THE CRYSTAL STRUCTURES

OF

SOME ORGANIC MOLECULES

(AN X-RAY STUDY)

THESIS
PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
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BY
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Ph.D. Thesis of H. N. Shrivastava

Some errors which have been noticed

p.2	The formula $C_{22}H_{26}N_2$ should be $C_{22}H_{26}N_4$. (The candidate may have copied an error in the paper by Robinson & Teuber, but if so he should have remarked on it).
p.49	Reference is made to Table 5, but this table has been omitted from the copy of the thesis submitted for examination.
p.51	cRO in the diagram should be a straight line and not angled as shown. - OST should be LOST
p.62	Pilzer should be Pitzer.
p.73(a)	The legends for figs. 3 and 4 are lacking.
p.75	Lüttke & Meeke should be Lüttke & Mecke.
p.116	The reference to Farmer should be J.Chem.Soc. and not J. Amer. Chem. Soc.

28th June, 1960

E. G. COX

PREFACE.

This thesis describes the determination of the crystal structures of calycanthine di-hydrochloride, quaterrylene and potassium hydrogen di-p-nitrobenzoate by X-ray diffraction methods. A section on hydrogen bonding and an appendix giving the unit cell parameters of Rb-H-di-O-nitrobenzoate are also included.

I wish to acknowledge my thanks to my supervisors, Professor J.M.Robertson and Dr. J.C.Speakman for the advice and criticism which they have offered throughout the course of this work. To the latter I am also grateful for initiating me to the techniques of X-ray crystallography and substantial encouragement thereafter.

I am grateful to the University of Saugar, India, for the grant of study leave and financial assistance during the earlier part of this work and to the University of Glasgow for similar assistance during the later part.

In the later period of this work, computations were carried out on the Glasgow University electronic computer 'DEUCE' using the programmes originally devised by Dr. J.S.Rollett, and I am indebted to

Dr. D. C. Gilles and the staff of the Computing Laboratory for facilities. Some minor programmes were also made available by Dr. J. C. Speakman, Dr. J. G. Sime and Dr. D. G. Watson to whom I am grateful and also to Mr. Findlay for preparing the photographs, and to Mrs. Gould for typing this thesis.

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SUMMARY.

The crystal structures of some organic molecules have been examined by X-ray diffraction methods. The thesis has been divided into four sections which are summarised by the following four paragraphs.

Calycanthine dihydrochloride, $C_{22}H_{28}N_4Cl_2.2H_2O$ crystallises in the space group D_2^4-$P\ 2_12_12_1$ with four molecules in the unit cell. Its isomorphism with calycanthine dihydrobromide has been established and a reliable electron-density projection obtained by the isomorphous replacement method. A benzenoid ring could be correctly picked up but extensive overlap prevented fuller interpretation. Similar difficulties were encountered in other projections and with Dr. T.A. Hamor taking up the analysis of the hydrobromide by three-dimensional methods, work on the hydrochloride was terminated. A joint communication giving the structure finally elucidated is appended.

Quaterrylene, $C_{40}H_{20}$ crystallises in the monoclinic system; space group $P\ 2_1/a$ with four molecules per unit cell. Its crystal structure has been determined by two-dimensional methods. A dimorph is found to occur.

The relation between crystal structure and morphology is of the usual type. In the polymorph examined, the lengths of the peri-bonds connecting the naphthalenic residues have been determined with moderate accuracy. The mean value is assessed at 1.53 ± 0.01 Å which is significantly larger than current theory predicts. Possible reasons for this difference are discussed.

The hydrogen bond: The major part of this section is a review and original comments are confined to the last three chapters, in one of which the structural features of some anomalous short hydrogen bonded structures have been examined.

Potassium hydrogen-di-p-nitrobenzoate, $K\text{-}H(C_7H_4NO_4)_2$, crystallises in the triclinic system; space group $P\bar{1}$, with two molecules per unit cell. Its structure has been determined via Patterson projection and Buerger minimum function maps. The third co-ordinates were obtained by trial and error methods and initially refined by generalised projections. Finally, a partial three-dimensional least squares refinement incorporating 992 reflexions has been carried out.

This structure reveals a short hydrogen bond of $2.49_2 \pm 0.02$ Å. Since the I.R. spectrum of this acid salt is of the superposition type, comparison of its structural features with those of the acid salts giving anomalous I.R. spectra reveals that the cause of the anomaly is not the short hydrogen bond but is, in some way, connected with the extensive networks which the formally symmetrical hydrogen bonds, together with carboxyl groups and alkali metal ions, invariably form in the acid salts of the latter type.

The benzenoid rings are substantially planar but the nitroxyl and the carboxyl groups are twisted the same way by 5° to 10° about the C - N and the C - C bonds. The oxygen atoms surrounding a potassium ion form a considerably distorted octahedron.

Mathematical derivations and explanatory notes have been included as appendices to the relevant sections. The unit cell parameters of Rb-H-di-o-nitrobenzoate are included as Appendix to Section IV.

References are given at the end of each section.

CONTENTS.

SECTION I: THE CRYSTAL STRUCTURE OF CALYCANTHINE-DI-HYDROCHLORIDE.

SECTION II: THE CRYSTAL AND MOLECULAR STRUCTURE OF QUATERRYLENE.

SECTION II: (Cont'd)

SECTION III: THE HYDROGEN BOND.

SECTION IV: CRYSTAL STRUCTURE OF AND HYDROGEN BONDING IN POTASSIUM HYDROGEN-DI-PARANITROBENZOATE.

SECTION I

THE CRYSTAL STRUCTURE OF CALYCANTHINE-DI-HYDROCHLORIDE.

The Crystal Structure of Calycanthine-di-hydrochloride.

($C_{22}H_{26}N_4.2HCl.2H_2O$)

The seeds of a shrub in Georgia, North Carolina and Tennessee, locally known as Carolina Allspice or bubby, killed cattle that happened to eat them. Eccles (1888) showed that the poisonous component in the shrub was an alkaloid from its seeds which he named Calycanthine. Gordin (1905) obtained crystals of pure calycanthine from these seeds. He mentions the shrub as Calycanthus glaucus (Willd) whereas Manske (1929) suggests that these could in fact be Calycanthus floridus L. Manske further found canycanthine in Meratia praecox, Rehd and Wils (order calycanthaceae) an ornamental shrub cultivated in China and Japan. This wider occurrence suggests a simple biogenesis. Gordin (1905) also showed that calycanthine forms salts with practically all acids and formulated it as $C_{11}H_{14}N_2$ and the hydrochloride and hydrobromide as $C_{11}H_{14}N_2.HCl.H_2O$ and $C_{11}H_{14}N_2.HBr.H_2O$. Späth and Stroh (1925) doubled these formulae whereas Barger et.al.(1939) revised it to $C_{22}H_{26}N_4$, the now accepted formula. They showed that a degradation product of usual occurrence is Calycanine, $C_{16}H_{10}N_2$, a base of great stability. Manske and Marion (1942) put forward a different formulation for calycanine which was shown to be inconsistent with the X-ray crystallographic data by Hargreaves (1943). A noteworthy feature of calycanthine is its remarkably high optical rotatory power $[\alpha]^{18}_{D\ \mathrm{ethereal}} = +684.3$ (Späth and Stroh, 1925); $[\alpha_D]^{22}_{\mathrm{acetone}} = +698$ (Gordin, 1905). Robinson and Teuber (1954) summarised the structural evidence, which may be stated in brief as follows.

> "Calycanthine, $C_{22}H_{26}N_4$ has two $N(Me)_2$ groups, I.R. absorption indicates O- disubstituted benzene rings and NH groups, coupling with diazo salts and other reactions show that there are two NH groups both joined directly to benzene rings. U.V. Spectra indicates dihydro indole. Heating, with soda-lime at 305° gives N.methyl tryptamine ($C_{11}H_{14}N_2$) and with CaO at 305° Norharman ($C_{11}H_8N_2$), these being interpreted to indicate an indoline type of structure. For calycanine, the usual degradation product, the structural formula proposed was:-
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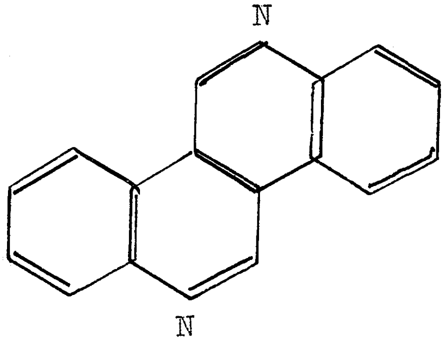
> 
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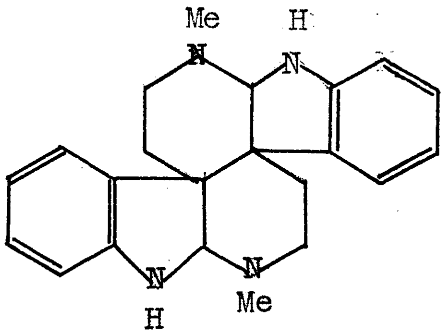
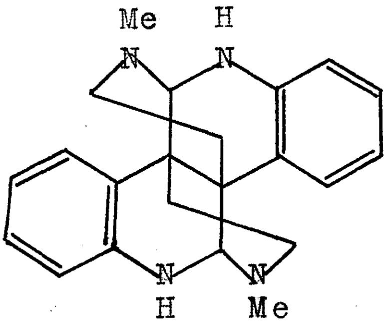
I may point out that both the U.V. spectra and the high temperature degradation are the weakest points in this chain and since only these support the indoline type of structure, this deduction is the most vulnerable.

Robinson and Teuber (1954) suggested that calycanthine may be (I) or some similar structure. The structure emerging from the X-ray investigations conducted under the direction of Prof. J.M.Robertson is (II). The following chapters of this section describe my part in these investigations.



(I)



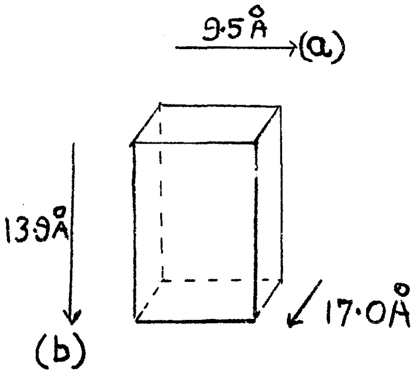
(II)

1. Introduction:

When Mr. Harley Mason provided excellent crystals of calycanthine and requested Professor J. Monteath Robertson to look into the structure, work on this problem started at Glasgow under the direction of Professor Robertson. When I joined, Mr. J.V. Silverton was examining the di-hydrobromide and I was asked to look into the di-hydrochloride.

2. Morphology:

Good crystals of calycanthine-di-hydrochloride were obtained by treating acetone solution of calycanthine with concentrated aqueous hydrochloric acid diluted with about three times its volume of alcohol and allowing slow crystallisation to take place over a couple of days. The substance crystallised in the orthorhombic system as rectangular plates with the longest morphological axis parallel to the orthorhombic crystallographic axis of medium length (13.9Å).



Some crystals have prominent $\{101\}$ forms. Two such crystals are shown overleaf.

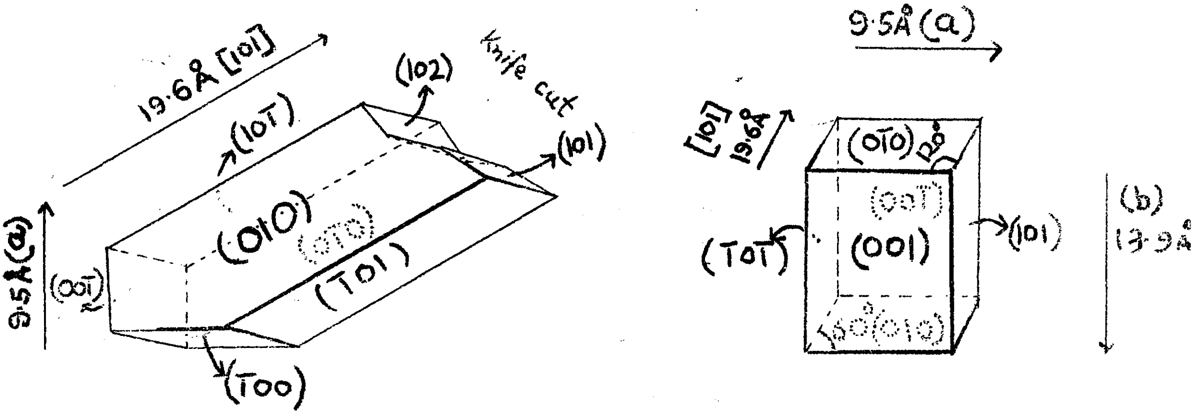


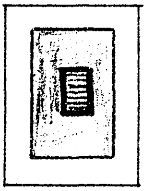
Fig.1.

(I)

Crystal standing with the longest morphological axis(b) nearly vertical.

(II)

Growth steps of the type shown on R.H.S. were observed on the {001} forms of some crystals. It is not possible to say whether these were spiral. The direction of easy cleavage is parallel to the longest morphological axis (b axis).



Note: For morphology of calycanthine see Gordin (1909).

The crystals showed no noticable sign of change during the course of the investigation (4 months).

3. Unit cell parameters, space group and intensity data.

The unit cell parameters and space group were determined using rotation and Weissenberg moving film photographs taken with crystals set parallel to each of the three axis. Rotation photographs about a few diagonals were also taken. Copper K_{α} radiation (λ=1.542Å) was used. The camera radius was in every case calibrated by superimposing on each film powder lines of copper for which 'a' was taken as 3.6146Å, thus correcting any errors due to film shrinkage. These results, together with those for the di-hydrobromide by Mr. J.V.Silverton, are given in Table I.

The cross section of the crystal used for collecting $(0k\ell)$ intensity data was $(0.10 \times 0.15)\mathrm{mm}^2$, rendering absorption corrections unnecessary. Intensities were estimated from Weissenberg moving film by visual comparison with standard spots and correlated using J.M.Robertson's (1943) multiple film technique. These (I_e) were processed in the usual way to give relative values of structure amplitudes. $|F'|$

$$I_e = \int_{\theta-E}^{\theta+E} I d\theta = \left(\frac{N\ e^2}{mc^2}\right)^2 \lambda^3\ |F|^2\ \frac{1 + \mathrm{Cos}^2 2\theta}{2\ \mathrm{Sin}\ 2\theta} \quad \mathrm{cm}^2$$

$$= |F'|^2\ \frac{1 + \mathrm{Cos}^2\ 2\theta}{2\ \mathrm{Sin}\ 2\theta} \quad \mathrm{cm}^2$$

(N = number of unit cells.)

TABLE I.

Formula	$C_{22}H_{26}N_4.2HCl.2H_2O$	$C_{22}H_{26}N_4.2HBr.2H_2O$
M	455.4	544.3
System	orthorhombic	
a(Å)	9.54 ± 0.02	9.61 ± 0.01
b(Å)	13.87 ± 0.04	14.13 ± 0.02
c(Å)	17.03 ± 0.07	16.97 ± 0.02
Unit cell vol.	2253	2304 Å^3
Mols.per cell	4	
d(calc.)	1.342	1.568
d(flotation)	1.335	1.568
Absent spectra	h00 when h is odd, 0k0 when k is odd, and 00ℓ when ℓ is odd.	
Space group	$D_2^4\,P_{2_1 2_1 2_1}$ (No.19)	
$F_{(000)}$	968	1112

4. Isomorphism with calycanthine-di-hydrobromide.

The close resemblance in Table I almost certainly points to isomorphism. The melting points are also almost identical (Gordin, 1905). However, to get an idea of the closeness of the isomorphism, which is important for the successful application of the isomorphous replacement method, the Patterson function for the projection down the short axis was calculated. This has symmetry pmm (Buerger, 1950) consequently its magnitude at $y/_b$, $z/_c$ is

$$P(y/_b, z/_c) = \frac{4}{Aa} \sum_k \sum_l \left|F_o\right|^2 \cos 2\pi k\, y/_b \,.\, \cos 2\pi l\, z/_c \,.$$

The summation was done on the machine designed by Robertson (1954). The resulting projection bears a close resemblance to the similar projection for the di-hydrobromide but the peaks expected on the line $z = c/_2$ from the bromine co-ordinates tentatively assigned are missing. As these peaks are hardly noticeable in the case of the dihydrobromide, this is not surprising, but if they are indeed Cl - Cl vector peaks they have a reasonable chance of appearing in the sharpened Patterson projection. A sharpened Patterson projection, incorporating the sharpening function:-

$$M(s) = \left(\hat{f} \exp \sin^2\theta/\lambda^2\right)^{-2}$$

is shown in fig.2. wherein these peaks appear as peak Nos. 6 and 10 confirming not only the isomorphism but also the correctness of the heavy atom co-ordinates. (Note: Sharpening functions are discussed in Section IV.)

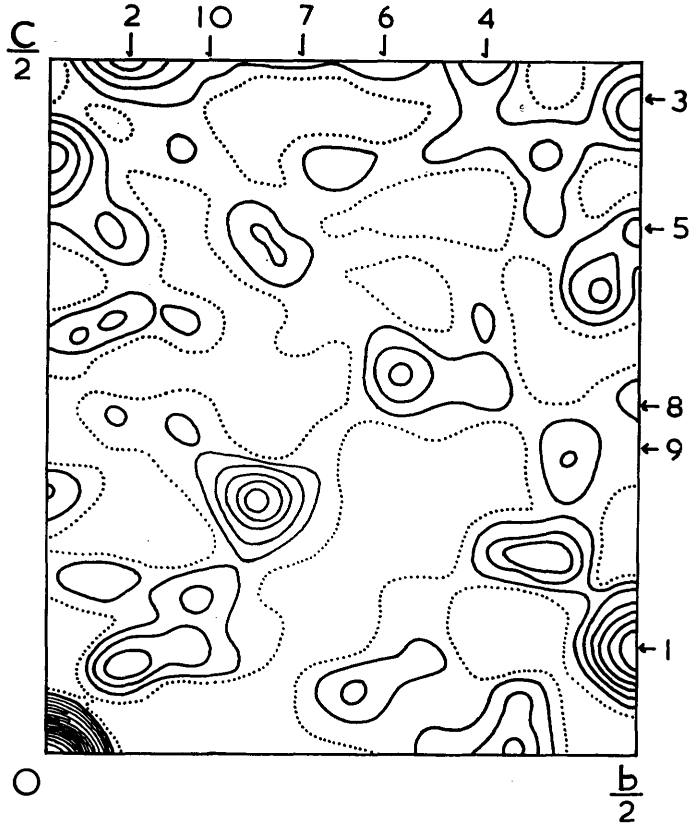


Fig. 2. Calycanthine-di-hydrochloride - sharpened Patterson projection on the (100) plane.

5. Analysis of sharpened Patterson projection.

After computing the sharpened Patterson projection it was decided to see what its independent analysis gives. A good account of the method is given by Beevers, C.A. and Robertson, J.H. (1950).
A simplified version for analysis of projections is presented in part (a) of this chapter, whereas part (b) describes its application.

(a)

The space group $P2_12_12_1$ is non-centred. Conventionally the origin chosen is between the pairs of three non-intersecting screw axes. The equivalent points are $x, y\ z$; $(\frac{1}{2} - x), \bar{y}, (\frac{1}{2} + z)$; $(\frac{1}{2} + x), (\frac{1}{2} - y), \bar{z}$ and $\bar{x}, (\frac{1}{2} + y), (\frac{1}{2} - z)$.
The symmetry of projections is pgg with origin on a screw axis perpendicular to the plane; consequently,

for the projection down(c)axis origin is at $(\frac{1}{4},0,0)$ whereby $x' = x - \frac{1}{4}$.
" " " " (a) " origin is at $(0,\frac{1}{4},0)$ whereby $y' = y - \frac{1}{4}$).
" " " " (b) " origin is at $(0,0,\frac{1}{4})$ whereby $z' = z - \frac{1}{4}$).

For the first of these the equivalent points are
x',y; $\bar{x}',\bar{y}$; $(x' + \frac{1}{2}), (\frac{1}{2} - y)$ and $(\frac{1}{2} - x'),(\frac{1}{2} + y)$.
From now on we will refer to this projection only.

The symmetry of the vector set is pmm with the origin as for the point set. The equivalent points are $2x', 2y$; $\overline{2x'}, \overline{2y}$; $\overline{2x'}, 2y$ and $2x', \overline{2y}$. An atom in general position produces sixteen vector peaks:-

1. $0, 0$; (and other three at the origin).
2. $2x' 2y$; (and other three equivalent peaks).
3. $\frac{1}{2}, (\frac{1}{2} - 2y)$; (and one symm. related and two coincident with these).
4. $(\frac{1}{2} - 2x'), \frac{1}{2}$; (do. do. do.)

Second atom in general position say x_1', y_1, will produce thirty two vector peaks, sixteen as detailed above and another sixteen by interaction with atom one and its equivalents. The latter sixteen are:-

5. $(x_1' + x'), (y_1 + y)$; (and three symm. related).
6. $(x_1' - x') + \frac{1}{2}, \frac{1}{2} - (y_1 + y)$; (do. do.).
7. $\frac{1}{2} - (x_1' + x'); (y_1 - y) + \frac{1}{2}$; (do. do.).
8. $(x_1' - x'), (y_1 - y)$; (do. do. do.).

Nos. 6 and 7 can also be written as:-

6. $\frac{1}{2} + (x_1' - x'), \frac{1}{2} + (y_1 + y)$; (do. do.).
7. $\frac{1}{2} + (x_1' + x'), \frac{1}{2} + (y_1 - y)$; (do. do.).

The location of two heavy atoms resolves into two operations:-

(s) Location of peaks of type 3 and 4 consistent with type 2.

(t) Checking the correctness of co-ordinates by looking for peaks of type 5,6,7 and 8 and rejecting the light-light atom vectors on peak height considerations.

(b) In Fig.2 we have five peaks each of type 3 and type 4, giving five values for each y' and z. As there are two atoms in general positions only two of the above y''s and z's refer to the heavy atoms. This choice can be made in 100 ways and corresponds to 25 possibilities for peaks of type 2. Actually there are only six such peaks corresponding to eleven combinations, i.e. any one of these combination can produce two of these six peaks.

Now, whereas the height of most peaks in the sharpened synthesis is more than twice that in the unsharpened synthesis, that of peak No.9 is nearly the same. Therefore this peak is not a heavy atom-heavy atom vector peak. Omitting this peak eliminates five combinations, all of which include peak No.7 also, indicating that the peaks 7 and 9 refer to the same atom but not the heavy atom. The remaining six combinations are given below (Table 2.) as combinations of peak Nos. marked in Fig.2 together with the corresponding y' and z co-ordinates in 60ths of cell edge.

TABLE 2.

(i)	(10,3)	and (2,1)	or	(11.0,0.6)	and (13.0,12.7)
(ii)	"	and (4,1)	"	"	and (4.0, 12.7)
(iii)	"	and (6,1)	"	"	and (7.0, 12.7)
(iv)	"	and (4,5)	"	"	and (4.0, 3.6)
(v)	(4,5)	and (6,1)	"	(4.0,3.6)	and (7.0, 12.6)
(vi)	"	and (2,1)	"	"	and (13.0,12.6)

Note: As it is not possible at this stage to differentiate between y' and $\frac{1}{2} - y'$ or between z and $\frac{1}{2} - z$, only values less than $\frac{1}{4}$ are listed.

Next, a table of peak heights for peaks of type 5, 6, 7 and 8 associated with each of these six combinations was prepared which showed that the combination (ii) is untenable and that combinations (i) and (vi) are associated with too low peaks. Of the remaining three, the combination associated with the strongest peak was (iii) followed by (iv) and (v). The relative average heights of peaks associated with these were 4.5, 3.5 and 3.1 respectively. This leads to the choice of combination (iii) which is also confirmed by the fact that only the peaks associated with this combination show a noticeable decrease in peak height in the di-hydrochloride as compared with the di-hydrobromide.

In performing operation (t) it was necessary to remember that some of the co-ordinates in Table 2 may be ($\frac{1}{2}$ - true co-ordinate). If we designate co-ordinates of peaks of the type 5, 6, 7 and 8 say by (c, d), we have also to keep in view peaks of the type c,($\frac{1}{2}$ - d); ($\frac{1}{2}$ - c),d and ($\frac{1}{2}$ - c),($\frac{1}{2}$ - d). For instance in the case of combination (iii) a prominent peak was always found for c,($\frac{1}{2}$ - d) indicating that some co-ordinate must be of the ($\frac{1}{2}$ - true co-ordinate) type. For the di-hydrobromide Mr. J.V.Silverton computed 2D electron density projections based on the signs of heavy atoms alone and obtained more accurate values of heavy atom co-ordinates:

1. Atom 1. $y' = 0.178$ Atom 2. $y' = 0.376$
$z = -0.063$ $z = 0.205$

which were used for the work described in the next chapter.

6. Solution of the phase problem using isomorphous replacement method.

The difference between the absolute intensities of equivalent reflexions from the two isomorphs will be due to the difference in the scattering factors of chlorine and bromine atoms. With a knowledge of the position of these atoms, the aforesaid difference together with its phase can be calculated. For the space group $P_{2_12_12_1}$ projections down orthogonal axes are centrosymmetric so that the reflexions determining them can only have phase angle 0° or 180°. Consequently, the problem reduces to one of determining the sign of a reflexion, its amplitude in the two isomorphs being known together with the amplitude and sign of the difference. This can be solved in a way similar to that used for metal-free phthalocyanine by Robertson and Woodward (1936).

The $0k\ell$ data for both the isomorphs were put on to an absolute scale by the statistical method of Wilson (1942), which gave a rather low temperature factor parameter ($B = 1.6$). The scaling thus achieved however was not accurate enough for the application of the isomorphous replacement method, and recourse was had to the more powerful method described by Hargreaves (1957).

With the structure factor formula given in International Tables Vol.I for the plane group pgg, Hargreaves' equations (4) and (5) can be written as (1) and (2) below:-

$$C_A\left\{\frac{F'A(hk0)}{P(hk0)}\right\} = C_B\left\{\frac{F'(hk0)}{P(hk0)}\right\} + \exp(-B\sin^2\theta/\lambda^2)\ldots.\quad(1)$$

Where,

$$P(hk0) = \sum_{m=1}^{M} 4\left\{(fo)_A - (fo)_B\right\}\cos 2\pi hx_m . \cos 2\pi ky_m$$

when $h + k = 2n$

<u>or</u>

$$= -\sum_{m=1}^{M} 4\left\{(fo)_A - (fo)_B\right\}\sin 2\pi hx_m . \sin 2\pi ky_m$$

when $h + k = 2n + 1$ ....(2)

$F'_A(hk0)$ and $F'_B(hk0)$ are observed structure factor amplitudes of the two isomorphs A and B and C_A and C_B the corresponding scale constants such that

$F_A(hk0) = C_A F'_A(hk0)$ and $F_B(hk0) = C_B F'_B(hk0)$

M is the number of replaced atoms in general position. For a small range of $\sin\theta$ the second term on R.H.S. in equation (1) is practically constant, and a plot of

$$\frac{F'_A(hk0)}{p(hk0)} \quad \text{against} \quad \frac{F_B(hk0)}{p(hk0)}$$

is linear with slope $\frac{C_B}{C_A}$ and intercept $\exp(-B \sin^2\theta/\lambda^2)$.

As a value of B = 1.6 was inferred by Wilson's method and as there is no reason to believe that it can be less than this, I actually used:

$$C_A\left\{\frac{F'_A(hk0)}{p'(hk0)}\right\} = C_B\left\{\frac{F'_B(hk0)}{p'(hk0)}\right\} + \exp\left\{(1.6 - B)\sin^2\theta/\lambda^2\right\}$$

where,

$$p'(hk0) = p(hk0) \quad \exp(-1.6 \sin^2\theta/\lambda^2),$$

an advantageous form, because it extends the range of $\sin\theta$ for which reflexions can be graphed on the same plot. The plot for the $\sin\theta$ range of 0 to 0.32 is shown in Fig. 3. The scale constants derived from these were $C_A = 1.25$ and $C_B = 1.65$, resulting in a successful sign determination of 70% of the reflexions. Values of $|F_A(0k\ell)|$, $|F_B(0k\ell)|$, and $p'(0k\ell)$ together with derived signs are listed in Table 3.

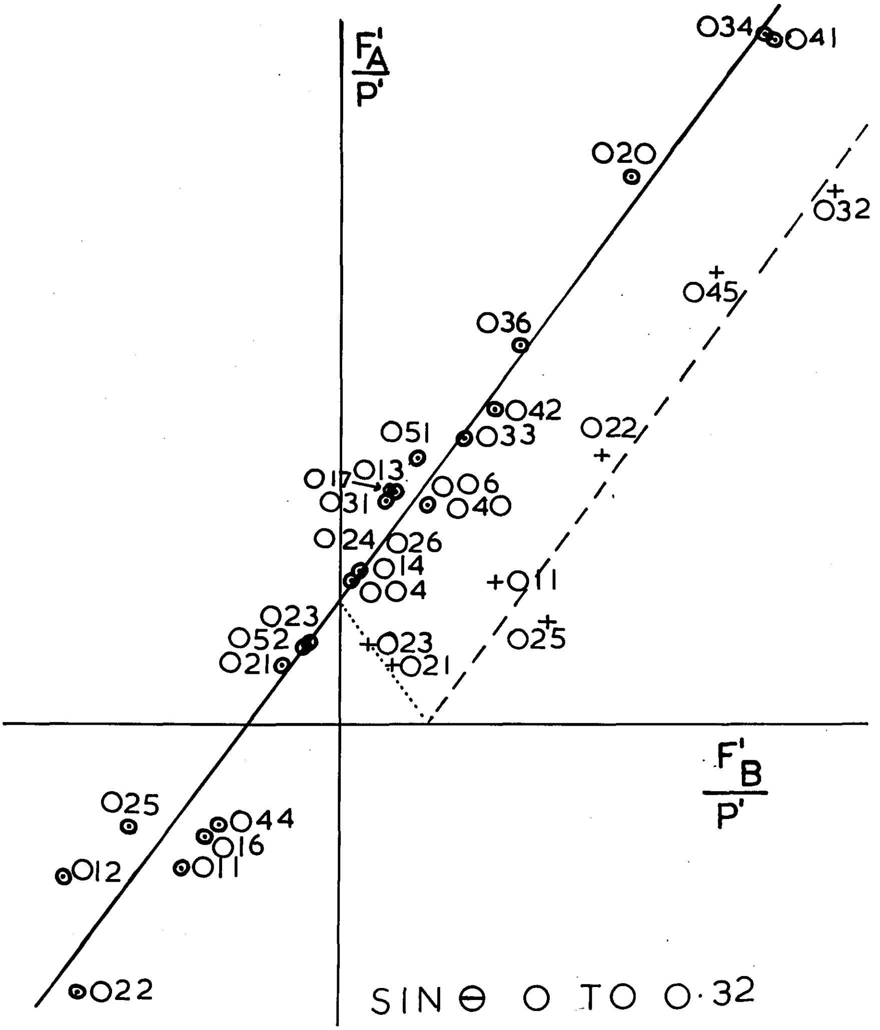


Fig. 3. Hargreaves' isomorphous replacement method of sign determination; plot for the sin θ range 0 to 0.32.

7. The electron density projection on the (100)plane.

This was calculated by the equation:-

$$\sigma\,(y,z) = \frac{4}{Aa}\left[\frac{F(000)}{4} + \sum_{k}\sum_{\ell}^{(k+\ell)=2n} F_{(0k\ell)}\cos 2\pi y.\cos 2\pi z - \sum_{k}\sum_{\ell}^{(k+\ell)=2n+1} F_{(0k\ell)}\sin 2\pi y.\sin 2\pi z\right].$$

and is shown in Fig. 4.

It was possible to pick up one six membered ring (20-21-22-23-24-25) from this, but further interpretation proved difficult because of extensive overlap. The superposition of co-ordinates later derived from 3D Fourier by Dr. T. Hamor confirmed the remarkable accuracy of this electron density projection, where peaks for all but one atom are present.

At this stage, Glasgow University acquired A DEUCE computer. As two bromine atoms are heavy enough for the successful application of the 'Heavy atom' method (Lipson & Cochran, 1953) to this structure, a three dimensional attack on the di-hydrobromide alone was made, which soon led to structure (II). This work was done by Dr. T. Hamor and is described elsewhere. (Hamor et al. 1960.)

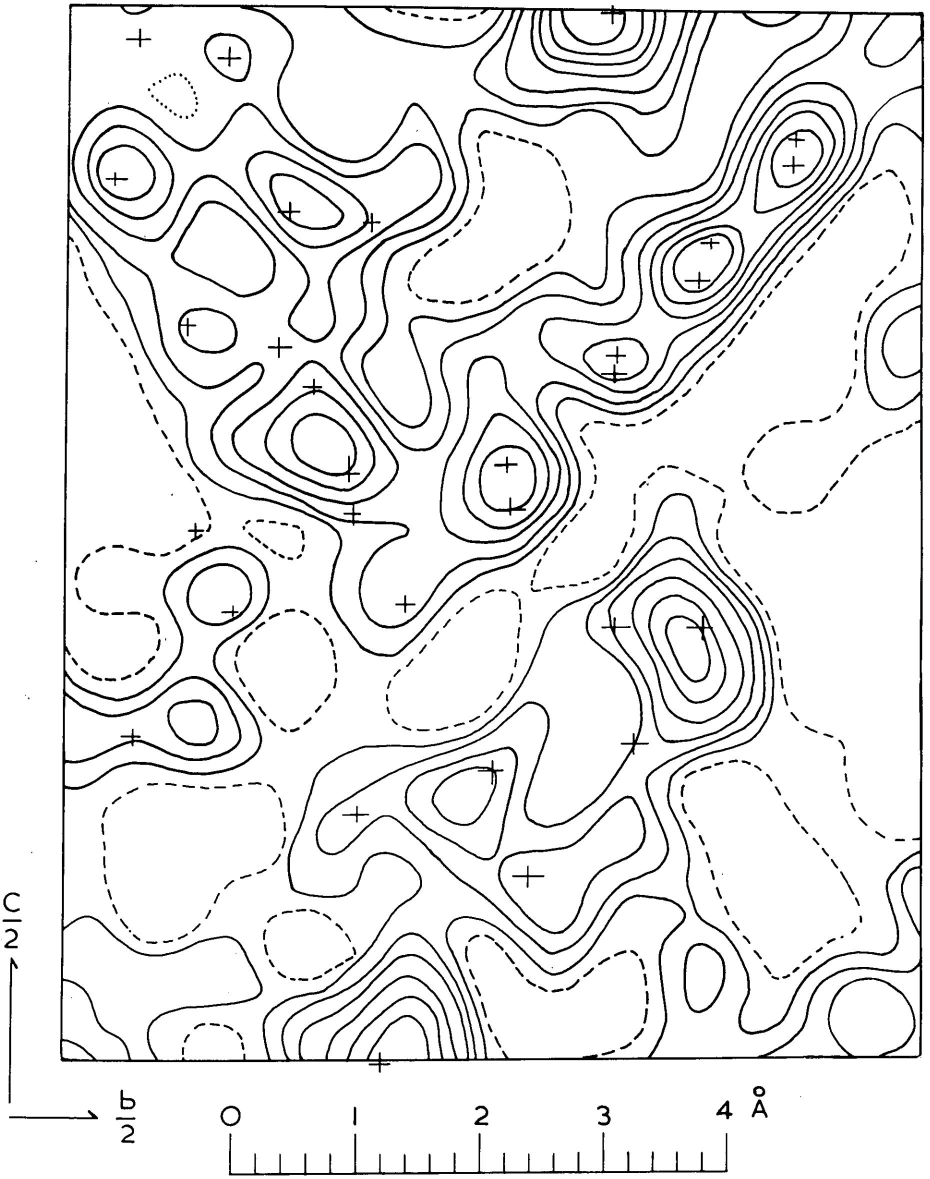


Fig.4. Calycanthine-di-hydrochloride - electron-density projection on the (100) plane.

TABLE 3.

Observed structure amplitudes for $(0k\ell)$ of calycanthine-di-hydrobromide (F_A) and the dihydrochloride (F_B) together with their calculated difference (p').

Index	$2F_A$	$2F_B$	$2p'$	Index	$2F_A$	$2F_B$	$2p'$
$0,0,\ell$				$0,2,\ell$			
2	290	254	24	5	- 30	- 60	28
4	195	22	175	6	- 119	- 36	- 75
6	212	106	125	7	153	39	57
8	107	20	35	8	- 166	- 98	- 60
10	302	85	200	9	- 152	- 14	- 56
12	d 73	d 72	- 1	10	- 125	- 44	- 64
14	145	97	104	11	87	d 21	92
16	- 40	-132	44	12	- 64	- < 20	- 50
18	45	19	21	13	d 97	d 97	- 41
20	40	- 21	68	14	- 75	d 25	- 75
				15	- 35	- 82	39
$0,1,\ell$				16	- 50	d 55	- 39
1	- 30	- 43	27	17	47	< 16	17
2	55	129	- 46	18	- 44	- 14	- 23
3	206	64	115	19	< 28	25	- 10
4	110	21	93				
5	d147	d140	- 30	$0,3,\ell$			
6	57	87	- 65	1	- 220	- 38	- 96
7	174	71	106	2	167	205	- 40
8	147	< 20	75	3	- 405	- 236	-183
9	d 41	d 59	2	4	315	255	58
10	d 27	d151	/	5	30	88	- 16
11	- 41	- 78	35	6	- 177	- 111	- 60
12	d131	d 65	6	7	- 312	- 215	-168
13	47	d 31	47	8	- 115	- 136	24
14	86	55	51	9	- 102	- 56	- 38
15	- 50	- 21	- 12	10	- 46	- 21	- 21
16	d 89	d 88	- 18	11	- 130	- 20	- 70
17	78	54	47	12	d < 42	d 27	- 17
18	75	13	42	13	- 120	- 20	- 82
19	< 28	- 12	32	14	- 39	- 62	18
20	d < 20	d 18	0	16	< 30	55	- 34
				17	- 85	- 35	- 71
$0,2,\ell$				18	< 28	30	- 17
0	-445	-313	-104	19	< 28	39	- 7
1	56	- 72	128	20	- < 20	10	- 16
2	160	206	- 77	21	- < 12	20	- 31
3	- 44	21	- 74				
4	- 90	- 37	- 87				

Index	$2F_A$	$2F_B$	2p'
$0,4,\ell$			
0	-390	-165	-144
1	-135	-113	- 25
2	219	142	89
3	d108	d183	7
4	42	64	- 53
5	112	124	- 32
6	- 32	- 15	- 19
7	-193	- 73	- 25
8	65	19	49
9	d 50	d 13	- 5
10	-137	- 81	- 78
11	<42	58	- 34
12	95	45	63
13	- 55	- 20	- 10
15	- 45	- 20	- 23
17	<30	24	- 18
18	-<30	- 23	11
19	d<28	d 12	11
20	-<28	<13	- 26
$0,5,\ell$			
1	240	90	115
2	32	-<16	- 52
3	53	d 22	52
4	-115	- 16	- 81
5	343	236	140
6	265	192	76
7	177	165	37
8	- 98	- 51	- 65
9	133	<13	90
10	-<40	- 63	10
11	95	<20	54
13	132	<20	30
14	- 45	d 36	- 42
16	43	24	29
17	35	14	12
19	41	<12	37
20	d<12	d 53	8
$0,6,\ell$			
0	253	106	100
1	-210	-100	- 94
2	103	55	52
3	87	<16	67
4	60	- 25	87
6	210	66	72
7	<30	46	- 23
8	105	51	45
9	43	- 36	70
10	180	94	72
11	-107	d110	- 50
12	48	<20	27
13	82	<20	70
15	37	46	- 9
17	<30	<15	7
20	40	15	28
$0,7,\ell$			
1	-100	- 81	- 50
2	35	<13	29
3	83	<13	39
4	- 37	- 13	- 23
5	-190	-125	- 93
7	205	126	44
8	<40	44	- 10
9	- 80	- 47	- 54
10	-<42	- 68	24
11	48	20	30
12	d<45	d 24	22
14	d<30	d 15	1
15	- 55	-<16	- 43
16	45	13	31
17	<28	21	- 15
19	- 30	-<10	- 19
$0,8,\ell$			
0	29	42	- 6
2	-313	- 99	-153
3	- 55	- 22	- 21

Index	$2F_A$	$2F_B$	$2p'$
$0,8,\ell$			
4	-128	- 35	- 49
5	d 63	d 13	6
6	-137	-<13	- 69
7	112	63	14
8	-123	-<20	-110
9	<42	61	- 19
12	d148	d 14	3
15	d<45	d 24	9
16	51	<16	42
18	- 40	- 22	- 37
19	d 12	d 34	- 5
$0,9,\ell$			
1	-113	- 13	- 48
2	73	21	43
3	- 48	- 31	- 21
4	- 43	- 72	70
5	- 85	- 69	- 59
6	- 67	- 13	- 55
7	<30	71	- 13
9	<30	106	- 46
10	d<42	47	- 44
11	- 72	- 47	- 25
12	d<45	d 27	- 1
13	d<45	d 15	- 14
14	-<45	- 47	40
16	- 30	-<16	- 21
18	<20	- 12	35
$0,10,\ell$			
0	d<42	- 49	46
1	117	53	56
2	112	84	38
3	-120	- 57	- 32
4	45	23	40
5	- 70	- 55	- 16
6	70	<23	37
7	100	83	30
8	-<45	- 51	29
9	-<45	25	- 60
10	d 50	d 47	32
$0,10,\ell$			
11	d 70	d 64	35
13	-<40	19	- 38
14	53	18	20
17	d<20	d 16	2
$0,11,\ell$			
1	125	53	79
3	- 45	- 40	15
4	47	31	13
5	180	29	112
6	-125	- 96	-105
7	-<45	- 47	35
8	d 75	d<20	10
9	49	- 37	72
10	d 48	d 25	0
11	87	56	29
12	d<30	d 19	0
15	43	- 24	55
16	- 17	-<20	- 4
$0,12,\ell$			
1	-<45	- 50	28
2	- 35	- 71	49
5	- 40	- 86	10
8	70	<35	35
9	d<30	- 29	30
10	- 67	-<16	- 25
11	<28	31	- 12
12	42	<13	36
13	40	33	27
15	d<12	d 32	- 3
16	d 12	d 7	8
$0,13,\ell$			
1	d<40	39	- 40
3	-<40	25	- 33
4	d<35	d 32	- 3
5	- 45	- 35	- 32
6	80	47	23
7	- 72	- 32	- 40
8	d<30	23	- 21

Index	$2F_A$	$2F_B$	$2p'$	Index	$2F_A$	$2F_B$	$2p'$
$0,13,\ell$				$0,15,\ell$			
11	d 37	d<13	N.C.	1	d<28	d 26	- 4
12	<28	31	9	2	d<28	d 29	- 4
14	d<12	d 17	N.C.	4	d<27	d 17	- 5
$0,14,\ell$				11	d 50	d 20	5
0	38	45	- 8	$0,16,\ell$			
1	- 38	- 14	- 33	0	d 23	- 44	51
7	d<28	18	- 15	1	<28	- 23	23
13	15	<13	12	2	d<26	- 16	12
				4	<24	- 15	40

<u>NOTE</u>:

d indicates a doubtful sign.

N.C. = not calculated.

<2F indicates that the structure amplitude is less than the minimum locally observable value F.

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The Structure of Calycanthine.

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The Structure of Calycanthine

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X-RAY work in this Department has led to a complete determination of the structure of the alkaloid calycanthine, $C_{22}H_{26}N_4$, by means of a crystal structure analysis of the dihydrobromide dihydrate, $C_{22}H_{28}N_4Br_2,2H_2O$. Our results are summarised in formula (I) for calycanthine, and in Fig. 2 which is a projection drawing of the molecule as it appears in the unit cell of the crystal.

Our *X*-ray work on this structure began in 1957 when Mr. Harley-Mason kindly supplied us with a quantity of the pure material and several crystalline salts. At that time, and indeed until now, the structures regarded as most probable for calycanthine were those represented by (II)[1] and (III)[2], although several other possibilities had been discussed.

We hoped that by the examination of several derivatives, employing two-dimensional methods and the isomorphous replacement or heavy-atom phase-determining techniques,[3] we might be able to obtain recognisable fragments of the molecule and finally elucidate the complete structure. To this end a number of derivatives were examined and these gave the approximate cell dimensions and symmetries listed in the Table.

There is evidently a fairly close similarity between the first three compounds, and especially between

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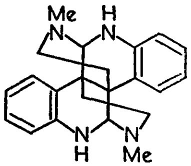
[1] Robinson and Teuber, *Chem. and Ind.*, 1954, 783.

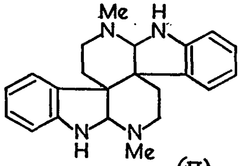
[2] Harley-Mason, personal communication.

[3] Robertson, *J.*, 1935, 615; 1936, 1195; Robertson and Woodward, *J.*, 1937, 219; 1940, 36.

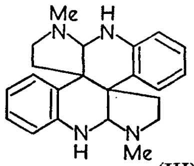
the dihydrochloride and dihydrobromide. These hydrates are liable to lose water in a dry atmosphere. The dihydroiodide, which does not appear to be hydrated, is unstable and difficult to prepare, and only very incomplete data were obtained. The hexachloroplatinate is readily prepared and forms red needles which appear dendritic but are in reality single crystals. The cell dimensions of this salt, however, indicate a rather complex structure.



(I)



(II)



(III)

Two-dimensional work on the dihydrochloride and dihydrobromide by the isomorphous replacement method yielded reliable electron-density projections but extensive overlap prevented full interpretation. The dihydrobromide was therefore selected for three-dimensional study and careful redetermination of the parameters by means of precession photographs and Mo–K_α radiation (λ 0·7107 Å) gave the following data:

		Space group	a	b	c (Å)	
Calycanthine		D_2^4–$P2_12_12_1$	10·5	13·3	14·5	
,,	dihydrochloride,$2H_2O$	D_2^4–$P2_12_12_1$	9·5	$13{\cdot}8_7$	17·0	
,,	dihydrobromide,$2H_2O$	D_2^4–$P2_12_12_1$	9·6	14·1	17·0	
,,	dihydroiodide	(Monoclinic)	9·5	13·8	8·9	$\beta = 120°$
,,	hexachloroplatinate	D_4^4–$P4_12_12$ (or D_4^8–$P4_32_12$)	13·4	13·4	31·9	

$C_{22}H_{28}N_4Br_2,2H_2O$. M, 544·3. Orthorhombic. $a = 9{\cdot}61 \pm 0{\cdot}01$, $b = 14{\cdot}13 \pm 0{\cdot}02$, $c = 16{\cdot}97 \pm 0{\cdot}02$ Å. Absent spectra, $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group D_2^4–$P2_12_12_1$. Four molecules per unit cell. Volume of unit cell = 2304 Å^3. d, calc. 1·568, measured by flotation in CCl_4 and benzene, 1·568. Total number of electrons per unit cell = $F(000)$ = 1112.

Intensities were estimated visually from several series of Weissenberg photographs by using Cu–K_α radiation and all the accessible layer lines from rotations about the principal axes. In all, 2111 independent structure factors were evaluated. A sharpened three-dimensional Patterson synthesis was first made to confirm the halogen positions.

With bromine phases alone a first three-dimensional Fourier synthesis (with R = 33·8%) enabled us to assign approximate co-ordinates to 15 of the 28 atoms (C, N, and O). When these in turn were inserted in the phasing calculations a second synthesis (R = 28%) placed 24 atoms with certainty.

The third three-dimensional synthesis (R = 22%) was therefore based on 24 atoms in addition to the bromine positions. Superimposed contour sections illustrating this synthesis, as projected on (001) are shown in Fig. 1. All the atoms are now resolved with considerable clarity and the positions are found to correspond to those required by formula (I). The atoms not inserted in the phasing calculations at this stage are the nitrogen atoms numbered 26 and 27 in the explanatory drawing in Fig. 2, and the two water molecules. These four atoms are, however, definitely resolved in this synthesis, the two nitrogen atoms being indicated by peaks of over 3 eÅ^{-3} and the water molecules by peaks of between 1 and 2 eÅ^{-3}. (In Fig. 1 the small nitrogen peak 26 is concealed below the methyl group, and the water molecules, which lie beyond the region of the calycanthine molecule, are not included.)

Further refinement of the structure is now in progress. Structure-factor calculations based on the atomic positions derived from the third synthesis, with all the C, N, and Br atoms inserted, give a discrepancy (R) over all planes of 18%. When the two water molecules are inserted as well, the discrepancy falls to 16%; and later refinement has now reduced this figure to 14·6%. These results indicate that the structure is now established beyond reasonable doubt.

The molecule which emerges from this analysis is a very compact three-dimensional structure in which the planes of the two benzene rings are inclined at about 60° to each other. The other four six-membered rings are all of "chair" form and fused *cis* to each other. The nitrogen atoms 10 and 16 can be distinguished from the carbon atoms by higher peak densities, although all the atoms were given equal weight in the phasing calculations. The other two nitrogen atoms, 26 and 27, which were entirely

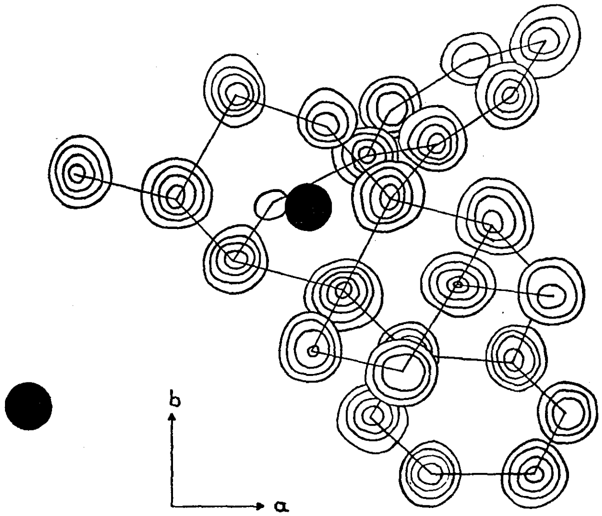


FIG. 1. *The third three-dimensional electron density distribution for calycanthine dihydrobromide shown by means of superimposed contour sections parallel to* (001). *Contours are at unit intervals but those below* 3 $e\text{Å}^{-3}$ *are omitted for clarity. (The contour scale is only approximately absolute.)*

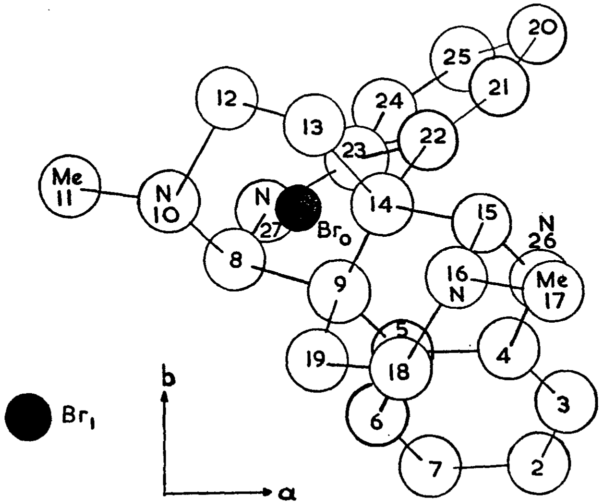


FIG. 2. *Drawing of the molecule in projection on* (001).

omitted from the phasing calculations, are of course of lower height at the present stage of refinement.

A full account of the stereochemistry with co-ordinates of all the atoms, together with the inter-molecular arrangement of the bromine ions and water molecules, will be given after further refinement has been completed. At the present stage standard deviations in co-ordinates are probably about 0·1 Å.

We are grateful to Mr. Harley-Mason for first suggesting this interesting problem and for supplies of material. The extensive numerical calculations involved were carried out on the Glasgow University Deuce computer by using the programmes originally devised by Dr. J. S. Rollett, and we are indebted to the Director of the Computing Laboratory, Dr. D. C. Gilles, and his staff for facilities.

(*Received, December* 18*th*, 1959.)

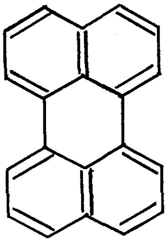
SECTION II.

THE CRYSTAL AND MOLECULAR STRUCTURE OF QUATERRYLENE.

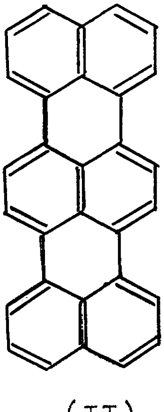
The Crystal and Molecular Structure of Quaterrylene.

1. Introduction:

Perylene (I), terrylene (II) and quaterrylene(III) form a series of peri-condensed naphthalene analogues. For these, a Kekulé type of structure with double bond in the *peri*-position cannot be written. For instance, eighty-one non excited Kekulé structures can be written for quaterrylene, by putting together the three possible structures for each naphthalenic residue in every possible combination, but none of these has a double bond linking these residues. The resulting structure should, therefore correspond to one formed by naphthalenic residues linked by single bonds. On the contrary, one may argue that the true picture might not be so simple. The possible excited structures may considerably out-number the stable forms as pointed out by Daudel and Pullman (1946).



(I)



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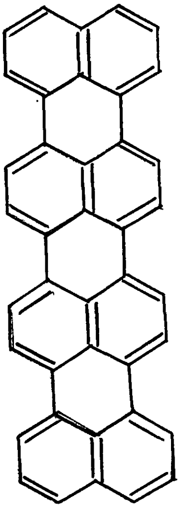


(III)

Some of these are likely to have a double bond in the peri-position and will, therefore, shorten this bond in the averaged structure. This, and the current discussion on the change of the covalent radius of carbon atom with the hybridisation type (Dewar and Schmeising, 1959; Mulliken, 1959) make it interesting to measure the peri-bond length accurately. Moreover, the structure of quaterrylene would be expected to provide interesting comparisons with naphthalene and perylene on the one hand and graphite on the other.

The structure of perylene (I) was studied by Donaldson, Robertson and White (1953). Clar, Kelly and Laird (1956) prepared terrylene (II) and quaterrylene (III). Clar and Speakman (1958) showed quaterrylene to be isostructural with perylene. This implies that difficulties due to partial overlap, similar to those encountered in perylene, will arise. On the other hand, we may expect that greater statistical significance would attach to the results, because of the presence of a larger number of similar bonds. For instance, in perylene only one of the two peri bonds was resolved in its most favourable projection, whereas in quaterrylene there are six peri bonds of which three would be resolved in the corresponding projection. We also hoped to carry the refinement further than that of perylene with the better methods now available.

2. Experimental, Crystal and Morphological Data.

Thin crystals of quaterrylene are green, whereas thick ones are almost blue black. They are very stable, sublimate on heating above 570°C. and are insoluble in all solvents. Consequently, the crystals supplied to us by Dr. E. Clar, to whom our thanks are due, had been grown by sublimation. Individual crystals differed widely in density, as was reported by Clar and Speakman (1958), but I got for their density a value somewhat higher than that cited by them. The most prominent form of these crystals was $\{001\}$.

A number of big crystals with apparently well formed faces gave many additional spots on Weissenberg moving film photographs, which although sharp deviated from integral or half integral reciprocal lattice positions. A few crystals, however, gave normal X-ray diffraction patterns with only two or three additional spots at $\frac{1}{3}$rd or $\frac{2}{3}$rd reciprocal lattice positions. While the structure determination could proceed with the latter variety (which later we call the α-modification) the character of the former remained puzzling for some time.

Following the procedure adopted by Ramachandran and Lonappan (1957) Laue photographs with the (001) plane // to the X-ray beam were taken. These however revealed no twinning across the (001) plane. No positive evidence of any other type of twinning could be obtained although some crystals appeared to develop deformities on cutting. I therefore suspected that different polymorphic (or polytypic) modifications might be present in the one piece. This was confirmed when a well-developed, uncut and accurately set crystal gave the Okℓ moving film Weissenberg photograph shown in Fig.1. A remarkable feature of this photograph is its two types of spots, (a) rectangular, (b) two thin parallel lines separated by a rectangular hollow into which the spot of the first type can be exactly fitted. Closer examination revealed that the spots of the type (a) correspond to a denser modification (which we called the β-modification) with the C- axis 0.7% shorter than that of the light modification. The lighter modification, giving spots of the type (b), is sited on the (001)-faces. No crystals of pure β form could be found. The formation of two modifications seems to be due to differences of vapour pressure and temperature during the earlier and later stages in the growth of these crystals by sublimation.

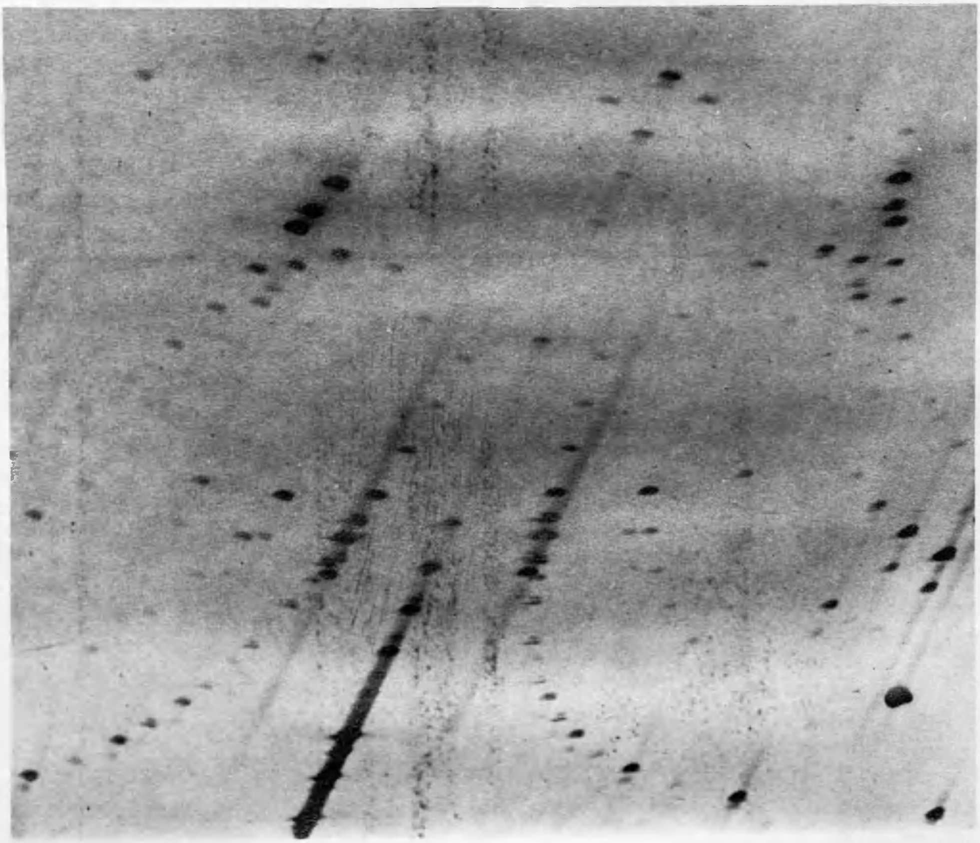


Fig.1. An (Okl) Weissenberg moving film photograph of a crystal of β-quaterrylene with the α-modification sited on the $\{001\}$ forms.

The unit cell parameters given below were determined from one crystal of the α-modification, whose structure we have determined. Crystal data were derived from single crystal rotation, oscillation and Weissenberg moving film photographs. Copper K_α radiation (1.542 Å) was used. Camera radii were standardised by superimposing powder lines from metallic copper (a = 3.614 Å). Some of these parameters differ from those given by Clar and Speakman(1958).

Quaterrylene (α-Modification), $C_{40}H_{10}$; mol.wt. 500.6.
Monoclinic prismatic, a = 11.25 ± 0.04, b = 10.66 ± 0.03,
c = 19.31 ± 0.07 Å, β = 100.6°; volume of unit cell =
2276.2 Å^3; d (flotation) 1.476 - 1.494 g./cc.;
Four molecules per unit cell; d (calc.) = 1.461.
Absorption coefficient for X-rays (λ = 1.542 Å) = 7.8 cm.^{-1};
Number of electrons per cell = $F_{(000)}$ = 1040.
Absent spectra; $h0\ell$ when h is odd; 0k0 when k is odd.
Space group, C^5_{2h}($P2_1/a$) No.14. Asymmetric unit - one molecule, i.e. no molecular symmetry required.
Equivalent points; x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}$ + x, $\frac{1}{2}$ - y, z;
and $\frac{1}{2}$ - x, $\frac{1}{2}$ + y, $\bar{z}$.

The unit cell parameters for the β-modification determined from composite crystals are

Quaterrylene (β-modification)

a = 11.21 ± 0.04; b = 10.67 ± 0.04; c sinβ = 18.85 ± 0.07

$d_{(\text{flotation})}$ 1.476-1.494g./cc. $d_{(\text{calc.})}$ = 1.472.

Morphological Data:

The most prominent form is $\{001\}$, occurring on almost all crystals examined. The next form of wide occurrence is $\{110\}$. It will be shown in Chapter 7 that these forms represent planes parallel to two van-der-Waals vectors holding the molecules together in the crystalline state. These can, therefore, be called "F" faces in the terminology of Hartman and Perdok (1955).

A number of crystals especially those containing both modifications cleave parallel to the (110) plane which was found to be the green reflecting plane in some of these crystals. Some crystals showed pleochroism, with oblique extinction and were rejected. In contrast to the crystals of the α-modifications, crystals containing both modifications exhibited many faces of the type $(hh\ell)$. The faces from two such crystals set along $[110]$ diagonal are given in a table below. Both are composite crystals but crystal 3 consists predominently of the β form.

Observed Angle from (001)plane	Crystal 4	Crystal 3	Index assigned	Calculated angle.
267°	Observed	Missing	$(\bar{6}\bar{6}1)$ $(\bar{5}\bar{5}1)$	266° 40' 267° 19'
264° 56'	"	"	$(\overline{10},\overline{10},1)$	265° 12'
262° 26'	"	"	$(\bar{1}\ \bar{1}\ 0)$	262° 44'
261° 23'	"	A row of Reflections From 262° to 259°30'	$(\overline{12},\overline{12},\bar{1})$	261° 2'
260° 41'	"		$(\overline{10},\overline{10},\bar{1})$	260° 45'
259° 30'	"		$(\bar{6},\bar{6},\bar{1})$	259° 13'
241°	Missing	Observed	$(\bar{5}\ \bar{5}\ \bar{6})$ $(\bar{1}\ \bar{1}\ \bar{1})$	240° 23' 242° 29'
235°	"	"	$(\bar{2}\ \bar{2}\ 3)$	234° 28'
184°	"	"		
180° 24'	Observed	Observed at 180°	$(00\bar{1})$	180° 0'
82° 30'	Missing	Observed	(110)	82° 44'
73°	"	"	(221)	72° 20'
0°	Observed	"	(001)	0°

The calculated angles listed here were derived by a graphical method explained in Appendix I.

Intensity data:

The dimensions of the crystal used for collecting $(h0\ell)$ data were 0.08, 0.16 and 0.7 mm. parallel to a,c' and b axes respectively. This gave an absorption correction range of only 0.89 to 0.95, rendering its application unnecessary. For $(0k\ell)$ and (hk0) data the same crystal was cut in two - approximately halving its length. Strictly, absorption corrections should be applied here.

However, because these data were used only for a one-stage refinement of the molecular orientational parameters, absorption corrections were not applied.

Intensities were estimated visually from Weissenberg moving-film photographs using Robertson's (1943) multiple film technique. Even after long exposures, only 123, 76 and 29 of the $h0\ell$, $0k\ell$ and $hk0$ reflexions could be recorded representing 44%, 28% and 18% coverages respectively.

Relative values of the structure amplitudes, derived in the usual way (see Section 1, p.6), were initially placed on an approximately absolute scale by Wilson's (1950) method, which gave a rather low value for the Debye temperature factor parameter ($B = 1.4\text{Å}^2$). Better scaling was obtained by subsequent comparison with the calculated values (which gave, initially, $B = 2.4\text{Å}^2$).

3. Determination of the structure.

The close resemblance of this structure with that of perylene implied that the best view, by 2D methods, would be obtained only in projection down the '<u>b</u>'-axis. The relevant strong planes in order of decreasing unitary structure factors are:- $8,0,\overline{15}$; $8,0,11$; $20\overline{9}$; 802; $10,0,\overline{16}$; $80\overline{7}$; $6,0,12$ and $0,0,18$. For a centred space group the phase problem reduces to one of sign determination and we hoped that an idea of the signs of a few of these strong reflexions would enable us to apply the strong plane method, as illustrated in the determination of the ovalene structure by Donaldson and Robertson (1953).

For this, we derived help partly from the similarity of the structure with perylene and partly from a simplified application of inequalities (particularly the Sayre-Cochran equation) as outlined by Lipson and Cochran (Book, 1953, p.255). For instance, the reflexion 8,0,11 in quaterrylene occupies a position in reciprocal space between the reflexions 805 and 806 of perylene, the former of which is strong. As 805 and 806 both have a positive sign in perylene, reflexion 8,0,11 in quaterrylene is likely to be positive. This was supported by inequalities which also indicated that both 6,0,12 and 0,0,18 must be positive.

Unfortunately, we had an ambiguity in the case of $8,0,\overline{15}$ - the reflexion with the largest unitary structure amplitude. This occupies a position, in reciprocal space between that of $80\overline{9}$ and $80\overline{8}$ in perylene, being more exactly matched by the latter which is too weak to be observed, whereas the former is a strong reflexion with negative sign. This circumstance makes an *a priori* allocation of negative sign to $8,0,\overline{15}$ not unexceptionable. (This difficulty arises because the inclination of the quaterrylene molecule to the *c*- axis is considerably different from that of perylene.) Inequalities also failed to provide an answer in this case.

However, trial and error indicated this sign to be negative, after which it was easy to fit two centro-symmetrically related and partially overlapping molecules of formula (III) to the *b*- axial projection of half the unit cell in a manner similar to that found in perylene. This structure gave an agreement index of 0.48 for the $h0\ell$ reflexions and was the starting point of refinement for the x- and z- co-ordinates.

4. Refinement of *x*- and *z*- co-ordinates.

To refine the structure we had to concentrate our efforts on the *b*- axial projection, since the other projections had neither sufficient number of reflexions to determine 80 parameters nor any resolution. This is however not a serious disadvantage because the length of most bonds, including the peri- bond, depend almost exclusively on their *x*- and *z*- co-ordinates.

Two cycles of refinement by electron-density projections reduced the agreement index from 0.43 to 0.25.

increase of the Debye temperature factor parameter(B) from $2.4\ \mathring{A}^2$ to $2.7\ \mathring{A}^2$ further decreased R to 0.214. The final electron density map, incorporating a few changes in the signs of weak reflexions indicated by subsequent stages of refinement, is reproduced in Fig.2a and interpreted in Fig.2b.

Two cycles of refinement by "difference synthesis", together with an increase of B to $3.0\ \mathring{A}^2$ and use of McWeeny(1951) scattering factor curves $\bar{f} = \frac{1}{3}(f'' + 2f^{\perp})$ brought down R to 0.14. Hydrogen atoms connected to the remote carbon atoms in the molecule could be seen in the second of these synthesis.

The introduction of all hydrogen atoms in the usual way at $1.05\ \mathring{A}$ from their appropriate carbon atoms did not alter the disagreement index R, but we thought it better to include them with a B value of $4.5\ \mathring{A}^2$ in the succeeding cycles of refinement by "difference synthesis". The third cycle, incorporating hydrogen atoms and some unobserved reflexions for which the calculated structure amplitude was relatively high, reduced R to 0.124.

In this projection 32 carbon atoms are resolved. For the remaining 8, refinement of positional parameters presented difficulties. In an attempt to overcome these, at this stage I made use of two tactics.

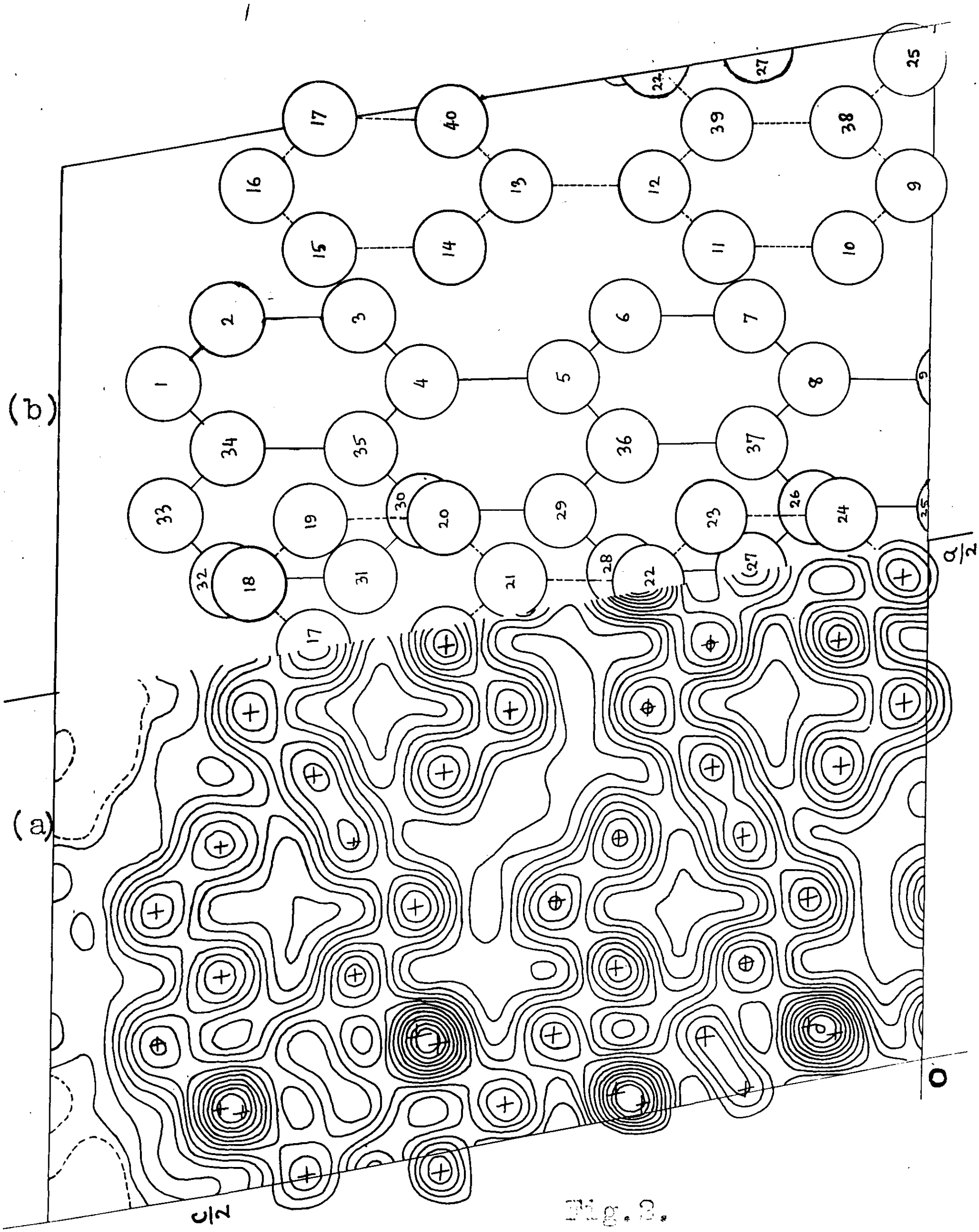


Fig. 2.

Projection down the *b*-axis in the crystal structure of quaterrylene: (a) an electron-density map with contour-line scale of 1 electron per sq. A., the zero line being broken: (b) the corresponding explanatory diagram, showing the numbering of the carbon atoms, with parts of three different molecules appearing.

First, in addition to good agreement between $\underline{F}_o$ and $\underline{F}_c$ for observed reflexions, a refined structure should give, for the unobserved reflexions, a value of $\underline{F}_c$ less than that minimum locally observable. We would expect the average $\underline{F}_c$ for such reflexions to be about half the average minimum locally observable value. Therefore all the unobserved terms in the circle of reflexion for which $\underline{F}_c$ was equal to or greater than $F_{(\mathrm{Loc.Min.})}$ were included in the 'difference synthesis' as $(\frac{1}{2}\underline{F}_{(\mathrm{Loc.Min.})} - \underline{F}_c)$. It is interesting to note that this procedure caused an improvement in the R value of the observed reflexions.

Secondly, in a 'difference map' when an electron-density gradient occurs near the site of an isolated atom, the atom is moved in the direction of "steepest ascent", but when such a gradient occurs in a projection near two overlapping atoms, the direction and magnitude of the shift indicated is the resultant of two shifts.

As this breakdown can be done in an infinite number of ways, a serious ambiguity arises. To solve this, the procedure followed was to distribute the total shift indicated by the 'difference map' between the four co-ordinates of the pair of atoms in such a way that the tendency would be towards the ideally symmetrical molecule. This procedure can be criticised on the grounds that it runs the risk of introducing false symmetry into the molecule; however, in the present analysis this cannot be serious because only 8 of the 40 atoms were involved (affecting 19 of the 50 bond lengths) and only small shifts (up to 0.015 Å) were made.

Two cycles of refinement by 'difference synthesis' incorporating the above tactics brought down R from 0.124 to 0.11. In the last of these cycles the carbon atoms were allocated individual isotropic temperature factor parameters (B), ranging from 2.65 to 3.85 $Å^2$, which in general were larger, the more distant the atom from the molecular centre of gravity.

The x- and z- co-ordinates together with the values of B are given in Table 1. A final 'difference synthesis', $^2/_3$rd of the shifts indicated by which have been applied in deriving the final x- and z- co-ordinates, is shown in Fig.3. The $|\underline{F}_o|$ and $\underline{F}_c$'s for the observed $h0\ell$ reflexions are listed in Table 2, for which R = 0.11. Nine unobserved reflexions for which $\underline{F}_c$ significantly exceeds $F_{(\mathrm{loc.min.})}$ are listed in Appendix to Table 2.

Cruickshank's (1949) method of assessing the accuracy of these co-ordinates is not strictly applicable when the atoms are not resolved. However, its application gave standard deviations

$$\sigma(\underline{x}) = 0.011, \quad \sigma(\underline{z}) = 0.010 \text{ Å}.$$

Internal consistency of molecular dimensions as discussed in a later chapter probably gives a better check on the accuracy of this analysis.

Note: To calculate atomic shifts (Δr_n) from the 'difference maps" the expression used was:-

$$r_n = \left(\frac{\delta \rho_o}{\delta r_n}\right) \Big/ 4pZn$$

(Lipson and Chochran.1953 Book,p.279)

p was taken to be 5, and, instead of Z_n, the peak height of the atom in the electron density synthesis ρ_n was used.

5. Estimation of y-co-ordinates:

From the refined x- and z- co-ordinates the picture that emerged agreed with the projection of a planar molecule consisting of regular hexagons except that the peri- bonds appeared considerably longer.

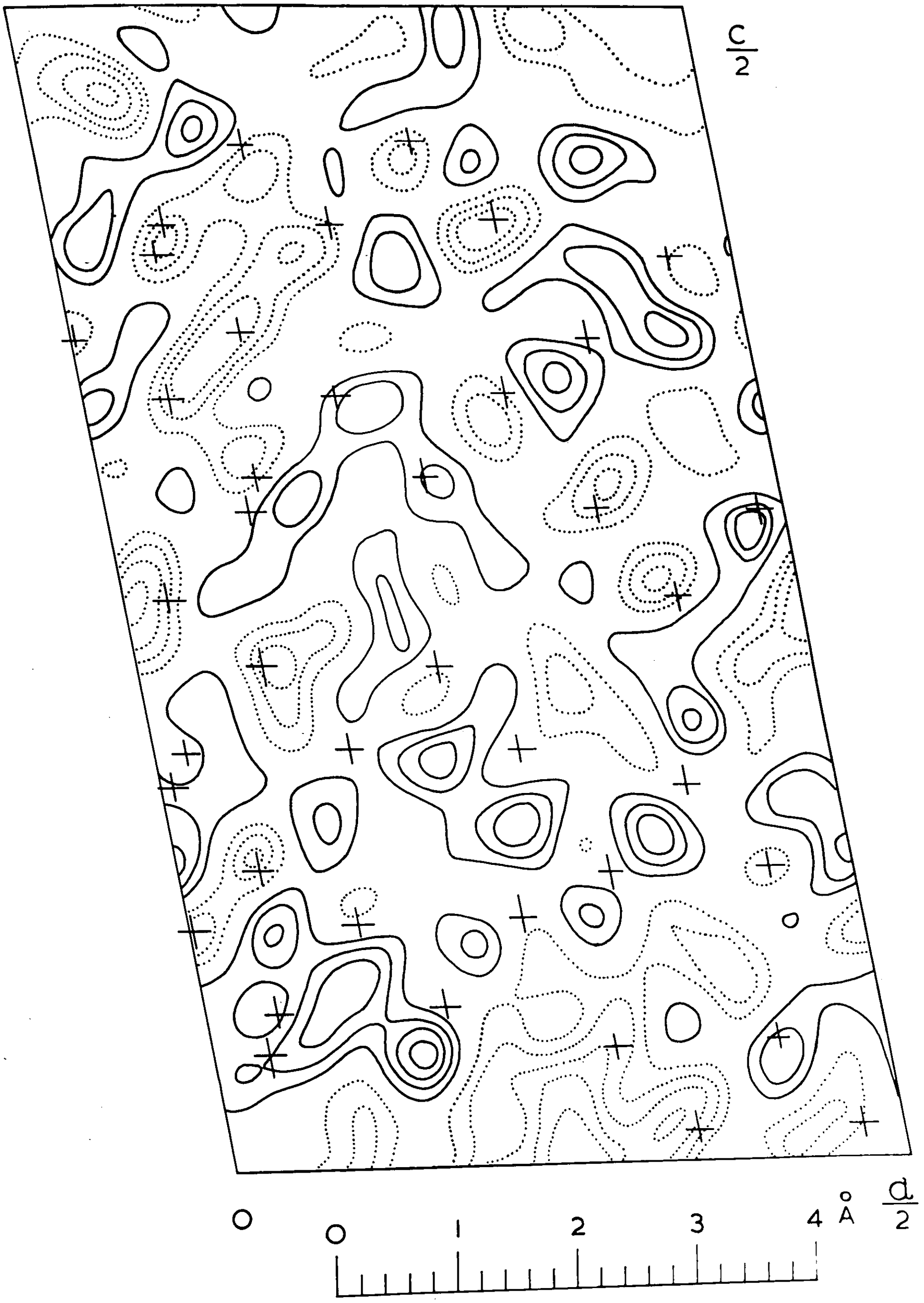


Fig.3. (F_o - F_c) synthesis map for the projection down b-axis of quaterrylene.

As the other projections suffer from overlap and as none of them have enough observed terms to determine unambiguously the co-ordinates of 40 atoms, refinement of individual y- co-ordinates by 2D methods is not possible.

However, if we accept that the molecule is planar, as suggested by its aforesaid projected aspect, the problem reduces to one of only three parameters. We chose these to be the y- co-ordinate of the centre of the molecule (y_c) and two angles ψ_M and ψ_L defining the tilt of the molecule to the *b*- axis.

Following the scheme used in perylene, let *L*, M, and N be three mutually perpendicular molecular axes, the first two being in the plane of the molecule with L along its length. Let χ, ψ and ω be the angles made by any one of these axes with the orthogonal crystal axes *a*-, *b*-, and *c*'- respectively (*c*'- being perpendicular to a and b). Three of the nine possible angles would, in general, define the molecular orientation but since the position of the molecule in its *b*- axial projection was known, two angles sufficed.

If ℓ, m and n represent co-ordinates along molecular axes and ℓ', m' and n' their projected lengths on the (010) plane it is easily seen that:-

$$y = y_c + \ell \cos\psi_L + m \cos\psi_M = y_c + \ell' \cot\psi_L + m' \cot\psi_M. \quad \ldots\ldots\ldots(1)$$

The projected aspect of the molecule shown in Fig.4 indicated that, while it was considerably foreshortened along M, it presented along the L- direction its estimated full length. The projected width and length were 2.768 Å and 28.90 Å, which on comparison with the estimated width and length of ~4.84 Å and ~28.92 Å gave $\psi_M = 34^\circ 56'$ and $\psi_L = 90^\circ$ approx.

Provided the molecular shape is sufficiently regular for a cross line, such as one drawn between atoms 2 and 34, to be perpendicular to L in the actual molecule, a more sensitive test for any deviation of ψ_L from 90° is provided by the angle ($\bar{\theta}_N$) between L and the cross line as they appear in projection. There were in all, eleven cross lines involving resolved atoms. The mean value of these angles measured in projection was 90.5°. By simple geometric considerations it can be shown that:

$$\left|\cos\bar{\theta}_N\right| = \cot\psi_M . \cot\psi_L$$

With the known value of ψ_M, we find that $\psi_L = 89.7^\circ$ which proves that ψ_L does not in fact significantly deviate from 90°.

With the lie of the molecule in projection and its inclination known, it was clear that y_c must depend on the perpendicular distance (d) between the pair of centro-symmetrically related molecules. Straightforward trigonometric methods revealed that when $\psi_L = 90^\circ$, y_c is given by

$$\pm\, y_c = \frac{d}{2}\operatorname{cosec}\psi_M - \frac{d'}{2}\cot\psi_M \quad \ldots\ldots\ldots \quad (2)$$

where d' is the distance in projection between the two parallel L- axes. (For derivation see Appendix 2 to this Section.)

The planar molecules of hydrocarbons are always stacked with a perpendicular distance more than that between the atomic layers in graphite (3.40 Å). This spacing was 3.48 Å in perylene (recalculated from Donaldson, Robertson and White's data, where an error in the listed value of ψ_N occurs). Reasons can be given for expecting a shorter value in quaterrylene. The greater stability at high temperatures suggests greater cohesion between parallel molecules increasing more than proportionately to the molecular area. The b- axial length in quaterrylene is shorter by 0.21 Å as compared to that in perylene. If the molecular width is supposed to be the same in both, there are only three ways of bringing about this contraction, namely a decrease in y_c, $\psi_M \rightarrow 90^\circ$ or $\psi_L \rightarrow 90^\circ$. The second of these modes calls for an increase in the 'a' translation, whereas there is actually a small decrease (0.1 Å). The third mode seems to have been used to the full but, as ψ_L in perylene (89.2°) was already close to 90°, it is unlikely to explain the entire contraction.

In view of the proximity of ψ_L to 90°, if we assume that equation (2) is also applicable to perylene, then for the same values of d and ψ_M the contraction Δy_c turns out to be 0.035 Å. As in perylene y_c was -1.55 Å, we should expect a value slightly less than -1.515 Å in quaterrylene. In quaterrylene, d' (see Fig. 5) is 1.068 Å; and when d is put equal to 3.44 Å y_c was calculated to be ± 1.481 Å, whereas when $d = 3.48$ Å $y_c = \pm 1.517$ Å. An initial value of $y_c = -1.513$ Å (final value $y_c = -1.508$ Å) was chosen. Structure amplitudes based on the y co-ordinates so derived (equation 1) gave a R- value of 0.23 for the $hk0$ and $0k\ell$ reflexions.

6. Least square refinement of parameters y_c, Ψ_M and Ψ_L.

In what follows, let $W'_L = 90^\circ - \Psi_L$. Let ΔF_c be a small change in F_c caused by small changes in y_c, $\cot \Psi_M$ and $\sin W'_L$ of the magnitude Δy_c, $\Delta \cot \Psi_M$ and $\Delta \sin W'_L$. Then

$$\Delta F_c = \left(\frac{\delta F_c}{\delta y_c}\right) \Delta y_c + \left(\frac{\delta F_c}{\delta \cot \Psi_M}\right) \Delta \cot \Psi_M + \left(\frac{\delta F_c}{\delta \sin W'_L}\right) \Delta \sin W'_L \quad \ldots\ldots\ldots (3)$$

The correct values of Δy_c, $\Delta \cot \Psi_M$ and $\Delta \sin W'_L$ are those which nearly equate ΔF_c to $(F_o - F_c)$ for all equations of this type within the limiting sphere, i.e. those for which $\sum \Delta F_c = \sum \Delta(F_o - F_c)$ . . . . . (4)

Now, multiplying (3) by $\frac{\delta F_c}{\delta y_c}$, $\frac{\delta F_c}{\delta \cot \Psi_M}$, and $\frac{\delta F_c}{\delta \sin W'_L}$ respectively and summing for all reflexions we get:-

$$\sum \frac{\delta F_c}{\delta y_c} \Delta F_c = \Delta y_c \sum \left(\frac{\delta F_c}{\delta y_c}\right)^2 + \Delta \cot \Psi_M \sum \frac{\delta F_c}{\delta \cot \Psi_M} \cdot \frac{\delta F_c}{\delta y_c} + \Delta \sin W'_L \sum \frac{\delta F_c}{\delta \sin W'_L} \frac{\delta F_c}{\delta y_c} \quad \ldots . (5)$$

$$\sum \frac{\delta F_c}{\delta \cot \Psi_M} \Delta F_c = \Delta y_c \sum \frac{\delta F_c}{\delta y_c} \cdot \frac{\delta F_c}{\delta \cot \Psi_M} + \Delta \cot \Psi_M \sum \left(\frac{\delta F_c}{\delta \cot \Psi_M}\right)^2 + \Delta \sin W'_L \sum \frac{\delta F_c}{\delta \sin W'_L} \cdot \frac{\delta F_c}{\delta \cot \Psi_M} \quad \ldots . (6)$$

$$\sum \frac{\delta F_c}{\delta \sin W'_L} \Delta F_c = \Delta y_c \sum \frac{\delta F_c}{\delta y_c} \cdot \frac{\delta F_c}{\delta \sin W'_L}$$

$$+ \Delta \cot \Psi_M \sum \frac{\delta F_c}{\delta \cot_M} \cdot \frac{\delta F_c}{\delta \sin W'_L} + \Delta \sin W'_L \sum \left(\frac{\delta F_c}{\delta \sin W'_L} \right)^2 \quad \ldots\ldots (7)$$

For the (hk0) reflexions, the necessary terms in equation 5, 6 and 7 were calculated and on solving them for Δy_c, $\Delta \cot \Psi_M$ and $\Delta \sin W'_L$ we got:-

$\Delta y_c = 0.005$ Å.

$\Delta \cot \Psi_M = 0.012$ Å, i.e. $\Delta \Psi_M = -13'$ in the range $\Psi_M = 35^\circ$.

$\Delta \sin W'_L = 0.0005$, i.e. $\Delta W'_L = 2'$ in the range $W'_L = 0$.

If cross terms are left out we get:-

$\Delta y_c = 0.0048$, and $\Delta \cot \Psi_M = 0.0113$.

With new y co-ordinates derived after applying these corrections to the orientational parameters, the structure amplitudes for the larger number of $0k\ell$ reflexions were calculated. These gave R = 0.20.

Structure amplitudes for hk0 reflexions have not been re-calculated but these must also give better agreement. These structure factors are listed in Table 4.

(Note: In Table 4, F_o for 00ℓ reflexions has been omitted as better values are in Table 2, and for 0k0 reflexions averaged structure amplitudes from (hk0) and $(0k\ell)$ zones are given; consequently values in this table indicate better values for R. than given above.)

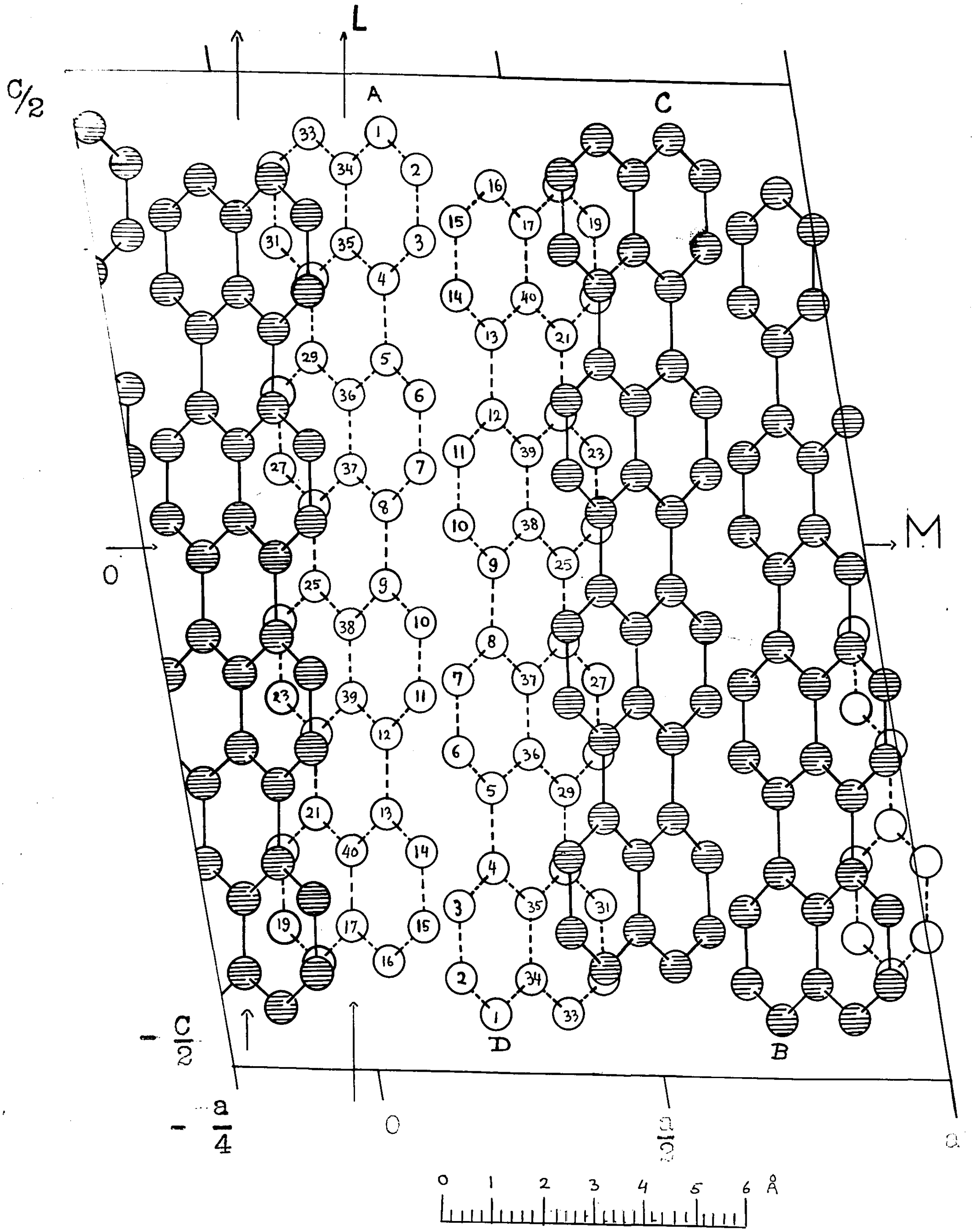
Final molecular orientational parameters are listed in Table 3, which need not be as comprehensive as that of perylene because $\psi_L = 90^\circ$. y- Co-ordinates are listed in Table 1, along with co-ordinates (in Å) with respect to orthogonal axes, X' and Y parallel to $\underline{x}$- and $\underline{y}$ respectively and Z' perpendicular to both.

7. Arrangement of molecules, intermolecular distances and explanation of morphology.

Four equivalent molecules, A(x_c,y_c,z_c), B($\bar{x}_c,\bar{y}_c\bar{z}_c$), C($\frac{1}{2} + x_c$, $\frac{1}{2} - y_c$, z), and D($\frac{1}{2} - x_c,\frac{1}{2} + y_c,\bar{z}$) as seen looking down the screw axis, are shown in Fig.4. Diagramatic representation of these molecules, when looking down the orthogonal axis C' together with the direction, length and multiplicity of the Van-der-waals intermolecular contacts is given in Fig.5, whereas Fig.6 shows the projection of two centro-symmetrically related molecules A and B on the plane of the molecule A.

The perpendicular distance between the planes of these parallel molecules is 3.47 Å which is slightly shorter than the distance in perylene. These molecules are displaced laterally to avoid near perpendicular contacts, such displacement being more in quaterrylene as compared to that in perylene. (See Fig.3 in the paper on perylene.)

Fig.4. Projection of the quaterrylene structure down the b-axis covering rather more than one complete unit cell and showing four overlapping molecules at different levels, viz. A(x, y, z), B(-x, -y, -z), C($\frac{1}{2}$ + x, $\frac{1}{2}$ - y, z), and D(at $\frac{1}{2}$ - x, $\frac{1}{2}$ + y, -z). The directions of the molecular axes L and M are also indicated.



The average length of sixteen such contacts (3.476 Å) represents the shortest van-der-Waals contacts in quaterrylene. There are sixteen contacts of similar length but different direction between the other pair of parallel molecules. In the terminology of Hartman and Perdok (1955), these represent two periodic bond chain vectors (P.B.C.-vectors) with components (2.864, -2.001, 0.301) Å and (2.864, 2.001, 0.301) Å respectively along the axes a-, b- and c-.

Since these P.B.C. vectors are nearly parallel to $\{001\}$ it can be described as a 'F-face'. There are a large number of other contacts lying in the range 3.67 to 3.97 Å as can be seen from Fig.6. Of these, the type III and V represent two P.B.C. vectors (of multiplicity 8 and 4 respectively), nearly parallel to $\{110\}$ Consequently, this form is also a 'F-face'. This explains the prominence of these forms in α-quaterrylene.

In the case of β-quaterrylene which exhibits a greater number of faces, it may be noted that a number of them make a small angle ($\sim 3^{\circ}$ see Table p.28) with the $(\bar{1}\bar{1}0)$ plane. If these be indeed genuine planes, this would imply a decrease in the multiplicity

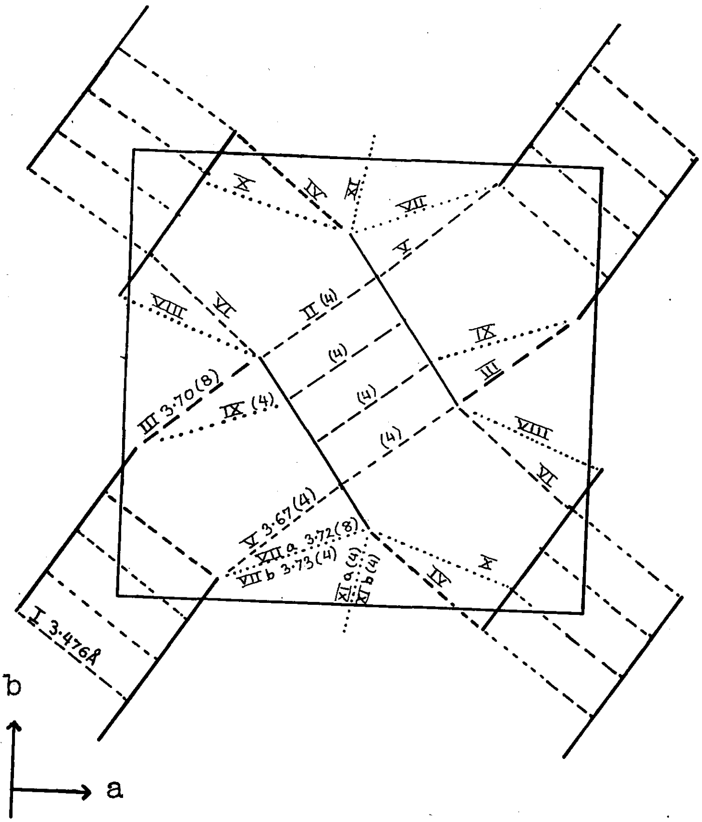


*Fig.5. Diagramatic representation of quaterrylene structure as viewed along the orthogonal axis c'. Molecules are indicated by solid lines whereas the broken lines indicate van der Waals intermolecular contacts.

* Multiplicity of contacts is given in parenthesis. The even numbered contacts are similar to the preceding odd number in length and multiplicity.

of P.B.C. vectors of type III and V accompanied by a generation of allied P.B.C. vectors.

8. van-der-Waals force function.

The existence of so many multiple van-der-Waals contacts between similar atoms, having a range of values from 3.476 Å to 3.92 Å, makes it likely that an examination of the equilibrium conditions may reveal whether the van-der-Waals force function between carbon atoms resembles an exponential function, similar to that found between hydrogen and argon atoms (see Cottrell, 1956), or a function based on Lennard-Jones' potential, as used by Pitzer and Catalano(1956).

The two drawbacks are:-

1. Existence of no van-der-Waals contacts in the range 3.48 Å to 3.67 Å.
2. H - - - C van-der-Waals intermolecular interactions.

A more detailed examination of this problem will be taken up some time later.

9. Molecular dimensions.

Bond lengths and bond angles calculated from the orthogonal co-ordinates listed in Table 1 are given in Fig.7. Length of bonds between atoms suffering from overlap in the b- axial projection are enclosed

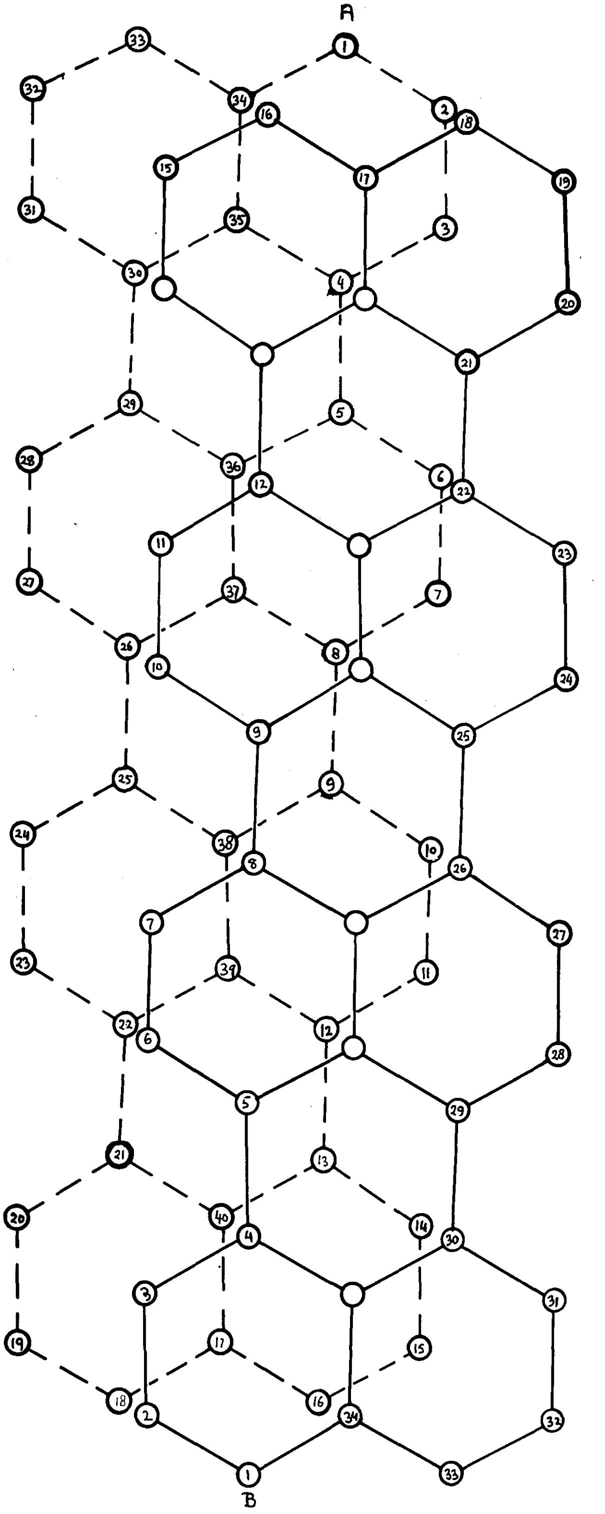


Fig. 6. Projection of two centre-symmetrically related planar quaterrylene molecules A and B on the plane of the molecule A which is shown by broken lines.

in parentheses. The estimated standard deviations of X' and Z' would imply that for a bond parallel to L σ is about ±0.015 Å. For other bonds σ should be increased to about ±0.030 Å.

It is quite likely that the individual y co-ordinates may be in error because of small deviations of the molecule from planarity, or of errors in the orientational parameters, but this will not cause serious errors in bond-lengths. Considerable distortions would be needed to compromise the lengths given for bonds parallel to L and any corrections would be positive.

Internal consistency within a set of equivalent or quasi-equivalent bonds can give a reasonably good estimate of the accuracy of its mean length. The six *peri*-bonds show no signs of systematic variation in different parts of the molecule. Their averaged length i~~f~~s 1.527 Å, with a r.m.s. deviation of 0.011 Å for any individual length and of ±0.0045 Å on their mean. If we omit three of these bonds, which suffer from overlap, the mean is 1.530 ± 0.0064 Å.

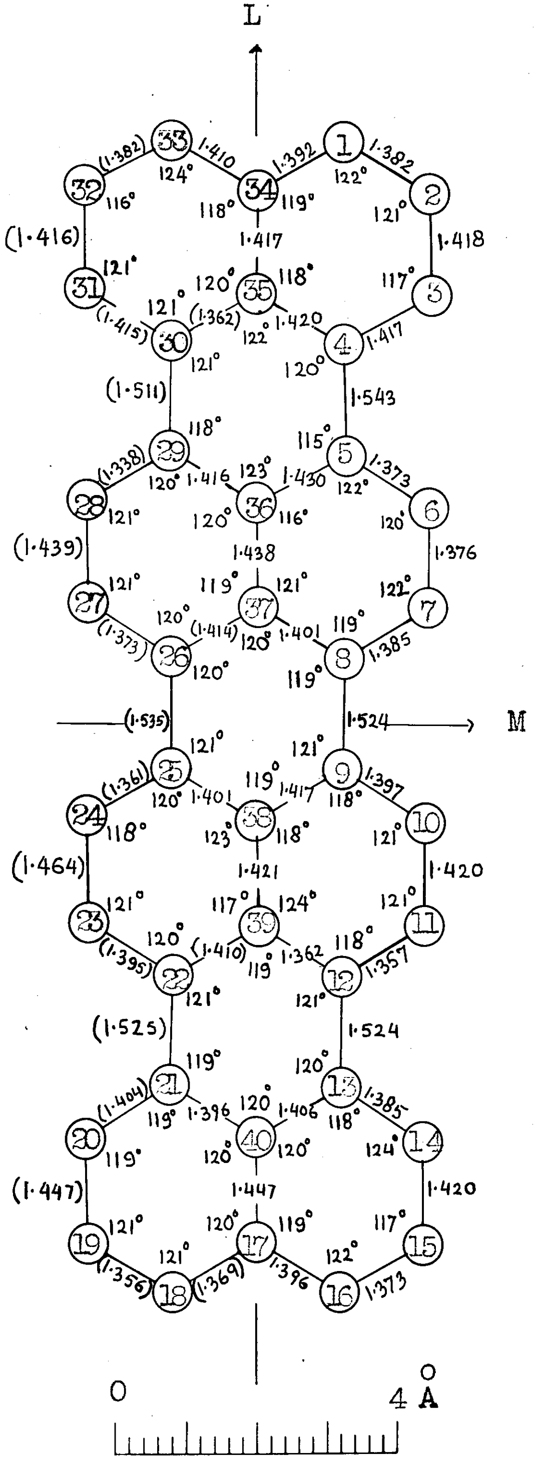


Fig.7. Bond-lengths and bond-angles in the molecule of quaterrylene and directions of the <u>L</u>- and <u>M</u>- molecular axes. The less reliable bond lengths are in parenthesis.

10. Discussion:

The accepted value for the length of the C-C single bond over the past decade has been 1.544 Å which is the distance found in diamond. This value applies only to the bond between carbon atoms in the sp^3 state of hybridisation..

Coulson (1948) estimated the bond between carbon atoms in the sp^2 state of hybridisation to be 1.50 Å. Recent estimates by Dewar and Schmeising(1959) and Mulliken (1959) are lower (1.48 Å). Any conjugation or π - bonding, such as in aromatic compounds, will further reduce this value.

Here it may be pointed out that Mulliken has agreed to Dewar and Schmeising's argument that the lengths of conjugated or hyperconjugated C-C single bonds are determined to a greater extent by the state of hybridization of the carbon σ-bond orbitals. This would imply that the true π-bond shortenings are much smaller than is currently estimated.

In valency bond terminology, we will say that so long as resonance occurs between unexcited canonical (Kekulé), structures the peri- bonds in this series of compounds have no double bond character. But for a large molecule like quaterrylene excited structures become more important (Daudel and Pullman, 1946), some of which will have double bond in the peri- position reducing its length. Whereas, according to Dewar and Schmeising's and Mulliken's argument, either the excited structures do not partake in resonance or their contribution is small.

A similar conclusion follows in terms of the molecular orbital theory. Molecular orbital calculations on perylene by Fernàndez-Alonso, Mira and Alcañiz (1957) gave a bond order of 0.3845 for the peri- bond, from which, by the Goodwin and Vand (1955) bond order bond length relation, we can derive a length of 1.478 Å for the peri bond.

It may be pointed out here that the procedure followed by Fernàndez-Alonso, et al. is not above criticism because of their use of a modifying function directly dependent on the measured bond length. Dr. Goodwin has now completed calculations on perylene and quaterrylene by a more objective method, wherein our measured values served only as an initial guide, and he reports a bond order of .310 and .334, and bond length of 1.485Å and 1.484Å for the peri- bond in perylene and quaterrylene respectively.

Thus it would be expected that the <u>peri</u>- bonds would be certainly shorter than 1.50 Å and possibly around 1.48 Å. That, on the contrary, these have been found to be significantly larger than the above values seems to indicate a failure of the first order theory. Here it is noteworthy that di-<u>peri</u>-naphthyleneanthracene analysed by Rossman (1959) contains two pairs of <u>peri</u>-bonds. The mean length of these bonds, calculated as explained previously is 1.545 ± 0.014 Å or 1.587 ± 0.006 Å, if the anomalously short value found between the atoms labelled H_2 and G_2 is ignored.

Bartell (1959) has pointed out that the C - C distance in a series of <u>n</u>-alkanes (1.533 Å) is significantly less than that in diamond (1.544 Å). He has showed this difference to be a consequence of enhanced repulsion in diamond due to <u>gauche</u> <u>interactions</u> as compared to only trans interactions between the C - C bonds branching from contiguous carbon atoms in the alkanes.

In perylene, quaterrylene and other polycyclic aromatic hydrocarbons there are <u>cis</u> interactions, which would cause a stronger repulsion between the bonded carbon atoms. In many cases resonance and/or conjugation masks this repulsion. But in the perylene series of compounds, where conjugation is forbidden, and resonance between non-excited (Kekulé) structures does not shorten the <u>peri</u>-bond, the repulsion will be effective. An additional repulsion will be operative because of overcrowding with respect to the hydrogen atoms attached to carbon atoms such as 3 and 6. Since in the molecule of 1:4-butadiene there is only one trans interaction, its central C - C distance (1.47 Å) can be only used for the discussion of bond shortening under similar conditions and not for aromatic molecules containing phenanthrenoid rings or cis interactions.

If the <u>peri</u>- bonds are true single bonds it immediately follows that resonance will be confined to the naphthalenic residues. The structure of these C_{10} units would therefore resemble that of the naphthalene molecule. As corresponding bond lengths in different units show no systematic differences they have been averaged. Mean values together with their r.m.s. deviations are collected in Table 5 and compared with the more accurate values for naphthalene derived by Cruickshank (1957).

The table also provides similar comparison with the corresponding, though less accurately measured, sets of bonds in perylene. Apart from the central (C - C') bond there is sufficient correspondence. In the second column of Table 5 are given the bond lengths in quaterrylene averaged on the assumption that the molecule has mmm symmetry. The figuresin parenthesis are the numbers of individual bonds averaged.

Clar (1958) has expressed the view that benzenoid character in such molecules as quaterrylene is localised, and that the "contact bonds" between benzenoid rings lack aromatic character altogether. This analysis supports this.

Much of the work in this section was done before Glasgow University acquired the 'DEUCE' computer. Fourier series summations were done on the machine designed by Robertson,J.M.(1954). I am very grateful to Professor J.M.Robertson, F.R.S. for his interest in this work and for access to the original photographs taken with perylene.

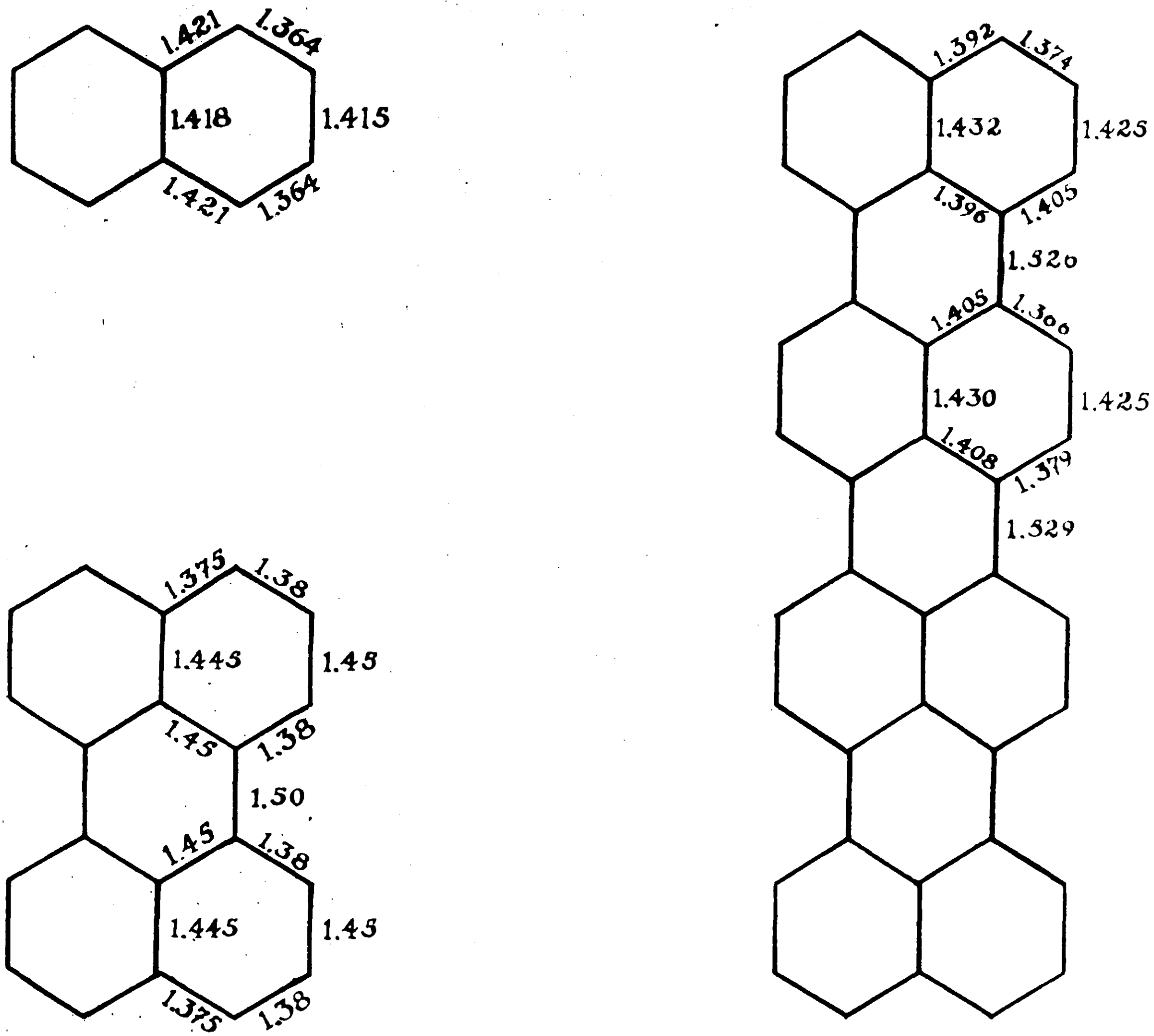


Fig.8. Bond lengths in naphthalene, perylene and the averaged bond-lengths in quaterrylene. (Note: The less reliable bond lengths have not been excluded in averaging - better values may be obtained by doing so.)

APPENDIX I.

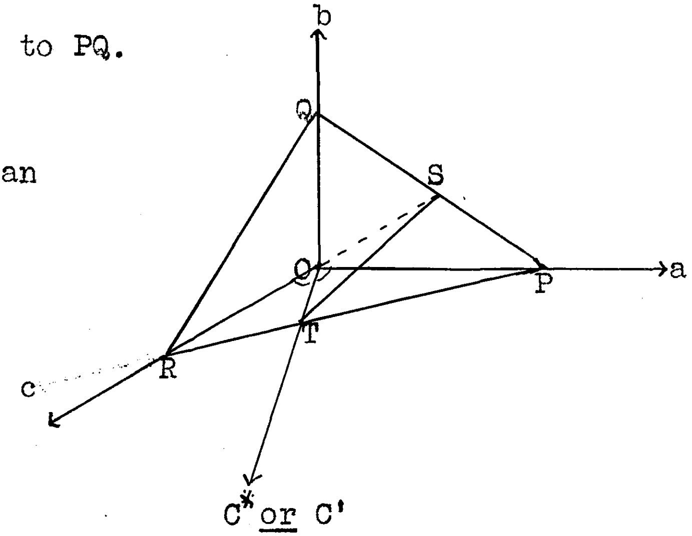
A simple graphical method of calculating the angle (θ) between the (001) plane and any other ($hk\ell$) plane of monoclinic crystals.

In the diagram below, PQR is the plane $hk\ell$ and T is the intersection of PR and the orthogonal axis OC'.

Let OS be perpendicular to PQ.
Join S and T.
By simple geometry it can be shown that TS is perpendicular to PQ whereby it follows that

$$\theta = \angle OST$$

or $\quad \mathrm{Tan}\,\theta = \dfrac{OT}{OS}$



The procedure consists of measuring OT and OS. A single measure of OS suffices for all planes of the type $(hk)_n\ L$ with common or multiple hk indices, because Tanθ for these is n times Tanθ for the corresponding planes where n = 1. Thus, within a group, the problem reduces to measuring OT graphically and can be tackled with considerable speed by plotting on graph paper using arbitrary scale.

APPENDIX 2.

Relation between molecular orientation and the projected interplanar distance.

In addition to the molecular orientational parameters defined in Chapter 5, let L', M' and N' be the projection of the molecular axes L, M and N on the plane AC'. As before, we will use χ, ψ and ω to denote the angles that the axes a, b and c' respectively make with these (i.e. whereas χ_L represents the angle between a and L; $\chi_{L'}$ represents the angle between a and L').

In the above terminology the equation for the plane of the molecule is:-

$$\cos\chi_N x_c + \cos\psi_N y_c + \cos\omega_N z_{c'} = p_1 \quad \ldots\ldots\ (1)$$

where p_1 is the perpendicular distance of this plane from the origin. Using elementary geometrical methods it can be shown that a general relationship between the direction cosines and sines of angles defined above is:-

$$\begin{aligned}\cos\omega_L,\ \omega_M \text{ or } \omega_N \quad &= \sin\psi_{L,M \text{ or } N} . \cos\omega_{L'},\ \omega_{M'} \text{ or } \omega_{N'} \\ \text{or } \chi_L,\ \chi_M \text{ or } \chi_N \quad & \qquad\qquad\qquad \text{or } \chi_{L'},\ \chi_{M'} \text{ or } \chi_{N'}\end{aligned}$$

$$\ldots\ldots\ldots\ldots\ldots\ (2)$$

Two of the six equations implied above are:-

$$\left.\begin{aligned}\cos\omega_N &= \sin\psi_N . \cos\omega_{N'} \\ \cos\chi_N &= \sin\psi_N . \cos\omega_{N'}\end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Substituting these in equation (1) we have :-

$$\sin\psi_N(\cos\chi_{N'}x_c + \cos\omega_{N'}z_c) + \cos\psi_N y_c = p' \qquad \ldots\ldots\ldots\ldots(4)$$

When $\psi_L = 90^\circ$

we have $\chi_{N'} = \omega_{L'}$ and $\omega_{N'} - \omega_{L'} = 90^\circ$

<u>or</u> $\cos\chi_{N'} = \cos\omega_{L'}$ and $\cos\omega_{N'} = -\sin\omega_{L'}$

Substituting these in equation (4) we have:-

$$\sin\psi_N(\cos\omega_{L'}x_c - \sin\omega_{L'}z_c) + \cos\psi_N y_c = p' \qquad \ldots\ldots\ldots\ldots(5)$$

It can be easily seen that $2(\cos\omega_{L'}x_c - \sin\omega_{L'}z_c)$ represents the perpendicular distance between the L' axes of two centrosymmetrically related pair of molecules and can be measured in projection. Call this distance d'. If d represents perpendicular distance between the two centrosymmetrically related pair of molecules - obviously

$$2p' = d.$$

$$\sin\psi_N \frac{d'}{2} + \cos\psi_N y_c = \frac{d}{2}$$

As $\psi_N + \psi_M = 90^\circ$ when $\psi_L = 90^\circ$ we can write:

$$\pm\, y_c = \frac{d}{2}\operatorname{cosec}\psi_M - \frac{d'}{2}\cot\psi_M \qquad \ldots\ldots\ldots\ldots(6)$$

The ± being introduced to leave the choice of the standard molecule open.

TABLE 1. Co-ordinates and temperature factor parameters.

x, y, and z are expressed as fractions of axial lengths in 10^{-4} unit; X', Y and Z' are orthogonal co-ordinates in Å (X'//X).

Carbon Atom	x	y	z	X'	Y	Z'	B
1	2771	-0481	4420	1.547	-0.513	8.389	3.30
2	3284	0453	4074	2.247	0.483	7.733	3.85
3	3109	0486	3328	2.315	0.518	6.317	3.10
4	2380	-0474	2960	1.626	-0.505	5.619	2.85
5	2193	-0447	2139	1.704	-0.477	4.079	2.90
6	2676	0470	1785	2.376	0.501	3.388	3.15
7	2469	0451	1060	2.401	0.481	2.012	3.10
8	1758	-0465	0678	1.737	-0.495	1.287	2.75
9	1529	-0486	-0124	1.764	-0.519	-0.236	3.20
10	2030	0432	-0500	2.461	0.460	-0.948	3.35
11	1817	0428	-1247	2.488	0.456	-2.368	2.75
12	1121	-0470	-1621	1.837	-0.501	-3.077	3.00
13	0903	-0476	-2424	1.877	-0.507	-4.601	3.15
14	1386	0427	-2808	2.557	0.455	-5.330	3.40
15	1199	0456	-3555	2.611	0.486	-6.748	3.10
16	0492	-0473	-3913	1.944	-0.504	-7.426	3.50
17	-0027	-1425	-3563	1.235	-1.508	-6.763	3.25
18	-0726	-2333	-3931	0.580	-2.487	-7.461	3.30
19	-1231	-3243	-3588	-0.110	-3.457	-6.811	3.85
20	-1043	-3277	-2827	-0.169	-3.493	-5.366	3.10
21	-0319	-2353	-2438	0.507	-2.508	-4.627	3.10
22	-0090	-2319	-1634	0.479	-2.472	-3.102	2.90
23	-0594	-3254	-1273	-0.216	-3.468	-2.415	3.35
24	-0408	-3272	-0502	-0.280	-3.488	-0.953	3.10
25	0297	-2357	-0145	0.385	-2.513	-0.275	3.25
26	0516	-2349	0664	0.344	-2.504	1.260	3.00
27	0018	-3257	1027	-0.345	-3.471	1.949	3.35
28	0228	-3259	1785	-0.378	-3.474	3.388	2.80
29	0908	-2368	2153	0.257	-2.524	4.086	3.15
30	1143	-2347	2949	0.239	-2.502	5.597	3.00
31	0614	-3297	3304	-0.483	-3.515	6.272	3.40
32	0807	-3327	4050	-0.530	-3.547	7.687	3.25
33	1514	-2378	4398	0.140	-2.534	8.348	3.50
34	2046	-1416	4057	0.861	-1.509	7.700	3.24
35	1840	-1430	3310	0.894	-1.524	6.283	2.85
36	1433	-1415	1796	0.974	-1.508	3.409	2.75
37	1243	-1400	1039	1.029	-1.492	1.972	2.70
38	0802	-1426	-0513	1.085	-1.520	-0.973	2.65
39	0622	-1393	-1259	1.192	-1.485	-2.390	3.00
40	0179	-1415	-2801	1.196	-1.508	-5.316	2.70

TABLE 1 (Cont'd).

Appendix: x and y for hydrogen atoms, expressed as fractions of axial length in 10^{-3} unit.

Hydrogen Atom	x	y	Hydrogen Atom	x	y
1	290	497	11	-089	-448
2	382	436	12	-176	-390
3	348	303	13	-140	-253
4	323	207	14	-114	-158
5	287	078	15	-078	-021
6	258	-021	16	-053	074
7	222	-015	17	-150	208
8	196	-253	18	006	302
9	159	-386	19	043	433
10	032	-447	20	169	495

TABLE 2. Observed(F_o) and calculated(F_c) structure factors.

$0,0,\ell$	F_o	F_c	$4,0,\ell$	F_o	F_c
0	--	1040.0	$\overline{19}$	4.7	5.8
1	--	77.7	$\overline{18}$	9.9	11.4
2	79.7	-72.9	$\overline{17}$	7.2	-8.2
3	79.7	85.3	$\overline{16}$	5.3	5.7
4	124.0	-112.3	$\overline{15}$	11.3	-11.4
5	18.7	23.4	$\overline{14}$	38.3	-39.0
6	32.5	-30.5	$\overline{10}$	22.8	20.3
7	32.9	32.5	$\overline{5}$	5.3	-4.5
8	31.7	-28.4	$\overline{4}$	6.5	10.0
9	28.0	-21.7	$\overline{3}$	8.3	-8.0
13	26.8	-25.0	$\overline{2}$	11.6	14.3
17	42.7	45.7	$\overline{1}$	89.5	91.9
18	46.0	44.2	1	5.1	-5.4
19	15.5	-15.5	2	11.0	14.6
20	7.5	7.0	3	49.8	-48.9
			4	11.2	-7.7
$2,0,\ell$			6	5.1	2.6
			7	11.6	-13.5
$\overline{25}$	9.5	4.1	8	20.5	-20.8
$\overline{24}$	5.1	-3.7	12	7.2	5.3
$\overline{22}$	5.9	-3.1	16	4.8	5.6
$\overline{12}$	5.7	-5.5			
$\overline{11}$	14.6	14.7	$6,0,\ell$		
$\overline{10}$	41.9	-40.5			
$\overline{9}$	113.7	-107.4	$\overline{24}$	6.2	-8.9
$\overline{8}$	20.0	21.4	$\overline{23}$	12.0	-13.6
$\overline{7}$	6.2	-7.4	$\overline{22}$	3.5	3.4
6	4.1	-3.8	$\overline{21}$	3.2	-0.7
$\overline{5}$	23.6	17.4	$\overline{20}$	1.7	0.4
$\overline{4}$	21.2	-24.2	$\overline{15}$	13.0	12.1
$\overline{3}$	31.7	27.3	$\overline{10}$	10.2	-12.5
$\overline{2}$	44.7	-54.4	$\overline{9}$	6.5	7.8
$\overline{1}$	127.6	121.2	$\overline{8}$	8.1	-7.5
0	75.8	74.4	$\overline{7}$	6.2	5.8
1	8.6	-13.2	$\overline{6}$	70.8	62.2
2	2.7	-3.0	$\overline{5}$	7.6	-2.7
3	6.7	2.0	$\overline{3}$	22.3	20.5
4	12.8	-9.7	$\overline{1}$	18.0	12.4
5	5.6	5.0	1	5.6	-5.0
7	5.6	-5.2	2	13.7	10.5
8	75.0	76.4	3	26.0	23.2
9	23.9	22.9	9	6.7	3.0
10	8.8	-11.6	10	12.0	-9.1
12	8.6	7.3	11	41.3	44.2
13	5.9	12.3	12	48.3	46.7
17	15.3	15.1	13	16.0	-16.0

TABLE 2 (Cont'd).

$6,0,\ell$	F_o	F_c	$10,0,\ell$	F_o	F_c
14	6.4	8.0	$\overline{16}$	45.1	-46.4
20	14.3	-16.2	$\overline{15}$	19.0	-18.2
			$\overline{14}$	3.2	4.3
$8,0,\ell$			$\overline{8}$	4.8	-5.5
			$\overline{7}$	16.9	-20.5
$\overline{19}$	7.4	11.7	1	19.5	-19.1
$\overline{18}$	10.5	-11.5	2	31.9	-32.5
$\overline{17}$	18.7	22.3	10	10.8	-11.4
$\overline{16}$	46.3	-45.3	11	8.0	-9.6
$\overline{15}$	102.9	-109.1			
$\overline{14}$	13.4	17.1	$12,0,\ell$		
$\overline{11}$	11.0	11.0			
$\overline{9}$	8.3	11.6	$\overline{11}$	6.2	-3.0
$\overline{8}$	18.7	-16.9	$\overline{8}$	4.3	5.5
$\overline{7}$	59.8	55.2	$\overline{4}$	4.5	-5.1
$\overline{6}$	42.6	36.0	$\overline{3}$	8.6	-9.8
$\overline{5}$	5.6	-7.8	3	7.4	-0.3
2	71.3	-71.5	5	4.8	-3.7
3	30.1	-30.1			
4	16.7	19.1	$14,0,\ell$		
5	12.9	-14.8			
6	8.6	10.5	$\overline{4}$	10.5	-11.2
7	14.5	-14.8	$\overline{3}$	6.5	-8.8
8	11.8	15.4	$\overline{2}$	2.7	3.7
9	14.7	-15.7			
10	20.4	21.9	Σ	2972.4	2931.0
11	95.6	100.5			
12	10.5	-4.1			

Appendix: Unobserved reflections with calculated structure factor significantly greater than the locally observable minimum.

$h,0,\ell$	$F_{loc.\,min.}$	F_c	$h,0,\ell$	$F_{loc.\,min.}$	F_c
0,0,10	3.4	10.0	6,0,4	3.9	-5.7
2,0,$\overline{14}$	3.9	-5.4	8,0,15	3.6	-9.5
4,0,10	3.9	-6.2	10,0,20	2.7	8.5
4,0, 9	3.7	6.2	10,0, 3	4.6	7.8

TABLE 3.

Orientation of the molecule
and
Co-ordinates of its centre.

	Fractional	In Å units	Orthogonal(Å)
x_c	0.1022	1.150 Å	1.058 Å
y_c	-0.1415	-1.508 Å	-1.508 Å
z_c	0.2578	0.489 Å	0.489 Å

$$\omega_L = -1.2^\circ, \quad \psi_L = 90^\circ, \quad \psi_M = 34.6^\circ$$

$$\cos\omega_L = 0.9997, \qquad \sin\omega_L = -0.0244$$

$$\cot\psi_M = 1.14491, \qquad \operatorname{cosec}\psi_M = 1.7610$$

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TABLE 4. Observed (F_o) and calculated (F_c) structure factors. (h,k,0 and 0,k,ℓ).

0,1,ℓ	F_o	F_c	0,5,ℓ	F_o	F_c
1	4.2	6.8	3	15.9	-12.0
2	12.3	-15.1	4	80.4	78.4
3	20.0	19.1	5	75.0	65.2
4	33.0	-30.7	6	28.5	-33.0
5	25.2	17.2	7	22.2	21.9
6	31.8	-27.3	8	18.3	-12.8
7	39.6	31.2	9	22.8	17.3
8	58.8	-60.7	10	12.0	-12.7
9	>80.0	-97.4	13	118.8	-131.1
10	12.3	15.5	14	27.9	-14.8
13	6.6	8.2	15	13.5	18.0
24	3.0	0.9	22	12.6	-13.8
0,2,ℓ			0,6,ℓ		
1	7.8	-3.1	3	11.7	13.7
4	7.8	-5.8	4	46.8	-37.8
5	6.6	-7.0	5	35.4	-21.6
9	15.6	5.4	13	23.1	-31.8
0,3,ℓ			0,8,ℓ		
1	6.3	-1.9	4	23.1	15.4
4	15.6	18.8	5	6.3	4.1
5	4.5	4.6			
9	21.0	23.0	0,9,ℓ		
0,4,ℓ			5	10.5	7.3
			8	13.5	-11.5
1	17.1	10.2	9	22.2	-15.4
2	6.6	-2.6			
3	15.0	-5.9	0,10,ℓ		
4	61.5	57.5			
5	46.8	40.7	1	17.7	-5.4
6	18.6	-18.2	2	9.6	8.2
7	9.6	10.6	3	6.6	-9.9
13	34.2	37.8	4	9.6	12.4
14	15.6	16.2			
15	9.6	-10.4			
22	17.1	-17.3			

TABLE 4 (CONT'D).

0,k,0	F_o	F_c	1,k,0	F_o	F_c
2	18.0	-17.5	2	102.0	92.0
4	47.0	57.0	4	65.0	-55.0
6	17.0	25.2	6	24.0	-24.0
8	25.0	-33.5	8	17.0	8.0
10	93.0	-91.0	10	22.0	6.0
12	19.2	-20.1			
			2,k,0		
1,k,0					
			1	80.0	122.0
1	140.0	127.0	3	29.0	27.0
3	76.0	46.0	5	9.0	7.0
5	25.0	-26.0	9	32.0	38.0
7	9.0	-9.0			
9	26.0	18.0	3,1,0	40.0	-81.0
11	59.0	-66.0			
			3,2,0	68.0	70.0
2,k,0					
0	34.0	22.0			
2	284.0	-255.0			
4	13.0	-24.0			
6	22.0	23.0			
8	25.0	22.0			
12	18.0	27.0			

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Table 5.

Comparison of Average bond-lengths (Å) in quaterrylene (assumed to have mmm molecular symmetry) with corresponding averaged bond-length in perylene and naphthalene.

Bond Type	Average Lengths, with numbers of bonds averaged.		Overall Average length in quaterrylene	Corresponding Length in Perylene (1953)	Overall Average Length in quaterrylene	Corresponding Length in Naphthalene (1957)
1 - 2	1·374 ± 0·007	(4)	1·374	1·38	1·381 ± 0·005	1·361 (A–B)
5 - 6	1·366 ± 0·012	(4)	1·384	1·38		
3 - 4	1·405 ± 0·008	(4)				
7 - 8	1·379 ± 0·008	(4)				
1 - 34	1·392 ± 0·009	(4)	1·392	1·375	1·400 ± 0·005	1·425 (B–C)
4 - 35	1·396 ± 0·012	(4)	1·403	1·45		
5 - 36	1·405 ± 0·015	(4)				
8 - 37	1·408 ± 0·005	(4)				
2 - 3	1·425 ± 0·004	(4)	1·425	1·45	1·425 ± 0·016	1·421 ([illegible]–B')
6 - 7	1·425 ± 0·013	(4)				
34 - 35	1·432 ± 0·015	(2)	1·431	1·445	1·431 ± 0·007	1·410 ([illegible])
36 - 37	1·430 ± 0·009	(2)				
4 - 5	1·526 ± 0·007	(4)	1·527	1·50	1·527 ± 0·005	
8 - 9	1·529 ± 0·006	(2)				

Table 5.

Comparison of Average bond-lengths (Å) in quaterrylene (assumed to have mmm molecular symmetry) with corresponding averaged bond-length in perylene and naphthalene.

Bond Type	Average Lengths, with numbers of bonds averaged.		Overall Average length in quaterrylene	Corresponding length in Perylene (1953)	Overall Average Length in quaterrylene	Corresponding Length in Naphthalene (195
1 - 2	1·374 ± 0·007	(4)	1·374	1·38		
5 - 6	1·366 ± 0·012	(4)	1·384	1·38	1·381 ± 0·005	1·361 (A-B)
3 - 4	1·405 ± 0·008	(4)				
7 - 8	1·379 ± 0·008	(4)				
1 - 34	1·392 ± 0·009	(4)	1·392	1·375		
4 - 35	1·396 ± 0·012	(4)	1·403	1·45	1·400 ± 0·005	1·425 (B-C)
5 - 36	1·405 ± 0·015	(4)				
8 - 37	1·408 ± 0·005	(4)				
2 - 3	1·425 ± 0·004	(4)	1·425	1·45	1·425 ± 0·016	1·421 (A-D')
6 - 7	1·425 ± 0·018	(4)				
34 - 35	1·432 ± 0·015	(2)	1·431	1·445	1·431 ± 0·007	1·410 (C-C')
36 - 37	1·430 ± 0·009	(2)				
4 - 5	1·526 ± 0·007	(4)	1·527	1·50	1·527 ± 0·005	
8 - 9	1·529 ± 0·006	(2)				

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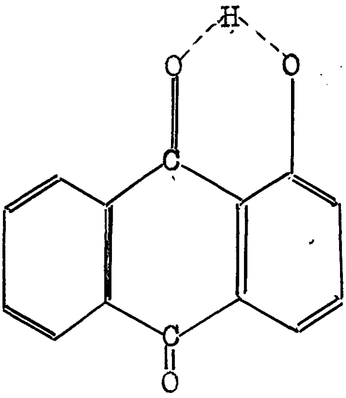
SECTION III.

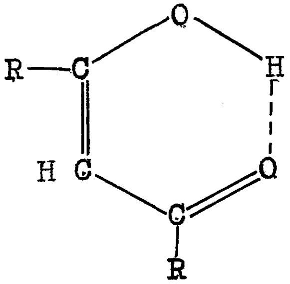
THE HYDROGEN BOND.

The Hydrogen Bond.

1. Introduction.

Oddo and Puxeddu (1906) suggested that the abnormal properties of the O- hydroxyazo-compounds are due to a divided hydrogen valency. Moore and Winmill (1912), Pfeiffer (1913), and Morgan and Reilly (1913) made use of formulations involving a doubly linked hydrogen atom to explain the weak basic nature of trimethyl ammonium hydroxide $(CH_3)_3 N - H - OH$, and the reduced combining power of hydroxyl in o-hydroxy quinones and enolised β-diketones:





The first clear presentation of hydrogen bonding as an explanation of the abnormal physical properties of associated liquids, such as the high dielectric constant of water and the small ionization of ammonium hydroxide, is due to Latimer and Rodebush (1920) and Huggins (1920) who were also the first to write an electronic formula (O:H:O). Pauling (1929) considered this valency picture to be inadmissible on the ground that only the 1 s hydrogen orbital is available for bond formation.

Pauling (1939) suggested that the hydrogen bond is essentially ionic in nature. This approach was largely successful but there have been difficulties. For instance, to account for the formation of the polymer H_6F_6 (Cady 1934) and the great difference between the thermal stabilities of the cubic and the ordinary forms of ice (Frank 1957) hydrogen bonds with some covalent character have been proposed. Tsubomura (1954) and Hofacker (1957) have pointed out other difficulties in taking a purely electrostatic view of hydrogen bonding.

In a m.o. formulation Leonello Paoloni (1959) includes a contribution from the 2 s and/or 2 p atomic orbitals of the hydrogen atom in addition to that from the 1 s orbital.

2. Characteristic properties of hydrogen bonds.

Scope and representation: The current representation of a hydrogen bond: X - H···Y implies a link weaker than the usual chemical bonds but stronger than the van der Waals type of hold. The atoms X and Y are usually the electronegative atoms F, O, N, or Cl but the S - H group forms a few weak hydrogen bonds (Sutton 1955) and the C - H group is reported to form one hydrogen bond (Pimentel, 1955).

Energy: Relatively few estimates of the energy of hydrogen bonds are available and even these are not exact (Davies 1946). For carboxylic acid dimers with an average O•••O distance of 2.65 Å the energy is 7 to 8 K Cal. per mole, for alcohols and phenols where the bridge length is about 2.70 Å it is about 6 K Cal. per mole, and for ice where the bridge length is 2.76 Å the energy is probably 4.5 K Cal. per mole (Rawlinson 1949). Bonds between nitrogen atoms are generally weak (energy 1 to 3 K Cal. per mole) but stronger bonds occur between nitrogen and oxygen.

Structural features: Most hydrogen bonds are linear or nearly so. In α-glycine (Albrecht and Corey 1939) a bifurcated hydrogen bond has been reported but such instances are rare.

Pauling (1939) pointed out that normal structural features, such as coplanarity of conjugated systems and tetrahedral values of bond angles for electronegative atoms would apply to hydrogen bonding. As a result of an extensive and thorough survey, Donohue (1952) concludes that the former expectation is usually fulfilled in the case of hydrogen bonds between carboxyl groups and the latter when O-H groups, H_2O molecules or - NH_3^+ ions are involved.

In amides and imides (Corey 1948) the three bonds around the nitrogen atoms are coplanar. This is a fact of great importance in formulating possible structures for the proteins.

Another observation, helpful in structure determination, is that all hydrogen atoms attached to electronegative groups partake in hydrogen bonding (Donohue 1952). This is known as 'the principle of maximum hydrogen bonding'. It does not apply to hydrogen bonds between nitrogen atoms.

Bernal (1959) points out that a hydrogen bond may be relatively free, that is, it easily submits to compression, dilation or bending. Some reasons to believe that the bending deformations are the ones most easily brought about are in Chapter 6.

The Nature of atoms X and Y and the effect of groups attached to the atom X :- The formation of a hydrogen bond implies a H•••Y attraction which has been attributed to a lone pair of electrons on the atom Y (Pople and Lennard-Jones 1951, Schneider 1955, and Brealey and Kasha 1955).

A restriction that the atom X should be one of the electronegative atoms listed earlier implies the importance of this property. The atom or group (R) attached to the atom X affects the strength of the hydrogen bond by modifying this property.

According to Bernal (1959) the chief role of the aforesaid group R is that of a proton activator, whereas the atom Y behaves as a proton acceptor.

I.R. and P.M.R. spectra: Hydrogen bonding causes an increase in the normal X - H distance (Pauling 1939, Clews and Cochran 1949, Bacon & Curry 1956), a broadening of the I.R. bond due to X - H stretching and a lowering of this stretching frequency (Gordy 1939, Lüttke and Mecke 1949). According to Smith and Creitz (1951) and Nakamoto, Margoshes and Rundle (1955) this lowering of the stretching frequency and the increase in the strength of the hydrogen bond depend on the X···Y distance.

Some short hydrogen bonded substances, in which the centre of the O···O bridge coincides with a crystallographic symmetry element, appear to form an exception to this rule. While examining these structures I noticed some common structural features which are set in Chapter 7.

In most cases hydrogen bonding shifts the P.M.R. signal of the hydrogen partaking in the bond to low field (Liddel and Ramsay 1951).

3. Classification of hydrogen bonded structures.

An obvious classification of hydrogen bonds is one based on the chemical nature of the different electronegative atoms and groups involved. For instance, Carpenter and Donohue (1950) subdivide the O···O hydrogen bonds into (1) those involving carboxyl groups, (2) those involving hydroxyl groups, and (3) those involving water molecules.

In addition to these, while classifying hydrogen bonded structures distinction should be made as to whether the hydrogen bonds hold the structure (a) in three dimensions, (b) in sheets, (c) in columns, or (d) in discrete units (Bernal 1959).

Blinc, Hadzi and Novak (1960) classify substances with a short O···O bridge of 2.41 Å to 2.61 Å, according to the nature of the P.E. curve, as ascertained from their I.R. and P.M.R. spectra, into four main types, viz.

(A) single symmetric minimum type	Acid salts.
(B) double minimum with small barrier	
(C) double minimum with large barrier	Carboxylic acids.
(D) asymmetric or unharmonic single minimum	Phenols.

The order A to D follows increasing average bridge lengths but the increase in going from A to B is within the experimental errors involved.

4. The isotope effect.

As the space requirement and the zero point energy of the deuterium atom is smaller than that of the hydrogen atom, substitution of hydrogen by deuterium is expected to permit a closer packing (Robertson 1953).

Such a contraction is actually observed in lithium hydride, where the structure is ionic, but in hydrogen bonded structures an expansion of the lattice in the direction of the hydrogen bond is observed. Gallagher (1959) points out that this isotope effect is a function of the O···O distance, being an expansion for short bonds and reversing to a contraction for long bonds.

5. Theoretical approaches to hydrogen bonding.

The forces operative in a hydrogen bond may be subdivided into:-

(A) electrostatic interaction
(B) delocalisation effects
(C) repulsive overlap forces
(D) dispersion forces.

Some or all of the five valence bond structures I to V have been included by various workers in their quantum-mechanical calculations (Coulson 1959).

(I) $\diagdown O_1 - H \quad O_2 <$ pure covalent, no charge transfer.

(II) $\diagdown O_1^- \quad H^+ \quad O_2 <$ pure ionic, no charge transfer.

(III) $\diagdown O_1^+ \quad H^- \quad O_2 <$ pure ionic, no charge transfer.

(IV) $\diagdown O_1^- \quad H - O_2^+ <$ charge transfer, long $H - O_2$ bond.

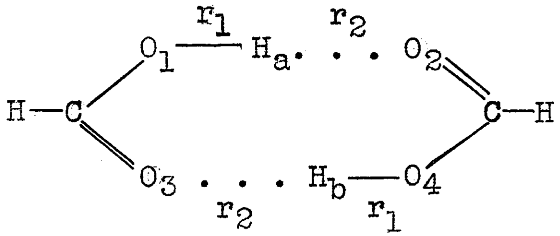
(V) $\diagdown \underbrace{O_1 \quad H^- \quad O}{}_2^+ <$ charge transfer, $O_1 - O_2$ bonding.

It is noteworthy that in addition to the structures, that would provide an oxygen atom with more than ten, or the hydrogen atom with more than two electrons, the structures requiring a movement of proton from O_1 to O_2 prior to their formation (VI and VII) have also been excluded. One may argue that the high charge density of a proton may permit such a movement in the case of short hydrogen bonded substances.

(VI) $\diagdown O_1 \cdots H^- \; O_2^+ \langle$ charge transfer, short $H^- \; O_2^+$ bond.
(VII) $\diagdown O_1^- \cdots H \; O_2^+ \langle$ charge transfer, short $H \; O_2^+$ bond.

6. Potential energy curves.

Coulson (1959) obtains different P.E. contour diagrams Fig.1 and 2 for hydrogen bonds occurring in single isolated groupings and those in multiple groupings such as in formic acid dimer. In the latter the motion of the protons is considered to be so correlated that a movement of H_a away from O_1 is accompanied by an equal movement of H_b away from O_4.



The dotted line in Fig.1 follows the change of P.E. as hydrogen is moved between two fixed oxygen atoms and suggests a highly anharmonic curve with a single minimum, whereas in Fig.2 it follows the change when two hydrogens are moved between four fixed oxygen atoms and suggests a curve with two minima and a sandwiched symmetrical maximum.

A noteworthy feature of Fig.1 and 2 is that the line radiating from the minima in the direction of

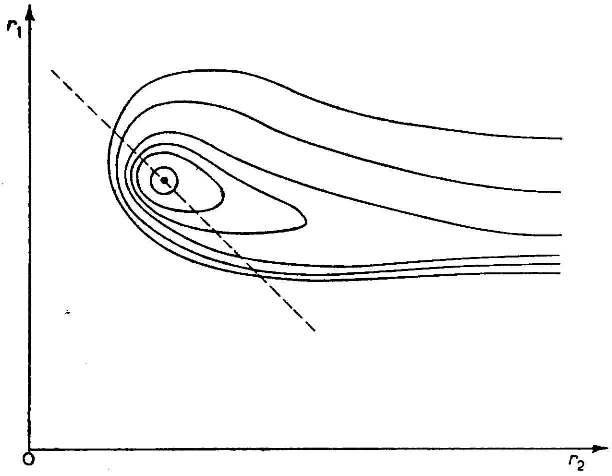


Fig. 2. **Contour diagram for the potential energy in an isolated H-bond system $O_1—H \cdots\cdots O_2$ ($O_1—H$ is r_1, $H \cdots\cdots O_2$ is r_2)**

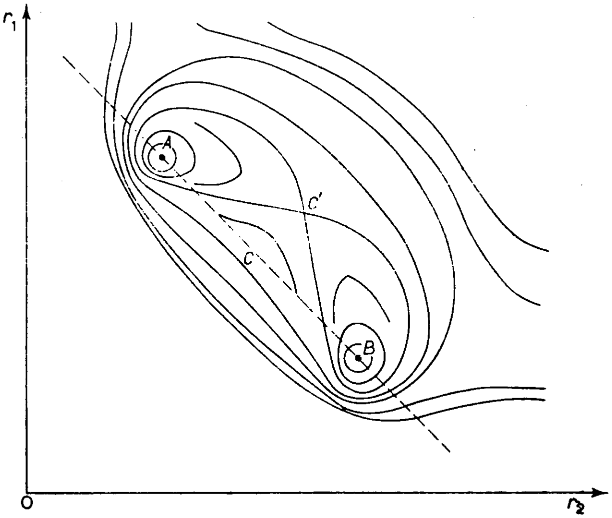
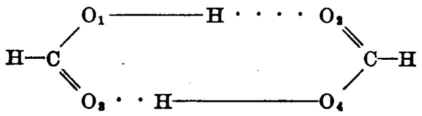


Fig. 3. Contour diagram for the correlated in-step motion of the two protons in a dimer-type system such as



$O_1H = O_4H = r_1$, $H \cdots O_2 = H \cdots O_3 = r_2$

the minimum potential energy gradient does not coincide with the line for constant $O_1 - O_2$ distance. In addition to the interpretation given by Coulson, I would consider this to suggest the relative ease of the bending vibrations of the hydrogen bond. Such a conclusion would be consistent with the results of Broadley et al.(1959) for succinic acid, the anisotropic thermal motion parameters of hydrogen bonded atoms in K-H-diparanitrobenzoate (next section) and other results.

Fig.2 can be fairly reproduced by superposing a tracing of Fig.1 with its r_1 and r_2 axis interchanged on Fig.1 itself. If Fig.2 actually represented a superposition function, it would only mean that a stable dimer can be formed with hydrogen atoms placed at distances corresponding to either of the two maxima. It is more likely that this circumstance is merely due to an oversimplification of the dimer model, where the four oxygen atoms have been treated as equivalent. (It appears that because of a typographical error, r_1 and r_2 have been interchanged in Fig. 1.)

7. Structural features of some anomalous short hydrogen bonded substances.

There is little difference between the average bridge lengths of substances referred to as of type (A) and (B) in Chapter 3, whereas the average O - H stretching frequencies differ widely, those of the former being smaller. The substances of the type (A), viz.

1. Na-H-diacetate, Speakman (1959).
2. K-H maleate, Peterson and Levy (1958).
3. K-H dibenzoate, Skinner et al. (1954).
4. Na-sesquicarbonate dihydrate, (Bacon & Curry (1956). (Brown et al.(1949).
5. K-H-bisphenyl acetate, Bacon and Curry (1957).
6. K-H-di-p-hydroxybenzoate hydrate, Skinner & Speakman (1951).

to which we may also add

7. Rb-H-diorthonitrobenzoate, Shrivastava and Speakman. (to be published)

have some common structural features:-

In all [illegible]

(a) the O . . . O bridge centre coincides with a crystallographic symmetry element (not necessarily a centre).

(b) In 3, 4, 5, 6 and 7, the hydrogen and the alkali ion bonded carboxyl groups form a <u>sheet</u> produced by chains infinitely extending along a direction, usually a crystallographic axis, and linked one over the other by alkali metal ions of one chain and carboxyl oxygens of the other (see fig.3). In 2 we have an intermolecular hydrogen-bond but the aforesaid sheets do exist with the difference that the hydrogen atom is not on the central plane of such a sheet. (see Fig.4).

Alternatively, we may say that:-

In 3, 4, 5, 6 and 7, alkali ions and the hydrogen atoms lie on a plane on both sides of which carboxyl groups are situated in columns placed alternately on either side.

In 2, the hydrogen bonds are on the surfaces of a sheet, the alkali ions are on the central plane of the sheet and the carboxyl groups link the surface of the sheet with its interior. Going parallel to the c-axis the hydrogen bonds occur alternately on each surface of the sheet.

(c) In 1, the hydrogen bonds form a fully interlinked 3D network.

(d) The smallest closed vibrating unit incorporating the hydrogen bond consists of two hydrogen bonds between four carboxyl groups and two alkali metal ions in all the compounds listed above except sodium hydrogen diacetate where this unit appears to be smaller.

See overleaf - page 73(a).

Fig. 3.

Fig. 4.

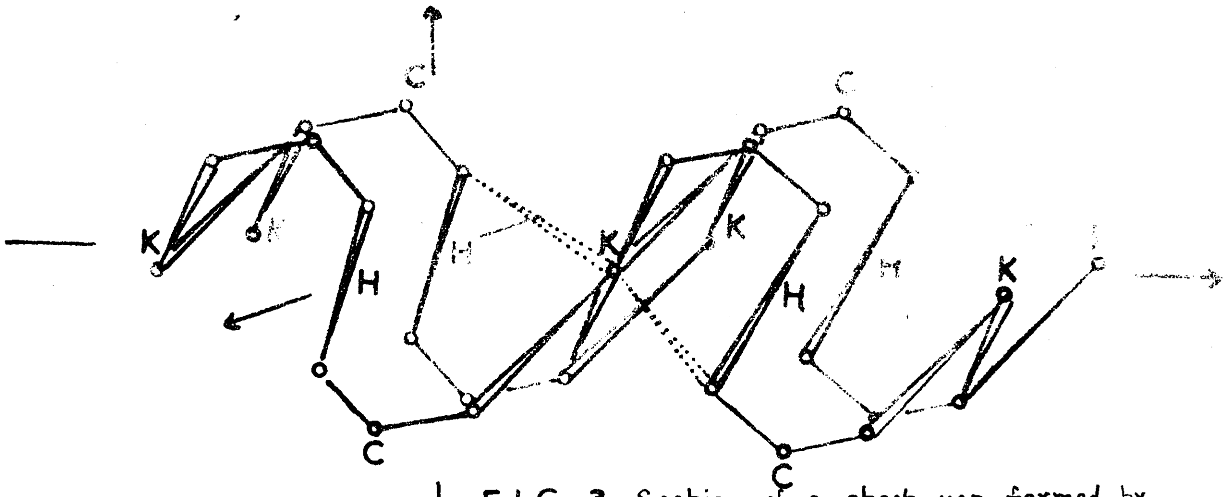


FIG. 3. Section of a sheet yoz formed by hydrogen atoms, potassium ions and carboxyl groups in the structure of K-H dibenzoate.

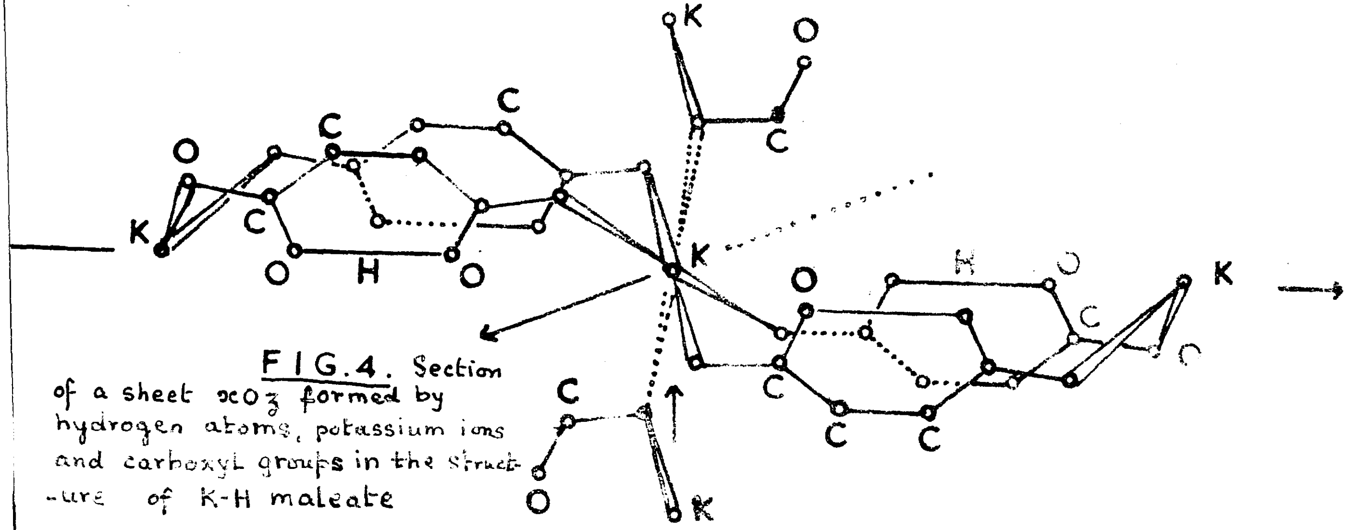


FIG. 4. Section of a sheet xOz formed by hydrogen atoms, potassium ions and carboxyl groups in the structure of K-H maleate

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SECTION IV.

CRYSTAL STRUCTURE OF AND HYDROGEN BONDING IN POTASSIUM HYDROGEN-DI-PARANITROBENZOATE.

Crystal structure of and hydrogen bonding in potassium hydrogen-di-paranitrobenzoate.

1. Introduction:

Many monocarboxylic acids HX form crystalline acid salts of the formula MHX_2 where M is a monovalent metal. These fall into two structural types, A and B. Most of these belong to the type A, of which potassium

$M^+ \quad X - \bar{H} - X \qquad\qquad M^+X^- \cdot HX$

(type A) (type B)

hydrogen bis-phenylacetate (1) is an example. In these the acid radical of the molecule HX and the anion X^- are crystallographically equivalent and indistinguishable. They are related to one another by a crystallographic symmetry element with which the centre of the hydrogen bond coincides and this bond appears to be formally symmetrical.

In type B, of which ammonium hydrogen disalicylate hydrate (2) is an example, the acid molecule HX is crystallographically distinct and unrelated to the anion X^-. The I.R. spectrum of ammonium hydrogen disalicylate hydrate is substantially a superimposition of the spectra of the free salicylic acid and its normal ammonium salt, whereas the compounds of the type A have I.R. spectra which cannot be regarded as superpositions and which show certain remarkable features.

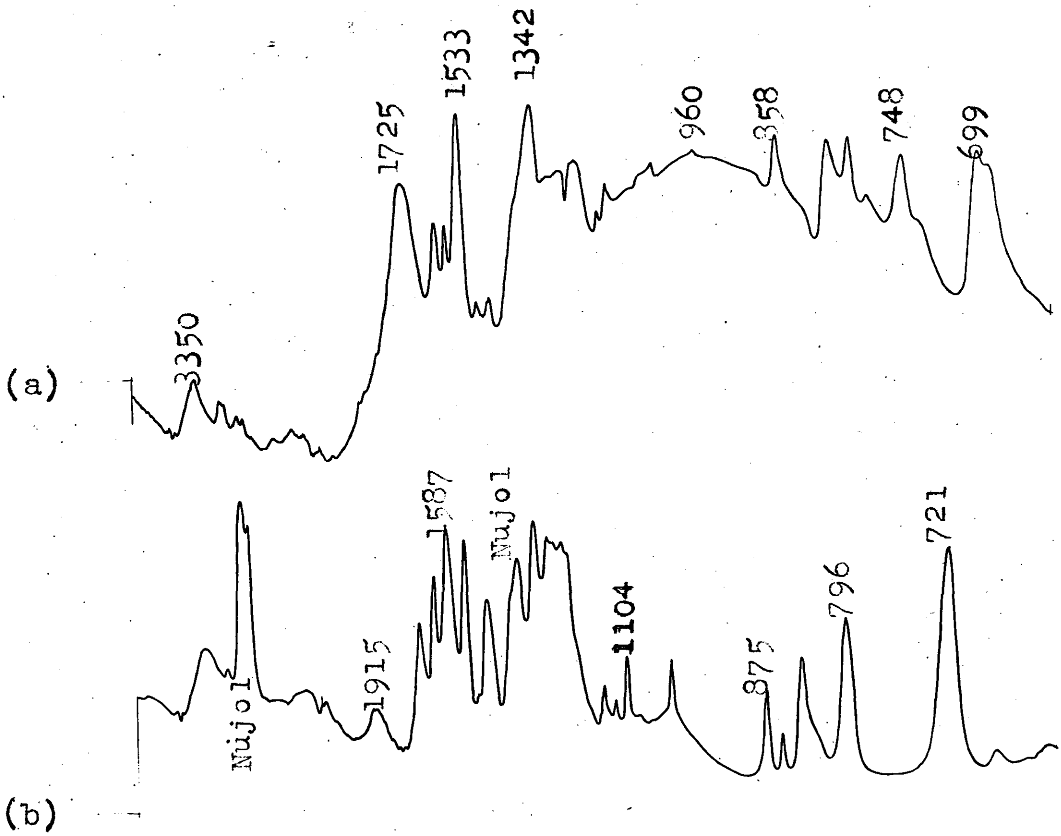


Fig.1. The I.R. Spectra of the potassium acid salts of o- and p-nitrobenzoic acids (a and b respectively). The spectrum (a) is taken with the specimen between KCl discs, whereas in (b) the specimen is in Nujol. Wave numbers (cm.$^{-1}$) of some peaks are indicated.

See overleaf - Page 78(a).

Fig. 1.

The I.R. spectra of the crystals of the potassium acid salts of o- and p-nitrobenzoic acids show this difference strikingly. Whereas the spectrum of the latter is of the superposition type, the former has a broad region of absorption somewhere between 860 and 1100 cm.$^{-1}$ (Fig. 1.) The OH stretching frequency is not easily recognisable and appears to have shifted to a much lower value than the normal one of about 3500 cm.$^{-1}$ These anomalies are presumed to be connected, in some way, with symmetrical hydrogen bonding on which basis Dr. Hadži (3) predicted that whilst the former (the o- compound) should have a structure of the type A, the latter must be of the type B.

My present analysis of K-H-di-p-nitrobenzoate together with the analysis of Rb-H-di-o-nitrobenzoate mainly by Dr. J.C.Speakman and in part myself confirms this prediction and also reveals the para-compound to be an interesting varient of the type B. (Note: The aforesaid types A and B correspond in part to similar types in a wider classification by Blinc, Hadži and Novak, Section 3, p.72.)

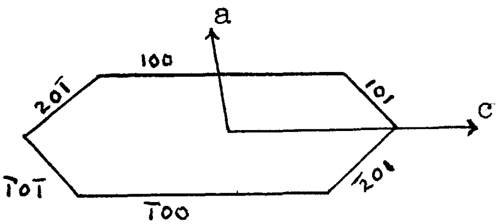
When I took up this work, Mr. N. Purdie (B.Sc. thesis, Glasgow, 1958) had estimated the h0ℓ intensities and applied to these the Wilson ratio and Rogers N(z) statistical tests which indicated centrosymmetry. He obtained a Patterson projection which could not be interpreted. Initially, I re-estimated and averaged these intensities. At a later stage it was found that the films used by Mr. Purdie had faded and I re-collected and re-averaged these data.

2. Preparation and characterisation:

The potassium acid salts of o- and p-nitrobenzoic acids can be easily prepared by adding half an equivalent of KOH or K_2CO_3 to a strong solution of the corresponding acid in hot aqueous alcohol and allowing the solution to cool. Care should be exercised, for sometimes the free acid (~~or the normal salt~~) crystallises out. These salts were first prepared by Farmer (4) who reported them to be flat prisms and pale yellow needles respectively, which soon decompose in water.

The crystals used in the present investigations were prepared by Dr. J. C. Speakman. Micro analysis results were in good agreement with the formula $C_{14}N_2O_8H_9K$ but could not exclude the possibility of H_2O or $\frac{1}{2}H_2O$ being present as water of crystallisation. I did an accurate flame photometric estimation of potassium. The resulting percentage of potassium was slightly higher than the calculated value, rendering the presence of any water of crystallisation very unlikely.

Good crystals from this specimen were pale yellow, almost colourless, laths which showed extinction at 30° to the lath axis, whereas most other crystals showed little or no extinction and appeared to be twinned. They had $\{100\}$ as their most prominent form. A crystal rotated about its vertically set lath-axis (b-axis) and viewed horizontally gave reflexions at 0°, 46°, 139°, 180°, 226° and 319°. These angles correspond to the planes:
(100), (101), $(\bar{2}01)$, $(\bar{1}00)$, $(\bar{1}0\bar{1})$ and $(20\bar{1})$ respectively.



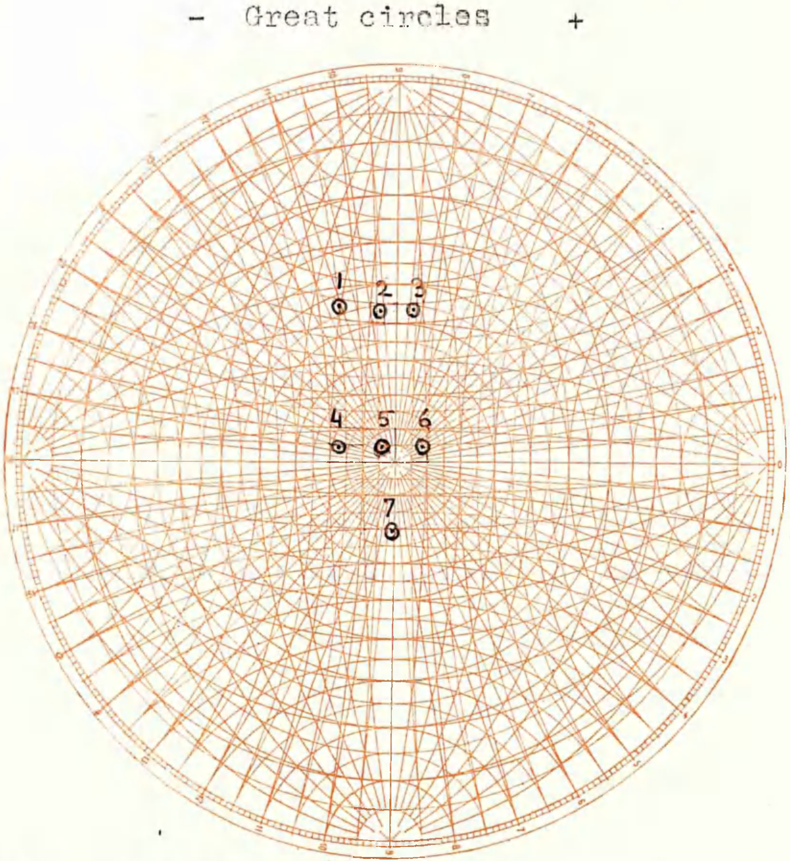
3. Unit cell parameters and the space group.

As the crystals belong to the triclinic system, determination of the parameters of the unit cell presented the usual difficulties which were overcome by determining the length of a large number of axes and plotting the corresponding goniometer-arc readings on a stereographic net. Fig. 2 is such a stereographic net obtained by plotting lower arc-readings on great circles and upper arc readings on little circles. A unit cell with $a^1 = 18.25$ Å, $b = 4.05$ Å, $c = 11.44$ Å, $\alpha^1 = 86.3^\circ$, $\beta^1 = 114.1^\circ$ and $\gamma^1 = 93.2$ Å was the first to be derived but was discarded in preference to the unit cell mentioned below.

Potassium Hydrogen di-p-nitrobenzoate, $KH(C_7H_4NO_4)_2$
Mol.wt. 372.3, Triclinic pinakoidal,
$a = 17.20$, $b = 4.05$, $c = 11.44$ Å,
$\alpha = 93.8^\circ$, $\beta = 104.1^\circ$, $\gamma = 90.5^\circ$.
Unit cell volume 771.3 Å^3,
Density observed 1.65 g./cc., density calculated 1.606g./cc.
$F(000) = 380$, absorption co-efficient for X-rays ($\lambda = 1.542$ Å) $= 35.4$ cm^{-1}. Space group $P\,\bar{1}$.

Statistical examination of the $h0\ell$ intensities yielded a value of 0.61 for the ratio of the square of the mean structure amplitude to the mean intensity (Wilson

Fig.2. Stereographic plot of arc-readings for a crystal of K-H-di-p-nitrobenzoate set along various axes.



1.	$[1\bar{1}0]$ axis,	17.56 Å	43°	and -20°20'
2.	[100] axis,	17.20 Å	43°	and - 6°50'
3.	[110] axis,	17.65 Å	43°	and + 6°30'
4.	[111] axis,	18.37 Å	4°30'	and -17°25'
5.	$[10\bar{1}]$ axis,	18.25 Å	5°	and - 4°30'
6.	$[11\bar{1}]$ axis,	18.87$_5$ Å	4°30'	and 8° 0'
7.	[102] axis,	25.18 Å	-20°	and - 2°40'

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ratio, (5)). Howells, Phillips and Rogers N(z) test (6) also indicated centrosymmetry, implying the space group P $\bar{1}$; which was borne out by the subsequent analysis.

4. Intensity data:

Intensity data were collected from equi-inclination Weissenberg moving film photographs, utilising the multiple film technique, and estimated visually. There was some uncertainty about the value of the film factor that ought to be used. This arose from the observation that the equi-inclination angle versus the film factor curve suggested by Rossman (7) passes through the observational point ($\nu^{o} = 35^{o}$, film factor = 4.00) considered doubtful by him. If we draw a smooth curve through the rest of Rossman's observational points it is in better agreement with Grenville-Wells' (8) calculated values. I used such a curve. The derived film factors of 3.25, 3.40 and 3.66 for the equi-inclination angles 0^{o}, 11^{o} and 22.4^{o} seemed to be in fairly good agreement with intensities estimated on two consecutive films of a series. Copper radiation was used throughout.

Initially some 234 $h0\ell$ reflexions were recorded. At a late stage in the refinement an additional 90 weak reflexions were observed on films that had received a long exposure. The total of 325 is 70% of those accessible. 241 $h1\ell$ and 180 $h2\ell$ reflexions representing 52 and 55% respectively of the totals accessible in these reciprocal nets were also recorded.

The cross-section of the crystal used was 0.05 x 0.08 mm^2. Calculations (Appendix I) indicated, for the $h0\ell$ reflexions, a maximum absorption correction of about 9%, whereas the estimated error in the observed intensities was about 15%. Absorption corrections for the $h1\ell$ and $h2\ell$ intensities would be more, but their estimated errors were also correspondingly more and the corrections were not applied. To correct for a systematic error due to the difference between the sizes of spots on the upper and the lower halves of the $h2\ell$ moving films, the two sets were separately scaled during the later stages of the least squares refinement. Similar errors in the $h1\ell$ data were not significant. Lorentz-polarisation factor (Sec. 2) and Tunell factor (9) corrections were applied in the usual way.

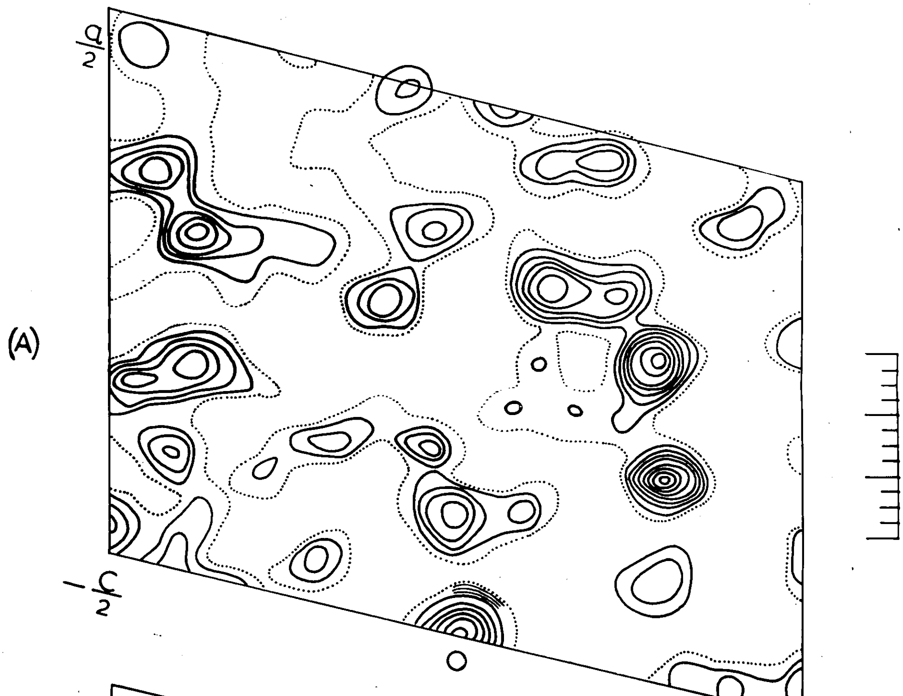
5. Determination of the projected structure:

As atoms were expected to be well resolved in a projection down the short axis (b-axis), initial efforts were confined to the determination of the structure in this projection. Solution of the phase problem presented difficulties. Repeated attempts to prepare the Rb or NH_4 isomorphs failed. It was also clear that potassium was not heavy enough for the successful application of the heavy atom method; the square of its atomic number being less than $\frac{1}{3}$rd the sum of the squares of the atomic numbers of the other atoms in the asymmetric unit (10).

The p-nitrobenzoate group has high pseudo-symmetry (*m m m*), so that its vector-set includes prominent peaks due to the coincidence - or near coincidence- of several interatomic vectors (11). Presence of two independent paranitro groups in the asymmetric unit further gives rise to prominent inter-group vector peaks. Actually in the Patterson projection there were seven prominent peaks of about the same height and it was difficult to say which of these is the true K - K vector peak.

Fig. 3a represents a moderately sharpened Patterson function computed by incorporating the sharpening function $\left\{\hat{f}_o \exp(\sin^2\theta/\lambda^2)\right\}^{-2}$ (see Appendix II). Relative increase in peak heights on sharpening together with the consideration of compactness of these peaks (inter-group peaks are usually diffuse) pointed to the correct K - K vector peak in addition to one or two other peaks.

Fig.3.(a) Sharpened Patterson synthesis map for the projection of K-H-di-p-nitrobenzoate structure along the b-axis.



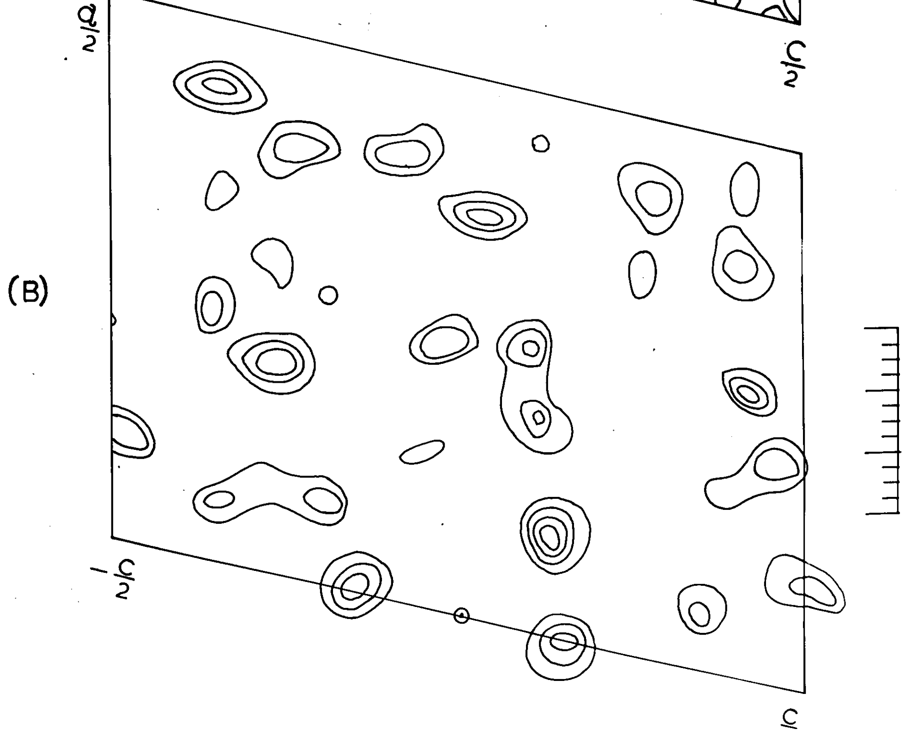


Fig.3. (b) Corresponding Buerger minimum function map obtained by superposing the true K-K vector peak on the origin.

Superposing the sharpened Patterson map on itself in such a way that the suspected K - K vector peak of one was coincident with the origin of the other, we obtained Buerger minimum function maps (12) for a number of peaks. One of these maps which contained the true structure is shown in Fig. 3b. However, the true structure was not recognised from this map until it had also been indicated by another approach.

The weighted vector diagram for a single p-nitrobenzoate residue was drawn to scale on tracing paper. This includes a high-weight vector about 6.9 Å from its origin, due to the pair of long O···O separations. The sharpened Patterson map contains 12 peaks which lie between 6.5 to 7.0 Å from the origin. The tracing was placed with its origin on that of the sharpened Patterson map and its high-weight vector coincident with each of these 12 peaks in turn. Each of these 12 positions was then given a figure-of-merit based on the number and weights of any other coincidences. (For every coincidence the weight of the peak on the tracing was noted, the sum of these being the aforesaid figure-of-merit. A slight tilt of the tracing was allowed whenever it improved coincidence.) Orientations at 76°, 156°

and 0 or 180° to the projected C axis had the highest figures of merit of 120, 100 and 100 respectively and were the most probable.

Next a search was made in the Patterson map for the centre-to-centre vector peaks between pairs of acid radicals related by a centre of symmetry. In view of the short b-axis, such peaks cannot lie too close to the origin. Their relative increase in height on sharpening is likely to be about the same or slightly less than that of the origin peak. It is also expected to be a relatively diffuse peak. On these grounds, it was possible to reject one peak which turned out to be the K - K vector peak.

The vector diagram, in each of its three most probable orientations was then placed with its origin, in turn, on each of the remaining peaks, figures-of-merit being allotted as before. Thus it became possible to reject all but two orientations and two peaks.

This information immediately led to the interpretation of the appropriate minimum function, Fig. 5b. The preliminary structure so derived gave an agreement index (R) of 0.33 between $|F_o|$ and F_c values calculated with a Debye factor (B) of 3.0 $\mathring{A}^2$. Throughout this work, atomic scattering factor curves published by Berghuis, et al. (13) were used.

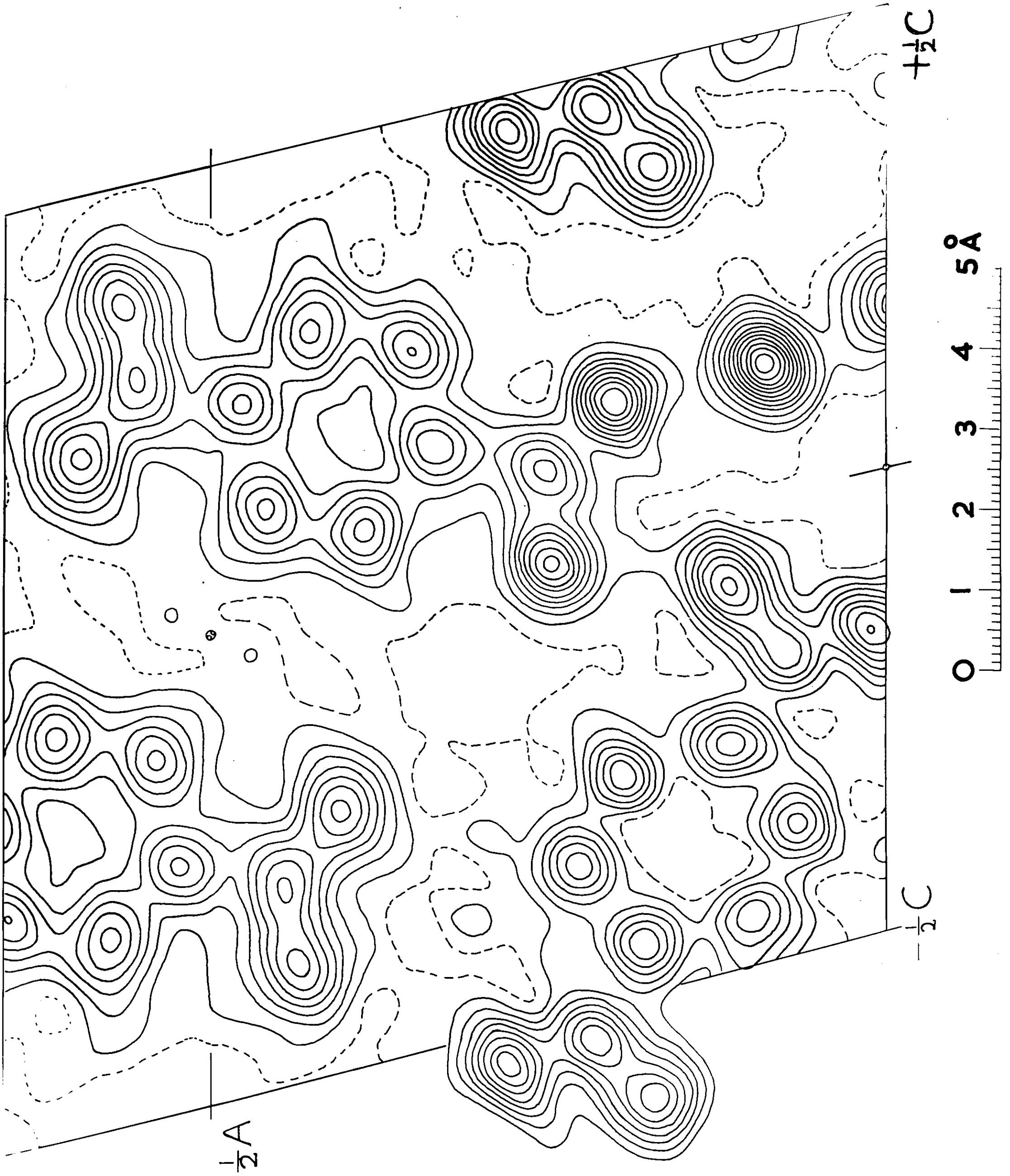


Fig.4. Electron-density synthesis for the projection of the K-H-di-p-nitrobenzoate structure down the b-axis.

6. Refinement of the projected structure.

Two cycles of refinement utilising electron-density synthesis brought down R to 0.19. Although no distinction was initially made between the carbon atoms of the carboxyl groups and the Nitrogen atoms of the nitroxyl groups, this became quite clear in the second electron density synthesis. This distinction is in agreement with the chemical expectation that the carboxyl group would make preferential contacts with the potassium ion.

The aforesaid electron-density synthesis included 232 of the then available 235 terms, two of which changed sign subsequently, and is reproduced in Fig.4. together with the key and the numbering of atoms in Fig.5.

Then followed three cycles of 'Difference synthesis' (14) with isotropic B allowed to vary for individual atoms. In the last of these, some unobserved reflexions giving a significantly high value for F_c were incorporated by giving to their F_o a value equal to the minimum locally observable value. At the end of these cycles R stood at 0.13 but calculation of the structure amplitudes of the unobserved reflexions within the circle of reflexion showed that many of these should have been observed. A long exposure series actually added 90 reflexions to those previously observed.

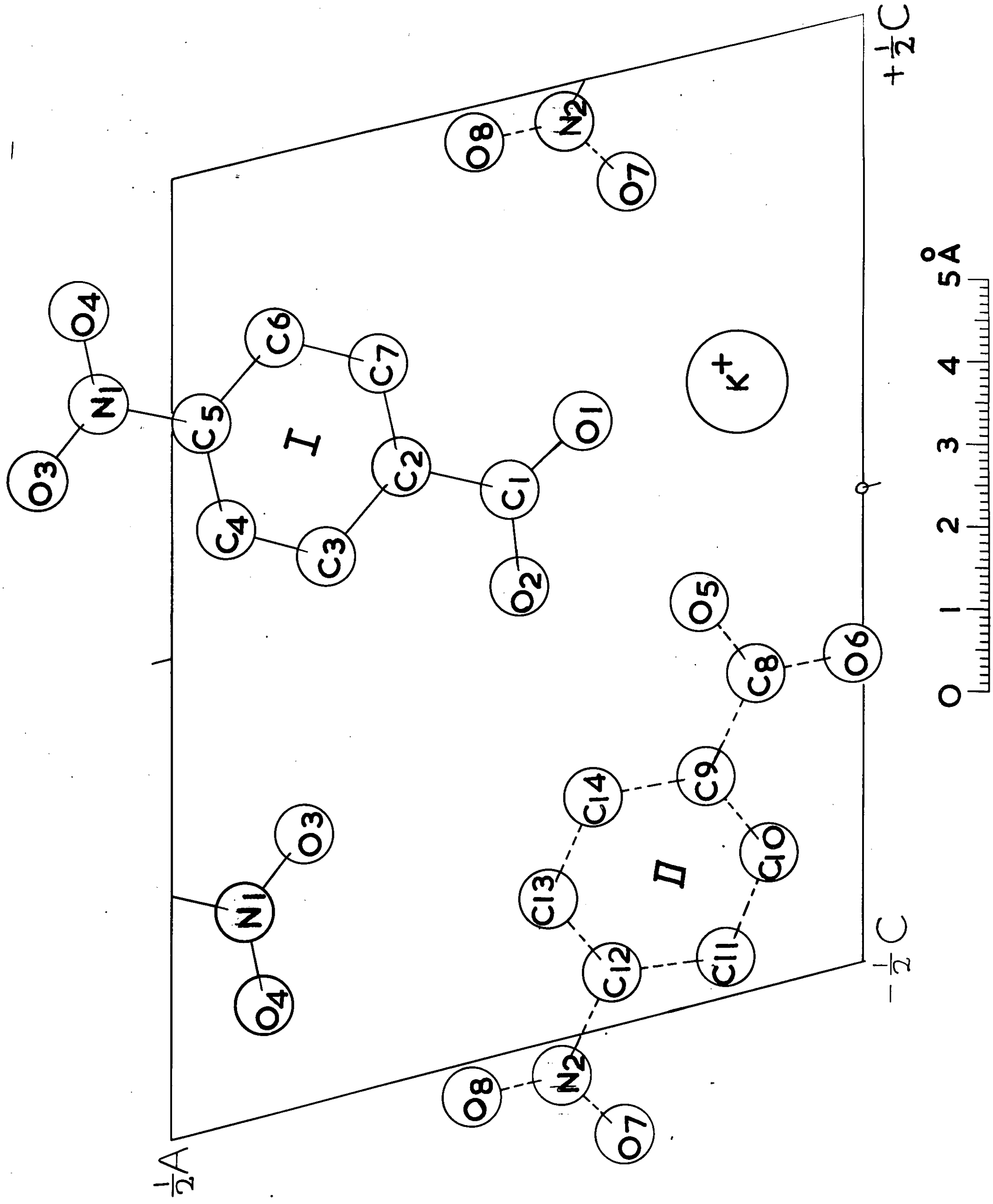


Fig.5. Key to electron-density map (Fig.4) and the numbering of atoms.

The intensities of these implied that the initial films had faded a little. As such fading affected the weak spots more than the stronger ones, the F_c values of the former were generally more than the observed, whereas those for the latter appeared to be less because of faulty scaling.

To improve the data another short exposure series was taken and best values arrived at by averaging the available estimates (as the previous values were averages from four different estimates they were not thrown away). In the final results the residual fading probably shows itself in a general increase of the anisotropic temperature factor parameters in the plane of this projection but the significance of their relative values is unlikely to be affected.

With the new and fuller $\underline{h0\ell}$ data a final "difference synthesis" was obtained. This included unobserved reflexions for which F_c was greater than the locally observable minimum value by assigning to them a structure amplitude of half this minimum. The hydrogen atoms attached to the benzenoid rings were also included in the F_c calculations. This synthesis is shown in Fig.6. It is interesting to note that there is a peak $1e/\text{Å}^2$ high near oxygen atom O(2), not far from the expected position of the hydrogen bonding hydrogen atom.

Note: 1. In cycles of refinement by "difference synthesis" atomic shifts of magnitude Δr_n were made in the direction of steepest electron density ascent corresponding to half shifts.

$$\Delta r_n = \left(\frac{\delta \rho_o}{\delta r_n}\right)_n \Big/ 4p(\rho_o)_n$$

where p was assumed to be 5. Actually $^2/_3$rd shifts would have given a better convergence, whereas full shifts would have overshifted the atoms (15).

2. Electron density at the point (x, z) was calculated from the expression

$$\rho(x,\ z) = \frac{1}{A_b}\Big\{F(000) + 2\sum_{h=1}^{\infty} F(h00)\ \cos 2\pi hx$$
$$+ \ 2\sum_{\ell=1}^{\infty} F(00\ell)\ \cos\ 2\pi \ell z$$
$$+ \ 2\sum_{h=1}^{\infty}\sum_{\ell=-\infty}^{\infty} F(h0\ell)\ \cos 2\pi(hx + \ell z).$$

Dr. J.S.Rollett's programme was used for summation on DEUCE. This gives half weight to the 0k0 terms when k<1 is included, in which case,

$$\rho(x,\ y) = \frac{2}{A_b}\Big\{F(000) + \sum_{h=0}^{\infty}\sum_{k=-\infty}^{\infty}(Accc - Assc)\Big\}$$

both 0k0 and 0$\bar{k}$0 were included.

(Indices had to be rearranged for computational purposes.)

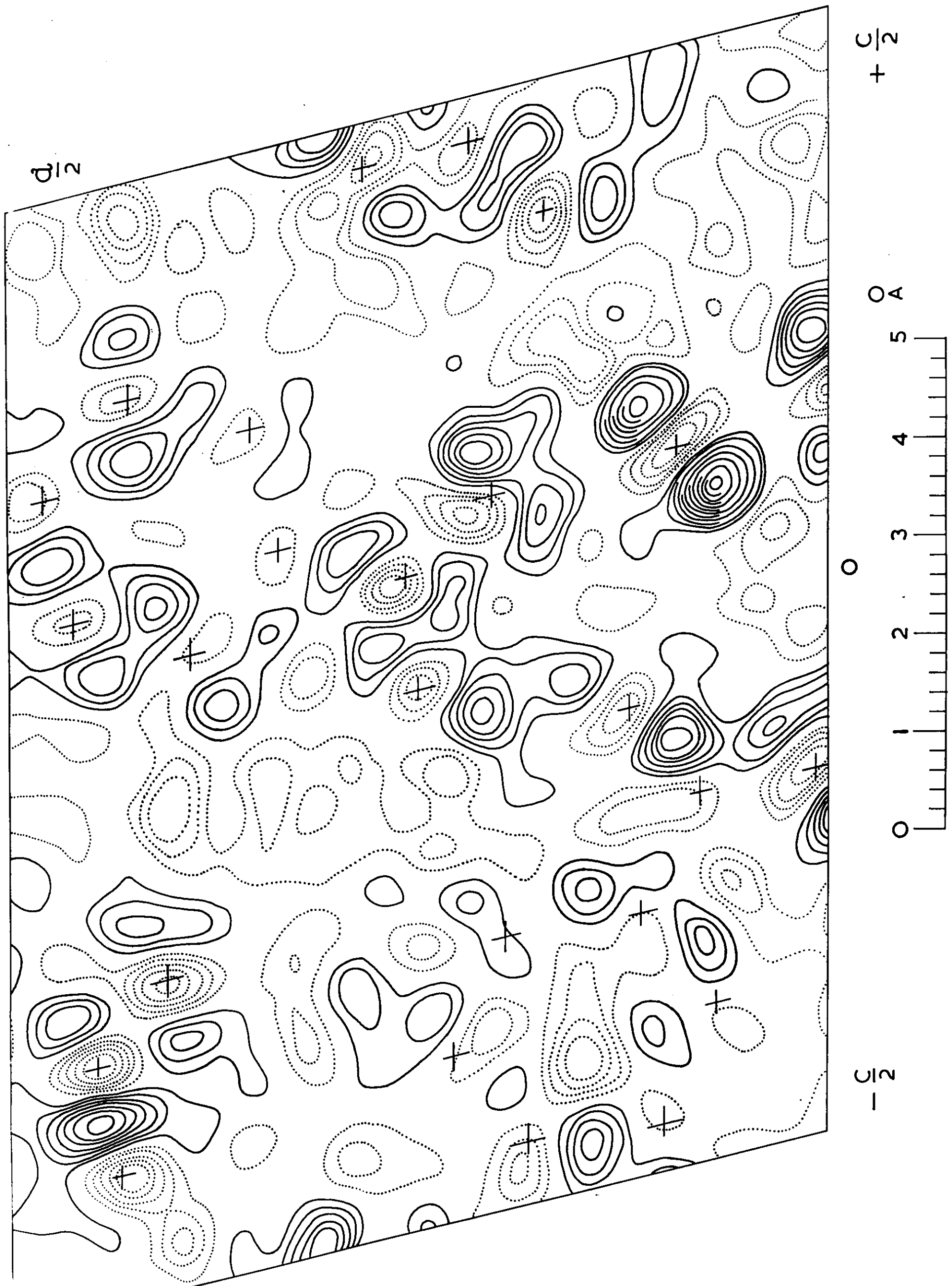


Fig.6. (Fo - Fc) synthesis map for the projection of K-H-di-p-nitrobenzoate [illegible]

7. Determination of the y- coordinates:

In view of the short projected distance (3.9 Å) between the two centro-symmetrically related potassium ions and the short b-axis, it seemed that potassium should be located about $\frac{b}{4}$ above or below the plane of projection. These positions are equivalent to a change of origin from (0,0,0) to (0,$\frac{1}{2}$,0). By arbitrarily choosing $H_K = b/4$ we merely fixed the origin (H_K represents height of atom K above the plane of projection).

Utilising the fact that the sum of the ionic radii of potassium and oxygen is about 2.68 Å, the shortness of the projected distances K-O(1), and K-O(6) suggested that O(1) and O(6) will be about b/2 above and below H_K and H_{K^1} respectively. Thus the central structure holding the two p-nitrobenzoate residues was approximately fixed; what remained was to decide their inclinations.

Assuming the distances between atoms such as C(3) and C(7) to be 2.42 Å and those between atoms such as C(2) and C(5) to be 2.80 Å, four possible inclinations can be assigned to each p-nitrobenzoate residue. In each case, two of these could be rejected as they did not correspond to the observed angle between lines such as C(3) -C(7) and C(2) - C(5).

Knowing the height H(r) of a standard atom r in each residue {O(1) in one and O(6) in the other} and the residue's inclination, the height H(n) of any atom <u>n</u> in the residue could be calculated from:-

$$H(n) = H(r) + (\ell^1 - \ell_r^{\,1})\cot\psi_L + (M^1 - M_r^{\,1})\cot\psi_M$$

where the meaning of the terms is the same as defined for quaterrylene (Sec. 2, p.36).

Further y was calculated from:-

$$y = \frac{H - zc\cos\alpha - xa\cos\gamma}{b}$$

and four preliminary trial structures postulated, one of which showed an agreement index (R) of 0.37 for the $|F_o|$ and F_c values of some 136 $hl\ell$ reflexions and served as a starting-point for the refinement of y co-ordinates.

8. <u>Refinement of y co-ordinates by generalised projections</u>:

With well established (though not yet final) values of x and z, the initial refinement of the y- co-ordinates was by way of the $h1\ell$ and $h2\ell$ generalised projections (16). (Appendix III). An initial <u>$h1\ell$</u> generalised projection (cosine part alone), utilising 136 strong reflexions, brought down <u>R</u> for these terms to 0.28; but a similar second cycle showed little improvement (R = 0.256).

Therefore in the succeeding two cycles co-ordinates were derived utilising both cosine and sine parts of the h1ℓ generalised projections. This brought down *R* for all the 241 *h1ℓ* reflexions to 0.20. Then followed two similar cycles, utilising the *h2ℓ* data, at the end of which R was 0.144 and 0.22 for all the *h1ℓ* and *h2ℓ* reflexions respectively.

So far a common isotropic Debye temperature factor parameter of B = 3 was used. When the individual isotropic B values obtained from the refinement in projection were substituted *R* improved to 0.138 and 0.214 respectively. This improvement is rather less than what would normally be expected and suggests that the thermal movements parallel to the b- axis may differ substantially from those in the projection. This was borne out by subsequent refinement. Fig.7 shows the cosine and sine parts of the final *h1ℓ* and *h2ℓ* generalised projections.

9. Partial 3D least squares refinement.

With the x- and z- co-ordinates refined as far as possible with isotropic temperature factor parameters and with the y- co-ordinates also fairly well refined, a least squares (17) refinement of these parameters, which also provided for anisotropic thermal motion, was carried out. In such a refinement the variable parameters are

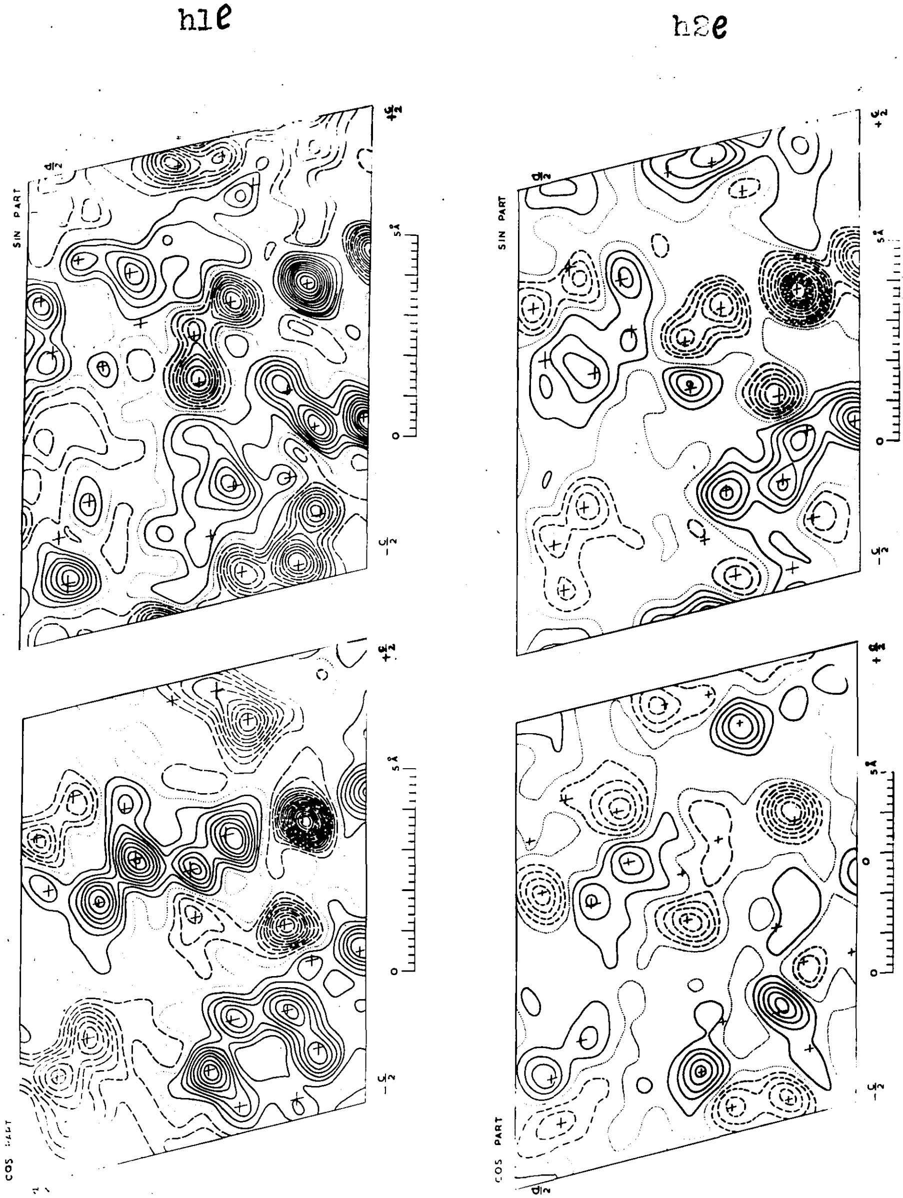


Fig.7. **Generalised** projections of **K-H-di-p-nitro**benzoate structure.
(a) h1ℓ cosine part
(b) h1ℓ sine part
(c) h2ℓ cosine part
(d) h2ℓ sine part.

nine per atom (three positional and six thermal) + the scale factor. Excluding the hydrogen atoms from refinement, we have 226 such variables and 750 observed structure amplitudes indicating that a reasonably good refinement should be possible.

The quantity minimised was:

$$\sum W_1(hk\ell)\left\{|F_o(hk\ell)| - |F_c(hk\ell)|\right\}^2$$

where $W_1(hk\ell)$ is the weight of a particular term $(hk\ell)$. If all the observational data are equally good no weighting should be necessary. On the other hand, a value of $\sqrt{W_1}$ equal to the inverse of the probable error of every datum may be expected to give 'best' results - if such errors are not systematic and can be reasonably estimated. In practice the latter requirement is not fulfilled by the usual *X*-ray data and it is convenient to give unit weight to all observations except those of *very* intense reflexions which may be given zero weight (17) and (18).

In the present refinement, the average values of $|F_o|$ for the *h0ℓ*, *h1ℓ* and *h2ℓ* reflexions were 12.0, 20.6 and 16.4 respectively, and reflexions with $|F_o| < 41.0$ were given unit weight, whereas those for which $|F_o| > 41.0$ were given a weight of $\frac{41.0}{|F_o|}$. Accidentally unobserved reflexions were excluded. The programme used was that developed by Dr. J.S. Rollett at the National Physical Laboratory (U.K.) and made available to us by the courtesy of the Director of the Mathematics Division.

Three cycles of refinement employing half atomic shifts were carried out. In the last two cycles 55 unobserved $\underline{h0\ell}$ reflexions for which $F_c > F_{(\text{local minimum observable})}$ were included by assigning to their structure amplitudes a value of half that locally observable. In the last cycle 192 unobserved $\underline{h1\ell}$ and $\underline{h2\ell}$ reflexions were similarly included. Also included were the 8 hydrogen atoms attached to the benzenoid rings by putting them in the mean plane of the benzenoid rings at about 1.05 Å from the respective carbon atoms in the usual way.

Agreement index (R) values for the observed $\underline{h0\ell}$, $\underline{h1\ell}$, and $\underline{h2\ell}$ reflexions which initially stood at 0.14, 0.138, and 0.214 respectively, with a total of 0.166, were reduced to 0.095, 0.086 and 0.137, with a total of 0.104. When the aforesaid unobserved reflexions are included these figures increase to 0.105, 0.144 and 0.161 with a total of 0.137. The final co-ordinates are given in Table 1, which also includes co-ordinates in Å units, with respect to orthogonal axes chosen with Y^1 parallel to y, Z^1 in the plane yz and perpendicular to y, and X^1 perpendicular to both Y^1 and Z^1.

Co-ordinates and orthogonal co-ordinates of some important symmetry related atoms are given as Appendix to Table 2.

The anisotropic temperature factor (T) is usually represented as:-

$$T = \exp\left\{-(\beta_1 h^2 + \beta_2 k^2 + \beta_3 \ell^2 + \beta_4 hk + \beta_5 k\ell + \beta_6 \ell h)\right\} \ldots .(1)$$

In Dr. Rollett's programme it is represented on the binary scale as:-

$$T = 2^{-(B_{11}h^2 + B_{22}k^2 + B_{33}\ell^2 + B_{12}hk + B_{23}k\ell + B_{31}\ell h)} \ldots .(2)$$

Therefore: $B_{11} = 1.4427\beta_1$; $B_{22} = 1.4427\beta_2$ etc.etc. .....(3)

The final B_{ij}'s are listed in Table 2.

If B is an isotropic thermal parameter giving the same value of T as equation (1) or (2), i.e. such that: $T = \exp - B(\sin^2\theta/\lambda^2)$

then (19) we have:

$$\frac{B}{4} = \frac{a^{*2}\beta_1 + b^{*2}\beta_2 + c^{*2}\beta_3 + 2a^*b^*\cos\gamma^*\beta_4 + 2b^*c^*\cos\alpha^*\beta_5 + 2a^*c^*\cos\beta^*\beta_6}{a^{*4} + b^{*4} + c^{*4} + 4a^*b^*\cos^2\gamma^* + 4b^{*2}c^{*2}\cos^2\alpha + 4a^{*2}c^{*2}\cos^2\beta^*} \ldots .(4)$$

This simply represents an averaging procedure which makes use of relations such as:-

$$\beta_1 = \frac{a^{*2}B}{4}, \quad \beta_2 = \frac{b^{*2}B}{4}, \quad \beta_3 = \frac{c^{*2}B}{4}$$

$$\beta_4 = a^*b^*\cos\gamma^* . \frac{B}{2} \text{ etc.} \qquad \ldots\ldots\ldots\ldots(5)^*$$

To get an approximate idea of the anisotropy of the thermal vibrations involved it may be helpful to represent the Bij parallel to the crystallographic axis in terms of the conventional isotropic B's. Such values calculated from the first three of the equations (5) are given in Table 3.

The numbering of the atoms in these tables is explained in Fig.5. The bond lengths and bond angles for one asymmetric unit are detailed in Fig.8, whereas Fig.9 shows one unit cell and the nearest atoms from the surrounding unit cells together with the length of the important intermolecular contacts. Table 4 shows the accuracy of results as assessed from the least squares totals, which included the 247 unobserved reflexions. The expressions used were:

$$\sigma^2(x/a) = (\Sigma W\Delta^2)/(n - s) \left[\Sigma W(dF/dx)^2\right]$$

Dunitz and Rollett (20).

$$\sigma(r) = \sqrt{\frac{\sigma^2(x) + \sigma^2(y) + \sigma^2(z)}{3}}$$

$$\sigma(\ell) = \left[\sigma_r^2(A) + \sigma_r^2(B)\right]^{\frac{1}{2}}$$

As the standard deviations for atoms of the same chemical type were generally similar these have

---

* <u>NOTE</u>: The values of $4B_{11}/1.4427a^{*2}$, $4B_{22}/1.4427b^{*2}$ and $4B_{33}/1.4427c^{*2}$ are $776.6\ B_{11}$, $45.2\ B_{22}$, and $346.6\ B_{33}$ respectively.

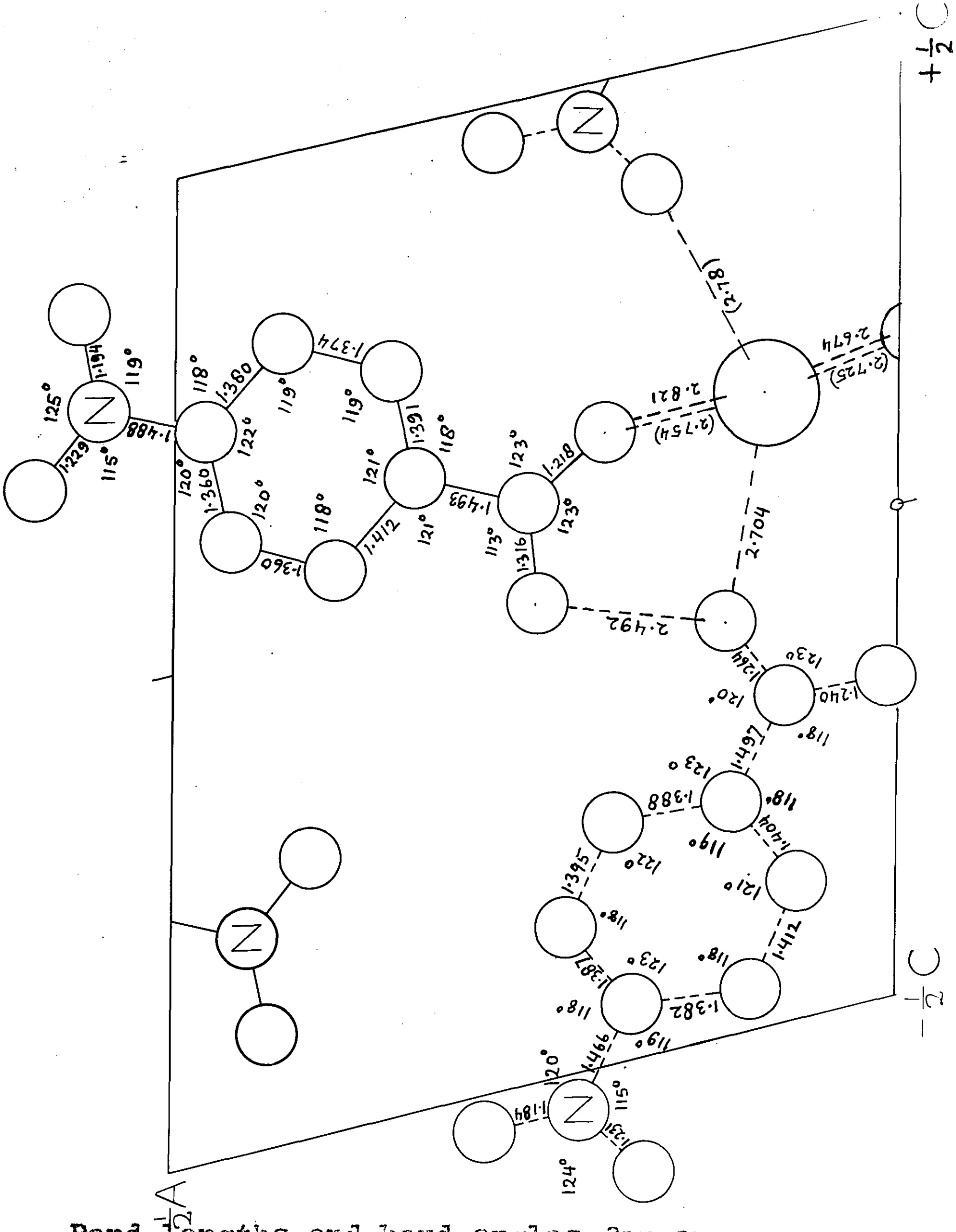


Fig.8. Bond-lengths and bond-angles for an asymmetric unit in the structure of K-H-di-p-nitrobenzoate.

been averaged. Standard deviations of bond angles (21) have not been calculated, but are estimated to be about 2°.

The comparatively larger tables of $|F_o|$ and F_c, which are being prepared, will be included in a paper to be published in J.Chem.Soc. In the meantime, a copy can be provided if required.

10. Discussion:

The original object of this investigation was to discover whether the structure of the acid nitrobenzoates differed in the way suggested by their I.R. spectra. In K-H-di-p-nitrobenzoate (see Fig.8) neither the potassium ion nor the centre of the hydrogen bond, between O(2) and O(5), lie on a crystallographic symmetry element. This alone suffices to prove that it does not belong to our type A. The present compound has a short hydrogen bond directly linking the two p-nitrobenzoate residues, whereas in ammonium hydrogen disalicylate hydrate (2), the only acid salt of the type B whose structure is known, such linking is via water molecules and the hydrogen bonds are long. Apart from this, all structural features support its assignment to the type B.

The two nitrobenzoate residues are crystallographically distinct. The residue I can be identified

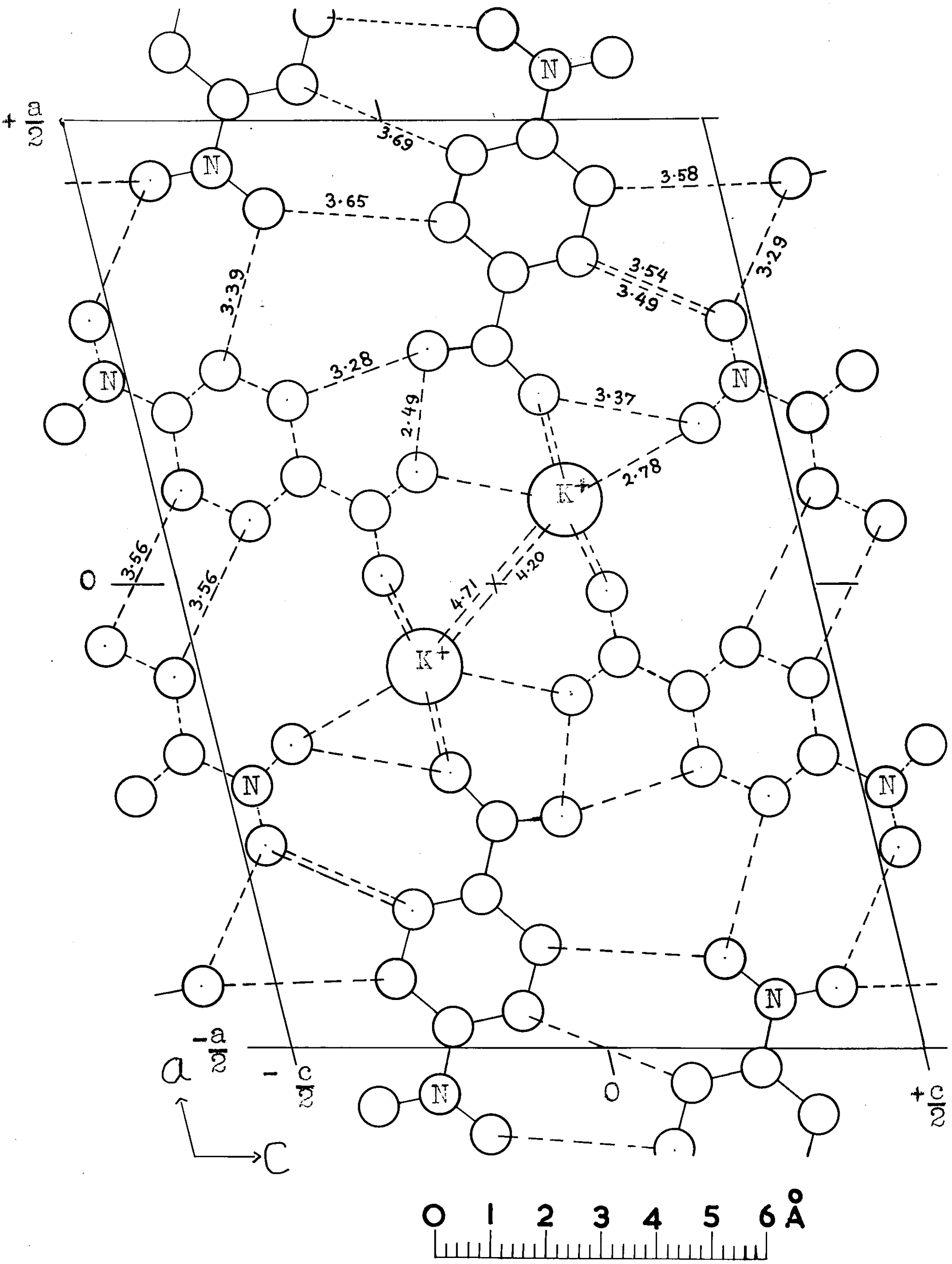


Fig.9. Projection of K-H-di-p-nitrobenzoate structure down the b-axis, showing a complete unit cell with the neighbouring atoms and the important intermolecular contacts.

as the neutral molecule HX because :

(a) it makes contact with potassium ions only through a single carboxylic oxygen atom, whereas the other makes contact through two carboxylic and one nitroxylic oxygen atoms.

(b) the bond C(1) - O(2) is the longest, whereas the bond C(1) - O(1) is the shortest of the four carbon-oxygen bonds, suggesting a predominently single bond character in the former. Similar distinction also observable in II is not so significant.

(c) the observation (b) suggests that the acid hydrogen atom should be near O(2) and indeed in the final difference map (Fig. 6.) we can locate a 1 e/$Å^2$ peak not far from the expected position.

(d) angle C(1)O(2)O(5) is 109.8^{o}.

Our *X*-ray work on Rb-H-di-O-nitrobenzoate, an isomorph of the potassium acid salt (22) has shown that it belongs to the type A. Thus the structural difference suggested by the I.R. spectra can be broadly considered as v~~a~~erified.

However, the hydrogen bond in potassium hydrogen di-p-nitrobenzoate is a very short one, 2.49_2 Å with a standard deviation of 0.02 Å which makes it shorter than or equal to the average value of 2.504 Å for the five acid salts of the type (A) listed in Sec. 3, p.72. (The average for all the seven compounds being 2.493 Å.) This <u>proves</u> that the shortness of the hydrogen bond is not the cause of the spectral anomaly shown by the compounds of the type (A). We have seen in Sec.3, p.72 that in the compounds of type (A) the hydrogen bond together with carboxyl groups and alkali metal ions forms an extensive network in two or three dimensions. In the present structure there is no such extensive network. The hydrogen bond together with carboxyl groups and the potassium ions forms a column. One nitroxylic oxygen atom of each anion $\bar{X}$ forms an electrostatic link with the potassium ion of a neighbouring column. The rest of the structure is then held together by van-der-Waals forces in such a way that the nitro group of the acid parts HX fit as closely as possible into the space available between nitrobenzoate residues.

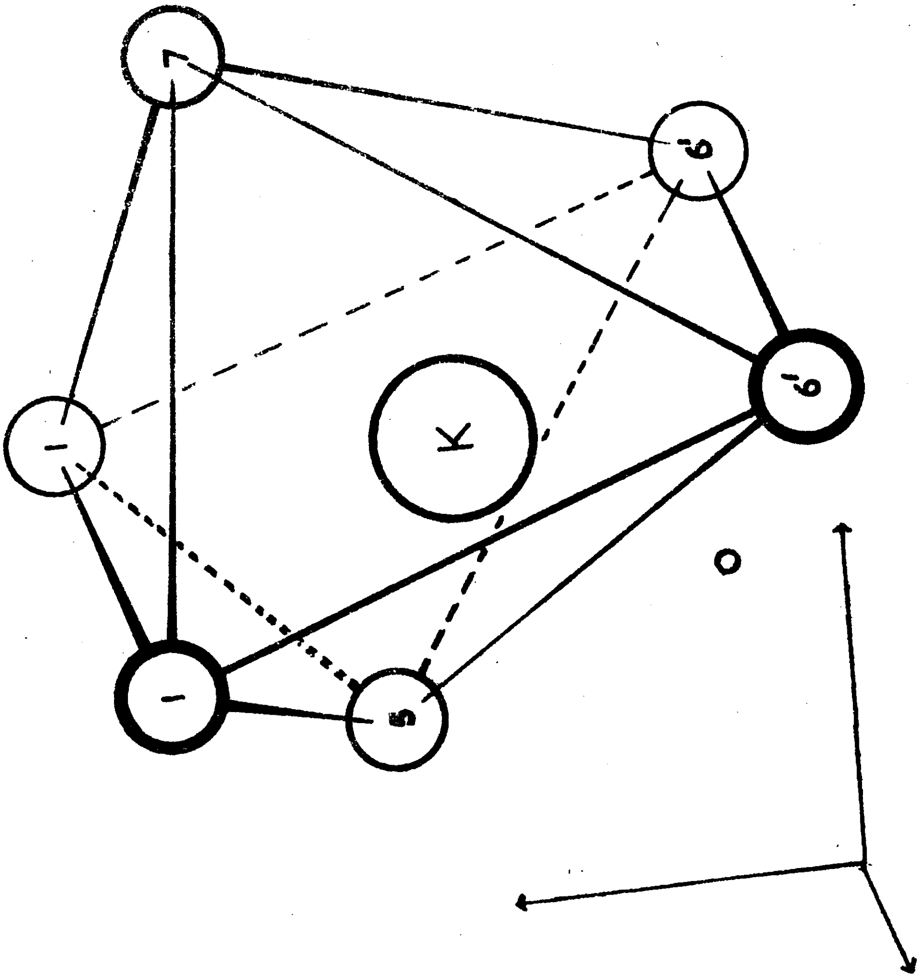
Increase in the size of an absorbing unit usually lowers the frequency of the radiation absorbed. It therefore appears that the broad band in the anomalous I.R. spectra of the compounds of the type (A) is due to the aforesaid extensive networks in these structures. In sodium hydrogen diacetate (22) which has the most extensive of such net works the anomaly is also most pronounced, whereas our present compound has no such network and the anomaly is also non-existent. This lends support to the view that the anomaly is intimately connected with the nature and expanse of this network.

Let us now consider other features of interest in the present structure. The potassium ion is surrounded by six oxygen atoms, five carboxylic and one nitroxylic, which form a distorted octahedron with an O(7)-K-O(5) angle of 137°. The face with the greatest area is opposite to a similar face of another symmetry related octahedron (see Fig.10).

The anisotropic temperature factor parameters (Table 3) indicate that the thermal vibrations parallel to the b-axis are relatively small for the potassium ion and the carboxyl oxygen atoms O(1) and O(6). This would suggest a firmer binding parallel to the b-axis and is in agreement with the fact that this axis is the longest morphological axis.

In contrast the hydrogen-bonding oxygen atom O(2) has the largest equivalent <u>B</u>- value parallel to the b-axis and its thermal displacement parallel to the hydrogen bond is relatively small. The other oxygen atom O(5) shows isotropic motion because it is

Fig.10. Surroundings of a potassium ion; the small circle shows the true origin from where the cubic cross axes are removed for clarity.



electrostatically bound to the potassium ion which inhibits movement parallel to b-axis. Thus we can conclude that the thermal vibrations of the hydrogen bonding oxygen atoms are appreciably less parallel to the bond. This is in agreement with results from more accurate studies on β-succinic acid (23) and ice (24).

The benzenoid rings are substantially planar. The standard deviation from the mean molecular plane are 0.028 Å and 0.009 Å for the benzenoid rings in the residue I and II respectively. With reference to the orthogonal axis defined earlier the equations for the mean plane of the benzenoid rings of the residues I and II are:-

$$-0.374\ X^1 + 0.809\ Y^1 - 0.213\ Z^1 + 2.092 = 0$$

$$-0.187\ X^1 + 0.795\ Y^1 - 0.420\ Z^1 - 1.473 = 0$$

where X^1 , Y^1 and Z^1 are the orthogonal co-ordinates in Å units.

The p-nitrobenzoate residues as a whole are not planar. The carboxyl and the nitroxyl groups are twisted about the C - C and the C - N bonds by $+10^\circ$ and $+5^\circ$ respectively in residue I and both by

+ 5° in residue II. In p-di-nitrobenzene (25) the observed twist of nitroxyl group is 9.5°. It is interesting that these twists are in the same sense, viz. in the residue II the nitroxyl and the carboxyl groups are in nearly the same plane. It is possible to give a plausible explanation for this in terms of steric hindrance, viz. the van der Waal's attractive and repulsive forces preventing the rotation of the benzenoid rings, from the intermolecular contacts shown in Fig.9.

The short $K^+ - K^+$ contact of 4.20 Å is rendered possible because of the cushioning effect of six oxygen atoms surrounding each K^+. Fig.9 also shows a short intramolecular contact of 3.28 Å between C(14) and O(2) and of 3.29 Å between O(8) and O(4). Similar short contacts have been reported in many other cases (26). Other intermolecular contacts are normal.

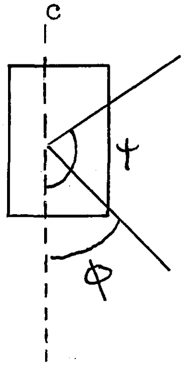
APPENDIX I.

Absorption Corrections.

Absorption corrections were calculated by a simplified version of Albrecht's method (Rev.Sci.Inst. 1939,10,221.) adopted for programming on DEUCE by Dr. J.C.Speakman. The cross-section of the K-H-di-p-nitrobenzoate crystal used for collecting data was 0.05 x 0.05 mm^2. The machine was to treat every 0.0135 mm. as a unit of 10^{-2}cm. by assuming the cross-section of the crystal to be 6 x 4 units and its absorption coefficient as 4.775 per unit. Calculated transmittance for 24 reflexions, listed in the following table, showed that the smallest value is 0.757 and the biggest 0.821. When the paper by Bond appeared (Acta Cryst 1959, 12, 375) the minimum and the maximum transmittance for cylinders of radius 0.026 and 0.041 mm. with μ = 35.37 per cm. could be seen to be 0.781 and 0.855. These values compare favourably.

<u>Substance. K-H-di-p-nitrobenzoate crystal 1.</u>

Indice	ϕ	ψ	Transmittance
8,0,2	6	.135	.771
10,0,3	10	124	.778
13,0,5	20	101	.791
$\bar{5}$,0,1	26	179	.757
$\overline{13}$,0,1	37	146	.779
$\bar{6}$,0,3	51	-165	.777
$\overline{18}$,0,1	53	125	.808
$\overline{10}$,0,4	55	178	.779
$\overline{13}$,0,6	68	168	.783
$\overline{19}$,0,5	72	134	.800
$\bar{5}$,0,5	76	-147	.797
$\overline{18}$,0,8	86	143	.805
1,0,3	89	-64	.820
3,0,5	87	-46	.809
8,0,6	88	-15	.789
$\bar{1}$,0,3	68	-88	.821
$\bar{1}$,0,7	60	-63	.812
2,0,9	61	-37	.796
1,0,12	42	-23	.776
$\bar{7}$,0,8	30	-80	.796
$\bar{9}$,0,12	14	-53	.779
$\overline{16}$,0,10	84	30	.799
3,0,2	68	-137	.803
4,0,4	83	-141	.804



ϕ and ψ are the angles that the incident and the diffracted rays make with the c- axis.

APPENDIX II.

The sharpened Patterson function.

The Patterson function $P_{S(r)}$ for a distribution of a number of points of weight Z_n and situated at r_n is given by :

$$P_S(r) = \frac{1}{V} \sum_H \frac{|F(H)|^2}{\hat{f}^2} \exp\left[-2\pi i H\cdot r\right] \quad \ldots\ldots.(1)$$

(Lipson & Cochran 153.3)

where

$$\hat{f} = \frac{\sum f_n}{\sum_1^n Z_n} = \frac{\sum f_o}{\sum_1^n Z_n} \exp - \tfrac{1}{4} BS^2 \quad \ldots\ldots..(2)$$

It represents a set of points of weight $Z_n Z_m$ at distances $r_n - r_m$. The introduction of any function of S (where S is $2\sin\theta/\lambda$) as a modifying function for $|F|^2$ effects neither the spherical symmetry nor the position of the centres of the peaks. However, to be useful such a function M(S) should increase the height of the central maxima without introducing subsidiary maxima.

Patterson (1935) suggested the function:

$$\sqrt{M(S)} = \sum_{j=1}^{N} Z_j \Big/ \sum_{j=1}^{N} f_{oj}$$

Lipson and Cochran (Book. p.172) suggest:

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 \exp\left[-\frac{\pi^2}{p}S^2\right]$$

and give very useful tables of p versus peak diameter. We may write the above as:

$$M(S) = \left(\frac{1}{\hat{f}_o}\right)^2 \exp\left[-\left(\frac{\pi^2}{p} - \tfrac{1}{2}B\right)S^2\right] \quad \ldots\ldots\ldots\ldots(3)$$

If we define B_e as the effective Debye temperature factor parameter incorporated in the sharpening function:

$$M(S) = \left(\frac{1}{\hat{f}_o}\right)^2 \exp\left[\tfrac{1}{2} B_e S^2\right] \quad \ldots\ldots\ldots\ldots(4)$$

it follows that:

$$Be = B - \frac{19.7}{p} \quad \ldots\ldots\ldots\ldots(5)$$

We can see that:

(1) For point sharpening $p = \infty$ and $B_e = B$

(2) For Patterson sharpening $p = \frac{19.7}{B}$ and $B_e = 0$

(3) For no sharpening $p = 0$ and $B_e = -\infty$

A serious criticism of sharpening a Patterson function is that it renders the Fourier series divergent and strictly speaking devoid of meaning. However, experience has shown that with a judicious choice of the sharpening function this process is helpful. The extent of sharpening usefully attainable in a particular case largely depends on the range of the observed intensities and their accuracy (especially the high $\sin\theta$ terms. As the initial $h0\ell$ intensities were based on a three film series, I preferred moderate sharpening and chose $B_e = -1$. With $B_e = -1$ the sharpening function can be written as:

$$M(S) = \left\{\hat{f}_o \exp(\sin^2\theta/\lambda^2\right\}^{-2}$$

This function is particularly useful if it is intended to apply superposition methods to the resulting distribution because it does not introduce subsidiary minima and maxima. Mr. Clune, who has subsequently used this sharpening function in his successful 3D analysis of isoclovene supports this.

APPENDIX III.

Generalised crystal structure projections.

Corresponding to the electron density:

$$\rho(x,y,z) = \frac{1}{V} \sum\sum\sum F(hk\ell) \exp\left\{-2\pi i(hx + ky + \ell z)\right\} \quad .....(1)$$

Cochran and Dyer (Acta. Cryst. 1952, **5**, 624) define generalised projection of this distribution on a plane perpendicular to the b- axis as:

$$\rho_K(x,z) = b\int_0^1 \rho(x,y,z) \exp\left[2\pi i\, K\, y\right]dy \quad ....(2)$$

Substituting the value of $\rho(x,y,z)$ in (2), and using the fact that:

$$\int_0^1 \exp\left[2\pi i(K - k)y\right]dy = 1, \quad \text{when } k = K$$

$$\text{and is } = 0, \quad \text{when } k \neq K$$

they further obtain:

$$\rho_K\ (x,z) = \frac{1}{A} \sum_h \sum_\ell F(hK\ell) \exp\left[-2\pi i(hx + \ell z)\right] \quad .....(3)$$

Now with:

$$F(hK\ell) = A(hK\ell) + i\, B(hK\ell)$$

and $\rho_K(x,z) = C_K(x,z) + i\, S_K(x,z)$ ....(3b)

for a centrosymmetric group where B = 0 we have:

$$C_K(x,z) = \frac{1}{A} \sum_h \sum_\ell \left\{F(hK\ell) \cos 2\pi(hx + \ell z)\right\} \quad ......(4)$$

$$S_K(x,z) = -\frac{1}{A} \sum_h \sum_\ell \left\{F(hK\ell) \sin 2\pi(hx + \ell z)\right\} \quad ......(4b)$$

If the structure is composed of spherical atoms:

$$F(hK\ell) = \frac{1}{A}\sum_{n=1}^{N} f_n(hK\ell) \exp\left\{2\pi i(hx_n + Ky_n + \ell z_n)\right\} \ldots\ldots(5)$$

substituting in equation (3) and re-arranging we see that:

$$\rho_K(x,z) = \frac{1}{A}\sum_h \sum_\ell \sum_{n=1}^{N} f_n(hK\ell) \exp\left[-2\pi i\left\{h(x-x_n) + \ell(z-z_n)\right\}\right] \exp 2\pi iKy_n \ldots\ldots\ldots\ldots(6)$$

Writing $\sigma_{nK}(x,z) = \frac{1}{A}\sum_h \sum_\ell f_n(hK\ell) \exp\left\{-2\pi i(hx + \ell z)\right)$

and utilising (3b) we can split (6) into its real and imaginary parts as:

$$C_K(x,z) = \sum_{n=1}^{N} \sigma_n K\ (x-x_n,\ z-z_n) \cos 2\pi Ky_n \ldots\ldots(7)$$

$$S_K(x,z) = \sum_{n=1}^{N} \sigma_n K\ (x-x_n,\ z-z_n) \sin 2\pi Ky_n \ldots\ldots(7b)$$

In a triclinic crystal, simplification of $\sigma_n K$ of the type indicated by Lipson and Cochran (p.224) cannot be made as $f_n(hK\ell) \neq f_n(\bar{h}K\bar{\ell})$. This is implied but not explicitly stated in the book. A similar omission occurs in the paper by Rossmann and Shearer (Acta Cryst. 1958, 11, 829) when they write generalised density as:

$$\sigma_K(x-x_n,\ z-z_n) = \frac{1}{A}\sum_h \sum_\ell f(hk\ell)\cos 2\pi\left[h(x-x_n) + \ell(z-z_n)\right]$$

The general formulation should have $\exp 2\pi i$ instead of $\cos 2\pi$ on the R.H.S.

However, from (7) and (7b) we see that:

$$\frac{S_K(x,z)}{C_K(x,z)} = \tan 2\pi K y_n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Dr. J.S. Rollett's Fourier programme could be used for summations (4) and (4b), but in the latter case A had to be treated as B. This however does not involve any extra labour.

APPENDIX IV.

The unit cell parameters of Rb-H-di-o-nitrobenzoate.

These have been measured in a way similar to that for K-H-di-p-nitrobenzoate.

$Rb\,H(C_7H_4NO_4)_2$, mol.wt. 418.7, Triclinic pinakoidal

$a = 13.8, \quad b = 4.74, \quad c = 6.08\ \text{Å}$;

$\alpha = 100.5^\circ, \quad \beta = 99.4^\circ, \quad \gamma = 95.0^\circ$;

Unit cell volume 383.0 Å^3 ; assuming one molecule per cell,

d (cal.) = 1.815 g./cc. F(000) = 208 ;

Absorption co-efficient for X-rays:

$(\lambda = 1.542\ \text{Å}) = 53.0\ \text{cm}^{-1}$.

The estimated error in the above parameters may be as high as ½% for the cell lengths and 1° for angles.

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TABLE 1. Co-ordinates and Orthogonal Co-ordinates.

x, y, and z are expressed as fractions of axial lengths in 10^{-5} unit; X', Y' and Z' are orthogonal co-ordinates in Å. Y' is parallel to y; Z' is in the plane yz and perpendicular to y, whereas X' is perpendicular to both Y' and Z'.

	x	y	z	X'	Y'	Z'
K	09075	34914	14252	1.5140	1.2932	1.2475
O(1)	20249	-13449	14498	3.3782	-0.6851	0.8086
O(2)	24954	-29750	-01429	4.1632	-1.2339	-1.2062
O(3)	59816	57259	21544	9.9794	2.0630	-0.0411
O(4)	56426	69715	38155	9.4138	2.4489	1.9968
O(5)	11834	39474	-07826	1.9743	1.6382	-1.3880
O(6)	00551	14065	-17499	0.0919	0.6993	-2.0206
O(7)	17253	-52368	-61787	2.8784	-1.6872	-7.7746
O(8)	28551	-28577	-53461	4.7633	-0.8039	-7.2964
N(1)	55283	55892	28326	9.2231	1.9643	0.9226
N(2)	21792	-35078	-53672	3.6356	-1.0548	-7.0379
C(1)	25553	-13531	09116	4.2631	-0.6567	-0.0275
C(2)	33435	04238	13938	5.5781	0.0144	0.1934
C(3)	38818	08298	06542	6.4762	0.2255	-0.8759
C(4)	46070	23061	11710	7.6860	0.7733	-0.5891
C(5)	47530	37792	23075	7.9296	1.2827	0.6472
C(6)	42284	34705	30373	7.0544	1.1116	1.6996
C(7)	34986	18937	25634	5.8368	0.5200	1.4637
C(8)	07646	22000	-16724	1.2756	1.0036	-2.2287
C(9)	11485	07500	-26249	1.9161	0.4814	-3.4765
C(10)	06697	-11652	-36086	1.1172	-0.2133	-4.3994
C(11)	10039	-25701	-45330	1.6748	-0.7186	-5.5943
C(12)	18103	-19924	-44415	3.0202	-0.5043	-5.8270
C(13)	23040	-01721	-34710	3.8438	0.1526	-4.9255
C(14)	19601	11568	-25640	3.2701	0.6286	-3.7463
H(1)	37500	-02101	-02621	6.2563	-0.1252	-1.8668
H(2)	50380	25001	06841	8.4051	0.3813	-1.3251
H(3)	44079	44200	40219	7.3539	1.4198	2.7486
H(4)	30956	17900	30779	5.1645	0.4460	2.2195
H(5)	00740	-15101	-36201	0.1235	-0.3426	-4.1635
H(6)	06316	-12301	-53670	1.0537	-0.1077	-6.3907
H(7)	29170	01500	-34470	4.8665	0.2716	-5.1543
H(8)	22330	25100	-17620	3.7254	1.1125	-2.9449
H(9)	-	-	-	-	-	-

APPENDIX TO TABLE 1:

Co-ordinates and orthogonal co-ordinates of some symmetry related atoms.
(Dash means inversion at the true origin.)

	x	y	z	X'	Y'	Z'
O(3') + a	40184	-57259	-21544	6.7041	-2.2221	-4.1392
O(4') + a	43574	-69715	-38155	7.2696	-2.6080	-6.1771
O(4')+a+c	43574	-69715	61845	7.2696	-3.3542	5.2384
O(7) + c	17253	-52368	38213	2.8784	-2.4334	3.6410
O(8) + c	28551	-28577	46539	4.7633	-1.5500	4.1191
N(1') + a	44717	-55892	-28326	7.4603	-2.1233	-5.1029
N(2') + a	21792	-35078	46328	3.6356	-1.8010	4.3776
C(4') + a	53930	-23061	-11710	8.9974	-0.9324	-3.5912
C(5')+a+b	52470	62208	-23075	8.7538	2.6081	-4.8275
C(10') - c	-06697	11652	-63914	-1.1180	0.9607	-7.0350
C(11') - c	-10059	25701	-54670	-1.6760	1.4650	-5.8370
C(12)+c+b	18103	80076	55585	3.0237	2.7983	5.6043
H(2') + a	49620	-25001	-06841	8.2783	-1.0404	-2.8552
H(5') - c	-00740	15101	-63799	-0.1234	1.0888	-7.2521
H(6') - c	-06316	12301	-46330	-1.0537	0.8539	-5.0248

NOTE:

The y co-ordinate of atom C(8) obtained from ℓ.S refinement was 0.205 which puts this atom about 0.06 Å out of the plane of the benzenoid ring. As the hlℓ data does not determine the y- co-ordinate in the proximity of $y = \frac{1}{4}$, the s.d. for such y- co-ordinates is appreciably large. It may be estimated at 0.044 Å. Thus, by moving this atom on to the plane of the benzenoid ring, we have made a shift $\frac{3}{2}$ times its estimated standard deviation.

TABLE 2. Anisotropic Temperature Factor Parameters.
(10^{-5} unit)

Ap	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
K	577	6106	1474	-964	764	-334
O(1)	535	4136	1841	-1233	780	-539
O(2)	603	11816	1033	-1310	514	394
O(3)	844	22600	2423	-48	822	-1791
O(4)	910	20671	2281	-1462	437	-2183
O(5)	631	10660	1395	-1182	699	-323
O(6)	627	5339	2106	-1294	1060	-44
O(7)	961	14223	1589	-1627	764	-1253
O(8)	843	15423	2120	-2694	1342	514
N(1)	711	20300	1683	123	717	-677
N(2)	772	10341	1493	-1150	618	-1841
C(1)	687	3499	1602	552	1015	935
C(2)	536	3365	1568	564	734	700
C(3)	545	3969	1614	102	768	1758
C(4)	536	7714	1943	1439	737	651
C(5)	564	9998	1765	409	535	452
C(6)	635	10696	1456	1591	463	988
C(7)	639	6713	1477	617	740	603
C(8)	466	9154	1671	717	826	-208
C(9)	644	2402	1159	-1309	765	479
C(10)	522	9170	1438	-232	546	-268
C(11)	659	2837	1464	1707	364	175
C(12)	761	5324	1143	-204	828	1266
C(13)	556	6489	1444	-699	665	-729
C(14)	430	7705	1220	67	534	-162

Note: $T = 2^{-(B_{11}h^2 + B_{22}k^2 + B_{33}\ell^2 + B_{23}k\ell + B_{31}\ell h + B_{12}hk)}$

TABLE 3. Equivalent Isotropic B Values.

Atom	B//a	B//b	B//c	Atom	B//a	B//b	B//c
K	4.5	2.8	5.1	C(1)	5.3	1.6	5.5
O(1)	4.2	1.9	6.4	C(2)	4.2	1.5	5.4
O(2)	4.7	5.3	3.6	C(3)	4.2	1.8	5.6
O(3)	6.6	10.0	8.4	C(4)	4.2	3.5	6.7
O(4)	7.1	9.3	7.9	C(5)	4.4	4.5	6.1
O(5)	4.9	4.8	4.8	C(6)	4.9	4.8	5.0
O(6)	4.9	2.4	7.3	C(7)	5.0	3.0	5.1
O(7)	7.4	6.4	5.5	C(8)	3.6	4.1	5.8
O(8)	6.5	6.9	7.3	C(9)	5.0	1.1	4.0
				C(10)	4.0	4.1	5.0
N(1)	5.5	9.1	5.8	C(11)	5.1	1.3	5.1
N(2)	6.0	4.7	5.2	C(12)	5.9	2.4	4.0
				C(13)	4.3	2.9	5.0
				C(14)	3.3	3.5	4.2

TABLE 4. Standard deviations of co-ordinates and bond lengths (Å units).

Averaged for	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	σ r.m.s.
K	0.005	0.006	0.005	0.005_5
O(carboxyl)	0.013	0.016	0.014	0.014_4
O(nitroxyl)	0.017	0.020	0.017	0.018
N	0.018_5	0.023	0.018	0.020
C	0.020	0.025	0.021	0.022

Bond type	s.d.	Bond type	s.d.
K - O(carboxyl)	0.015	N - O	0.027
K - O(nitroxyl)	0.019	C - O	0.026
O - O(hydrogen bond)	0.020	C - C	0.031

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