9	37.3
5	8	4	51.6	45.8
5	9	4	26.7	34.7
5	10	4	27.5	29.2
5	11	4	28.3	27.0
5	12	4	20.5	18.6
6	1	4	49.8	40.9
6	2	4	44.5	33.2
6	3	4	31.6	27.9
6	4	4	31.9	28.2
6	5	4	45.7	47.9
6	6	4	26.3	26.3
6	7	4	37.5	36.9
6	9	4	38.3	32.8
6	10	4	28.5	33.6
7	0	4	29.1	38.6
7	1	4	24.2	19.0
7	2	4	38.6	36.2
7	3	4	19.5	12.9
7	4	4	24.6	20.5
7	5	4	24.8	28.4
7	8	4	50.2	47.6
7	9	4	26.1	28.0
7	10	4	26.5	29.0
7	11	4	21.5	27.8
0	3	5	38.6	42.1
0	6	5	16.2	24.8
0	8	5	30.1	38.9
1	0	5	40.2	42.2
1	2	5	50.6	34.4
1	3	5	8.5	15.5
1	4	5	50.1	55.7
1	5	5	48.6	56.8
1	6	5	24.8	26.5
1	7	5	24.6	27.4
1	8	5	53.7	44.6
1	9	5	36.6	32.8
2	1	5	45.9	46.5
2	2	5	34.6	32.3
2	3	5	33.5	40.6
2	5	5	39.3	42.8
2	6	5	47.5	49.0
3	0	5	79.8	64.1
3	1	5	27.1	25.3
3	2	5	27.8	25.4
3	4	5	60.1	60.9
3	6	5	41.7	43.4
4	5	5	62.9	58.6
5	0	5	46.1	38.4

Part III

The Structure of Benzilmonoxime:

The Crystal Structure of the

Para-Bromobenzoate of Benzilmonoxime

3.1 INTRODUCTION

The currently accepted structures of the two monoximes
of benzil are shown here
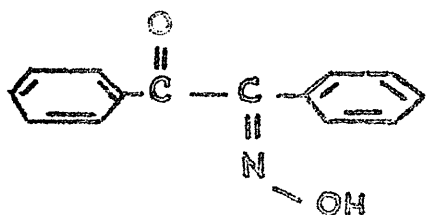
α   m.p. 138°C I
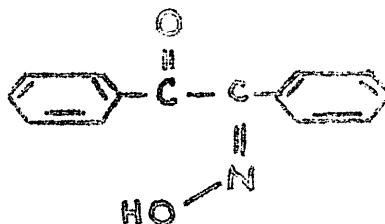
β   m.p. 107°C II
(114°C polymorph)

This configurational assignment, made by Meisenheimer (1921),
was based on the fact that the benzoate of the β-oxime, IV,
is formed from the ozonisation of triphenylisoxazole, III.
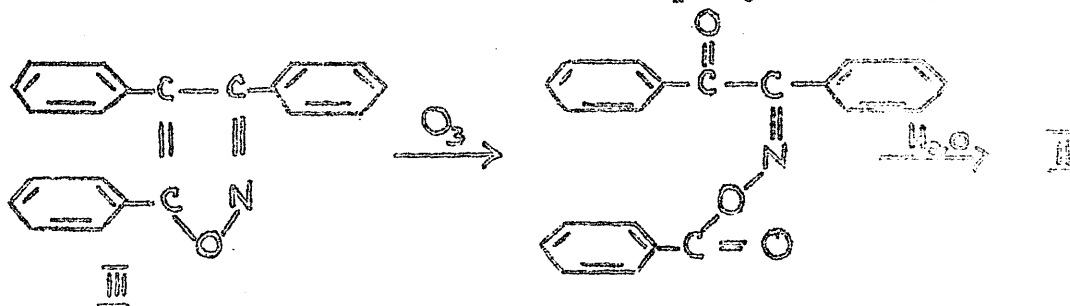
There is some evidence that the configurations should be
reversed.   The acetate of β-benzilmonoxime is stable at
190°C, whereas that of the α-oxime undergoes thermal
decomposition at 140°C.   When the reaction products are
treated with water, acetic acid, benzoic acid and
benzonitrile are formed, indicating that the initial products
were probably benzonitrile and acetic-benzoic anhydride.
Such thermal decompositions often occur by intramolecular

cyclic mechanisms, viz.
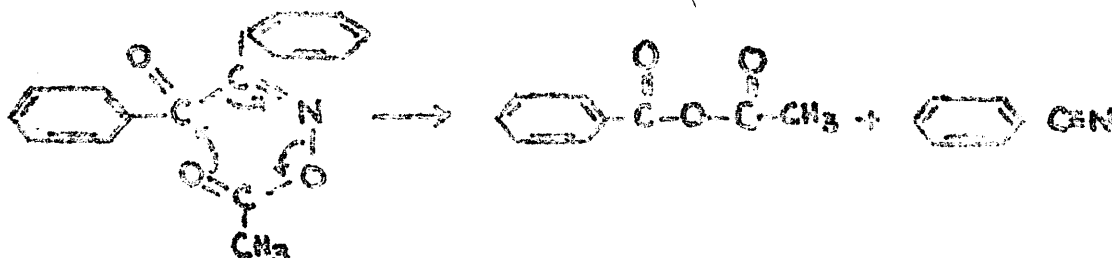
This would imply that the hydroxyl group in the α-oxime **was _cis_ to the carbonyl group.**

Some spectroscopic evidence would seem to support this argument. An investigation of some α- and β-oximes by infra-red spectroscopy (Palm and Werbin, 1953), shown that with each isomeric pair, the β-oxime has the higher melting point and the higher conductivity. This increase in acidity of the O-H bond is accompanied by a shift to lower frequencies of the I.R. absorption bands associated with the O-H stretching mode. In most isomeric oximes the β-oxime absorbs at lower frequency than the α-isomer. Benzilmonoxime is an exception on two counts. In solution of benzene and chloroform, the β-oxime absorbs at higher frequencies than the α-oxime. The melting point of the ~~para bromobenzoate of the~~ β-oxime is only 107°C as compared with 106°C in the case of the α isomer.

Other anomalies in the behaviour of these two compounds include an abnormal Beckmann rearrangement (Blatt, 1931) and abnormal reaction of the oxime with trifluoro-acetic acid and with polyphosphoric acid (Forbes, and Kuhla, 1959).

N.M.R. studies undertaken at Ohio State University
seemed to support a change in the configuration but these
were not conclusive (M.S. Newman, private communication).
Professor Newman requested an X-ray analysis and sent
a sample alleged to be the para-bromobenzoate of β-
benzilmonoxime (m.p. 105-106°C). Barnes (1938) reports
melting points of the para bromobenzoates of α and β-
monoxime. His values are as follows:

α form 105°C ,

β form 147°C .

That the sample provided was the para-bromobenzoate of the
α-form of the oxime was further confirmed by the fact that
attempted hydrolysis of the para-bromobenzoate did not
yield the parent oxime. (M.S. Newman, private communication).
This behaviour is typical of derivatives of α-oximes.

The crystals provided by Professor Newman were long
white needles and showed sharp extinction along the direction
of the needle axis. Unfortunately, they showed a very
strong tendency to grow together as twins. The specimen
chosen for analysis had one individual of the twin
sufficiently smaller than the other to allow accurate
indexing. It had been intended to solve the structure
by the usual heavy atom method. This approach failed.
The structure was finally solved by combining a heavy

atom-phased Fourier synthesis with a "minimum function"
derived from a three-dimensional, sharpened Patterson
function. Three electron density distributions were
calculated to refine the atomic positions. Further
improvement of the positional and thermal parameters
was obtained by the method of least squares. The final
R-value was 16·0% for 1258 independent, non-zero reflections.

The results of this analysis show that the para-
bromobenzoate of the α-benzilmonoxime (m.p. 105-106°C)
has the para-bromobenzoate group trans relative to the
carbonyl group (Figure 10).
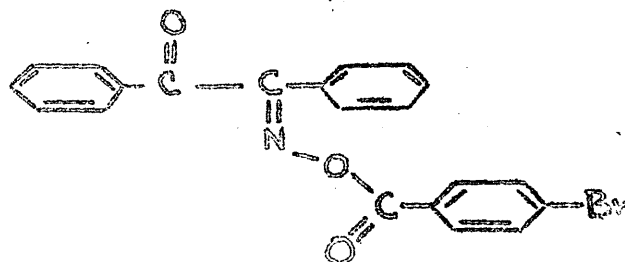
This confirms Meisenheimer's assignment of structure
to the oximes, I and II, of benzil.

3.2. EXPERIMENTAL

The para-bromobenzoate of α-benzilmonoxime yields
long colourless, needle-shaped crystals when crystallised
from ethanol solutions. These melt sharply at 106°C
on a hot-stage microscope. When examined under a
polarising microscope, they show sharp extinction along
the needle direction.

3.2.1. CHOICE OF CRYSTAL

Preliminary photographs showed that the compound crystallises in the triclinic system, with space group P1 or P$\bar{1}$. (Subsequent calculations have shown that the space group is P$\bar{1}$). Weissenberg photographs of the hk0 zone were taken in the usual manner with multiple film packs (Robertson, 1943). Photographs of the hk1 and hk2 reciprocal lattice nets showed that the crystals were twinned. This twinning occured in such a way that there was exact registry of points in the zero layer of the reciprocal lattice, but complete disregistry in other layers. In the crystal chosen for analysis, one individual of the twin was sufficiently larger than the other to allow accurate indexing. The spot shape of the reflections in the photographs was very poor.

3.2.2. CHOICE OF UNIT CELL

In the triclinic system, the choice of unit cell is not dictated by symmetry considerations. For this reason there are an infinite number of ways of choosing a primitive cell in a triclinic lattice. However, for any crystal, there is one cell that is unique. This particular cell is called the "reduced cell" and is defined by the three shortest, non-coplanar translations in the lattice. In such a cell, each cell edge is shorter than

reciprocal lattice points into the sphere of reflection.
Thus both the $\underline{a}^*\underline{b}^*$ plane and the $\underline{a}^*\underline{c}^*$ plane can be photographed
with the same mounting. The dihedral angle between the
planes is the complement of the angle between the plane
normals: e.g. $[\underline{a}^*\underline{b}^*] \perp \underline{c}$ and $[\underline{a}^*\underline{c}^*] \perp \underline{b}$; therefore, the
angle between the planes is $180-\alpha$. In the monoclinic
case and in systems of higher symmetry $\alpha^* = 180-\alpha$. In the
triclinic case

$$\alpha^* = \cos^{-1} (\cos \beta^* \cos \gamma^* - \sin \beta^* \sin \gamma^* \cos \alpha).$$

Thus the six reciprocal cell dimensions are available
from a single mounting. The real cell dimensions can then
be calculated from the formulae given by Buerger (1942,
p.360).

3.2.4. CRYSTAL DATA

Formula	$C_{21}NO_3Br$	F.W. 395.23 gm.
System	triclinic	
Space group	$P1$ or $P\bar{1}$	
Lattice constants	$a = 8 \cdot 78$ Å	
	$b = 17 \cdot 01$ Å	
	$c = 6 \cdot 27$ Å	
	$\alpha = 95 \cdot 11°$	
	$\beta = 91 \cdot 08°$	
	$\gamma = 102 \cdot 34°$	

reciprocal lattice points into the sphere of reflection. Thus both the a^*b^* plane and the a^*c^* plane can be photographed with the same mounting. The dihedral angle between the planes is the complement of the angle between the plane normals: e.g. $[a^*b^*] \perp c$ and $[a^*c^*] \perp b$; therefore, the angle between the planes is $180-\alpha$. In the monoclinic case and in systems of higher symmetry $\alpha^* = 180-\alpha$. In the triclinic case

$$\alpha^* = \cos^{-1} (\cos \beta^* \cos \gamma^* - \sin \beta^* \sin \gamma^* \cos \alpha).$$

Thus the six reciprocal cell dimensions are available from a single mounting. The real cell dimensions can then be calculated from the formulae given by Buerger (1942, p.360).

3.2.4. CRYSTAL DATA

Formula	$C_{21}NO_3Br$	F.W. 395.23 gm.
System	triclinic	
Space group	P1 or P$\bar{1}$	
Lattice constants	$a = 8.78$ Å	
	$b = 17.01$ Å	
	$c = 6.27$ Å	
	$\alpha = 95.11°$	
	$\beta = 91.08°$	
	$\gamma = 102.34°$	

Volume	931 Å
Density(obs)	1·47 gm/cc
Molecules/ cell	2
Density(calc)	1·49 gm/cc
F(000)	416
μ(Cu Kα)	35·9 cm^{-1}

3.2.3. INTENSITY DATA

Intensity data were obtained for the reciprocal lattice nets hk0 to hk5 using a Nonius Weissenberg camera and multiple film packs. To avoid the spot shape correction necessary if data are obtained from upper and lower halves of the same film, two sets of photographs were taken of each layer, one displaced from the other by a rotation of 180°. The two sets were scaled to one another by comparison of common reflections. The various reciprocal lattice nets were given a common relative scale by comparison by axial reflections from the Weissenberg data with common reflections from the precession photographs of the 0kl zone. Lorentz and polarization corrections had been calculated on the DEUCE computer for the Weissenberg data. These corrections had been applied to the precession data by means of a template. (Buerger, 1960, p.189).

3.2.6. ANALYSIS OF THE STRUCTURE

Projected Patterson syntheses, P(UV) and P(VW), were calculated to determine three coordinates of the heavy atom. The median axis projection, calculated from precession data, showed two large peaks. Neither of these gave satisfactory agreement with the major peak in the short axis projection. A three-dimensional vector map, P(UVW), showed two major peaks corresponding to the two peaks in the projected function, P(UV). The larger of these was a diffuse peak, very much extended in a direction roughly parallel to the median axis. Since the smaller peak was the usual Gaussian shape it was assumed to represent the Br-Br interaction. The bromine coordinates derived from this peak were;

$$x = 0.3246, \quad y = 0.0826, \quad z = 0.3573.$$

Structure factors were calculated with phases determined by the heavy atom. Sim's ratio, r, for this compound is

$$r = \left(\frac{\Sigma f^2_{Br}}{\Sigma f^2_L}\right)^{\frac{1}{2}} = \left(\frac{1225}{1012}\right)^{\frac{1}{2}} = 1.10 .$$

indicating that about 20% of the data will have the wrong sign in a calculation based on the heavy atom alone. (Sim, 1957). To avoid introducing errors in to the electron density distribution by including terms with the wrong sign, all structure factors with

$$\left| F_o \right| - \left| F_c \right| > \frac{1}{2} \left| F_c \right|$$

were excluded from the first Fourier synthesis. The

R-value for the terms actually included in the summation
was 53.7%.

The first Fourier map was calculated in sections along
the median axis.   There were 40 peaks with heights between
two and six electrons/$\overset{\circ}{A}{}^3$.   Other than the bromine atom,
none of the known features of the molecule could be
recognised.

A minimum function was derived from the three-dimensional
Patterson function in the manner described in Part I (1.4).
Both the Fourier map and the minimum function were plotted
on glass sheets, but the only obvious similarities between
them were the positions of the bromine atoms and very
pronounced streaks of electron density running diagonally
across the maps.   Although the minimum function was not
well resolved, it was possible to reduce the number of
atomic sites by comparing the two functions, one section
at a time.   Only 27 of the 40 peaks in the Fourier map
corresponded to positive regions in the minimum function.

These 27 peaks were plotted in
three-dimensions using long wires
supported by a cork base.   Two
coordinates were defined by the
positions of the wires relative to
a grid drawn on the base.   The
vertical coordinate was marked by
a small piece of fibre glass along
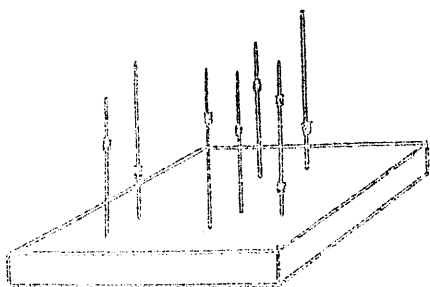
insulation sheathing. Tentative locations were assigned
to 9 of the atoms in the molecule. Five of these were
used in a structure-factor calculation with hk0 reflection
data. The R-value increased. The three-dimensional
data were "sharpened" by applying the Lorentz-polarisation
function to the Patterson coefficients, $|F|^2$. This gives
a sharpening function of the form shown on the left. The
sharpened Patterson function was used to give an improved
position for the bromine atom and to derive a minimum function.
The bromine-phased electron density calculation and the
Patterson synthesis were repeated in sections along the short
axis because it seemed likely that the streaking observed
in the previous maps represented unresolved, steeply
tilted benzene rings. The resolution of the minimum
function had been much improved by the sharpening process.
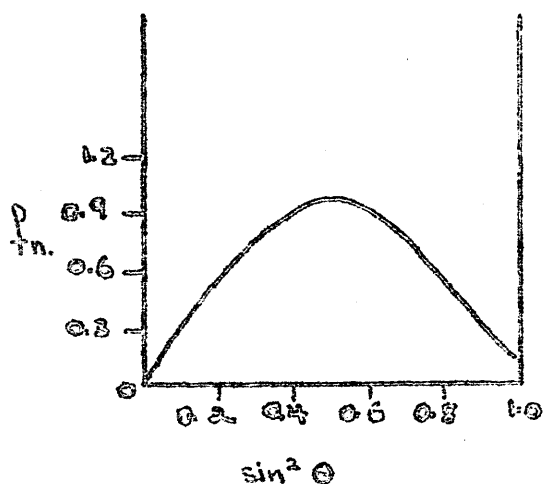
The electron density distribution and the minimum
function were superimposed by plotting equivalent sections
from the two functions on the same glass sheet. This
composite map revealed the positions of the 25 light atoms.
Since the structure of the molecule was known, all of the
atoms could be identified. When they were analysed

in the next structure factor calculation with scattering factors appropriate to their chemical types, the R-value dropped to 34.8%. Another cycle of Fourier refinement gave a further improvement to 30.1%. No further calculations were done on the DEUCE computer at Glasgow University.

3.2.7. REFINEMENT OF THE STRUCTURE

The Glasgow Structure Factor Least Squares program was available before the Fourier program. For this reason refinement was continued by least squares in spite of the high R-value.

The first cycle of least squares used unit weights for each reflection and served to provide a rough over all scale factor for the data. The R-value was 35.7%. For all subsequent calculations, Cruickshank's (1961) weighting scheme was used:

$$\sqrt{w} = (1/p_1 + F + p_2 F^2 + p_3 F^3)^{\frac{1}{2}} \quad .$$

The initial values of the parameters were

$$p_1 = 6.0, \; p_2 = 9.9 \times 10^{-3}, \; p_3 = 1.25 \times 10^{-4} \quad .$$

These values were adjusted slightly during the course of refinement. The final values were

$$p_1 = 4.2, \; p_2 = 1.6 \times 10^{-2}, \; p_3 = 3.8 \times 10^{-4} \quad .$$

After four cycles of isotropic block-diagonal least-squares refinement, the R-value had been reduced to 26.6%. The data were rescaled. After two more cycles the R-value was 24.6%.

A program for refining projections by the "minimum
residual" method of Bhuiya and Stanley (1963) was written
by K.W. Muir of this Department. When this program
became available, it was used to refine the projections
along the short and median axes. The R-values for the two
zones improved from 25% to 23% and from 27% to 22%
respectively. Three-dimensional structure factors based
on positions from the two projections showed an R-value
of 21.9%. Three cycles of least squares reduced this
to 18.2%. Anisotropic temperature factors were allowed
to refine for 4 cycles of block diagonal least squares.
Refinement was terminated at this point. The R-value
was 16.0% for 1258 independent reflections. Unobserved
reflections were not included in the analysis.

3.3 MOLECULAR DIMENSIONS AND DESCRIPTION OF THE STRUCTURE

The configuration of the para-bromobenzoate of benzil monoxime is best displayed when the crystal structure is viewed in projection along the short axis (Figure 10). Van der Waals forces are important in determining the packing arrangement of the molecule, but a very short contact between the oxygen of the carbonyl group and the carbon of the carboxyl group would seem to indicate that dipole-dipole interactions may also be important. Intermolecular contacts are seen most easily in the projection along the median axis (Figure 11). Figure 14 is an enlargement of a portion of the median axis projection.

Table 8 lists the final atomic coordinates and their standard deviations as given by the least-squares refinement. The coordinates and their standard deviations are quoted with the same number of significant figures. No significance should be attached to the last figure as it has been included only to allow derived quantities to be calculated without loss of accuracy. It should be noted that the standard deviations of the heavy atom coordinates are an order of magnitude smaller than those of the light atoms.

Anisotropic temperature parameters are shown in Table 9. These are the parameters of the equations

$$\exp \left(-B \sin^2\theta/\lambda^2\right) = \exp \left[-2\pi^2 \left(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2}\right.\right.$$

$$\left.\left. + 2U_{23}k\ell b^*c^* + 2U_{31}\ell h c^*a^* + 2U_{12}hka^*b^*\right)\right]$$

The factor of 2 has been included in the cross-terms.
Bond lengths and their standard deviations are given in Table
10; bond angles are shown in Table 11. These are shown
diagramatically in Figure 12.

Table 12 is a list of ρ_{ij}, the correlation coefficients
between the coordinates of each atom. The correlation
coefficient between the ith and j^{th} parameters in a least-
squares calculation is defined as

$$\rho_{ij} = (a^{-1})_{ij}/[(a^{-1})_{ii}(a^{-1})_{ij}]^{\frac{1}{2}},$$

where $(a^{-1})_{ij}$ is the jth element of the ith row of the matrix
inverse to a_{ij}, the matrix of the normal equations. The
intra-atomic correlations arise primarily from non-orthogonality
of the axes and from anisotropy of the thermal parameters.

Standard deviations of bond lengths in this structure
lie between 0·03 and 0·04 Å. Most of the observed bond
lengths are very near their expected values. Individual
bond lengths in the benzene rings vary between 1·30 and 1·51 Å.
with an average length of 1·41 Å. The C-Br bond length
is 1·85 Å. Both of these values compare favourably with
the expected values of 1·397 and 1·85 Å, respectively (Sutton,
1965). There are three $C(sp_2)-C(sp_2)$ single bonds in the

structure with an average length of 1·49 Å, and two C=O
bonds with an average length of 1·21 Å. These measurements
are in agreement with the values of 1·492 and 1·210 Å,
respectively for bonds of these types in benzil (Brown and
Sadanaga, 1965). The C-O bond length of 1·38 Å is close
to the value of 1·358 Å reported for the long bond in esters
and acids (Sutton et al., 1958). The N-O bond length of
1·42 Å is similar to the value 1·408 Å, reported in formaldoxime
(Levine, 1963), and to the value 1·415 Å, reported in formamide
oxime (Hall, 1965).

In a summary of oxime structures, Hamilton (1961) lists
various lengths for the C=N bond between 1·225 and 1·29 Å.
The value predicted from Pauling's radii is 1·265 Å. The
measured bond length of 1·39±·03 Å seems to be significantly
longer than the predicted length. This may be real or it
may reflect an under-estimate of the standard deviation of
the bond length. Hodgson and Rollett (1963) have shown that
when the variances of parameters are calculated from the
inverse of the block matrices, standard deviations of bond
lengths can be underestimated by as much as 80%. If the
difference is real, it implies that this is not a pure
double bond but that it is taking part in some sort of resonance
interaction. This is not the case. Resonance interaction
with the benzene ring is precluded because both the C and the
N deviate significantly from the plane through the

ring (Table 13). Resonance with the carbonyl group is impossible. The root mean square distance from the "best" plane through C(8), C(9) N(22) and O(23) is more than ±0·25 Å. This would indicate that the difference is not real and that the standard deviation of this bond length and been under-estimated.

"Best" planes have been calculated for the three benzene rings and for the carboxyl group. Deviations from these planes are shown in Table 13 and Figure 13. It is interesting to note that C(17) and Br(26) lie in the plane of benzene ring A, but that the oxygens of the carboxyl group have been displaced from this plane by a rotation of 13°.

Pauling's figures for the Van der Waals radii of carbon (1·70 Å), nitrogen (1·50 Å) and oxygen (1·40 Å) predict that the shortest inter-molecular contacts will be as follows:

| C....C | 3·40 Å | C....N | 3·20 Å |
| C....O | 3·12 Å | O....O | 2·80 Å |

The only contact that is significantly shorter than the corresponding Van der Waals radius is that between O(23) and C(7). The calculated standard deviation of this measurement is just under 0·03 Å, but the difference between the observed and calculated distances is large enough to be significant even if the standard deviation were as high as 0·04 Å. Contacts as short as 2·77 Å between sp_2-hybridised carbon and the oxygen of a carbonyl group have been observed in other

compounds where there is no possibility for hydrogen bonding.
(Davies and Blum, 1955; Ohm, Jeffrey and Sakurai, 1962;
Bolton, 1963, 1964, 1965). Bolton has studied this effect
and has suggested that it occurs when dipole-dipole or
dipole-induced-dipole interactions are quite strong. The
shortest contacts occur when the bond of the carbonyl group
is approximately collinear with the π-bond of a carbon atom
in an adjacent molecule. In the compounds studied by
Bolton, the carbon atom is in an aromatic system with at
least two carbonyl substituents. The average length of the
$O....C$ contact is 2·82 Å, and the average value of the $C-O....C$
angle is 15f. In the present study, the carbon atom involved
in the contact is an sp_2-carbon in a carboxyl group. There
is no large inductive effect present, but neither of the
$C=O$ groups in the molecule seem to be involved in any
appreciable resonance interaction. It seems reasonable
to expect a certain amount of dipole-dipole interaction
between the two groups. This interaction would not be as
strong as in alloxan and the other molecules studied by Bolton;
the $C=O...C$ angle (116°) is less favourable and the contact
is longer than those he observed.

Kihara (1963) has shown that the structures of many
polar molecular crystals are governed by electrostatic forces
between the molecules. He has determined correct crystal
structures for a number of relatively simple molecules by
building models with shape and magnetization appropriate

to the particular molecule and allowing the models to "crystallise".   This would seem to indicate, that electrostatic forces play an important role in determining the crystal structures of a fairly broad category of molecules.   This general observation, coupled with the fact that the carboxyl group in the present structure has been rotated out of the plane of the benzene ring in a direction that would make a more favourable angle between the π-orbital of the carbon atom and the σ-orbital of the oxygen, suggests that the close contact is real.

Figure 10
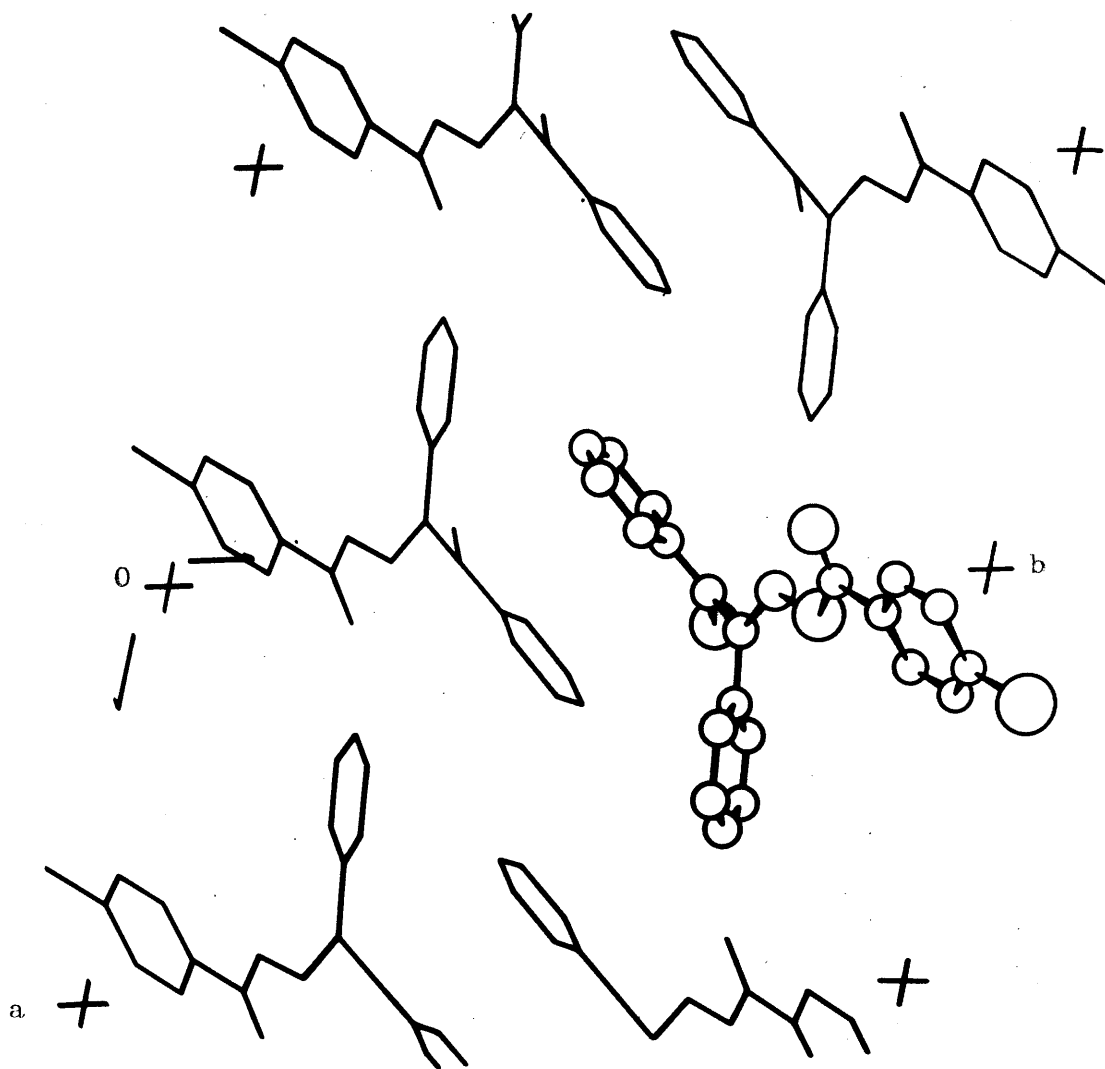
Packing diagram of the _para_-bromobenzoate of
benzil monoxime, viewed along the _c_-axis

Figure 11
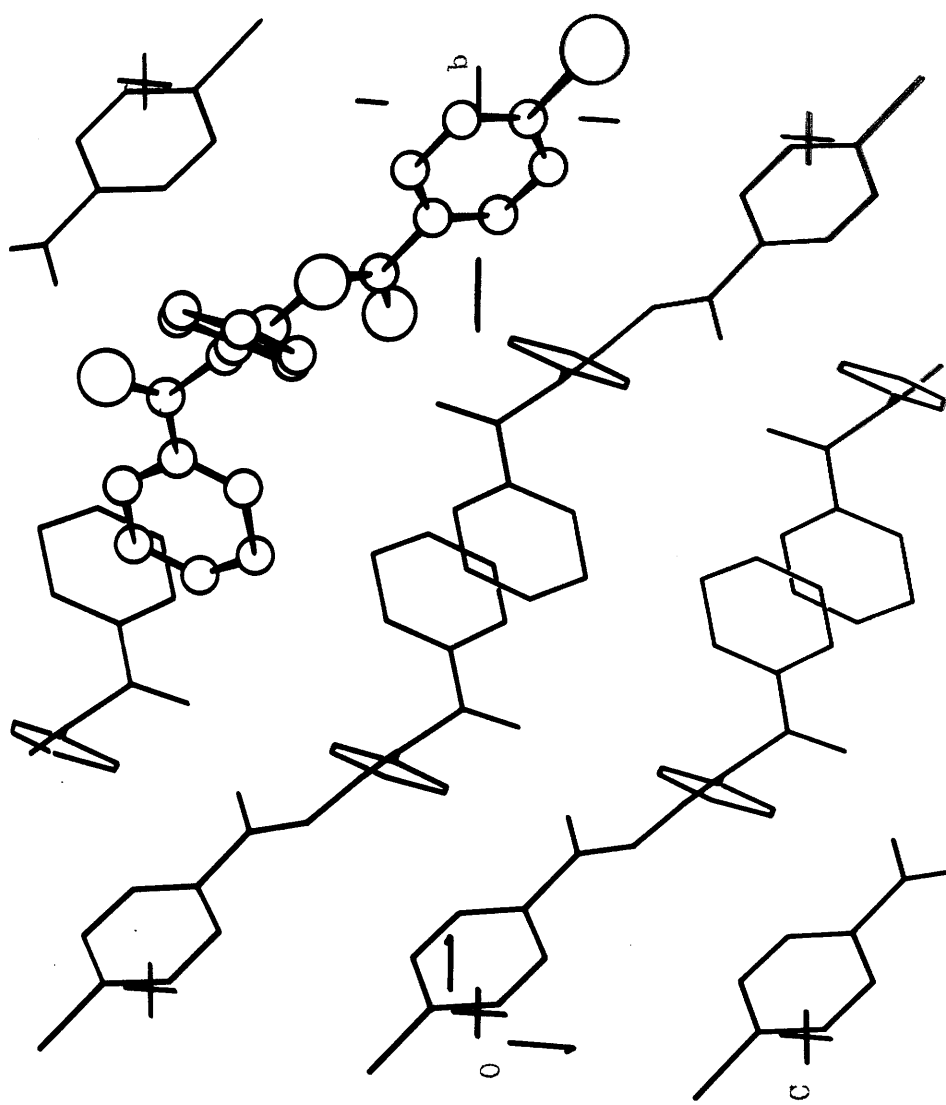
Molecular packing of the para-bromobenzoate of benzilmonoxime viewed in projection along the a-axis.

Para-Bromobenzoate of benziisomethine

Final fractional atomic coordinates with their
estimated standard deviations. No significance
should be attached to the last figure as it
has been included only to allow derived quantities
to be calculated without loss of accuracy.

C(1)	0.2293(35)	-0.0607(16)	1.1303(36)
C(2)	0.3015(30)	-0.0077(16)	0.9457(46)
C(3)	0.2336(29)	-0.0692(17)	0.7802(40)
C(4)	0.0974(27)	-0.1240(14)	0.8345(46)
C(5)	0.0197(31)	-0.1105(17)	1.0511(47)
C(6)	0.0634(31)	-0.0550(15)	1.2051(47)
C(7)	0.0109(26)	-0.1892(14)	0.6924(37)
C(8)	0.1373(25)	-0.2880(13)	0.2285(35)
C(9)	0.0504(27)	-0.3420(14)	0.0465(41)
C(10)	-0.0801(27)	-0.4029(13)	0.0837(37)
C(11)	-0.1020(29)	-0.4360(12)	0.2827(47)
C(12)	-0.2271(36)	-0.5044(16)	0.3169(51)
C(13)	-0.3264(33)	-0.5339(18)	0.1435(50)
C(14)	-0.3040(36)	-0.5019(20)	-0.0518(51)
C(15)	-0.1702(28)	-0.4330(17)	-0.0557(50)
C(16)	0.3110(23)	-0.2735(14)	0.2423(32)
C(17)	0.4064(24)	-0.2459(14)	0.0701(37)
C(18)	0.5663(33)	-0.2455(16)	0.0955(40)
C(19)	0.6244(28)	-0.2642(16)	0.2731(39)
C(20)	0.5243(26)	-0.2907(15)	0.4507(43)
C(21)	0.3674(26)	-0.2909(15)	0.4399(40)
N(22)	0.0373(21)	-0.2576(11)	-0.1263(29)
O(23)	0.1123(18)	-0.3256(10)	0.5207(23)
O(24)	0.1148(16)	-0.2029(09)	0.7229(28)
O(25)	-0.1135(19)	-0.2309(10)	0.7229(28)

Br(26) 0.31968(41)   0.08090(18)   1.3570(49)

Table 9

Para-bromobenzoate of Benzilmonoxime: Anisotropic
Temperature Parameters

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.156	0.073	0.063	-0.064	0.035	0.085
C(2)	0.079	0.086	0.116	-0.010	-0.009	0.028
C(3)	0.060	0.103	0.139	0.010	-0.004	0.009
C(4)	0.074	0.079	0.082	0.006	0.030	0.045
C(5)	0.095	0.110	0.087	0.014	0.024	0.069
C(6)	0.115	0.063	0.082	-0.0 7	0.025	-0.007
C(7)	0.072	0.087	0.079	-0.039	0.038	0.023
C(8)	0.067	0.075	0.064	-0.007	0.022	0.029
C(9)	0.087	0.083	0.052	0.041	0.040	-0.004
C(10)	0.083	0.074	0.076	0.011	0.078	0.039
C(11)	0.088	0.046	0.114	0.005	0.041	0.022
C(12)	0.120	0.077	0.126	0.001	0.022	-0.022
C(13)	0.090	0.089	0.153	-0.008	0.013	0.022
C(14)	0.108	0.123	0.120	0.002	0.012	0.050
C(15)	0.053	0.138	0.077	-0.062	-0.023	-0.005
C(16)	0.054	0.080	0.086	-0.020	-0.020	0.016
C(17)	0.047	0.088	0.084	0.019	-0.001	-0.044
C(18)	0.105	0.092	0.076	0.020	-0.016	-0.036
C(19)	0.083	0.097	0.069	-0.018	-0.010	0.001
C(20)	0.050	0.089	0.116	-0.026	-0.002	-0.003
C(21)	0.061	0.090	0.097	-0.020	0.026	0.012
N(22)	0.074	0.071	0.070	0.022	0.010	0.005
O(23)	0.080	0.110	0.088	0.015	0.009	-0.003
O(24)	0.059	0.093	0.083	-0.042	0.010	-0.004
O(25)	0.090	0.098	0.110	-0.020	0.065	-0.004
Br(26)	0.136	0.096	0.102	-0.060	-0.011	0.014.

Table 10

Para-bromobenzoate of Benzilmonoxime:

Bond lengths in angstroms, with standard
deviations given as units in the last place.

Br(26)	C(1)	1.845(25)
C(1)	C(2)	1.448(37)
C(2)	C(3)	1.390(39)
C(3)	C(4)	1.446(35)
C(4)	C(5)	1.449(35)
C(5)	C(6)	1.301(36)
C(6)	C(1)	1.477(39)
C(4)	C(7)	1.507(33)
C(7)	O(25)	1.197(28)
C(7)	O(24)	1.377(27)
O(24)	N(22)	1.417(23)
N(22)	C(8)	1.354(28)
C(8)	C(16)	1.495(30)
C(16)	C(17)	1.433(32)
C(17)	C(18)	1.387(35)
C(18)	C(19)	1.316(35)
C(19)	C(20)	1.475(35)
C(20)	C(21)	1.377(32)
C(21)	C(16)	1.357(34)
C(8)	C(9)	1.456(30)
C(9)	O(23)	1.217(26)
C(9)	C(10)	1.469(32)
C(10)	C(11)	1.420(34)
C(11)	C(12)	1.447(38)
C(12)	C(13)	1.375(44)
C(13)	C(14)	1.380(46)
C(14)	C(15)	1.511(41)
C(15)	C(10)	1.323(33)

Figure 12
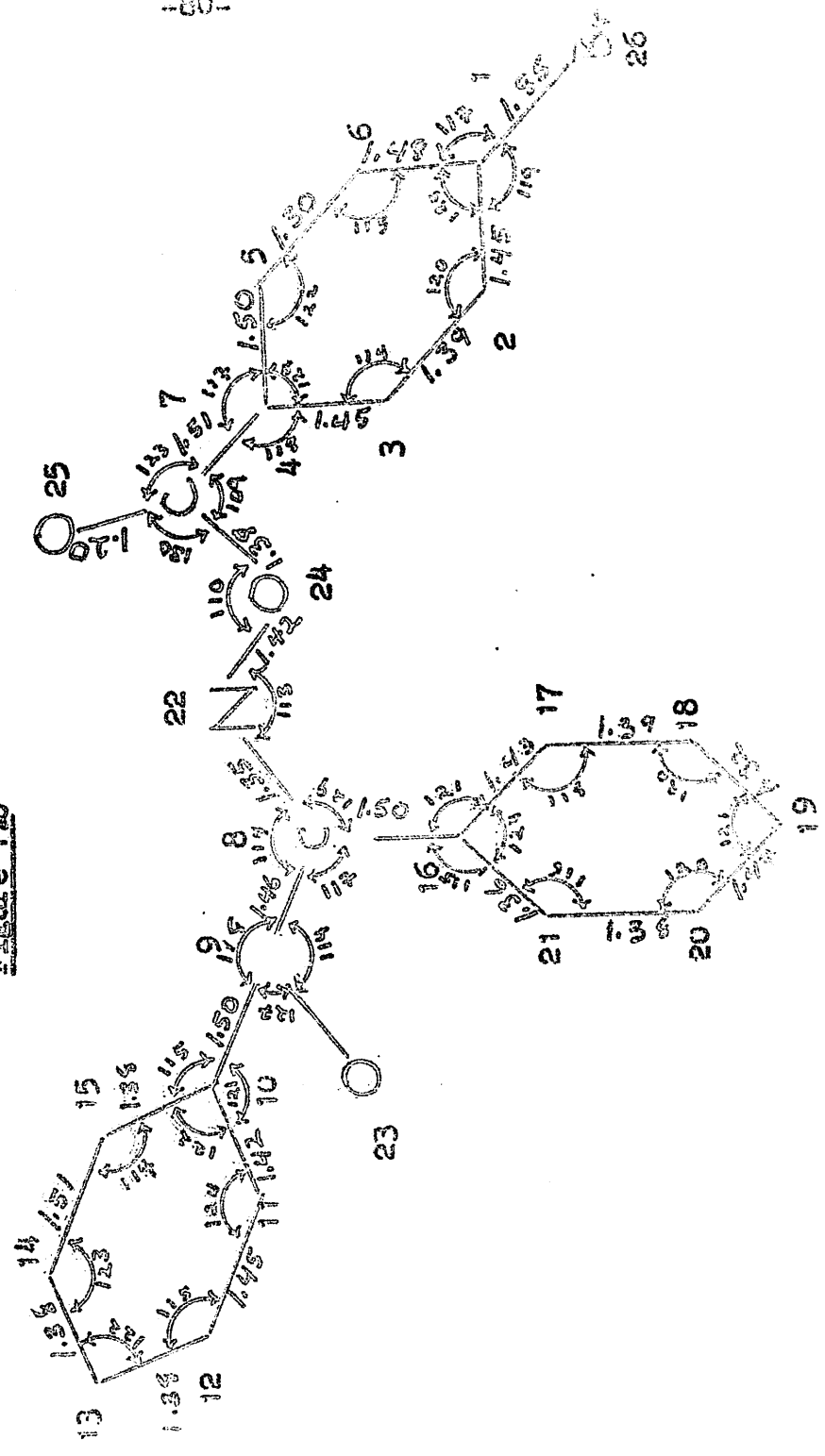
Para-Bromobenzoate of Benzilmonoxime: Bond Lengths and Angles.

Table 11

Para-Bromobenzoate of Benzilmonoxime

Bond angles with their estimated standard
deviations given as units in the last place.

			ANGLE	E.s.d.
Br(26)	C(1)	C(2)	119.5	2.0
C(1)	C(2)	C(3)	119.7	2.4
C(2)	C(3)	C(4)	114.3	2.5
C(3)	C(4)	C(5)	1.24	2.3
C(3)	C(4)	C(7)	117.7	2.1
C(7)	C(5)	C(6)	116.9	2.0
C(4)	C(5)	C(6)	121.8	2.4
C(5)	C(6)	C(1)	115.4	2.3
C(6)	C(1)	Br(26)	116.7	1.8
C(6)	C(1)	C(2)	123.7	2.2
C(4)	C(7)	O(25)	122.9	2.1
C(4)	C(7)	O(24)	108.7	1.8
O(24)	C(7)	O(25)	129.9	2.2
C(7)	O(24)	N(22)	110.5	1.5
O(24)	N(22)	C(8)	112.7	1.6
N(22)	C(8)	C(16)	129.3	1.9
C(8)	C(16)	C(21)	115.0	2.0
C(8)	C(16)	C(17)	120.7	1.9
C(16)	C(17)	C(18)	117.6	2.1
C(17)	C(18)	C(19)	120.2	2.4
C(18)	C(19)	C(20)	120.8	2.3
C(19)	C(20)	C(21)	120.4	2.3
C(20)	C(21)	C(16)	115.8	2.3
C(21)	C(16)	C(17)	124.3	2.0
C(16)	C(8)	C(9)	117.0	1.9
C(8)	C(9)	O(23)	114.5	2.0
O(23)	C(9)	C(10)	126.7	2.0
C(8)	C(9)	C(10)	118.3	1.8
C(9)	C(10)	C(11)	121.5	2.0
C(10)	C(11)	C(12)	123.6	2.3
C(11)	C(12)	C(13)	114.8	2.7
C(12)	C(13)	C(14)	121.8	2.8
C(13)	C(14)	C(15)	123.1	2.7
C(14)	C(15)	C(10)	114.3	2.3
C(15)	C(10)	C(11)	122.3	2.2
C(15)	C(10)	C(9)	115.3	2.0

Table 12

Para-Bromobenzoate of Benzilmonoxime:

Correlation Coefficients

C(1)	0.29998	0.14586	-0.16655
C(2)	0.11987	0.06582	0.01953
C(3)	0.08878	0.04642	0.07248
C(4)	0.18409	0.17467	0.07385
C(5)	0.25684	0.12183	0.09247
C(6)	0.00550	0.12405	0.05836
C(7)	0.13869	0.18289	-0.07714
C(8)	0.16573	0.12154	0.03710
C(9)	0.01546	0.16854	0.21003
C(10)	0.18099	0.30766	0.08628
C(11)	0.11643	0.18964	0.06149
C(12)	-0.02487	0.09343	0.09301
C(13)	0.12420	0.09403	0.05286
C(14)	0.17601	0.07558	0.06221
C(15)	0.03727	-0.03303	-0.13106
C(16)	0.09594	-0.00379	0.00554
C(17)	-0.10309	0.05197	0.13689
C(18)	-0.09101	-0.02412	0.15814
C(19)	0.05061	-0.01672	0.01787
C(20)	0.05333	0.07842	-0.03691
C(21)	0.07686	0.13350	-0.01227
N(22)	0.07201	0.09923	0.13674
O(23)	0.05114	0.08290	0.11462
O(24)	0.04473	0.08099	-0.06906
O(25)	0.04323	0.24747	0.02315
Br(26)	0.04472	0.00410	-0.16339

Table 13

Para-Bromobenzoate of Benzilmonoxime: deviations in angstroms × 10⁻³ from planes through the molecule.

A		B		C		D
Atoms included in plane						
C(1)	-19	C(16)	2	C(10)	19	O(24)
C(2)	8	C(17)	-29	C(10)	-19	O(24)
C(3)	30	C(18)	12	C(12)	13	O(27)
C(4)	-60	C(19)	7	C(13)	-9	
C(5)	50	C(20)	18	C(14)	-7	
C(6)	-9	C(21)	36	C(15)	22	

Root mean square deviation:
34   27   14

Atoms not included in plane:

C(7)	-43	C(8)	205	C(9)	159
Br(26)	70	C(9)	-559	O(23)	525
O(24)	312	N(22)	1347		
O(25)	154				

Equations of planes. X,Y,Z are atomic coordiates orthogonalized according to the following formulae:

$X = \underline{a}x + \underline{c}z \cos \beta$,
$Y = \underline{b}y$,
$Z = \underline{c}z \sin \beta$.

A $-0.5217X + 0.7644Y - 0.3788Z = -4.4150$

B $-0.1411X -0.9093Y -0.3914Z = 3.8857$

C $0.5917X -0.7604Y -0.2677Z = 4.5940$

D $-0.4404X +0.6219Y -0.6475Z = -4.9788$

Figure 13

-83-A-

Para-Bromobenzoate of Benzilmonoxime: Deviations from the
plane through the benzene rings are given in units of angstroms x10⁻³

Table 14

Para-Bromobenzoate of Benzilmonoxime

Inter-molecular Contacts < 3.60 A.

Equivalent position 1 refers to the molecule whose coordinates are listed in Table 5; position 2 refers to the molecule related to this one by a centre of inversion.

C(9)	O(25)	1	(0, 0,-1)	3.42
C(13)	C(14)	2	(-1,-1, 0)	3.49
C(14)	C(14)	2	(-1,-1, 0)	3.53
C(19)	O(25)	1	(1, 0, 0)	3.53
C(20)	O(25)	1	(1, 0, 0)	3.49
N(22)	C(5)	1	(0, 0,-1)	3.30
O(23)	C(4)	1	(0, 0,-1)	3.57
	C(7)	1	(0, 0,-1)	2.99
	C(12)	2	(0,-1, 0)	3.33
	C(13)	2	(0,-1, 0)	3.39
	C(21)	1	(0, 0,-1)	3.56
	O(24)	1	(0, 0,-1)	3.14
	O(25)	1	(0, 0,-1)	3.00
O(24)	C(6)	1	(0, 0,-1)	3.42
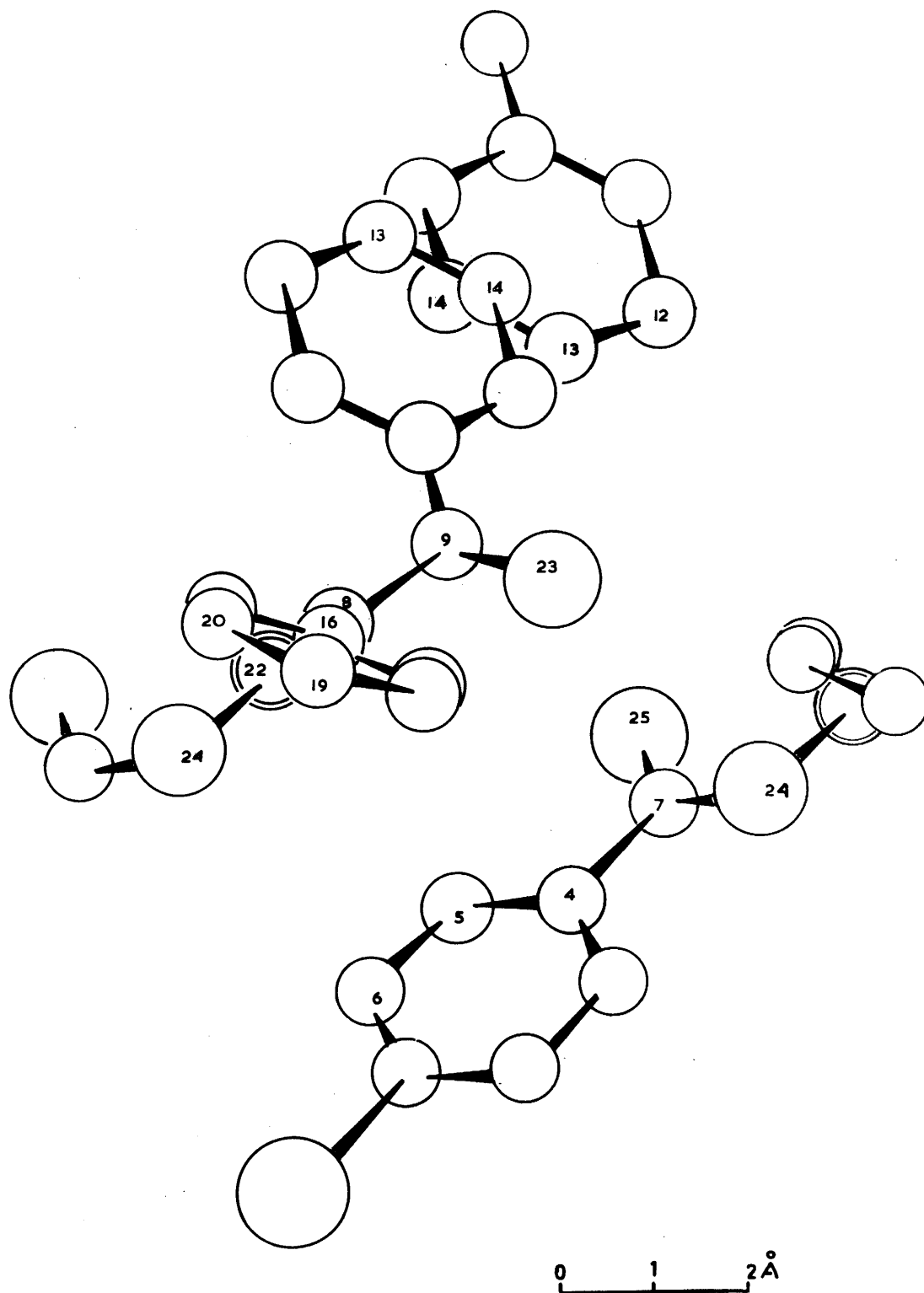
Inter-molecular contacts (median axis projection)

Table 15

Para-Bromobenzo te of Be izilmonoxime

H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc

Table 15 Ctd.

H	K	L	|Fo|	Fc
4	-5	1	27.2	30.6
4	-4	1	16.5	-15.3
4	-3	1	36.9	-37.4
4	-2	1	12.7	-12.1
4	-1	1	20.3	-19.0
4	0	1	20.6	-23.4
4	2	1	19.5	17.2
4	3	1	18.1	17.9
4	4	1	10.4	13.6
4	5	1	22.2	26.4
4	6	1	16.5	17.9
4	7	1	8.5	10.0
4	8	1	15.7	-18.6
4	9	1	6.4	5.8
4	10	1	5.9	4.6
4	11	1	6.7	-7.0
4	12	1	7.4	-10.4
5	-7	1	7.1	-9.4
5	-6	1	17.5	-22.9
5	-5	1	5.3	-6.8
5	-4	1	13.1	-14.0
5	-3	1	16.5	-5.8
5	-2	1	10.3	-9.3
5	-1	1	7.3	7.1
5	0	1	21.4	21.0
5	1	1	28.0	28.5
5	2	1	3.9	5.5
5	3	1	9.0	-7.7
5	4	1	4.7	2.9
5	5	1	9.6	-9.2
5	6	1	18.1	-23.1
5	7	1	10.2	-13.9
5	8	1	13.2	-16.2
5	10	1	6.6	6.5
6	-5	1	10.5	9.6
6	-4	1	10.5	11.5
6	0	1	6.0	-5.3
6	1	1	8.6	-8.2
6	3	1	18.2	-20.5
6	5	1	8.3	-6.4
7	-2	1	9.1	-9.4
7	0	1	8.3	-7.4
7	4	1	10.5	12.5
1	-13	-2	14.9	-20.3
1	-12	-2	11.0	-8.7
1	-11	-2	8.3	8.0
1	-9	-2	13.3	10.9
1	-8	-2	46.4	44.7
1	-7	-2	33.8	35.7
1	-6	-2	34.7	33.9
1	-5	-2	17.2	19.2
1	-4	-2	8.5	-5.9
1	-3	-2	17.2	-15.0
1	-2	-2	15.0	-23.0
1	-1	-2	50.8	-61.3
1	0	-2	27.4	-54.4
1	1	-2	12.7	-15.3
1	2	-2	16.3	21.5
1	3	-2	11.8	-11.7
1	4	-2	11.7	9.5
1	5	-2	48.8	43.1
1	6	-2	33.8	31.9
1	8	-2	5.3	-5.2
1	9	-2	5.0	3.9
1	11	-2	21.2	-17.2
1	12	-2	6.2	-2.4
1	13	-2	7.2	-5.3
1	14	-2	4.6	4.2
1	16	-2	5.0	2.4
1	17	-2	4.7	3.6
2	-16	-2	10.0	-7.2
2	-14	-2	7.3	5.7
2	-13	-2	12.8	11.8
2	-12	-2	9.9	8.8
2	-11	-2	27.6	25.6
2	-10	-2	14.4	12.0
2	-9	-2	7.4	4.9
2	-7	-2	16.5	-14.1
2	-6	-2	40.3	-34.0
2	-5	-2	37.2	-37.0
2	-4	-2	8.2	-11.4
2	-3	-2	9.6	8.2
2	-2	-2	13.0	11.6
2	-1	-2	19.7	23.4
2	0	-2	35.6	46.6
2	1	-2	26.0	33.4
2	2	-2	31.0	38.5
2	3	-2	4.9	3.8
2	4	-2	5.4	-6.5
2	5	-2	21.6	-25.5
2	6	-2	18.4	-19.6
2	7	-2	18.8	-18.7
2	8	-2	25.2	-28.8
2	9	-2	10.9	-9.1
2	10	-2	4.6	4.7
2	11	-2	9.1	8.8
2	12	-2	6.2	6.3
2	13	-2	5.8	3.7
2	14	-2	8.2	9.6
2	15	-2	4.5	2.5
3	-14	-2	10.4	7.2
3	-13	-2	8.1	5.1
3	-12	-2	5.6	-5.3
3	-11	-2	10.7	-7.4
3	-10	-2	18.6	-16.9
3	-9	-2	25.4	-23.0
3	-8	-2	14.9	-13.8
3	-7	-2	12.4	-13.6
3	-4	-2	29.3	29.5
3	-3	-2	52.9	55.5
3	-2	-2	32.2	40.9
3	-1	-2	8.5	7.9
3	0	-2	10.9	-9.0
3	1	-2	9.9	11.7
3	2	-2	6.4	-8.2
3	3	-2	35.5	-42.2
3	4	-2	29.2	-29.9
3	9	-2	17.0	20.0
3	10	-2	5.5	4.2
3	11	-2	4.5	3.4
3	15	-2	5.4	-3.7
4	-15	-2	14.5	-11.0
4	-14	-2	13.0	-8.5
4	-13	-2	13.0	-8.8
4	-12	-2	11.4	-9.3
4	-11	-2	7.8	-5.4
4	-10	-2	6.7	-7.8
4	-8	-2	9.1	16.3
4	-7	-2	17.0	18.3
4	-6	-2	4.0	4.0
4	-5	-2	11.1	-9.5
4	-2	-2	21.0	-21.8
4	-1	-2	20.9	-21.7
4	0	-2	26.5	-31.2
4	1	-2	9.2	-8.0
4	2	-2	4.7	-7.0
4	3	-2	6.2	4.1
4	4	-2	9.1	8.5
4	5	-2	15.4	14.1
4	6	-2	14.3	16.5
4	7	-2	5.9	3.4
4	10	-2	8.1	-8.7
4	11	-2	9.7	-7.4
4	12	-2	7.7	-5.9
4	13	-2	5.0	-3.0
4	14	-2	3.8	2.4
5	-16	-2	3.7	-2.2
5	-15	-2	8.7	-6.6
5	-13	-2	7.3	5.2
5	-12	-2	3.6	3.2
5	-11	-2	12.8	9.8
5	-10	-2	7.9	5.9
5	-9	-2	14.0	12.3
5	-6	-2	12.8	-13.0
5	-5	-2	25.3	-23.5
5	-4	-2	15.4	-13.5
5	-3	-2	8.4	-8.2
5	-2	-2	3.7	3.7
5	-1	-2	13.4	13.6
5	0	-2	13.5	12.6
5	1	-2	4.3	4.2
5	2	-2	4.9	5.8
5	3	-2	14.4	16.1
5	5	-2	11.9	-12.6
5	6	-2	6.9	-4.3
5	7	-2	5.6	-5.8
5	8	-2	4.6	-5.3
5	10	-2	6.5	-5.6
6	-17	-2	4.9	4.2
6	-16	-2	4.8	5.2
6	-13	-2	4.5	3.5
6	-11	-2	4.6	-4.3
6	-8	-2	12.6	-11.1
6	-6	-2	12.2	9.7
6	-5	-2	5.4	-4.4
6	-4	-2	4.7	-3.5
6	-3	-2	17.0	14.1
6	-2	-2	30.9	30.8
6	-1	-2	4.2	5.3
6	0	-2	6.7	6.6
6	1	-2	8.5	7.0
6	2	-2	7.7	-7.2
6	3	-2	12.4	-10.4
6	4	-2	3.6	-2.1
6	5	-2	7.3	-5.6
6	7	-2	3.7	-4.3
6	8	-2	9.1	7.0
6	9	-2	12.7	9.8
7	-13	-2	6.0	-6.1
7	-11	-2	4.6	-4.2
7	-7	-2	4.1	2.3
7	-5	-2	10.2	8.1
7	-4	-2	18.5	-14.6
7	-2	-2	5.7	3.9
7	-1	-2	10.2	8.4
7	0	-2	3.6	-3.7
7	1	-2	12.9	-12.7
7	3	-2	10.3	10.3
7	5	-2	5.8	-4.7
7	6	-2	6.4	6.0
8	-4	-2	16.6	-12.5
8	-3	-2	9.1	-6.6
0	-16	2	5.1	-3.1
0	-15	2	8.2	-4.6
0	-14	2	9.6	-6.6
0	-13	2	9.3	-6.9
0	-11	2	4.5	3.6
0	-10	2	31.0	20.7
0	-9	2	36.9	28.1
0	-8	2	34.0	27.9
0	-7	2	27.1	22.3
0	-6	2	7.4	-6.4
0	-5	2	2.9	-4.5
0	-4	2	30.8	-31.6
0	-3	2	28.9	-31.0
0	-2	2	45.4	-54.7
0	2	2	52.8	52.6
0	3	2	34.7	38.2
0	4	2	17.5	15.2
0	5	2	31.6	34.8
0	6	2	55.7	51.6
0	7	2	18.7	-16.7
0	8	2	22.8	-21.2
0	9	2	17.1	-17.9
0	10	2	12.9	-14.2
0	11	2	17.3	-16.4
0	12	2	10.0	-9.5
0	13	2	4.6	4.0
0	14	2	4.2	3.6
0	15	2	9.0	8.0
1	0	2	24.6	29.1
1	1	2	44.2	39.2
1	2	2	9.6	12.0
1	3	2	9.7	-6.0
1	6	2	14.5	-19.0
1	7	2	25.0	-21.5
1	8	2	19.1	-15.5
1	10	2	13.5	12.2
1	11	2	25.7	24.7
1	12	2	13.0	14.9
1	13	2	9.5	8.9
2	0	2	9.1	-11.6
2	1	2	32.5	-27.5
2	2	2	57.3	-45.2
2	4	2	12.9	-16.9
2	5	2	25.9	25.0
2	6	2	31.0	25.8
2	7	2	18.2	18.3
2	8	2	11.9	12.8
2	9	2	14.1	16.0
2	10	2	8.3	-9.2
2	13	2	9.0	-2.8
3	0	2	11.7	12.5
3	1	2	28.7	25.5
3	2	2	34.1	33.5
3	4	2	25.0	20.8
3	5	2	13.0	12.9
3	6	2	19.8	20.7
3	7	2	4.4	4.4
3	8	2	3.4	-4.4
3	11	2	18.8	-20.3
4	0	2	39.7	37.1
4	1	2	17.8	17.0
4	2	2	7.2	7.2
4	3	2	17.1	17.9
4	5	2	29.6	-29.0
4	6	2	27.5	-29.3
4	7	2	7.8	6.6
4	8	2	8.1	-7.6
5	0	2	6.9	-6.1
5	2	2	21.2	-21.2
5	3	2	13.4	-12.3
5	4	2	6.2	-6.8
5	5	2	9.0	-8.9
5	6	2	14.6	-16.4
5	7	2	11.7	13.7
5	9	2	9.4	11.8
6	0	2	8.0	7.6
6	4	2	19.0	17.8
1	-1	2	41.7	43.1
1	-2	2	20.0	19.2
1	-3	2	17.9	18.8
1	-4	2	17.7	-24.2
1	-5	2	11.0	-16.3
1	-6	2	28.1	-40.8
1	-7	2	27.5	-36.1
2	-2	2	18.4	-16.5
2	-3	2	27.1	31.5
2	-4	2	41.6	44.6
2	-5	2	6.6	8.7
2	-8	2	6.4	8.7
2	-9	2	19.2	23.4
2	-10	2	8.0	-10.0
2	-11	2	15.2	-15.2
3	-1	2	11.5	-15.2
3	-2	2	41.9	-47.4
3	-3	2	17.9	-18.7
3	-4	2	20.8	-24.8
3	-5	2	10.2	-11.7
3	-6	2	12.6	15.0
3	-7	2	16.4	16.4
3	-10	2	7.0	7.4
4	-2	2	16.9	15.0
4	-4	2	6.0	-3.8
4	-5	2	9.7	-10.4
4	-6	2	14.5	-14.6
4	-8	2	8.8	8.2
5	-2	2	6.1	5.8
5	-4	2	10.8	9.3
5	-5	2	8.7	10.7
5	-8	2	15.9	17.2
5	-9	2	9.7	-10.8
5	-10	2	14.1	-18.3
5	-11	2	7.2	-7.3
6	-1	2	9.8	-9.6
6	-2	2	5.5	-4.2
6	-3	2	7.6	-5.7
6	-4	2	12.2	-13.1
6	-6	2	7.8	8.9
6	-7	2	8.9	8.5
7	-1	2	10.5	10.5
7	-3	2	6.6	-7.8
2	3	2	18.0	-15.2
2	9	2	12.6	-14.8
5	1	2	15.9	-14.6
0	-2	2	18.1	28.1
1	-8	2	8.1	-10.1
3	-8	2	32.9	40.3
3	-9	2	21.7	25.0
4	-1	2	9.4	8.0
4	6	3	6.4	6.0
4	7	3	12.8	11.9
5	1	3	13.4	11.5
5	-2	3	16.2	-15.7
1	0	3	15.7	-17.7
1	1	3	51.5	-47.4
1	2	3	51.8	-46.3
1	3	3	16.0	-14.4
1	5	3	8.2	-5.9
1	6	3	23.7	22.0
1	7	3	19.2	16.9
1	8	3	27.3	23.9
1	9	3	20.5	19.3
1	12	3	6.7	-7.9
1	13	3	24.4	20.3
2	0	3	13.5	12.2
1	14	3	7.1	-11.0
2	2	3	10.2	-10.4
2	3	3	26.2	22.9
2	4	3	30.4	29.7
2	5	3	26.6	24.5
2	6	3	8.5	-3.6
2	7	3	12.7	-13.0
2	8	3	6.1	-6.9
2	10	3	12.5	-11.6
3	0	3	14.5	-17.2
3	12	3	9.2	-10.8
3	0	3	40.3	42.2
3	1	3	21.9	21.8
3	4	3	10.5	-12.9
3	6	3	19.0	-18.9
3	7	3	21.1	-18.3
3	8	3	20.8	-17.9
3	9	3	7.1	-10.1
3	10	3	5.8	-2.2
3	12	3	9.2	11.4
4	0	3	7.1	9.3
4	1	3	5.8	4.2
4	2	3	10.6	-8.1
4	3	3	17.3	-17.7
4	4	3	14.3	-16.0
4	5	3	5.3	-3.1
4	8	3	11.7	9.8
4	9	3	7.4	6.6
4	10	3	5.7	5.4
5	3	3	11.4	13.4
5	4	3	11.5	11.4
5	7	3	5.8	2.9
6	1	3	6.6	-5.7
6	3	3	12.9	10.7
6	4	3	13.0	14.9
1	-1	3	9.2	-9.2
1	-2	3	4.8	4.9
1	-3	3	10.7	-13.4
1	-4	3	10.7	15.9
1	-5	3	23.2	33.2
1	-6	3	26.1	35.0
1	-7	3	5.6	6.5
1	-8	3	13.9	19.8
1	-9	3	7.3	-10.3
1	-10	3	5.6	-6.7
2	-1	3	16.5	-18.3
2	-2	3	27.8	-33.8
2	-3	3	7.9	-10.9
2	-4	3	10.5	-11.9
2	-5	3	7.9	-10.8
2	-6	3	4.3	5.2
2	-7	3	10.3	16.1
2	-8	3	4.4	8.6
2	-9	3	4.7	3.9
2	-10	3	10.0	13.2
3	-1	3	29.5	29.0
3	-2	3	13.1	12.1
3	-4	3	4.5	-3.8
3	-5	3	5.1	-6.7
3	-6	3	8.5	-10.7
3	-7	3	12.6	-15.4
3	-8	3	7.4	-8.0
3	-9	3	4.9	-2.4
3	-10	3	6.6	7.8
4	-1	3	9.0	-8.4
4	-2	3	8.4	4.9
4	-3	3	8.0	8.7
4	-4	3	8.4	8.4
4	-5	3	13.1	14.1
4	-6	3	10.6	11.1

Table 15 Ctd.

H	K	L	|Fo|	Fc
5	-1	3	22.0	-25.6
5	-4	3	11.5	-9.5
5	-5	3	5.2	-4.6
5	-7	3	5.4	6.7
6	-1	3	5.7	7.8
6	-2	3	11.3	8.0
6	-4	3	8.9	-8.5
6	-7	3	9.0	-9.7
7	-3	3	9.2	7.3
7	-4	3	9.2	7.9
1	-13	-3	4.5	4.3
1	-12	-3	5.0	2.4
1	-11	-3	3.8	-4.2
1	-10	-3	17.6	-21.4
1	-9	-3	22.5	-19.4
1	-8	-3	26.4	-22.0
1	-7	-3	14.4	-12.2
1	-5	-3	10.8	11.4
1	-4	-3	28.3	26.3
1	-3	-3	28.1	27.7
1	-2	-3	34.7	37.0
1	-1	-3	9.2	11.2
1	1	-3	30.6	-36.3
1	2	-3	16.4	-25.3
1	3	-3	36.2	-39.3
1	4	-3	12.7	-14.4
1	5	-3	21.5	-13.5
1	6	-3	17.6	-11.5
1	7	-3	13.6	8.5
1	8	-3	25.1	17.1
1	9	-3	15.9	11.0
1	10	-3	7.1	3.5
1	11	-3	12.7	7.7
1	12	-3	7.7	5.8
1	13	-3	6.2	-4.8
1	15	-3	7.8	-5.6
2	-14	-3	6.2	-8.5
2	-8	-3	12.5	16.8
2	-7	-3	28.1	27.4
2	-6	-3	20.9	23.1
2	-5	-3	30.6	26.7
2	-4	-3	6.9	-6.8
2	-3	-3	18.5	-18.2
2	-2	-3	6.0	-8.3
2	0	-3	27.5	-32.2
2	1	-3	35.3	-38.0
2	2	-3	8.6	8.2
2	3	-3	13.9	15.9
2	4	-3	11.9	11.1
2	5	-3	18.2	20.6
2	6	-3	15.6	13.7
2	7	-3	14.9	16.2
2	9	-3	5.6	5.1
2	10	-3	17.7	-17.1
2	11	-3	3.8	2.4
2	12	-3	6.2	-2.4
2	13	-3	6.3	-4.5
3	-12	-3	7.1	11.7
3	-11	-3	15.7	23.6
3	-10	-3	12.8	17.1
3	-7	-3	5.8	4.6
3	-6	-3	11.7	-15.6
3	-5	-3	23.7	-25.9
3	-4	-3	20.1	-21.7
3	-1	-3	22.8	25.5
3	0	-3	22.8	23.3
3	1	-3	15.4	12.0
3	2	-3	7.0	7.6
3	3	-3	13.9	11.0
3	4	-3	11.0	9.5
3	5	-3	5.5	-2.1
3	6	-3	5.1	-3.4
3	7	-3	13.0	-10.0
3	8	-3	7.2	-4.7
3	10	-3	9.7	-9.5
3	11	-3	5.6	5.0
3	13	-3	4.5	1.5
3	14	-3	4.7	2.8
3	15	-3	4.0	3.1
4	-13	-3	4.5	-6.2
4	-10	-3	3.8	-7.0
4	-9	-3	9.4	-16.4
4	-8	-3	10.2	-16.1
4	-7	-3	7.0	-9.7
4	-4	-3	8.8	9.4
4	-3	-3	10.8	14.9
4	-2	-3	6.7	7.9
4	-1	-3	16.0	16.6
4	0	-3	6.7	9.0
4	1	-3	12.9	-12.9
4	2	-3	22.6	-20.6
4	3	-3	24.7	-22.8
4	4	-3	14.2	-14.3
4	5	-3	14.7	-17.0
4	6	-3	9.0	11.5
4	7	-3	8.3	-8.9
4	8	-3	4.9	3.0
4	9	-3	8.8	9.2
4	10	-3	7.9	5.6
4	11	-3	4.5	1.5
5	-13	-3	4.9	-10.1
5	-12	-3	4.5	-6.7
5	-11	-3	4.0	-3.3
5	-8	-3	4.8	4.9
5	-7	-3	9.4	6.4
5	-4	-3	3.5	5.1
5	-2	-3	7.6	-9.2
5	-1	-3	6.8	-8.8
5	2	-3	13.5	-18.0
5	3	-3	6.5	-5.8
5	6	-3	11.0	10.5
5	11	-3	3.8	-1.0
6	-11	-3	5.0	7.4
6	-8	-3	3.9	5.0
6	-6	-3	5.5	-6.7
6	-5	-3	9.7	-11.0
6	-2	-3	7.6	-9.7
6	0	-3	20.5	21.3
6	1	-3	16.3	22.1
6	2	-3	6.1	-8.3
6	3	-3	4.4	4.7
7	-8	-3	4.5	-6.0
7	-7	-3	4.5	-5.4
7	-2	-3	7.1	8.1
7	0	-3	4.5	5.4
7	1	-3	8.9	11.4
7	3	-3	4.5	-5.3
8	-7	-3	3.7	1.2
8	-6	-3	4.1	-1.6
8	-1	-3	5.4	-5.7
0	-12	3	25.7	15.0
0	-11	3	8.1	7.3
0	-10	3	8.5	-4.6
0	-9	3	15.2	-11.8
0	-8	3	3.3	1.5
0	-7	3	11.5	-6.9
0	-6	3	37.7	-28.4
0	-5	3	7.6	-9.5
0	-4	3	7.9	5.7
0	-3	3	11.2	11.2
0	-2	3	13.0	18.1
0	1	3	15.7	16.0
0	2	3	6.1	6.1
0	3	3	35.3	-31.0
0	4	3	22.2	-20.3
0	5	3	35.6	-31.0
0	6	3	29.0	-22.9
0	7	3	45.2	-31.1
0	9	3	7.1	6.4
0	10	3	15.0	9.8
0	11	3	15.7	15.3
0	12	3	8.9	13.2
1	-9	4	10.6	11.1
1	-7	4	5.1	5.3
1	-6	4	4.2	2.8
1	-4	4	8.4	-11.0
1	-3	4	13.2	-20.0
1	-2	4	9.5	-8.9
1	-1	4	7.5	-7.7
1	1	4	18.6	16.0
1	2	4	20.9	17.2
1	3	4	23.3	27.0
1	4	4	25.6	26.0
1	5	4	8.8	11.5
1	8	4	6.6	-9.8
1	9	4	11.5	-19.5
1	10	4	6.3	-9.7
2	-10	4	10.2	2.1
2	-9	4	6.1	-5.7
2	-8	4	11.5	-11.3
2	-7	4	8.6	-6.6
2	-6	4	6.3	-5.1
2	-2	4	26.3	28.6
2	-1	4	13.3	12.6
2	0	4	6.2	8.8
2	1	4	9.2	11.0
2	2	4	14.0	11.9
2	3	4	5.9	-5.2
2	4	4	20.1	-20.0
2	5	4	9.5	-12.0
2	6	4	9.0	-10.9
2	7	4	9.4	-12.4
2	8	4	6.2	-5.3
2	10	4	7.0	9.0
2	11	4	6.6	8.6
2	12	4	5.2	9.1
3	-11	4	7.6	-5.7
3	-10	4	6.6	-3.2
3	-9	4	8.0	-6.6
3	-8	4	6.9	-3.5
3	-6	4	7.8	4.3
3	-5	4	8.5	7.1
3	-4	4	8.3	8.1
3	-3	4	7.3	8.1
3	-2	4	7.3	8.5
3	-1	4	4.1	-5.4
3	0	4	4.2	-11.0
3	1	4	17.5	-18.0
3	2	4	10.2	-12.5
3	3	4	7.5	-4.4
3	4	4	8.9	-7.2
3	6	4	6.1	5.0
3	7	4	10.9	14.5
3	8	4	7.0	7.9
4	-4	4	15.0	-10.3
4	-3	4	9.4	-8.2
4	-2	4	5.4	-3.8
4	-1	4	5.4	4.2
4	0	4	6.1	-4.3
4	2	4	11.4	13.1
4	3	4	13.1	14.8
4	4	4	8.5	11.0
4	5	4	6.9	7.0
5	-4	4	10.5	-10.8
5	-2	4	9.4	8.0
5	-1	4	8.4	6.1
5	0	4	8.4	3.3
5	1	4	6.1	5.3
5	2	4	9.4	9.6
6	-5	4	7.0	5.8
6	-4	4	7.0	4.1
6	0	4	6.1	-1.1
6	1	4	11.0	-11.0
6	2	4	7.0	-8.0
0	1	4	21.9	-13.9
0	2	4	27.8	-24.7
0	3	4	10.2	-10.5
0	5	4	10.0	7.7
0	6	4	15.5	14.0
0	7	4	8.3	7.5
0	8	4	4.5	4.9
0	9	4	8.2	7.1
0	10	4	5.3	4.1
0	11	4	4.9	-5.9
0	-2	4	4.3	-6.9
0	-3	4	2.8	2.7
0	-4	4	17.5	17.3
0	-5	4	18.0	13.7
0	-6	4	11.5	9.0
0	-7	4	14.1	12.0
0	-8	4	4.9	1.6
0	-9	4	11.7	-10.0
0	-10	4	7.8	-5.4
0	-12	4	9.4	8.1
0	-13	4	9.0	-6.6
0	-14	4	5.3	4.8
1	1	-4	8.2	15.9
1	2	-4	10.5	15.6
1	3	-4	5.4	-5.5
1	5	-4	7.0	8.3
1	6	-4	4.9	-3.6
1	7	-4	18.9	-18.9
1	8	-4	12.8	-7.7
1	9	-4	4.4	-1.4
1	10	-4	11.4	-9.6
2	2	-4	6.4	-9.0
2	3	-4	10.9	-11.9
2	4	-4	13.1	-15.6
2	5	-4	3.2	-3.2
2	6	-4	6.1	8.2
2	7	-4	5.1	5.5
2	8	-4	4.9	6.1
2	9	-4	6.4	6.5
2	11	-4	7.6	7.5
3	1	-4	12.2	-13.7
3	2	-4	3.1	-3.1
3	3	-4	4.1	5.3
3	4	-4	6.4	5.3
3	6	-4	18.9	22.2
3	7	-4	8.8	7.6
3	13	-4	9.0	-4.0
4	1	-4	4.5	6.1
4	2	-4	8.1	8.7
4	4	-4	7.7	-7.9
4	5	-4	7.9	-10.3
4	6	-4	6.4	8.3
4	7	-4	5.9	-6.0
5	2	-4	6.4	-7.1
5	4	-4	16.7	-15.7
5	5	-4	15.0	-15.5
6	2	-4	4.9	-5.3
6	3	-4	6.0	6.7
6	7	-4	5.2	4.6
7	3	-4	4.1	4.6
7	5	-4	3.9	-3.2
1	0	-4	9.6	14.0
1	-1	-4	7.7	9.2
1	-2	-4	10.0	-11.0
1	-3	-4	18.0	-19.1
1	-4	-4	14.3	-16.5
1	-5	-4	28.0	-22.2
1	-6	-4	30.4	-24.3
1	-7	-4	25.9	-21.7
1	-8	-4	11.0	-7.6
1	-9	-4	14.4	13.0
1	-10	-4	16.8	12.5
1	-11	-4	10.7	10.1
1	-12	-4	4.9	5.6
2	0	-4	4.8	6.6
2	-1	-4	15.6	20.2
2	-2	-4	10.4	11.7
2	-3	-4	14.1	18.7
2	-4	-4	13.5	16.0
2	-5	-4	7.3	8.5
2	-7	-4	21.0	-16.4
2	-8	-4	19.6	-16.2
2	-11	-4	4.3	-5.0
2	-13	-4	4.7	-7.6
3	0	-4	10.7	-10.1
3	-1	-4	3.0	-3.4
3	-2	-4	19.6	-14.3
3	-4	-4	8.4	9.8
3	-5	-4	17.6	14.9
3	-6	-4	16.5	10.6
3	-7	-4	5.5	6.1
3	-8	-4	14.2	14.9
3	-9	-4	16.6	16.4
3	-11	-4	5.4	-7.0
3	-12	-4	4.2	-3.4
3	-13	-4	5.2	-5.9
4	-3	-4	6.5	-9.0
4	-4	-4	9.3	-13.0
4	-5	-4	10.8	-15.2
4	-7	-4	6.4	-8.7
4	-9	-4	8.5	10.4
4	-10	-4	5.4	7.2
5	-1	-4	4.5	6.2
5	-2	-4	10.0	8.3
5	-3	-4	5.7	5.4
5	-8	-4	6.7	-6.8
6	-8	-4	4.2	-4.1
6	0	-4	4.2	-4.0
7	-1	-4	6.0	5.9
7	-6	-4	5.3	-6.1
1	1	-5	6.6	-5.9
1	2	-5	7.5	-7.7
1	4	-5	6.0	6.0
1	5	-5	7.1	7.8
1	8	-5	9.6	8.2
1	11	-5	4.0	-4.0
2	1	-5	6.7	7.2
2	2	-5	8.7	8.2
2	3	-5	9.0	9.4
2	7	-5	6.8	-6.4
2	10	-5	8.0	-4.6
3	2	-5	7.8	-6.1
3	8	-5	8.0	5.5
3	9	-5	9.0	7.4
4	2	-5	9.7	-8.1
1	-1	-5	17.5	-17.7
1	-2	-5	13.1	-11.1
1	-3	-5	4.4	5.3
1	-4	-5	8.5	6.3
1	-5	-5	20.1	-14.1
1	-6	-5	9.5	8.1
1	-7	-5	13.8	12.4
2	0	-5	5.3	4.8
2	-1	-5	4.3	2.5
2	-5	-5	20.5	-21.4
2	-10	-5	9.0	6.4
2	-11	-5	5.5	6.6
3	0	-5	7.6	8.0
3	-1	-5	7.7	8.4
3	-2	-5	9.9	12.8
3	-3	-5	11.3	11.7
3	-8	-5	7.2	-8.9
4	-1	-5	8.4	-8.4
5	-4	-5	10.2	-11.0
5	-3	-5	7.1	-9.2
0	-6	5	4.7	6.1
0	-5	5	11.4	-16.6
0	1	5	11.0	20.0
0	2	5	9.4	11.8
0	4	5	14.3	17.3
0	5	5	13.7	13.7
0	6	5	8.5	-6.9
0	7	5	7.1	-6.9
0	8	5	8.1	-7.4
0	9	5	10.3	-12.4
1	-7	5	7.0	-12.8
1	-2	5	6.1	12.3
1	-1	5	6.9	17.0
1	1	5	9.5	11.5
1	3	5	6.8	5.7
1	4	5	6.4	-4.5
1	5	5	9.5	-10.6
1	6	5	11.1	-12.2
2	-7	5	6.5	2.6
2	-6	5	7.0	3.7
2	-4	5	7.5	7.9
2	-3	5	5.2	8.8
2	-1	5	5.1	-6.2
2	0	5	5.2	-7.6
2	1	5	10.3	-12.4
2	2	5	9.6	-11.9
2	5	5	7.1	-6.9
2	6	5	7.2	7.8
2	7	5	7.3	9.5
2	8	5	10.3	7.7
2	9	5	7.9	2.3
3	-2	5	11.3	-10.6
3	-1	5	5.7	-5.9
3	1	5	9.1	-10.8
3	2	5	5.3	2.4
3	3	5	6.3	6.6
3	4	5	6.3	5.3
3	5	5	8.0	8.3
4	5	5	9.1	9.8
4	-1	5	8.8	2.7
4	0	5	7.9	6.9
4	6	5	7.9	-5.8

SECTION II

A Comparative Study of

1,1'-Binaphthyl and the

β-Form of Perylene

INTRODUCTION

Coulson has pointed out that a bond in a conjugated system may be regarded as a superposition of a σ- bond and a fractional π- bond. For a particular type of hybridization, the length of a bond can be expected to vary with change in π- bond order. Various empirical relationships have been suggested to correlate bond length with bond order. Since most of the accurate structure determinations have involved bonds of intermediate π- bond order, agreement between theory and experiment is very good in this region but becomes less reliable for extreme bond orders.

Binaphthyl, I, and perylene, II, are examples of molecules that contain bonds of very low π- bond order. Both of these molecules can be regarded as composed of two naphthalene residues connected by long bonds.

I   II
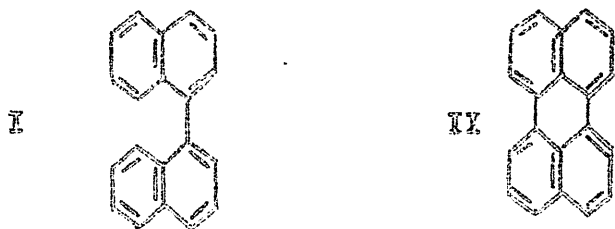
There are nine unexcited Kekulé structures for each molecule, representing the various combinations of three Kekulé structures of each naphthalene nucleus. None of these structures attributes double bond character to the linking bonds. Thus simple valence bond theory predicts that the long bonds are pure sp_2-sp_2 single bonds with no π bond character. Molecular orbital theory predicts

that the π bond order will be low, but it cannot be zero
since this theory assumes that there is always some interaction
between π bonds on adjacent atoms.

A study of these two compounds provides a fairly stringent
test of the hypothesis that the aromatic character of the
perylene molecule is localised in the naphthalene residues.
Perylene is planar but binaphthyl is not. The angle
between the planes, of the naphthalenic residues is about
66°, sufficiently large to preclude any π - bonding interaction
between the two ring systems. If there are significant
differences between the dimensions of the two molecules,
this could be interpreted as evidence for interaction
between the naphthalenic residues in perylene.

THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1'-BINAPHTHYL

The crystal structure of 1,1'-binaphthyl (m.p. 148°C) was first established from projection data by Brown, Trotter and Robertson (1961). They have reported that the molecular configuration is cis with an angle of about 73° between the planes of the two ring systems, and have suggested that the variety of melting points reported in the literature corresponds to different crystalline forms. Brown has refined the structure in two projections by differential synthesis but his results have not been published.

Badar, Chua, Cook and Harris (1968) have shown that the compound has at least two distinct crystalline forms. The higher melting form (m.p. 157-159°C) was prepared by deamination of (+)-4,4'-naphthidine and is optically active. When melted and resolidified it is converted into the low melting form (m.p. 145°C). Infra-red spectra of the two forms are identical in carbon disulphide, in carbon tetrachloride and in cyclohexane, but there is an extra peak in the solid state spectrum of the low melting form. The authors attribute this to C-H out-of-plane vibrations caused by H...H and C...H interactions inherent in the cis configuration. They suggest that the higher melting form corresponds to the trans configuration of the molecule.

1.1. EXPERIMENTAL

Dr. Harris kindly provided samples of two crystalline modifications of 1,1'-binaphthyl. The high-melting form

does not show extinction when examined under a polarizing
microscope.   When a "single" crystal is photographed by
the usual rotation method the result is a rather "spotty"
powder diagram, typical of coarse, randomly-oriented
crystallites.   Recrystallisation from light petroleum
did not improve the crystals.

The low-melting form crystallises as colourless
plates that show sharp extinction and can be cut without
apparent deformation.   Weissenberg and precession photographs
of one of these crystals mounted about its unique axis were used
to check cell dimensions and space group.   Cell dimensions
were further confirmed by measuring reciprocal lattice
spacings of high angle reflections on the linear diffractometer.

1.1.1. CRYSTAL DATA

Formula $C_{20}H_{14}$ F.W. 254.3

System   monoclinic
Lattice constants $a = 20.97_8$ Å
                        $b = 6.35_1$ Å
                        $c = 10.12_8$ Å
                        $\beta = 105.17°$
Absent Spectra hkl if $h+k$ odd
                        $h0l$ if l odd
                        $0k0$ if k odd
Space group   Cc or C2/c
Volume 1302.3 Å^3

Density(obs.)	1·299 gm./cc
Molecules/cell	4
Density(calc.)	1·297 gm./cc

Linear absorbtion coefficient, $\mu = 0.86$ cm^{-1}

(Mo Kα, λ = 0·7107 Å)

1.1.2. REFLECTION DATA

Reflection data from eight reciprocal lattice nets,
h0ℓ to h7ℓ, were collected with Mo Kα radiation on a
Hilger-Watts linear diffractometer of the type described
by Arndt and Phillips (1961).   Peak height and background
were measured at least twice for each reflection.   Planes
with intensities smaller than ten counts per minute were
considered unobserved and were not included in the refinement.
Lorentz-polarization corrections were applied to the
observed data by computer program using the formula appropriate
to equi-inclination Weissenberg geometry.

1.1.3.   THE HILGER-WATTS DIFFRACTOMETER

The diffractometer is of the moving-crystal-stationary-
counter type and can be described as a mechanical model of
the reciprocal lattice.   Its main components are three
slides driven by a system of tapes, pulleys and gears.
The motions of the crystal and the slides are coupled in
such a way that any plane, hkℓ, can be brought into the
reflecting position by setting the coordinates of the
corresponding reciprocal-lattice point, ha*, kb*, ℓc*, on

on the three slides.   The oscillation motor then rotates

the crystal through a small arc.   During each oscillation,

three counts are recorded.   The first and third are

background counts (time, t) recorded at the two extremes

of the oscillation.   The middle count (time, 2t) is

recorded while the crystal oscillates through a small, pre-set

arc.   A minimum of two oscillations, one with each of the

$SrO-ZrO_2$ balanced filters, is required to measure peak and

background for a single reflection.   This type of counting

mechanism should produce similar standard deviations for

most measurements.   However, spring and backlash in the

mechanisms cause setting errors that increase with decrease

in the cylindrical coordinate, ζ.   This has two consequences:

in terms of operation of the diffractometer, it means that

reflections from planes with low sin θ values must be

measured by hand; in terms of quality of the data, it implies

that absolute errors in the intensity data will show some

systematic dependence on sin θ.

1.2. REFINEMENT OF THE STRUCTURE

Brown's (1961, unpublished) coordinates from

differential synthesis refinement of two projections were

used as starting point for the three-dimensional refinement

of 1,1'-binaphthyl.   The initial R-value was 36.2%, but

this was reduced to 18.7% by three cycles of isotropic full-

matrix least squares refinement with Cruickshank's (1961)

weighting scheme;

$$\sqrt{w} = (1/p_1 + F_o + p_2 F^2 + p_3 F^3)^{\frac{1}{2}}.$$

The values of the parameters were:

$$p_1 = 4 \cdot 20, \quad p_2 = 0 \cdot 011, \quad p_3 = 0.$$

One further isotropic refinement cycle improved R to 14·6%.

The coordinates of the seven hydrogen atoms were calculated by hand. When these were included in the structure-factor calculation, the R-value was 15·8%. One further refinement cycle reduced R to 14·6%. At this point, the parameters of the weighting scheme were changed slightly;

$$p_1 = 2 \cdot 56, \quad p_2 = 0 \cdot 011, \quad p_3 = 0.$$

The refinement continued with isotropic temperature factors for hydrogen atoms and anisotropic temperature factors for carbon atoms. Because of the size of the matrix involved, the block-diagonal approximation was used. After five cycles, the refinement seemed to be near convergence: the R-value had fallen to 9·37%; indicated parameter shifts for carbon atoms were between 1/5 and 1/10 of the corresponding estimated standard deviations; and the weighting analysis showed that the average value of $\overline{w\Delta^2}$ was reasonably constant when analysed as a function of either $\sin \theta/\lambda$ or $|F_{obs}|$. However, some of the hydrogen atoms showed unlikely temperature factors and had moved to unacceptable locations.

Stewart, Davidson and Simpson (1965) have pointed out
that if hydrogen atom form factors calculated from a
simple 1s wave function are used in least-squares refinement,
isotropic temperature factors will be abnormally low and
the C-H bond distances will be short. **The scattering
factors used in the present calculations are those tabulated
by Hanson, Herman, Lea and Skillman (1964).** Another
possible source of difficulty in the refinement of the
hydrogen parameters is the choice of weighting scheme.
Cruickshank's (1961) weighting scheme was designed for
film data and is probably not applicable in this case. The
particular parameters used tend to give high relative weights
to planes with small intensities.

The positions of the hydrogen atoms were recalculated
by a computer program. Each atom was placed $1 \cdot 10$ Å along
the external bisector of the angle subtended at the
corresponding carbon atom. Further refinement was attempted
using these calculated positions with a scattering curve
appropriate to bonded hydrogen (Stewart et al., 1965) and
a new weighting scheme of the form,

$$\sqrt{w} = [1 - \exp(2\sin^2\theta / \lambda^2)]^{\frac{1}{2}}$$

The anisotropic refinement of carbon parameters converged
in two cycles to an R-value of $9 \cdot 36\%$, but the weighting
analysis was not satisfactory. A more successful
weighting scheme was devised after examination of the

unweighted structure factors as a function of the magnitude
of F_{obs}, the magnitude of $\sin \theta/\lambda$ and the index of the
reciprocal lattice net, as shown in Table 1. The
R-value is high for reflections with small values of $|F_{obs}|$.
The increase in R with increase in layer index is caused
by the large number of weak reflections observed at high
angles. The absolute error in the structure factors is
constant for most categories of reflections, but increases
for large values of $|F_{obs}|$ and for low values of $\sin \theta/\lambda$.
The weighting scheme adopted after this examination of the
data gives unit weights to most reflections, but

if $\sin^2 \theta / \lambda^2 < 0.16$ then $w = (\sin^2 \theta / \lambda^2)/0.16$;

if $|F_{obs}| > 20$ then $w = 20/|F_{obs}|$.

Reflections with $|F_{calc}| < 1/3 |F_{obs}|$ were considered to be
unreliably phased and were given a weight of zero. This
effectively removes 45 of the 1315 reflections from the
refinement. The value of $\Sigma w\Delta^2$ was 1543.86.

After two full-matrix calculations involving only
the parameters of the carbon atoms, R was 9.30%. Positions
and isotropic temperature factors of hydrogen atoms were
allowed to refine for four block-diagonal cycles. Refinement
was terminated at this point with R = 8.50% and $\Sigma w\Delta^2$ = 1007.60.
Indicated shifts of carbon parameters were less than 1/10
of the corresponding estimated standard deviations; shifts
of hydrogen parameters were between 1/3 and 1/5 of their
e.s.d.

TABLE

1,1'-Binaphthyl: Analysis of Observed and Calculated Structure Amplitudes

A. As function of $|F_{obs}|$

F_o	$\Sigma|F_o|$	$\Sigma|F_c|$	$\Sigma|\Delta|$	N	R	
2	33·10	37·9	11·03	20	0·333	0·5?
4	1194·63	1007·5	377·65	381	0·316	0·99
6	1150·58	1095·6	194·83	235	0·169	0·8?
8	1278·04	1255·3	136·21	183	0·107	0·7?
10	933·00	905·8	73·73	105	0·079	0·70
12	694·00	699·63	53·15	64	0·077	0·??
14	826·93	836·40	66·63	64	0·080	1·??
17	1004·84	956·69	54·95	65	0·05?	0·??
24	1487·98	1493·25	81·81	74	0·05?	?·??
33	1859·24	1800·14	102·14	66	0·055	?·??
67	2193·30	2162·35	78·63	50	0·036	1·5?
110	648·36	666·89	23·71	8	0·037	2·??

As function of $\sin\theta/\lambda$

·20	845·15	819·40	50·72	27	0·060	?·??
·30	2190·96	2149·28	125·62	93	0·05?	?·??
·40	2399·49	2270·33	204·60	184	0·08?	?·??
·45	1705·99	1706·12	109·37	119	0·064	0·??
·50	1476·63	1520·34	131·63	140	0·08?	?·??
·55	1241·24	1257·40	105·52	151	0·085	0·7?
·60	1196·40	1157·24	144·68	184	0·12?	0·7?
·65	1061·34	1024·54	137·36	181	0·129	0·7?
·70	646·91	581·60	109·93	114	0·16?	0·??
·75	342·37	293·47	67·06	68	0·195	0·??
·80	146·09	98·13	53·70	34	0·368	1·??
1·00	41·87	29·47	15·36	11	0·367	1·??

As function of reciprocal lattice index

0	1642·53	1636·29	116·78	94	0·071	?·??
1	2897·20	2816·72	222·64	213	0·077	1·??
2	2693·17	2632·49	201·38	209	0·073	0·??
3	1792·01	1741·73	155·26	167	0·087	0·8?
4	1674·48	1642·12	152·26	180	0·091	0·??
5	1142·88	1106·89	137·57	157	0·120	0·4?
6	814·94	778·61	125·27	146	0·154	0·??
7	677·23	593·92	146·65	149	0·221	0·??

1.3. MOLECULAR DIMENSIONS AND DESCRIPTION OF THE STRUCTURE

Final atomic coordinates and temperature parameters
are listed in Tables 2 and 3, respectively, with standard
deviations given as units in the last place. Bond lengths
and angles and their standard deviations are shown in
Figure 1 and in Tables 4 and 5.

The molecular structure of 1,1'-binaphthyl viewed
in projection along the c axis is shown in Figure 2.
The planar naphthalene residues are linked by a bond across
the diad axis, b. The length of this bond $(1.475\pm0.005\ \text{Å})$
is very close to the value of $1.479\ \text{Å}$ predicted by Dewar
and Schmeising (1959) and to the value of $1.477\ \text{Å}$ predicted
by Pauling's method with a new order-length curve
(Cruickshank and Sparks, 1960).

The equation of the best plane through the naphthalene
nucleus is

$$0.0512X + 0.5596Y - 0.8272Z = -1.6754$$

where X, Y and Z are orthogonal axes defined in the
following formulae:

$$X = ax + cz\cos\beta;$$

$$Y = by;$$

$$Z = cz\sin\beta;$$

Deviations from this plane are shown in Table 8. A χ^2
test with 7 degrees of freedom has a significance level
of 0.10, indicating that the naphthalene ring systems

are essentially planar.   If a mean plane is calculated
through either of the benzene rings of the naphthalene
system, three of the carbon atoms in the other ring show
very large deviations from that plane.   This does not
imply that the naphthalene system is buckled; it just
shows that the "best" planes through the individual rings
are slightly different from the best plane through the
whole system.

In Tables 6 and 7, some of the more important intra
and inter-molecular contacts are shown.   Primed numbers
refer to atoms whose positions are generated by the symmetry
operation of the diad axis.   It seems likely that the
most important intra-molecular forces are carbon-carbon
repulsions between $C(2)\ldots C(2)'$, $C(8)\ldots C(8)'$, and $C(8)\ldots C(9)'$
whereas, the most important inter-molecular forces arise
from the very large number of $C\ldots H$ interactions.   Each
naphthalene residue has 32 non-bonded $C\ldots H$ contacts shorter
than 3·50 $\overset{\circ}{A}$.   The compromise between inter- and intra
molecular forces produces an angle of 68° between the planes
of the two ring systems.

Badar et al.(1965) have interpreted the solid state
(nujol mull) infra-red spectrum of the low melting form
of 1,1'-binaphthyl in terms of a short non-bonded contact
between $H(17)$ and $C(8')$.   Present calculations show that
$H(17)$ has two short intra-molecular contacts, and four
inter-molecular contacts with the portion of the molecule

at $-x, -y, -z$ in cell $(0,1,1)$:

H(17)...C(9)'	2·813 Å	H(17)...C(8)	2·991 Å
...C(8)'	2·991	...C(7)	3·057
		...H(17)	2·464
		...H(16)	2·555

The extra peak in the spectrum of the low melting form
may be caused by C...H interactions but both inter- and
intra-molecular contacts are involved.   This would seem
to cast some doubt on the argument that the high melting
form must have a _trans_- configuration since it lacks this
peak in its spectrum.   The authors have reported that
the high melting form is optically-active.   This implies
that it cannot crystallise in a centrosymmetric space
group.   Any crystal modification that reduced the number
of C...H contacts would probably reduce inter-molecular
repulsion forces.   If this allowed the angle between
the planes to expand, it would decrease the intra-molecular
interactions involving H(17).   It is not necessary to
postulate a change in molecular configuration to explain
the differences in the two spectra.   However, the point
will remain "not proven" until suitable crystals of the
high melting polymorph become available for X-Ray analysis.

1.4.   COMPARISON OF THEORY AND EXPERIMENT

Cruickshank and Sparks (1960) have shown that
Pauling valence bond theory and Huckel molecular orbital
theory give very good agreement with experiment for

naphthalene, anthracene and various alternant hydrocarbons.
They have recommended that a correlation of the form,

$$r = 1 \cdot 477 - (1 \cdot 477 - 1 \cdot 337) \frac{1 \cdot 333p}{0 \cdot 333p + 1} ,$$

be used for valence-bond calculations, and have suggested
that a linear variation between m=0·40 at r = 1·46 and
m = 0·85 at r = 1·34 would improve the performance of
simple molecular orbital theory.   In these relationships,
r is the bond length, p is the π-bond order calculated by
the Pauling superposition method and m is the π-bond order
calculated by the molecular orbital method.   Trotter
(1964) has recently used these order-length correlations
to compare theoretical predictions with experimental results
for a large number of aromatic molecules.

Table 9 shows π-bond orders for the various bonds
in the asymmetric unit of 1,1'-binaphthyl.   The numbering
used corresponds to the normal convention for naphthalene.
The H.M.O. bond orders quoted here have been taken from
Coulson and Streitwieser (1965)

Valence bond theory predicts that the bond-lengths
in the naphthalene nuclei of 1,1'-binaphthyl will be
the same as those in naphthalene itself.   For this reason,
it is interesting to compare the lengths obtained in the
present study with the values obtained by Cruickshank and
Sparks for naphthalene and with those predicted by the two

theories.   These lengths are compared in Table 10,
and the root mean square differences are shown at the
foot of each column.

A χ^2 test with 10 degrees of freedom shows that the
dimensions of the napthalenic residue are not significantly
different from those of naphthalene.   However, the
differences between observed and theoretical values are
highly significant.   In both cases, agreement is worse
for the short bonds than it is for the long ones and the
major source of disagreement is the very short $C(5)-C(6)$
bond.   It is likely that the discrepancies will be
reduced when the experimental values are corrected for
vibrational oscillation.   Some of the bonds that show
worst agreement are the ones likely to be most affected
by this correction.

Table 2

1,1'-Binaphthyl: Final Fractional Atomic Coordinates.
Standard deviations are given as units in the last place

	x	y	z
C(1)	0.03550(10)	0.1057(44)	0.25298(25)
C(2)	0.06095(12)	-0.05065(44)	0.18985(29)
C(3)	0.12841(14)	-0.06107(48)	0.19519(31)
C(4)	0.17047(12)	0.08794(48)	0.25514(29)
C(5)	0.18919(11)	0.41283(47)	0.10531(29)
C(6)	0.16698(13)	0.56895(47)	0.47141(30)
C(7)	0.09985(13)	0.57849(44)	0.46830(29)
C(8)	0.05754(10)	0.43030(40)	0.39799(26)
C(9)	0.07905(10)	0.26431(38)	0.34733(23)
C(10)	0.04702(10)	0.25500(41)	0.33171(24)

Final coordinates and isotropic temperature parameters
for the hydrogen atoms.

	x	y	z	B
H(11)	0.0301(15)	-0.1522(49)	0.1337(30)	0.0385
H(12)	0.1443(17)	-0.1673(55)	0.1494(35)	0.0517
H(13)	0.2179(18)	0.0827(58)	0.2679(36)	0.0579
H(14)	0.2320(18)	0.4007(60)	0.4043(37)	0.0590
H(15)	0.1965(17)	0.6831(55)	0.5195(36)	0.0534
H(16)	0.0827(16)	0.6920(53)	0.5167(33)	0.0485
H(17)	0.0152(16)	0.4322(57)	0.3985(34)	0.0516

Table 3

Anisotropic temperature parameters of the carbon atoms.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.0301	0.0360	0.0370	0.0071	0.0158	0.0051
C(2)	0.0379	0.0432	0.0501	-0.0071	0.0217	0.0114
C(3)	0.0435	0.0526	0.0542	-0.0078	0.0321	0.0325
C(4)	0.0262	0.0566	0.0492	0.0140	0.0149	0.0089
C(6)	0.0359	0.0501	0.0529	-0.0042	0.0185	0.0195
C(7)	0.0380	0.0461	0.0457	-0.0115	0.0186	0.0089
C(8)	0.0270	0.0435	0.0407	-0.0062	0.0241	0.0015
C(9)	0.0278	0.0395	0.0332	0.0093	0.0155	0.0090
C(10)	0.0280	0.0451	0.0370	0.0174	0.0182	0.0062

Figure 2
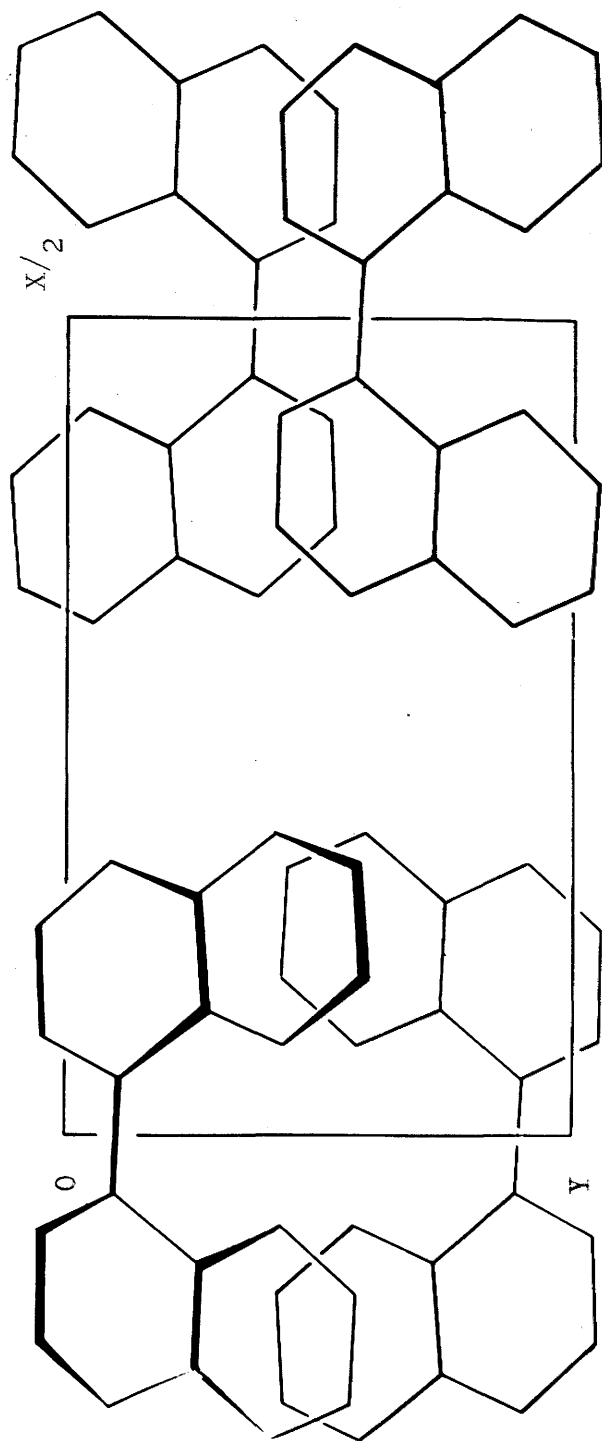
The crystal structure of 1,1'-Binaphthyl : orthogonal projection along $\underline{c}^*$
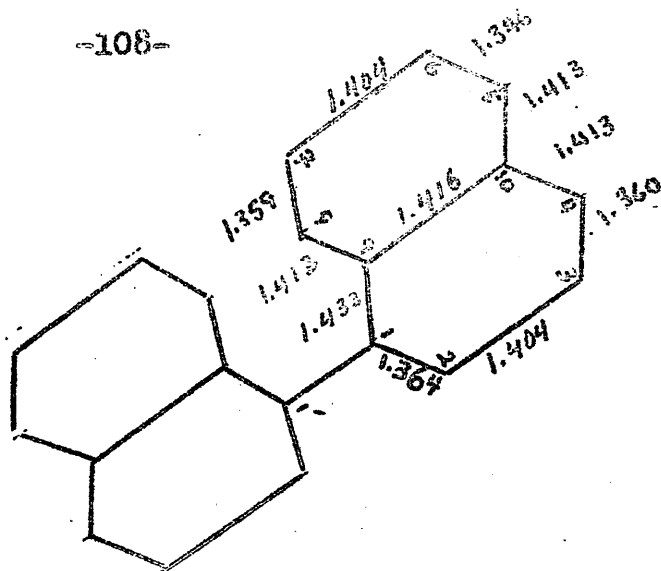
Table 4

1,1'-Binaphthyl: Bond Lengths.

Standard deviations are given as

units in the last place,

C(1)	C(1')	1.4748(46) Å
C(1)	C(2)	1.3645(37)
C(2)	C(3)	1.4036(38)
C(3)	C(4)	1.3598(41)
C(4)	C(10)	1.4127(39)
C(10)	C(5)	1.4135(37)
C(5)	C(6)	1.3450(42)
C(6)	C(7)	1.4037(38)
C(7)	C(8)	1.3590(37)
C(8)	C(9)	1.4128(35)
C(9)	C(10)	1.4162(29)
C(9)	C(1)	1.4328(32)

Bonds involving hydrogen.

C(2)	H(11)	0.983(31) Å
C(3)	H(12)	0.929(35)
C(4)	H(13)	0.989(37)
C(5)	H(14)	0.904(37)
C(6)	H(15)	0.995(36)
C(7)	H(16)	0.987(34)
C(8)	H(17)	0.889(34)

Table 5

1,1'-Binaphthyl: Bond Angles.(°)

C(1)	C(2)	C(3)	122.09(25)
C(2)	C(3)	C(4)	119.84(27)
C(3)	C(4)	C(10)	120.79(24)
C(4)	C(10)	C(9)	119.33(22)
C(4)	C(10)	C(5)	122.43(21)
C(9)	C(10)	C(5)	118.23(22)
C(10)	C(5)	C(6)	122.30(22)
C(5)	C(6)	C(7)	119.81(26)
C(6)	C(7)	C(8)	119.66(26)
C(7)	C(8)	C(9)	122.11(21)
C(8)	C(9)	C(10)	117.88(21)
C(8)	C(9)	C(1)	123.07(19)
C(10)	C(9)	C(1)	119.04(21)
C(9)	C(1)	C(2)	118.95(20)

Bond angles involving hydrogen.

C(1)	C(2)	H(11)	118.1(1.8)
H(11)	C(2)	C(3)	119.7(1.8)
C(2)	C(3)	H(12)	120.3(2.1)
H(12)	C(3)	C(4)	119.8(2.1)
C(3)	C(4)	H(13)	120.2(2.2)
H(13)	C(4)	C(10)	119.0(2.2)
C(10)	C(5)	H(14)	114.8(2.4)
H(14)	C(5)	C(6)	122.8(2.4)
C(5)	C(6)	H(15)	121.9(2.1)
H(15)	C(6)	C(7)	118.2(2.1)
C(6)	C(7)	H(16)	120.5(1.9)
H(16)	C(7)	C(8)	119.8(1.9)
C(7)	C(8)	H(17)	120.2(2.3)
H(17)	C(8)	C(9)	117.7(2.3)

Table 6

1,1'-Binaphthyl: Intra-molecular contacts <3.50 A.

C(1)	C(2)	2.456
C(1)	C(9)	2.534
C(1)	H(11)	2.595
C(1)	H(17)	2.631
C(1)	C(8)	2.971
C(2)	H(11)	3.008
C(2)	C(2)	3.107
C(2)	H(17)	3.470
C(8)	H(17)	2.999
C(8)	C(8)	3.321
C(8)	C(9)	3.333
C(9)	H(17)	2.813
C(9)	C(9)	3.277
H(11)	H(11)	2.951
H(17)	H(17)	2.906

Table 7

Inter-molecular contacts. Equivalent position numbers refer to the following transformations.

1.	$x, y, z,$		5.	$1/2+x, 1/2+y, z$
2.	$-x, y, 1/2-z$		6.	$1/2-x, 1/2+y, 1/2-z$
3.	$-x, -y, -z$		7.	$1/2-x, 1/2-y, -z$
4.	$x, -y, -1/2+z$		8.	$1/2+x, 1/2-y, -1/2+z$

C-H contacts < 3.15 A.

C(1)	H(16)	4	(0,1,0)	3.100
C(2)	H(16)	4	(0,1,0)	2.983
C(3)	H(16)	4	(0,1,0)	2.962
C(4)	H(16)	4	(0,1,0)	3.040
C(4)	H(15)	4	(0,1,0)	3.051
C(5)	H(14)	7	(0,0,1)	2.958
C(5)	H(13)	6	(0,0,0)	3.135
C(7)	H(17)	3	(0,1,1)	3.057
C(8)	H(17)	3	(0,1,1)	2.999
C(8)	H(11)	4	(0,0,1)	3.140
C(10)	H(16)	4	(0,1,0)	3.140

C-C contacts < 3.60 A.

C(2)	C(7)	1	(0,-1,0)	3.600
C(3)	C(6)	1	(0,-1,0)	3.580
C(5)	C(5)	7	(0,0,1)	3.450
C(6)	C(3)	1	(0,1,0)	3.580
C(7)	C(2)	1	(0,1,0)	3.600

H-H contacts < 2.50 A.

H(17)	H(17)	3	(0,1,1)	2.46

Table 8

1,1'-Binaphthyl: Mean Planes.

Deviations from the planes are shown in units of
angstroms X 10⁻⁴.

A. Plane through naphthalene residue:
$$0.0512X + 0.5396Y - 0.8272Z = -1.6754$$

B. Plane through atoms 1,2,3,4,9,10:
$$0.0567X + 0.5544Y - 0.8303Z = -1.6774$$

C. Plane through atoms 5,6,7,8,9,10 :
$$0.0451X + 0.5653Y - 0.8237Z = -1.6536$$

	A	B	C
C(1)	99	10	3
C(2)	-6	14	-222
C(3)	-97	1	-400
C(4)	-105	-40	-371
C(5)	117	32	16
C(6)	-6	-197	12
C(7)	-127	396	-23
C(8)	-62	299	6
C(9)	77	-48	22
C(10)	110	63	-32

Root mean square deviation from planes,

90	37	20
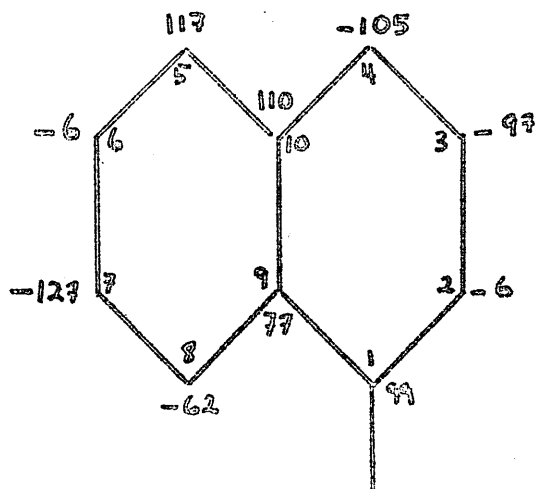
Table 9

1,1'-Binaphthyl: π-Bond Orders.

Normal naphthalene numbering is used.

		V.B.	H.M.O.
C(1)	C(2)	0.667	0.659
C(2)	C(3)	0.333	0.621
C(3)	C(4)	0.667	0.712
C(4)	C(10)	0.333	0.550
C(10)	C(5)	0.333	0.554
C(5)	C(6)	0.333	0.722
C(6)	C(7)	0.333	0.607
C(7)	C(8)	0.667	0.717
C(8)	C(9)	0.333	0.569
C(9)	C(10)	0.333	0.523
C(1)	C(9)	0.333	0.507
C(1)	C(1)'	0.000	0.404

Table 10

A comparison of bond lengths.

		Binaphthyl	naphthalene	V.B.	H.M.O.
C(1)	C(2)	1.364	1.364	1.375	1.391
C(2)	C(3)	1.404	1.415	1.421	1.401
C(3)	C(4)	1.360	1.364	1.375	1.377
C(4)	C(10)	1.413	1.421	1.421	1.420
C(10)	C(5)	1.413	1.421	1.421	1.419
C(5)	C(6)	1.346	1.364	1.375	1.374
C(6)	C(7)	1.404	1.415	1.421	1.405
C(7)	C(8)	1.359	1.364	1.375	1.376
C(8)	C(9)	1.413	1.421	1.421	1.415
C(9)	C(10)	1.416	1.418	1.421	1.427
C(9)	C(1)	1.433	1.421	1.421	1.432
C(1)	C(1)'	1.475		1.477	1.459

Root mean square difference

			0.009	0.014	0.015

1,1-Binaphthyl Structure Factor Tables Ctd.

H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc
18	2	3	10.7	-11.3	9	3	8	4.9	4.2	7	3	1	28.4	27.4	-22	4	4	2.6	2.0	-1	5	9	3.8	-1.7
12	2	3	2.3	2.1	11	3	7	5.7	5.6	5	3	1	27.3	-26.3	-16	4	4	22.7	21.5	-3	5	9	5.1	5.2
10	2	3	25.4	-23.4	9	3	7	17.1	-17.4	3	3	1	31.9	-29.1	-14	4	4	11.3	11.0	-3	5	9	4.3	2.2
8	2	3	43.2	-40.2	7	3	7	12.5	-13.0	1	3	1	3.4	5.3	-12	4	4	6.2	-6.0	-7	5	9	4.9	-4.4
6	2	3	23.8	24.0	3	3	7	24.9	-25.1	-3	3	1	0.9	-1.3	-10	4	4	2.9	3.1	-11	5	9	2.7	3.7
4	2	3	26.7	24.8	1	3	7	30.4	30.1	-5	3	1	80.5	-88.6	-8	4	4	4.6	-3.0	-15	5	9	4.5	2.0
2	2	3	14.8	14.8	-1	3	7	69.2	70.3	-7	3	1	16.5	-15.5	-6	4	4	10.5	-9.4	-21	5	8	3.3	-0.6
0	2	3	54.4	56.4	-3	3	7	7.2	-7.9	-9	3	1	17.6	15.1	-4	4	4	6.4	7.2	-23	5	8	2.8	0.8
-2	2	3	8.7	-8.5	-5	3	7	11.8	-11.6	-11	3	1	16.7	-16.9	-2	4	4	10.0	11.1	-21	5	8	2.8	-0.2
-4	2	3	42.7	42.0	-9	3	7	23.8	-25.4	-13	3	1	51.9	51.8	2	4	4	19.5	-19.6	-19	5	8	12.1	11.2
-6	2	3	26.7	25.7	-11	3	7	5.8	-6.6	-15	3	1	46.7	46.1	2	4	4	25.6	-27.2	-17	5	8	4.9	4.9
-8	2	3	28.5	-27.7	-15	3	7	5.3	-6.6	-17	3	1	25.4	-24.2	6	4	4	2.2	1.8	-15	5	8	6.0	-5.0
-10	2	3	4.3	5.9	-17	3	7	4.0	5.1	-19	3	1	7.4	-7.2	6	4	4	2.8	2.3	-13	5	8	2.8	1.0
-12	2	3	22.0	-21.5	-19	3	7	3.7	2.8	-23	3	1	10.7	-10.9	8	4	4	3.6	3.5	-11	5	8	3.2	2.1
-14	2	3	32.8	-33.6	-27	3	6	3.1	-1.5	-25	3	1	2.9	2.1	10	4	4	11.0	12.2	-9	5	8	2.5	-0.9
-18	2	3	6.5	6.4	-11	3	6	5.6	-6.0	27	3	0	3.7	-1.3	16	4	4	1.8	1.5	1	5	8	2.8	-4.2
-26	2	2	6.8	3.7	-9	3	6	5.6	-5.1	23	3	0	3.3	-2.6	18	4	4	4.5	4.6					
-28	2	2	6.0	6.6	-7	3	6	3.2	-2.3	15	3	0	14.1	14.3	20	4	3	5.8	5.2					
-24	2	2	8.2	-8.3	-5	3	6	5.7	-6.2	13	3	0	10.2	11.3	22	4	3	3.7	3.6					
-22	2	2	4.7	-3.9	-3	3	6	8.8	9.9	9	3	0	2.9	3.2	20	4	3	3.7	1.9					
-18	2	2	4.8	-3.8	-1	3	6	21.9	22.0	7	3	0	9.9	-9.1	18	4	3	7.9	-6.7					
-16	2	2	10.1	11.0	1	3	6	3.6	3.4	5	3	0	17.7	-16.4	16	4	3	5.8	-4.7					
-14	2	2	7.1	7.0	7	3	6	8.8	-7.9	3	3	0	10.5	-9.2	14	4	3	3.2	3.5					
-12	2	2	4.8	-5.0	9	3	6	5.4	-5.5	0	3	0	5.4	6.0	12	4	3	8.0	9.0					
-10	2	2	10.7	12.3	11	3	6	2.7	-2.7	-2	4	11	7.2	7.3	10	4	3	7.4	-8.1					
-8	2	2	2.3	-2.7	19	3	6	3.1	-2.5	-4	4	11	2.6	-3.3	8	4	3	16.0	-16.2					
-6	2	2	33.2	-30.9	19	3	5	13.1	14.0	-10	4	11	10.6	-10.6	6	4	3	8.7	8.5					
-2	2	2	22.1	21.2	15	3	5	5.9	5.6	-18	4	11	3.7	-2.2	4	4	3	6.5	5.7					
0	2	2	15.5	14.5	17	3	5	7.4	-6.2	-20	4	10	7.0	-5.1	2	4	3	3.0	-2.5					
2	2	2	33.8	-32.7	15	3	5	7.7	-8.4	-12	4	10	4.1	-1.2	0	4	3	10.2	11.7					
4	2	2	35.6	-33.8	13	3	5	15.2	15.9	-10	4	10	6.1	-6.3	-2	4	3	4.1	3.8					
6	2	2	25.0	23.6	11	3	5	26.9	27.4	-4	4	10	3.1	-2.4	-4	4	3	27.0	26.4					
8	2	2	2.8	-3.7	9	3	5	9.7	-9.4	-6	4	10	3.2	3.2	-6	4	3	9.5	8.7					
10	2	2	7.5	7.1	7	3	5	10.0	-10.0	-8	4	10	14.0	14.0	-8	4	3	22.1	-21.8					
12	2	2	40.2	38.6	5	3	5	6.1	-6.6	-12	4	10	3.8	1.9	-12	4	3	16.0	-15.5					
14	2	2	4.5	-5.1	3	3	5	37.5	-37.5	-14	4	10	3.6	-4.5	-14	4	3	17.3	-17.4					
16	2	2	27.6	-27.3	1	3	5	5.8	-3.8	-16	4	10	3.2	1.8	-16	4	3	15.4	15.1					
18	2	2	4.3	-3.6	-1	3	5	6.4	7.0	-18	4	9	4.3	5.4	-18	4	3	9.7	9.7					
20	2	2	9.7	9.4	-3	3	5	5.3	-5.2	8	4	9	7.0	7.0	-28	4	2	3.4	-1.9					
22	2	2	4.9	5.0	-5	3	5	10.2	9.1	6	4	9	6.1	-6.0	-24	4	2	8.9	9.5					
26	2	2	3.6	4.4	-7	3	5	2.2	1.4	2	4	9	7.1	-7.6	-22	4	2	5.5	5.3					
24	2	1	6.7	-7.8	-9	3	5	4.0	4.2	0	4	9	24.4	-25.2	-20	4	2	4.6	-4.6					
22	2	1	8.6	-7.9	-11	3	5	7.7	8.4	-4	4	9	15.6	15.6	-18	4	2	7.6	7.7					
20	2	1	11.8	11.7	-17	3	5	8.6	8.7	-8	4	9	4.6	4.7	-16	4	2	13.0	-12.5					
18	2	1	10.2	-9.4	-21	3	5	6.5	5.7	-12	4	9	4.0	-2.8	-14	4	2	28.9	-28.6					
16	2	1	18.4	18.2	-23	3	5	13.9	-12.3	-18	4	9	3.2	-3.3	-10	4	2	3.2	-3.1					
14	2	1	42.6	43.1	-25	3	5	5.8	-5.5	-22	4	9	6.7	5.2	-8	4	2	4.2	-4.0					
12	2	1	2.9	-3.9	-27	3	4	2.9	-1.9	-24	4	9	3.3	2.0	-6	4	2	25.2	23.9					
10	2	1	4.4	2.9	-25	3	4	2.9	-4.7	-20	4	8	8.6	7.4	-4	4	2	11.4	10.5					
8	2	1	2.3	-0.3	-23	3	4	12.0	10.9	-18	4	8	5.6	4.8	-2	4	2	3.3	-3.4					
4	2	1	16.5	-15.6	-15	3	4	13.1	13.1	-16	4	8	5.6	-1.7	0	4	2	6.7	-6.1					
0	2	1	15.0	13.9	-13	3	4	3.6	-2.6	-12	4	8	3.6	3.3	2	4	2	11.1	10.0					
-2	2	1	31.3	-25.3	-11	3	4	3.7	-3.2	-10	4	8	12.8	13.2	4	4	2	23.6	22.6					
-4	2	1	19.9	-19.8	-9	3	4	5.3	-5.8	-6	4	8	4.5	-5.1	6	4	2	2.3	1.4					
-6	2	1	5.0	5.2	-5	3	4	2.6	-1.8	-2	4	8	14.9	-16.0	10	4	2	19.0	-19.5					
-10	2	1	1.5	-0.3	-3	3	4	7.5	-4.5	0	4	8	16.4	-17.1	12	4	2	7.9	-8.3					
-12	2	1	17.3	-18.1	-1	3	4	2.2	-1.9	2	4	8	2.8	3.6	14	4	2	7.7	7.3					
-14	2	1	4.4	4.7	1	3	4	6.1	5.5	8	4	8	6.6	8.4	16	4	2	7.8	-7.3					
-16	2	1	37.9	38.3	9	3	4	7.7	5.4	10	4	7	3.2	-3.9	20	4	2	6.7	-7.2					
-18	2	1	5.9	7.0	13	3	4	4.4	-3.6	8	4	7	8.9	-8.9	24	4	1	3.8	-5.3					
-22	2	1	6.2	7.3	15	3	4	3.2	2.2	8	4	7	5.1	4.7	22	4	1	9.1	7.4					
-24	2	1	12.5	-11.9	17	3	4	3.4	4.2	2	4	7	5.1	5.4	20	4	1	17.9	17.4					
-26	2	1	3.5	-3.8	19	3	3	5.1	5.1	2	4	7	2.2	1.5	16	4	1	26.8	25.9					
-28	2	1	3.4	-1.8	23	3	3	12.6	-12.5	0	4	7	8.5	-8.1	14	4	1	13.5	-12.6					
28	2	0	4.4	-6.8	21	3	3	8.9	-8.9	-2	4	7	3.8	3.0	12	4	1	8.0	-7.2					
26	2	0	13.5	-14.1	19	3	3	9.5	-9.3	-4	4	7	5.6	5.8	10	4	1	3.6	-4.3					
24	2	0	3.7	-1.6	15	3	3	2.6	0.2	-8	4	7	9.9	11.1	8	4	1	36.4	-34.0					
22	2	0	2.4	-0.4	11	3	3	11.9	10.0	-12	4	7	11.9	-13.2	6	4	1	3.7	-3.7					
18	2	0	24.6	25.8	7	3	3	8.3	5.7	-20	4	7	7.0	-5.4	4	4	1	22.2	24.5					
16	2	0	17.2	18.9	5	3	3	14.7	-14.8	-22	4	7	5.1	-5.8	2	4	1	7.9	8.4					
14	2	0	25.3	-27.0	3	3	3	18.3	-20.1	-24	4	7	6.8	7.1	0	4	1	8.8	-7.3					
12	2	0	12.9	-13.3	1	3	3	18.6	21.2	-26	4	7	4.9	4.5	-2	4	1	1.6	-1.6					
10	2	0	5.0	-5.9	-1	3	3	6.9	7.2	-22	4	6	2.7	-1.0	-4	4	1	8.1	7.7					
8	2	0	25.4	-24.8	-3	3	3	7.1	7.5	-20	4	6	2.7	-1.2	-6	4	1	2.5	-3.8					
6	2	0	12.0	11.7	-5	3	3	31.4	29.7	-18	4	6	14.0	-12.7	-10	4	1	21.9	-20.9					
4	2	0	6.3	3.6	-9	3	3	2.9	-2.2	-16	4	6	7.2	-6.3	-12	4	1	5.9	-4.6					
1	3	11	4.0	4.5	-11	3	3	18.3	18.6	-14	4	6	7.3	7.6	-14	4	1	32.2	31.0					
-7	3	11	2.6	2.2	-13	3	3	7.6	7.2	-10	4	6	8.7	-10.4	-16	4	1	7.4	7.8					
-11	3	11	4.7	-3.6	-15	3	3	67.0	-67.7	-8	4	6	6.6	-8.2	-18	4	1	8.1	8.4					
-21	3	11	11.2	-10.0	-17	3	3	24.1	-24.6	-6	4	6	2.0	2.0	-22	4	1	9.4	-9.1					
-21	3	10	3.6	-2.1	-19	3	3	19.4	19.1	-2	4	6	5.4	-4.5	-24	4	1	6.7	-6.4					
-19	3	10	2.7	-3.2	-21	3	3	6.4	-5.6	0	4	6	9.4	9.6	-26	4	1	3.3	1.7					
-11	3	10	2.5	-2.8	-23	3	3	15.1	14.6	4	4	6	30.8	31.9	28	4	0	2.6	-2.5					
-9	3	10	3.1	-2.4	-25	3	3	17.4	16.7	4	4	6	4.1	-5.2	22	4	0	3.4	1.0					
-1	3	10	3.8	3.7	-27	3	3	4.5	-4.6	6	4	6	3.2	2.6	20	4	0	7.7	-7.3					
9	3	9	3.2	0.7	-27	3	2	2.9	0.2	8	4	6	3.4	3.4	18	4	0	3.1	1.3					
7	3	9	3.8	3.4	-25	3	2	3.0	4.5	8	4	6	11.6	-11.2	16	4	0	12.1	11.5					
3	3	9	4.1	3.6	-23	3	2	4.4	4.1	10	4	6	7.1	-7.3	12	4	0	8.8	-8.5					
-1	3	9	10.3	10.6	-21	3	2	2.8	4.2	18	4	6	5.4	-5.0	10	4	0	8.3	7.4					
-3	3	9	20.5	-21.5	-17	3	2	4.8	-5.0	12	4	5	5.9	-6.5	8	4	0	15.3	-13.0					
-5	3	9	19.7	-19.4	-15	3	2	14.8	-14.3	8	4	5	6.6	7.4	6	4	0	32.7	30.7					
-7	3	9	4.3	3.2	-13	3	2	16.2	-16.5	6	4	5	2.1	2.4	4	4	0	22.5	-18.4					
-9	3	9	10.5	-10.9	-11	3	2	3.6	-3.6	4	4	5	11.8	11.8										
-11	3	9	7.1	7.1	-9	3	2	4.7	4.2	2	4	5	30.8	31.7										
-13	3	9	22.9	24.4	-7	3	2	4.9	4.1	0	4	5	20.3	-21.2										
-15	3	9	6.2	-6.8	-5	3	2	18.0	17.0	-2	4	5	35.8	-36.8										
-19	3	9	10.6	9.0	-3	3	2	17.9	16.8	-4	4	5	1.7	-1.9										
-21	3	9	7.7	7.2	-1	3	2	2.6	-3.0	-6	4	5	13.7	-14.3										
-23	3	8	7.2	-8.0	1	3	2	10.0	-9.2	-8	4	5	12.3	13.6										
-19	3	8	2.6	2.9	5	3	2	6.4	5.4	-10	4	5	2.7	2.1										
-17	3	8	3.8	-3.4	7	3	2	3.1	-3.6	-12	4	5	25.4	24.8										
-15	3	8	3.5	-3.3	9	3	2	2.8	2.7	-14	4	5	12.5	13.0										
-13	3	8	4.7	4.2	11	3	2	3.4	3.1	-16	4	5	19.3	-19.5										
-11	3	8	8.0	7.9	19	3	2	5.4	-6.2	-18	4	5	3.4	-3.9										
-9	3	8	3.6	2.9	25	3	1	3.4	0.3	-20	4	5	2.9	-2.9										
-3	3	8	7.1	-7.7	23	3	1	2.7	3.4	-22	4	5	8.6	-8.6										
-1	3	8	12.0	-11.4	17	3	1	6.8	7.6	-24	4	5	5.1	4.8										
1	3	8	7.9	-8.2	13	3	1	2.0	1.7	-26	4	5	5.0	4.8										
5	3	8	3.4	-4.2	9	3	1	11.9	11.1	-24	4	4	9.5	-9.2										
7	3	8	3.9	3.1																				

1,1-Binaphthyl Structure Factor Tables Ctd.

Column group 1:

H	K	L	|Fo|	Fc
18	2	3	10.7	-11.3
12	2	3	2.3	2.1
10	2	3	25.4	-23.4
8	2	3	43.2	-40.2
6	2	3	23.8	24.0
4	2	3	26.7	24.8
2	2	3	14.8	14.8
0	2	3	54.4	56.4
-2	2	3	8.7	-8.5
-4	2	3	42.7	42.0
-6	2	3	26.7	25.7
-8	2	3	28.5	-27.7
-10	2	3	4.3	5.9
-12	2	3	22.0	-21.5
-14	2	3	32.8	-33.6
-18	2	3	6.5	6.4
-26	2	3	2.8	3.7
-28	2	2	8.0	6.6
-24	2	2	8.2	-8.3
-22	2	2	4.7	-3.9
-18	2	2	4.8	-3.8
-16	2	2	10.1	11.0
-14	2	2	7.1	7.0
-12	2	2	4.8	-5.0
-10	2	2	10.7	12.3
-8	2	2	2.3	-2.7
-6	2	2	33.2	-30.9
-2	2	2	22.1	21.2
0	2	2	15.5	14.5
2	2	2	33.8	-32.7
4	2	2	35.6	-33.8
6	2	2	25.0	23.6
8	2	2	2.8	-3.7
10	2	2	7.5	7.1
12	2	2	40.2	38.6
14	2	2	4.5	-5.1
16	2	2	27.6	-27.3
18	2	2	4.3	-3.6
20	2	2	9.7	9.4
22	2	2	4.9	5.0
26	2	2	3.6	4.4
24	2	1	6.7	-7.8
22	2	1	8.6	-7.9
20	2	1	11.8	11.7
18	2	1	10.2	-9.4
16	2	1	18.4	18.2
14	2	1	42.6	43.1
12	2	1	2.9	-3.9
10	2	1	4.4	2.9
8	2	1	2.3	-0.3
4	2	1	16.5	-15.6
0	2	1	15.0	13.9
-2	2	1	31.3	-25.3
-4	2	1	19.9	-19.8
-6	2	1	5.0	5.2
-10	2	1	1.5	-0.3
-12	2	1	17.3	-18.1
-14	2	1	4.4	4.7
-16	2	1	37.9	38.3
-18	2	1	5.9	7.0
-22	2	1	6.2	7.3
-24	2	1	12.5	-11.9
-26	2	1	3.5	-3.8
-28	2	1	3.4	-1.8
28	2	0	4.4	-6.8
26	2	0	13.5	-14.1
24	2	0	3.7	-1.6
22	2	0	2.4	-0.4
18	2	0	24.6	25.8
16	2	0	17.2	18.9
14	2	0	25.3	-27.0
12	2	0	12.9	-13.3
10	2	0	5.0	-5.9
8	2	0	25.4	-24.8
6	2	0	12.0	11.7
4	2	0	6.3	3.6
1	3	11	4.0	4.5
-7	3	11	2.6	2.2
-11	3	11	4.7	-3.6
-21	3	11	11.2	-10.0
-21	3	10	3.6	-2.1
-19	3	10	2.7	-3.2
-11	3	10	2.5	-2.8
-9	3	10	3.1	-2.4
-1	3	10	3.8	3.7
9	3	10	3.2	0.7
7	3	9	3.8	3.4
3	3	9	4.1	3.6
-1	3	9	10.3	10.6
-3	3	9	20.5	-21.5
-5	3	9	19.7	-19.4
-7	3	9	4.3	3.2
-9	3	9	10.5	-10.9
-11	3	9	7.1	7.1
-13	3	9	22.9	24.4
-15	3	9	6.2	-6.8
-19	3	9	10.6	9.0
-21	3	9	7.7	7.2
-23	3	9	7.2	-8.0
-19	3	8	2.6	-2.9
-17	3	8	3.8	-3.3
-15	3	8	3.5	-3.3
-13	3	8	4.7	4.2
-11	3	8	8.0	7.9
-9	3	8	3.6	2.9
-3	3	8	7.1	-7.7
-1	3	8	12.0	-11.4
1	3	8	7.9	-8.2
5	3	8	3.4	4.2
7	3	8	3.9	3.1

Column group 2:

H	K	L	|Fo|	Fc
9	3	8	4.9	4.2
11	3	7	5.7	5.6
9	3	7	17.1	-17.4
7	3	7	12.5	-13.0
3	3	7	24.9	-25.1
1	3	7	30.4	30.1
-1	3	7	69.2	70.3
-3	3	7	7.2	-7.9
-5	3	7	11.8	-11.6
-9	3	7	23.8	-25.4
-11	3	7	5.8	-6.6
-15	3	7	5.3	-6.6
-17	3	7	4.0	5.1
-19	3	7	3.7	2.8
-27	3	6	3.1	-1.5
-11	3	6	5.6	-6.0
-9	3	6	5.6	-5.1
-7	3	6	3.2	-2.3
-5	3	6	5.7	-6.2
-3	3	6	8.8	9.9
-1	3	6	21.9	22.0
1	3	6	3.6	3.4
7	3	6	8.8	-7.9
9	3	6	5.4	-5.5
11	3	6	2.7	-2.7
19	3	6	3.1	-2.5
19	3	6	13.1	14.0
17	3	5	5.9	5.6
15	3	5	7.4	-6.2
13	3	5	7.7	-8.4
11	3	5	15.2	15.9
9	3	5	26.9	27.4
7	3	5	9.7	-9.4
5	3	5	10.0	-10.0
3	3	5	6.1	-6.6
1	3	5	37.5	-37.5
-1	3	5	5.8	-3.8
-3	3	5	6.4	7.0
-5	3	5	5.3	-5.2
-7	3	5	10.2	9.1
-9	3	5	2.2	1.4
-11	3	5	4.0	4.2
-17	3	5	7.7	8.4
-21	3	5	8.6	8.7
-23	3	5	6.5	5.7
-25	3	5	13.9	-12.3
-27	3	5	5.8	-5.5
-25	3	4	2.9	-1.9
-23	3	4	5.8	-4.7
-15	3	4	12.0	10.9
-13	3	4	13.1	13.1
-11	3	4	3.6	-2.6
-9	3	4	3.7	-3.2
-5	3	4	5.3	-5.8
-3	3	4	2.6	-1.8
-1	3	4	7.5	-4.5
1	3	4	2.2	-1.9
3	3	4	6.1	5.5
9	3	4	7.7	5.4
13	3	4	4.4	-3.6
15	3	4	3.2	2.2
17	3	4	3.4	4.2
19	3	3	5.1	5.1
21	3	3	12.6	-12.5
19	3	3	8.9	-8.9
15	3	3	9.5	-9.3
11	3	3	2.6	0.2
7	3	3	11.9	10.0
5	3	3	8.3	5.7
3	3	3	14.7	-14.8
1	3	3	18.3	-20.1
-1	3	3	18.6	21.2
-3	3	3	6.9	7.2
-5	3	3	31.4	29.7
-7	3	3	2.9	-2.2
-9	3	3	18.3	18.6
-11	3	3	7.6	7.2
-13	3	3	67.0	-67.7
-15	3	3	24.1	-24.6
-17	3	3	19.4	19.1
-19	3	3	6.4	-5.6
-21	3	3	15.1	14.6
-23	3	3	17.4	16.7
-25	3	3	4.5	-4.6
-27	3	2	2.9	0.2
-27	3	2	3.0	4.5
-25	3	2	4.4	4.1
-23	3	2	2.8	4.2
-21	3	2	4.8	-5.0
-17	3	2	14.8	-14.3
-15	3	2	16.2	-16.5
-13	3	2	3.6	-3.6
-11	3	2	4.7	4.2
-9	3	2	3.9	4.1
-7	3	2	18.0	17.0
-5	3	2	17.9	16.8
-3	3	2	2.6	-3.0
-1	3	2	10.0	-9.2
1	3	2	6.4	5.4
5	3	2	3.1	-3.6
7	3	2	2.8	2.7
9	3	2	3.4	3.1
11	3	2	5.4	-6.2
19	3	2	3.4	0.3
25	3	1	2.7	3.4
23	3	1	6.8	7.6
17	3	1	2.0	1.7
9	3	1	11.9	11.1

Column group 3:

H	K	L	|Fo|	Fc
7	3	1	28.4	27.4
5	3	1	27.3	-26.3
3	3	1	31.9	-29.1
1	3	1	3.4	5.3
-3	3	1	0.9	-1.3
-5	3	1	80.5	-88.6
-7	3	1	16.5	-15.5
-9	3	1	17.6	15.1
-11	3	1	16.7	-16.9
-13	3	1	51.9	51.8
-15	3	1	46.7	46.1
-17	3	1	25.4	-24.2
-19	3	1	7.4	-7.2
-23	3	1	10.7	-10.9
-25	3	1	2.9	2.1
27	3	0	3.7	-1.3
23	3	0	3.3	-2.6
15	3	0	14.1	14.3
13	3	0	10.2	11.3
9	3	0	2.9	3.2
7	3	0	9.9	-9.1
5	3	0	17.7	-16.4
3	3	0	10.5	-9.2
0	4	11	5.4	6.0
-2	4	11	7.2	7.3
-4	4	11	2.6	-3.3
-10	4	11	10.6	-10.6
-18	4	11	3.7	-2.2
-20	4	10	7.0	-5.1
-12	4	10	6.1	-6.3
-10	4	10	6.1	-6.3
-6	4	10	3.1	-2.4
-4	4	10	3.2	3.2
-2	4	10	14.0	14.0
0	4	10	3.8	1.9
2	4	10	3.6	-4.5
12	4	9	3.2	1.8
10	4	9	4.3	5.4
8	4	9	7.0	5.0
6	4	9	6.1	-6.0
2	4	9	7.1	-7.6
0	4	9	24.4	-25.2
-4	4	9	15.6	15.6
-8	4	9	4.6	4.7
-12	4	9	4.0	-2.8
-18	4	9	3.2	-3.8
-22	4	9	6.7	5.2
-24	4	9	3.3	2.0
-20	4	8	8.6	7.4
-18	4	8	5.6	4.8
-16	4	8	3.4	-1.7
-12	4	8	3.6	3.2
-10	4	8	12.8	13.2
-6	4	8	4.5	-5.0
-2	4	8	14.9	-16.0
0	4	8	16.4	-17.1
2	4	8	2.8	3.6
8	4	7	6.6	8.4
10	4	7	3.2	-3.9
8	4	7	8.9	-8.9
6	4	7	5.1	4.7
4	4	7	5.1	5.4
2	4	7	2.2	1.5
0	4	7	8.5	-8.1
-2	4	7	3.8	3.0
-4	4	7	5.6	5.8
-8	4	7	9.9	11.1
-12	4	7	11.9	-13.2
-20	4	7	7.0	-5.4
-22	4	7	5.1	-5.8
-24	4	7	6.5	7.1
-26	4	7	6.8	2.6
-26	4	6	4.9	4.5
-22	4	6	2.7	-1.0
-20	4	6	14.0	-12.7
-18	4	6	7.2	-6.3
-16	4	6	7.3	7.6
-14	4	6	8.7	-10.4
-10	4	6	6.6	-8.2
-8	4	6	6.0	2.0
-6	4	6	9.4	9.6
-4	4	6	30.8	31.9
0	4	6	4.1	-5.2
2	4	6	3.4	3.4
6	4	6	11.6	-11.2
8	4	6	7.1	-7.3
10	4	6	5.9	-6.5
12	4	5	2.1	2.4
12	4	5	11.8	-8.7
4	4	5	30.8	31.7
2	4	5	20.3	-21.2
-2	4	5	35.8	-36.8
-4	4	5	13.7	-14.3
-6	4	5	12.3	13.6
-10	4	5	2.7	2.1
-12	4	5	25.4	24.8
-14	4	5	12.5	13.0
-16	4	5	19.3	-19.5
-18	4	5	3.4	-3.9
-20	4	5	2.9	-3.9
-22	4	5	8.6	-8.6
-24	4	5	5.1	4.8
-26	4	5	5.0	4.8
-24	4	4	9.5	-9.2

Column group 4:

H	K	L	|Fo|	Fc
-22	4	4	2.6	2.0
-16	4	4	22.7	21.5
-14	4	4	11.3	11.0
-12	4	4	6.2	-6.0
-10	4	4	2.9	3.1
-8	4	4	4.6	-3.0
-6	4	4	10.5	-9.4
-4	4	4	6.4	7.2
-2	4	4	10.0	11.1
0	4	4	19.5	-19.6
2	4	4	25.6	-27.2
2	4	4	2.2	1.8
4	4	4	2.8	2.3
6	4	4	3.6	3.5
8	4	4	11.0	12.2
10	4	4	1.8	1.5
16	4	4	4.5	4.6
18	4	4	5.8	5.2
20	4	3	3.7	3.6
22	4	3	3.7	1.9
20	4	3	7.9	-6.7
18	4	3	5.8	-4.7
16	4	3	3.2	3.5
14	4	3	8.0	9.0
12	4	3	7.4	-8.1
10	4	3	16.0	-16.2
8	4	3	8.7	8.5
6	4	3	6.5	5.7
4	4	3	3.0	-2.5
2	4	3	10.2	11.7
-2	4	3	4.1	3.8
-4	4	3	27.0	26.4
-6	4	3	9.5	8.7
-8	4	3	22.1	-21.8
-12	4	3	16.0	-15.5
-14	4	3	17.3	-17.4
-16	4	3	15.4	15.1
-18	4	2	9.7	9.7
-28	4	2	3.4	-1.9
-24	4	2	8.9	9.5
-22	4	2	5.5	5.3
-20	4	2	4.6	-4.6
-18	4	2	7.6	7.7
-16	4	2	13.0	-12.5
-14	4	2	28.9	-28.6
-10	4	2	3.2	-3.1
-8	4	2	4.2	-4.0
-6	4	2	25.2	23.9
-4	4	2	11.4	10.5
-2	4	2	3.3	-3.4
0	4	2	6.7	-6.1
2	4	2	11.1	10.0
4	4	2	23.6	22.6
6	4	2	2.3	1.4
10	4	2	2.2	-1.5
12	4	2	19.0	-19.5
14	4	2	7.9	-8.3
16	4	2	7.7	-7.3
20	4	2	7.8	-7.3
24	4	1	6.7	-7.2
22	4	1	3.8	-5.3
20	4	1	9.1	7.4
16	4	1	17.9	17.4
14	4	1	26.8	25.9
12	4	1	13.5	-12.6
10	4	1	8.0	-7.2
8	4	1	3.6	-4.3
6	4	1	36.4	-34.0
4	4	1	3.7	-3.7
2	4	1	22.2	24.5
0	4	1	7.9	8.4
-2	4	1	8.8	-7.3
-4	4	1	1.6	-1.6
-6	4	1	8.1	7.7
-10	4	1	2.5	-3.8
-12	4	1	21.9	-20.9
-14	4	1	5.9	-4.6
-16	4	1	32.2	31.0
-18	4	1	7.4	7.8
-22	4	1	8.1	8.4
-24	4	1	9.4	-9.1
-26	4	1	6.7	-6.4
28	4	0	3.3	1.7
22	4	0	2.6	-2.5
20	4	0	3.4	1.0
18	4	0	7.7	-7.3
16	4	0	3.1	1.3
12	4	0	12.1	11.5
10	4	0	8.8	-8.5
8	4	0	8.3	7.4
6	4	0	15.3	-13.0
14	4	0	32.7	30.7
4	4	0	22.5	-18.4
-1	5	9	3.8	-1.7
-3	5	9	5.1	5.2
-7	5	9	4.3	2.2
-11	5	9	4.9	-4.4
-15	5	9	2.7	3.7
-21	5	9	4.5	2.0
-23	5	8	3.3	-0.6
-21	5	8	2.8	0.8
-19	5	8	3.2	-0.2
-17	5	8	12.1	11.2
-15	5	8	4.9	4.9
-13	5	8	6.0	-5.4
-11	5	8	2.8	2.1
-9	5	8	2.5	-0.9
-3	5	8	2.8	-4.2

1,1'-Binaphthyl Structure Factor Tables Ctd.

H	K	L	|Fo|	Fc
5	5	8	7.3	-7.4
9	5	8	3.8	4.1
13	5	8	7.5	7.5
15	5	8	4.9	4.9
17	5	8	4.6	-3.1
17	5	7	8.6	8.6
13	5	7	3.6	-4.6
9	5	7	3.4	-2.6
7	5	7	4.3	-3.7
3	5	7	2.5	-3.9
1	5	7	2.7	2.5
-1	5	7	10.8	10.8
-9	5	7	6.2	-6.0
-11	5	7	2.5	-0.8
-13	5	7	9.5	-8.8
-15	5	7	4.1	-5.3
-17	5	7	15.7	15.5
-19	5	7	12.4	11.0
-21	5	7	3.1	-1.6
-25	5	7	4.3	-3.2
-23	5	6	5.9	5.7
-21	5	6	7.8	-6.1
-19	5	6	3.1	2.1
-15	5	6	16.4	-15.8
-13	5	6	6.6	-5.5
-11	5	6	4.7	-5.9
-9	5	6	4.4	-4.3
-7	5	6	15.8	15.9
-5	5	6	8.2	8.0
1	5	6	2.8	3.5
3	5	6	7.7	7.8
13	5	6	3.6	-0.9
15	5	6	7.6	-6.4
17	5	6	3.0	-4.4
15	5	5	4.6	3.9
11	5	5	3.2	-2.8
9	5	5	2.3	1.8
5	5	5	7.4	-6.6
3	5	5	2.9	2.4
1	5	5	14.2	14.0
-1	5	5	6.7	6.7
-3	5	5	13.7	-13.7
-5	5	5	3.2	-2.8
-7	5	5	7.7	7.7
-9	5	5	6.8	-7.7
-11	5	5	6.6	6.7
-13	5	5	15.2	15.6
-15	5	5	10.4	-10.9
-17	5	5	16.7	-15.7
-21	5	5	6.2	5.7
-23	5	5	4.5	3.6
-27	5	5	4.7	3.1
-25	5	4	3.9	0.7
-23	5	4	3.6	-4.3
-19	5	4	7.5	7.1
-17	5	4	3.3	-3.3
-13	5	4	5.4	5.4
-11	5	4	9.6	10.5
-9	5	4	19.5	20.2
-7	5	4	2.5	-2.3
-5	5	4	13.8	-14.2
-3	5	4	9.5	-9.2
-1	5	4	22.9	-23.5
1	5	4	2.0	2.2
3	5	4	2.6	3.2
5	5	4	12.5	-12.5
7	5	4	8.1	8.2
13	5	4	15.2	15.3
17	5	4	4.1	-4.0
23	5	4	4.2	-0.0
23	5	3	3.4	0.7
21	5	3	5.0	-4.7
19	5	3	2.7	-0.4
17	5	3	6.3	-6.4
15	5	3	12.7	-13.1
13	5	3	10.6	10.4
9	5	3	5.4	5.5
7	5	3	6.2	5.6
4	5	3	4.0	3.8
3	5	3	33.0	-32.5
1	5	3	32.1	-33.2
-1	5	3	14.7	15.9
-3	5	3	18.3	18.4
-5	5	3	3.4	-3.3
-7	5	3	5.5	7.6
-9	5	3	3.7	4.3
-11	5	3	4.0	-5.2
-15	5	3	7.5	-7.5
-19	5	3	4.7	4.4
-21	5	3	3.0	-2.9
-25	5	3	4.0	4.2
-27	5	3	3.1	-1.4
-21	5	2	5.6	-6.2
-17	5	2	2.6	-0.1
-15	5	2	3.3	-4.0
-13	5	2	4.1	-5.1
-9	5	2	5.0	-4.9
-7	5	2	4.4	-4.8
-1	5	2	16.3	17.0
-3	5	2	31.4	32.6
-5	5	2	8.8	-8.7
5	5	2	6.5	-6.2
5	5	2	4.6	4.4
7	5	2	4.4	4.3
9	5	2	11.2	-11.9
11	5	2	8.0	7.1
13	5	2	8.3	-7.5
15	5	2	21.2	-21.1
23	5	2	7.4	7.1
25	5	1	3.1	-4.4
23	5	1	3.2	5.3
17	5	1	17.1	16.9
13	5	1	26.1	-26.4
11	5	1	12.2	-12.6
9	5	1	6.0	6.6
7	5	1	3.0	3.7
5	5	1	7.0	7.0
3	5	1	14.1	14.9
-1	5	1	5.2	-7.5
-3	5	1	2.7	-3.0
-5	5	1	12.4	-11.6
-7	5	1	3.6	-3.9
-9	5	1	5.5	5.6
-11	5	1	1.7	0.6
-13	5	1	3.9	3.7
-21	5	1	4.0	-2.7
-23	5	1	3.8	-0.7
-27	5	1	6.4	-5.3
-25	5	0	6.8	-6.3
23	5	0	7.9	-7.9
21	5	0	8.4	7.8
19	5	0	7.4	6.9
17	5	0	3.8	4.1
14	5	0	6.6	3.6
13	5	0	1.8	1.6
11	5	0	7.2	7.8
9	5	0	3.4	2.6
7	5	0	5.8	-6.1
5	5	0	1.5	-2.3
3	5	0	7.7	-7.9
-4	6	9	5.2	4.7
-6	6	9	5.1	4.4
-8	6	9	3.2	3.8
-10	6	9	3.5	1.6
-12	6	9	3.4	-2.5
-14	6	9	7.5	-6.3
-16	6	9	8.2	-8.1
-18	6	9	6.6	-6.9
-16	6	8	6.5	5.9
-14	6	8	14.2	13.6
-10	6	8	2.4	2.6
-8	6	8	13.2	-12.4
-6	6	8	3.9	-3.5
-4	6	8	5.8	5.2
-2	6	8	2.5	1.7
0	6	8	5.4	-5.5
2	6	8	6.4	-6.4
4	6	8	4.3	3.4
6	6	8	4.0	2.5
12	6	8	7.2	5.8
14	6	7	4.4	5.5
12	6	7	3.0	1.0
10	6	7	2.6	-2.0
6	6	7	6.2	-5.4
4	6	7	3.0	-2.4
-4	6	7	5.7	-5.8
-6	6	7	7.6	6.9
-14	6	7	6.8	7.4
-16	6	7	3.5	-0.6
-20	6	6	2.6	2.1
-16	6	6	2.3	-1.3
-12	6	6	3.8	-4.6
-10	6	6	8.0	-8.8
-8	6	6	5.9	6.5
-4	6	6	2.7	3.6
-2	6	6	2.7	-3.1
0	6	6	2.9	-3.1
2	6	6	12.0	11.6
4	6	6	8.2	7.7
6	6	6	5.2	-4.9
8	6	6	8.2	-7.3
12	6	6	15.0	-14.8
14	6	6	3.9	3.9
16	6	6	5.7	4.6
18	6	6	3.0	2.7
20	6	5	2.8	0.1
18	6	5	4.3	-2.7
16	6	5	9.0	-8.6
14	6	5	9.3	-9.9
12	6	5	2.8	3.0
8	6	5	3.4	2.6
6	6	5	9.8	10.1
4	6	5	8.3	8.8
2	6	5	5.4	-5.6
-2	6	5	1.9	1.7
-4	6	5	1.7	2.4
-6	6	5	4.4	-2.1
-8	6	5	2.4	0.5
-10	6	5	2.9	1.0
-12	6	5	3.7	-0.5
-16	6	5	4.2	-5.3
-18	6	5	5.2	-4.3
-20	6	5	2.9	-0.8
-22	6	5	4.8	1.6
-26	6	5	3.3	3.9
-26	6	4	4.4	-3.1
-24	6	4	3.3	-3.1
-22	6	4	4.4	4.4
-20	6	4	9.2	7.6
-18	6	4	2.7	-1.8
-14	6	4	2.7	1.9
-12	6	4	4.1	4.4
-8	6	4	5.6	-6.3
-6	6	4	2.5	-2.1
-4	6	4	2.1	3.1
-2	6	4	3.7	3.2
0	6	4	4.6	-4.6
2	6	4	7.3	-7.2
12	6	4	7.1	-8.1
14	6	4	15.0	14.6
16	6	4	14.7	14.7
18	6	4	3.9	-4.2
10	6	3	10.7	11.0
12	6	3	6.2	6.9
10	6	3	3.0	-2.9
6	6	3	2.6	-2.3
4	6	3	3.6	-2.9
0	6	3	8.5	-8.6
-2	6	3	3.1	-3.8
-6	6	3	2.9	-3.2
-8	6	3	1.7	2.7
-10	6	3	5.8	6.0
-16	6	3	2.3	2.5
-18	6	3	6.9	5.8
-20	6	3	3.2	4.4
-24	6	2	3.8	3.8
-22	6	2	5.6	-5.2
-20	6	2	9.6	-8.2
-18	6	2	5.6	-5.2
-16	6	2	3.8	3.5
-14	6	2	6.5	-7.2
-12	6	2	6.5	-7.2
-10	6	2	19.5	-19.0
-8	6	2	2.4	2.2
-6	6	2	7.9	8.3
-4	6	2	1.2	0.9
-2	6	2	19.2	21.5
0	6	2	6.8	7.5
2	6	2	11.9	-12.9
4	6	2	2.0	0.7
6	6	2	2.0	-1.8
8	6	2	1.9	-1.9
14	6	2	2.8	0.7
16	6	2	2.6	-3.0
18	6	2	3.0	-2.9
20	6	2	3.6	-3.5
22	6	2	4.1	-3.9
24	6	2	4.7	3.7
16	6	1	3.7	0.3
14	6	1	7.7	-8.4
10	6	1	5.6	-5.6
8	6	1	6.3	-5.9
6	6	1	5.3	-6.0
2	6	1	13.2	14.4
0	6	1	13.7	20.6
-2	6	1	6.9	8.3
-4	6	1	1.7	2.4
-6	6	1	3.3	-3.0
-8	6	1	7.7	-7.3
-10	6	1	9.2	-8.4
-12	6	1	6.8	-6.4
-14	6	1	2.6	2.6
-16	6	1	4.5	5.1
-18	6	1	3.5	-3.6
-20	6	1	1.1	-3.4
-22	6	0	3.8	2.8
26	6	0	3.9	0.1
20	6	0	3.4	0.1
18	6	0	2.8	-1.5
16	6	0	2.7	0.6
14	6	0	4.4	3.2
12	6	0	4.1	-4.8
10	6	0	7.3	7.1
8	6	0	12.9	12.6
6	6	0	3.3	-3.1
4	6	0	15.2	15.2
1	7	11	5.1	-3.8
-3	7	11	2.7	0.1
-5	7	11	3.5	-0.5
-7	7	11	3.1	-3.6
-11	7	11	4.0	1.1
-15	7	11	4.1	4.4
-17	7	11	3.8	3.3
-17	7	10	3.7	-2.2
-13	7	10	3.1	-3.2
-9	7	10	3.8	-0.5
1	7	10	3.1	-1.5
5	7	9	3.9	2.2
3	7	9	3.5	3.9
-7	7	9	3.4	3.4
-13	7	9	1.8	-1.8
-15	7	9	4.2	-4.9
-17	7	9	10.2	-9.4
-21	7	9	4.7	-1.9
-17	7	9	4.9	-1.5
-17	7	8	7.1	-1.4
-15	7	8	3.1	-1.9
-15	7	8	9.1	-8.0
-13	7	8	3.4	-2.5
-11	7	8	3.3	2.6
-7	7	8	2.4	2.6
-5	7	8	4.1	3.8
5	7	8	5.1	-4.8
11	7	8	5.6	-3.9
13	7	8	4.4	4.7
15	7	7	4.5	3.3
13	7	7	6.8	7.5
9	7	7	4.7	-2.1
7	7	7	3.7	-4.5
3	7	7	2.3	0.9
1	7	7	3.2	2.2
-1	7	7	2.2	-0.9
-3	7	7	6.8	-6.3
-5	7	7	4.4	-3.4
-11	7	7	7.9	6.6
-15	7	7	10.7	9.5
-25	7	7	3.2	-1.8
-23	7	7	3.3	3.0
-21	7	6	3.7	-1.5
-17	7	6	3.3	-3.6
-15	7	6	6.5	-5.4
-13	7	6	3.2	2.9
-11	7	6	2.6	2.3
-7	7	6	6.7	5.7
-5	7	6	2.3	0.5
-3	7	6	7.7	-6.6
-1	7	6	4.3	-2.7
1	7	6	3.3	3.4
5	7	6	2.7	-3.1
7	7	6	3.1	-0.2
11	7	6	4.5	4.8
13	7	6	5.9	5.8
15	7	6	4.6	-4.4
17	7	6	3.4	-4.2
19	7	6	3.1	0.2
13	7	5	8.4	-8.6
9	7	5	2.9	-1.6
3	7	5	8.4	7.4
1	7	5	3.0	3.4
-3	7	5	5.1	5.6
-5	7	5	6.5	5.3
-7	7	5	3.3	-2.7
-11	7	5	5.1	-5.1
-13	7	5	4.3	-2.8
-15	7	5	3.6	0.4
-19	7	5	2.9	-1.3
-23	7	5	3.1	0.7
-21	7	4	4.6	-2.7
-13	7	4	5.7	-5.8
-11	7	4	1.9	3.2
-9	7	4	8.0	8.1
-7	7	4	2.7	-1.4
-3	7	4	2.1	2.3
-1	7	4	5.0	-5.9
1	7	4	2.4	-2.3
3	7	4	4.2	-3.5
5	7	4	4.4	-3.7
7	7	4	6.8	5.4
9	7	4	2.7	2.4
11	7	4	3.8	2.5
13	7	4	5.1	3.5
15	7	4	5.5	-5.2
17	7	4	6.1	-4.4
19	7	3	3.6	-2.4
17	7	3	2.9	1.8
15	7	3	9.9	8.6
13	7	3	4.6	3.5
11	7	3	2.1	2.7
9	7	3	1.9	-0.9
7	7	3	2.8	-2.6
5	7	3	2.1	-1.3
3	7	3	4.5	-4.3
-1	7	3	11.3	-11.9
-3	7	3	5.4	-5.6
-5	7	3	3.7	3.8
-7	7	3	5.6	5.0
-9	7	3	5.3	5.6
-11	7	3	2.1	-1.9
-13	7	3	5.6	1.7
-17	7	3	5.6	4.8
-19	7	3	3.7	-1.2
-23	7	3	3.2	-1.9
-25	7	2	3.2	3.5
-17	7	2	4.2	4.9
-11	7	2	2.1	5.0
-9	7	2	4.6	-4.0
-5	7	2	16.3	-17.3
-3	7	2	17.4	18.8
-1	7	2	1.6	2.0
5	7	2	1.7	2.3
7	7	2	4.5	4.0
9	7	2	7.0	-6.8
11	7	2	3.2	-2.1
13	7	2	5.4	-4.3
15	7	2	6.4	-5.9
17	7	2	3.9	-3.7
19	7	1	4.2	-4.9
17	7	1	2.9	-3.0
11	7	1	7.0	-7.0
9	7	1	3.4	-3.5
7	7	1	2.8	3.1
5	7	1	7.9	12.3
1	7	1	2.1	-3.7
-3	7	1	2.0	-1.7
-5	7	1	1.5	1.5
-7	7	1	10.8	-10.5
-9	7	1	4.2	-4.6
-11	7	1	2.2	-2.2
-13	7	1	4.6	-0.9
-17	7	1	7.7	-5.8
-19	7	1	3.0	-0.4
-23	7	1	3.7	-1.6
-25	7	1	3.6	3.5
21	7	0	3.1	2.0
19	7	0	3.2	-1.6
15	7	0	2.7	-2.0
11	7	0	7.2	7.2
9	7	0	4.2	-3.6
7	7	0	6.7	-6.6
5	7	0	1.4	-1.4

THE CRYSTAL AND MOLECULAR STRUCTURE OF PERYLENE

In 1963, Tanaka discovered a second crystalline form of perylene which he designated as the β-form. From studies of absorption and fluorescence spectra of the two polymorphs, he concluded that the previously known α-form is a ground-state-excited-state dimer. To support his arguments, he determined the crystal structure of β-perylene in two projections. The h0l projection is well resolved and was refined to an R-value of 17%. The y-coordinates were derived by assuming that the molecule is planar and has a structure similar to the α-form. Because there is serious overlap in the 0kl projection, the y-parameters were not refined. The R-value for this zone was 27%. In view of the current interest in molecules containing bonds with extreme π-bond orders, it seemed worth-while to extend Tanaka's study to three dimensions.

The crystal structure of α-perylene was first established from projections along two axes by Donaldson, Robertson and White in 1953. Their measurement of 1·50±0·03 Å for the length of the peri bonds was in very good agreement with Coulson's (1951) theoretical prediction of 1·50 Å. Camerman and Trotter (1964) have made a three-dimensional study of α-perylene using counter data. They report the value of 1·471±0·006 Å for the length of the long bonds and state that the molecule is significantly

distorted from planarity.

There are no other detailed analyses of perylene itself in the literature, but the molecule forms donor-acceptor complexes with a wide variety of acceptor molecules including fluoranil and pyromellitic dianhydride. The crystal structures of the π-molecular complexes of perylene with these two compounds have been determined (Hanson, 1963; Boeyens and Herbstein, 1965).

The two polymorphs exhibit fluorescence when excited under ultra-violet light. This provides an easy method for distinguishing between them, since the fluorescence from the α-form is red and that from the β-form is green.

2.1. EXPERIMENTAL

There were a few crystals of the β-form in the sample of analytical grade perylene obtained from Koch-Light Laboratories. Since these were not suitable for single crystal studies, they were set aside to be used as seed crystals. When portions of the sample were recrystallized from benzene and from petroleum ether, the first "crop" consisted mainly of the α-form. If the supernatant liquid was decanted and seeded with crystals of the β-form, it yielded a good crop of very thin hexagonal plates that were too brittle to be cut. However, it was possible to grow very large crystals by allowing benzene solution to evaporate slowly for several months. Crystals grew

in this manner were cut to the shape of a uniform rod and used to obtain cell dimensions and intensity data.

2.1.1. CRYSTAL DATA

Formula	$C_{20}H_{12}$	F.W.	252.9
System	monoclinic		
Lattice constants	$a = 9.77_7$ Å		
	$b = 5.90_4$		
	$c = 10.58_9$		
	$\beta = 96.75°$		
Absent Spectra	h0ℓ if ℓ odd		
	0k0 if k odd		
Space group	$P2_1/c$		
Volume	607.0 Å^3		
Density(obs.)	1.38 gm/cc		
Molecules/cell	2		
Density(calc.)	1.380 gm/cc		
Linear absorption coefficient μ,		0.920 cm^{-1}	
(Mo Kα; $= 0.7107$ Å)			

Since there are two molecules per unit cell, the centre of the molecule must lie on a centre of inversion.

The cell dimensions listed here have been measured from precession and Weissenberg photographs and have been confirmed by checking reciprocal lattice spacings of high angle reflections on the diffractometer. The length of the a-axis is considerably shorter than Tanaka's value

of 11·27 Å but the pattern of intensities is in agreement
with the reflection data quoted in his paper.

2.1.2. REFLECTION DATA

Reflection data were obtained on a Hilger-Watts
linear diffractometer using Mo Kα radiation. The
diffractometer is equipped with SrO-ZrO$_2$ balanced filters
and a scintillation counter. Two crystals were used.
Data from reciprocal lattice nets h0ℓ to h4ℓ were
collected on one crystal and data from nets h5ℓ to h7ℓ
were collected on the second. After Lorentz-polarisation
corrections had been applied, the scale of the observed
structure amplitudes was approximately twice the absolute
scale. All data were included in the refinement. There
are no "unobserved" planes because reflections with
negative net counts are given an intensity of +1 by the data
processing program.

2.2. REFINEMENT OF THE STRUCTURE

Although the cell dimensions determined in the
present study were substantially different from those
measured by Tanaka, the intensities of the reflections
in the h0ℓ zone agreed with the values quoted in Tanaka's
paper. It seemed reasonable to use his coordinates as
the starting point for the refinement of the structure.

When the "minimum residual" method of Bhuiya and

Shenley (1943) was applied to the unique axis projection of the R-value fell from 37% to 16% in eight cycles. Further x- and z-coordinates from this projection were combined with Tanaka's calculated y-coordinates and used to compute structure factors for the five reciprocal lattice nets, h0ℓ to h4ℓ. The initial R-value was 54%, but this was reduced to 21·5% after three cycles of Fourier refinement. After termination-of-series corrections had been applied to the atomic parameters, refinement was continued by the method of least squares. Three isotropic least-squares calculations with unit weights improved the R-value to 18·9%. At this point, a weighting function of the form,

$$w = 1-\exp(-2\sin^2\theta/\lambda^2),$$

was applied. R was reduced to 15·0% by two further isotropic calculations but was improved by only 0·5% when the temperature factors of the carbon atoms were allowed to refine anisotropically. When hydrogen atoms were included in the structure-factor calculations, R fell to 13·0% and dropped to 12·7% after two cycles of anisotropic refinement.

Data from layers h5ℓ to h7ℓ were included at this point. Three full-matrix least-squares cycles were calculated to refine the scale factor between the two batches of data. In order to avoid a singularity in the matrix, the U_{22} temperature parameters were held constant

The R-value was 16·4% for 1805 reflections.

The unweighted structure factors were analysed as a function of $\sin\theta/\lambda$, the index of the reciprocal lattice layer and the magnitude of F_{obs} as shown in Table 11. The weighting scheme devised from this examination of the data had the following form:

if $\sin^2\theta/\lambda^2 \leqslant 0\cdot16$, then $w = (\sin^2\theta/\lambda^2)/0\cdot16$;

if $|F_{obs}| \geqslant 7\cdot0$, then $w = 7/|F_{obs}|$,

Planes with $|F_{calc}| \leqslant 1/3\ |F_{obs}|$ were considered to be unreliably phased and were given a weight of zero.

A separate analysis of the weak reflections showed that R was over 200% for reflections with $|F_{obs}| < 0\cdot5$ electrons and over 80% for reflections with $0\cdot5 \leqslant |F_{obs}| \leqslant 1\cdot0$. Most of the reflections with structure amplitudes smaller than one electron were among those that had been given an intensity of one count per minute by the data processing program because the net count was negative. It is therefore surprising to find that $|F_{calc}|$ is larger than $|F_{obs}|$ for nearly all of them. This may indicate that there is some systematic error in the measurement of the weak reflections. In order to investigate this point it will be necessary to alter the programs and to process the data again. As a temporary expedient the 488 planes with $|F_{obs}| < 1\cdot0$ were excluded from the refinement. Of the remaining 1317 planes, 126 had been given a weight of zero. The R-value was 13·8% and $\Sigma w\Delta^2$ was 498·31. After

Table 11

β-Porylones   Analysis of Observed and Calculated
Structure Amplitudes for Reflections with $F_o \not> 1 \cdot 0$

As a function of $|F_{obs}|$

	$\Sigma |F_o|$	$\Sigma |F_d|$	$\Sigma |\Delta|$	N	R	$\bar{\Delta}$
2	930·90	823·96	196·50	933	0·533	0·53
3	643·56	547·49	172·37	262	0·268	0·66
4	488·46	461·19	80·93	141	0·166	0·57
8	1548·57	1534·66	153·33	273	0·099	0·56
16	1352·16	1297·64	97·74	123	0·072	6·79
33	1386·67	1355·39	73·08	64	0·053	1·14
111	381·81	391·05	26·56	9	0·070	2·95

As a function of $\sin\theta/\lambda$

·20	491·51	494·32	51·01	32	0·104	1·59
·40	2170·07	2089·89	234·40	279	0·108	0·84
·50	1469·36	1489·22	150·42	298	0·102	0·50
·60	1169·82	1133·33	196·38	441	0·168	0·44
·70	962·06	887·18	262·68	490	0·272	0·54
·80	406·60	286·39	173·66	228	0·425	0·76
1·00	57·71	31·05	32·58	37	0·564	0·88

As a function of reciprocal lattice index

0	939·05	930·39	99·06	140	0·105	0·71
1	1512·15	1489·49	163·62	260	0·108	0·63
2	1393·97	1351·83	165·52	262	0·119	0·63
3	782·22	740·37	131·03	254	0·168	0·52
4	777·81	752·31	125·58	237	0·162	0·53
5	618·68	595·58	140·14	240	0·226	0·58
6	356·25	282·97	129·42	208	0·363	0·62
7	352·00	258·44	146·14	204	0·415	0·72

three further cycles of least squares, R was 13·3%,
$\Sigma w\Delta^2$ was 460·56 and the refinement of the carbon atoms had
converged.

2.3. INTERIM RESULTS

Atomic coordinates are listed in Table 12 with their
standard deviations.   Temperature parameters are shown
in Table 13.   The hydrogen atoms were placed by a computer
program and have not been refined;   their temperature factors
are probably slightly low.

Table 14 is a list of bond lengths and bond angles
derived from the parameters of the carbon atoms.   All
C-H bonds are 1·09 Å long.

The perylene molecule is remarkably planar as is
shown in Table 15.   The equation of the "best" plane
through the whole molecule is

$$0·2633X - 0·5793Y - 0·7714Z = 0 ,$$

where X,Y and Z are orthogonal axes defined by the
equations

$$X = ax + czcos\beta,$$

$$Y = by,$$

$$Z = czsin\beta .$$

The root mean square deviation from this plane ($3·4 \times 10^{-3}$ Å)
is less than the average estimated standard deviation of
atomic position.   A more severe test of planarity is
provided by the magnitude of the deviations from a plane

Table 12

β -Perylene: Final Fractional Atomic
Coordinates.   Standard deviations are given
as units in the last place.

C(1)	0.05911(30)	-0.16889(61)	0.08899(27)
C(2)	0.11785(36)	-0.32806(75)	0.17450(35)
C(3)	0.26034(33)	-0.32329(70)	0.21807(34)
C(4)	0.34271(31)	-0.16218(67)	0.17535(29)
C(5)	0.37200(36)	0.17590(68)	0.04415(33)
C(6)	0.31745(31)	0.33318(56)	-0.03908(27)
C(7)	0.17620(30)	0.33403(57)	-0.08412(28)
C(8)	0.08948(35)	0.17241(68)	-0.04359(34)
C(9)	0.14413(37)	0.00226(78)	0.04423(37)
C(10)	0.28757(39)	0.00439(76)	0.08855(37)

Calculated poitions of hydrogen atoms (not refined).

H(11)	0.0531	-0.4611	0.2082
H(12)	0.3032	-0.4486	0.2876
H(13)	0.4531	0.1654	0.2080
H(14)	0.4065	0.0082	0.0767
H(15)	0.3844	0.4609	-0.0748
H(16)	0.1347	0.4640	-0.1514

Table 13

Anisotropic Temperature Parameters of Carbon Atoms.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	0.0307	0.0377	0.0312	0.0001	0.0104	0.0020
C(2)	0.0353	0.0551	0.0452	0.0027	-0.0001	0.0146
C(3)	0.0287	0.0520	0.0439	-0.0123	0.0072	-0.0119
C(4)	0.0294	0.0449	0.0347	-0.0181	0.0079	0.0021
C(5)	0.0402	0.0427	0.0438	-0.0021	0.0084	-0.0237
C(6)	0.0328	0.0338	0.0310	-0.0017	0.0115	0.0006
C(7)	0.0315	0.0341	0.0333	-0.0096	0.0087	0.0098
C(8)	0.0363	0.0437	0.0480	0.0077	0.0117	0.0118
C(9)	0.0352	0.0566	0.0519	0.0066	0.0105	-0.0344
C(10)	0.0436	0.0507	0.0495	0.0271	0.0068	0.0234

Table 14

β-Perylene: Bond Lengths. (Å)

Standard deviations are given as units
in the last place.

C(1)	C(2)	1.3822(54)
C(2)	C(3)	1.4154(50)
C(3)	C(4)	1.3574(54)
C(4)	C(10)	1.4093(58)
C(10)	C(5)	1.4209(59)
C(5)	C(6)	1.3516(51)
C(6)	C(7)	1.4052(44)
C(7)	C(8)	1.3781(51)
C(8)	C(9)	1.4292(60)
C(9)	C(10)	1.4256(56)
C(9)	C(1)	1.4245(56)
peri-bonds		1.4758(52)

C-H bonds are all 1.09 Å long.

Bond-Angles with their standard deviations.

C(1)	C(2)	C(3)	121.13(37)
C(2)	C(3)	C(4)	120.36(37)
C(3)	C(4)	C(10)	120.64(32)
C(4)	C(10)	C(5)	121.37(35)
C(4)	C(10)	C(9)	119.65(38)
C(9)	C(10)	C(5)	118.99(39)
C(10)	C(5)	C(6)	120.52(34)
C(5)	C(6)	C(7)	121.21(32)
C(6)	C(7)	C(8)	120.68(31)
C(7)	C(8)	C(9)	119.52(33)
C(8)	C(9)	C(10)	119.08(38)
C(8)	C(9)	C(1)	121.80(33)
C(10)	C(9)	C(1)	119.12(38)
C(9)	C(1)	C(2)	119.11(31)

Table 15

β -Perylene: Mean Planes.

Deviations are shown in Ångstroms $\times 10^{-4}$.

Plane A is the plane through the whole carbon skeleton.

Plane B is the plane through the central ring.

	A	B
C(1)	29	-8
C(2)	-1	-72
C(3)	-58	-141
C(4)	46	-14
C(5)	-45	-45
C(6)	36	70
C(7)	-16	31
C(8)	-32	-8
C(9)	20	8
C(10)	20	-4

Root mean square deviation:
34
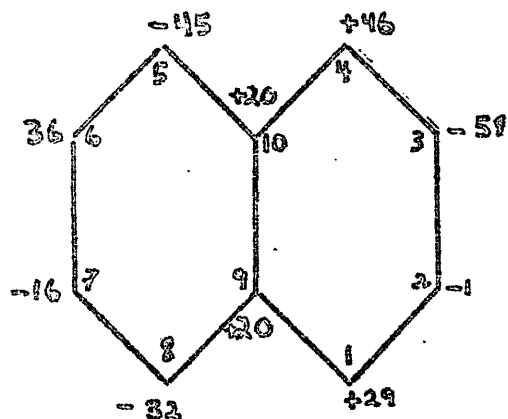
through the central ring of the molecule. Some of the atoms deviates significantly from this plane, which is defined by the equation.

$$0.2630X - 0.5773Y - 0.7730Z = 0.$$

The crystal structure of β-perylene is analogous to those of naphthalene and anthracene (Abrahams, Robertson & White, 1949 ; Sinclair, Robertson & Mathieson, 1950). The orthogonal projections shown in Figures 2 and 3 illustrate this similarity. Figure 2 is a projection of the whole unit cell on to the (100) plane. Figure 3 shows half of the projection on to (010).

It is interesting to compare the results of this analysis with theoretical predictions and with other crystallographic studies. Table 16 lists the bond lengths in β-perylene with those predicted by various theories. Table 17 summarises the results of X-ray studies on α-perylene; and Table 18 compares the dimensions of β-perylene with those of quaterrylene, naphthalene and 1,1'-binaphthyl.

The H.M.O. bond-lengths in Table 16 have been obtained by combining the π-bond orders tabulated by Coulson and Brauman (1965) with the order-length relationship suggested by Cruickshank and Sparks (1960). Bond-lengths predicted by the Pariser-Parr-Pople (P.P.P.) method and the split π orbital (S.P.O.) method were taken from a paper by Bower and Fletcher (1969). Bond-lengths given

Figure 2
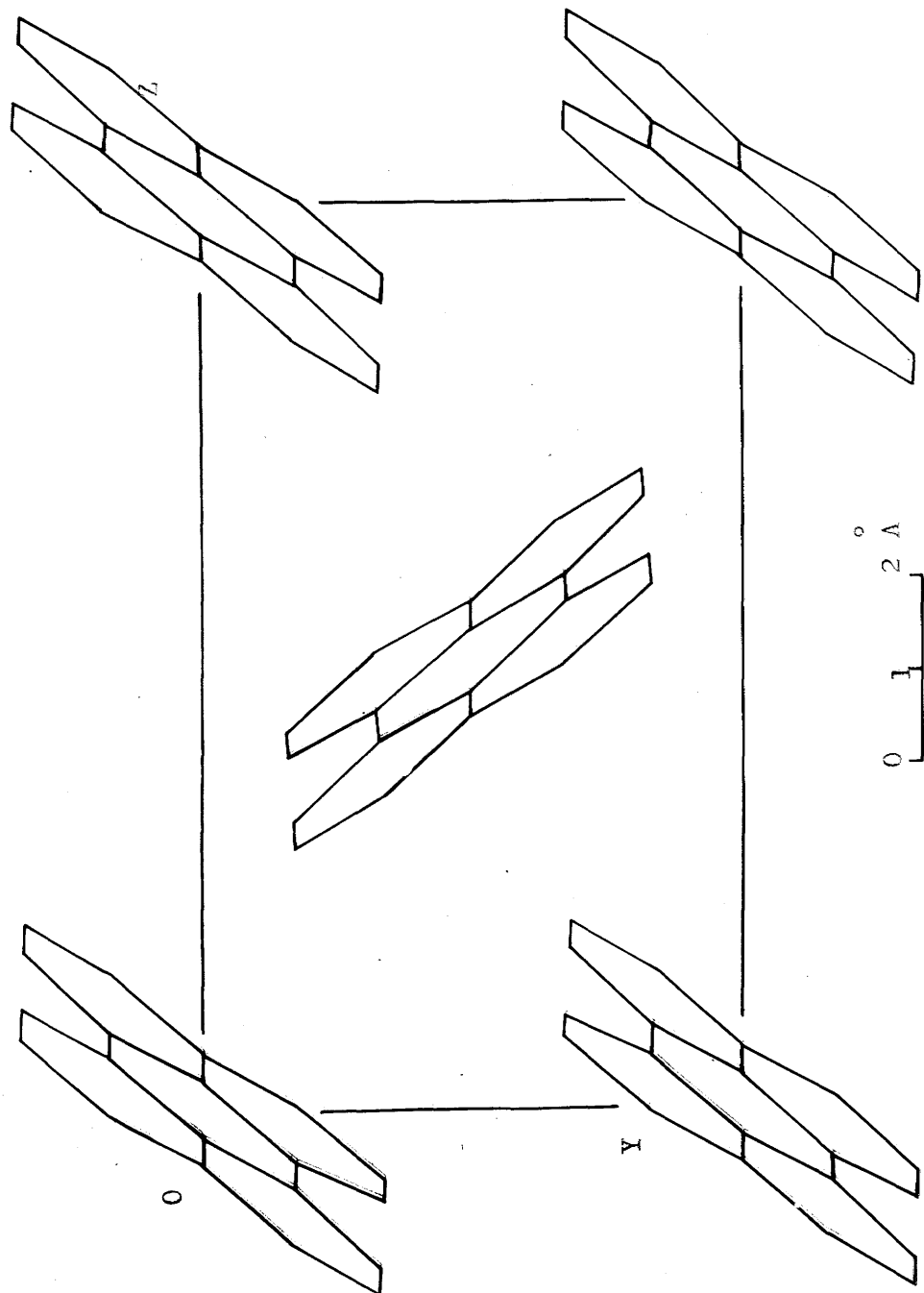
β-perylene: orthogonal projection on to (100)

Fig 3
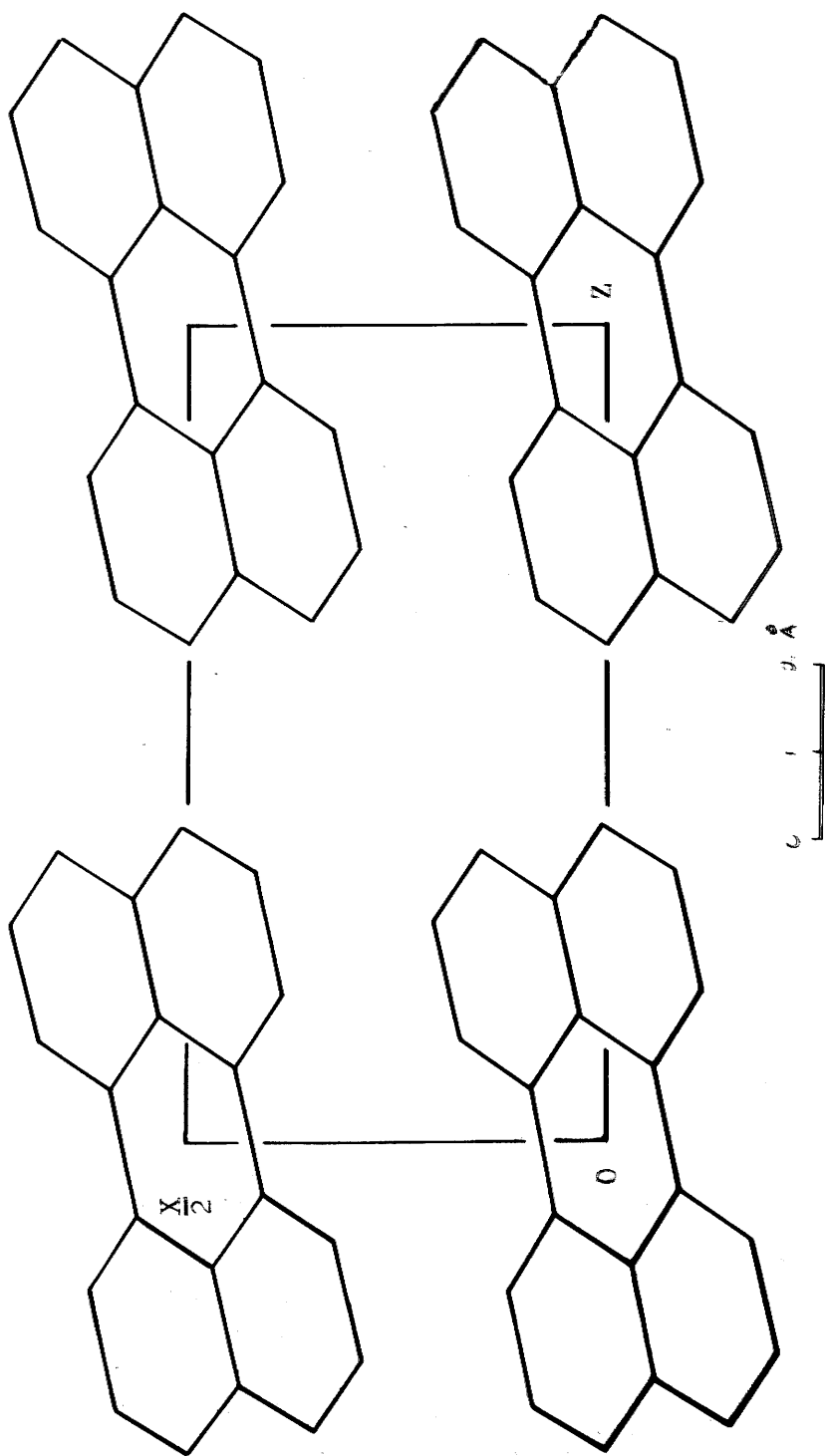
3-perylene orthogonal projection on to (010)

differences between experimental and theoretical lengths
are shown at the foot of each column. The goodness-of-fit
becomes worse as the theory becomes more elegant. The
length of the peri-bonds is the main source of disagreement
but even when this bond is not considered, the same
general trend is observed. The relative π-bond orders
predicted by molecular orbital theory follow the observed
variations in bond length very closely.

The more elegant P.P.P. and S.P.O. calculations
predict that the central bond in the naphthalenic residue
should be shorter than the two outer bonds but the reverse
situation is observed in the experiment. The 9-10 bond
in β-perylene is longer than either the 2-3 bond or the
6-7 bond. Although these differences are not large
enough to be significant, they are probably real since they
are observed in 1,1'-binaphthyl and in the complexes of
perylene listed in Table 17.

The dimensions of the perylene molecule obtained
from various three-dimensional X-Ray studies are shown
in Table 17. The average standard deviation of bond
length appears at the top of each column; the root mean
square difference is shown at the bottom. The perylene
molecule is necessarily centrosymmetric in β-perylene, in
the perylene-fluoranil complex (Hanson, 1963), and in the
perylene-PMDA complex (Boeyens and Herbstein, 1965)
but not in α-perylene (Camerman and Trotter, 1964). Re-

β -Perylene: Bond Length Comparisons

Table 16

		β-perylene	V.B.	H.M.O.	P.P.P.	S.P.O.
C(1)	C(2)	1.380	1.375	1.395	1.381	1.375
C(2)	C(3)	1.410	1.421	1.399	1.413	1.419
C(3)	C(4)	1.355	1.375	1.378	1.375	1.371
C(4)	C(10)	1.415	1.421	1.420	1.421	1.425
C(9)	C(10)	1.426	1.421	1.427	1.404	1.397
C(9)	C(1)	1.427	1.421	1.426	1.422	1.426
peri-bonds		1.476	1.477	1.457	1.456	1.462

Root mean square difference: peri-bonds included.
                                 0.010   0.013   0.014   0.015

Root mean square difference: peri-bonds excluded.
                                 0.010   0.011   0.012   0.013

Table 17

		β-perylene $\sigma = 0.005$	perylene-fluoranil $\sigma = 0.005$	perylene PMDA $\sigma = 0.010$	α-perylene $\sigma = 0.011$
C(1)	C(2)	1.382	1.380	1.393	1.381
C(2)	C(3)	1.415	1.419	1.407	1.401
C(3)	C(4)	1.357	1.350	1.364	1.360
C(4)	C(10)	1.409	1.406	1.366	1.412
C(10)	C(5)	1.421	1.415	1.445	1.396
C(5)	C(6)	1.352	1.364	1.366	1.362
C(6)	C(7)	1.405	1.401	1.383	1.405
C(7)	C(8)	1.378	1.379	1.381	1.384
C(8)	C(9)	1.429	1.427	1.407	1.427
C(9)	C(10)	1.426	1.434	1.443	1.434
C(9)	C(1)	1.424	1.431	1.423	1.420
peri-bonds		1.476	1.473	1.493	1.473

Root mean square difference:
                                 0.005   0.019   0.009

Table 18

		β-perylene	quaterrylene	naphthalene	1,1'- binaphthyl
C(1)	C(2)	1.380	1.384	1.364	1.364
C(2)	C(3)	1.410	1.425	1.415	1.404
C(3)	C(4)	1.355	1.374	1.364	1.355
C(4)	C(10)	1.415	1.392	1.421	1.413
C(9)	C(10)	1.426	1.431	1.418	1.416
C(9)	C(1)	1.427	1.403	1.421	1.433
peri-bonds		1.476	1.527		1.475

Root mean square difference including peri-bonds:

| 0.025 | 0.009 | 0.008 |

Root mean square difference excluding peri-bonds

| 0.015 | 0.009 | 0.008 |

bond lengths listed for α-perylene are the results of
Mason's (private communication) refinement of the data
published by Camerman and Trotter.   It should be noted
that the average standard deviation reported here is
approximately twice the estimate quoted in the original
paper, despite a much lower R-value.

In Table 18, β-perylene is compared with quaterrylene
(Shrivastava and Speakman, 1960), naphthalene (Cruickshank
and Sparks, 1960), and 1,1'binaphthyl.   The root mean
square differences between the dimensions of β-perylene
and those of the other molecules are small except in the
case of quaterrylene.   This is likely to be a reflection of
the fact that the structure of quaterrylene was determined
from two projections;   it does not necessarily imply a
real difference in molecular structure.

DISCUSSION

Although the analyses of these structures are not
yet complete, the precision of the measured bond-lengths
(0·003 to 0·005 Å) is sufficient to allow a certain amount
of discussion.

Cruickshank (1956) has shown that when libration
corrections are neglected, the apparent bond lengths are
systematically shorter than their true values.   In 1,1'-
binaphthyl, the thermal vibrations are markedly anisotropic
and libration corrections have not yet been applied.   The
bond that is likely to be most affected by these corrections

is the 5-6 bond.   In the perylene structure, libration
corrections will probably be very small since there is
little anistropy in the thermal parameters.   In the
present state of the analysis, the molecule appears to
have its maximum vibration amplitude almost perpendicular
to the plane of the ring.   This unlikely situation can
be explained in terms of a poor scale factor between
the two batches of data.

The dimensions of 1,1'-binaphthyl and β-perylene
are very similar.   The root mean square difference
is only 0·008 when "chemically equivalent" bonds are
averaged.   If the individual bond lengths are compared,
the root mean square difference increases to 0·011.
However, none of the differences between corresponding
bond-lengths is significant.

The lengths of the $sp_2 \cdot sp_2$ bonds reported in this
study are 1·473±0·005 Å in 1,1'-binaphthyl and 1·476±0·008 Å
in β-perylene.   These lengths are in good agreement with
the value of 1·472±0·005 Å in the perylene-fluoranil
complex and the value of 1·472±0·010 Å in α-perylene (Mason's
refinement) but they are in disagreement with the values
of 1·53 Å in quaterrylene, 1·493±0·010 Å in the perylene-
PMDA complex, and 1·493±0·015 Å from electron diffraction
measurements of perylene in the vapour phase (Trætteberg,
1965).

The peri-bond length quoted for quaterrylene is
the average value of six independent bond lengths and
would be expected to be very accurate in spite of the
fact that the structure was determined from two projections.
The discrepancy between this value and the 1·48 Å single
bond length predicted by Dewar and Schmeising (1959) has
been attributed to a stretching of the linking bonds
caused by steric repulsions between the hydrogen atoms
in the ortho-positions.   However, recent studies suggest
that hydrogen contacts of this type are "softer" than
had been supposed.   Bailey and Mason (1963) have reported
H...H contacts of 1·85 Å in 1,8-bisdehydro-[14]-annulene.
Hirshfeld, Rabinovich and Hodgman (1965) have found that
the mean separation of the inner hydrogens in [16]-annulene
is 1·97 Å.   There is no apparent deformation of C-C
bonds in either structure.   Agreement between the lengths
of the linking bonds in the two molecules in the present
study would seem to confirm that H...H contacts of this
type do not cause significant lengthening of C-C bonds.

Differences between the lengths quoted in this work
and those observed in the perylene-PMDA complex are,
in general, quite large; but certain experimental details
in the latter study should be considered.   Thermal
vibration amplitudes in the complex are large and anisotropic;
limited computer capacity made it necessary to refine the
parameters of only 6 atoms in each least-squares cycle;
the refinement was terminated before convergence.

It seems likely that the standard deviations have been underestimated.

The electron diffraction study is difficult to evaluate. Perylene is a very large molecule to be investigated by this method, and certain simplifying assumptions must be made. Traetteberg has assumed that the naphthalenic residues in perylene have the same molecular dimensions as naphthalene itself and has determined the lengths of the peri-bonds by subtracting the molecular intensity function of naphthalene from the radial distribution function for perylene. Results obtained from a calculation of this type are extremely sensitive to changes in the model. On the other hand, it is possible that there are real differences in the dimensions of the molecule in the vapour phase (300°C) and in the solid.

It is interesting to note that the trend in π-bond orders predicted by the Huckel molecular orbital method is very close to the trend in the bond lengths observed in this study. (See Figure 4). This suggests that the goodness-of-fit will probably improve as more accurate bond-length determinations become available and better order-length curves are devised. The most serious discrepancy between the experimental bond lengths in β-perylene and the predictions of P.P.P. and S.P.O. calculations is the relative π-bond order of the central

Figure 4
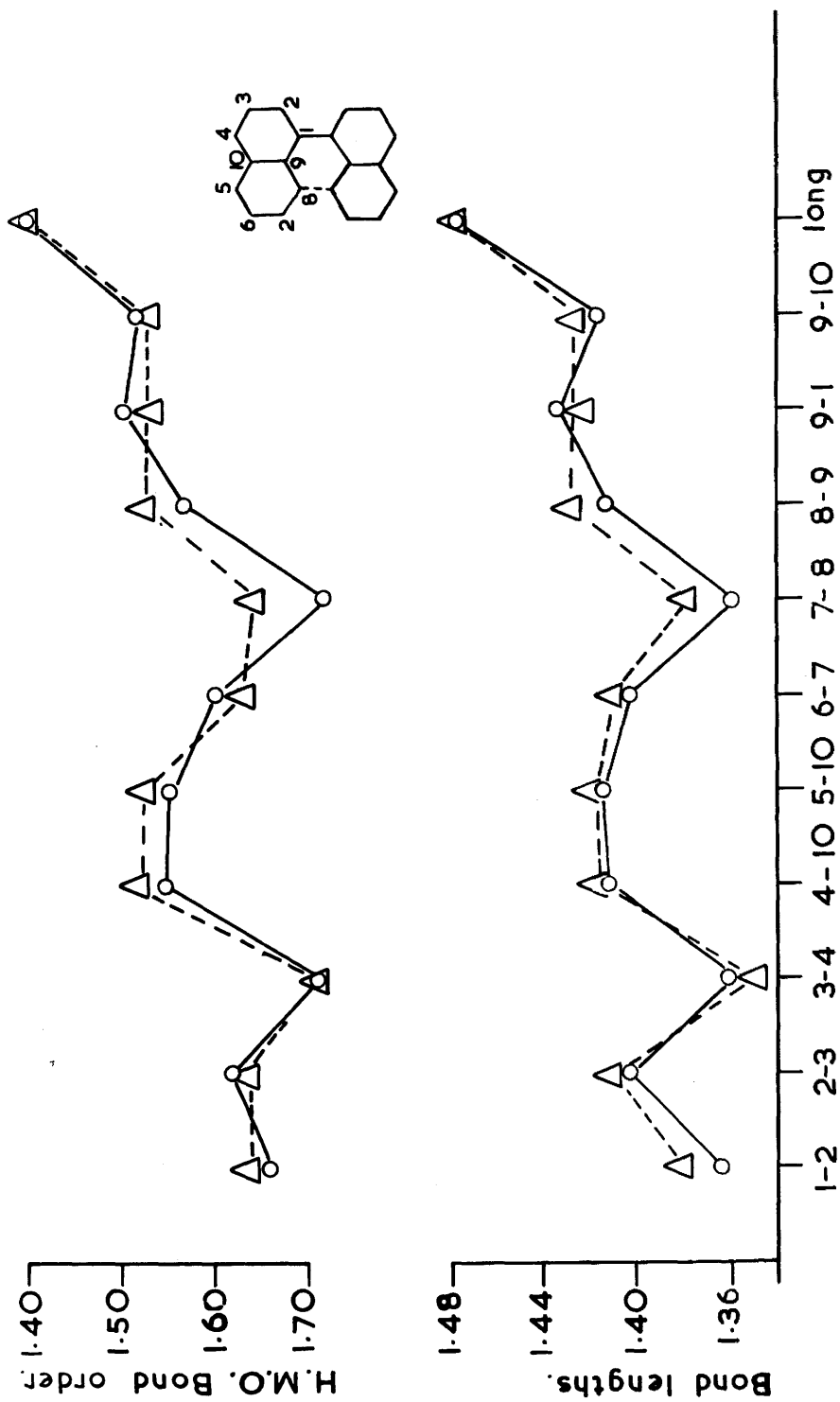
Trend in π – bond order and observed bond length

s-perylene –o– 1,1'–binaphthyl ....Δ........

bond of the naphthalenic residue. According to these two theories, this bond should be shorter than the outer bonds, but the reverse situation is observed in the four structures involving the perylene molecule and in the structure of 1,1'-binaphthyl.

The agreement between the dimensions of the two polymorphs of perylene and between perylene and 1,1'-binaphthyl is better than one would expect from the size of the standard deviations estimated for the individual structure determinations. None of the differences between these molecules is significant at the level of precision of the analyses. The dimensions of the naphthalenic residues do not differ, significantly, from those of naphthalene itself.

CONCLUSIONS

The results of the present work show that the bond lengths in the naphthalenic residues of 1,1'-binaphthyl and β-perylene are the same, within the experimental error, as those of naphthalene itself. This can be interpreted as direct evidence that the aromatic character of the perylene molecule is localised in the naphthalenic residues.

The average value for the sp_2-sp_2 single bond lengths in these two structures is 1.475 ± 0.005 Å.

β-Perylene Structure Factor Tables

H	K	L	|Fo|	Fc
12	0	4	7.3	6.7
12	0	2	1.7	-1.0
12	0	-2	2.2	-2.0
11	0	0	3.4	2.9
11	0	4	2.2	-2.2
10	0	6	1.0	0.8
10	0	4	3.8	4.3
10	0	2	2.5	3.3
10	0	0	1.6	-3.6
10	0	-2	2.6	3.1
10	0	-4	6.2	-6.3
10	0	-6	2.8	3.3
10	0	-10	2.8	-3.1
9	0	-10	1.4	-0.9
9	0	-8	7.2	7.7
9	0	-6	29.2	29.8
9	0	-4	10.1	9.2
9	0	-2	2.8	2.5
9	0	0	5.1	-6.1
9	0	2	14.8	-15.8
9	0	4	2.1	-2.3
9	0	6	1.2	-0.1
9	0	8	6.7	-6.6
9	0	10	4.4	-4.8
8	0	10	6.8	-6.6
8	0	6	1.7	2.2
8	0	4	5.3	-6.8
8	0	2	8.2	-10.1
8	0	-2	4.3	-4.0
8	0	-4	21.5	20.9
8	0	-6	15.9	16.0
8	0	-8	1.9	-1.6
8	0	-10	1.0	-0.7
8	0	-12	4.7	-5.0
7	0	-12	1.8	0.7
7	0	-6	8.8	-9.0
7	0	-2	9.2	-9.0
7	0	2	3.4	4.0
7	0	4	1.1	1.3
7	0	6	2.8	2.8
7	0	12	1.0	1.1
6	0	8	6.4	-6.6
6	0	6	1.9	2.0
6	0	4	7.9	-7.8
6	0	2	13.2	9.2
6	0	-2	3.5	3.3
6	0	-4	3.1	3.9
6	0	-6	6.9	7.6
6	0	-12	1.6	0.7
6	0	-14	2.3	-2.3
5	0	-14	8.2	7.7
5	0	-10	1.0	1.1
5	0	-8	16.0	-15.2
5	0	-6	12.0	-11.6
5	0	-4	4.9	2.9
5	0	-2	1.0	2.6
5	0	0	36.1	-31.2
5	0	2	7.8	-4.8
5	0	4	6.6	-6.2
5	0	6	5.6	4.7
5	0	8	22.3	22.1
5	0	10	19.0	19.1
4	0	8	26.1	26.7
4	0	4	3.5	4.2
4	0	2	47.7	-46.2
4	0	0	40.7	-40.8
4	0	-2	1.2	-1.4
4	0	-4	8.8	-6.8
4	0	-6	30.2	-26.8
4	0	-8	6.5	-6.1
4	0	-12	6.8	6.4
4	0	-14	12.4	12.2
3	0	-12	4.0	3.1
3	0	-10	4.4	-3.9
3	0	-8	4.5	3.4
3	0	-4	5.4	5.0
3	0	-2	17.3	17.5
3	0	0	22.2	23.8
3	0	2	13.0	-10.6
3	0	4	2.5	1.5
3	0	6	2.0	0.3
3	0	8	6.1	-6.4
3	0	10	2.5	6.2
3	0	12	1.8	-1.4
2	0	14	1.1	-0.5
2	0	10	2.0	-2.7
2	0	8	1.7	1.6
2	0	6	6.3	6.2
2	0	4	1.6	2.6
2	0	2	16.4	15.2
2	0	0	46.4	-46.4
2	0	-2	5.9	-8.4
2	0	-6	3.8	4.2
2	0	-8	5.5	4.9
1	0	-12	2.1	2.1
1	0	-10	2.7	-3.4
1	0	-8	8.3	-7.5
1	0	-6	3.4	3.7
1	0	-4	30.2	-29.2
1	0	2	24.7	-24.9
1	0	4	13.3	11.3
1	0	6	16.1	-16.6
1	0	10	3.5	3.3
1	0	14	2.1	-2.5
0	0	14	5.1	-5.0
0	0	12	1.7	-0.7
0	0	10	3.8	-3.5
0	0	8	25.5	-26.3
0	0	6	15.3	-16.2
0	0	4	2.9	2.8
12	1	4	4.3	4.8
12	1	3	1.7	1.0
12	1	0	1.2	0.2
12	1	-1	4.3	-3.9
11	1	0	4.0	-3.9
11	1	1	1.9	2.0
11	1	2	1.4	-0.7
10	1	5	2.0	-2.0
10	1	4	1.8	2.4
10	1	3	2.9	2.7
10	1	1	1.1	-0.5
10	1	0	5.5	5.4
10	1	-1	4.3	-4.7
10	1	-2	3.2	3.5
10	1	-3	4.1	-4.8
10	1	-4	5.4	-5.3
10	1	-5	2.5	-1.5
10	1	-7	2.5	2.5
10	1	-8	8.7	-8.5
10	1	-9	6.9	7.1
10	1	-10	3.3	-3.4
10	1	-10	2.1	-1.0
9	1	-9	4.5	4.8
9	1	-8	11.3	-12.1
9	1	-7	8.1	8.0
9	1	-5	6.8	6.3
9	1	-4	4.3	5.7
9	1	-3	1.2	-0.2
9	1	-2	2.6	-2.5
9	1	-1	5.6	-6.3
9	1	0	7.9	8.8
9	1	1	4.1	-4.7
9	1	3	2.8	-2.9
9	1	4	1.9	-2.2
9	1	5	1.0	0.8
9	1	6	4.8	4.7
9	1	7	3.5	-3.2
9	1	8	5.2	5.2
9	1	9	2.6	-2.6
9	1	9	1.1	-1.8
8	1	6	5.1	-5.5
8	1	5	5.0	-5.6
8	1	4	8.6	-9.8
8	1	3	2.8	-3.5
8	1	2	1.0	-1.2
8	1	0	2.0	1.2
8	1	-1	5.7	5.9
8	1	-2	13.4	12.9
8	1	-3	19.2	20.0
8	1	-4	22.9	22.9
8	1	-5	8.5	8.7
8	1	-7	1.1	0.8
8	1	-8	1.0	1.2
8	1	-9	3.0	-3.8
8	1	-10	3.1	-2.9
8	1	-11	4.2	-4.4
8	1	-12	2.7	-3.4
8	1	-10	3.6	-4.3
7	1	-8	1.4	-1.3
7	1	-5	1.3	-2.1
7	1	-4	2.2	2.0
7	1	-3	8.4	7.7
7	1	-2	7.7	8.0
7	1	-1	11.6	9.9
7	1	0	5.7	-4.6
7	1	1	6.6	-5.4
7	1	4	2.8	-2.5
7	1	5	5.4	-5.5
7	1	6	3.1	2.7
7	1	7	3.8	-3.9
7	1	8	1.1	0.7
7	1	9	2.0	2.4
7	1	10	1.8	0.8
6	1	11	1.1	-0.6
6	1	6	6.2	-5.8
6	1	5	11.2	11.7
6	1	3	1.1	-0.1
6	1	2	5.1	5.1
6	1	1	5.3	-5.6
6	1	0	4.1	-5.9
6	1	-1	3.1	-3.1
6	1	-2	5.2	3.9
6	1	-3	13.6	-11.6
6	1	-4	1.0	-2.5
6	1	-5	3.5	4.0
6	1	-7	3.3	3.0
6	1	-8	2.0	0.0
6	1	-9	2.1	-1.9
6	1	-10	5.4	5.1
6	1	-11	2.1	-2.4
6	1	-12	1.6	-0.3
6	1	-13	1.6	-0.9
6	1	-13	2.2	1.5
5	1	-12	1.0	-0.5
5	1	-11	3.3	-3.6
5	1	-10	4.1	4.1
5	1	-9	6.9	-6.7
5	1	-8	10.4	9.8
5	1	-7	6.1	-5.2
5	1	-6	1.6	-1.5
5	1	-5	1.4	0.4
5	1	-4	7.1	7.2
5	1	-3	5.5	-4.9
5	1	-2	26.2	26.2
5	1	-1	21.1	-17.8
5	1	0	19.3	18.5
5	1	1	1.2	0.6
5	1	2	2.2	-2.3
5	1	3	1.3	1.8
5	1	4	2.2	1.1
5	1	5	16.5	16.5
5	1	6	23.4	-24.8
5	1	7	13.4	14.1
5	1	8	6.2	-7.2
5	1	9	2.3	2.4
5	1	11	2.1	-1.7
5	1	12	1.5	-1.5
4	1	12	3.8	4.2
4	1	11	6.6	6.6
4	1	10	12.4	12.2
4	1	9	7.6	7.2
4	1	8	6.8	-6.3
4	1	7	5.5	5.9
4	1	6	2.7	-2.7
4	1	5	5.6	-5.2
4	1	4	9.2	-7.9
4	1	3	17.2	-16.1
4	1	2	23.1	-21.1
4	1	1	10.6	-9.9
4	1	0	14.6	12.1
4	1	-1	6.8	-8.5
4	1	-2	2.6	-4.1
4	1	-3	4.1	-4.6
4	1	-4	24.0	-23.4
4	1	-5	14.8	-13.2
4	1	-6	10.4	-9.3
4	1	-7	2.0	-2.0
4	1	-8	4.7	4.8
4	1	-10	1.3	1.8
4	1	-11	7.0	7.0
4	1	-12	9.6	9.8
4	1	-13	6.7	7.0
3	1	-13	2.2	2.0
3	1	-12	6.4	6.6
3	1	-11	9.6	9.1
3	1	-10	4.6	4.7
3	1	-9	3.4	2.7
3	1	-8	2.7	-2.3
3	1	-7	2.7	-2.4
3	1	-5	5.1	-5.2
3	1	-4	13.9	-12.4
3	1	-3	20.6	-24.2
3	1	-2	5.7	-3.7
3	1	-1	8.1	9.5
3	1	0	4.5	-3.5
3	1	1	2.9	3.2
3	1	2	7.2	-6.9
3	1	3	13.7	-14.6
3	1	4	23.5	-24.1
3	1	5	10.1	-10.5
3	1	6	2.2	1.7
3	1	7	1.9	-2.6
3	1	10	6.1	6.1
3	1	11	6.2	6.7
3	1	12	7.6	7.5
3	1	13	5.1	4.6
3	1	13	1.1	1.1
2	1	12	1.0	0.7
2	1	11	3.0	-2.8
2	1	10	2.5	-2.5
2	1	8	1.5	0.5
2	1	7	5.9	-4.9
2	1	6	5.9	4.1
2	1	4	2.3	4.1
2	1	3	4.1	5.6
2	1	1	16.1	14.2
2	1	0	11.7	9.8
2	1	-1	12.1	-12.1
2	1	-2	19.6	16.8
2	1	-3	7.1	5.0
2	1	-4	6.6	-6.4
2	1	-5	9.1	6.5
2	1	-6	7.8	7.6
2	1	-7	9.1	-7.4
2	1	-8	2.4	-1.8
2	1	-10	7.9	-8.7
2	1	-11	1.5	1.2
2	1	-12	1.8	-2.0
2	1	-13	1.1	-1.1
1	1	-13	1.1	0.4
1	1	-12	3.3	3.2
1	1	-11	5.8	-5.8
1	1	-10	8.8	8.5
1	1	-9	4.1	-4.0
1	1	-8	2.3	2.0
1	1	-6	4.6	5.0
1	1	-5	11.7	11.2
1	1	-4	27.9	-27.1
1	1	-1	24.8	25.2
1	1	1	7.9	-8.7
1	1	2	29.6	-31.7
1	1	3	24.2	-23.8
1	1	4	17.7	16.0
1	1	5	18.2	-18.7
1	1	6	16.4	15.5
1	1	7	3.3	-3.3
1	1	9	1.9	1.9
1	1	10	3.5	3.5
1	1	11	2.7	-2.1
1	1	12	4.3	4.1
1	1	13	3.4	-4.1
0	1	14	2.1	2.7
0	1	13	2.3	-2.2
0	1	12	2.2	2.1
0	1	10	2.2	-2.2
0	1	9	5.1	-5.2
0	1	8	5.1	-5.2
0	1	7	7.0	-7.1
0	1	6	15.5	16.4
0	1	5	10.8	-10.3
0	1	4	4.3	-2.7
0	1	3	16.0	16.8
12	2	1	1.7	-1.9
12	2	0	1.0	-3.3
11	2	0	2.6	-3.3
11	2	3	1.5	1.7
11	2	4	2.8	-2.7
11	2	5	1.9	0.6
10	2	5	6.2	6.0
10	2	4	4.7	-4.4
10	2	3	2.2	2.2
10	2	2	1.1	-0.9
10	2	0	2.2	1.0
10	2	-1	4.5	4.9
10	2	-2	4.6	-5.1
10	2	-3	7.0	7.0
10	2	-4	1.8	-1.0
10	2	-7	1.6	0.2
10	2	-9	6.4	-4.6
10	2	-10	6.6	7.2
9	2	-10	1.3	2.0
9	2	-9	1.5	-1.6
9	2	-8	4.2	4.0
9	2	-7	1.6	1.1
9	2	-6	4.4	-3.8
9	2	-5	2.5	-2.5
9	2	-3	1.5	-0.5
9	2	-2	6.2	-6.2
9	2	-1	5.4	-5.0
9	2	1	4.4	-4.7
9	2	2	2.2	-2.2
9	2	5	3.5	3.5
9	2	7	1.8	1.7
9	2	8	3.7	3.7
9	2	8	1.8	0.8
8	2	7	2.2	-2.3
8	2	6	2.2	-2.1
8	2	5	3.3	-3.4
8	2	4	3.6	-3.7
8	2	3	5.1	4.8
8	2	1	2.5	-2.4
8	2	0	2.2	1.6
8	2	-2	10.6	10.3
8	2	-3	12.5	12.0
8	2	-4	4.2	4.2
8	2	-5	2.1	1.3
8	2	-6	3.8	-3.6
8	2	-9	2.9	-3.1
8	2	-10	2.2	-2.8
8	2	-11	3.3	-3.5
8	2	-12	1.3	-1.3
8	2	-10	1.6	0.7
7	2	-9	1.7	-1.6
7	2	-8	6.9	-7.2
7	2	-7	4.9	-5.1
7	2	-6	3.9	-4.5
7	2	-5	3.0	-2.5
7	2	-3	3.2	3.5
7	2	-2	1.9	2.3
7	2	-1	17.1	17.6
7	2	0	27.0	27.8
7	2	1	17.1	17.3
7	2	2	9.5	9.1
7	2	3	9.5	9.0
7	2	4	4.7	-4.7
7	2	5	2.4	-2.1
7	2	6	3.9	3.0
7	2	7	6.9	-7.3
7	2	8	7.4	-7.1
7	2	10	2.8	-3.5
7	2	11	1.4	-1.8
7	2	11	1.0	0.6
6	2	11	4.6	4.2
6	2	10	1.8	-1.8
6	2	7	1.1	-0.5
6	2	6	1.7	2.1
6	2	5	11.1	-11.5
6	2	4	18.0	19.0
6	2	3	25.4	-26.0
6	2	2	9.6	8.1
6	2	1	5.8	4.5
6	2	0	3.7	2.9
6	2	-2	8.4	-8.0
6	2	-3	8.6	7.5
6	2	-4	13.8	-13.2
6	2	-5	10.4	9.8
6	2	-6	5.9	-4.9
6	2	-8	5.2	-2.4
6	2	-9	2.3	1.3
6	2	-10	1.9	-2.3
6	2	-11	5.3	5.2
6	2	-12	3.2	-3.8
6	2	-13	1.4	2.3
5	2	-11	1.6	1.0
5	2	-10	5.5	-5.9
5	2	-6	2.1	3.0
5	2	-4	4.0	-3.3
5	2	-3	16.5	15.4
5	2	-2	6.5	-5.0
5	2	-1	3.1	-0.7
5	2	0	1.4	-0.3
5	2	1	1.1	-0.9
5	2	2	2.6	-3.0
5	2	3	5.2	-5.2
5	2	5	11.5	11.5
5	2	5	11.7	-12.0
5	2	7	9.9	9.4
5	2	7	2.7	2.6
5	2	8	3.2	-2.9

β-perylene Structure Factor Tables

H	K	L	|Fo|	Fc
5	2	10	1.6	0.1
4	2	12	2.9	2.2
4	2	10	2.0	-0.3
4	2	8	3.8	-4.0
4	2	7	3.2	2.7
4	2	6	2.1	2.1
4	2	4	8.7	-7.6
4	2	3	6.6	7.0
4	2	2	5.3	6.4
4	2	0	8.6	7.0
4	2	-1	6.2	4.3
4	2	-3	12.3	-12.1
4	2	-4	1.8	-1.6
4	2	-5	1.3	1.2
4	2	-6	2.9	3.3
4	2	-8	1.9	-1.5
4	2	-10	3.3	2.8
4	2	-11	4.4	3.8
4	2	-12	2.6	2.6
4	2	-13	1.7	-1.3
3	2	-12	1.6	2.4
3	2	-11	7.4	7.3
3	2	-10	13.0	12.9
3	2	-9	17.3	17.3
3	2	-8	7.7	6.7
3	2	-7	1.3	-0.2
3	2	-6	1.9	2.3
3	2	-5	8.5	8.4
3	2	-4	16.9	-15.0
3	2	-3	14.9	-12.6
3	2	-2	24.7	-22.1
3	2	-1	28.1	-23.5
3	2	0	11.7	-10.3
3	2	1	1.4	1.3
3	2	2	2.7	0.9
3	2	3	9.3	-8.9
3	2	4	4.9	-5.2
3	2	5	16.6	-15.9
3	2	6	12.1	-12.0
3	2	7	6.2	-6.9
3	2	8	2.2	-1.5
3	2	11	1.1	1.0
3	2	12	7.1	7.0
3	2	13	6.8	6.8
2	2	13	2.9	2.4
2	2	12	1.1	0.1
2	2	10	4.0	-4.9
2	2	9	3.6	4.1
2	2	8	5.5	-5.8
2	2	7	7.0	-6.9
2	2	6	6.8	-7.7
2	2	5	4.1	-3.1
2	2	4	3.6	-2.6
2	2	3	22.4	22.2
2	2	2	20.1	-16.2
2	2	1	14.9	13.7
2	2	0	8.9	-5.0
2	2	-1	22.4	-20.1
2	2	-2	8.1	-8.3
2	2	-3	1.6	-1.8
2	2	-4	22.0	19.9
2	2	-5	35.3	-35.2
2	2	-6	21.2	18.9
2	2	-7	5.7	-4.9
2	2	-8	9.1	8.6
2	2	-9	9.4	9.2
2	2	-10	1.8	2.1
2	2	-12	4.0	-3.6
2	2	-13	4.1	3.9
1	2	-13	2.9	2.9
1	2	-12	3.2	-3.4
1	2	-11	3.8	3.8
1	2	-10	4.9	-5.2
1	2	-9	3.7	-3.7
1	2	-6	6.8	7.8
1	2	-5	30.3	-32.3
1	2	-4	37.4	41.0
1	2	-3	22.1	-21.3
1	2	-2	11.0	8.7
1	2	-1	16.5	15.0
1	2	0	2.4	-3.9
1	2	1	3.3	2.4
1	2	2	7.0	-9.0
1	2	3	21.8	19.9
1	2	4	19.3	-19.5
1	2	5	9.2	8.6
1	2	6	3.8	4.6
1	2	9	1.9	3.0
1	2	10	2.9	-3.1
1	2	11	6.2	6.6
1	2	12	3.5	-3.9
1	2	14	1.2	1.0
0	2	13	1.6	1.8
0	2	8	4.4	3.3
0	2	7	4.1	-3.7
0	2	6	4.4	-5.1
0	2	5	10.0	-10.3
0	2	4	4.5	-5.6
0	2	3	1.9	-0.9
0	2	2	5.8	6.7
0	2	1	15.7	-15.0
12	3	3	1.9	1.1
12	3	2	1.5	1.1
12	3	1	1.2	-1.9
12	3	0	1.2	1.1
12	3	-1	2.3	0.9
11	3	-1	1.3	-0.6
11	3	1	8.0	-7.8
11	3	3	7.9	-7.5
11	3	4	1.5	-0.4
10	3	5	2.5	-2.5
10	3	4	1.5	0.4
10	3	3	7.0	-6.6
10	3	1	1.3	1.1
10	3	0	1.0	-0.1
10	3	-1	2.6	2.8
10	3	-3	1.6	-2.3
10	3	-5	4.3	-4.1
9	3	-9	2.4	-1.4
9	3	-8	1.7	0.7
9	3	-7	1.6	1.6
9	3	-5	2.5	2.0
9	3	-4	2.3	1.4
9	3	-3	1.4	-0.0
9	3	-2	1.5	1.0
9	3	-1	2.2	1.7
9	3	1	2.3	-2.0
9	3	2	2.1	0.4
9	3	3	3.2	2.9
9	3	5	1.0	-0.1
9	3	7	2.6	2.1
9	3	8	1.5	1.1
8	3	5	2.8	2.5
8	3	3	6.7	-7.1
8	3	1	5.8	-6.1
8	3	0	4.0	-4.4
8	3	-1	2.8	2.2
8	3	-2	2.2	-2.3
8	3	-3	6.8	-6.9
8	3	-5	3.0	3.3
8	3	-6	1.6	1.0
8	3	-10	1.8	0.8
7	3	-10	1.3	-0.4
7	3	-9	2.3	-1.9
7	3	-7	11.1	-12.1
7	3	-6	1.9	1.0
7	3	-5	4.8	-5.1
7	3	-3	4.0	-3.6
7	3	-2	1.3	-0.7
7	3	-1	8.5	7.5
7	3	1	33.0	33.2
7	3	2	1.2	-1.6
7	3	3	5.3	5.5
7	3	5	1.0	2.0
7	3	6	1.1	-1.5
7	3	7	3.6	-3.4
7	3	9	6.8	-6.6
7	3	10	1.8	0.0
6	3	9	6.4	-6.2
6	3	8	1.2	-1.2
6	3	7	1.4	-0.5
6	3	5	2.2	-2.2
6	3	4	1.5	1.3
6	3	3	24.9	25.2
6	3	1	27.3	26.8
6	3	0	3.8	4.1
6	3	-3	1.1	1.3
6	3	-4	1.6	1.0
6	3	-5	13.3	-13.9
6	3	-6	2.1	0.1
6	3	-7	6.9	-7.5
6	3	-8	1.5	-1.0
6	3	-9	1.2	0.9
6	3	-10	1.2	-0.9
6	3	-11	1.7	-1.5
6	3	-13	4.2	-4.4
6	3	-12	1.4	0.6
5	3	-11	1.1	0.1
5	3	-7	3.0	2.9
5	3	-8	1.2	-0.3
5	3	-4	1.3	-0.6
5	3	-2	1.0	-1.0
5	3	-1	1.9	-1.7
5	3	1	1.4	1.4
5	3	2	10.9	-10.6
5	3	3	4.1	3.3
5	3	4	1.6	-1.8
5	3	5	5.6	-6.1
5	3	7	1.3	1.9
5	3	9	2.1	-2.1
5	3	10	1.2	0.8
4	3	11	1.6	0.5
4	3	9	1.3	-1.2
4	3	3	3.7	3.6
4	3	2	1.0	-1.3
4	3	0	6.1	6.1
4	3	-1	1.1	1.2
4	3	-1	5.1	4.2
4	3	-2	2.0	1.6
4	3	-3	2.5	2.4
4	3	-5	1.1	0.8
4	3	-6	1.7	-1.8
4	3	-7	9.5	-9.4
4	3	-11	2.2	-2.4
4	3	-13	1.3	-0.4
3	3	-13	1.3	-0.7
3	3	-11	1.8	-2.8
3	3	-10	1.7	-1.4
3	3	-9	14.2	13.8
3	3	-8	2.1	-1.7
3	3	-7	15.3	15.1
3	3	-5	2.4	-1.9
3	3	-4	1.7	2.6
3	3	-3	6.9	7.2
3	3	-2	1.1	0.4
3	3	-1	23.5	-22.7
3	3	0	2.5	2.4
3	3	1	7.5	-7.6
3	3	4	2.4	2.7
3	3	7	7.4	-8.0
3	3	11	1.1	-1.0
3	3	12	1.2	0.3
3	3	13	2.3	1.9
3	3	13	1.3	1.0
2	3	12	1.7	-0.7
2	3	11	1.2	-0.7
2	3	8	11.3	-13.0
2	3	7	12.0	-13.0
2	3	6	1.2	-0.5
2	3	4	1.5	-0.7
2	3	1	42.8	-40.3
2	3	0	7.1	-4.9
2	3	0	2.6	-2.3
2	3	-1	16.2	-14.3
2	3	-5	14.7	13.3
2	3	-6	3.4	-3.2
2	3	-7	38.6	40.9
2	3	-9	7.8	8.6
2	3	-11	1.3	0.4
2	3	-12	1.4	1.3
2	3	-13	3.1	-3.3
1	3	-13	2.6	-2.4
1	3	-11	1.0	1.1
1	3	-10	1.0	0.3
1	3	-9	4.2	-4.3
1	3	-8	1.1	0.5
1	3	-7	2.0	2.1
1	3	-6	2.0	2.0
1	3	-5	9.6	10.2
1	3	-4	1.9	1.7
1	3	-3	14.6	-15.3
1	3	-2	2.0	1.9
1	3	-1	5.2	4.5
1	3	3	1.0	-1.6
1	3	4	1.4	-1.1
1	3	5	7.0	7.2
1	3	7	2.7	3.7
1	3	9	5.1	-4.9
1	3	10	1.1	-0.1
1	3	11	1.7	-1.3
1	3	12	1.8	-1.3
1	3	13	1.4	0.6
0	3	13	2.0	1.8
0	3	12	1.0	0.8
0	3	9	2.4	3.0
0	3	8	1.3	1.4
0	3	5	5.4	-6.1
0	3	3	1.0	-0.6
0	3	2	2.8	-3.0
10	4	4	2.5	-3.2
10	4	3	2.9	-1.9
10	4	-1	4.9	-3.5
10	4	-3	5.8	-5.2
10	4	-4	2.5	-2.5
10	4	-8	1.6	2.0
10	4	-9	3.5	3.5
9	4	-8	1.8	1.3
9	4	-6	2.7	-2.0
9	4	-5	1.3	0.7
9	4	-4	1.8	0.7
9	4	-3	2.2	-2.2
9	4	-2	2.0	-1.1
9	4	-1	2.8	3.1
9	4	0	2.7	-2.5
9	4	1	2.0	2.3
9	4	2	2.4	3.0
9	4	7	1.5	1.2
9	4	8	2.4	-2.5
8	4	7	1.3	2.4
8	4	6	2.9	-2.7
8	4	5	3.2	2.9
8	4	3	3.4	-3.9
8	4	2	1.9	-1.8
8	4	0	2.3	2.2
8	4	-1	9.0	-8.5
8	4	-2	10.8	10.8
8	4	-3	2.9	-3.0
8	4	-4	3.2	3.4
8	4	-5	2.6	2.2
8	4	-9	1.8	-1.6
8	4	-10	2.7	2.9
8	4	-11	2.7	-3.1
8	4	-11	1.5	0.6
8	4	-11	1.1	0.3
7	4	-9	4.6	5.1
7	4	-8	2.9	-3.4
7	4	-7	4.4	4.9
7	4	-6	1.5	-1.8
7	4	-2	7.1	6.8
7	4	-1	18.9	-18.3
7	4	0	10.4	9.6
7	4	2	2.0	1.3
7	4	3	2.2	-1.7
7	4	4	1.5	-1.7
7	4	5	4.5	-3.9
7	4	6	3.5	-2.3
7	4	8	1.8	0.0
7	4	9	2.6	-0.4
7	4	10	1.1	-1.8
6	4	9	1.7	-0.6
6	4	7	2.2	1.6
6	4	6	3.8	3.4
6	4	5	7.2	7.3
6	4	4	10.5	10.2
6	4	3	19.0	18.4
6	4	2	9.2	8.4
6	4	1	2.7	-3.1
6	4	0	2.3	2.0
6	4	-2	5.0	-5.1
6	4	-3	4.0	-4.2
6	4	-4	5.5	-6.6
6	4	-5	6.9	-7.3
6	4	-6	4.3	-3.9
6	4	-7	1.7	0.7
6	4	-8	1.5	-0.8
6	4	-9	1.6	-2.0
6	4	-10	2.2	-1.3
6	4	-11	4.1	-3.6
6	4	-12	2.5	-2.5
5	4	-13	1.1	0.2
5	4	-11	1.7	-1.5
5	4	-10	4.0	-3.2
5	4	-8	1.4	0.1
5	4	-7	1.3	-0.8
5	4	-6	1.5	1.4
5	4	-5	1.0	-1.6
5	4	-4	3.1	-3.3
5	4	-3	8.0	-8.5
5	4	-2	2.1	-2.1
5	4	0	1.7	-0.6
5	4	1	1.7	1.0
5	4	3	6.6	6.2
5	4	4	8.0	7.5
5	4	5	9.7	9.0
5	4	7	1.2	-0.6
5	4		1.0	-1.0
4	4	12	2.7	2.6
4	4	10	1.4	-0.4
4	4	8	1.2	-0.7
4	4	7	2.2	-2.9
4	4	5	5.5	-5.6
4	4	3	3.1	-2.9
4	4	0	3.4	3.2
4	4	-1	2.5	-1.8
4	4	-2	2.7	-3.2
4	4	-3	6.9	6.3
4	4	-4	2.9	-2.8
4	4	-6	1.3	-0.3
4	4	-7	1.4	1.2
4	4	-9	1.5	-0.8
4	4	10	3.9	-0.4
4	4	-11	3.4	-3.6
4	4	-12	4.2	3.5
4	4	-13	1.1	0.5
3	4	-13	1.6	0.0
3	4	-12	3.2	2.4
3	4	-11	4.8	-5.1
3	4	-10	7.1	7.7
3	4	-9	14.2	-14.8
3	4	-5	5.1	5.6
3	4	-4	4.4	-4.7
3	4	-3	7.0	7.1
3	4	-2	10.1	-9.2
3	4	-1	15.2	13.7
3	4	0	4.5	-3.6
3	4	2	2.6	2.1
3	4	3	4.7	5.2
3	4	4	1.6	-2.7
3	4	5	7.2	8.7
3	4	6	5.8	-7.1
3	4	7	4.1	4.9
3	4	9	1.1	-0.7
3	4	12	3.5	3.5
3	4	13	5.4	-4.8
2	4	13	2.1	-1.6
2	4	11	3.3	-3.9
2	4	8	3.6	5.6
2	4	7	4.6	5.6
2	4	6	1.6	-1.8
2	4	5	1.0	1.0
2	4	3	10.5	-10.5
2	4	2	7.0	-6.4
2	4	1	7.5	-7.4
2	4	0	4.4	-3.7
2	4	-1	8.9	9.1
2	4	-2	1.3	-1.4
2	4	-4	7.4	7.0
2	4	-5	17.4	18.3
2	4	-6	11.0	11.1
2	4	-7	1.3	2.5
2	4	-8	4.3	4.7
2	4	-9	0.8	-6.7
2	4	-10	2.2	0.8
2	4	-12	2.3	-2.4
2	4	-13	1.3	-2.1
1	4	-13	3.0	-2.5
1	4	-12	2.3	-2.7
1	4	-11	2.7	-2.7
1	4	-10	1.7	-1.7
1	4	-9	3.2	3.6
1	4	-8	5.8	-0.9
1	4	-6	5.8	8.6
1	4	-5	17.1	19.2
1	4	-4	7.9	8.6
1	4	-3	5.1	4.8
1	4	-2	1.6	-1.2
1	4	2	5.2	-5.9
1	4	3	11.7	-11.5

3-perylene Structure Factor Tables

H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc	H	K	L	|Fo|	Fc
1	4	4	10.0	-10.5	4	5	5	1.3	-0.8	7	6	8	2.4	-0.2	8	7	1	1.7	-0.8
1	4	5	3.4	-2.9	4	5	4	2.8	3.9	7	6	9	2.8	0.3	8	7	-1	2.1	2.0
1	4	7	1.4	-0.9	4	5	3	5.2	-6.7	6	6	9	1.1	-0.1	8	7	-2	2.9	3.4
1	4	8	1.6	0.3	4	5	2	4.7	4.7	6	6	8	1.8	-1.3	8	7	-4	6.3	5.5
1	4	9	1.4	-2.0	4	5	1	4.2	-4.4	6	6	7	2.5	-2.5	8	7	-6	1.5	-1.1
1	3	10	2.4	-0.1	4	5	0	2.7	-3.3	6	6	4	2.0	-2.5	8	7	-7	2.1	-0.7
1	4	11	5.5	-5.7	4	5	-1	2.6	-3.0	6	6	3	1.5	-1.0	7	7	-9	1.5	-0.2
1	4	12	2.4	-2.6	4	5	-2	1.3	-0.6	6	6	2	1.2	2.6	7	7	-6	1.7	0.5
1	4	14	1.6	-1.2	4	5	-3	3.1	-2.9	6	6	-1	1.1	1.5	7	7	-5	2.3	0.2
0	4	14	1.3	-0.2	4	5	-4	8.1	7.8	6	6	-2	1.5	0.2	7	7	-2	2.1	1.8
0	4	9	1.7	1.3	4	5	-5	4.9	-5.3	6	6	-3	2.4	1.4	7	7	-1	1.1	0.9
0	4	8	2.6	2.8	4	5	-6	3.7	3.9	6	6	-5	2.3	1.4	7	7	3	1.1	-0.6
0	4	7	2.2	2.0	4	5	-8	2.7	-1.0	6	6	-7	1.9	0.1	7	7	4	1.7	-0.9
0	4	6	3.5	-3.9	4	5	-9	1.5	-0.9	5	6	-10	1.1	0.1	7	6	5	1.2	-0.7
0	4	5	2.9	3.1	4	5	-10	2.0	-1.7	5	6	-11	1.6	-0.6	7	6	4	2.8	-2.5
0	4	3	2.2	-3.0	4	5	-11	3.0	4.9	5	6	-11	3.3	1.2	7	6	3	1.5	-1.1
0	4	2	3.2	3.8	4	5	-12	5.6	-5.4	5	6	-9	1.4	0.7	7	6	1	1.5	0.7
12	5	4	2.1	-1.9	3	5	-12	1.9	-3.1	5	6	-6	5.1	4.0	6	6	6	2.2	-2.5
12	5	3	1.5	-1.0	3	5	-11	3.4	5.3	5	6	-5	3.3	-3.7	6	6	5	1.6	-1.1
12	5	2	1.7	-0.5	3	5	-10	2.0	-2.2	5	6	-5	1.3	0.0	6	6	3	1.5	-0.7
12	5	-1	2.2	-2.9	3	5	-9	1.8	2.4	5	6	2	6.3	-6.9	6	6	2	1.5	-0.7
11	5	0	1.9	2.2	3	5	-7	1.5	-1.9	5	6	3	1.5	-2.3	7	7	3	1.2	-0.6
11	5	2	1.4	0.0	3	5	-5	1.5	-1.6	5	6	4	1.9	-1.7	7	7	-3	1.3	-0.6
10	5	2	1.5	0.6	3	5	-4	3.4	2.9	5	6	5	2.0	-1.6	7	7	-8	1.8	0.2
10	5	0	1.7	-2.4	3	5	-3	7.4	-7.2	5	6	6	2.9	2.0	7	7	-9	1.1	-1.1
10	5	-2	1.7	-1.1	3	5	-2	1.3	1.2	5	6	6	8.6	7.9	7	7	-3	2.4	2.6
10	5	-4	1.7	2.0	3	5	-1	1.7	2.3	5	6	8	1.3	-0.9	5	5	7	2.4	2.6
10	5	-7	1.8	1.8	3	5	1	1.1	1.6	5	6	10	7.5	7.0	5	5	-2	1.3	0.9
9	5	-7	4.4	5.0	3	5	3	1.3	-2.3	5	6	10	3.4	0.5	5	5	-1	3.4	4.1
9	5	-5	4.6	5.2	3	5	4	6.1	7.2	4	6	9	10.0	9.1	5	5	-3	3.5	4.3
9	5	-4	3.9	-4.7	3	5	5	4.9	-5.0	4	6	9	1.1	-1.2	5	5	-4	3.5	4.5
9	5	-1	5.2	-4.9	3	5	7	1.1	0.2	4	6	8	1.6	-1.2	5	5	-5	2.3	2.2
9	5	0	4.8	-4.4	3	5	8	1.5	-1.5	4	6	2	9.1	-9.4	5	5	-6	4.2	3.8
9	5	1	2.4	-2.5	3	5	10	1.8	-2.0	4	6	1	1.1	-0.6	5	5	-6	4.2	3.6
9	5	3	2.8	-2.8	3	5	11	4.0	3.2	4	6	0	6.6	-7.1	4	5	-4	3.5	3.5
9	5	4	1.0	1.6	3	5	12	3.8	-3.6	4	6	-1	1.8	-1.2	3	5	6	2.2	-2.2
9	5	5	1.7	-0.5	3	5	13	3.0	2.0	4	6	-3	1.1	-1.4	3	5	7	1.1	-1.1
9	5	6	2.8	-2.6	3	5	12	1.4	-0.4	4	6	-4	1.3	-1.8	3	5	9	3.5	-0.2
9	5	7	1.8	-2.4	2	5	7	1.9	2.2	4	6	-6	7.4	-7.4	3	5	10	1.9	-3.4
9	5	8	2.2	-2.3	2	5	6	2.0	2.3	4	6	-7	1.2	-0.7	3	7	9	1.9	0.0
8	5	7	1.8	-0.4	2	5	1	3.3	3.7	4	6	-8	3.1	-2.9	3	7	7	1.6	-1.3
8	5	6	1.1	0.1	2	5	0	1.1	-0.8	4	6	-9	1.2	-0.7	3	7	4	4.1	-4.3
8	5	6	2.7	2.2	2	5	-2	2.9	-2.3	4	6	-10	1.3	-0.2	3	7	3	2.6	-2.1
8	5	4	2.8	-2.3	2	5	-5	2.0	1.7	4	6	-11	1.1	-0.2	3	7	1	2.1	-0.8
8	5	1	5.1	5.1	2	5	-6	3.6	-3.5	4	6	-12	1.6	2.7	3	7	-3	3.3	-2.0
8	5	0	2.0	0.8	2	5	-7	5.6	-5.6	3	6	-12	2.8	1.3	3	7	-4	3.4	-2.2
8	5	-1	1.6	1.1	2	5	-8	1.2	-0.0	3	6	-11	1.3	-0.4	3	7	-5	2.3	2.1
8	5	-2	2.6	2.2	1	5	-14	1.1	0.3	3	6	-10	1.9	-1.2	3	7	-11	3.2	-0.3
8	5	-3	6.2	-6.2	1	5	-12	1.5	-0.3	3	6	-9	2.4	1.0	2	7	-11	1.3	-0.3
8	5	-4	9.0	9.7	1	5	-11	2.0	-2.5	3	6	-2	1.3	1.0	2	7	-9	1.8	-0.0
8	5	-5	9.9	-9.9	1	5	-10	4.5	-3.6	3	6	-2	2.3	2.4	2	7	-5	1.8	-2.2
8	5	-7	3.3	2.7	1	5	-9	2.5	-1.8	3	6	1	1.1	-1.3	2	7	-4	1.5	-2.0
8	5	-9	1.0	0.3	1	5	-5	3.7	3.2	3	6	2	2.2	-2.3	2	7	-3	2.1	-0.2
8	5	-10	2.1	-2.4	1	5	-4	9.0	9.1	3	6	4	1.0	-0.9	2	7	-1	1.3	-0.7
8	5	-10	2.0	2.0	1	5	-3	16.0	16.5	3	6	6	1.1	1.1	2	7	5	1.8	-1.4
7	5	-5	1.6	-0.7	1	5	-2	16.4	16.0	3	6	10	3.1	2.9	2	7	10	2.0	-0.3
7	5	-4	1.2	-0.1	1	5	2	3.3	3.2	3	6	11	1.1	0.0	2	7	12	1.2	-0.3
7	5	-3	3.5	4.3	1	5	3	6.8	-7.2	3	6	10	1.0	0.9	2	7	13	1.3	-0.8
7	5	-2	2.6	-3.4	1	5	4	4.0	-4.6	2	6	4	1.1	1.1	1	7	11	1.7	-0.5
7	5	-1	5.7	6.0	1	5	5	6.2	-5.9	2	6	-1	1.2	-1.7	1	7	10	1.6	0.8
7	5	0	1.9	2.3	1	5	6	5.6	-5.4	2	6	-4	2.5	-2.4	1	7	8	1.6	0.8
7	5	1	3.8	-3.4	1	5	7	2.3	-2.0	2	6	-5	1.3	-1.2	1	7	5	3.3	-2.6
7	5	3	1.1	-0.0	1	5	8	1.2	1.4	2	6	-7	1.4	1.0	1	7	4	3.1	-2.1
7	5	4	1.9	-0.4	1	5	10	1.4	-1.0	2	6	-8	1.1	1.6	1	7	3	1.3	-1.7
7	5	5	4.3	-4.1	1	5	12	2.5	-1.8	1	6	-10	1.7	-0.6	1	7	1	2.5	3.7
7	5	6	1.0	-0.8	1	5	13	2.4	-2.1	1	6	-13	1.7	-0.4	1	7	-1	3.6	-4.2
7	5	7	1.0	-1.4	1	5	13	1.4	-2.0	1	6	-11	1.5	0.4	1	7	-4	1.7	-2.6
7	5	9	1.8	0.9	0	5	12	1.6	-1.0	1	6	-8	3.2	-3.1	1	7	-5	2.4	-2.8
6	5	10	2.1	0.5	0	5	10	2.9	3.2	1	6	-7	1.6	1.0	1	7	-6	1.7	-4.7
6	5	9	1.7	0.0	0	5	9	3.7	-2.9	1	6	-5	2.2	-2.1	1	7	-7	2.6	2.6
6	5	7	1.0	-0.4	0	5	7	2.7	-2.3	1	6	-4	4.7	-4.4	1	7	-10	2.0	-1.5
6	5	6	2.5	2.5	0	5	6	6.2	-6.0	1	6	-3	1.5	-1.8	1	7	-11	1.7	-0.9
6	5	5	4.1	3.5	0	5	5	5.0	-4.7	1	6	-2	8.0	8.5	1	7	-12	1.1	-0.7
6	5	3	1.8	-1.8	0	5	4	1.8	-2.0	1	6	-1	2.0	-0.3	0	7	-12	1.1	-0.3
6	5	2	1.8	-1.7	0	5	3	6.5	6.8	1	6	2	1.5	-2.1	0	7	-8	1.6	-1.1
6	5	1	4.0	-4.5	0	5	2	12.7	-14.2	1	6	4	1.9	-2.1	0	7	-7	1.9	-1.9
6	5	-1	1.5	-0.0	0	5	0	8.0	10.8	1	6	6	4.2	-4.3	0	7	-6	2.4	-2.3
6	5	-2	1.3	-1.4	0	5	3	2.4	-0.5	1	6	7	1.2	1.3	0	7	-5	1.5	-1.2
6	5	-3	3.3	-3.4	4	5	11	3.8	4.3	1	6	8	1.4	-0.9	4	7	-3	1.3	1.2
6	5	-5	1.9	2.6	1	5	-1	4.4	5.1	1	6	10	1.3	-0.2	4	7	9	2.6	2.4
6	5	-6	1.1	0.2	1	5	-1	1.5	1.6	0	6	12	1.6	-0.2	4	7	7	1.8	-1.4
6	5	-8	1.4	-0.4	12	6	1	2.2	0.4	0	6	9	2.0	0.2	4	7	6	1.8	-1.5
6	5	-9	1.3	-0.1	11	6	1	2.0	-0.8	0	6	8	7.9	-7.5	4	7	4	1.1	-1.3
6	5	-10	2.5	-1.9	10	6	1	1.7	1.3	0	6	7	1.5	-0.0	4	7	2	1.1	-2.2
5	5	-10	2.1	-0.8	10	6	-1	1.1	0.9	0	6	3	4.2	-4.2	4	7	1	2.5	-3.0
5	5	-9	2.2	-1.9	10	6	-3	1.3	0.8	12	7	1	2.4	-0.3	4	7	-2	1.3	-0.4
5	5	-8	4.2	-4.2	10	6	-5	2.1	-0.4	12	7	-1	2.4	-0.8	4	7	-4	3.6	-3.5
5	5	-8	3.1	-3.4	9	6	-6	10.2	10.3	10	7	0	2.9	1.6	4	7	-5	1.9	-2.0
5	5	-7	3.3	-3.3	9	6	-4	3.9	4.1	10	7	-1	1.1	-1.7	4	7	-6	2.7	-1.7
5	5	-6	2.0	0.8	9	6	1	2.5	0.0	10	7	-3	1.7	-1.3	4	7	-9	2.5	1.0
5	5	-5	1.3	-1.7	9	6	2	5.3	-5.6	10	7	-4	1.1	-1.0	4	7	-10	1.8	1.3
5	5	-4	1.6	-2.4	9	6	4	2.7	-0.0	10	7	-5	2.2	-1.1	4	7	-11	3.0	2.3
5	5	-2	7.0	-8.6	8	6	2	3.7	-4.1	10	7	-6	2.1	-1.1	4	7	-13	2.1	1.9
5	5	-1	5.7	-5.9	8	6	1	1.3	-1.3	9	7	-6	2.7	-2.1	1	7	-2	9.5	-10.3
5	5	0	3.4	-4.2	8	6	0	1.7	-0.7	9	7	-3	2.6	0.8					
5	5	1	2.1	-2.0	8	6	-1	1.7	0.3	9	7	-3	1.6	-0.1					
5	5	3	1.3	-0.5	8	6	-5	2.9	-0.1	9	7	-1	1.9	2.4					
5	5	5	2.6	2.1	8	6	-6	6.1	6.2	9	7	0	3.1	0.3					
5	5	5	9.7	10.0	8	6	-7	2.6	1.3	9	7	2	1.8	0.3					
5	5	6	11.0	10.8	8	6	-10	2.0	-0.5	9	7	5	1.7	-0.5					
5	5	7	6.5	6.6	7	6	-11	2.6	-0.5	8	7	7	1.7	-0.5					
5	5	8	3.4	3.6	7	6	-6	1.3	-1.9	8	7	5	3.4	-0.9					
5	5	9	3.7	3.5	7	6	-2	2.3	-2.3	8	7	4	2.9	-2.6					
5	5	10	1.1	-1.5	7	6	-1	1.0	0.4	8	7	2	1.7	-1.4					
4	5	11	5.5	4.3	7	6	1	1.7	1.2	8	7	2	2.6	-0.4					
4	5	10	5.7	-4.9	7	6	3	2.4	1.2										
4	5	9	4.2	3.6	7	6	6	1.6	1.2										
4	5	8	3.9	4.1															
4	5	6	2.4	2.0															

Appendix I

Comments on Choice of
Unit Cell in a Triclinic Lattice

CHOICE OF UNIT CELL IN A TRICLINIC SYSTEM

In the triclinic system, the choice of unit cell
is not dictated by symmetry considerations; thus there
are an infinite number of ways of choosing primitive cells
in a triclinic lattice.   However, each lattice is
uniquely described by the Bravais "reduced cell"; the
cell whose edges are the three shortest non-co-planar
translations in the lattice.   For purposes of compilation,
it is desirable to describe the lattice in terms of this
reduced cell.   The two most common algorithms for deriving
a reduced cell from any arbitrary primitive cell are the
Delaunay reduction and the Dirichlet reduction.   There
are certain reasons for preferring the latter.

In any parallelopiped, sets of angles occur in
enantiomorphous pairs at opposite corners.   One pair
of corners has the angles α, β, γ homogeneous; that is,
they are all obtuse (or all acute).   The other three
pairs of corners are of mixed types α, β', γ' or α', β, γ',
where α', β', γ' are the acute (or obtuse) supplements of
α, β, γ.   If we define vectors $\underline{a}, \underline{b}, \underline{c}$ along the edges from
a homogeneous corner, the scalar products $\underline{a} \cdot \underline{b}$, $\underline{b} \cdot \underline{c}$, and
$\underline{a} \cdot \underline{c}$ all have the same sign.   This allows a cell to be
defined uniquely in terms of the homogeneous triplet
with the three shortest translations.   Within the limits
imposed by the condition that the angles be homogeneous,

these are two possible parallelopipeds - one obtuse and
the other acute. Only one of these corresponds to the
Bravais-reduced cell with edges shorter than any face-
or body-diagonal.

The Delaunay reduced cell is tri-obtuse and so will
correspond to the Bravais-reduced cell only when the
latter happens to be obtuse. When the Bravais-reduced
cell is tri-acute, the Delaunay-reduced cell will have
diagonals shorter than its edges. In the first edition
of Crystal Data the Delaunay reduced cell was used as
the standard cell. In 20% of the cases reported, the
cell has angles that differ from 90° by more than 20°;
in some cases the difference is as much as 60°, and there
seems to be no theoretical reason why the Delaunay reduction
could not produce a cell with angles approaching 180°. If
the Bravais-reduced cell is tri-acute, the Delaunay
reduction can be applied to the reciprocal cell (Delaunay
1937), though Buerger has shown that the shortest a,b,c
in reciprocal space do not necessarily correspond to the
shortest a,b,c in direct space.

The Dirichlet reduction will always produce the
cell with the three shortest translations. Given any
triplet, a,b,c it forms the reduced triplet by using
multiples of each vector in turn in attempts to shorten
the other two edges. The steps can be performed in any

order and they are repeated until there is no further
change.   Their order convention adopted ($a<b<c$ or $c<a<b$)
has no effect on the reduction.

In the second edition of Crystal Data the Bravais-
reduced cell is used as the standard cell in all cases;
but the condition imposed is that α and β be non-acute.
In the case of a tri-acute parallelopiped, this corresponds
to a shift of origin to the "right-handed" corner whose
angles are α',β',γ'.

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