PHYSICO-CHEMICAL STUDIES OF SOME ORGANIC MOLECULES.

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in fulfilment of the requirements for the
degree of

Doctor of Philosophy

by

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PREFACE

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A.L.P.
<table>
<thead>
<tr>
<th>CONTENTS.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>i</td>
</tr>
<tr>
<td>Summary</td>
<td>1</td>
</tr>
<tr>
<td>The Crystal and Molecular Structures of Tiglic and Angelic Acids.</td>
<td></td>
</tr>
<tr>
<td>Nomenclature</td>
<td>2</td>
</tr>
<tr>
<td>Introduction</td>
<td>3</td>
</tr>
<tr>
<td>The Fourier Transforms of the two 2-methyl-2-butenic acids</td>
<td>9</td>
</tr>
<tr>
<td>The Crystal and Molecular Structure of Tiglic Acid</td>
<td>13</td>
</tr>
<tr>
<td>Crystal Data</td>
<td>14</td>
</tr>
<tr>
<td>Experimental Measurements</td>
<td>15</td>
</tr>
<tr>
<td>Structure determination and ( b )-axis projection</td>
<td>16</td>
</tr>
<tr>
<td>Refinement of ( b )-axis projection and location of hydrogen atoms</td>
<td>18</td>
</tr>
<tr>
<td>( a )-axis projection</td>
<td>26</td>
</tr>
<tr>
<td>( c )-axis projection</td>
<td>28</td>
</tr>
<tr>
<td>Coordinates, molecular dimensions and orientation of the molecule in the unit cell</td>
<td>30</td>
</tr>
<tr>
<td>Estimation of accuracy</td>
<td>34</td>
</tr>
<tr>
<td>Discussion</td>
<td>37</td>
</tr>
<tr>
<td>Table of observed and calculated structure factors</td>
<td>44</td>
</tr>
<tr>
<td>The Crystal and Molecular Structure of Angelic Acid.</td>
<td>50</td>
</tr>
<tr>
<td>Crystal Data</td>
<td>51</td>
</tr>
<tr>
<td>Experimental Measurements</td>
<td>52</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>----</td>
</tr>
<tr>
<td>Angelic acid and the Fourier transform of 2-methyl-cis-2-butenic acid</td>
<td>54</td>
</tr>
<tr>
<td>a-axis projection</td>
<td>59</td>
</tr>
<tr>
<td>b-axis projection</td>
<td>64</td>
</tr>
<tr>
<td>c-axis projection</td>
<td>67</td>
</tr>
<tr>
<td>Coordinates, molecular dimensions and orientation of the molecule in the unit cell</td>
<td>69</td>
</tr>
<tr>
<td>Conclusion</td>
<td>74</td>
</tr>
<tr>
<td>Table of observed and calculated structure factors</td>
<td>77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The Crystal and Molecular Structure of Tetrabenzo-2:3-6:7-2':3'-6':7'-heptfulvalene.</th>
<th>83</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>84</td>
</tr>
<tr>
<td>Crystal Data</td>
<td>85</td>
</tr>
<tr>
<td>Experimental Measurements</td>
<td>86</td>
</tr>
<tr>
<td>Attempts to determine the crystal structure</td>
<td>87</td>
</tr>
<tr>
<td>Fractional atomic coordinates of postulated structure</td>
<td>95</td>
</tr>
<tr>
<td>Table of observed and calculated structure factors</td>
<td>96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A Molecular Orbital Study of Pteridine and a Correlation Curve for Carbon-nitrogen Bonds.</th>
<th>98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>99</td>
</tr>
<tr>
<td>The secular equations of Pteridine</td>
<td>100</td>
</tr>
<tr>
<td>Solution of the secular equations and the permitted energy levels for the ( \pi )-electrons of pteridine</td>
<td>104</td>
</tr>
</tbody>
</table>
The secular coefficients for each energy level 108
The bond orders of pteridine 110
\( \pi \)-electron distributions for the ground state of pteridine 111
Effect of variation of arbitrary parameters on the calculations 112
A correlation curve for carbon–nitrogen bonds and bond lengths of pteridine 114

References 123
SUMMARY

This thesis describes investigations of the molecular structures of a number of organic compounds using physicochemical methods. Two main methods are employed. These are

1) Methods of X-ray structural analysis.
2) Theoretical methods (molecular orbital calculations).

Three compounds are considered under the first heading. These are

a) Tiglic Acid
b) Angelic Acid
c) Tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene.

Tiglic and angelic acids are cis-trans isomers which were known from chemical evidence to have the formula \( \text{CH}_3\text{CHCH}_2\text{COOH} \). However, chemical methods of deciding which acid is the cis and which is the trans isomer were based on results which, by themselves, were of doubtful value although when considered collectively indicated the trans structure for tiglic acid and the cis structure for angelic acid.

X-ray analyses of both acids are described in the thesis. A novel method of distinguishing between cis and trans isomers by means of molecular Fourier transforms, which may be applicable in the case of planar molecules is described.

Unit cell and space group data are given for both compounds and a complete and accurate analysis of tiglic acid is described. This analysis shows tiglic acid to be the trans acid I.

\[
\begin{align*}
\text{I} & : \quad \text{HC} - \text{CH} \\
\text{II} & : \quad \text{HC} - \text{CH}_3 \\
\text{III} & : \quad \text{H}_2\text{C} - \text{C} - \text{COOH} \\
\end{align*}
\]
thereby confirming the formula usually accepted — although not proved — for this acid.

Owing to various experimental difficulties the analysis of the angelic acid structure is not as accurate as that of tiglic acid, but the work confirms the formula II for the acid. The complete determination of the structure of angelic acid has been hindered somewhat by unusual difficulties involving homometric projections. Work is still proceeding on the compound and it is believed that the described solution of the problem is essentially correct. Three dimensional analysis at low temperatures may be necessary to achieve high accuracy.

The thesis also describes some work carried out on Tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene (III). If a planar model of this molecule is built up using aromatic bond lengths of 1.4Å, and assuming rings A and B to be regular heptagons and rings C, D, E and F to be regular hexagons, then it is found that the starred carbon atoms approach to within about 1.3Å of one another.

Such a close distance of approach is impossible and so the atoms of the molecule cannot be coplanar. The object of the work on this compound was to find the actual shape of the molecule. Unit cell and space group data for III are described in the thesis and a discussion on the probable conformation/
conformation is given. This part of the work is not yet finished but the structure postulated is chemically reasonable and fits in with a number of experimental observations.

The second type of method used in the investigations was the application of molecular orbital theory. By this means, \( \pi \)-electron distributions, bond orders, and bond lengths for pteridine(IV) have been derived. A new bond order – bond length curve for carbon–nitrogen bonds is proposed.
THE CRYSTAL AND MOLECULAR STRUCTURES

OF

TIGLIC AND ANGELIC ACIDS.
NOTE ON NOMENCLATURE

For the purpose of clarifying configurations, it will be convenient to use an adaptation of the rules suggested by the I.U.P.A.C. Commission of Nomenclature of Organic Chemistry (1) and now generally adopted. In these rules, in the case of 2-methyl-2-alkenoic acids the prefix cis- or trans- is used to describe the configuration of the unsubstituted alkenoic acid chain. Thus the name 2-methyl-trans-2-butenic acid is obtained for I, while the acid II will be 2-methyl-cis-2-butenic acid.

CH₃ –CH         2-methyl-trans-2-butenic acid.
\\
CH₃ –C – COOH

I

CH₃ –CH
\\
HOOC– C – CH₃

2-methyl-cis-2-butenic acid.

II

II
INTRODUCTION

As a result of the identification of the biologically active fraction of the fatty acids from the tuberculosis bacillus with C₂₇-phthienoic acid(2) and the assignment of a structure including the features of a 2-methyl-2-alkenoic acid(3,4) \( R\cdot CH_2\cdot CH=CH\cdot COOH \), there has followed an extensive study of the methods of preparation and properties of such unsaturated acids(5,6,7,8). However, in spite of considerable synthetic activity in this field, there has not yet developed a reliable method for assigning geometrical configurations to either the synthetic 2-methyl-2-alkenoic acids or to the naturally occurring C₂₇-phthienoic acid.

In two recent papers(7,9) assignments of geometric configuration have been based primarily on correlation of infra-red and ultra-violet spectral data with those of the simplest members of the series - tiglic and angelic acids (\( R = H \)). However, the geometric configuration to be assigned to tiglic and angelic acids themselves were by no means conclusive, and it was with the object of removing the uncertainties in the configurations of these acids that this work was undertaken.

Chemical evidence indicates that tiglic and angelic acids are 2-methyl-2-butenic acids. Tiglic acid is believed to be the trans- acid and angelic acid is believed to be the cis- acid thus

\[
\begin{align*}
\text{Tiglic Acid} & \quad \begin{array}{c} \text{CH}_3 - \text{CH} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{COOH} \end{array} \\
\text{Angelic Acid} & \quad \begin{array}{c} \text{HC} - \text{CH}_3 \\ \parallel \\ \text{H} \text{C} - \text{C} - \text{COOH} \end{array}
\end{align*}
\]
The main evidence on which these configurations are assigned is based mainly on the work of Sudborough and Davies (10) on esterification of the acids with methanol and hydrochloric acid, on the work of Von Auwers and Wissebach (11) on the configurations of the crotonic acids and on the work of Pfeiffer(12) on the dibromo derivatives of tiglic and angelic acids.

Sudborough and Davies showed that angelic acid is esterified at a slower rate than tiglic acid. Consequently, they said, angelic acid must have more groups blocking the carboxyl group than has tiglic acid. Hence angelic acid is the cis-acid.

Von Auwers and Wissebach established the configurations of the crotonic acids by relating them via the intermediate \( \gamma,\gamma'-\text{trichlorocrotonic acids} \) to maleic and fumaric acids. They thus showed that solid crotonic acid is the trans-form and isocrotonic acid is the cis-form. By comparing the physical properties of this pair of isomers with the same properties of the pair of isomers, tiglic and angelic acids, they then came to the conclusion that tiglic acid is the 2-methyl-trans-crotonic acid and angelic acid is the 2-methyl-cis-crotonic acid thus.

\[
\begin{align*}
\text{Crotonic Acid} & \quad \begin{array}{c} 
\text{H}_2\text{C} - \text{CH} \\
\parallel \\
\text{H} - \text{C} - \text{COOH}
\end{array} \\
\text{m.pt. 72}^\circ\text{C;} & \quad \text{pK}_a = 4.70 \\
\text{Heat of combustion} & \quad = 478 \text{ Kg.cals/mole.}
\end{align*}
\]

\[
\begin{align*}
\text{Isocrotonic Acid} & \quad \begin{array}{c} 
\text{H} - \text{C} - \text{CH}_3 \\
\parallel \\
\text{H} - \text{C} - \text{COOH}
\end{array} \\
\text{m.pt. 15.5}^\circ\text{C;} & \quad \text{pK}_a = 4.44 \\
\text{Heat of combustion} & \quad = 486 \text{ Kg.cals/mole.}
\end{align*}
\]
Pfeiffer studied the elimination of hydrogen bromide from a number of bromo-substituted alkenes and came to the conclusion that trans elimination occurred more readily than cis elimination. On this basis, he assigned the trans-methyl configuration to the 2-bromo-2-butene which boiled at 87 - 88°C., since it gave crotonylene more readily than the 2-bromo-2-butene which boiled at 93 - 94°C.

Having established the configurations of the 2-bromo-2-butenes in this manner, he then went on to deduce the configurations of tiglic and angelic acids as follows:

\[
\begin{align*}
\text{H}_3\text{C} - \text{C} - \text{H} & \quad \text{KOH} \quad \text{H}_3\text{C} - \text{C} - \text{H}_3 \\
\text{Br} - \text{C} - \text{CH}_3 & \quad \text{HBr} \quad \text{C} - \text{CH}_3 \\
\text{2-bromo-} & \quad \text{Crotonylene} \\
\text{trans-2-butene} & \quad \text{b.p.t.} = 87 - 88°C. \\
\text{H}_3\text{C} - \text{C} - \text{COOH} & \quad \text{Na}_2\text{CO}_3 \quad \text{H}_3\text{C} - \text{C} - \text{Br} + \text{CO}_2 + \text{NaBr} \\
\text{H}_3\text{C} - \text{C} - \text{COOH} & \quad \text{Br} - \text{C} - \text{COOH} \\
\text{2-bromo-} & \quad \text{C} - \text{CH}_3 \\
\text{cis-2-butene} & \quad \text{b.p.t.} = 93 - 94°C. \\
\end{align*}
\]

Tiglic Acid

\[
\begin{align*}
\text{I} & \quad \text{II}
\end{align*}
\]
Tiglic and angelic acids on treatment with bromine yield different racemic dibromo derivatives. On treatment of these with sodium carbonate CO$_2^-$ and Br$^-$ ion are eliminated to yield the 2-bromo-2-butenes of known configuration. Tiglic acid gives 2-bromo-trans-2-butene (II) whilst angelic acid gives 2-bromo-cis-2-butene (IV). Pfeiffer assumed that the elimination of the CO$_2^-$ and Br$^-$ ion from the dibromo-acids could only take place if the bromine atom and the carboxyl group concerned were in a trans-conformation. If this were so, then tiglic acid and angelic acid must have the configurations shown. Pfeiffer's ideas are easily followed if the dibromo-acids are viewed along the C$_b$ - C$_c$ bonds. Along this view the reactions become

\[
\begin{align*}
\text{Tiglic Acid} & \quad \text{III} \\
\text{Angelic Acid} & \quad \text{IV}
\end{align*}
\]

i.e. Bromine adds on trans across the double bond of tiglic acid to give the dibromotiglic acid (I). For elimination of CO$_2^-$ and Br$^-$ ion a trans conformation of -Br and -COOH is required so rotation about the bond C - C takes place. The -CH$_3$ groups are now in a trans conformation also and so on elimination of CO$_2^-$ and Br$^-$.
ion 2-bromo-trans-2-butene (II) is obtained.

The similar reaction in the case of angelic acid is

\[ \text{H}_3\text{C} - \text{Br} + \text{Li} \rightarrow \text{H}_3\text{C} - \text{Li} \]

\[ \text{H}_3\text{C} - \text{Li} \rightarrow \text{H}_3\text{C} - \text{CH}_3 \]

\[ \text{H}_3\text{C} - \text{CH}_3 + \text{CO}_2 \rightarrow \text{H}_3\text{C} - \text{COOH} \]

These are the main lines of evidence on which the suggested configurations for tiglic and angelic acids were based when this work was started but more recently Dreiding and Pratt(13) have obtained more conclusive chemical evidence from a study of the carboxylation of trans-2-butenyl-lithium, a reaction which they consider to afford a stereospecific synthesis of angelic acid.

None of these is by itself, conclusive evidence as to the configurations of tiglic and angelic acids, although when taken together they would indicate that tiglic acid is the trans- acid and angelic acid is the cis- acid. Nevertheless, a much more direct determination of the configurations of these acids is clearly desirable.
The methods of X-ray structure analysis afford an excellent means of solving such a problem since by this method the spacial positions of all the atoms in the molecules can be uniquely determined and hence the configurations obtained directly.

In particular it would be expected, at least to a first approximation, that these molecules would be planar and so the methods of the molecular Fourier transform could be employed. The problem would then reduce to finding out which reciprocal lattice fitted which transform.
The Fourier Transforms of the two 2-methyl-2-butenic acids (14, 15)

Experience shows that most organic acids occur as centrosymmetric dimers in the crystal, with hydrogen bonding between adjacent carboxyl groups. If this is so, we can then say that the structure factor $P(hkl)$ is given by

$$P(hkl) = 2\sum_{j=1}^{n} f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

Here $h$, $k$ and $l$ are indices representing points on a reciprocal lattice and $x_j$, $y_j$ and $z_j$ are scaled coordinates (with centre of symmetry as origin) representing the position of the atom $j$ in the unit cell. $f_j$ is the atomic scattering factor of atom $j$ for the reflection $(hkl)$ and the summation is taken over half the number of atoms of the unit cell. The structure factor $F(hkl)$ is a discontinuous function and when solving a crystal structure the whole problem degenerates to finding both the amplitude and the phase angle of the structure factors for each of the points of the reciprocal lattice.

Suppose now we take any centrosymmetric constellation of atoms. Choose an origin at the centre of symmetry through which pass any three non-coincident axes defined by the unit vectors $\xi_i, \eta_i, \zeta_i$ and consider the function.

$$G(X^*, Y^*, Z^*) = 2\sum_{j=1}^{n} f_j \cos 2\pi((\xi_j X^* + \eta_j Y^* + \zeta_j Z^*))$$

where $\xi_j, \eta_j, \zeta_j$ are coordinates of the atom $j$ referred to the set of axes $\xi_i, \eta_i, \zeta_i$ and $X^*, Y^*$ and $Z^*$ are points on a set of axes reciprocal to the frame $\xi_i, \eta_i, \zeta_i$. Unlike $h, k$ and $l$, the values of $X^*, Y^*$ and $Z^*$ are not restricted to integers.
G(X*Y*Z*) is the Fourier transform of the given constellation of atoms. It will be obvious that although F(hkl) is a discontinuous function, G(X*Y*Z*) is continuous and in fact F(hkl) can be obtained by placing F(hkl) and G(X*Y*Z*) on the same scale, origin to origin, and sampling G(X*Y*Z*) at the points of the reciprocal lattice. It should be noted that the axes of the reciprocal unit cell of the crystal and the axes of the function G(X*Y*Z*) need not necessarily be the same so that the reciprocal unit cell of the crystal and the function G(X*Y*Z*) may be tilted during the sampling process.

It would be an extremely laborious task to work out the three-dimensional functions G(X*Y*Z*) over the whole of reciprocal space but the problem is very much simplified when the atoms of the constellation concerned are coplanar. When this is the case, take \( \xi \) and \( \eta \) in the plane of the constellation and \( \gamma \) at right angles to it. All values of \( \gamma \) are now zero and the transform becomes

\[
G(X*Y*Z*) = 2 \sum_{j} \frac{f_j}{e} \cos 2 \pi \left( \xi_j X^* + \eta_j Y^* \right)
\]

i.e. the function now consists of "cylinders" of contours with constant sections since its value is independent of \( Z^* \).

If all the atoms are assumed to be the same, say carbon atoms, then we can write

\[
G(X*Y*Z*) = \frac{T(X*Y*Z*)}{f} = 2 \sum_{j} \frac{f_j}{e} \cos 2 \pi \left( \xi_j X^* + \eta_j Y^* \right)
\]

or, if the atoms are not the same but of nearly the same atomic number

\[
G(X*Y*Z*) = \frac{T(X*Y*Z*)}{f} = 2 \sum_{j} \frac{f_j}{e} w_j \cos 2 \pi \left( \xi_j X^* + \eta_j Y^* \right)
\]

where \( f \) is an atomic scattering factor for carbon.
Idealised Dimer of 2-methyl-trans-2-butene acid (I).

Idealised Dimer of 2-methyl-cis-2-butene acid (II).

Figure 1.
\( w \) is a weighting factor whose value is 1 for \( j = \) carbon and whose value is \( \frac{N_j}{6} \) for any other atom of atomic number \( N_j \).

i.e., instead of comparing the observed values of \( F(hkl) \) with \( G(X*Y*Z*) \), in practice the observed value of \( \frac{F(hkl)}{T} \) is compared with the calculated function \( T(X*Y*Z*) \).

Even with this simplification the calculation would be very laborious and so a further simplification is introduced. The way in which this is done is shown for the examples actually used here.

We are interested in calculating the Fourier transforms of the two 2-methyl-2-butenic acids. If instead of calculating the transforms of the actual acids we calculate the transforms of the two idealised constellations of atoms shown, then a great simplification in labour will result. (See Figure 1)

It will be seen that in these idealised constellations all coordinates can be expressed as multiples of 0.7\( \text{Å} \) along the \( \xi \)-direction and 1.21\( \text{Å} \) along the \( \eta \)-direction. Hence it follows that the function

\[
T(X*Y*Z*) = 2 \sum_{i,j} w_j \cos \frac{\pi}{T}(\xi_j \cdot X + \eta_j \cdot Y)
\]

will be periodic with period \( \frac{2\pi}{0.7} \text{Å}^{-1} \) along the \( X^* \) direction and period \( \frac{2\pi}{1.21} \text{Å}^{-1} \) along the \( Y^* \) direction, and can easily be evaluated by means of Beevers-Lipson strips in a manner analogous to that used for estimating electron densities by the normal method of Fourier analysis.

The problem of deciding which of the two 2-methyl-2-butenic acids is tiglic acid and which angelic acid then degenerates to finding out whether the reciprocal lattice of the acid concerned fits the \( T(X*Y*Z*) \) function of I or II.

The first acid to be dealt with is tiglic acid.
THE CRYSTAL AND MOLEULAR STRUCTURE OF TIGLIC ACID
1. Crystal Data

Tiglic Acid, $C_5H_9O_2$; Molecular weight = 100.1; m.pt. = 64.5°C.

Density calculated = 1.162 gms/cc.

Density observed (by flotation in potassium iodide solution)

$$= 1.163 \text{ gms/cc.}$$

$$a = 7.70 \pm 0.02 \text{ Å}$$
$$b = 5.23 \pm 0.02 \text{ Å}$$
$$c = 7.42 \pm 0.02 \text{ Å}$$

$$\alpha = 96.6^\circ \pm 0.5^\circ$$
$$\beta = 86.5^\circ \pm 0.5^\circ$$
$$\gamma = 106^\circ \pm 0.5^\circ$$

No systematic absences. Space group is P1 or P1.

Two molecules per unit cell. No molecular symmetry required.

Volume of unit cell ($V$)

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}}$$

$$= 285.6 \text{ Å}^3$$

Absorption coefficient for X-rays ($\lambda = 1.542\text{Å}$) $\mu = 8.56 \text{ cm}^{-1}$.

Total number of electrons per unit cell = $P(000) = 108$.

The crystals were obtained by slow recrystallation from 60–80 petroleum-ether. This resulted in thick needles developed along the $b$-axis.

The morphology has been described by Haushofer(16) who gives


$$\alpha = 99^\circ01\text{'}; \beta = 137^\circ54\text{'}; \gamma = 85^\circ03\text{'}.$$

No correlation between the two cells has been found.
2. Experimental Measurements

Tiglic acid is extremely volatile and so some method of protecting the crystal whilst the X-ray photographs are being taken is necessary. This was done by encapsulating the crystal on its glass fibre with a Park—Davis number 0 gelatine capsule and adding extra crystals of tiglic acid under the capsule to build up a vapour pressure. Rotation, oscillation and moving-film photographic measurements were employed using copper Kα radiation (λ = 1.542Å). The cell dimensions were determined by rotation and equatorial layer line moving-film photographs. The angles α, β and γ of the unit cell were obtained by two methods.

a). Directly, by measuring the unit translations along diagonals of the unit cell and thence employing the simple triangulation formulae of the type

\[
[110]^\perp = a^\perp + b^\perp - 2ab\cos γ
\]

b). Indirectly, by means of reciprocal angles α*, β*, γ* obtained from equatorial layer line moving-film photographs and thence employing formulae of the type

\[
\cos α = \frac{\cos β* \cos γ* - \cos α*}{\sin α* \sin γ*}
\]

The mean values of α, β and γ obtained by these methods have been quoted.

The reflexions were estimated visually by means of the multiple film technique(17). The structure factors evaluated by the usual mosaic crystal formula from the estimated intensities are given in table VI(pp. 44-49).

In the solid state, most organic acids exist as centro-symmetric dimers. Tiglic acid contains two molecules per unit cell and it was assumed that these would form dimers in the usual manner, i.e. the space group was assumed to be P1, with the centre of inversion between the carboxyl groups of a symmetrical dimer. Hence the discussion already given on Fourier transforms applies to this problem.

Since the b-axis is the shortest of the unit cell translations it was expected that a projection of the structure down this axis would give the best resolution and so this projection was considered first.

109 planes out of a possible 151 were observed in the (hol) section of the reciprocal lattice and it was found that this reciprocal lattice net fitted the Fourier transform of I but a fit could not be obtained on the transform of II (fig. I. p. 11.).

It is obvious that, since the constellations of atoms, I and II, have much in common, their Fourier transforms will also have some common features. However, although parts of the (hol) reciprocal lattice net of tiglic acid fitted parts of the transform of II, serious discrepancies existed and there was no doubt that this reciprocal lattice net was a sample from the transform of I. Hence tiglic acid is 2-methyl-trans-2-butenic acid thus confirming the formula assigned to it on chemical grounds.

The orientation of the (hol) reciprocal lattice net on the transform of I is shown on fig. II.

Computation of the electron density projected on to a plane
Fourier Transform of Idealised Dimer of 2-methyl-trans-2-butene acid with the $a^*$ and $c^*$ reciprocal axes of triglic acid superimposed.
perpendicular to the $b$-axis by summation of the Fourier series

$$\rho(xoz) = \frac{1}{A} \sum_{h,-\infty}^{+,\infty} \sum_{l,-\infty}^{+,\infty} F(hol) \cos 2\pi(hx + lz)$$

using the phase angles derived from the transform and the observed structure factor amplitudes, resulted in an electron density map which showed all of the atoms to be clearly resolved. Structure factors calculated using atomic coordinates obtained by picking out atomic centres from the electron density map resulted in a discrepancy

$$R = \frac{100 \sum |F_o| - |F_c|}{\sum |F_o|}$$

of 21% at this stage.

4. Refinement of the projection down the $b$-axis and location of the hydrogen atoms.

Further refinement of this projection of the structure was carried out by successive difference Fourier synthesis,

$$D(xoz) = f_o(xoz) - f_c(xoz)$$

$$= \frac{1}{A} \sum_{h,-\infty}^{+,\infty} \sum_{l,-\infty}^{+,\infty} \left[ F_o(hol) - F_c(hol) \right] \cos 2\pi(hx + lz)$$

Difference methods have been used by several authors from time to time (e.g., 18, 19, 20) and Booth (21), in a theoretical investigation of the function advocated its use. However, the full potentialities of the method were established by Cochran (22) only in 1951.

The corrections to the atomic coordinates may be derived as follows. The electron density distribution of an atom, to a first approximation, is Gaussian and may be represented by the equation

$$f_o(r) = \rho_o(0) \exp[-pr^2]$$

where $f_o(r)$ is the electron density at a distance $r$ from the centre of the atom where the electron density is $\rho_o(0)$. 
\[ f_0(r) = f_0(0) \left\{ 1 - pr^2 + \frac{D^2}{2} - \cdots \right\} \]

\[ \approx f_0(0) \left\{ 1 - pr^2 \right\} \quad \text{when } r \text{ is small.} \]

If the origin is taken at the point assumed to be the atomic centre in calculating the structure factors then the calculated electron density at \( r \) will differ from the true electron density at this point by an amount \( D(r) \) given by

\[ D(r) = \rho_o(r) - \rho_c(r). \]

where \( \rho_o(r) \) is the observed electron density at \( r \), calculated by using the observed values of the structure factors and \( \rho_c(r) \) is the electron density at \( r \) obtained by making use of the calculated values of the structure factors. The position of \( \rho_o(0) \) will differ from that of \( \rho_c(0) \) by a small amount \( \Delta \), where \( \Delta \) is the required correction to the atomic centre. Hence we may now write

\[ D(r) = \rho_o(r) - \rho_c(r) \]

\[ = \rho_o(0) \left\{ 1 - p(r - \Delta)^2 \right\} - \rho_c(0) \left\{ 1 - p'r^2 \right\}. \]

If the correct scattering curve has been used so that \( \rho_o(0) = \rho_c(0) \) and \( p = p' \) then

\[ D(r) = 2 \rho_o(0) p r \Delta \]

\[ \Delta = \left( \frac{\frac{dD}{dr}}{2p \rho_o(0)} \right)_{r=0} \]

The factor \( p \) depends upon the thermal motion of the atoms and is derived experimentally from the equation

\[ \rho_o(r) = \rho_o(0) \exp \left[ -pr^2 \right] \]

i.e. \( \log \rho_o(r) = \log \rho_o(0) - pr^2 \)

or \( \log \rho_o(r) = -pr^2 + \text{constant}. \)
Hence if $\log f_0(r)$ is plotted against $r^2$, a straight line graph should be obtained. The gradient of this line is $-p$, and and at $r = 0$, $\log f_0(0)$ and hence $f_0(0)$ may be obtained.

The direction of shift of the atomic coordinates is along the line of steepest ascent and the magnitude is obtained by measuring the slope of $D(r)$ at the atomic site and dividing by $2p f_0(0)$.

The process of refinement will come to an end when the function $D$ has zero slope at the atomic centres. The coordinates will then be free from termination of series errors except in so far as the scattering curves used to calculate the $F_c$'s are incorrect.

The atomic scattering curves employed during the preliminary stages of the refinement process were of the form

$$f_j = f_{j0} \exp \left\{ -B \left( \frac{\sin \theta}{\lambda} \right)^2 \right\}$$

where $f_{j0}$ is the theoretical curve for atom $j$ (valence states) at rest given by McWeeny(23) and the Debye-Waller factor $B$ was assumed to be $4.8 \times 10^{-6}$ for all atoms.

The first difference syntheses showed that the coordinates of several atoms required to be adjusted but when these atomic shifts were allowed for, it soon became obvious that the Debye-Waller factors for all the atoms were not the same, so the value of $B$ for each atom was adjusted until the difference between the observed and calculated electron densities($f_o - f_c$) at each atom was as small as possible. The method of adjusting the $B$ values was that employed by Cochran(22) who defined a quantity $\delta = \frac{B}{\lambda^2}$ and showed that on the average a small change $\Delta \delta$ in $\delta$ of 0.1 for carbon(or oxygen) atoms results in a change in $(f_o - f_c)$ of about
Fig. 11a.

Tiglic acid - b-axis projection.

Difference between the electron density in the crystal and that calculated for carbon, oxygen and hydrogen atoms.

Contours of intervals of 0.2 e/Å². 

± 0.1 Å contour omitted.
Tiglic Acid - b-axis projection.
Difference between the electron density in the crystal and that calculated for carbon and oxygen atoms.
Contours at intervals of 0.2 e/Å². Zero contour dotted.
0.35 e/Å² at the centre of the atom.

Application of the methods outlined above to successive difference syntheses resulted in a final discrepancy $R$ for the (hol) net of the reciprocal lattice of 10.8%.

At this stage, there still remained small difference peaks on atoms $C_3$ and $C_4$, but since the main object of refining the structure this far was to obtain accurate coordinates for the carbon and oxygen atoms and to detect the hydrogen atoms, neither of which is affected by these small peaks, they were not removed.

The values of $B$ obtained in this way were

<table>
<thead>
<tr>
<th>Atom</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$O_4$</th>
<th>$O_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>5.1</td>
<td>4.8</td>
<td>4.2</td>
<td>4.4</td>
<td>4.8</td>
<td>5.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The final $(\rho_a - \rho_c)$ map is shown in Fig. III. It represents the difference between the electron density existing in the crystal and that calculated for carbon and oxygen atoms only. The significant peaks are due to the hydrogen atoms. There is very little resolution of the individual atoms on this map but although it is not possible to say exactly where a hydrogen atom is situated it is possible to say how many such atoms are in a given neighbourhood. The electron density of the hydrogen atom of the carboxyl group which is responsible for the hydrogen bonding between the molecules of the dimer is very much smeared out, as would be expected since the $-O-H$ bond has a high electrovalent character, but the map indicates clearly a peak of 0.6e much nearer to $O_6$ than to $O_7$, i.e. the hydrogen bond is asymmetric and the hydrogen atom concerned is bonded to $O_6$. 
Tiglic acid - b-axis projection. Final electron density map.
Contours at intervals of 1 e/Å².; contour dotted.
The final electron density map of the projection of the structure on to the plane perpendicular to the \( b \)-axis is shown in fig. IV. This in addition to showing all the atoms in the molecule to be clearly resolved, shows evidence of repulsion between the methyl groups attached to \( C_2 \) and \( C_3 \). In the projection, bonds \( C_2 = C_3 \) and \( C_4 = O_7 \) are parallel to one another. So also are \( C_5 = C_3 \) and \( C_4 = O_6 \). However, bonds \( C_5 - C_2 \) and \( C_3 - C_4 \) are not parallel in projection. Hence they cannot be parallel in space, i.e. repulsion of the methyl groups has resulted in distortion of the \( sp^3 \) bond angles of the idealised formula. This point will be dealt with in detail again.

Although the individual features of the projection were investigated as thoroughly as in the case of the plane, they are not the correct ones of our model combined into the whole round in the form projection of the idea that in this structure, the molecule is a unit vibrating slightly above its conical axis. Changes of this main vibration have a tendency for one atom under vibrations of its own, the mechanism of vibration can favor the motion of another external atom to which
5. Projection of the structure on to the plane perpendicular to the $a$-axis of the triclinic cell.

The method of dealing with this projection was the same as that already employed for the $b$-axis projection. 73($hkl$) reflections out of a total of 97 possible were observed and estimated. Phase angles for these were obtained from the transform and combined with the observed structure amplitudes to give a representation of the electron density in the crystal projected on to the plane perpendicular to the $a$-axis. Atomic coordinates were picked out from the resultant electron density map, structure factors calculated, and the structure refined in the usual way by successive difference syntheses. After four cycles of refinement the discrepancy $R$, fell to 13.2% and stopped there. Again, McWeeny atomic scattering factor curves corrected for temperature vibration were used and the value of $B$ employed for each atom was

<table>
<thead>
<tr>
<th>Atom</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$O_6$</th>
<th>$O_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>6.2</td>
<td>5.1</td>
<td>4.0</td>
<td>3.8</td>
<td>5.8</td>
<td>5.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Although the temperature factors for this projection were not investigated as thoroughly as in the case of the projection down the $b$-axis, they are of the correct order of magnitude and when combined with the values found in the first projection support the idea that in this structure, the molecule as a unit is vibrating randomly about its centre of mass. Superimposed on top of this main vibration there is a tendency for each atom to execute random vibrations of its own, the amplitude of vibration being greater the fewer the number of carbon (or oxygen) atoms to which the atom
Tiglic Acid - a-axis projection. Final electron density map.
Contours at intervals of $1e/A^2$. $1e/A^2$ contour dotted.
concerned is bonded.

The final electron density map of this projection is shown in fig. V.

6. Projection of the structure on to a plane perpendicular to the c-axis of the triclinic cell.

As a check on the results already obtained, coordinates from the a and b-axes projections were combined to give coordinates for a projection of the structure on to a plane perpendicular to the c-axis. These were then used to calculate structure factors and the structure factors thus obtained were employed to compute the electron density projected on to the plane under consideration. The atomic scattering factors used were of the form

\[ f_j = f_j^0 \exp \left\{ -5.7 \left( \frac{\sin \theta}{\lambda} \right)^2 \right\} \]

for all atoms. This resulted in a discrepancy \( R = 15.9\% \) over 76 planes observed and estimated out of a possible 109.

The electron density map computed in this way (fig. VI) shows no resolution of the individual atoms but demonstrates quite clearly the arrangement of the molecules in the unit cell. In particular, it shows clearly the existence of a very pronounced cleavage plane, the (210) plane of the unit cell.

The observed and calculated structure factors are tabulated on pp. 44-49.
Fig. 1.

Tiglic acid - c-axis projection. Final electron density map.

Contours at intervals of 1e/Å². 1e/Å²: contour dotted.
7. Coordinates, Molecular Dimensions and Orientation of the molecule in the unit cell.

The final coordinates of the carbon and oxygen atoms are shown in table 1. \( x_p, y_p, z_p \) are fractional coordinates of an atom \( P \) and \( X_p, Y_p, Z_p \) are corresponding coordinates in Angstrom units referred to the oblique frame \( a, b, c \) of the triclinic unit cell. There are two independent estimates of \( Z_p \) (from projections down the \( a \) and \( b \) axes respectively). The average deviation from the mean of the two independent determinations is 0.008\( \AA \) and can be taken as a measure of the accuracy to be expected of the atomic coordinates. The mean value of \( Z_p \) is quoted in table 1.

In order to make use of the usual formulae of 3-dimensional coordinate geometry it was necessary to transform \( (X_p, Y_p, Z_p) \) into rectangular coordinates \( (X'_p, Y'_p, Z'_p) \). This was done in the following manner.

We are given a point \( P \) whose rectangular coordinates are \( (X'_p, Y'_p, Z'_p) \) and whose coordinates referred to oblique axes
a, b, c at angles $\alpha, \beta, \gamma$ to one another, as shown in the diagram,
are $(X_p, Y_p, Z_p)$. $Oa$ and $OX'$ are coincident and the $aOb$ and $X'OY'$
planes are identical.

\[
\begin{align*}
QR &= X'_P \quad ; \quad OR = Y'_P \quad ; \quad QP = Z'_P \\
MN &= X_P \quad ; \quad ON = Y_P \quad ; \quad MP = Z_P
\end{align*}
\]

$X_p, Y_p, Z_p$ are known, and $X'_P, Y'_P, Z'_P$ are required in terms of
these. This can be done quite easily by means of ordinary three
dimensional geometry and the transformation formulae turn out to be

\[
\begin{align*}
X'_P &= X_P + Y_P \cos \gamma + Z_P \cos \beta \\
Y'_P &= Y_P \sin \gamma + Z_P \left\{ \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \gamma} \right\} \\
Z'_P &= Z_P \cos \gamma \left( 1 - \cos \alpha - \cos \beta - \cos \gamma \right)
+ 2 \cos \alpha \cos \beta \cos \gamma \right)^{1/2}
\end{align*}
\]

Table 1. $X_p, Y_p, Z_p, X'_P, Y'_P, Z'_P$, are in Angstrom units.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$X_p$</th>
<th>$Y_p$</th>
<th>$Z_p$</th>
<th>$X'_P$</th>
<th>$Y'_P$</th>
<th>$Z'_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.7000</td>
<td>0.3254</td>
<td>0.5557</td>
<td>5.3900</td>
<td>1.7018</td>
<td>5.1725</td>
</tr>
<tr>
<td>O2</td>
<td>0.7863</td>
<td>0.5333</td>
<td>0.4298</td>
<td>6.0545</td>
<td>2.7892</td>
<td>5.4803</td>
</tr>
<tr>
<td>O3</td>
<td>0.7667</td>
<td>0.5095</td>
<td>0.2523</td>
<td>5.9036</td>
<td>2.6647</td>
<td>5.2834</td>
</tr>
<tr>
<td>O4</td>
<td>0.8707</td>
<td>0.7155</td>
<td>0.1450</td>
<td>6.7044</td>
<td>3.7421</td>
<td>5.7387</td>
</tr>
<tr>
<td>O5</td>
<td>0.6440</td>
<td>0.2710</td>
<td>0.1506</td>
<td>4.9588</td>
<td>1.4173</td>
<td>4.6364</td>
</tr>
<tr>
<td>O6</td>
<td>0.9773</td>
<td>0.9290</td>
<td>0.2310</td>
<td>7.5252</td>
<td>4.8587</td>
<td>6.2907</td>
</tr>
<tr>
<td>O7</td>
<td>0.8530</td>
<td>0.6980</td>
<td>0.0217</td>
<td>6.5681</td>
<td>3.6505</td>
<td>0.1610</td>
</tr>
</tbody>
</table>
The bond lengths and valency angles in the tiglic acid molecule calculated from the values of $X'$, $Y'$, $Z'$ are shown in fig. VIII. It will be obvious that the hydrogen of the carboxyl group is to be associated with O₆ rather than with O₇ thus confirming the position assigned to this atom on the basis of difference syntheses.

It will be noticed that

\[ C_2 \hat{C}_3 C_4 + C_3 \hat{C}_5 C_7 + C_5 \hat{C}_3 C_4 = 360.1^\circ \]
\[ C_3 \hat{C}_4 O_6 + O_6 \hat{C}_4 O_7 + O_7 \hat{C}_3 C_3 = 360.4^\circ \]

Hence it follows that bonds $C_2 - C_3$, $C_3 - C_4$, $C_5 - C_7$ lie approximately in one plane and bonds $C_3 - C_4$, $C_4 - O_6$, $C_4 - O_7$ in another plane.

It does not follow that these planes are the same since the one may be rotated with respect to the other about their common line $C_3 - C_4$.

However, calculation showed the two planes to be identical and the equation of the common plane of atoms $C_2$, $C_3$, $C_4$, $C_5$, $O_6$ and $O_7$ to be

\[ 0.8907X' - 0.4348Y' - 0.1324Z' - 3.4373 = 0 \ldots (i) \]
This equation is given in the form $lx + my + nz + p = 0$ where $l, m, n,$ are the direction cosines of the normal to the plane and $p$ is the perpendicular distance from the origin to the plane. The mean distance of atoms $C_1, C_3, C_4, C_5, O_6,$ and $O_7$ from the plane is 0.008Å whereas $C_1$ is 0.098Å away from it. Hence, it follows that all of the atoms of the tiglic acid molecule lie in one plane except for $C_1$.

Table II Distances (d) of the atoms from the plane defined by (i)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$O_6$</th>
<th>$O_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>+0.098</td>
<td>-</td>
<td>0.008</td>
<td>+0.016</td>
<td>+0.003</td>
<td>0.014</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The orientation of the molecule in the cell may be defined by

a) stating the equation of the molecular plane.

and

b) fixing the position of a line in the molecule in this plane.

The equation of the plane has already been given above, and, as will be shown later is very nearly, although not quite, the $(210)$ plane. The orientation of the molecule in this plane will be defined by stating the angle between $C_3-C_4$ and the $c$-axis of the triclinic cell. This angle was found to be 52.8°.

The standard deviations of the atomic coordinates, bond lengths, bond angles and electron density were estimated by the methods described by Cruickshank(24,25), Ahmed and Cruickshank(26), Cruickshank and Robertson(27). The essentials of these methods are as follows

a) Standard Deviation of Atomic Coordinates is given by the equation

$$\sigma(X_p) = \frac{2\pi}{a\cdot A\cdot C_a} \left( \sum_{c} h^2 (F_o - F_c) \right)^{\frac{1}{2}}$$

where $\sigma(X_p)$ is the standard deviation of the atomic coordinate of an atom $P$ measured in the direction of the $a$-axis of the triclinic cell.

$a$ is the length of the projected $a$-axis of the cell.

$A$ is the area of the plane of projection.

$C_a$ is the curvature of atom $P$ measured in the direction of the projected $a$-axis.

$h$, $F_o$ and $F_c$ have their usual meanings.

Similar expressions obtain for $\sigma(Y_p)$ and $\sigma(Z_p)$.

Use of these expressions give $\sigma(X_p) = \sigma(Y_p) = \sigma(Z_p)$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$O_6$</th>
<th>$O_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma(X_p)$</td>
<td>0.012A</td>
<td>0.009A</td>
<td>0.009A</td>
<td>0.009A</td>
<td>0.012A</td>
<td>0.007A</td>
<td>0.007A</td>
</tr>
</tbody>
</table>

Table III

i.e. the accuracy of the positions obtained from the atoms is in the order oxygen more accurate than $sp^2$ carbon which in turn is more accurate than $sp^3$ carbon.
Standard Deviation of Bond Lengths.

If \( \sigma(X_{1}'), \sigma(Y_{1}'), \sigma(Z_{1}') \) represent the standard deviations of the atomic coordinates of atom 1 and \( \sigma(X_{2}'), \sigma(Y_{2}'), \sigma(Z_{2}') \) represent the standard deviations of the atomic coordinates of atom 2, and \( l, m, n \) are the direction cosines of the bond joining atoms 1 and 2 then the standard deviation of bond length \( \sigma(d) \) is given by

\[
\sigma^2(d) = \left\{ \sigma^2(X_{1}') + \sigma^2(X_{2}') \right\} l^2 + \left\{ \sigma^2(Y_{1}') + \sigma^2(Y_{2}') \right\} m^2 + \left\{ \sigma^2(Z_{1}') + \sigma^2(Z_{2}') \right\} n^2
\]

if, as is very nearly the case in this analysis, \( \sigma(X_{1}') = \sigma(Y_{1}') = \sigma(Z_{1}') \)

then

\[
\sigma(d) = \left\{ \frac{\sigma^2(X_{1}') + \sigma^2(X_{2}')}{2} \right\} \left\{ l^2 + m^2 + n^2 \right\}
\]

i.e.

\[
\sigma(d) = \sigma(X_{1}') + \sigma(X_{2}')
\]

This formula gives the following values for the standard deviations of bond lengths.

<table>
<thead>
<tr>
<th>Bond</th>
<th>( C_1-C_2 )</th>
<th>( C_2-C_3 )</th>
<th>( C_3-C_4 )</th>
<th>( C_3-C_5 )</th>
<th>( C_4-O_6 )</th>
<th>( C_4-O_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma(d) )</td>
<td>0.015Å</td>
<td>0.013Å</td>
<td>0.013Å</td>
<td>0.015Å</td>
<td>0.012Å</td>
<td>0.012Å</td>
</tr>
</tbody>
</table>

Table IV

Standard Deviation of Bond Angles

The standard deviation of bond angles is given by

\[
\sigma^2(\theta) = \frac{\sigma^2(\theta)}{d_{AB}^2} + \sigma^2(B) \left\{ \frac{1}{d_{AB}^2} - \frac{2 \cos \theta}{d_{AB} d_{BC}} + \frac{1}{d_{BC}^2} \right\} + \sigma^2(C)
\]

where \( d_{AB} \) and \( d_{BC} \) are the lengths of the bonds joining atoms \( A, B \) and \( C \).
\( \theta \) is the angle between these bonds.

\( \sigma(A), \sigma(B), \sigma(C) \) are the standard deviations of the positions of A, B and C.

\( \sigma(\theta) \) radians is the standard deviation of \( \theta \)

Use of this equation gives values of \( \sigma(\theta) \) for the bond angles of tiglic acid of the order of 0.8°.

**Standard Deviation of Electron Density.**

The standard deviation of the projected electron density \( \sigma(\rho) \) is given by

\[
\sigma(\rho) = \frac{1}{n} \left( \sum (F_o - F_c)^2 \right)^{1/2}
\]

giving a value of 0.14/\( \AA \) for the \( \beta \)-axis projection and a value of 0.3/\( \AA \) for the \( \alpha \)-axis projection.

The displacement of atoms $C_2$, $C_3$, $C_4$, $C_5$, $O_6$, and $O_7$ from the plane of the molecule varies from zero to 0.016Å. These deviations have no significance. However, $C_1$ is situated 0.098Å away from the plane. Hence it follows that $C_1$ is not coplanar with the rest of the molecule. If all the atoms lay in the same plane and all the bond angles were 120°, as would be expected if the structure were that of the idealised chemical formula, then $C_1$ and $C_5$ would approach to within 2.8Å. Apparently this distance of approach is far too close and the methyl groups have repelled one another until they are separated by a distance of 3.04Å. $C_5$ obviously cannot move very far otherwise it would come into the field of $O_7$ and so most of the repulsion has centred round $C_1$. The bond angle $C_1C_2C_3$ has widened out until it becomes 126.3°. Bond $C_2 - C_1$ has rotated slightly about $C_3 - C_2$ as axis in an anticlockwise direction until its direction makes an angle of 4° with the plane of the rest of the molecule.

The angle $C_2C_3C_5$ has widened out to 123.4° i.e. it is wider than the sp² bond angle although the distortion is not as large as in the case of $C_1C_2C_3$.

$C_2 = C_3$ and $C_4 - O_7$ are conjugated. Consequently it would be expected that $C_3 - C_4$ should differ from a pure single bond. A shortening of 0.06Å from the pure single sp² bond length of 1.50Å has been observed and since this difference is five times the standard deviation to be expected in this bond the result shows that a considerable degree of conjugation does in fact exist.
The system is found in other acids whose structures have been accurately worked out by X-ray methods and it is interesting to compare the results observed for tiglic acid with some other acids of similar type. Thus

\[
\begin{array}{cccccccc}
\text{Salicylic Acid (28)} & 1.46 \text{Å} & 1.33 \text{Å} & 1.24 \text{Å} & 117.0^\circ & 122.7^\circ & 120.2^\circ & 2.63 \text{Å} \\
\text{Benzoic Acid (29)} & 1.46 \text{Å} & 1.29 \text{Å} & 1.24 \text{Å} & 118.0^\circ & 122.0^\circ & 122.0^\circ & 2.64 \text{Å} \\
\text{Tiglic Acid} & 1.44 \text{Å} & 1.31 \text{Å} & 1.24 \text{Å} & 117.7^\circ & 121.4^\circ & 121.3^\circ & 2.64 \text{Å} \\
\end{array}
\]

Table V.

The coordinates listed in table I (p. 31) are those of a molecule lying at the \([110]\) corner of the triclinic cell. The corner of the unit cell is the centre of symmetry of the dimer. However, the centre of symmetry does not lie on the molecular plane defined by equation (1). It lies at a perpendicular distance of 0.05Å away from the plane. It follows therefore that the two molecules comprising a dimer of tiglic acid do not lie in the same plane. Instead, the planes of the two halves of the dimer are displaced 0.1Å from one another to give what might be called a "stepped" arrangement of hydrogen bonding in the dimers.

\[
0.8907X' - 0.4348Y' - 0.1324Z' - 3.4373 = 0 \quad \ldots \ldots \ldots (i)
\]
is very nearly, although not quite, the (210) plane. It lies 0.05A from the [110] corner of the triclinic cell and is 3.44A from the origin of this cell.

It now follows that the plane of the associated molecule comprising the dimer at [110] must lie at a perpendicular distance of 3.34A from the origin and these planes are parallel to one another. This stepped arrangement exists right through the crystal. Consequently the structure can be considered as being made up of alternating pairs of sheets of molecules. The members of each pair are joined by hydrogen bonds and are separated by a perpendicular distance of 0.1A from each other. The pairs of sheets are held together by

Fig 18.
Van der Waals forces and are 3.29Å apart (fig. X). However, it does not follow that non-bonded atoms are 3.29Å apart.

![Fig X]

Fig. XI shows the arrangement of the dimers whose centres of symmetry lie on the (010) plane. In this arrangement, the shortest intermolecular distances are those between carbon and oxygen atoms, the shortest being a methyl to oxygen distance of 3.58Å.

Fig. XII shows the arrangement of the dimers whose centres of symmetry lie on the (001) plane and demonstrates the closest distance of approach between the doubled sheets of molecules. The closest distance of approach is again a methyl to oxygen distance - this time of 3.63Å.

The closest carbon to carbon non-bonded distance of approach is demonstrated in fig. XII and is between methyl groups related to each other by centres of symmetry. This distance is 3.70Å and is somewhat less than should be expected from the radius of 2Å assigned to a methyl group by Pauling (30) and the corresponding value of 3.87Å observed in Durene and Hexamethylbenzene (31,32). However, shorter non-bonded methyl to methyl distances than these have been observed before e.g. in 2,3,5,6 - Tetramethyl Pyrazine (33) a distance of 3.72Å has been observed and a value of 3.64Å has been quoted for dl - Alanine (34). As Corey has stated (34) when longer non-bonded methyl to methyl distances are involved it is probable that the rotations of the methyl groups are independent of one another. As the
Tiglic Acid.

Arrangement of molecules on (010) plane.
non-bonded methyl to methyl distance decreases the rotations will tend to synchronise and the carbon—hydrogen bonds will act like the teeth of two cog-wheels revolving round each other.

Whether or not this explanation for the close distance of approach of methyl groups belonging to adjacent molecules is correct, it must be true for methyl groups belonging to the same molecule if these are rotating. The distance between methyl groups in the same molecule in this case, is only 3.04Å and so it follows immediately that the hydrogen atoms of these methyl groups must have a staggered configuration. If these methyl groups rotate independently of one another then sooner or later the hydrogen atoms will approach to within about 1.8Å. Since the Van der Waals radius of hydrogen is 1.2Å such a close distance of approach is inconceivable and consequently if the methyl groups are rotating it must follow that the rotations of the methyl groups in the same molecule are synchronised.

It is interesting to note that a similar explanation of the mode of rotation of the methyl groups in Hexamethylbenzene was put forward by Mack as long ago as 1932. (36).
Table VI  
Observed (Fo) and Calculated (Fc) Structure Factors of Tigliic Acid.

\[ F(\text{o}k\ell) \]

| Plane. | 2sin\(\theta\) | \(|Fo|\) | Fc  | Plane. | 2sin\(\theta\) | \(|Fo|\) | Fc  |
|--------|---------------|---------|------|--------|---------------|---------|------|
| 001    | 0.207         | 6.3     | + 7.3 | 020    | 0.615         | 5.6     | - 7.2 |
| 002    | 0.415         | 1.1     | + 0.5 | 021    | 0.675         | 11.1    | - 11.7|
| 003    | 0.623         | 10.3    | -11.8 | 022    | 0.785         | 7.6     | - 6.6 |
| 004    | 0.835         | 9.0     | + 9.4 | 023    | 0.930         | 5.4     | - 5.2 |
| 005    | 1.050         | 6.5     | + 6.4 | 024    | 1.100         | 8.5     | + 7.9 |
| 006    | 1.255         | 1.6     | - 1.2 | 025    | 1.285         | 1.2     | + 1.4 |
| 007    | 1.465         | 4.2     | + 4.0 | 026    | 1.470         | 3.4     | - 2.8 |
| 008    | 1.672         | 1.2     | + 1.5 | 027    | 1.667         | 2.6     | - 2.0 |
| 009    | 1.878         | 1.2     | + 0.8 | 021    | 0.622         | 16.1    | - 16.8|
| 010    | 0.305         | 16.8    | -18.0 | 022    | 0.697         | 16.4    | - 19.8|
| 011    | 0.395         | 14.0    | +15.8 | 023    | 0.820         | 7.8     | + 8.6 |
| 012    | 0.550         | 17.1    | -20.6 | 024    | 0.973         | 1.9     | + 1.8 |
| 013    | 0.730         | 4.1     | - 3.2 | 026    | 1.325         | 10.7    | - 10.5|
| 014    | 0.928         | 7.5     | - 5.7 | 027    | 1.515         | 2.4     | - 1.9 |
| 016    | 1.332         | 2.3     | - 1.7 | 030    | 0.915         | 5.9     | + 5.8 |
| 017    | 1.535         | 5.2     | - 4.1 | 031    | 0.963         | 10.9    | +11.4 |
| 018    | 1.738         | 0.6     | - 0.8 | 032    | 1.050         | 4.6     | + 5.1 |
| 011    | 0.348         | 2.3     | + 3.1 | 033    | 1.170         | 2.7     | - 1.9 |
| 012    | 0.490         | 1.7     | - 2.9 | 034    | 1.315         | 2.1     | - 1.6 |
| 013    | 0.665         | 1.8     | - 1.2 | 035    | 1.480         | 4.2     | + 3.5 |
| 014    | 0.855         | 9.2     | + 8.3 | 036    | 1.650         | 3.8     | + 3.4 |
| 015    | 1.055         | 1.4     | - 1.2 | 031    | 0.910         | 1.4     | - 0.9 |
| 016    | 1.255         | 4.2     | + 4.0 | 032    | 0.957         | 5.5     | + 5.2 |
| 017    | 1.460         | 2.3     | - 1.8 | 033    | 1.040         | 1.8     | + 2.1 |
| 018    | 1.645         | 2.1     | + 1.4 | 034    | 1.155         | 0.8     | + 0.6 |
| Plane. 2sinθ. | |Fo| | Fc | Plane. 2sinθ. | |Fo| | Fc |
|---|---|---|---|---|---|---|---|
| 035 | 1.300 | 2.9 | -2.7 | 048 | 1.930 | 2.2 | +1.6 |
| 036 | 1.455 | 1.0 | +1.6 | 050 | 1.530 | 5.9 | -5.9 |
| 037 | 1.610 | 1.2 | +1.1. | 054 | 1.835 | 1.1 | -1.1 |
| 040 | 1.220 | 5.9 | +5.5 | 051 | 1.517 | 3.8 | -3.0 |
| 041 | 1.265 | 4.1 | +3.8 | 053 | 1.573 | 2.0 | +1.6 |
| 043 | 1.435 | 3.8 | -2.6 | 054 | 1.650 | 0.8 | -0.8 |
| 044 | 1.555 | 1.6 | -1.4 | 055 | 1.737 | 1.8 | -1.9 |
| 042 | 1.240 | 1.4 | -1.7 | 061 | 1.870 | 0.8 | -1.0 |
| 043 | 1.300 | 1.6 | +1.0 | 062 | 1.925 | 1.1 | +0.7 |
| 044 | 1.390 | 1.6 | +1.6 | 061 | 1.820 | 0.7 | -0.3 |
| 046 | 1.625 | 0.6 | +0.6 | 063 | 1.860 | 1.2 | +1.2 |
| 047 | 1.770 | 2.3 | +2.4 | |

\[
R = 100 \left( \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \right)
\]

\[
= 13.2\%
\]
| Plane | $2\sin \theta$ | $|F_o|$ | $F_o$ | Plane | $2\sin \theta$ | $|F_o|$ | $F_o$ |
|-------|-------------|---------|------|-------|-------------|---------|------|
| 001   | 0.215       | 7.4     | + 7.9| 001   | 0.460       | 16.2    | + 16.1|
| 002   | 0.420       | 1.2     | + 1.6| 002   | 0.580       | 20.7    | - 22.7|
| 003   | 0.630       | 12.6    | - 13.2| 003   | 0.745       | 3.3     | - 3.0 |
| 004   | 0.835       | 9.1     | + 8.7| 004   | 0.920       | 7.8     | - 5.5 |
| 005   | 1.050       | 5.9     | + 6.5| 005   | 1.300       | 3.0     | - 1.3 |
| 006   | 1.250       | 1.7     | - 1.7| 006   | 1.495       | 5.4     | - 5.0 |
| 007   | 1.460       | 3.9     | + 3.9| 007   | 0.480       | 5.2     | + 6.2 |
| 008   | 1.670       | 1.3     | + 1.0| 008   | 0.605       | 4.4     | - 5.3 |
| 009   | 1.880       | 1.1     | + 0.9| 009   | 0.770       | 1.2     | - 0.1 |
| 100   | 0.210       | 21.0    | + 21.9| 100   | 0.950       | 6.6     | + 7.1 |
| 101   | 0.295       | 35.5    | + 34.6| 101   | 1.145       | 0.9     | - 1.4 |
| 102   | 0.460       | 4.5     | + 4.6| 102   | 1.340       | 3.4     | + 3.3 |
| 103   | 0.660       | 3.4     | - 3.9| 103   | 1.540       | 1.8     | - 1.8 |
| 104   | 0.850       | 2.3     | + 2.2| 104   | 1.740       | 1.2     | + 1.0 |
| 105   | 1.060       | 1.3     | + 0.9| 105   | 0.630       | 0.6     | + 0.7 |
| 106   | 1.260       | 3.3     | - 3.3| 106   | 0.655       | 4.1     | - 4.5 |
| 107   | 1.460       | 3.4     | - 3.3| 107   | 0.740       | 5.9     | - 5.7 |
| 108   | 1.670       | 1.6     | + 1.9| 108   | 0.870       | 7.4     | - 7.2 |
| 109   | 1.880       | 1.1     | + 1.1| 109   | 1.020       | 2.9     | - 3.5 |
| 110   | 0.310       | 12.9    | - 11.8| 110   | 1.190       | 5.2     | - 4.7 |
| 111   | 0.480       | 16.5    | - 16.4| 111   | 1.370       | 3.4     | - 2.7 |
| 112   | 0.675       | 7.9     | + 8.2| 112   | 1.560       | 1.7     | - 0.5 |
| 113   | 0.870       | 13.5    | + 12.9| 113   | 0.670       | 7.6     | - 9.4 |
| 114   | 1.080       | 6.1     | + 6.5| 114   | 0.770       | 14.4    | - 15.5|
| 115   | 1.280       | 1.8     | + 1.3| 115   | 0.910       | 8.9     | - 8.9 |
| 116   | 1.480       | 2.5     | + 2.0| 116   | 1.070       | 2.2     | + 2.1 |
| 117   | 2.420       | 17.3    | - 16.9| 117   | 1.250       | 3.0     | + 2.5 |
| Plane | $2\sin \beta$ | $|F_0|$ | $F_0$ | Plane | $2\sin \beta$ | $|F_0|$ | $F_0$ |
|-------|--------------|--------|------|-------|--------------|--------|------|
| 307   | 1.625       | 1.7    | -2.0 | 600   | 1.250       | 2.5    | +3.4 |
| 401   | 0.855       | 13.3   | -12.5| 601   | 1.260       | 6.5    | +7.1 |
| 402   | 0.910       | 2.9    | -2.9 | 602   | 1.300       | <1.0   | -0.6 |
| 403   | 1.020       | 3.9    | -5.1 | 604   | 1.470       | 2.1    | -1.9 |
| 404   | 1.150       | 10.7   | +8.5 | 605   | 1.590       | 5.2    | +4.5 |
| 405   | 1.300 <1.0  | -0.4   |      | 606   | 1.725       | 1.5    | +0.9 |
| 406   | 1.470       | 3.7    | -3.1 | 607   | 1.280       | 1.8    | -1.1 |
| 407   | 1.640       | 2.9    | -1.6 | 700   | 1.665       | 1.6    | +1.7 |
| 408   | 0.880       | 9.1    | -11.5| 701   | 1.660       | <0.9   | +0.9 |
| 409   | 0.955       | 14.4   | -14.2| 702   | 1.690       | 0.9    | -1.0 |
| 410   | 1.075       | 3.0    | +3.3 | 703   | 1.670       | 1.9    | -2.2 |
| 411   | 1.210       | 1.0    | +1.6 | 704   | 1.875       | 1.3    | +1.6 |
| 412   | 1.375       | 2.1    | +2.1 | 705   | 1.480       | 2.5    | +1.8 |
| 413   | 1.545       | 6.3    | -6.2 | 706   | 1.540       | 1.0    | +1.4 |
| 414   | 1.730 <0.9  | -1.4   |      | 800   | 1.665       | 1.6    | +1.7 |
| 500   | 1.045       | 3.9    | +2.7 | 801   | 1.660       | <0.9   | +0.9 |
| 501   | 1.060       | 1.6    | +1.7 | 802   | 1.690       | 0.9    | -1.0 |
| 502   | 1.105       | 8.5    | -7.7 | 803   | 1.755       | 2.6    | -1.6 |
| 503   | 1.200       | 3.5    | -3.0 | 805   | 1.920       | 1.0    | -0.8 |
| 504   | 1.300       | 4.5    | +3.6 | 807   | 1.690       | 2.7    | +2.6 |
| 505   | 1.040       | 6.7    | +6.7 | 808   | 1.740       | 1.7    | -1.6 |
| 506   | 1.750       | 1.4    | -1.3 | 900   | 1.880       | <0.7   | +0.9 |
| 507   | 1.080       | 2.2    | -2.2 | 901   | 1.880       | <0.7   | +1.2 |
| 508   | 1.150       | 1.0    | -1.0 | 903   | 1.950       | 0.4    | -0.7 |
| 509   | 1.245       | 3.0    | +3.3 | 904   | 1.905       | 1.0    | -1.5 |
| 510   | 1.520       | 3.1    | -3.5 | 905   | 1.950       | 0.4    | -1.0 |

$$R = 100\left\{ \frac{\sum|F_0|}{\sum|F_0|} - 1 \right\}$$

$$= 10.8\%$$
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<td>&lt;0.7</td>
<td>+0.8</td>
</tr>
<tr>
<td>730</td>
<td>1.905</td>
<td>1.1</td>
<td>+0.8</td>
<td>940</td>
<td>1.960</td>
<td>0.6</td>
<td>+1.6</td>
</tr>
<tr>
<td>710</td>
<td>1.410</td>
<td>1.5</td>
<td>+1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$R = 100 \left( \frac{\Sigma |F_{o1}| - |F_{o2}|}{\Sigma |F_o|} \right)$$

$$= 15.9\%$$
THE CRYSTAL AND MOLECULAR STRUCTURE

OF

ANGELIC ACID
The Crystal and Molecular Structure of Angelic Acid.

1. Crystal Data.

Angelic Acid, C$_5$H$_8$O$_2$; Molecular Weight = 100.1; m.pt. = 45.5°C.

Density calculated = 1.139 gms/cc.

Density observed (by flotation in phosphoric acid solution) = 1.141 gms/cc.

$\alpha = 7.66 \pm 0.02\text{A}$  $\quad b = 11.60 \pm 0.02\text{A}$  $\quad c = 6.67 \pm 0.02\text{A}$

$\alpha = 90^\circ$  $\quad \beta = 100^\circ \pm 0.5^\circ$  $\quad \gamma = 90^\circ$

Systematic absences:— (h0l) when h = 2n + 1; (oko) when k = 2n + 1

Crystal system:— Monoclinic.

Space group:— P 2$_1$/a.

Four molecules per unit cell. No molecular symmetry required.

Centre of symmetry between two molecules.

Volume of unit cell (V) = abc sin $\beta = 583.7\text{A}^3$.

Absorption coefficient for X-rays ($\lambda = 1.542\text{A}$) /$\mu = 8.39\text{cm}^{-1}$.

Total number of electrons per unit cell = F(000) = 216.

The crystals were obtained by slow recrystallisation from 60 – 80 petroleum ether. This resulted in thin plates with the {001} face prominent.

The above data agree reasonably well with that found by Schimper(37) who gives

$\quad a : b : c = 0.6494 : 1 : 1.1393$

$\quad \beta = 100^\circ 33'$

The X-ray data give

$\quad a : b : c = 0.6603 : 1 : 0.5750$

i.e. Schimper's cell is twice the size of the true unit cell.
2 Experimental Measurements.

Angellic acid is very volatile and exists as soft, distorted plates. These plates cleave readily along the (20\bar{1}) plane and so thin needles with the needle axis parallel to the \( b \)-axis of the unit cell can easily be cut.

However, difficulty was experienced in obtaining specimens suitable for taking rotation photographs with the crystals rotating about either the a or c axes since attempts to cut the crystals in any other direction usually resulted in grossly distorted specimens.

Since the acid is volatile, some method of protecting the crystals whilst the X-ray photographs are being taken is necessary. As in the case of tiglic acid, the crystal on its glass fibre, was encapsulated in a Park-Davis gelatine capsule and extra crystals of angellic acid were added under the capsule to build up the vapour pressure. It was found the capsule acted as a permeable membrane and the crystal volatilised steadily whilst the photographs were being taken. As a result, the crystals had to be sealed in thin walled glass capillary tubes. This method proved to be perfectly satisfactory and in this way the crystals could be kept indefinitely.

Rotation, oscillation and moving-film photographs were taken using Cu - \( K\alpha \) radiation(\( \lambda = 1.542\AA. \)). The unit cell dimensions were obtained by means of rotation and equatorial layer line moving-film photographs. The reflections were estimated visually by/
by the multiple film technique (17). The structure factors evaluated from the estimated intensities by means of the usual mosaic crystal formula are given in table (VIII).
3. Correlation of the Reciprocal Lattice of Angelic Acid with the Fourier Transform of the Idealised 2-methyl-cis-2-butenic acid, the dimensions of which are given on page 11.

The Fourier Transforms of the idealised dimers of the two 2-methyl-2-butenic acids have already been calculated and it has been shown that tiglic acid is 2-methyl-trans-2-butenic acid. Consequently, it follows on the basis of chemical evidence, that angelic acid should be 2-methyl-cis-2-butenic acid.

However, the unit cell of angelic acid contains four molecules, i.e. two centrosymmetric dimers of angelic acid, and so the reciprocal lattice of the acid can not be obtained by simple sampling of the transform of the idealised dimer. Instead, the weighted reciprocal lattice is obtained by sampling the sum of two transforms correctly orientated with respect to one another. However, there is no need to consider two separate transforms. The solution of the structure can be obtained from the transform of one dimer by the following methods.

In the space group P 2₁/a, projection of the structure on to the (010) plane results in a projected arrangement of molecules similar to that shown in fig. (XIII).
i.e. The problem now reduces to consideration of a simple oblique cell half the size of the true cell and so the procedure employed in fitting the triclinic reciprocal lattice of tiglic acid to the Fourier Transform of the dimer of 2-methyl-trans-2-butene acid can again be used.

Unfortunately, in the particular case of angelic acid, it was obvious from the strength of the reflection from the $(20\overline{1})$ plane that on looking down the $b$-axis the molecule would be seen end on and it would be useless to try to solve the structure by making use of this projection.

Consequently, solution of the problem was approached by considering projection on to a plane perpendicular to the $a$-axis instead.

In this projection of the space group $P \overline{2}_1/a$ the projected arrangement of the molecules is as shown in fig. (XIV).

The symmetry of the projection gives rise to the equivalent points

\[(y, z), \left[\frac{1}{2}+y, z\right], \left[\frac{1}{2}+y, z\right], \left[\frac{1}{2}-y, z\right]\]

Hence, using the same notation as before, we get

\[F(\mathbf{kl}) = \sum w_{ij} \cos 2\pi (ky_{ij} + lz_{ij}) + \sum w_{ij} \cos 2\pi (ky_{ij} + lz_{ij})\]

where the first term on the right hand side is to be summed over the
atoms of the first dimer and the second term is summed over the dimer 2 related to the first by means of the reflection line \( y = \frac{1}{2} \).

Expanding the expression and dropping the subscripts 1 and 2 gives

\[
\frac{F(\omega k l)}{f_\omega} = \sum_{n} w_n \cos 2\pi(ky_n + lz_n) + \sum_{n} w_n \cos 2\pi\left\{ k\left(\frac{1}{2} + y_n\right) - lz_n\right\}
\]

\[
= \sum_{n} w_n \cos 2\pi(ky_n + lz_n) + \sum_{n} w_n \cos 2\pi\left( ky_n - lz_n\right)
\]

Hence the approximate value of \( \frac{F(\omega k l)}{f_\omega} \) for angelic acid can be obtained by correctly orientating the reciprocal lattice frame of the acid on the Fourier Transform of the idealised 2-methyl-cis-2-butenic acid, reading off the values of the transform at the points \((\omega k l)\) and \((\omega k l)\), and adding these if \( k \) is even or subtracting if \( k \) is odd.

\[\text{i.e. when } k = 2n, \frac{F(\omega k l)}{f_\omega} = T(\omega k l) + T(\omega k l)\]
when \( k = 2n + 1 \), \( \frac{F(\text{o}k\text{l})}{f_0} = T(\text{o}k\text{l}) - T(\text{o}k\text{l}) \)

It should be noted that

\[ \frac{F(\text{o}0\text{l})}{f_0} = 2T(\text{o}0\text{l}) \text{ for all values of } l, \]

and \( \frac{F(\text{o}k\text{o})}{f_0} = 2T(\text{o}k\text{o}) \text{ when } k \text{ = even} \)

= 0 when \( k \text{ = odd} \).

Although \( \frac{F(\text{o}k\text{o})}{f_0} = 0 \text{ when } k \text{ = odd} \), it does not follow that the value of the transform \( T(X*Y*Z*) \) at the point \( (\text{o}k\text{o}) \) is zero when \( k \text{ = odd} \). The zero values for \( \frac{F(\text{o}k\text{o})}{f_0} \) arise because a particular value of the \( T(X*Y*Z*) \) function is being subtracted from itself.
Fourier transform of idealised atoms of 2-methyl- 
\[ \text{cis}-2\text{-butyric acid} \]
with the \( b^* \) and \( c^* \) reciprocal axes of 
\( \text{angelic acid} \) superimposed.
4. The Structure of Angelic Acid.

Projection on to the Plane perpendicular to the a-axis of the unit cell.

The discussion just given, holds only if the orientation of the reciprocal lattice on the Fourier transform is known. This is precisely the problem being considered and so, at first sight it would seem that what has been said would be of no immediate use in solving the structure of angelic acid. Nevertheless, a number of clues to the way in which the (okl) reciprocal lattice net is arranged on the transform, are given by the discussion.

First of all, the values of $F(oko)$ and $F(ool)$ are twice the values of $T(oko)$ and $T(ool)$ read off from the transform and so addition and subtraction of terms need not be considered for these when seeking the correct orientation.

Secondly, strong values of $F(okl)$ must correspond with large

\[ \sum_{\text{fc}} T(okl) + (-1)^k T(OKI) \]

and weak values must correspond with small sums.

Forty-six independent (okl) reflections out of a possible 102 were observed and estimated. The intensities of these reflections were placed on an approximately absolute scale by means of the Wilson method, and with the above rules concerning the (oko) and (ool) reflections, coupled with the stronger general reflections (011), (032), (041), (042), (055), a reasonable fit of the reciprocal lattice net on to the transform was soon obtained.

Fig. (XV) shows the Fourier transform of an idealised dimer of
Fig. XVI.

Angelic acid, $a$-axis projection.

The electron density was computed using phase angles obtained from the Fourier transform of the idealised chlorine of $\alpha$-methyl - cis - 2- butyric acid.

Contours at intervals of 1$e/A^2$. 1$e/A^2$ contour dotted.
2-methyl-cis-2-butenic acid with the \( b^* \) and \( c^* \) reciprocal axes of angelic acid superimposed on it.

Phase angles obtained from the transform, combined with the observed structure factor amplitudes were then used to calculate the electron density projected on to the plane perpendicular to the \( a \)-axis.

Atomic centres in positions consistent with the expected geometry of the angelic acid molecule were then picked out from this map and structure factors were evaluated from these.

The discrepancy \( (R) \) at this stage was 36.2\%.

At a similar stage in the analysis of the tiglic acid structure, the discrepancy was 21\% and so it seemed likely at this point that the true angelic acid structure differed more from the idealised dimer of 2-methyl-cis-2-butenic acid than did tiglic acid from the corresponding trans acid.

This projection was then refined by successive difference syntheses until no further refinement could be effected. At this stage, the final value of the discrepancy was \( R = 8\% \).

An electron density map of the projected structure is shown in fig. 1 (XVI).

The projection of the crystal structure on to the plane perpendicular to the \( a \)-axis should have given two reasonably accurate atomic coordinates \( (y_p, z_p) \) for each atom P. The dimensions of the angelic/
angelic acid molecule should be expected to be roughly those of the idealised 2-methyl-cis-2-butene acid and are therefore known approximately. Hence, it should be quite a simple matter to calculate the third coordinate \( x^p \) for each atom and so refine the other two views of the molecule obtained by projecting the structure down the \( b \) and \( c \) - axes respectively.

This process was carried out and attempts were made to refine the \( c \)-axis projection. In this, the calculated coordinates \( x^p \) were combined with the coordinates \( y^p \) obtained from the \( a \)-axis projection. The resultant discrepancy between the observed and calculated structure factors \( F(hko) \) was 39.8%. Successive refinements by means of difference syntheses brought down the value (\( R \)) in the sequence 39.8% → 35.2% → 31.5% → 27.9% and when hydrogen atoms were included in the calculations, \( R \) fell to 23% at which point the projection stopped refining any further. A map of the electron density computed at this point, exhibited so much distortion that it was obvious that something was wrong with the structure.

A re-examination of the electron density map obtained from the \( a \)-axis projection gave no indication what could be wrong. There seemed no other way of choosing a constellation of atoms from this map which was consistent with the X-ray data and at the same time was chemically reasonable. Consequently, the work up to this point was abandoned for the moment and it was decided to try to find a new structure.
Angelic acid - b - axis projection showing final electron density map (corresponding to structure A), and the alternative structures A and B.

Contours at intervals of 1e/Å². 1e/Å². contour dotted.
Projection on to the (010) plane of the unit cell.

At this stage, the best hope of finding a new structure seemed to be to tackle the \(h\)-axis projection. The reflected beam obtained from the \((20\bar{1})\) plane is so very strong that all the atoms in the unit cell must lie on, or very nearly on this plane.

To solve the structure therefore, it is only necessary to place a model of the idealised 2-methyl-cis-2-butenic acid on this plane, with the centre of symmetry of the dimer coincident with the crystallographic centre of symmetry, and rotate the dimer in this plane about an axis through the centre of symmetry until the observed and calculated structure factors agree.

This was done and it soon became obvious that there were only two arrangements in space which gave reasonable agreement between observed and calculated structure factors. These orientations are shown in figure (XVII). It will be noted that arrangements A and B are almost identical in this projection, and as a result, on the basis of the \((h0l)\) reflections alone, the X-ray data do not give a unique solution.

However, when the \((hko)\) reflections are considered it becomes quite obvious that arrangement B is unacceptable and orientation A is consistent with both the \((h0l)\) and \((hko)\) structure factors.

Structure A was refined by means of successive difference syntheses. The refinement process was accomplished very rapidly at this point and the discrepancy R fell in the sequence \(R = 31.6\% \rightarrow 19.6\% \rightarrow 13.2\%\), at which stage no further refinement/
refinement was attempted. All the atoms in the unit cell (carbon, hydrogen and oxygen) were included in the structure factor calculations and a Debye-Waller factor \( B = 8.5 \times 10^{-16} \text{ cm}^2 \) was employed.

Only 22 (h0l) reflections out of a possible total of 63 in the \( \text{Cu} - K_\alpha \) sphere of reflection were observed and estimated. This small percentage of observed reflections is due to two effects. First, the large amount of overlapping of atoms in the projection and secondly, the apparently high temperature factor will both cause the structure factors of planes with small spacings to be very small and hence the X-ray beams reflected from these planes will be so weak that they will be unobserved on the photographs.

Because of this, it should be expected that large errors might be associated with coordinates derived from this projection, and this appears to be borne out by the observation that in this projection, moving an atom quite a considerable distance in one direction can be compensated for in the difference syntheses by movements of neighbouring atoms so that the overall discrepancy is varied by only a small amount.

Even so, because of the good agreement between observed and calculated structure factors the structure appears to be essentially correct.

The final electron density map obtained by projecting the structure on to the (010) plane is shown in figure(XVII) and the atomic coordinates obtained from the projection are given in table (VII).
Fig. XVIII

Angelic acid, c-axis projection. Final electron density map. Contours at intervals of 1e/Å². 1e/Å² contour dotted.
Projection of the Structure on to the plane perpendicular to the c-axis of the unit cell.

The atomic coordinates \((x_p, z_p)\) obtained from the \(b\)-axis projection should not be expected to be very accurate but they should be accurate enough to provide an approximate \(y_p\) coordinate to be used in a model set up for refinement of the \(c\)-axis projection.

Such a model was obtained and refined by successive difference syntheses. The refinement process proceeded in the sequence
\[
R = 39.9\% \rightarrow 31.4\% \rightarrow 27.8\% \rightarrow 24.2\% \rightarrow 22.3\% \rightarrow 19.9\%.
\]
No further refinement was attempted because it was found that the calculated structure factors were insensitive to movements of up to 0.1A. in the coordinates of \(C_2\) and it was felt that the small percentage of observed reflections (39 independent reflections out of a possible 112) was insufficient to justify any claim of higher accuracy.

The temperature factor used was \(B = 8.5 \times 10^{-16}\text{cms.}^2\) for all atoms except \(C_4\) for which a value of \(3.5 \times 10^{-16}\text{cms.}^2\) was used.

The final electron density map of the \(c\)-axis projection is shown in figure (XVIII). The calculated and observed structure factors are quoted in table (VIII).

When the high temperature factor is considered together with the facts that angelic acid crystals melt at 45°C., are extremely volatile, and, in general, are very distorted, it would appear that at room temperatures the crystal lattice is tending to break down/
down and disorder is setting in. The result is that only reflections from planes of low order spacings are observed. If the disorder is increased by addition of a small amount of impurity to the acid then the melting point falls sharply. This explains why impure acids of this type tend to exist as oils and will only solidify if the impurity is removed.

\[ (x, y, z) \] are coordinates of a point in a lattice in which the unit vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are parallel to the unit cell translations \(a\) and \(b\) and the vector \(\mathbf{a}_3\) is in \((00l)\) plane at right angles to the plane \((h0l)\).

The transformations are the analogs of the analogous of the analogous of the analogous...
Coordinates, Molecular Dimensions and Orientation of the molecule in the unit cell.

The final coordinates obtained by projection of the structure down the b and c-axes respectively, are quoted in table (vii).

These two projections were refined independently of one another and since errors in atomic coordinates of up to 0.1Å can be expected in both cases, the sets of coordinates obtained from the projections are given independently.

\((x_p, y_p, z_p)\) are the fractional coordinates of atom P.
\((X_p, Y_p, Z_p)\) are the same coordinates expressed in Angstrom units, \((X_p\) is obtained from the average value of \(x_p\) from the two independent measurements) referred to the frame of the monoclinic unit cell.

\((X'_p, Y'_p, Z'_p)\) are coordinates of P referred to a rectangular frame in which the unit vectors \(OY'\) and \(OZ'\) are coincident with the unit cell translations \(b\) and \(c\) and the vector \(OX'\) lies in the \((01\ell)\) plane at right angles to the plane \(Y'OZ'\).

The transformations from the monoclinic to the rectangular frame are

\[
X'_p = X_p \sin \beta \\
Y'_p = Y_p \\
Z'_p = Z_p + X_p \cos \beta.
\]
## Table (VII)

### Fractional Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>(X_p)</th>
<th>(Z_p)</th>
<th>Atom</th>
<th>(X_p)</th>
<th>(Y_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>0.1257</td>
<td>0.0913</td>
<td>C₁</td>
<td>0.1000</td>
<td>0.3633</td>
</tr>
<tr>
<td>C₂</td>
<td>0.1667</td>
<td>0.3100</td>
<td>C₂</td>
<td>0.1833</td>
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<td>0.2103</td>
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<td>C₄</td>
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<td>0.1273</td>
</tr>
<tr>
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<td>C₅</td>
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</tr>
<tr>
<td>O₆</td>
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<td>0.0467</td>
<td>O₆</td>
<td>0.0033</td>
<td>0.1447</td>
</tr>
<tr>
<td>O₇</td>
<td>0.1500</td>
<td>0.2117</td>
<td>O₇</td>
<td>0.1230</td>
<td>0.0240</td>
</tr>
</tbody>
</table>

#### Coordinates in \(\text{A.}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Monoclinic Coords.</th>
<th>Rectangular Coords.</th>
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<tbody>
<tr>
<td></td>
<td>(X_p) (Y_p) (Z_p)</td>
<td>(X_p^{\prime}) (Y_p^{\prime}) (Z_p^{\prime})</td>
</tr>
<tr>
<td>C₁</td>
<td>0.865 4.214 0.609</td>
<td>0.852 4.214 0.459</td>
</tr>
<tr>
<td>C₂</td>
<td>1.341 3.480 2.068</td>
<td>1.320 3.480 1.835</td>
</tr>
<tr>
<td>C₃</td>
<td>1.612 2.440 2.528</td>
<td>1.587 2.440 2.248</td>
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<tr>
<td>C₄</td>
<td>0.880 1.477 1.223</td>
<td>0.867 1.477 1.070</td>
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<tr>
<td>C₅</td>
<td>2.308 1.771 3.620</td>
<td>2.273 1.771 3.219</td>
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<tr>
<td>O₆</td>
<td>0.128 1.679 0.312</td>
<td>0.126 1.679 0.289</td>
</tr>
<tr>
<td>O₇</td>
<td>1.046 0.278 1.412</td>
<td>1.030 0.278 1.231</td>
</tr>
</tbody>
</table>
Molecular Dimensions.

The standard deviation from the mean of the two independent measurements of $X_p$ is 0.08Å and the largest deviation is 0.14Å. This means, therefore, that a standard deviation of about 0.12Å should be associated with measured bond lengths and differences between observed and expected bond lengths of two and a half times this will have no significance.

The standard deviation in bond angles is 10°.

The observed bond lengths and bond angles are

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1 - C_2$</td>
<td>1.63Å</td>
<td>$C_1 C_2 C_3$ 140°</td>
</tr>
<tr>
<td>$C_2 - C_3$</td>
<td>1.16Å</td>
<td>$C_2 C_3 C_4$ 99°</td>
</tr>
<tr>
<td>$C_3 - C_4$</td>
<td>1.69Å</td>
<td>$C_2 C_3 C_5$ 142°</td>
</tr>
<tr>
<td>$C_3 - C_5$</td>
<td>1.36Å</td>
<td>$C_4 C_5 C_6$ 116°</td>
</tr>
<tr>
<td>$C_4 - O_6$</td>
<td>1.10Å</td>
<td>$C_3 C_4 C_7$ 132°</td>
</tr>
<tr>
<td>$C_4 - O_7$</td>
<td>1.22Å</td>
<td>$O_6 C_4 O_7$ 111°</td>
</tr>
</tbody>
</table>
The equation of the plane through atoms C₂, C₃, C₄, C₅, O₆, and O₇ is

$$0.8154 X^* + 0.0669 Y^* - 0.5742 Z^* - 0.1675 = 0 \quad \ldots \ldots \ldots (1)$$

The distance (d) of the atoms from this plane are

<table>
<thead>
<tr>
<th>Atom</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>O₆</th>
<th>O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(A)</td>
<td>0.55</td>
<td>0.09</td>
<td>-</td>
<td>0.02</td>
<td>-0.04</td>
<td>-0.12</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The hydrogen bonded O-.O distance in the dimers is 2.73Å. Hence it follows that the molecule has essentially the shape expected from the chemical formula with one important difference. C₁ does not lie in the plane (1) of the rest of the molecule. Bond C₂ - C₁ has rotated about C₂ = C₃ as axis, in a clockwise direction until C₁ is 0.55Å. from the plane (1) and although large errors are associated with the atomic coordinates this rotation is highly significant.

The consequences of this rotation of bond C₁ - C₂ are rather interesting. It means that if the sp² hybridisation at carbon atoms C₂ and C₃ is preserved, and the axes of the 7π-orbitals are still perpendicular to the planes of the sp² orbitals, then in angelic acid, the axes of the 7π-orbitals of C₂ and C₃ are not parallel to one another. Hence the overlap of these 7π-orbitals is not as extensive in the planar system \( \text{C}=\text{C} \) of the normal double bond.

This probably accounts, at least to some extent, for the differences in the relative stabilities of tiglic and angelic acids and of their derivatives.
If some mechanical stress is exerted on $C_1$ so that $C_1 - C_2$ is caused to rotate even further (e.g. by overcrowding of $C_1$ due to a large group attempting to attach itself to the carboxyl group) or, if the distortion of the $\equiv C=\equiv$ system is increased by attempted substitution, then the resultant overlap of the $\pi$-orbitals may be so small that effectively the $\pi$-electrons will be localised on $C_2$ and $C_3$. Free rotation will then take place about $C_2 - C_3$ and a mixture of tiglic acid and angelic acid (or derivatives of these) will be obtained with the tiglic acid (or tiglic acid derivative) predominating.

The ready isomerization of angelic acid (and its derivatives) to tiglic acid (and its derivatives) is observed in practice. (39).

**Molecular Orientation.**

The molecular orientation can be defined by stating
a) the mean plane through atoms $C_2$, $C_3$, $C_4$, $C_5$, $O_6$, and $O_7$ and
b) fixing the position of a line in the molecule in this plane.

The equation of the plane has already been given and it is very nearly, although not quite, the (201) plane. The orientation of the molecule in this plane will be defined by stating the angle between $C_3 - C_4$ and the positive direction of the $b$-axis of the monoclinic unit cell. This angle is found to be $55^\circ$. 
Conclusion.

The atomic coordinates obtained from the b and c axial with projections respectively, are consistent with one another and the chemical formulation 2-methyl-cis-2-butenio acid assigned to angelic acid. The packing of the molecules in the unit cell is reasonable. The hydrogen bonded $O...H$ distance is 2.73Å, and the closest distances of approach of non-bonded atoms of neighbouring dimers are all of the expected dimensions.

However, these results are not consistent with the a-axis projection originally obtained by considering the Fourier transform of the idealised dimer.

There are two ways of explaining this inconsistency.

1. The projections down the b and c axes are completely wrong and the a axis projection is correct.
2. The projections down the b and c axes are correct and the a axis projection is wrong.

There are a number of reasons for assuming that explanation (2) is correct. It explains why the structure based on the a axis projection could not be refined when the other projections were considered. Combination of the b and c axial projections result in a structure which, if allowance is made for the inaccuracies involved, is both chemically and crystallographically reasonable. In these projections there are no serious discrepancies between the observed and calculated values of the structure factors. Furthermore, if the b and c axial projections were completely wrong then there would be no agreement between the observed and calculated structure/
Angelic acid. a-axis projection.

- = original interpretation of projected electron density obtained from the Fourier Transform.

- - = projected structure expected on the basis of the b- and c-axial projections.
structure factors for the general (hkl) planes. A comparison of the observed and calculated (hlA) structure factors shows a general agreement between the two sets of values and when it is remembered that the standard deviation of the atomic coordinates obtained from the b and c axial reflections is of the order 0.1Å., then the agreement is very reasonable.

Hence, it follows that the b and c axial projections must be essentially correct but the interpretation of the electron density projection obtained on looking down the a-axis is wrong.

Figure (XIX) compares the original interpretation of this projection with that expected on the basis of the b and c axial projections. It will be observed that the alternative explanations of the projected electron density have much in common. It is thought that the wrong interpretation has arisen because the true structure of the dimer is somewhat different from the idealised dimer on which the Fourier transform was based. As a result, a number of incorrect phase angles have been obtained from the transform and the refinement process involving combination of these incorrect phase angles with the structure factor moduli has biased the refinement towards a pseudohomometric constellation which has much in common with the correct structure.

The a-axis projection will, therefore, require to be reinvestigated.

Table (viii) lists the observed and calculated structure factors of the (hol), (hko), (hlA), reflections. The atomic coordinates obtained on projection down the a-axis and the calculated and observed structure factors based on these coordinates are also given.
Observed (|Fₒ|) and Calculated (Fₒ) Structure Factors of Angelic Acid. (Table VIII).

\[ h + k = 2n \]

\[ F(hkl) = F(hkl) \]
\[ F(\bar{h}k\bar{l}) = F(h\bar{k}\bar{l}) + F(hkl) \]

\[ h + k = 2n + 1 \]

\[ F(hkl) = -F(hkl) \]
\[ F(\bar{h}k\bar{l}) = -F(h\bar{k}\bar{l}) + F(hkl) \]
\[ F(hkl) = 0 \text{ when } h = 1 = 0 \text{ or } k = 0. \]
\[ R = \frac{100\left( \sum |F_o| - |F_c| \right)}{\sum |F_o|} \]

\[ R = 13.2\% \]
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\[
R = \frac{100 \left( \sum |F_o| - |F_c| \right)}{\sum |F_o|}
\]

= 19.9%
| Plane | $2\sin \theta$ | $|F_o|$ | $F_o$ | Plane | $2\sin \theta$ | $|F_o|$ | $F_o$ |
|-------|----------------|--------|--------|-------|----------------|--------|--------|
| 011   | 0.270          | 55.6   | 59.3   | 210   | 0.430          | 34.1   | 43.4   |
| 012   | 0.478          | 15.8   | 26.0   | 211   | 0.520          | 11.7   | 8.0    |
| 013   | 0.715          | 9.6    | 9.2    | 211   | 0.450          | 31.5   | 27.2   |
| 014   | 0.955          | < 4.8  | 10.4   | 212   | 0.575          | 16.9   | 8.3    |
| 110   | 0.240          | 23.9   | 22.6   | 310   | 0.625          | < 4.9  | 1.6    |
| 111   | 0.360          | 5.2    | 0.1    | 311   | 0.700          | 7.9    | 7.8    |
| 112   | 0.565          | 17.1   | 17.4   | 312   | 0.840          | 8.9    | 12.6   |
| 113   | 0.780          | 20.4   | 7.2    | 313   | 0.860          | 15.3   | 12.8   |
| 114   | 1.000          | 6.5    | 10.0   | 314   | 0.715          | 13.5   | 23.7   |
| 111   | 0.315          | 27.7   | 39.9   | 410   | 0.850          | 4.8    | 0.4    |
| 112   | 0.495          | 5.6    | 0.7    | 411   | 0.825          | 10.7   | 11.3   |
| 113   | 0.715          | 11.4   | 15.8   | 412   | 0.880          | 20.3   | 16.4   |
| 114   | 0.935          | 8.7    | 1.7    |
Atomic Coordinates and Structure Factors obtained from incorrect interpretation of the projection down the a-axis.

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\[ R = \frac{\sum |Z| |F_o| - |F_o|^2}{\sum |F_o|} = 15.8\% \]
THE CRYSTAL AND MOLECULAR STRUCTURE

OF

TETRABENZO-2:3-6:7-2'3'-6':7'-HEPTAFULVALENE.
The Crystal and Molecular Structure of
Tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene.

1. Introduction.

As a result of much accurate work carried out on the structures of organic compounds by means of the methods of X-ray and electron diffraction analysis, coupled with parallel progress in theoretical calculations, it has become possible to predict with fair accuracy such things as bond lengths, bond angles, charge distributions and ultra-violet absorption bands of many molecules.

In particular, for conjugated condensed ring hydrocarbons, calculations by means of the molecular orbital theory have been found to be in reasonable agreement with observation.

Tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene (I) is such a condensed ring hydrocarbon and molecular orbital calculations have been reported for it. These calculations are based on the assumption that all the atoms lie in one plane. If, however, the atoms do not lie in the same plane then the calculations may be in serious error. The magnitude of this error will depend on how far the molecule deviates from planarity. If the deviations are marked then predictions based on the
assumption of a planar molecule may be quite wrong.

This is in fact what is found to happen in the case of tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene for certain predictions made on the basis of these calculations are not in accord with observation.

The reason for this is quite simple. If a planar model is built up using bond lengths of 1.4A. and assuming the rings A and B to be regular heptagons and the rings C,D, E and F to be regular hexagons, then it is found that the centres of the starred pairs of carbon atoms approach to within 1.3A. of one another.

Such a close distance of approach of carbon atoms is impossible and so the atoms of the molecule can not be coplanar.

The object of this work is to determine the shape of the tetrabenzo-2:3-6:7-2':3'-6':7'-heptafulvalene molecule.

From now on, the compound will be referred to as T.B.H.F.

2. **Crystal Data.**

T.B.H.F., C$_{30}$H$_{20}$; Molecular Weight = 380.5.

Density calculated = 1.224 gms/cc.

Density observed (by flotation in potassium iodide solution) = 1.245 gms/cc.

a = 13.52 ± 0.02A. b = 8.38 ± 0.02A. c = 10.41 ± 0.02A.

α = 90° β = 118°50' ± 0.5° γ = 90°

Volume of unit cell = 1033A.$^3$

Number of molecules per unit cell = 2.

Systemmatic absences: (hol) when h = 2n + 1.

(oko) when k = 2n + 1.
Space group = P 2\textsubscript{1}/a
Absorption coefficient for X-rays (\(\lambda = 1.542\text{Å}\)) \(\mu = 6.4\text{cm}^{-1}\).
Total number of electrons per unit cell \(F(000) = 400\).

Crystals were obtained in the form of small, diamond-shaped plates by refluxing the material with toluene until solution was complete and allowing the toluene to evaporate off overnight at room temperature. The diamond-shaped face is the (001) face and the \(a\) and \(b\) axes lie along the diagonals of the face.

Harnik, Herbstein, Schmidt and Hirshfield\(^4\) have reported the existence of another form of T.B.H.F. with
\[
\begin{align*}
a &= 11.3\text{Å} \\
b &= 16.6\text{Å} \\
c &= 11.6\text{Å} \\
\alpha &= 90^\circ \\
\beta &= 107^\circ 30' \\
\gamma &= 90^\circ
\end{align*}
\]
Space group = P 2\textsubscript{1}/n.
Density calculated = 1.22 gms/cc. Density observed = 1.25 gms/cc.
4 molecules per unit cell.

These authors call the compound Bisdibenzosuberenylidene.

The existence of more than one form of these complex condensed ring hydrocarbons seems to be not unusual, e.g.
\(\alpha\) and \(\beta\) forms of 3:4-5:6-dibenzophenanthrene (\(41, 42\)).
\(\alpha\) and \(\beta\) forms of dixanthyldiene (\(41\)).
\(\alpha\) and \(\beta\) forms of difluorenyldiene (\(43, 44\)).

3. **Experimental Measurements.**

Rotation, oscillation and moving-film photographic measurements have been employed. The radiation used was copper K\(_\alpha\) (\(\lambda = 1.542\text{Å}\)). The cell dimensions were determined by means of rotation and equatorial layer line moving-film photographs. The reflections were estimated visually by means of the multiple film technique. Structure factors for the (h0l) reflections calculated by the usual mosaic crystal formula are given in pp(96, 97).
4. Attempts to determine the structure of T.B.H.F.

Since the space group is $P 2_1/a$ with two molecules per unit cell, it follows that the asymmetric unit is half the molecule and the molecule possesses a centre of symmetry. The centre of symmetry must lie at the mid-point of the bond joining the seven-membered rings, and the asymmetric unit is

It should be expected that the most stable state of the molecule would be attained when the conjugation is a maximum and so, rather than merely have the starred atoms knock one another out of the plane of the rest of the molecule, it seemed more likely that the rings C, D, E and F would move out of the plane of rings A and B. In addition, it is unlikely that only rings C and E say, will move. It is more likely that at the overcrowded positions, one ring will be twisted up whilst the other is twisted down. If ring C is up out of the plane of rings A and B then ring F will be twisted downwards. Hence, since the molecule is centrosymmetrical, the plane of ring D will be up and the plane of ring E will be down from the plane of rings A and B, i.e. the molecule may have a shape similar to that shown below.
The next step forward in the investigation was an attempt to fit a model of this sort into the unit cell in such an orientation as to fit the observed data.

It was assumed, on analogy with results obtained for dibiphenylene-ethylene (II) (43), that the atoms at the overcrowded positions would have to be at least 2.5Å apart - possibly further - and so, for the trial structure it was postulated that in the asymmetric unit consisting of rings C, A and D, ring A was planar and rings C and D were folded up out of the plane of ring A and at angles of about 45° to it.

In spite of a great deal of work carried out in trying to obtain the correct crystal structure based on such a model, no satisfactory structure could be obtained.

All structures based on this model gave very large discrepancies \( R = \frac{\sum |F_o - |F_c|}{\sum |F_o|} > 65\% \).

Then it was noticed that the ultra-violet absorption spectra of tetraphenyl-ethylene and T.B.H.F. were reported to be very similar (40).
The ultra-violet absorption spectra are defined by the electronic energy levels of the compounds. These energy levels are defined, to the first approximation, by the extent of the conjugation of the \( \pi \)-electrons of the molecule. If the ultra-violet spectra are similar then the \( \pi \)-electron conjugations must be similar. Tetraphenylethylene is just T.B.H.F. minus atoms 4, 5, 4' and 5'. Consequently, in T.B.H.F., atoms 4, 5, 4' and 5' can not be adding a large contribution towards the resonating structure of the remaining \( \pi \)-electrons.

In tetraphenylethylene, the steric strain due to overcrowding can be overcome by simply rotating the six membered rings about axes along the bonds joining them to the central "ethylenic" system, and so it seems reasonable to assume that something of this sort will take place in T.B.H.F.

At this stage, the original trial structure was abandoned.

Inspection of the calculated structure factors of the trial structures using the rejected molecular model revealed one structure where the calculated values of \( F(001) \) agreed reasonably well with the scaled observed structure factors for these planes. This suggested that the \( z_p \) coordinates of this structure were correct but did not indicate whether any particular coordinate had a positive or negative value nor did it indicate which atom should be associated with a particular value of \( z_p \).

Consequently, on a scale diagram of the (010) plane, a grid consisting of lines drawn parallel to the \( a \)-axis and passing through the \( z_p \) coordinates of this trial structure was drawn up.
The asymmetric unit consisting of rings A, C and D was then divided up into four parts:

(i) Ring C   (ii) Ring D   (iii) Atom 1 of ring A  
(iv) Atoms 4 and 5 of Ring A.

The structure factors of the planes (401), (400), (401) and (402) are 32.0, 43.0, 5.8 and 22.6 respectively and because of the sudden fall in the value of |F(401)| as compared with the others, it was felt that if a structure could be obtained which yielded calculated F values for these planes in this sequence, as well as accounting satisfactorily for the (00\ell) planes, then this might prove to be the correct structure.

Experience with the numerous trial structures already considered showed an orientation of the molecule which yielded calculated F values for the above mentioned (401) planes in the correct sequence. On placing the four parts of the asymmetric unit on to the grid already discussed and sliding them into the approximate orientation to give calculated values of F(401) in agreement with the observed values, a feasible trial structure was obtained. This gave a discrepancy of 49%.

This may or may not prove the correct structure.

The extent of the buckling is not certain but the broad features of this postulated molecular structure are as shown in figure (XX). The puckering of the seven membered rings in the diagram is very much over-exaggerated to make the distortions clear.

The main features of this structure are
Postulated structure of T.B.H.F.
a) There is a central ethylenic system, the atoms of which are coplanar or very nearly so. This system is made up of atoms 1, 2, 7, 1', 2', 7'.

b) The six membered rings are turned about axes along the bonds which attach them to the ethylenic system (a) until their planes are at about 40° to that of the plane 1, 2, 7, 1', 2', 7'.

c) This results in atoms 2, 3, 6, 7 of ring A being approximately coplanar and the planes of rings C and D lie at about 40° to this plane. Plane 2, 3, 6, 7 make an angle of about 40° with the plane 1, 2, 7, 1', 2', 7'.

d) Atoms 3, 4, 5 and 6 lie approximately in one plane in such a way that 4 and 5 bridge across the space between 3 and 6 which is left as a consequence of operations (a), (b) and (c). Rings C and D therefore, lie on opposite sides of the plane 2, 3, 6, 7 from atoms 1, 4 and 5. Hence the seven-membered rings are puckered in a manner analogous to that of the boat form of the cyclohexane molecule.

This process means that bonds 1-1', 4-5, 4'-5' must be true double bonds. Bromine does add on to this molecule although the number of atoms of bromine which do add to the structure is not known.

It is also interesting to note that in this structure there is no steric strain due to distortion of bond angles. Neither is there distortion of the sp² bond angles of the six membered rings nor is there any associated with the ethylene systems.

There is no overcrowding of atoms. The closest distance of approach of non-bonded carbon atoms is 2.8Å and is between atoms 2 and 7'. The next closest distance of approach is between atoms 2 and 15' which are about 3Å apart.
The structure can be considered to be tetrphenyl ethylene plus atoms 4, 5, 4', 5'. Hence the similarity reported for the ultra-violet spectra of the two compounds.

It is interesting to note that this postulated structure is very similar to that found by Harnik and Schmidt (45) for dianthronylidene. In this compound, "A molecular model has been obtained approximating to symmetry 2/m in which the centre to centre distance of 2.9Å between the "overcrowded carbon atoms 4, 8' and 8, 4' is achieved by a 40° "rotation of the benzene rings out of the plane of the central "ethylenic system. This rotation is accompanied by a compression "of the angle to 113° and by "deflection of the exocyclic bonds "to the carbonyl carbon by 8° out "of the planes of their respective "benzene rings".

Both dianthronylidene and T.B.H.F. have four six-membered rings and a central ethylenic system in common. They differ only in the nature of the group spanning the space between the six-membered rings. The postulated model of T.B.H.F. was not based on Harnik and Schmidt's work. It is a model which has emerged in the process of putting together parts of a molecule in such a way as to account for the experimentally observed structure factors.

Although at the moment there is no direct proof that the model proposed for the T.B.H.F. molecule is correct all the above pieces
of evidence, which by themselves do not mean very much, all fit in with it. Consequently, the proposed structure may possibly be correct and it may be well worth while attempting to refine this structure further.

The fractional coordinates of the carbon atoms in this projection are given in table (1x). A comparison of the calculated structure factors with those observed for the (hol) reciprocal lattice net of T.B.H.F. are given on pages(96-97).
Fractional Atomic Coordinates for the Atoms of the Asymmetric Unit of T.B.H.F.

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### Observed (|Fo|) and Calculated (Fo) Structure Factors of T.B.H.F.

#### $F(hol)$

| Plane  | 2sin$^\theta$ | |Fo|  | Fo |
|--------|--------------|-----------------|-----|-----|
| 200    | 0.255        | 7.2             | -17 |     |
| 201    | 0.365        | 11.2            | 11  |     |
| 202    | 0.510        | 5.8             | 8   |     |
| 203    | 0.660        | 22.0            | 4   |     |
| 204    | 0.820        | 18.1            | -4  |     |
| 205    | 0.980        | 9.1             | 12  |     |
| 206    | 1.135        | 8.9             | 14  |     |
| 207    | 1.305        | 13.8            | -18 |     |
| 208    | 1.215        | 13.3            | 14  |     |
| 209    | 1.380        | 5.7             | 2   |     |
| 400    | 0.510        | 43.0            | 54  |     |
| 401    | 0.615        | 5.8             | -4  |     |
| 402    | 0.735        | 22.6            | -14 |     |
| 403    | 0.875        | -               | 14  |     |
| 404    | 1.015        | -               | -4  |     |
| 405    | 1.165        | 13.0            | -4  |     |
| 406    | 1.320        | 6.2             | -29 |     |
| 407    | 1.480        | 10.8            | -17 |     |

<p>| Plane  | 2sin$^\theta$ | |Fo|  | Fo |
|--------|--------------|-----------------|-----|-----|
| 401    | 0.460        | 32.0            | 34  |     |
| 402    | 0.460        | 18.8            | -15 |     |
| 403    | 0.510        | 13.3            | -7  |     |
| 404    | 0.610        | 21.0            | -15 |     |
| 405    | 0.735        | 25.0            | -25 |     |
| 406    | 0.865        | 11.6            | 9   |     |
| 407    | 1.010        | 13.0            | 2   |     |
| 408    | 1.160        | 11.3            | -4  |     |
| 409    | 1.290        | 10.7            | 17  |     |
| 410    | 1.480        | 8.6             | 14  |     |
| 411    | 1.630        | 5.0             | -   |     |
| 600    | 0.775        | 6.0             | 3   |     |
| 601    | 0.870        | 7.4             | 7   |     |
| 602    | 0.980        | 8.5             | 15  |     |
| 603    | 1.105        | 10.0            | 14  |     |
| 604    | 1.235        | 17.0            | 14  |     |
| 605    | 1.385        | 5.2             | 9   |     |
| 606    | 0.710        | 4.0             | -10 |     |
| 607    | 0.680        | 8.9             | -20 |     |
| 608    | 0.685        | 4.0             | 2   |     |
| 609    | 1.300        | 5.0             | 6   |     |</p>
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* This may be due to extinction.
A MOLECULAR ORBITAL STUDY OF PTERIDINE

AND

A CORRELATION CURVE FOR CARBON–NITROGEN BONDS.
A Molecular Orbital Study of Pteridine and a Correlation Curve for Carbon-Nitrogen Bonds.

1. Introduction

There are a number of experimental techniques which can be employed in measuring bond lengths and each one of them shows that bonds of a similar type between any two given atoms are more or less constant in length.

The transition in bond type is gradual in character and many organic molecules can be assigned bond orders intermediate between single and double bonds. The lengths of these bonds can be estimated experimentally by any of the usual methods and so a relationship between bond orders and bond lengths can be obtained. Hence, if a bond length between two atoms is known the bond order can be predicted.

Conversely, if the bond order is known, then the bond lengths can be estimated.

In this work, the attempt is made to calculate these bond orders for pteridine (which is formulated as above) and so predict the bond lengths to be expected.

It is the electrons which form the bonds in a molecule and so one obvious way of estimating bond orders is to estimate the
distribution of electrons in the molecule.

In pteridine, for each carbon and nitrogen atom, there are three \( sp^3 \) hybridised orbitals lying in one plane at 120° to each other. Two of these overlap with \( sp^2 \) orbitals of nearest neighbours of the condensed ring system giving rise to the axially symmetrical \( \sigma \) bonds between carbon and nitrogen atoms, whilst the third, in the case of carbon atoms, is linked up with the 1s orbital of a hydrogen atom, and in the case of nitrogen atoms it contains a lone pair of \( sp^3 \) electrons.

The remaining electron of each atom lies in the 2p\( _z \) orbital which is at right angles to the planar framework of the \( sp^2 \) orbitals. When 2p\( _z \) orbitals overlap a \( \pi \)-bond is formed.

The \( \sigma \)-electrons are usually regarded as being effectively localised whereas the \( \pi \)-electrons are regarded as being the property of the molecule as a whole.

Hence, the problem of calculating the distribution of electrons in the pteridine molecule now degenerates to a consideration of the distribution of the \( \pi \)-electrons over the molecule.

2. The Secular Equations of Pteridine.

Electrons are particles which show some of the properties of waves and in order to correlate the particulate idea of an electron with its wave-like properties it is postulated that the probability of finding an electron in space is defined by a wave function \( \Psi \), where \( \Psi \, dV \) represents the probability of finding an electron in the volume element \( dV \) of space.

There are several ways of attempting to find this electron
distribution and in the linear combination of atomic orbitals
molecular orbital approach the \( n \)-electrons are considered to be
under the influence of all the atoms of the condensed ring system.
The molecular orbitals are then supposed to be given by
\[
\Psi_j = \sum_{\alpha}^\infty (c_{\alpha,j} \psi_\alpha)
\]
where \( c_{\alpha,j} \) are constants representing the contribution which the
atomic orbitals \( \psi_\alpha \) make towards the molecular orbital \( \Psi_j \) and the
normalising condition \( \sum (c_{\alpha,j})^2 = 1 \) is obeyed. \( c_{\alpha,j} \) then
represents the contribution of the \( n \)-electron \( j \) to the electron density
on atom \( r \).

In pteridine there are ten atoms contributing to the molecular
orbital and so this linear combination of atomic orbitals leads,
in the well-known manner, to ten secular equations, the first of
which is
\[
c_1 (H_{1,j} - E S_{1,j}) + c_2 (H_{2,j} - E S_{2,j}) + \cdots + c_{10} (H_{10,j} - E S_{10,j}) = 0
\]
where \( E_j \) is the energy of the \( j \)th \( n \)-electron,
\( H_{rs} = \int \psi_r \psi_s d\gamma \) and is known as the "Exchange Integral" or
"Resonance Integral" since it is a measure of the stability
which the system attains through exchange of an electron between atoms
\( r \) and \( s \),
\( H_{rr} = \int \psi_r \psi_r d\gamma \) is the "Coulomb Integral" and is the energy
which the \( n \)-electron in question would have if it were confined to
the atom \( r \) instead of resonating round the ring of the pteridine
molecule,
\( S_{rs} = \int \psi_r \psi_s d\gamma \) and is the "Overlap Integral". It is a measure
of the extent of the overlap of the atomic orbitals \( r \) and \( s \),
\( S_{rr} = \int \psi_r^2 d\gamma \) is the "Normalisation Integral" and since \( \psi_r^2 d\gamma \)
represents the probability of finding an electron in volume \( d\gamma \) of
space \( S_{rr} = 1 \),
now let $H_{rs} = \beta$ when $r$ and $s$ are neighbouring atoms no matter whether $r$ and $s$ are carbon or nitrogen atoms. When $r$ and $s$ are not nearest neighbours $H_{rs}$ is assumed to be so small that it can be neglected.

The value of the "Overlap Integral" $S_{rs}$ is only about 0.25 and is neglected since by doing so the arithmetic involved is appreciably shortened.

Let the energy which $\mu$-electron would have if it were confined to a carbon atom, be $\alpha$ (i.e. $H_{rr} = \alpha$ for carbon atoms) and let $(\alpha - E_j)$ be some multiple of $\beta$ - say $x_1 \beta$.

Let $(H_{rr} - E_j)$ be some other multiple of $\beta$ - say $(x - h) \beta$ when $r$ = nitrogen(n)

i.e. $\frac{H_{nn} - E_j}{\beta} = \frac{\alpha - E_j}{\beta} - \frac{\alpha - H_{nn}}{\beta} = x - h$

Therefore $h$ depends on the value of $\alpha - H_{nn}$ which, in turn, depends on the difference in the electronegativity of carbon and nitrogen. In this case $h$ is assumed to be $-\frac{1}{2}$

i.e. $H_{nn} - E_j = (x + \frac{1}{2})\beta$

Slightly different values for the exchange and coulomb integrals of carbon-nitrogen bonds and nitrogen atoms respectively have been quoted in the literature (46, 47, 48) on the grounds that these give approximately the correct dipole moments for heterocyclic molecules containing nitrogen: in this work, these figures are rounded off to ease the computation involved.

Hence, on substitution, and elimination of $\beta$, the secular equations now reduce to
\begin{align*}
(1) & \quad c_1 (x + \frac{1}{2}) \cdot c_2 + c_{10} = 0 \\
(2) & \quad c_1 + c_2 x + c_3 = 0 \\
(3) & \quad c_2 + c_3 (x + \frac{1}{2}) + c_4 = 0 \\
(4) & \quad c_3 + c_4 x + c_5 = 0 \\
(5) & \quad c_4 + c_5 x + c_6 + c_{10} = 0 \\
(6) & \quad c_5 + c_6 (x + \frac{1}{2}) + c_7 = 0 \\
(7) & \quad c_6 + c_7 x + c_8 = 0 \\
(8) & \quad c_7 + c_8 x + c_9 = 0 \\
(9) & \quad c_8 + c_9 (x + \frac{1}{2}) \cdot c_{10} = 0 \\
(10) & \quad c_9 + c_{10} x = 0
\end{align*}
3. The Permitted Energy Levels for the $\mu$-electrons of Pteridine.

The secular equations give rise to the 10th order secular determinant $\Delta$.

$$
\begin{vmatrix}
(c_i) & c_1 & c_2 & c_3 & c_4 & c_5 & c_6 & c_7 & c_8 & c_{10} \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & (x+\frac{1}{3}) & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & x & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & (x+\frac{1}{3}) & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & x & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & (x+\frac{1}{3}) & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & x & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\end{vmatrix} = 0
$$

Now let $y = 2x$ and get

$$
\begin{vmatrix}
(y+1) & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 \\
2 & y & 2 & 2 & y & 2 & 2 & y & 2 & 2 \\
2 & (y+1) & 2 & 2 & (y+1) & 2 & 2 & (y+1) & 2 & 2 \\
2 & y & 2 & 2 & y & 2 & 2 & y & 2 & 2 \\
2 & (y+1) & 2 & 2 & (y+1) & 2 & 2 & (y+1) & 2 & 2 \\
2 & y & 2 & 2 & y & 2 & 2 & y & 2 & 2 \\
\end{vmatrix} = 0
$$

(10)
These determinants are of the variety known as continuants of the form

\[
\begin{vmatrix}
y & 2 \\
2 & y \\
\end{vmatrix} = 2^n
\]

with a number of decorations added.

A number of very useful properties of determinants of this type have been worked out by Goodwin and Vand\(^{(4,4)}\) and by making use of these relations, \(\Delta\) can be expressed in terms of unitary continuants \(S_n\) in the form

\[
\Delta = 1024S_{10} + 2048S_9 - 512S_8 - 1536S_7 - 960S_6 - 2048S_5 - 6272S_4
\]

\[
- 6528S_3 - 3456S_2 - 3200S_1 - 4288
\]

\(= 0\)

In order to solve this equation and find the roots within the range \(-2 < x < +2\), \(\Delta\) is now converted into a series of multiple cosines by making the substitution \(x = 2\cos \theta\) which gives rise \((\Rearrange 5)\) to the formula

\[
S_n = 2 \left[ \cos n\theta + \cos(n-2)\theta + \cos(n-4)\theta + \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
\[ \Delta(x+h) = \Delta(x) + \frac{h}{1!} \Delta'(x) + \frac{h^2}{2!} \Delta''(x) + \ldots = 0 \]

where \( \Delta(x) \) is the value of \( \Delta \) using the approximate root \( x \) and \( h \) is the correction to be applied.

The derivatives \( \frac{dS_n}{dx} \) can be obtained from the formula

\[ \frac{dS_n}{dx} = nS_{n-1} + (n-2)S_{n-3} + (n-4)S_{n-5} + \ldots + (1 \text{ or } 0) \]

the final term depending on whether \( n \) is odd or even.

Successive approximations of this type lead to exact values for the roots \( x \) of the secular equations and roots which lie outside the range \(-2 < x < +2\) can then be obtained from the theory of equations. These exact values for \( x \) are

\[
\begin{align*}
  x &= \pm 2.15775; \pm 1.45460; \pm 1.07655; \pm 0.90997; \pm 0.33221; \\
  &= -0.91874; -1.10302; -1.58342; -1.84220; -2.48377
\end{align*}
\]

But \( E_j = \alpha - x \beta \) and so the permitted energy levels for the \( \pi \)-electrons of pteridine are, in ascending order of magnitude (since \( \beta \) is negative).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( E_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>( \alpha +2.48377 \beta )</td>
</tr>
<tr>
<td>(2)</td>
<td>( \alpha +1.84220 \beta )</td>
</tr>
<tr>
<td>(3)</td>
<td>( \alpha +1.58342 \beta )</td>
</tr>
<tr>
<td>(4)</td>
<td>( \alpha +1.10302 \beta )</td>
</tr>
<tr>
<td>(5)</td>
<td>( \alpha +0.91874 \beta )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( i )</th>
<th>( E_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6)</td>
<td>( \alpha -0.33221 \beta )</td>
</tr>
<tr>
<td>(7)</td>
<td>( \alpha -0.90997 \beta )</td>
</tr>
<tr>
<td>(8)</td>
<td>( \alpha -1.07655 \beta )</td>
</tr>
<tr>
<td>(9)</td>
<td>( \alpha -1.45460 \beta )</td>
</tr>
<tr>
<td>(10)</td>
<td>( \alpha -2.15775 \beta )</td>
</tr>
</tbody>
</table>

Table (X)

Pteridine has 10 \( \pi \)-electrons and each energy level can hold two electrons (with opposite spins). Hence, to obtain the energy level for the molecule whilst in its ground state the electrons are filled in two at a time, starting with the lowest level and working upwards,
until each of the electrons has been accounted for.

In this way, the permitted energy levels for the \( \pi \) -electrons of pteridine when the molecule is in the ground state are shown to be

<table>
<thead>
<tr>
<th>( i )</th>
<th>( E_i )</th>
<th>Number of electrons in each level</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \alpha + 2.48377 \beta )</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha + 1.84220 \beta )</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>( \alpha + 1.58342 \beta )</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>( \alpha + 1.10302 \beta )</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>( \alpha + 0.91874 \beta )</td>
<td>2</td>
</tr>
</tbody>
</table>
4. The Secular Coefficients for each Energy Level.

By means of a process of successive elimination, the secular equations on p.(103) can be reduced to

(10) \[ c_1 + c_5 + c_9 + xc_{10} = 0 \]
(3) \[ 2c_2 + (2x+1)c_3 + 2c_4 = 0 \]
(4) \[ c_3 + xc_4 + c_5 = 0 \]
(5) \[ c_4 + xc_5 + c_6 + c_{10} = 0 \]
(6) \[ 2c_5 + (2x+1)c_6 + 2c_7 = 0 \]
(7) \[ c_6 + xc_7 + c_8 = 0 \]
(8) \[ c_7 + xc_8 + c_9 = 0 \]
(9) \[ 2c_8 + (2x+1)c_9 + 2c_{10} = 0 \]

(1) \[ (8x^7 + 12x^6 - 34x^5 - 43x^4 + 42x^3 + 35x^2 - 12x)c_9 + (8x^6 + 8x^5 - 30x^4 - 20x^3 + 46x^2 + 16x - 24)c_{10} = 0 \]

(2) \[ (8x^8 + 12x^7 - 50x^6 - 63x^5 + 106x^4 + 98x^3 - 84x^2 - 43x + 20)c_9 + (8x^7 + 8x^6 - 46x^5 - 32x^4 + 92x^3 + 36x^2 - 54x + 8)c_{10} = 0 \]

and all of the coefficients can, by substituting the correct values of \( x \), be expressed in terms of \( c_{10} \).

The normalising condition \( \sum (c_{r,j})^2 = 1 \) can then be employed and hence \( c_{10} \) estimated. In this way, absolute values of the coefficients for each energy level can be obtained.
These values were found to be

<table>
<thead>
<tr>
<th>Energy Level ($E_j$)</th>
<th>$a_{1,j}$</th>
<th>$a_{2,j}$</th>
<th>$a_{3,j}$</th>
<th>$a_{4,j}$</th>
<th>$a_{5,j}$</th>
<th>$a_{6,j}$</th>
<th>$a_{7,j}$</th>
<th>$a_{8,j}$</th>
<th>$a_{9,j}$</th>
<th>$a_{10,j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha +2.48377 \beta$</td>
<td>+0.34532</td>
<td>+0.24379</td>
<td>+0.26013</td>
<td>+0.27224</td>
<td>+0.41606</td>
<td>+0.31985</td>
<td>+0.21844</td>
<td>+0.22272</td>
<td>+0.33473</td>
<td>+0.44131</td>
</tr>
<tr>
<td>$\alpha +1.84220 \beta$</td>
<td>-0.29466</td>
<td>-0.42432</td>
<td>-0.48705</td>
<td>-0.22939</td>
<td>+0.06446</td>
<td>+0.31929</td>
<td>+0.36410</td>
<td>+0.35145</td>
<td>+0.28334</td>
<td>+0.02885</td>
</tr>
<tr>
<td>$\alpha +1.58342 \beta$</td>
<td>+0.37720</td>
<td>+0.08588</td>
<td>-0.24089</td>
<td>-0.34687</td>
<td>-0.30835</td>
<td>-0.46401</td>
<td>-0.19436</td>
<td>+0.15625</td>
<td>+0.44202</td>
<td>+0.32263</td>
</tr>
<tr>
<td>$\alpha +1.10302 \beta$</td>
<td>+0.21515</td>
<td>-0.22189</td>
<td>-0.45989</td>
<td>-0.05543</td>
<td>+0.39874</td>
<td>+0.46632</td>
<td>-0.34388</td>
<td>+0.15041</td>
<td>+0.40686</td>
<td>+0.22339</td>
</tr>
<tr>
<td>$\alpha +0.91874 \beta$</td>
<td>-0.35026</td>
<td>-0.37004</td>
<td>+0.01029</td>
<td>+0.37950</td>
<td>+0.14863</td>
<td>-0.45989</td>
<td>-0.37004</td>
<td>+0.01029</td>
<td>+0.37950</td>
<td>+0.14863</td>
</tr>
</tbody>
</table>
5. The Bond Orders of Pteridine.

The mobile bond order $p_{rs}$ between atoms $r$ and $s$ is defined as

$$p_{rs} = \sum \frac{n_j c_{r,j} c_{s,j}}{E_j}$$

where $n_j$ is the number of electrons in energy level $E_j$ (2 in this case) $c_{r,j}$ and $c_{s,j}$ are the coefficients of the secular equations for atoms $r$ and $s$ for the $j$th level, and the summation is taken over all the energy levels,

i.e.  

$$p_{rs} = \sum c_{r,j} c_{s,j}$$

Use of this equation gives the following values for the mobile bond orders of pteridine.

<table>
<thead>
<tr>
<th>Bond $r$-$s$</th>
<th>1-2</th>
<th>1-10</th>
<th>2-3</th>
<th>3-4</th>
<th>4-5</th>
<th>5-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{rs}$</td>
<td>0.709</td>
<td>0.558</td>
<td>0.599</td>
<td>0.706</td>
<td>0.549</td>
<td>0.552</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond $r$-$s$</th>
<th>5-10</th>
<th>6-7</th>
<th>7-8</th>
<th>8-9</th>
<th>9-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{rs}$</td>
<td>0.519</td>
<td>0.722</td>
<td>0.590</td>
<td>0.715</td>
<td>0.551</td>
</tr>
</tbody>
</table>
6. \( \bar{\mu} \)-electron Distributions\( (q_r) \) in the Ground State of Pteridine.

\( (c_{r,j})^2 \) represents the contribution of electron \( j \) to the \( \bar{\mu} \)-electron density at atom \( r \). Hence, the total \( \bar{\mu} \)-electron density at atom \( r \) is given by

\[
q_r = \sum_j n(c_{r,j})^2
\]

the summation being taken over all the occupied energy levels and \( n \) is the number of electrons in each level. This results in

the following \( \bar{\mu} \)-electron densities for pteridine.

<table>
<thead>
<tr>
<th>( r )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_r )</td>
<td>1.224</td>
<td>0.829</td>
<td>1.194</td>
<td>0.831</td>
<td>0.962</td>
<td>1.126</td>
<td>0.905</td>
<td>0.872</td>
<td>1.166</td>
<td>0.891</td>
</tr>
</tbody>
</table>

Carbon atoms 2 and 4 are therefore, most deficient in electrons and any nucleophilic substitution should occur at these points

[Chalvet and Sandorfy (47) by algebraic superposition of results for compounds containing fewer nitrogen atoms in different positions find \( C_4 \) the more deficient.]
7. The Effect of Variation of the Values Assigned to the Arbitrary Parameters on the Calculations.

In the process of obtaining the bond orders of the pteridine molecule in the ground state, a number of arbitrary assumptions have been made about the values to be assigned to the parameters $H_{rr}$, $H_{rs}$, $S_{rs}$. These have all been expressed in terms of $\alpha$ and $\beta$ (the Coulomb integral for carbon and the Exchange integral for carbon-carbon bonds respectively) or else have been neglected in the calculations.

It is of interest to know what effect varying the values assigned to these parameters has on the final results obtained for the bond orders and $\pi$-electron distribution of pteridine.

$H_{nn}$ is usually assigned a value of $(\alpha + 0.6\beta)$ since this reproduces correctly the dipole moments of simple heterocycles containing nitrogen ($47, 48$). A value of $H_{nn} = \alpha + \frac{\beta}{2}$ has been used in this work on pteridine. A comparison of calculations carried out by the author on pyridine using $H_{nn} = \alpha + \frac{\beta}{2}$ with those of Chalvet and Sandorfy ($47$) using $H_{nn} = \alpha + 0.6\beta$ shows that this minor variation results in differences in $\pi$-electron distributions and mobile bond orders of 0.015e and 0.002 units respectively - differences of no importance.

The Exchange integral for a carbon-nitrogen bond will be slightly greater than that of a carbon-carbon bond, although in this work the two Exchange integrals have been assumed to be equal. To determine the effect of varying $H_{C-N}$ on the calculations, they have been reperformed using an extreme - and erroneous - value of $H_{C-N}$ equals $1\frac{1}{2}\beta$. This makes a serious difference in the permitted energy levels of as much as $0.8\beta$ although the average differences which result in the $\pi$-electron distributions for carbon atoms is only 0.03e and for
nitrogen is 0.05e. This variation in the Exchange integral for carbon—nitrogen bonds also results in small differences on the average of 0.03 units in mobile bond order.

Recently, (51), it has been pointed out that under certain circumstances nitrogen may be slightly more electropositive than carbon. Under these circumstances $H_{NN}$ and $H_{CN}$ will be less than $\alpha$ and $\beta$ respectively. However, nitrogen will only be less electronegative than carbon if, in some way, a high negative charge is resident on the atom. This situation seems to obtain in some five-membered ring systems and consequently, doubts as to the values to be assigned to $H_{NN}$ and $H_{CN}$ must arise in such cases. However, in pteridine the nitrogen atoms are undoubtedly more electronegative than carbon and so the values of $H_{NN}$ and $H_{CN}$ which have been used are those appropriate to this problem.

The Overlap integral $S_{rs}$ has been neglected in this work. The justification for this is to be found in a paper by D.W. Davis (52) in which the effect of overlap in molecular orbital calculations of heterocyclic molecules is examined. Davis finds that, by including overlap in the calculations, the change produced in the $\bar{n}$—electron distributions is extremely small, (of the order of 0.001 — 0.003e) and so also is the effect on the mobile bond orders (of the order of 0.002 — 0.007 bond units).

Hence, as far as varying the values assigned to the parameters $H_{rr}$, $H_{rs}$, $S_{rs}$ is concerned, the effect on the $\bar{n}$—electron distributions and mobile bond orders is negligible although the permitted energy levels are more sensitive to such changes.
8. **A Correlation Curve for Carbon-Nitrogen Bonds and Bond Lengths of Pteridine.**

So far, a discussion of the study of the pteridine molecule by means of molecular orbital theory has been given up to the point of estimation of mobile bond orders and it has been shown that these bond orders derived by this method should be very reliable.

In order to convert bond orders into bond lengths a correlation curve is necessary. For the carbon-carbon bonds this curve is well established (51) but the position for carbon-nitrogen bonds is much less satisfactory. The curve of Cox and Jeffrey (54) has often been used in this connection but is unsatisfactory since the intermediate points (pyridine and melamine) are in error. Since Cox and Jeffrey published their paper, however, a number of compounds containing accurately measured C—N bonds have been reported. These, and the results for them are listed below.
Compound | PC-N | Bond Lengths | Method of Measurement
--- | --- | --- | ---
Melamine I (ring C-N) | 0.563(55) | 1.343±0.05Å | X-ray (56)
(side C-N) | 0.520(55) | 1.353±0.05Å | X-ray (57)
s-Triazine II | 0.654(55) | 1.319±0.005Å | X-ray (59)
α-Phenazine III | 0.603(55) | 1.345±0.009Å | X-ray (61)
Pyrimidine IV | 0.656(6e) | 1.33Å | X-ray (6e)
Pyridine V | 0.654(6e) | 1.340Å | Micro-wave (62)

The extremities of the single bond - double bond range are not very satisfactory. Cox and Jeffrey quote a pure single bond length of 1.475Å. but in the aliphatic amines which they quote as the source of this measurement the hybridisation is sp³ whereas sp² hybridisation is involved in condensed ring compounds. Coulson(41) has considered the variation of length in carbon-carbon bonds as the hybridisation changes and has shown that the length of 1.54Å. for the tetrahedral C-C becomes 1.50Å. in the trigonal hybrid. It is, therefore, suggested that a similar shortening is to be expected for the C-N bond. Hence, 1.435Å. has been taken for the sp² carbon-nitrogen bond of zero order.

For the pure bond of π-order 1, Cox and Jeffrey select a length of 1.28Å. and the covalent radii values of Stevenson and Schomaker (44) with the electro-negativity correction according to Gordy (45) give 1.27Å.

In building up the bond order - bond length curve in this work, however, another method of determining the point for the pure bond of mobile order 1, has been employed. The six intermediate points listed above, mean that any reasonable curve must pass through or very near to the point (0.600, 1.336).
Fig XXI.

Bond Order - Bond Length Curves

Bond Lengths (Å)

- Carbon - Carbon
- Carbon - Nitrogen

Mobile Bond Orders
This point has, therefore, been taken as a datum for developing the carbon-nitrogen bond order - bond length curve. In the carbon-carbon correlation curve \((\xi_3)\) the bond lengths corresponding to orders 0 and 0.6 are 1.50\(\text{Å}\) and 1.406\(\text{Å}\). The carbon-nitrogen curve has been obtained by displacing and proportionally compressing the carbon-carbon curve so that it passes through \((0,1.435)\) and \((0.600,1.336)\). The curve shown in fig.\((\times1)\) results and passes through the points \((0.1,1.431), (0.2,1.425), (0.3,1.418), (0.4,1.407), (0.5,1.375), (0.6,1.336), (0.7,1.312), (0.8,1.291), (0.9,1.277)\) and \((1.0,1.267)\). The last of these gives the length of the pure double bond and agrees closely with the values assigned to this bond length by the authors already mentioned.

The justification for this procedure is that the carbon-carbon curve has been found to be very reliable and it is expected that the variation in carbon-nitrogen bond length with bond order would follow a path similar to the carbon-carbon curve.

It is difficult to decide just how accurate bond lengths obtained from the curve throughout its whole length will be, since this obviously depends on the accuracy with which the reference points on the curve have been obtained. However, in the case of pteridine the effective region of the curve to be used lies within the range in C-N mobile bond orders from \(0.73 - 0.55\). This range lies very near to the datum point \((0.6,1.336)\) and so it is believed that the error associated with bond lengths derived from this curve will not be greater than \(\pm 0.02\text{Å}\).

On making use of the C-C and C-N curves discussed above the bond lengths obtained for the ground state of the
pteridine molecule are found to be

![Diagram of pteridine molecule]

<table>
<thead>
<tr>
<th>Bond r-s</th>
<th>Derived Length</th>
<th>Observed Length</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>1.310 A.</td>
<td>1.34 A.</td>
<td>0.03 A.</td>
</tr>
<tr>
<td>1-3</td>
<td>1.349</td>
<td>1.40</td>
<td>0.05</td>
</tr>
<tr>
<td>2-3</td>
<td>1.337</td>
<td>1.40</td>
<td>0.06</td>
</tr>
<tr>
<td>3-4</td>
<td>1.311</td>
<td>1.28</td>
<td>-0.03</td>
</tr>
<tr>
<td>4-5</td>
<td>1.425</td>
<td>1.42</td>
<td>-0.01</td>
</tr>
<tr>
<td>5-6</td>
<td>1.351</td>
<td>1.39</td>
<td>0.04</td>
</tr>
<tr>
<td>5-7</td>
<td>1.435</td>
<td>1.35</td>
<td>-0.09</td>
</tr>
<tr>
<td>6-7</td>
<td>1.307</td>
<td>1.36</td>
<td>0.05</td>
</tr>
<tr>
<td>7-8</td>
<td>1.410</td>
<td>1.39</td>
<td>-0.02</td>
</tr>
<tr>
<td>8-9</td>
<td>1.309</td>
<td>1.32</td>
<td>0.01</td>
</tr>
<tr>
<td>9-10</td>
<td>1.352</td>
<td>1.41</td>
<td>0.06</td>
</tr>
</tbody>
</table>

This table compares the derived lengths with those obtained in an X-ray crystallographic investigation of pteridine by Hamor and Robertson (66). In it, $\Delta$ signifies measured length minus derived length. The results give a mean value $|\Delta|_{\text{mean}} = 0.04$. The observed lengths are nearly always greater than the derived lengths and this would appear, at first sight, to indicate that correlation curves should be raised slightly. However, the standard deviation in observed bond lengths has been quoted by Hamor and Robertson to be 0.03 A., so the mean discrepancy is well within the limits of
experimental error. The observed length for bond $C_5 - C_{10}(1.35\text{A})$ is obviously too short and it is of interest to note that if atoms 5 and 10 are equally displaced along the line joining them so that they become separated by the distance $1.435\text{A.}$ indicated by the calculations, then the discrepancies in the bonds $N_9 - C_{10}, C_{10} - N_1, C_5 - N_6, C_5 - C_4$ are greatly reduced to 0.04, 0.02, 0.01, and $-0.03\text{A}.$ respectively.

Again, much the shortest bond measured is $N_3 - C_4(1.28\text{A.}),$ a length which would mean that bond $N_3 - C_4$ was almost, if not quite, a pure double bond—a state of affairs which, according to molecular orbital theory is impossible in this type of compound.

Occasionally in the literature during comparison of observed and calculated bond lengths one comes across statements to the effect that discrepancies in the results obtained by the two methods of approach may be due to (a) the effect of formal charges on bond lengths, or, (b) the compounds under consideration are not planar, or, (c) the bonds, although co-planar, are distorted from the simple $sp^2$ hybridised type which has been assumed in performing the calculations.

It is true that all of these effects do alter bond lengths but these effects have been neglected in the calculations since their effects were believed to be small. The justification for this procedure is in two papers published by Coulson on this subject. In the first paper (47) Coulson deals with the effect of formal charge distribution on bond lengths and shows that an estimate of this effect can be obtained from the equation
where the bond length in the absence of any charges on the atoms is \( r \) and \( \Delta r \) is the change in \( r \) when charges \( q_1 \) and \( q_2 \) are placed on atoms 1 and 2. \( e \) is the electronic charge. \( K \) is the effective dielectric constant for the medium surrounding the bond and \( k \) is the force constant for the bond \( 1-2 \). In the case of pteridine the greatest formal charges are on \( N_1 \) and \( C_2 \) and are \(-0.224e\) and \(+0.171e\) respectively. If \( K \) is assumed to be about 2, \( r = 1.31\text{\AA} \), \( k = 6 \times 10^5 \text{ dynes/cm} \), then \( \Delta r \) turns out to be \(-0.005\text{\AA}\). i.e. a contraction of \( 0.005\text{\AA} \) in bond length occurs. Obviously, this as a source of discrepancy between observed and calculated bond lengths is of no importance.

Provided the molecule deviates only very slightly from planarity effects (b) and (c) can be considered together. The effect of variation in hybridisation on atomic radius is discussed by Coulson (61). The molecular orbital description of a hybrid bond for a carbon atom is defined by the expression

\[
\Psi(\lambda) = \frac{s + \lambda p}{\sqrt{(1 + \lambda^2)}}
\]

where \( s \) and \( p \) denote carbon \( 2s \) and \( 2p \) orbitals respectively and the square root ensures normalisation.

In rough terms it might be said that the amounts of \( s \) and \( p \) atomic orbitals in the hybrid orbital \( \Psi(\lambda) \) are \( \frac{1}{1 + \lambda^2} \) and \( \frac{\lambda^2}{1 + \lambda^2} \). When the hybridisation ratio \( \lambda \) is 1, an sp hybrid orbital results and when \( \lambda = 2 \) or 3, sp\(^2\) or sp\(^3\) hybrids are obtained.
The variation of atomic radius for carbon atoms as the hybridisation changes from sp through sp² to sp³ is known accurately from spectroscopic data and hence a correlation curve of atomic radius of carbon against \( \lambda \) can be obtained. Coulson has derived expressions relating \( \lambda \) to trigonometric functions of the angles between the bonds radiating from an atom. Hence if these bond angles are known, \( \lambda \) can be calculated and then by reference to the correlation curve the atomic radius for the carbon atom can be obtained. The difference of this radius from that of the atom when in the pure sp² hybrid state can then be estimated and thence the contribution of this atom to the shortening (or lengthening) of a bond can be obtained (it is assumed that a small variation from the pure sp² type in nitrogen atoms produces a shortening or lengthening of the nitrogen radius by an amount which is the same as that found for carbon).

By arguing in this way it is readily shown that the order of correction due to effects (b) and (c) in pteridine is about 0.002\( \text{Å} \). Clearly these changes are insignificant.

A summary of the calculated bond orders, \( \pi \)-electron distributions and calculated bond lengths obtained for pteridine is shown in figure (XXII).
**Fig XXII.**

**Bond Lengths.**

**Bond Orders.**

**π-electron Distributions.**
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