THE CRYSTAL & MOLECULAR STRUCTURES
OF
p-TOLUIC ACID & 2-NITRO-4-METHYL BENZOIC ACID BY X-RAY DIFFRACTION

A Thesis submitted to the
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by

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MG. Takwale

(Murlidhar Gowind Takwale)

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ABSTRACT

In the present work, the crystal and molecular structures of p-toluic acid and 2-nitro-4-methyl benzoic acid have been determined by X-ray diffraction.

Crystals of p-toluic acid, $CH_3C_6H_4COOH$, are triclinic, space group $P\bar{1}$, with

$$a = 8.88, \quad b = 7.87, \quad c = 7.59\ \text{Å};$$
$$\alpha = 121.4^\circ, \quad \beta = 118.7^\circ, \quad \gamma = 93.9^\circ;$$
$$\rho_o,\ 1.251\ \text{gm.cm}^{-3}; \quad \rho_c \text{ for } Z = 2, \quad 1.256\ \text{gm.cm}^{-3}.$$

The trial structure was obtained from the (010) sharpened Patterson map. The structure was refined by the method of least squares to an R value of 0.106 for 852 observed reflections. The molecular dimensions are compared with those of related molecules. The average length of the aromatic bonds is 1.392 Å; the central bonds C(2)-C(3) and C(5)-C(6) are both 1.379 Å. The central bonds C(2)-C(3) and C(5)-C(6) are shorter than the average bond length of the remaining four aromatic bonds. The molecules as usual form dimers; the C-O bonds of the carboxylic group are both 1.292 ± 0.008 Å long. The carboxylic group has pronounced torsional oscillation with a root-mean-square amplitude of about 12°; the methyl group has a considerable vibration normal to the C-C bond.

Crystals of 2-nitro-4-methyl benzoic acid, $CH_3C_6H_3$ COOH NO_2, are monoclinic, space group $C_{2/c}$ with

a = 13.281, b = 11.048, c = 11.414 Å; β = 95.9°, ρ_o, 1.440 gm.cm^{-3}; ρ_c for Z = 8, 1.432 gm.cm^{-3}.

The structure was solved by direct methods and refined by the method of least squares to an R value of 0.089 for 1315 observed reflections. The molecular dimensions are compared with those of o-nitrobenzoic acid. The average C-C bond length of the aromatic ring is 1.388 Å. As in the case of p-toluic acid, the molecules form dimers; the C-O bonds of the carboxylic group are nearly equal (1.276 ± 0.004 Å and 1.265 ± 0.004 Å). The carboxylic group and the nitro group are out of the aromatic plane by 46.2° and 35.8° respectively.

A paper entitled "The structure of p-toluic acid" by M.G. Takwale and L.M. Pant is published in Acta Cryst. (1971), B27, 1152.

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LIST OF DIAGRAMS

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INTRODUCTION

The study of the internal arrangement of atoms in crystals began with the discovery of X-ray diffraction by crystals by Laue, Friedrich and Knipping in 1912. Their experiments proved the wave nature of X-rays as well as the triperiodic arrangement of atoms in crystals. The diffraction spots observed in the X-ray photographs were explained by W.L. Bragg as arising due to the reflection of X-rays by various sets of lattice planes in the crystal. W.H. Bragg (1915) suggested that since a crystal is periodic in three dimensions, it can be represented by a suitable Fourier series; each component of the Fourier series is a sinusoidal electron density distribution. If the magnitudes and relative phases of these electron density waves are known the structure can be obtained by summing the Fourier series. However, only the amplitudes of the electron density waves are known from the intensity data; the information about the phases is lost while recording the diffraction pattern of the crystal.

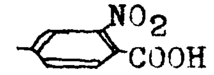
An attempt to overcome this difficulty was made by A.L. Patterson (1935). If the observed intensities are used as the coefficients of the Fourier series, the resultant synthesis gives a map of interatomic vectors rather than the atomic positions themselves; from this map it is generally possible to determine the structure.

Direct methods of determining crystal structures have been suggested by Karle and Hauptmann, Harker and Kasper, Goedkoop, Sayre and others since 1950. The direct methods of structure determination are based on the general relationship between the structure factors which must hold because of the physical nature of the crystals. For example, if all the atoms in the crystal lie on the crests of the electron density waves corresponding to the (h,k,l), (h',k',l') and (h+h', k+k', l+l') planes (i.e. if unitary structure factors U(h,k,l), U(h',k',l') and U(h+h', k+k', l+l') are all unity), the phases of the first two electron density waves will add up to that of the third. Sayre (1952) gave a set of relationships which exist among the structure factors of a crystal containing atoms of approximately equal diffracting power. The structure of 2-nitro-4-methyl benzoic acid described in this thesis was solved by using the Sayre's relations.

The parameters obtained from the trial structure are generally refined either by the difference synthesis or by the method of least squares. To obtain the difference Fourier map, the differences between the observed and calculated structure factors are used as the Fourier coefficients;

in the resulting map, incorrect positioning of the atoms is indicated when they lie on steep gradients. The method of 'Least Squares' is based on the minimisation, by adjusting the atomic and thermal parameters, of a weighted sum of squares of discrepancies between the observed and the calculated structure factors.

Owing to the development of fast electronic computers and of automatic diffractometers in recent years, it has become possible to determine complicated structures of biochemical interest such as proteins and nucleic acids. There is also considerable interest in determining simple structures in great detail so that a comparison of the structure with the results of quantum chemical calculations could be made. The accurate determination of simple structures can lead to a physical description of the chemical bond in terms of the electron density distribution between the bonded atoms. In this connection, mention may be made of the structure analyses of triazine (Coppens, 1967), oxalic acid dihydrate (Coppens, Sabine, Delaplane and Ibers, 1971) and Cyanuric acid (Verschoor and Keulen, 1971). In all these studies the final electron density difference maps show the bonding effects clearly.

In the present work, the precise structure analyses of p-toluic acid (CH$_3$COOH) and 2-nitro-4-methyl benzoic acid ( $CH_3C_6H_3(NO_2)COOH$) are undertaken in order to study the influence of methyl group substitution on the molecular structure. Methyl group is a weak electron donor group. The influence of NH_2 which is a strong electron donor has been studied in the structures of p-aminobenzoic acid, NH_2COOH (Lai and Marsh, 1967) and p-nitroaniline, NH_2NO_2 (Trueblood, Goldish and Donohue, 1961). It is of interest to study the influence of the methyl group in similar structures.

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PART - I : CRYSTAL AND MOLECULAR STRUCTURE OF p-TOLUIC ACID.

CHAPTER - I

EXPERIMENTAL

Crystals suitable for X-ray work were obtained by crystallizing the compound from toluene at room temperature. The crystals were colourless plates parallel to (001) face. They were cut into suitable sizes and the accurate setting of the crystal was done by the method of double oscillation (Davies, 1950). The preliminary values of axial lengths were obtained from rotation photographs taken with CuK_α radiation and the crystals oscillated about the three crystallographic axes in turn. Weissenberg photographs about three axes showed that the crystal belongs to the triclinic system; from these photographs α^*, β^* and γ^* were also determined.

Accurate determination of unit cell dimensions :

The accurate determination of cell dimensions was done with the help of high angle reflections in equatorial Weissenberg photographs because the large Bragg angles are very sensitive to small changes in cell dimensions; besides, the errors in the cell dimensions introduced due to non-coincidence of the camera axis and the axis of rotation of the crystal, as well as due to absorption and divergence of the X-ray beam, and due to film shrinkage become negligible at large θ. For p-toluic acid, the values of the spacings d_{100}, d_{010} and d_{001} determined from several high angle reflections were plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$ (Henry, Lipson and Wooster, 1961). The extrapolated values of spacings were in turn used to obtain more accurate values and they were again extrapolated to $\sin^2\theta = 1$. The values of the spacings d_{100}, d_{010} and d_{001} were calculated from the following relations :

For hk0 reflections,

$$d_{100} = \frac{\lambda}{2\sin\theta}\left[h^2 + \left(\frac{d_{100}}{d_{010}}\right)^2 k^2 + 2hk\left(\frac{d_{100}}{d_{010}}\right)\cdot\cos\gamma^*\right]^{1/2}$$

$$d_{010} = \frac{\lambda}{2\sin\theta}\left[\left(\frac{d_{010}}{d_{100}}\right)^2 h^2 + k^2 + 2hk\left(\frac{d_{010}}{d_{100}}\right)\cdot\cos\gamma^*\right]^{1/2}$$

For hol reflections,

$$d_{100} = \frac{\lambda}{2\sin\theta}\left[h^2 + \left(\frac{d_{100}}{d_{001}}\right)^2 l^2 + 2hl\left(\frac{d_{100}}{d_{001}}\right)\cos\beta^*\right]^{1/2}$$

$$d_{001} = \frac{\lambda}{2\sin\theta}\left[\left(\frac{d_{001}}{d_{100}}\right)^2 h^2 + l^2 + 2hl\left(\frac{d_{001}}{d_{100}}\right)\cos\beta^*\right]^{1/2}$$

For okl reflections,

$$d_{010} = \frac{\lambda}{2\sin\theta}\left[k^2 + \left(\frac{d_{010}}{d_{001}}\right)^2 l^2 + 2kl\left(\frac{d_{010}}{d_{001}}\right)\cos\alpha^*\right]^{1/2}$$

$$d_{001} = \frac{\lambda}{2\sin\theta}\left[\left(\frac{d_{001}}{d_{010}}\right)^2 k^2 + l^2 + 2kl\left(\frac{d_{001}}{d_{010}}\right)\cos\alpha^*\right]^{1/2}$$

The results are summarized in Tables I-1(a), I-1(b) and I-1(c) and corresponding graphs are shown in the Figures I-1(a), I-1(b) and I-1(c). From these spacings the cell dimensions were calculated by using the following relations:

$$a = \frac{d_{100}\sin\alpha^*}{A} \qquad b = \frac{d_{010}\sin\beta^*}{A} \qquad c = \frac{d_{001}\sin\gamma^*}{A},$$

where $A = \left[1+2\cos\alpha^*\cos\beta^*\cos\gamma^* - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^*\right]^{1/2}$.

The inter-axial angles α, β and γ were calculated by using the following formulae:

$$\cos\alpha = \frac{\cos\beta^*\cdot\cos\gamma^* - \cos\alpha^*}{\sin\beta^*\cdot\sin\gamma^*}$$

$$\cos\beta = \frac{\cos\alpha^*\cdot\cos\gamma^* - \cos\beta^*}{\sin\alpha^*\cdot\sin\gamma^*}$$

$$\cos\gamma = \frac{\cos\alpha^*\cdot\cos\beta^* - \cos\gamma^*}{\sin\alpha^*\cdot\sin\beta^*}$$

The final cell dimensions are

$a = 8.88$ Å $\alpha = 121.4^\circ$
$b = 7.87$ $\beta = 118.7$
$c = 7.59$ $\gamma = 93.9$

Table I-1(a) : Determination of d_{100}

h	k	l	θ	$\sin\theta$	$\sin^2\theta$	d_{100}
8	1	0	69.4°	0.9361	0.876	7.047 Å
$\bar{9}$	1	0	69.4	0.9361	0.876	7.054
$\bar{9}$	2	0	64.8	0.9048	0.819	7.047
$\overline{10}$	0	2	70.4	0.9421	0.888	7.051
$\overline{11}$	0	4	75.0	0.9659	0.933	7.053

The extrapolated value of d_{100} at $(\sin^2\theta=1)$= 7.057 ± 0.002 Å.

Table I-1(b) : Determination of d_{010}

h	k	l	θ	$\sin\theta$	$\sin^2\theta$	d_{010}
$\bar{2}$	8	0	70.8°	0.9444	0.892	6.063 Å
$\bar{4}$	8	0	67.4	0.9228	0.851	6.057
$\bar{5}$	8	0	68.3	0.9291	0.863	6.056
0	$\bar{4}$	8	74.6	0.9641	0.929	6.070

The extrapolated value of d_{010} at $(\sin^2\theta=1)$= 6.078 ± 0.001 Å.

Table I-1(c) : Determination of d_{001}

h	k	l	θ	$\sin\theta$	$\sin^2\theta$	d_{001}
$\bar{2}$	0	7	69.3°	0.9354	0.873	5.136 Å
$\bar{7}$	0	8	73.1	0.9568	0.910	5.145
$\bar{8}$	0	8	75.0	0.9659	0.933	5.147
0	$\bar{4}$	8	74.0	0.9613	0.929	5.148

The extrapolated value of d_{001} at $(\sin^2\theta=1)$ = 5.159 ± 0.001 Å.

The crystal density :

The crystal density was measured by the flotation method using a solution of lithium bromide in water. The observed density is 1.251 gm.cm^{-3}.

Number of molecules in a unit cell :

The number of molecules per unit cell (n) was obtained from the formula

$$n = \frac{VN\rho}{M}$$, where N = Avogadro's number,
M = the molecular weight,
V = volume of the unit cell,
and ρ = observed density.

The value of n was found to be 2 molecules per unit cell. The calculated density for Z = 2 is 1.256 gm.cm^{-3}.

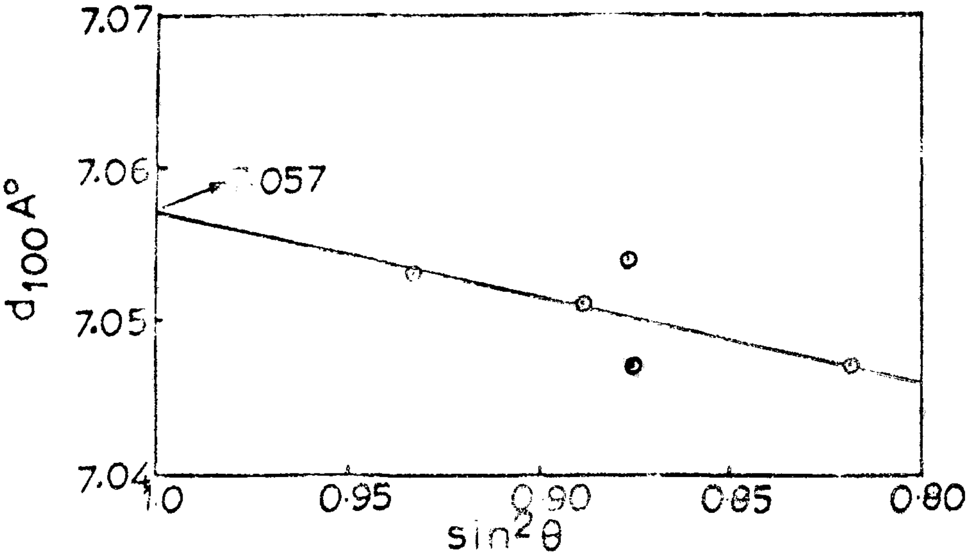
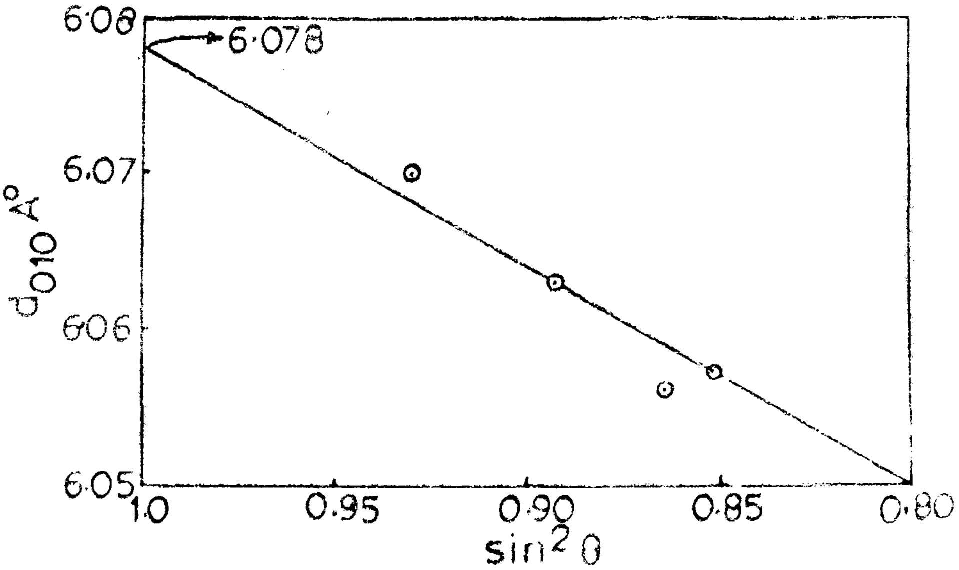
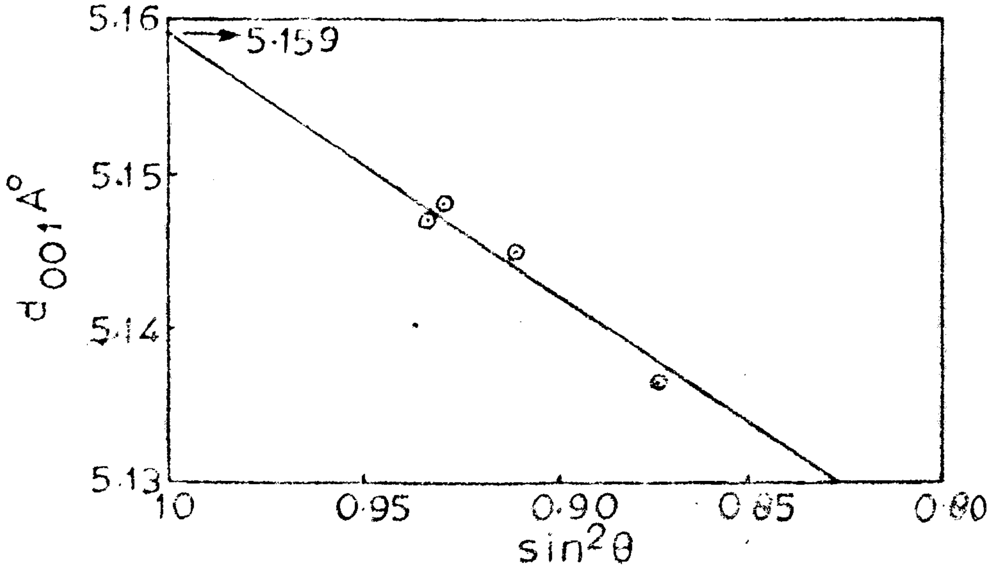


FIG 1·1(a)

FIG·1·1(b)





FIG·1·1(c)

FIG·1·1(a),(b),(c): EXTRAPOLATION GRAPHS FOR THE ACCURATE DETERMINATION OF d_{100}, d_{010} and d_{001}.

Linear absorption coefficient :

The linear absorption coefficient for CuK_α radiation was calculated by the formula

$$\mu = \rho \cdot \frac{\sum n \cdot \mu_g}{\sum n \cdot W}$$

where n is the number of atoms having atomic weight W and gram atomic absorption coefficient μ_g; the summation is done over all types of atoms present. Linear absorption coefficient for p-toluic acid is 9.2 cm^{-1}.

Collection of data :

The three dimensional intensity data were collected by the equi-inclination Weissenberg method using unfiltered copper radiation; sets of photographs were taken with different exposure times, using packs of three or four films in order to get all the reflections within the range of visual measurement. Zero to fourth layer Weissenberg photographs were taken with the crystal oscillated about the b axis, and zero to sixth layer photographs were taken with the crystal oscillated about the c axis. The crystals used for the two sets of photographs had the cross sections 0.5 x 0.5 mm^2 and 0.6 x 0.9 mm^2 and lengths 0.9 mm and 2 mm respectively. For each higher layer, two sets of photographs were taken; the oscillation range for the first set of photographs was 0-210° and for the second, 180°-360°. From the two sets of photographs (about the two axes) 1152 reflections were recorded out of which 300 were common to both the sets.

Estimation of intensity :

The intensities of the reflections were estimated visually with the help of calibrated intensity scales prepared with the same crystals. To prepare the intensity scale, a strong reflection from the zero layer Weissenberg photograph, having a good spot shape and which was sufficiently separated from the other reflections as well as from the β reflection of the same plane, was isolated within 10° oscillation range. By keeping the film cassette stationary, the exposure was given for one oscillation. The cassette was shifted by 5 mm and the next exposure was given for two oscillations. By increasing the number of oscillations each time, a series of 20 exposures were recorded on the film. Thus a set of diffraction spots of known relative intensities was obtained. This strip was used for the visual estimation of intensities. X-rays were generated by the stabilized X-ray generator (Philips PW1010), therefore errors in the intensity scale due to current and voltage fluctuations are not expected to be large. The visually estimated intensities were corrected for the following effects.

Lorentz and Polarization factor :

When an unpolarized X-ray beam is scattered by the crystal, the scattered X-ray beam is partially polarized;

the degree of polarization depends upon the Bragg angle θ. The polarization factor p, used to correct for the uneven diminution of intensity of the reflection having Bragg angle θ is given by

$$p = \frac{1}{2}(1 + \cos^2 2\theta)$$

The reciprocal lattice point has a finite size due to the mosaic character of the crystal. Therefore the reciprocal lattice point which passes through the Ewald sphere at grazing angle will have longer time to diffract the X-ray beam, than the one which passes through the Ewald sphere in the direction normal to the surface. Similarly the higher layers of reciprocal lattice points will have different speeds when they pass through the surface of Ewald sphere; both these effects are taken into account by the Lorentz factor, which for equi-inclination Weissenberg photograph is given by

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

where μ is the equi-inclination setting angle. Since Lorentz and polarization factor always occur together, it is convenient to combine them. The observed intensity is multiplied by $1/L_p$ to account for the Lorentz-polarization factor.

Effect of spot-extension :

When the mosaic-broadened reciprocal lattice point passes through the Ewald sphere, the moving cylindrical camera while recording upper layer reflections will, by its motion, tend to compress and sharpen the spots on one side of the film and broaden the spots on the other half of the film. When the film motion and spot growth are in the same direction, the spots get extended and when they are in opposite direction the spots are contracted. The intensity corrected for the effect of spot extension is given by $I = w.I_e$ where I_e is the intensity of the extended spot and w is the spot extension correction given by $w = \frac{A+\Delta A}{A}$, where A is the area of spot when the camera is stationary. The combined correction factors (w/L_p) were taken from the International Tables for X-ray Crystallography Vol. III. The correction was applied graphically.

Absorption correction :

When a crystal diffracts X-rays, the primary beam as well as diffracted beam is absorbed. As a result of absorption the diffracted beam is weaker than if there were no absorption; hence to account for the absorption of X-rays, the observed intensity is multiplied by absorption factor A^* given by

$$A^* = 1/A ,$$

where A is the transmission factor given by

$$A = \frac{1}{V} \int_V \exp\left[-\mu(p+q)\right] dV ,$$

where p and q are the lengths of the path of the incident and reflected beam in the crystal and μ is the linear absorption coefficient of the crystal.

For cylindrical crystals, the absorption factors A^* are tabulated in the International Tables for X-ray Crystallography Vol.II for various values of μR, where R is the radius of the crystal. For upper level equi-inclination Weissenberg photographs the correction can be found by using $\mu \sec \nu$ in place of μ and $\frac{\Upsilon}{2}$ in place of θ; $\frac{\Upsilon}{2}$ is given by $\sin \frac{\Upsilon}{2} = \sec \nu \, (\sin^2\theta - \sin^2\nu)^{1/2}$, where ν is the angle between the generator of the given layer line and the equatorial plane, and Υ is the angle between the projections of the incident and diffracted beams on the equatorial plane. The resultant correction for upper levels has to be multiplied by the factor $\sec \nu$, since the irradiated volume is greater by the factor $\sec \nu$ than the volume irradiated during the recording of zero-level.

In the present work, the intensities of the higher layer Weissenberg photographs were measured from the extended spots. The observed intensities were corrected for the effects of Lorentz-polarization factor, spot extension and absorption by the graphical method.

The corrected intensities from the data about the two axes were brought to the same scale by comparing intensities of the common reflections.

Scaling and temperature factor :

The observed intensities corrected for Lorentz and polarization factors are only relative. These can be put on an approximately absolute scale by Wilsons statistical method (1942). The observed intensity I can be expressed by

$$kI = I_o \exp\left[-2B\sin^2\theta/\lambda^2\right] ,$$

where k is the overall scale factor, I_o the absolute intensity and B the overall temperature factor.

Wilson showed that the average intensity $\langle I_o \rangle$ for a group of reflections having different hkl values but approximately the same value of sinθ is given by

$$\langle I_o \rangle = \sum_{j=1}^{n} f_j^2$$

where f_j is the atomic scattering factor for the mean value of sinθ range and the summation is taken over all the atoms in the unit cell. The mean value $\langle I \rangle$ in the region of sinθ is given by

$$\langle I \rangle = \frac{\sum I}{N} ,$$

where N is the number of reflections in the region and $\sum I$ is the sum of the intensities of the reflections in the corresponding sinθ range. Thus we can write

$$k.\langle I \rangle = \langle I_o \rangle \exp(-2B \sin^2\theta/\lambda^2)$$

$$k.\langle I\rangle = \left[\sum_{j=1}^{n} f_j^2\right] \exp\left(-2B \sin^2\theta/\lambda^2\right)$$

$$\log_e C = \log_e K + 2B \sin^2\theta/\lambda^2$$

where $$C = \sum_{j=1}^{n} f_j^2 \Big/ \langle I\rangle$$

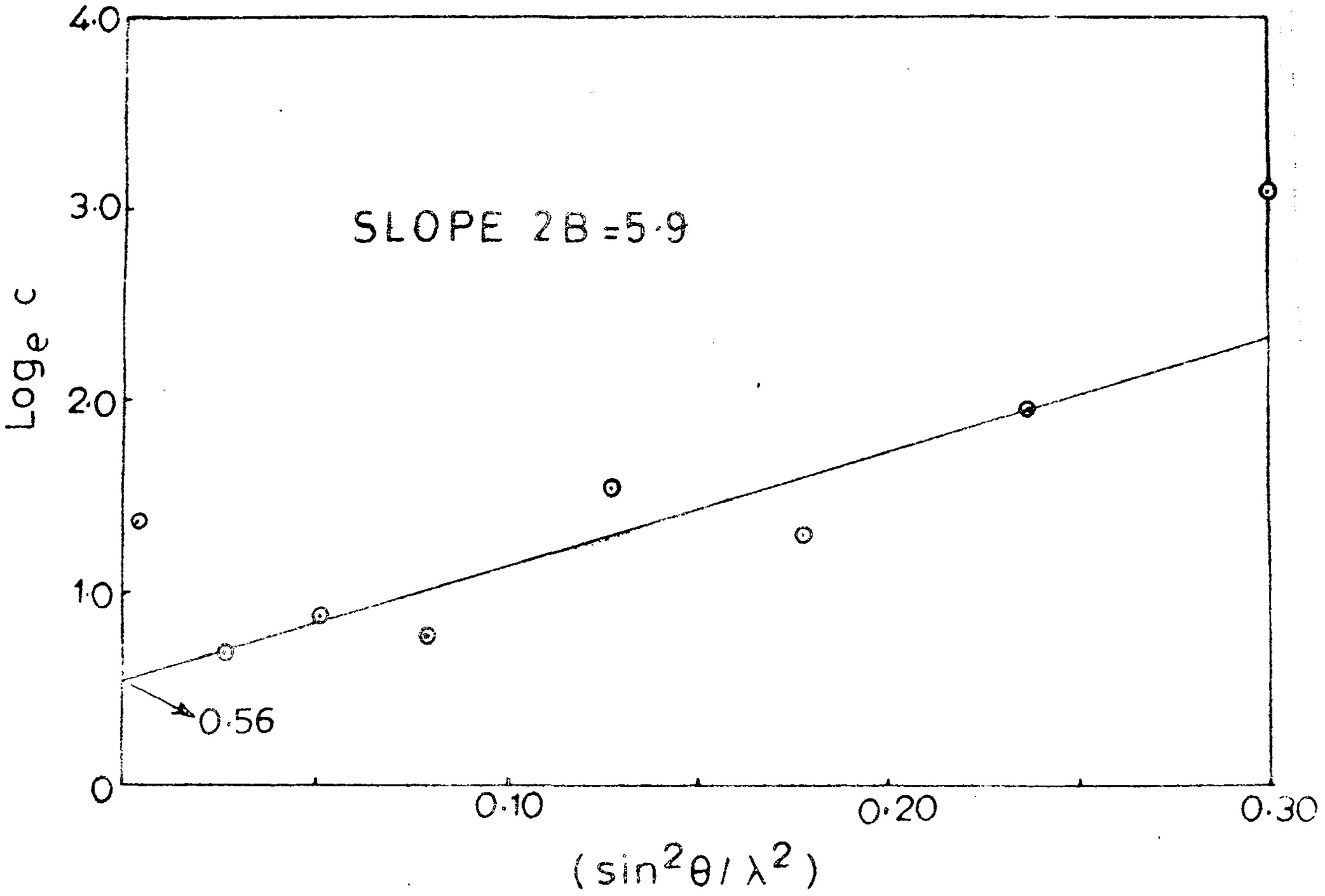
The graph of $\log_e C$ versus $\sin^2\theta/\lambda^2$ is a straight line whose intercept on the $\log_e C$ axis leads to the scale factor k and slope gives the value of 2B.

To obtain the scale factor and the temperature factor, the reflections from three dimensional data were divided into eight zones of sinθ (Table I-2).

Table I-2 : Determination of overall scale factor and temperature factor B.

sinθ zone	sinθ	$\sin^2\theta/\lambda^2$	$\sum f_j^2$	$\langle I_o\rangle$	C	$\log_e C$
0-0.20	0.10	0.004	740	188	3.938	1.371
0.20-0.30	0.25	0.026	440	224	1.963	0.674
0.30-0.40	0.35	0.052	287	120	2.392	0.872
0.40-0.50	0.45	0.085	179	85	2.105	0.744
0.50-0.60	0.55	0.127	117	25	4.752	1.559
0.60-0.70	0.65	0.178	85	23	3.637	1.291
0.70-0.80	0.75	0.237	70	9	7.352	1.995
0.80-0.90	0.85	0.304	59	3	22.380	3.108

For each zone, $\sum f_j^2$ was calculated by using the values of atomic scattering factors given in the International Tables



FIG·1·2: STATISTICAL DETERMINATION OF OVERALL SCALE FACTOR AND TEMPERATURE FACTOR B, FROM THREE DIMENSIONAL DATA for X-ray Crystallography Vol. III. The graph of $\log_e C$ was plotted against the mean value of $\sin^2\theta/\lambda^2$ (Figure I-2). From the graph, the overall scale factor is 1.75 and the temperature factor is 2.9 $\mathring{A}^2$.

Space group determination :

For the triclinic crystal the space group is either P1 or P$\bar{1}$. The structure analysis was done by assuming the space group to be P$\bar{1}$; further analysis of the structure confirmed this assumption.

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CHAPTER - II

STRUCTURE DETERMINATION

Fourier series :

A crystal can be regarded as a continuous distribution of electron density, which reaches to a maximum at the atomic centre and falls off asymptotically to zero in the space between the atoms. Since a crystal is a three dimensional periodic array of scattering matter, the electron density $\rho(x,y,z)$ at a point having fractional coordinates (x,y,z) within the crystal can be represented by a three dimensional Fourier series;

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{\infty} F(hkl) \exp\left\{-2\pi i(hx+ky+lz)\right\}, \qquad \ldots\ldots \text{II-1.}$$

where V is the volume of the unit cell. The Fourier coefficients $F(hkl)$, called structure factors, are in general complex and equal to $|F(hkl)| \cdot \exp(i\,\delta_{hkl})$. It can be shown that δ_{hkl} is the phase and $|F(hkl)|$ is the amplitude of the radiation scattered in the order h,k,l by the contents of one unit cell, taking the amplitude of the radiation scattered by a single classical electron under the same conditions as unity. To every reflection hkl given by the crystal, there corresponds one term in the Fourier series; each such term represents a plane sinusoidal distribution of scattering matter. If the amplitude and relative phase of each F(hkl) is known, the distribution of scattering matter can be determined by summing the Fourier series. In practice only magnitudes of structure factors are known from intensity data; the information about relative phases is lost while recording the intensities. One way to get rid of this difficulty is to use $|F(hkl)|^2$ as the Fourier coefficients instead of structure factors (Patterson, 1935).

Patterson series :

Patterson defined a function P(u,v,w) as

$$P(u,v,w) = V \iiint_0^1 \rho(x,y,z)\cdot\rho(x+u,\ y+v,\ z+w)\cdot dxdydz\,, \qquad \ldots\ldots\ \text{II-2.}$$

where $\rho(x,y,z)$ and $\rho(x+u,\ y+v,\ z+w)$ are the electron densities at points (x,y,z) and $(x+u,\ y+v,\ z+w)$ respectively. By substituting the values of $\rho(x,y,z)$ and $\rho(x+u,y+v,z+w)$ from equation II-1, the equation II-2 is reduced to

$$P(u,v,w) = \frac{1}{V}\sum_h \sum_k \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \exp 2\pi i(hu + kv + lw). \qquad \ldots\ldots\ \text{II-3.}$$

Since values of $|F(hkl)|^2$ are experimentally available, the series can be summed up without the knowledge of relative phases. It is clear from equation II-2 that the peaks in the Patterson map correspond to the interatomic vectors of the structure. Thus a pair of atoms A and B gives rise to the vectors $\underline{\underline{AB}}$ and $\underline{\underline{BA}}$ which are equal in magnitude but opposite in direction, and appear as peaks at (u,v,w) and $(\bar{u},\bar{v},\bar{w})$. The Patterson map will always be centrosymmetrical regardless of the space group of the crystal. Patterson map of a crystal containing N atoms in the unit cell will show N^2 peaks, out of which N peaks will fall at the origin, since they correspond to the interaction of these atoms with themselves. The remaining N(N-1) peaks are distributed over the unit cell of the same size as that of the crystal; half of these peaks are related to the other half by a centre of symmetry. The symmetry of the Patterson map of a crystal can be obtained by replacing all the translational symmetry elements of the space group of the crystal by the corresponding non-translational ones, and by adding a centre of symmetry in case of non-centrosymmetric structures. The Patterson map of a triclinic crystal will show $P\bar{1}$ symmetry while that of a monoclinic crystal will show 2/m symmetry. The peak height is proportional to the product of atomic numbers of the two atoms involved.

Since in the Patterson map N(N-1) peaks are distributed through the cell, there is generally a great deal of overlap among them. Therefore for a crystal structure containing moderate number of atoms of almost equal diffracting power, these peaks are not all resolved, hence the derivation of the original set of atoms which gives rise to the particular vector set becomesdifficult. In order to sharpen the Patterson peaks, various modifying functions are used (Kaelble; 1967). The modifying function M(s) used in the present work is given by

$$M(s) \quad = \quad (2\sin\theta)^{2} \quad = \quad S^{2},$$

where S in the reciprocal lattice vector of the corresponding reflection. The Patterson map is obtained by using $|F(hkl)|^2 \cdot S^2$ as the coefficients of the series. The modification reduces greatly the influence of low angle terms on the Patterson function which is useful when they are likely to be in error through extinction. However, the sharp peaks are surrounded by diffraction rings arising from the effects of series termination.

Sharpened Patterson map for (010) projection :

For (010) projection, Patterson function given by equation II-3 reduces to

$$P(u,o,w) \quad = \quad \frac{1}{A} \sum_{h} \sum_{l} |F(hol)|^{2} \cos 2\pi\,(hu + lw), \quad \ldots\ldots \quad \text{II-4.}$$

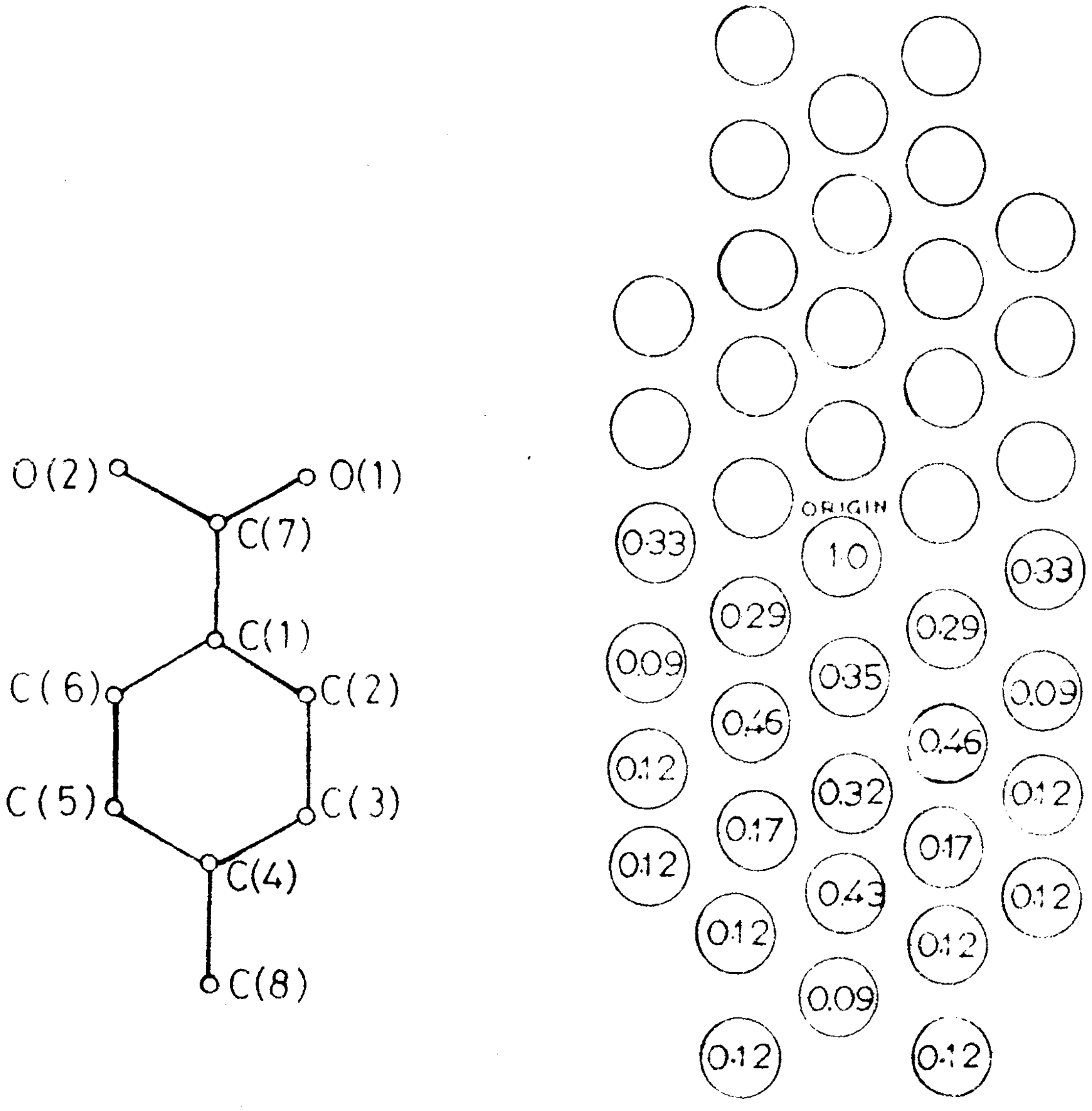
where A is the area of projected cell on (010) plane. The (010) sharpened Patterson map for p-toluic acid structure was obtained optically with the help of von Eller photosommateur (Figure II-2). The relative positions of atoms in one molecule are shown in Figure II-1(a). The molecule was assumed to be planar with usual bond lengths and angles. The corresponding weighted vector set is shown in Figure II-1(b). The heights of C-C, C-O and O-O Patterson peaks are assumed to be in the ratio 36:48:64. Since there are 20 non-hydrogen atoms in a unit cell, there will be 380 peaks distributed over the projected cell. This number is greatly reduced due to the presence of identical vectors in the molecule. For example vectors C(1)-C(2), O(2)-C(7) and C(5)-C(4) will give rise to the same Patterson peak. The orientation of the molecule in (010) projection could be fixed without difficulty and is shown on the Patterson map (Figure II-2). Assuming that the molecules form centrosymmetrical dimers, the positions of the atoms in the carboxylic group were fixed. The trial structure based on (010) Patterson map is shown in Figure II-3.

The atomic parameters obtained from the trial structure were used to calculate the structure factors, using the following formula :

$$F(hol) = \sum_{j=1}^{n} 2f_j \cos 2\pi(hx_j+lz_j), \qquad \ldots\ldots \quad II\text{-}5.$$

where n is the number of atoms in the molecule. The R factor for 36 reflections was 0.31. The phases obtained from the calculated structure factors were used to obtain (010) Fourier map, using the following relation :

$$\rho(x\ o\ z) = \frac{2}{A} \sum_{h} \sum_{l} F(hol) \cos 2\pi\,(hx+lz). \qquad \ldots\ldots \quad II\text{-}6.$$



(a)

(b)

FIG II 1(a) A MOLECULE OF p-toluic ACID, THE MOLECULE WAS ASSUMED TO BE PLANAR

(b) THE RELATIVE POSITIONS AND WEIGHTS OF THE PEAKS WHICH WILL OCCUR NEAR THE ORIGIN OF THE PATTERSON MAP OF p-toluic ACID

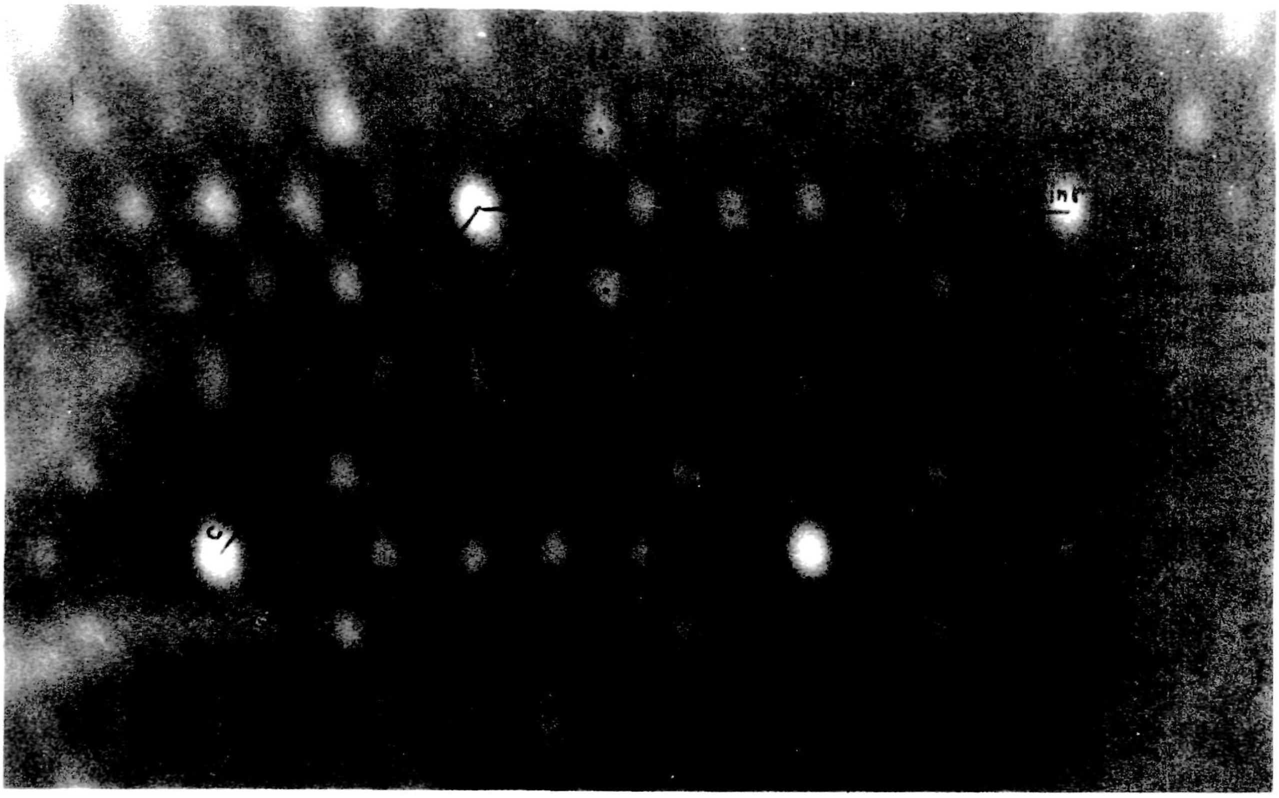


FIG-II-2: (010) PATTERSON MAP

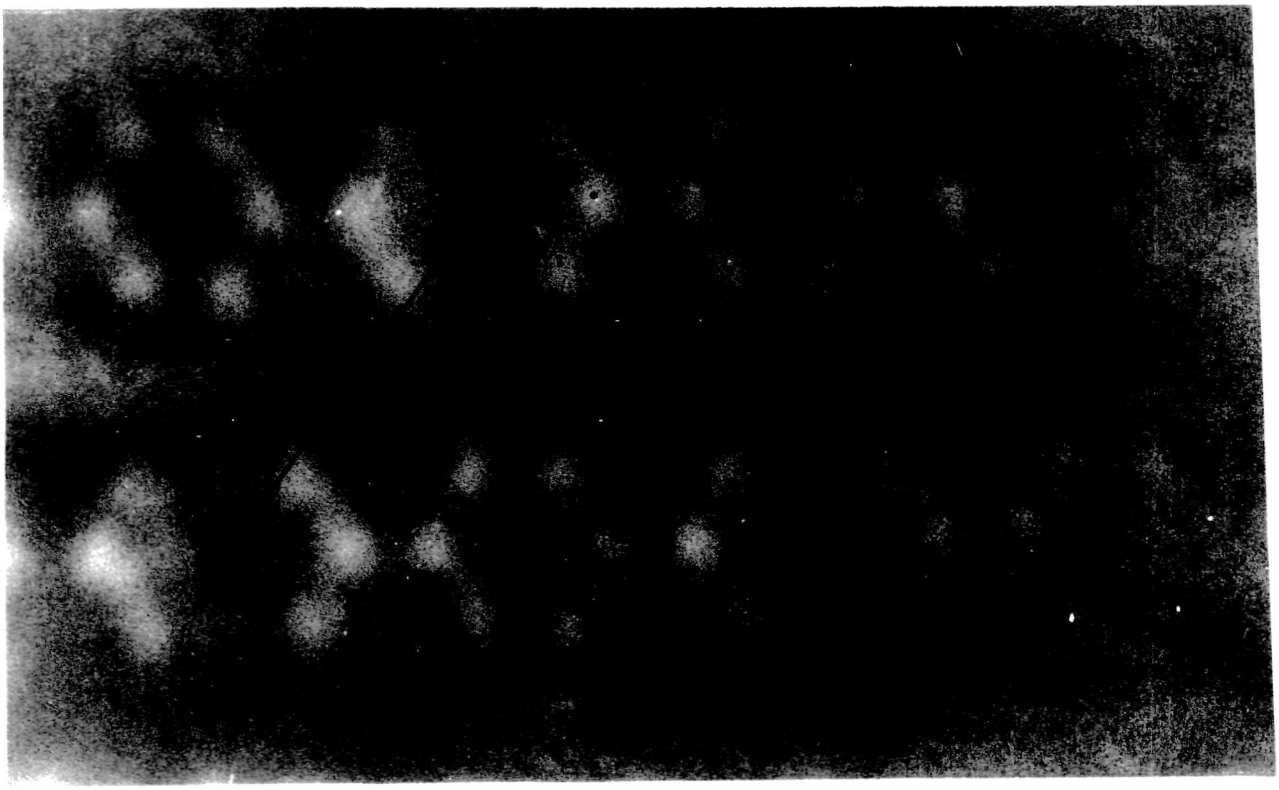


FIG-II-4: (010) FOURIER MAP

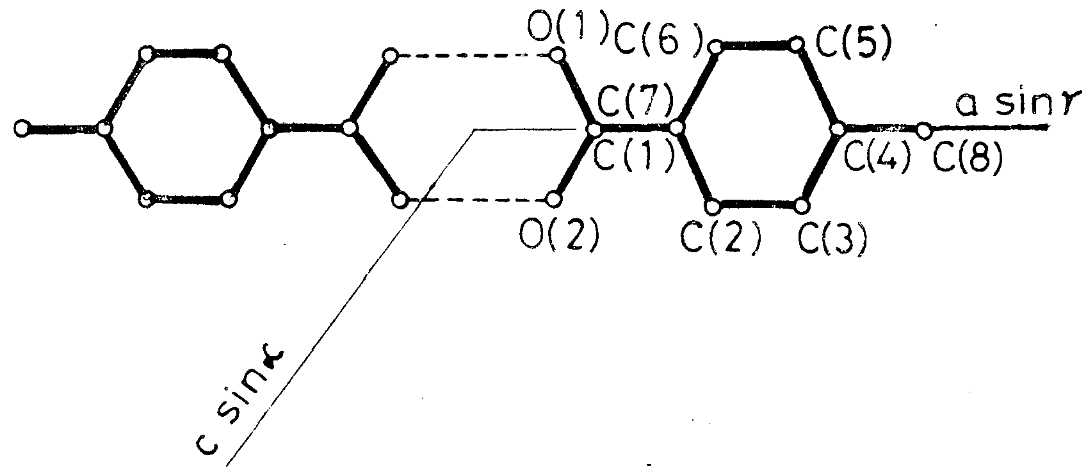


FIG-II-3: TRIAL STRUCTURE OF p-toluic ACID BASED ON (010) SHARPENED PATTERSON MAP.

The (010) Fourier map obtained by using von Eller Photosommateur is shown in Figure II-4. Since there was overlap of the peaks in the (010) Fourier map, the x and z parameters obtained from this projection were not refined further. The x and z atomic parameters were used to find the y parameter from stereochemical considerations. The y coordinates thus obtained were used to calculate hko structure factors; the R factor for 40 reflections was 0.35. The x, y and z parameters were refined from (100) and (001) projections.

The refinement of (x,y,z) parameters :

Difference Fourier map :-

The difference Fourier map is obtained by using F_o-F_c values as Fourier coefficients. When the position and temperature factor of an atom are correct, the difference Fourier map will be relatively smooth in the region near the atomic site. The incorrect position of the atom is indicated when assumed atomic position lies on a gradient $\partial\rho/\partial x_j$ in the difference Fourier map. The position of the atom can be corrected by shifting the atom along and up the gradient $\partial\rho/\partial x_j$. Also the incorrect temperature factor is indicated by a presence of residual electron density or hole at the assumed atomic position. Difference Fourier synthesis has two advantages, one is that when the phases are correct, it provides a direct measure of the errors between the model used and the true structure implied by the F_o's. The second advantage is that it is free from the effects of series termination.

The x and y parameters were refined by repeated difference Fourier maps in (001) projection, the corrections given to the atomic parameters were obtained approximately by trial. The R factor for 83 reflections was reduced from 0.35 to 0.19 by five cycles of refinement. At this stage temperature factor and scale factor were refined by Wilsons method and when new scale and temperature factors were used, R factor reduced to 0.17. The z coordinates were refined by using (100) difference Fourier maps. During the refinement of z parameters, y parameters were kept constant; three cycles of refinement brought R factor for 60 reflections from 0.26 to 0.20. The x, y and z parameters thus obtained (Table II-1) were used for further refinement by using three dimensional data.

Table II-1 : Fractional coordinates and temperature factors after the refinement

Atom	x	y	z	B Å^2
C(1)	0.364	0.179	0.005	2.9
C(2)	0.535	0.305	0.242	2.9
C(3)	0.688	0.383	0.247	2.9
C(4)	0.664	0.323	0.014	2.9
C(5)	0.474	0.197	-0.232	2.9
C(6)	0.324	0.118	-0.237	2.9
C(7)	0.209	0.097	0.000	2.9
C(8)	0.822	0.401	0.019	2.9
O(1)	0.246	0.156	0.228	2.9
O(2)	0.045	-0.032	-0.233	2.9

===

CHAPTER - III

REFINEMENT OF THE STRUCTURE

The refinement of atomic and thermal parameters was carried out on CDC-3600-160A computer at the Tata Institute of Fundamental Research, Bombay by the method of 'Least Squares', using three dimensional data.

The method of Least squares refinement :

Apart from the errors of measurements and any error in the atomic scattering factors used in the calculations, the difference between the observed and the calculated structure factor arises because of the errors in the atomic and thermal parameters as well as due to any error in the scale factor K. Assuming individual isotropic temperature factors, one may say that

$$\Delta F = F_o - F_c = \sum_{j=1}^{n} \left(\frac{\partial F}{\partial x_j} \Delta x_j + \frac{\partial F}{\partial y_j} \Delta y_j + \frac{\partial F}{\partial z_j} \Delta z_j + \frac{\partial F}{\partial B_j} \Delta B_j \right) + \frac{\partial F}{\partial k} \Delta k , \qquad \text{..... III-1.}$$

where n is the total number of atoms in an asymmetric unit in the crystal. Multiplying both the sides of equation III-1 by $w_{hkl} \dfrac{\partial F}{\partial x_j}$ and summing up for all hkl reflections, we get

$$\left.\begin{aligned}
\sum_{hkl} w_{hkl}\frac{\partial F}{\partial x_j}\Delta F &= \sum_{hkl} w_{hkl}\left(\frac{\partial F}{\partial x_j}\right)^2 \Delta x_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial x_j}\frac{\partial F}{\partial y_j}\Delta y_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial x_j}\frac{\partial F}{\partial z_j}\Delta z_j \\
&\quad + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial x_j}\frac{\partial F}{\partial B_j}\Delta B_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial x_j}\frac{\partial F}{\partial k}\Delta k . \\
&\text{Similarly} \\
\sum_{hkl} w_{hkl}\frac{\partial F}{\partial y_j}\Delta F &= \sum_{hkl} w_{hkl}\frac{\partial F}{\partial y_j}\cdot\frac{\partial F}{\partial x_j}\Delta x_j + \sum_{hkl} w_{hkl}\left(\frac{\partial F}{\partial y_j}\right)^2 \Delta y_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial y_j}\cdot\frac{\partial F}{\partial z_j}\Delta z_j \\
&\quad + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial y_j}\frac{\partial F}{\partial B_j}\Delta B_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial y_j}\cdot\frac{\partial F}{\partial k}\Delta k \\
\sum_{hkl} w_{hkl}\frac{\partial F}{\partial z_j}\Delta F &= \sum_{hkl} w_{hkl}\frac{\partial F}{\partial z_j}\frac{\partial F}{\partial x_j}\Delta x_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial z_j}\frac{\partial F}{\partial y_j}\Delta y_j + \sum_{hkl} w_{hkl}\left(\frac{\partial F}{\partial z_j}\right)^2 \Delta z_j \\
&\quad + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial z_j}\frac{\partial F}{\partial B_j}\Delta B_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial z_j}\cdot\frac{\partial F}{\partial k}\Delta k . \\
\sum_{hkl} w_{hkl}\frac{\partial F}{\partial B_j}\Delta F &= \sum_{hkl} w_{hkl}\frac{\partial F}{\partial B_j}\frac{\partial F}{\partial x_j}\Delta x_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial B_j}\frac{\partial F}{\partial y_j}\Delta y_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial B_j}\frac{\partial F}{\partial z_j}\Delta z_j \\
&\quad + \sum_{hkl} w_{hkl}\left(\frac{\partial F}{\partial B_j}\right)^2 \Delta B_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial B_j}\cdot\frac{\partial F}{\partial k}\Delta k \\
\sum_{hkl} w_{hkl}\frac{\partial F}{\partial k}\Delta F &= \sum_{hkl} w_{hkl}\frac{\partial F}{\partial k}\frac{\partial F}{\partial x_j}\Delta x_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial k}\frac{\partial F}{\partial y_j}\Delta y_j + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial k}\frac{\partial F}{\partial z_j}\Delta z_j \\
&\quad + \sum_{hkl} w_{hkl}\frac{\partial F}{\partial k}\frac{\partial F}{\partial B_j}\Delta B_j + \sum_{hkl} w_{hkl}\left(\frac{\partial F}{\partial k}\right)^2 \Delta k .
\end{aligned}\right\}\text{III-2}$$

w_{hkl} is the weight given to the hkl reflection. Equations III-2 represents a system of 4n+1 equations linear in 'S with 4n+1 unknowns. If anisotropic temperature factors of the form exp $(-\ b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl\ )$ are used for each atom, we will similarly have a system of 9n+1 linear equations in 9n+1 unknowns. We can determine 'S by solving these simultaneous equations. The equations III-2 may be represented in matrix notation as follows:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1m} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2m} \\ \vdots & \vdots & \vdots & & \vdots \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mm} \end{pmatrix} \times \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_m \end{pmatrix} = \begin{pmatrix} V_1 \\ V_2 \\ \vdots \\ V_m \end{pmatrix} \qquad \ldots\ldots \text{ III-3.}$$

The elements of the matrix are defined as

$$a_{11} = \sum_{hkl} w_{hkl} \left(\frac{\partial F}{\partial x_1}\right)^2, \quad a_{12} = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial y_1}, \quad a_{13} = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial z_1},$$

$$a_{14} = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_1} \frac{\partial F}{\partial B_1}, \quad a_{15} = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial x_2}, \quad \text{-----------},$$

$$a_{1m} = \sum_{hkl} w_{hkl} \left(\frac{\partial F}{\partial k}\right)^2, \quad a_{12} = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial y_1} \cdot \frac{\partial F}{\partial x_1}, \quad a_{22} = \sum_{hkl} w_{hkl} \left(\frac{\partial F}{\partial y_1}\right)^2,$$

$$\text{-----------------}, \ a_{mm} = \sum_{hkl} w_{hkl} \left(\frac{\partial F}{\partial k}\right)^2.$$

$X_1 = \Delta x_1, \quad X_2 = \Delta y_1, \quad X_3 = \Delta z_1, \quad X_4 = \Delta B_1,$
$X_5 = \Delta x_2, \text{-----------------}, X_m = \Delta k.$

$$V_1 = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_1} \Delta F, \quad V_2 = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial y_1} \Delta F,$$

$$V_3 = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial z_1} \Delta F, \quad V_4 = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial B_1} \Delta F,$$

$$V_5 = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial x_2} \Delta F, \text{-----------}, V_m = \sum_{hkl} w_{hkl} \frac{\partial F}{\partial K} \Delta F.$$

A short notation of equation III-3 is

$$A.X = V \qquad \ldots\ldots \quad \text{III-4.}$$

A is a mxm symmetrical matrix because $a_{ij} = a_{ji}$. The solution of equation III-4 is given by

$$X = A^{-1} V \qquad \ldots\ldots \quad \text{III-5.}$$

where A^{-1} is the inverse matrix of A. From equation III-5, we get

$$\begin{array}{ccccccccc}
\Delta x_1 = X_1 & = & C_{11}V_1 & + & C_{12}V_2 & + & C_{13}V_3 & + \text{----------} + & C_{1m}V_m \\
\Delta y_1 = X_2 & = & C_{21}V_1 & + & C_{22}V_2 & + & C_{23}V_3 & + \text{----------} + & C_{2m}V_m \\
\vdots & & \vdots & & \vdots & & \vdots & & \vdots \\
\Delta k = X_m & = & C_{m1}V_1 & + & C_{m2}V_2 & + & C_{m3}V_3 & + \text{----------} + & C_{mm}V_m
\end{array}$$

$$\ldots\ldots \quad \text{III-6.}$$

The corrections given by equations III-6 are applied to the atomic and thermal parameters and to the scale factor; the refinement is repeated till the R factor converges to the lowest value. Some of the off-diagonal terms of matrix A can be omitted to reduce the computation. A commonly used approximation is that of omitting all off-diagonal terms except those between the atomic parameters of the same atom and those between b_{ij}'s of the same atom. In this way a 3 x 3 matrix and a 6 x 6 matrix are computed for each atom. Since the overall scale factor K is highly correlated to the mean isotropic temperature factor, the term giving interaction between these two parameters must also be included in the calculation when refinement involves individual isotropic temperature factors (Rollett, 1965).

Refinement using isotropic temperature factor :

For the refinement of atomic parameters and individual isotropic temperature factors, 851 observed reflections were used; the reflection 001 appears to be subject to extinction and was excluded from the refinement. Structure factors were calculated from the following expression :

$$F_c(hkl) = \sum_{j=1}^{n} 2f_j \exp\left(-B_j \sin^2\theta/\lambda^2\right)\cdot\cos 2\pi\,(hx_j+ky_j+lz_j) \qquad \ldots\ldots \text{III-7.}$$

The atomic scattering factor f_j was calculated by using formula

$$f_j = A \exp(-ap^2) + B \exp(-bp^2) + C \quad \ldots\ldots \quad \text{III-8.}$$

where $p = \sin\theta/\lambda$. The five analytical constants A, a, B, b and C for the elements were taken from F. H. Moore's Tables (1963) and are tabulated in Table III-1.

Table III-1 : Analytical constants for atomic scattering factors for Cu range

Element	A	a	B	b	C
C	1.620	6.785	2.988	28.126	1.380
N	2.708	7.081	2.810	23.810	1.474
O	3.811	6.363	2.633	21.191	1.550
H	0.4629	9.077	0.5148	33.154	0.0207

The positional parameters were refined by using 3 x 3 matrix for each atom. The individual isotropic temperature parameters were refined by diagonal approximation; the term giving the interaction between the scale and the temperature factor was included in the calculations (Rollett, 1965). The R factor for all reflections using an overall temperature factor (2.9 Å^2) obtained by Wilson's method was 0.31; it reduced to 0.23 after six cycles of refinement. The structure was further refined after removing some numerical errors, R came down to 0.195. The anisotropic temperature factors were then introduced in the calculation. The individual isotropic temperature factors of the last cycle of refinement are given in the Table III-2.

Table III-2

Atom	B	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	3.19	0.0160	0.0217	0.0304	0.0079	0.0162	0.0133
C(2)	4.10	0.0206	0.0279	0.0390	0.0102	0.0208	0.0171
C(3)	4.31	0.0217	0.0293	0.0410	0.0107	0.0219	0.0180
C(4)	4.64	0.0233	0.0315	0.0442	0.0115	0.0236	0.0194
C(5)	4.42	0.0222	0.0300	0.0421	0.0109	0.0224	0.0185
C(6)	4.22	0.0212	0.0287	0.0402	0.0105	0.0214	0.0176
C(7)	3.32	0.0167	0.0226	0.0316	0.0082	0.0169	0.0139
C(8)	5.91	0.0297	0.0401	0.0562	0.0146	0.0300	0.0247
O(1)	4.24	0.0213	0.0288	0.0404	0.0105	0.0215	0.0177
O(2)	4.20	0.0211	0.0285	0.0400	0.0104	0.0213	0.0176

Refinement using anisotropic temperature factor :

The expression for the structure factor F(hkl) in terms of anisotropic thermal parameters b_{ij} for the space group P$\bar{1}$ is given by

$$F(hkl) = 2 \sum_{j=1}^{n} f_j \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)\right] \cdot \cos 2\pi (hx_j + ky_j + lz_j)$$

..... III-9.

b_{ij}'s corresponding to the isotropic temperature factor B were obtained as follows:

The isotropic temperature factor of an atom for a reflection having Bragg angle θ is given by

$$T = \exp\left(\frac{-B\sin^2\theta}{\lambda^2}\right) = \exp\left(-\frac{B}{4} \cdot \left(\frac{2\sin\theta}{\lambda}\right)^2\right) = \exp\left(-\frac{BS^2}{4}\right)$$

..... III-10.

where S $\left(= \frac{2\sin\theta}{\lambda}\right)$ is the reciprocal lattice vector, it is given by

$$S = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*,$$

i.e. $$S^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hk\, a^*b^* \cos\gamma^* + 2kl\, b^*c^*\cos\alpha^* + 2hl\, a^*c^*\cos\beta^*$$

..... III-11.

Substituting the value of S in equation III-10 we get

$$T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)\right] \quad \ldots\ldots \text{ III-12.}$$

where

$$b_{11} = \frac{Ba^{*2}}{4}, \qquad b_{22} = \frac{Bb^{*2}}{4}, \qquad b_{33} = \frac{Bc^{*2}}{4},$$

$$b_{12} = \frac{Ba^{*}b^{*}\cos\gamma^{*}}{4}, \quad b_{23} = \frac{Bb^{*}c^{*}\cos\alpha^{*}}{4}, \quad b_{13} = \frac{Ba^{*}c^{*}\cos\beta^{*}}{4}.$$

The values of b_{ij}'s for different atoms are given in Table III-2. These b_{ij}'s were used as starting thermal parameters for the further refinement.

The refinement of the atomic and thermal parameters was carried out by using 3 x 3 matrix for the atomic parameters of each atom and 6 x 6 matrix for anisotropic thermal parameters of each atom; unit weight was applied to all the reflections. Six cycles of refinement brought R value to 0.126.

The positions of the hydrogen atoms attached to the benzene ring were calculated from geometrical considerations of the molecule, assuming C-H distance to be equal to 1.08 Å. The hydrogen atoms of the methyl group were located from the three difference Fourier projections. The temperature factors of the hydrogen atoms were assumed to be the same as those of the carbon atoms to which they are attached; only their atomic parameters were refined. The hydrogen atom attached to the carboxylic group could not be located in the difference maps.

About 300 unobserved reflections were included in the structure factor calculations. The unobserved reflections for which F_c was greater than the minimum observable value were included in the refinement. All absent reflections were excluded from the estimation of R factor. For the further refinement of the structure, the following weighting scheme (Hughes, 1941) was used,

$$w \propto \frac{1}{|F_o|^2} \quad \text{for} \quad F_o > 4\,|F_{min}|$$

$$w \propto \frac{1}{16\,|F_{min}|^2} \quad \text{for} \quad F_o < 4\,|F_{min}| \; .$$

Four more cycles of refinement were given after including the hydrogen atoms of the benzene ring and of the methyl group. The final value of R for the observed reflections was 0.106. The final atomic and thermal parameters along with their estimated standard deviations are given in Table III-3. The standard deviations are given by (Stout and Jensen, 1968)

$$\sigma_{pi} = \sqrt{c_{ii}\left(\sum_{hkl} w_{hkl}\,\Delta F^2\right)/(m-n)}$$

where σ_{pi} is the standard deviation for a parameter p_i, c_{ii} is the ith diagonal element of the inverse matrix A^{-1},

Table III-3 : Final atomic and thermal parameters

The anisotropic thermal parameters ($\times 10^4$) are of the form $T = \exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2 + 2b_{12}hk+2b_{23}kl+2b_{13}hl)\right]$

The e.s.d.'s are given in parentheses and refer to last significant figures.

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	0.3607 (6)	0.1762 (7)	0.0007 (8)	175 (9)	296 (14)	348 (19)	93 (9)	226 (15)	158 (12)
C(2)	0.5453 (6)	0.3086 (8)	0.2299 (9)	200 (11)	325 (16)	390 (21)	90 (11)	215 (16)	172 (13)
C(3)	0.6910 (7)	0.3828 (8)	0.2307 (10)	181 (10)	332 (17)	505 (25)	67 (11)	248 (18)	177 (14)
C(4)	0.6588 (7)	0.3264 (8)	0.0039 (11)	240 (12)	324 (16)	719 (31)	148 (12)	363 (20)	314 (17)
C(5)	0.4754 (7)	0.1973 (9)	-0.2229 (11)	263 (13)	490 (22)	545 (27)	190 (14)	373 (22)	272 (17)
C(6)	0.3268 (7)	0.1204 (9)	-0.2298 (10)	233 (12)	437 (20)	438 (23)	132 (12)	349 (19)	206 (14)
C(7)	0.2030 (6)	0.0964 (7)	-0.0031 (9)	195 (10)	293 (15)	448 (22)	108 (10)	256 (16)	205 (13)
C(8)	0.8208 (8)	0.4053 (10)	0.0097 (10)	302 (15)	528 (25)	915 (41)	190 (16)	542 (29)	391 (22)
O(1)	0.2385 (4)	0.1586 (6)	0.2099 (6)	208 (8)	448 (13)	389 (14)	66 (8)	246 (12)	185 (9)
O(2)	0.0376 (4)	-0.0311 (6)	-0.2187 (6)	154 (7)	499 (14)	372 (14)	49 (8)	273 (12)	123 (8)

continued .....

Table III-3 (continued)

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
H(1)	0.580 (7)	0.322 (9)	0.382 (10)						
H(2)	0.809 (7)	0.459 (9)	0.377 (10)						
H(3)	0.455 (8)	0.171 (10)	-0.335 (11)						
H(4)	0.202 (8)	0.025 (10)	-0.393 (11)						
H(5)	0.778 (9)	0.420 (10)	-0.103 (11)						
H(6)	0.891 (9)	0.345 (10)	0.038 (11)						
H(7)	0.897 (9)	0.560 (10)	0.129 (11)						

m the number of structure factors used for refinement, and n the number of parameters.

The observed structure factors F_o, and the structure factors F_c calculated on the basis of final atomic and thermal parameters are given in Appendix A.

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CHAPTER - IV

RESULTS AND DISCUSSION

SECTION A : CRYSTAL AND MOLECULAR STRUCTURE

The bond lengths and bond angles are given in Table IV-1, and are also shown in the Figure IV-1. The C(7)-O(1), C(7)-O(2) and C(4)-C(8) bond lengths have been corrected for the effects of librational motion; the method of applying the correction is given in Section B of this chapter (p.56). The standard deviations in the bond lengths are given by

$$\sigma^2(l_{12}) = \sigma^2(x_1) + \sigma^2(x_2), \qquad \ldots\ldots \quad \text{IV-1.}$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the deviations in the atomic positions of atoms (1) and (2) respectively, and $\sigma(l_{12})$ is the standard deviation of the length between them. The standard deviations in atomic positions are assumed to be isotropic. The standard deviation $\sigma(\theta)$ in the bond angle is given by

$$\sigma^2(\theta) = \frac{\sigma^2(x_1)}{l_{12}^2} \quad \frac{l_{13}^2}{l_{12}^2 \cdot l_{23}^2}\,\sigma^2(x_2) + \frac{\sigma^2(x_3)}{l_{23}^2} \qquad \ldots\ldots \quad \text{IV-2.}$$

where θ is the angle subtended at atom (2) by the bonds from atoms (1) and (3). $\sigma(x_1)$, $\sigma(x_2)$ and $\sigma(x_3)$ are the standard

Table IV-1 : Intramolecular bond lengths and angles.

	Bond length (Å)			Angle	
	Uncorrected	Corrected	E.s.d.		
C(1)-C(2)	1.394 Å		0.009 Å	C(6)-C(1)-C(2)	118.7 ± 0.7°
C(2)-C(3)	1.379		0.009	C(1)-C(2)-C(3)	120.2 ± 0.7
C(3)-C(4)	1.398		0.010	C(2)-C(3)-C(4)	121.4 ± 0.7
C(4)-C(5)	1.383		0.010	C(3)-C(4)-C(5)	118.5 ± 0.7
C(5)-C(6)	1.379		0.010	C(4)-C(5)-C(6)	121.5 ± 0.7
C(6)-C(1)	1.421		0.009	C(5)-C(6)-C(1)	119.8 ± 0.7
C(1)-C(7)	1.476		0.009	C(3)-C(4)-C(8)	120.2 ± 0.8
C(4)-C(8)	1.499	1.514 Å	0.011	C(5)-C(4)-C(8)	121.4 ± 0.8
C(7)-O(1)	1.272	1.292	0.008	C(2)-C(1)-C(7)	120.9 ± 0.7
C(7)-O(2)	1.275	1.292	0.008	C(6)-C(1)-C(7)	120.5 ± 0.7
O(1)-O'(2) $(x,y,z)-(\bar{x},\bar{y},\bar{z})$	2.629		0.006	C(1)-C(7)-O(1)	118.3 ± 0.6
				C(1)-C(7)-O(2)	118.8 ± 0.6
C(2)-H(1)	0.98		0.07	O(1)-C(7)-O(2)	122.9 ± 0.6
C(3)-H(2)	0.89		0.07	C(7)-O(1)-O'(2) $(\bar{x},\bar{y},\bar{z})$	117.2 ± 0.6
C(5)-H(3)	0.68		0.08		
C(6)-H(4)	0.97		0.07		
C(8)-H(5)	0.83		0.09		
C(8)-H(6)	0.82		0.09		
C(8)-H(7)	0.96		0.09		

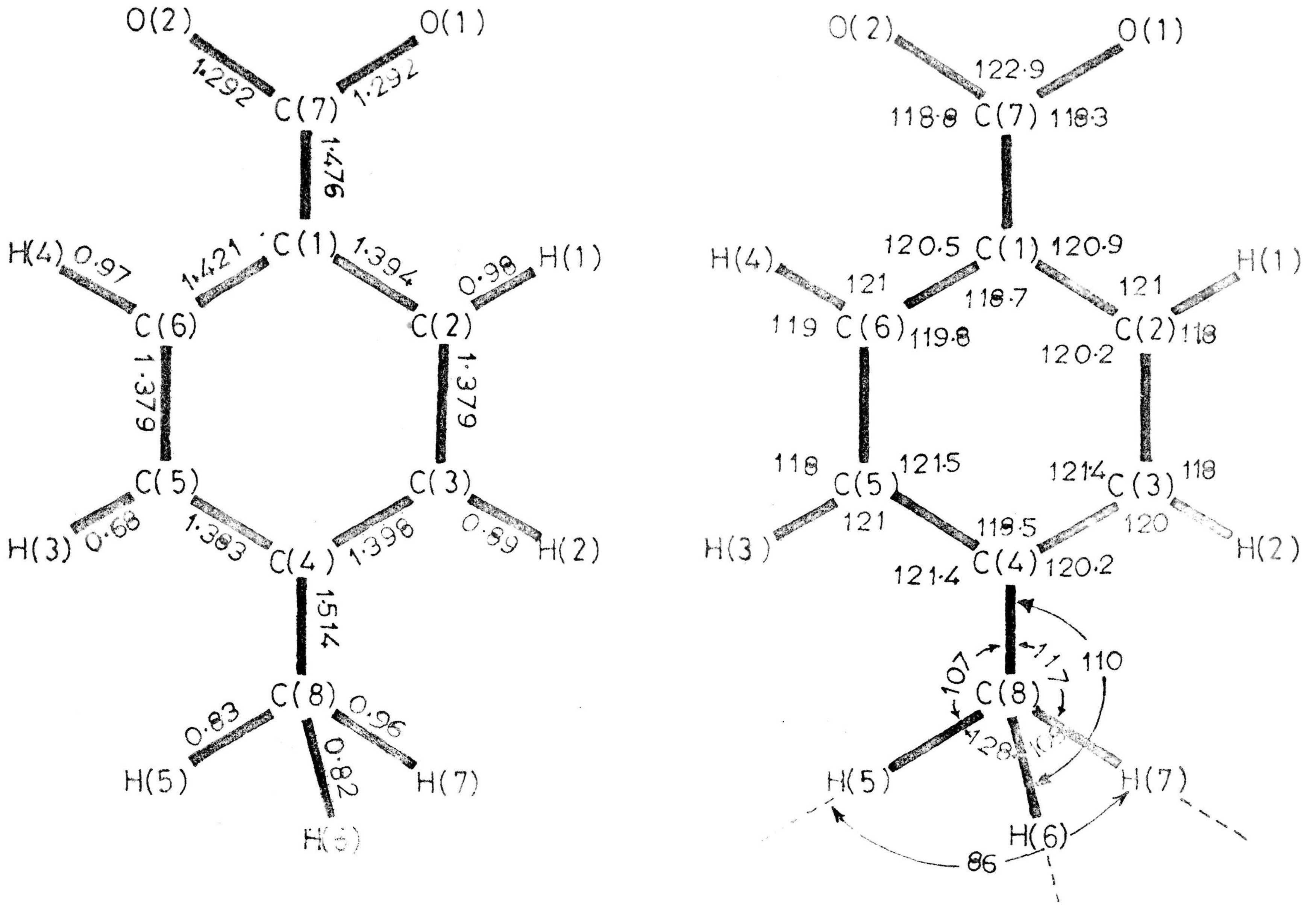


FIG-IV·1: BOND LENGTHS (A°) AND BOND ANGLES (°) OF p-toluic ACID deviations of the coordinates of the atoms (1), (2) and (3), and l_{12}, l_{13} and l_{23} are the lengths of bonds between atoms (1) and (2), atoms (1) and (3) and atoms (2) and (3) respectively.

The equations of various planes referred to the a, b', c' orthogonal axes such that ab and ab' planes are the same, are given in Table IV-2. The transformation equations are given by

$$\left.\begin{aligned}
x' &= x + y\cos\gamma + z\cos\beta \\
y' &= y\sin\gamma + \frac{z\,(\cos\alpha - \cos\beta\,.\cos\gamma)}{\sin\gamma} \\
z' &= \frac{z\,(1-\cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\,.\,\cos\beta\cdot\cos\gamma)^{1/2}}{\sin\gamma}
\end{aligned}\right\} \qquad \ldots\ldots \quad \text{IV-3.}$$

The equations of planes were obtained by the method of Schomaker, Waser, Marsh and Bergman (1959). The angles between these planes and deviations of atoms from different planes are also given in Table IV-2.

DISCUSSION :

Molecular Structure

(a) The aromatic ring

The aromatic ring in the p-toluic acid molecule is planar within 0.007 Å. The average length of the aromatic bonds is normal (1.392 Å). The estimated standard deviations

Table IV-2 : Equations of planes.

(1) Benzene ring	$-0.4052\,x' + 0.8810\,y' + 0.2442\,z' - 0.0377 = 0$
(2) Plane through O(1), O(2), C(7) and C(1)	$-0.4070\,x' + 0.8923\,y' + 0.1954\,z' - 0.0312 = 0$
(3) Plane through O(1), O(2) and Origin	$-0.3850\,x' + 0.9024\,y' + 1932\,z' = 0$

Angles between different planes.

	(2)	(3)
(1)	2.9°	3.4°
(2)	-	1.6°

Deviations of atoms from different planes (Å)

Atom	Planes (1)	(2)	(3)
C(1)	- 0.003	0.000	0.049
C(2)	0.000		
C(3)	0.005		
C(4)	- 0.007		
C(5)	0.005		
C(6)	0.000		
C(7)	0.000	- 0.001	0.014
C(8)	- 0.034		
O(1)	0.057	0.000	0.000
O(2)	- 0.052	0.000	0.000
Dimer Centre	0.038	0.031	0.000

(e.s.d.) of the C-C bond lengths are from 0.009 Å to 0.010 Å. The central bonds C(2)-C(3) and C(5)-C(6) are both 1.379 Å long while the average length of the other four aromatic bonds is 1.399 Å. The general picture thus resembles that found in the cases of p-aminobenzoic acid, β-p-nitrophenol, p-nitrotoluene, p-nitroaniline, β-sulphanilamide, terephthalic acid and p-nitrobenzoic acid (Table IV-3). The Figures IV-2(a) and (b) show the molecular dimensions of some of these compounds and Table IV-3 gives the averages of the two central bonds and the averages of the remaining four bonds of the aromatic ring in these molecules. In all these molecules the central bonds of the aromatic ring are shortened.

For a molecule having an electron donor and an electron acceptor group in para positions, cooperative interaction between the para-substituents is expected as shown below:

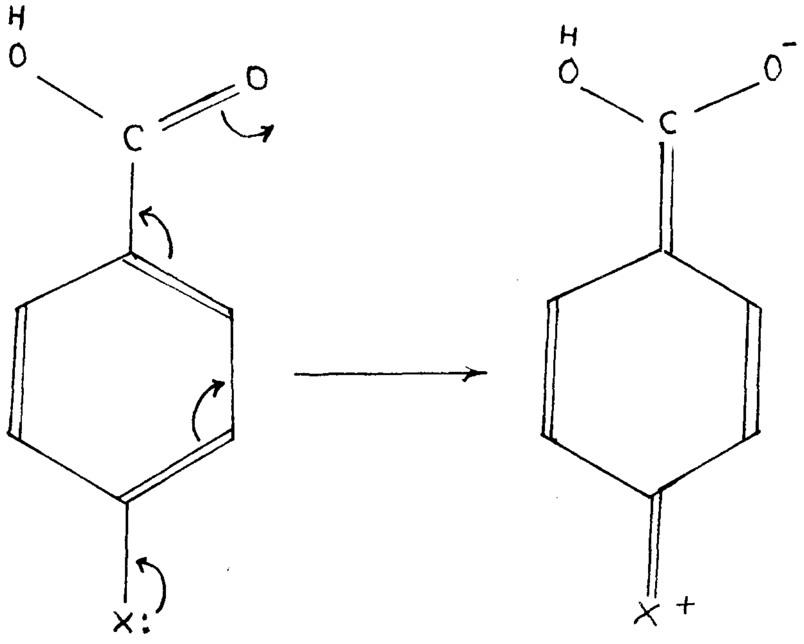
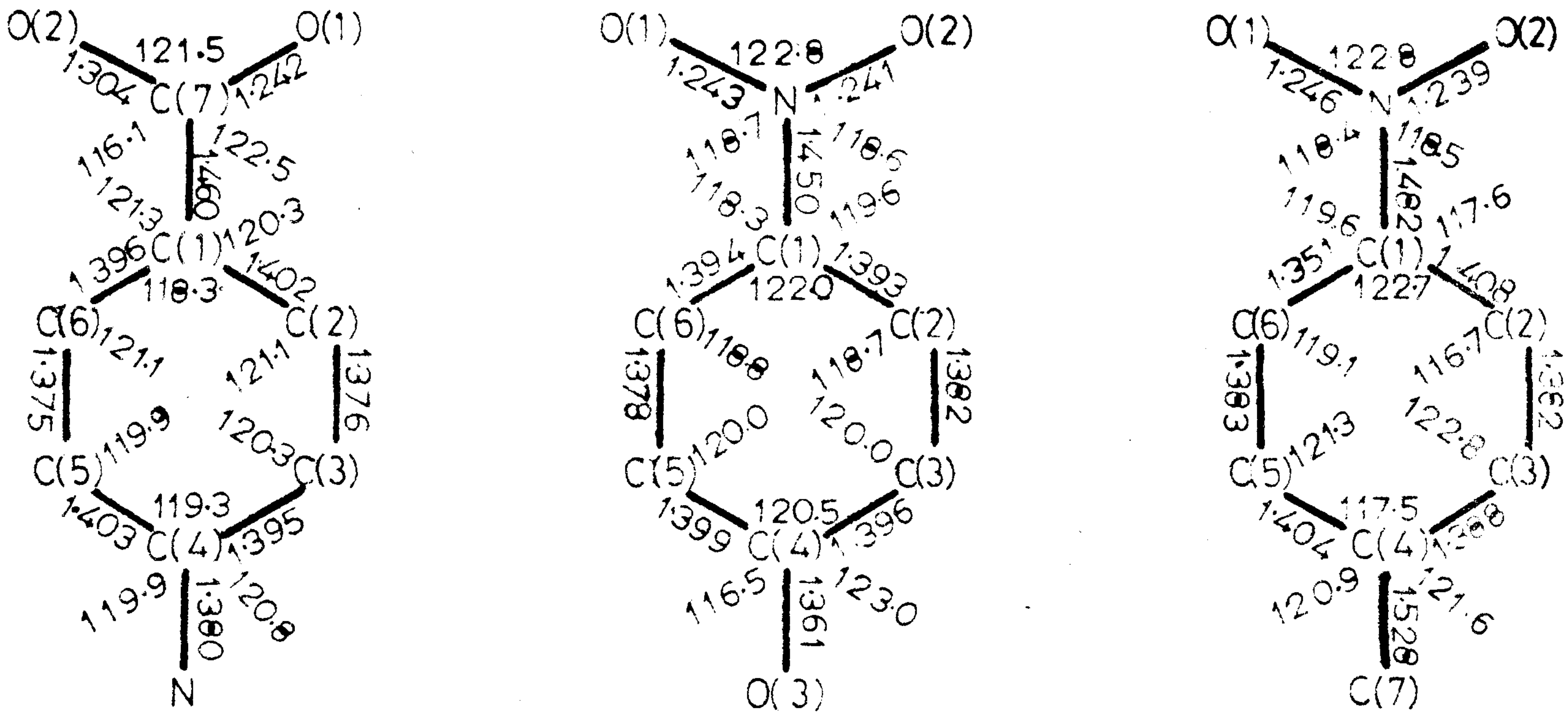


Table IV-3

Compound	Average bond length of central bonds in aromatic ring	Average bond length of remaining four aromatic bonds	Reference
p-Toluic acid	1.379 Å	1.399 Å	Present work. Takwale and Pant (1971)
p-Aminobenzoic acid	1.375	1.399 *	Lai and Marsh (1967)
p-Nitrophenol (β form)	1.380	1.396	Coppens and Schmidt (1965)
p-Nitrotoluene	1.382	1.400 **	Barve and Pant (1971)
p-Nitroaniline	1.375	1.402	Trueblood, Goldish and Donohue (1961)
β-Sulphanilamide	1.381	1.397	O'Connell and Maslen (1967)
Terephthalic acid	1.370	1.403	Bailey and Brown (1967)
p-Nitrobenzoic acid	1.383	1.396	Tavale and Pant (1971)

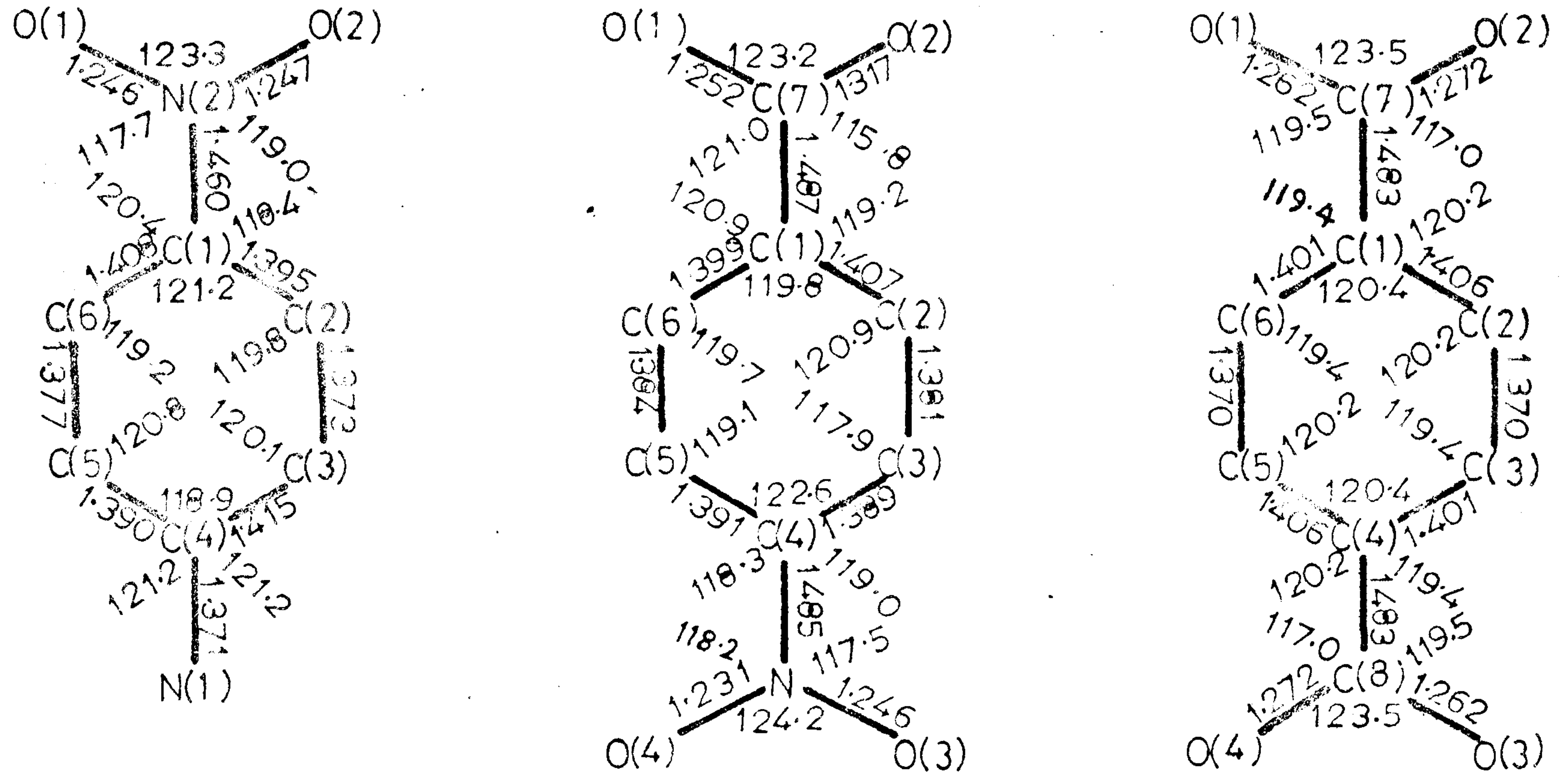
* The structure consists of two molecules per asymmetric unit; average for the two molecules is taken.

** C(5)-C(6) bond is very short (1.351 Å); it is excluded from the average.



p-Aminobenzoic acid p-Nitrophenol(β form) p-Nitrotoluene

FIG-IV·2(a): BOND LENGTHS (A°) AND ANGLES (°) IN SOME RELATED COMPOUNDS



p-nitroaniline p-Nitrobenzoic acid Terephthalic acid

FIG·IV·2(b): BOND LENGTHS (A°) AND ANGLES (°) IN SOME RELATED COMPOUNDS.

[X is an electron donor group such as NH_2, OH or CH_3; COOH is an electron acceptor group, NO_2 is also an acceptor group.] The interaction is expected to cause a shortening of the central bonds of the aromatic ring. Among the compounds discussed above, all except terephthalic acid and p-nitrobenzoic acid have an electron donor and an acceptor group in para positions. The cooperative electronic interaction between the para substituents discussed above explains the shortening of the central bonds of the aromatic ring in these compounds (except terephthalic acid and p-nitrobenzoic acid). However, the presence of the central bond shortening in p-nitrobenzoic acid and terephthalic acid as well implies that cooperative electronic interaction between the para substituents must be only partly responsible for the shortening of the central bonds of the aromatic ring.

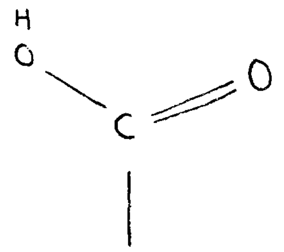
(b) Methyl group

The carbon atom C(8) of the methyl group is 0.034 Å away from the aromatic plane. The C(4)-C(8) bond length, 1.514 ± 0.011 Å (1.499 Å without correction for librational effects) agrees with the corresponding lengths in 2-amino-3-methyl benzoic acid, 1.501 ± 0.002 Å (Brown and Marsh; 1963), 1,1-di-p-tolylethylene, 1.503 ± 0.005 Å and 1.509 ± 0.005 Å (Casalone, Gavezzotti, Mariani, Mugnoli and Simonetta; 1970) and in p-nitrotoluene, 1.528 ± 0.009 Å (Barve and Pant, 1971). The bond lengths in 2-amino-3-methyl benzoic acid and 1,1-di-p-tolylethylene are not corrected for librational effects.

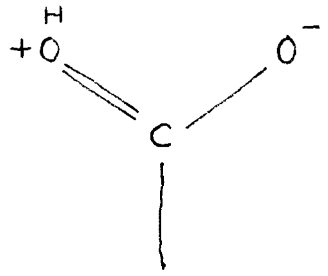
(c) Carboxylic group

The molecules form centrosymmetrical dimers with OH----O hydrogen bonds of length 2.63 Å. The carboxylic group is coplanar with the attached carbon atom C(7) of the benzene ring; it makes an angle of 2.9° with the aromatic plane (Table IV-2). The C(1)-C(7) bond length, 1.476 ±0.009 Å agrees with that found in terephthalic acid, 1.483 ± 0.003 Å and p-nitrobenzoic acid, 1.487 ± 0.006 Å but is a little longer than its values in the two crystallographically independent molecules of p-aminobenzoic acid, 1.455 ± 0.006 Å and 1.464 ± 0.006 Å. The two C-O bond lengths of the carboxylic group are both 1.292 ± 0.008 Å (1.272 and 1.275 Å without correction for librational effects).

The equality of the two C-O bonds probably implies that there is nearly equal contribution in the molecule from the following two structures:



(I)



(II)

In the structures of terephthalic acid and 3-aminobenzoic acid hydrochloride (Arora, Sunderlingam and others, 1973) as well, the two C-O bonds of the carboxylic group are nearly equal; the two C-O bond lengths are 1.262 ± 0.003 and

1.272 ± 0.003 Å in terephthalic acid, and 1.259 ± 0.004 and 1.267 ± 0.004 Å in 3-aminobenzoic acid hydrochloride. This symmetry is a reflection of the disorder in the location of the acidic proton. This is confirmed by the difference Fourier section $\rho(x,y,0.215)$ shown in Figure IV-3; the section is taken at z = 0.215 because the z parameters of O(1)-(x,y,z) and O(2)-($\bar{x},\bar{y},\bar{z}$) (which form the hydrogen bond) are both near the section. The peaks corresponding to two half hydrogen atoms are clearly seen in the difference map; the hydrogen atom occupies with nearly equal probability the two sites (marked by crosses in the difference map) associated with covalent bonding to O(1)-(x,y,z) and O(2)-($\bar{x},\bar{y},\bar{z}$).

(d) C–H bond distances

The average C-H bond length is 0.91 ± 0.09 Å (C(5)-H(3) bond length is omitted from the average since it is very short); the value of C-H distance is typical for X-ray diffraction investigation, being somewhat shorter than the values given by neutron diffraction and spectroscopic methods. The positions of the hydrogen atoms as shown by X-ray diffraction are affected by bonding because an appreciable part of the charge on the hydrogen atom is displaced towards the bond centre, therefore the centre of electron density does not coincide with the centre of the proton. In the present case the standard deviations in the bond lengths are high, hence little reliance can be placed on individual values of

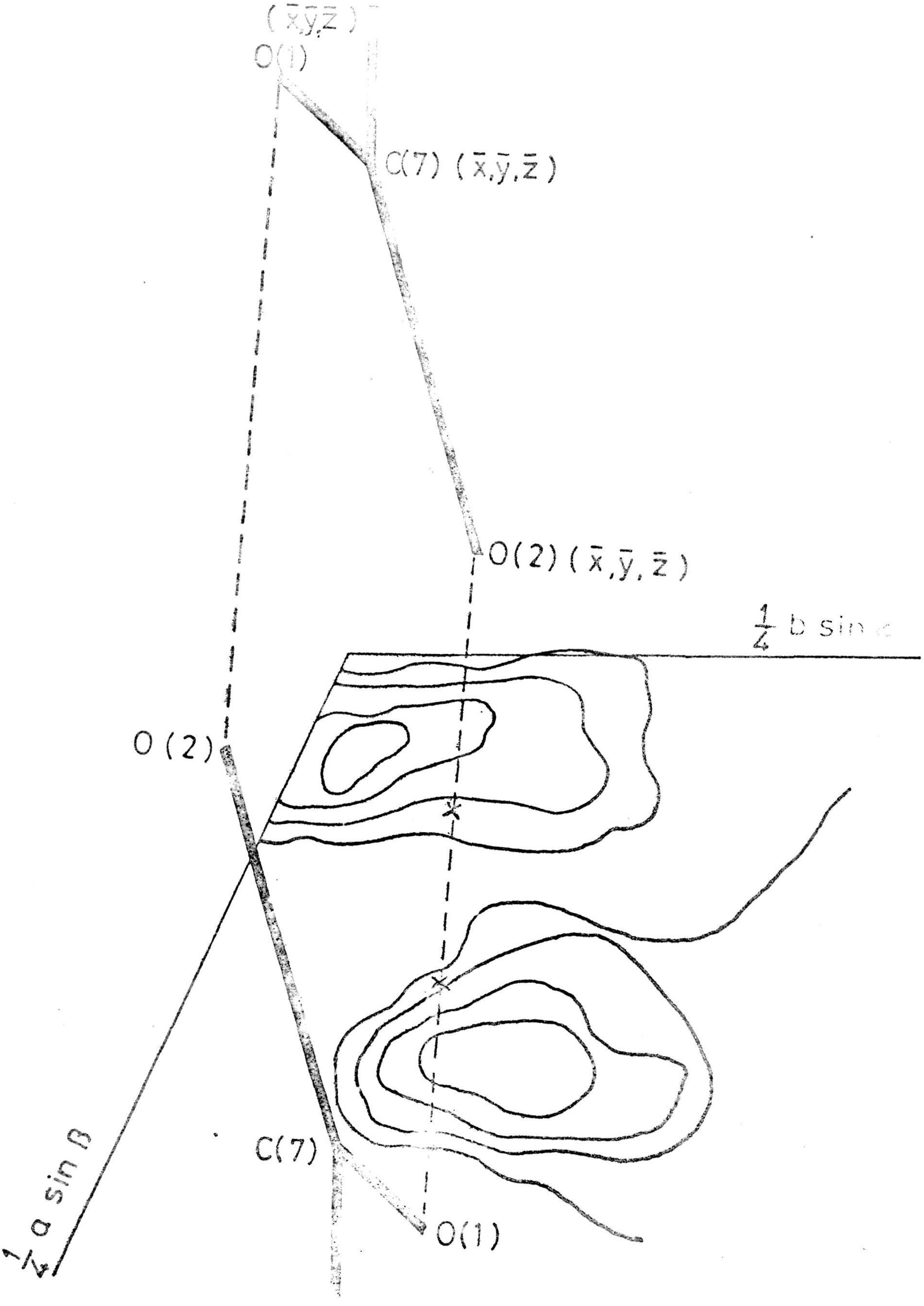


FIG-IV 3: DIFFERENCE FOURIER SECTION AT $Z = 0{\cdot}215$, THE CONTOURS ARE DRAWN AT INTERVALS OF 0·05 $e/\mathring{A}^3$, STARTING FROM 0·1 $e/\mathring{A}^3$

C-H bond lengths.

Crystal structure :

The projections of the structure on (001) and (100) planes are shown in Figures IV-4(a) and (b). In (010) projection, the molecules are overlapping, hence the projection is not shown. The principal intermolecular distances (< 3.8 Å) are also given in these figures. The crystal structures of p-toluic acid and terephthalic acid are quite similar; in these structures, infinite chains of molecules are held together by normal van der Waals interactions. In p-toluic acid, the molecules in any chain are bonded with neighbouring molecules by double OH--O hydrogen bonds of length 2.63 Å on one side and by van der Waals bonds between methyl groups (C-C distance, 3.50 Å) on the other side; in terephthalic acid, however, the molecules in any chain are bonded with the neighbouring molecules by double OH---O hydrogen bonds of length 2.67 Å on both sides.

SECTION B : THERMAL ANISOTROPY

The atomic scattering factor of an atom in thermal motion for hkl reflection is given by

$$f = f_o \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)\right] \qquad \ldots\ldots \quad \text{IV-4.}$$

The coordinates (x^*, y^*, z^*) of the hkl reciprocal lattice point are

$$x^* = ha^*, \qquad y^* = kb^*, \qquad z^* = lc^*.$$

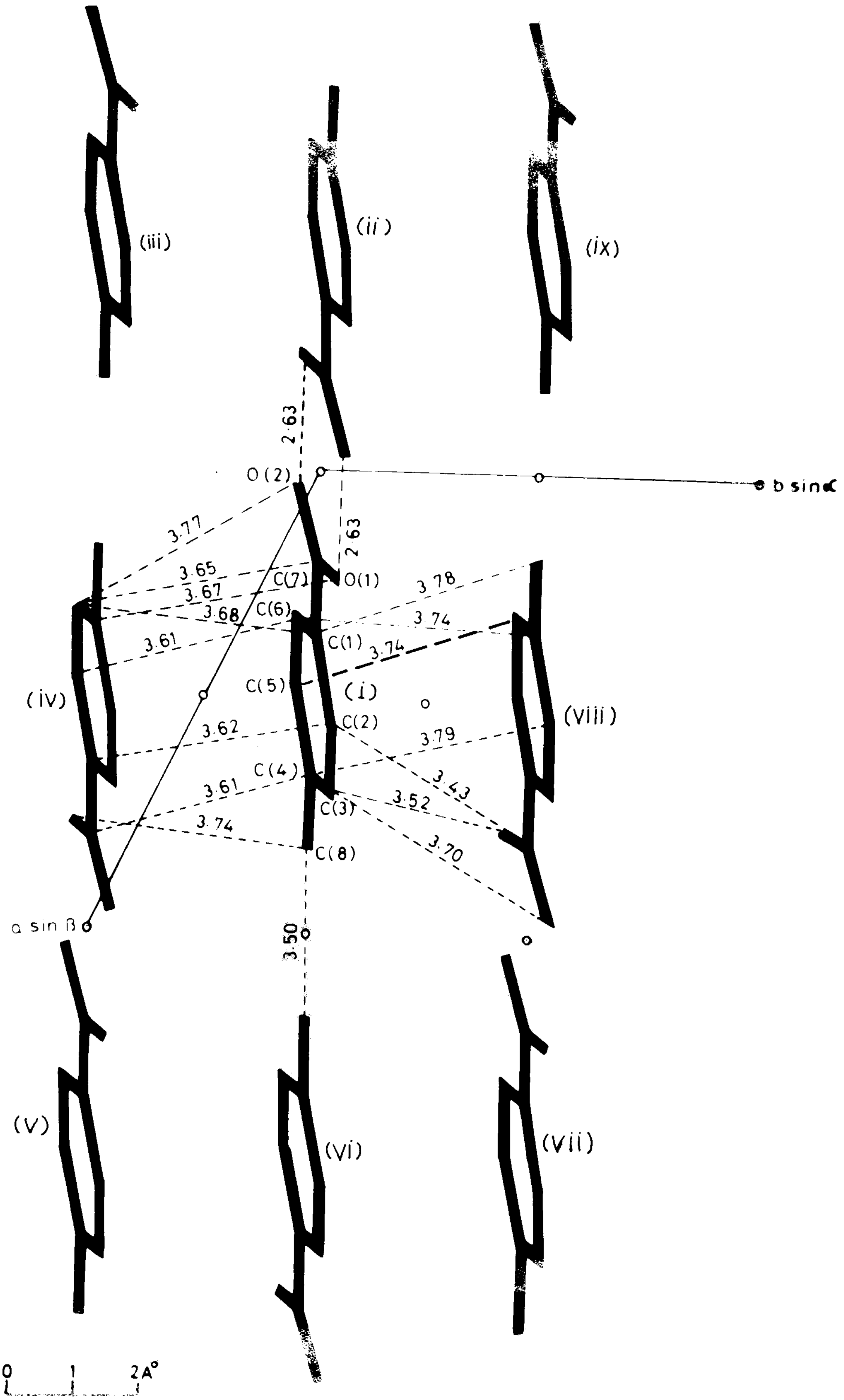


FIG. IV-4(a): THE STRUCTURE PROJECTED ALONG THE c-AXIS. SYMMETRY CODE: i) x, y, z ; ii) $\bar{x}, \bar{y}, \bar{z}$; iii) x-1, y-1, z ; iv) 1-x, $\bar{y}, \bar{z}$; v) 1+x, y, z ; vi) 2-x, 1-y, $\bar{z}$; vii) 1+x, 1+y, z ; viii) 1-x, 1-y, $\bar{z}$; ix) x-1, y, z.

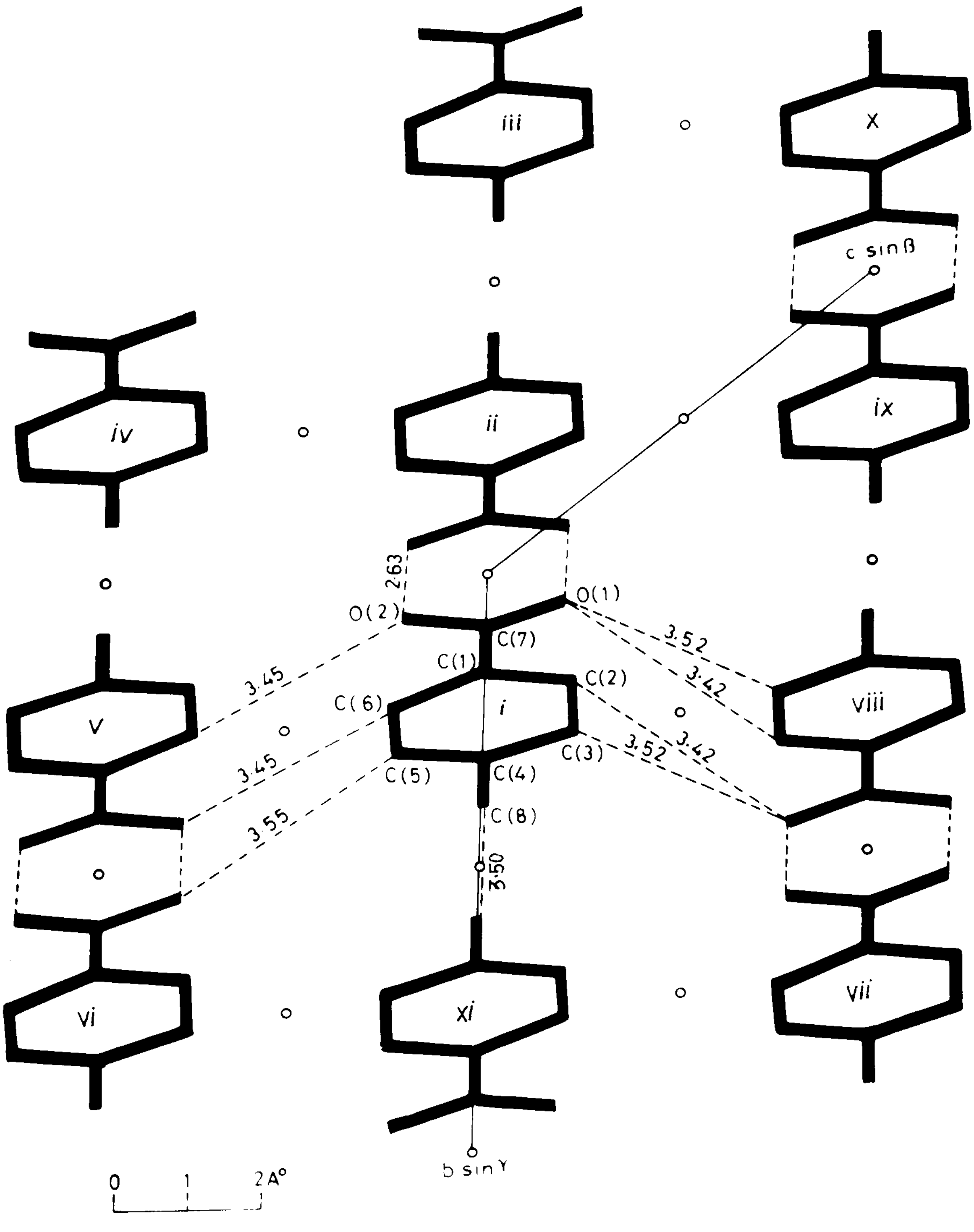


FIG. IV-4(b): THE STRUCTURE PROJECTED ALONG THE a-AXIS.

SYMMETRY CODE: i) x, y, z; ii) $\bar{x}, \bar{y}, \bar{z}$; iii) $x, y-1, z$;
iv) $x, -1-y, -1-z$; v) $x, \bar{y}, -1-z$; vi) $x, y, -1+z$; vii) $x, 1+y, 1+z$;
viii) $\bar{x}, 1-y, 1-z$; ix) $x, y, 1+z$; x) $\bar{x}, \bar{y}, 1-z$; xi) $\bar{x}, 1-y, \bar{z}$.

In terms of (x^*, y^*, z^*), f is given by

$$f = f_o \exp \left[-\left(\frac{b_{11}}{a^{*2}} x^{*2} + \frac{b_{22}}{b^{*2}} y^{*2} + \frac{b_{33}}{c^{*2}} z^{*2} + \frac{2b_{12}}{a^*b^*} x^*y^* + \frac{2b_{23}}{b^*c^*} y^*z^* + \frac{2b_{13}}{a^*c^*} x^*z^* \right) \right] \qquad \ldots\ldots \quad \text{IV-5.}$$

With reference to the axes of the reciprocal lattice of the triclinic unit cell, the equation of the ellipsoid on which the temperature factor is unity, is given by

$$\frac{b_{11}}{a^{*2}} x^{*2} + \frac{b_{22}}{b^{*2}} y^{*2} + \frac{b_{33}}{c^{*2}} z^{*2} + \frac{2b_{12}}{a^*b^*} x^*y^* + \frac{2b_{23}}{b^*c^*} y^*z^* + \frac{2b_{13}}{a^*c^*} x^*z^* = 1 \qquad \ldots\ldots \quad \text{IV-6.}$$

When referred to the orthogonal reciprocal axes a'^*, b'^*, c^* such that b^*c^* and b'^*c^* planes are the same, the equation IV-6 transforms as follows:

$$a_{11}X^{*2} + a_{22}Y^{*2} + a_{33}Z^{*2} + 2a_{12}X^*Y^* + 2a_{23}Y^*Z^* + 2a_{13}X^*Z^* = 1 \qquad \ldots\ldots \quad \text{IV-7.}$$

where

$$a_{11} = \left[\frac{b_{11}}{a^{*2}} + \frac{b_{22}}{b^{*2}} C^2 + \frac{b_{33}}{c^{*2}} (\cos\beta^* - \cos\alpha^* C)^2 - \frac{2b_{12}}{a^*b^*} C + \frac{2b_{23}}{b^*c^*} C\,(\cos\beta^* - \cos\alpha^* C) - \frac{2b_{13}}{a^*c^*} (\cos\beta^* - \cos\alpha^* C) \right] \frac{\sin^2\alpha^*}{D^2}$$

$$a_{22} = \left[\frac{b_{22}}{b^{*2}} + \frac{b_{33}}{c^{*2}}\cos^2\alpha^* - \frac{2b_{23}}{b^*c^*}\cos\alpha^*\right]\frac{1}{\sin^2\alpha^*}$$

$$a_{33} = \frac{a_{33}}{c^{*2}}$$

$$a_{12} = \left[-\frac{b_{22}}{b^{*2}}C + \frac{b_{33}}{c^{*2}}\cos\alpha^*(\cos\beta^* - \cos\alpha^* C) + \frac{b_{12}}{a^*b^*}\right.$$

$$\left. - \frac{b_{23}}{b^*c^*}(\cos\beta^* - 2\cos\alpha^* C) - \frac{b_{13}}{a^*c^*}\cos\alpha^*\right]\frac{1}{D}$$

$$a_{23} = \left[-\frac{b_{33}}{c^{*2}}\cos\alpha^* + \frac{b_{23}}{b^*c^*}\right]\frac{1}{\sin\alpha^*}$$

$$a_{13} = \left[-\frac{b_{33}}{c^{*2}}(\cos\beta^* - \cos\alpha^* C) - \frac{b_{23}}{b^*c^*}C + \frac{b_{13}}{a^*c^*}\right]\frac{\sin\alpha^*}{D},$$

where $C = (\cos\gamma^* - \cos\beta^* \cdot \cos\alpha^*)/\sin\alpha^*$

$$D^2 = 1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^* . \cos\beta^* . \cos\gamma^*$$

The orthogonal reciprocal axes a'*, b'*, c* coincide with the axes a, b', c' respectively with respect to which the equations of various planes (benzene ring, carboxylic group etc.) are determined. The transformation from equation IV-6 to equation IV-7 was effected using the following equations:

$$\left.\begin{aligned} X^* &= x^*(D/\sin\alpha^*) \\ Y^* &= y^*\sin\alpha^* + x^*C \\ Z^* &= z^* + y^*\cos\alpha^* + x^*\cos\beta^* \end{aligned}\right) \quad \ldots\ldots \quad \text{IV-8.}$$

Direction cosines of the maximum, medium and minimum vibration direction :

The major, medium and minor axes of the ellipsoid given by equation IV-7 are parallel to the directions of minimum, medium and maximum vibrations of the atom respectively. The direction cosines of the principal axes of the ellipsoid are obtained from the matrix formed with six a_{ij}'s in the following way (Nye, 1957).

The direction cosines of the maximum vibration direction are obtained from the following matrix:

$$U = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

where $a_{12} = a_{21}$, $a_{13} = a_{31}$ and $a_{23} = a_{31}$. The largest column of matrix U is multiplied by the matrix U, which results in a column matrix. Successive multiplication of the matrix by the product matrix is done till the elements of the product matrix become constant. The normalization of the matrix gives the values of direction cosines of maximum vibration direction. The normalizing condition is

$$l^2 + m^2 + n^2 = 1$$

where l, m and n are the direction cosines of the vibration direction. Similarly the direction cosines of the minimum vibration direction are obtained by performing the same operation on U^{-1} matrix.

If l m n and p q r are the direction cosines of maximum vibration direction and minimum vibration direction respectively, then the direction cosines of medium vibration direction are given by (mr-qn), (pn-lr) and (lq-pm).

<u>Root mean square amplitude</u> :

The equation of the ellipsoid with respect to its own axes is given by

$$A_{11}X^{*2} + A_{22}Y^{*2} + A_{33}Z^{*2} = 1.$$

A_{11}, A_{22} and A_{33} are obtained by successively multiplying the matrix U by the direction cosines of the three axes of the ellipsoid. The root mean square amplitudes of maximum, medium and minimum vibrations are given by

$$\left.\begin{array}{lll} \text{Maximum vibration} & : \sqrt{\bar{u}^2_{11}} & = \sqrt{A_{11}/2\pi^2} \\ \text{Medium vibration} & : \sqrt{\bar{u}^2_{22}} & = \sqrt{A_{22}/2\pi^2} \\ \text{Minimum vibration} & : \sqrt{\bar{u}^2_{33}} & = \sqrt{A_{33}/2\pi^2} \end{array}\right) \quad \ldots\ldots \quad \text{IV-9.}$$

The Table IV-4 gives the magnitudes and direction cosines of the principal axes of the atomic vibration ellipsoids, the angles between the principal axes and the aromatic plane, and those between the principal axes and the molecular axis (i.e. the C(1)-C(4) direction). In Table IV-5, mean square displacements along certain directions are given for

Table IV-4 : Magnitudes and direction cosines of the principal axes of the atomic vibration ellipsoids, the angles between the principal axes and the aromatic plane and those between the principal axes and the molecular axis (i.e. C(1)-C(4) direction)

Atom	Axis	$\sqrt{\bar{u}^2}$ (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with molecular axis
C(1)	1	0.238	-0.267	0.748	0.608	66°	86°
	2	0.210	-0.728	0.256	-0.635	21	56
	3	0.189	0.631	0.612	-0.476	10	34
C(2)	1	0.257	-0.300	0.950	0.089	79	83
	2	0.229	-0.082	0.067	-0.994	9	87
	3	0.220	0.950	0.306	-0.058	7	8
C(3)	1	0.270	-0.399	-0.048	0.916	20	68
	2	0.266	-0.379	0.918	-0.117	69	88
	3	0.202	0.835	0.394	0.385	6	22
C(4)	1	0.312	-0.002	-0.086	0.996	10	88
	2	0.221	-0.643	0.763	0.064	72	74
	3	0.191	0.766	0.640	0.056	15	16
C(5)	1	0.304	0.086	0.732	0.676	51	67
	2	0.248	-0.466	0.629	-0.622	36	80
	3	0.220	0.881	0.262	-0.395	13	25

continued....

Table IV-4 (continued)

Atom	Axis	$\sqrt{\bar{u}^2}$ (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with mole-cular axis
C(6)	1	0.291	-0.292	0.718	0.631	65	88
	2	0.241	-0.865	0.083	-0.495	18	41
	3	0.175	0.408	0.691	-0.597	17	49
C(7)	1	0.247	0.014	0.206	0.978	25	84
	2	0.222	-0.569	0.806	-0.162	64	79
	3	0.192	0.822	0.555	-0.129	7	12
C(8)	1	0.355	-0.104	0.203	0.974	27	90
	2	0.278	-0.612	0.759	-0.223	60	76
	3	0.203	0.784	0.619	-0.045	12	14
O(1)	1	0.321	-0.385	0.916	0.120	82	88
	2	0.232	-0.391	-0.044	-0.919	6	68
	3	0.196	0.836	0.400	-0.375	4	22
O(2)	1	0.334	-0.367	0.887	0.279	87	86
	2	0.217	0.371	0.414	-0.831	1	66
	3	0.195	0.853	0.202	0.481	3	30

Table IV-5 : Some mean square displacements ($\mathring{A}^2 \times 10^3$)

Atom	Direction of displacement**				
	Normal to the plane*	In the plane normal to the bond		Parallel to the bond	
O(1)	102	65		45	
C(7)	51	a) 50	O(1)	47	O(1)
		b) 41	O(2)	75	O(2)
O(2)	111	39		42	
C(4)	49	98		38	
C(8)	86	117		44	

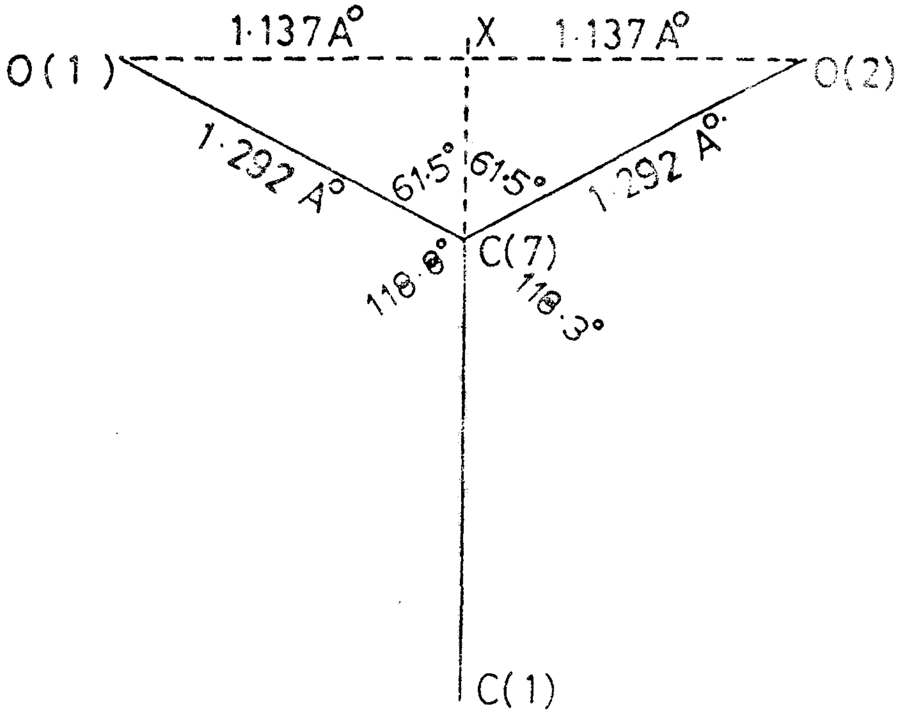
* The vibration directions of O(1), O(2) and C(7) are with respect to the plane through C(1), C(7), O(1) and O(2) whereas the vibration directions of C(4) and C(8) are with respect to the benzene plane.

** Values parallel and normal to the bond for C(4) are given only for C(4)-C(8) bond. The atoms listed besides certain values in the table indicate the direction of the bond in question.

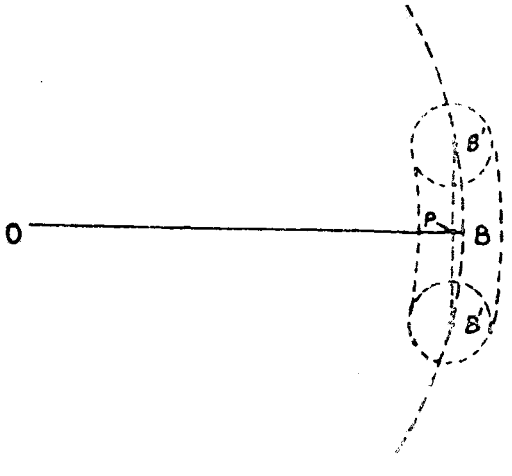
atoms O(1), O(2), C(7), C(4) and C(8). These are required in order to apply corrections to C(7)-O(1), C(7)-O(2) and C(4)-C(8) bond lengths arising from librational motion.

DISCUSSION OF THERMAL ANISOTROPY :

It is seen from the Table IV-4 that the oxygen atoms of carboxylic group have large root mean square amplitudes nearly normal to the aromatic plane. The mean square displacements of the atoms O(1), O(2) and C(7) normal to the plane are 0.102, 0.111 and 0.051 Å respectively. In order to see whether the carboxylic group is oscillating about the C(1)-C(7) bond as a rigid body, the amplitudes of torsional oscillation of the C(7)-O(1) and C(7)-O(2) bond about the C(1)-C(7) bond were calculated as follows: The mean square amplitude of torsional oscillation of C(7)-O(1) bond about the C(1)-C(7) direction is given by the difference between the mean square amplitudes of atoms C(7) and O(1) normal to the plane of carboxylic group. Hence the root mean square amplitude of torsional oscillation of C(7)-O(1) bond about C(1)-C(7) direction is given by $(0.051)^{1/2}/1.137$ radians or 11.5° (Figure IV-5). Similarly the root mean square amplitude of torsional oscillation of C(7)-O(2) bond about C(1)-C(7) direction is given by $(0.060)^{1/2}/1.137$ radian or 12.3°. Since the angle of torsional oscillations of C(7)-O(1) and C(7)-O(2) bonds about the C(1)-C(7) direction are both about 12°, it may be concluded that the carboxylic group behaves as a rigid body and oscillates about the



FIG·IV-5: CALCULATION OF THE ROOT MEAN SQUARE AMPLITUDES OF TORSIONAL OSCILLATION OF C(7)-O(1) AND C(7)-O(2) BONDS ABOUT THE C(1)-C(7) DIRECTION



FIG·IV·6: DISPLACEMENT OF THE MAXIMUM ELECTRON DENSITY BY LIBRATIONAL MOTION

C(1)-C(7) direction with a root mean square amplitude of 12°. Similar behaviour is shown in p-nitrobenzoic acid (Tavale and Pant, 1971) where the angle of torsional oscillation of the carboxylic group is 9° and o-methyl amino benzoic acid (Dhaneshwar and Pant, 1972) where the angle is 9°. The root mean square amplitude of carbon atom of methyl group has large value perpendicular to the molecular axis (0.355 Å). A comparison of Table IV-4 with Table 4 of Barve and Pant (1971) shows that the magnitudes of the principal axes of the atomic vibration ellipsoids of the carbon atoms of the methyl group in the two structures are similar, the corresponding values being 0.355, 0.278 and 0.203 Å in p-toluic acid, and 0.351, 0.313 and 0.206 Å in p-nitrotoluene; the orientations of the vibration ellipsoids with respect to the benzene plane and the molecular axis are also the same within 12°.

Bond length corrections :

The interatomic distance between a pair of atoms is apparently decreased due to librational motion. Consider an atom whose equilibrium position is B (Figure IV-6). If the atom oscillates about O so that the atom is displaced along the arc B' B B", the time averaged centre of electron density distribution will shift from B to a point P towards O. The error Δy (= PB) in atomic position is given by (Cruickshank, 1956)

$$\Delta y = \frac{1}{2r} \quad \frac{s^2}{1 + (s^2/q^2)} + \frac{t^2}{1 + (t^2/q^2)} \qquad \ldots\ldots \quad \text{IV-10.}$$

where q^2 is the breadth parameter and s^2 and t^2 are the mean square displacements of atom perpendicular to the bond normal to the plane and in the plane respectively. The errors introduced by librational motion for bonds C(7)-O(1), C(7)-O(2) and C(4)-C(8) were calculated by using the mean square displacements given in Table IV-5; the errors are given in Table IV-6.

Table IV-6 : Corrections for bond lengths due to librational motion.

Bond	Uncorrected bond length	Correction	Corrected bond length
C(7)-O(1)	1.272 Å	0.020 Å	1.292 Å
C(7)-O(2)	1.275	0.017	1.292
C(4)-C(8)	1.499	0.015	1.514

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PART - II : CRYSTAL AND MOLECULAR STRUCTURE OF 2-NITRO-4-METHYL BENZOIC ACID.

CHAPTER - V

EXPERIMENTAL

The crystals of 2-nitro-4-methyl benzoic acid were obtained by crystallizing the compound from alcohol. The preliminary Weissenberg photographs taken by oscillating the crystal about the three crystallographic axes in turn showed that the crystal belongs to the monoclinic system.

Cell dimensions :

The accurate determination of cell dimensions was done by using several high angle reflections in equatorial Weissenberg photographs taken along the b and c axes. The values of $a \sin\beta$, b and $c \sin\beta$ obtained from these reflections were plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$. To eliminate the error due to film shrinkage and any error introduced in the radius of the camera due to the finite thickness of the film, Straumanis (1936) mounting of the film was used. In this method the positions on the film corresponding to $\theta = 0^\circ$ and $\theta = 90^\circ$ can be located accurately. If r is the distance between the positions corresponding to $\theta = 0$ and $\theta = 90^\circ$, the angle θ for high angle reflection is multiplied by $(90/r)$ to get the correct value of θ.

Table V-1(a) : Determination of spacing a sinβ .

h	k	l		θ	sinθ	sin$^2\theta$	a sin
16	0	$\bar{2}$	α_1	68.73°	0.9319	0.8684	13.196 Å
14	0	$\bar{8}$	α_1	70.20°	0.9409	0.8853	13.198
16	0	$\bar{4}$	α_1	71.70°	0.9494	0.9014	13.199
16	0	2	α_1	72.72°	0.9549	0.9118	13.202
			α_2	73.20°	0.9573	0.9164	13.202
16	0	4	α_1	83.73°	0.9941	0.9882	13.209
			α_2	85.24°	0.9965	0.9930	13.211

The extrapolated value of
a sinβ (at sin$^2\theta$ = 1) = 13.211 ± 0.001 Å

Table V-1(b) : Determination of spacing b.

h	k	l		θ	$\sin\theta$	$\sin^2\theta$	b
5	13	0	α_1	72.32°	0.9528	0.9078	11.029 Å
0	14	0	α_1	77.67°	0.9770	0.9545	11.038
			α_2	78.31°	0.9793	0.9590	11.038
2	14	0	α_1	79.50°	0.9833	0.9669	11.042
			α_2	80.30°	0.9857	0.9716	11.044

The extrapolated value of b (at $\sin^2\theta=1$) = 11.048 ± 0.002 Å.

Table V-1(c) : Determination of spacing c sinβ .

h	k	l		θ	sinθ	$\sin^2\theta$	c·sin
6	0	12	α_1	66.26°	0.9154	0.8380	11.335 Å
$\bar{2}$	0	14	α_1	71.40°	0.9478	0.8983	11.342
0	0	14	α_1	71.95°	0.9508	0.9040	11.341
			α_2	72.37°	0.9530	0.9082	11.343
$\bar{4}$	0	14	α_1	73.50°	0.9588	0.9193	11.344
			α_2	73.98°	0.9612	0.9239	11.344
8	0	12	α_1	76.85°	0.9738	0.9483	11.346
			α_2	77.40°	0.9759	0.9524	11.347
$\bar{6}$	0	14	α_1	79.55°	0.9835	0.9676	11.350
			α_2	80.40°	0.9860	0.9722	11.349

The extrapolated value of c sinβ (at $\sin^2\theta = 1$) = 11.353 ± 0.001 Å.

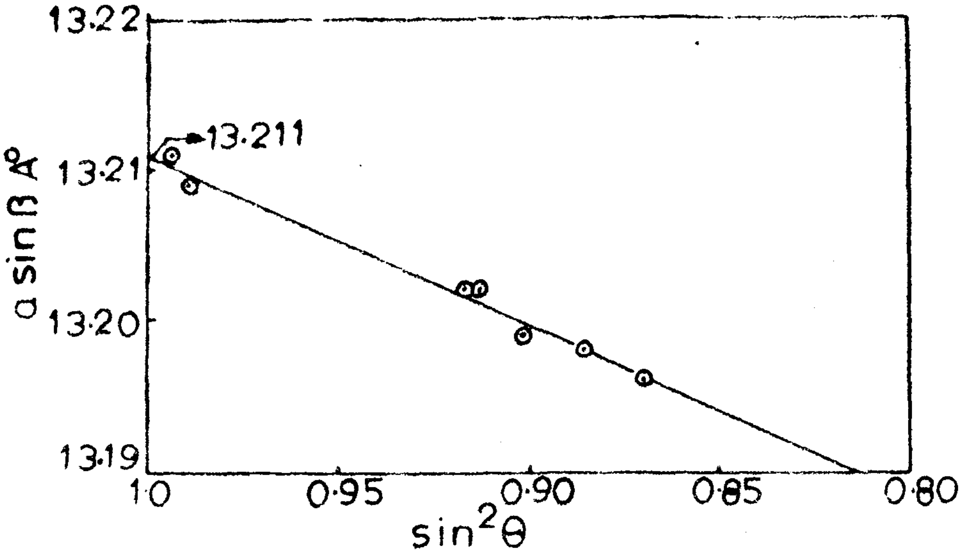
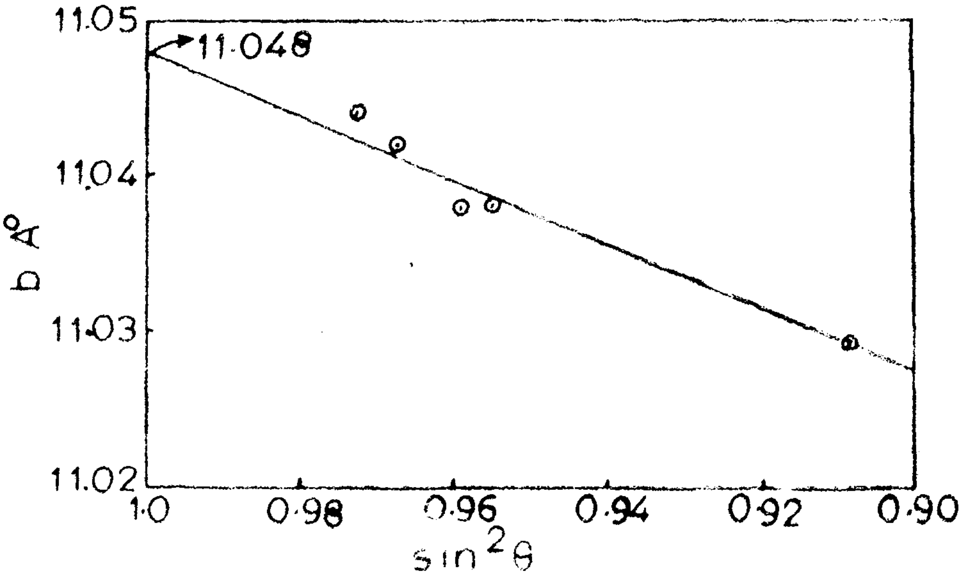


FIG V·1(a)

FIG V-1(b)



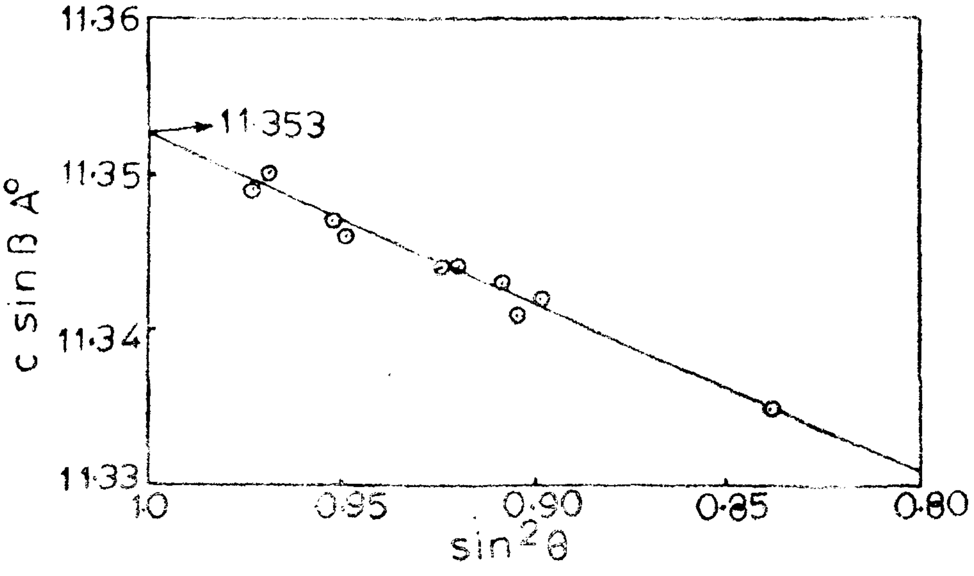


FIG V·1(c)

FIG·V·1(a),(b),(c): EXTRAPOLATION GRAPHS FOR THE ACCURATE DETERMINATION OF a sinβ, b and c sin β.

The expression used to calculate $a\sin\beta$, b and $c\sin\beta$ is given by

$$\left(\frac{2\sin\theta}{\lambda}\right)^2 = \frac{h^2}{a^2\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2\beta} - \frac{2hl\cos\beta}{a\,c\sin^2\beta}$$

The results are given in Table V-1(a), (b) and (c) and corresponding graphs are given in Figures V-1(a), (b) and (c).

The angle β^* was obtained by the method of triangulation using the $(\overline{10}\ 0\ 12)$ reflection (having $\theta = 73.7^\circ$) (Jeffery, 1971).

The final cell dimensions are

$a = 13.281 \pm 0.006$ Å
$b = 11.048 \pm 0.002$ $\quad\beta = 95.9 \pm 0.3^\circ$
$c = 11.414 \pm 0.005$

The density of crystal :

The density of the crystal measured by the flotation method is 1.440 $\mathrm{gm.cm^{-3}}$. The calculated density of $Z = 8$ is 1.432 $\mathrm{gm.cm^{-3}}$.

The linear absorption coefficient :

The linear absorption coefficient, calculated as described in Chapter II, is 10.3 $\mathrm{cm^{-1}}$.

Collection of data and estimation of intensity :

The three dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with unfiltered Cu-radiation. Zero to nineth layer Weissenberg photographs were taken with the crystal oscillated about the b axis and zero to fourth layer photographs were taken with the crystal oscillated about the c axis. The crystals used for the two sets of photographs had the cross sections 0.40 x 0.45 mm^2 and 0.61 x 0.70 mm^2 and lengths 0.75 mm and 1.04 mm respectively. The intensities of the reflections were estimated visually with the help of intensity scales prepared with the same crystals.

The estimated intensities were corrected for the effects of Lorentz-polarization factor, spot extension and absorption. The computer program suitable for CDC-3600 computer was written by using the following formulae:

$$\frac{W}{L_p} = \frac{2\,\xi\cos\theta}{1+\cos^2(2\theta)}\left[1+\frac{180}{4\pi}\,\frac{\zeta\,\left[(4-\zeta^2)/\xi^2-1\right]^{1/2}}{\left[2R_1/(4-\zeta^2)^{1/2}+R_2\right]}\right]$$

$$\zeta = -2\sin\mu \text{ (for equi-inclination Weissenberg)}$$

$$\xi^2 = 4\sin^2\theta - \zeta\,,$$

where μ is equi-inclination setting angle, R_1 is the camera radius and R_2 is the distance between crystal and first-pinhole (75.0 mm). To obtain the absorption correction factors, tables of absorption correction factors versus sinθ for each layer were supplied to the computer and the correction factors were obtained by interpolation.

The data from the two sets of photographs were brought to the same scale by comparing the intensities of common reflections; 1323 independent reflections were observed from the two sets.

Scale and temperature factor :

The intensities of the reflections were put on the absolute scale by the Wilson's statistical method as discussed in the Chapter I. The results are given in Table V-2; the corresponding graph is shown in Figure V-2. The temperature factor B = 2.9 Å and scale factor K = 12.2 were obtained from the graph.

Space group determination :

The systematic absences observed in the Weissenberg photographs are

h o o for h odd
o k o for k odd
h k o for h+k odd
o k l for k odd
h o l for h odd and l odd
h k l for h+k odd

From these systematic absences the space group could be either C_c or $C_{2/c}$. The space group C_c is non-centrosymmetrical while

Table V-2 : Wilson's statistical determination of scale and temperature factor

$\sin\theta$ range	$\sin\theta$	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$\langle I \rangle$	$\sum f_n^2$	c	$\log_e c$
0.1 - 0.3	0.20	0.017	122.3	3123.7	25.54	3.240
0.3 - 0.5	0.40	0.067	63.9	1369.3	21.43	3.065
0.5 - 0.6	0.55	0.127	25.2	736.4	29.22	3.375
0.6 - 0.7	0.65	0.178	19.8	514.2	25.97	3.257
0.7 - 0.8	0.75	0.236	9.8	384.0	39.18	3.666
0.8 - 0.9	0.85	0.304	3.6	305.6	84.89	4.442

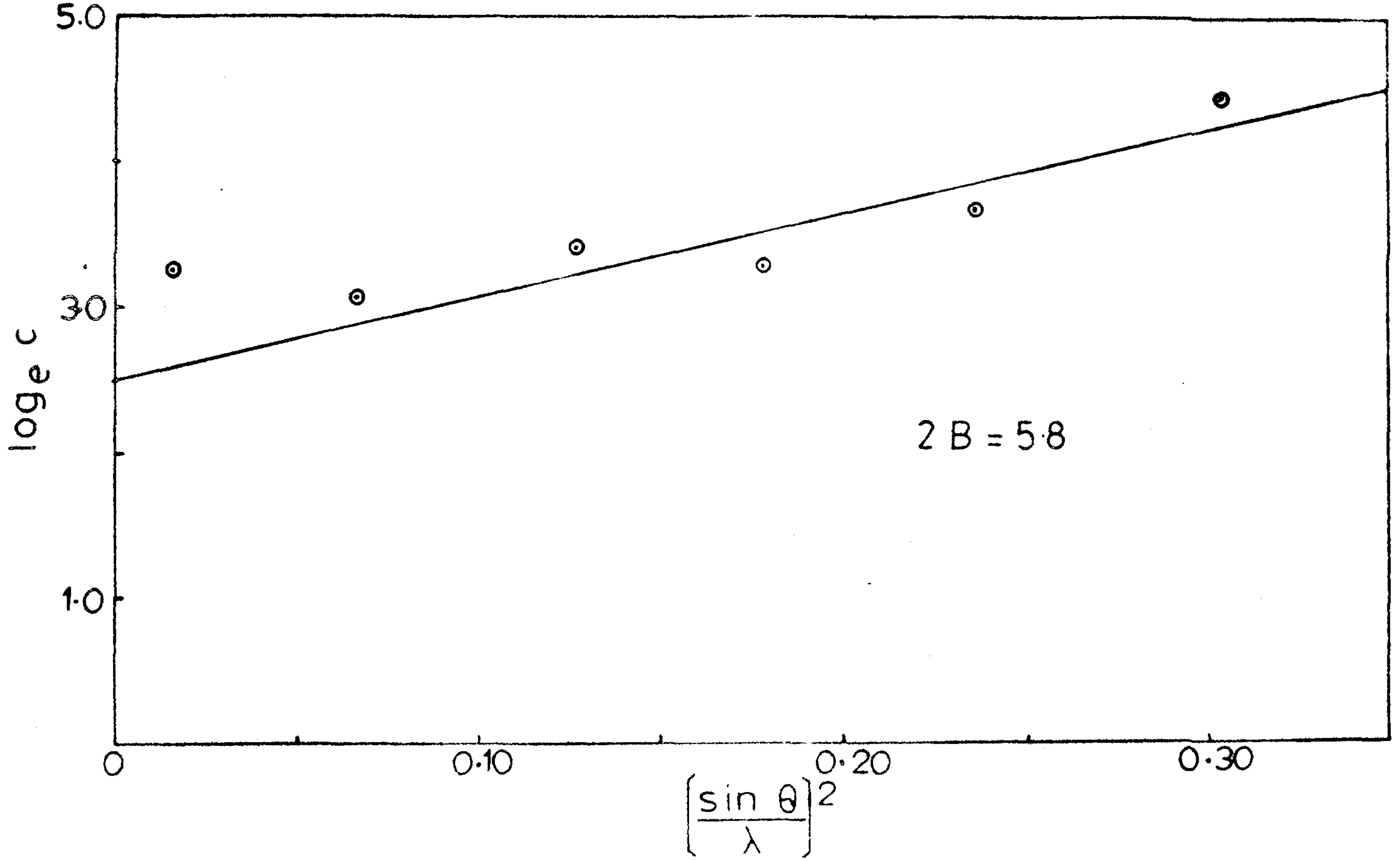


FIG-V-2: STATISTICAL DETERMINATION OF OVERALL SCALE AND TEMPERATURE FACTOR FROM THREE DIMENSIONAL DATA.

$C_{2/c}$ is centrosymmetrical. The N(z) test based on three dimensional intensity statistics was carried out to see whether the crystals belong to the centrosymmetrical space group or the non-centrosymmetrical one (Phillips, Rogers and Howells, 1950).

The fractions N(z) of reflections whose intensities are equal to or less than a fraction z of the local average are given by

$N(z) = 1-\exp(-z)$ for non-centrosymmetrical crystal,

and $N(z) = \mathrm{erf}\,(\frac{1}{2}z)^{\frac{1}{2}}$ for centrosymmetrical crystals,

where 'erf' means the error function (Jahnke and Emde, 1933). These functions are tabulated in Table V-3, and are plotted in Figure V-3, for centrosymmetrical as well as for non-centrosymmetrical structures.

The N(z) values for 2-nitro-4-methyl benzoic acid obtained from three dimensional intensity data are given in Table V-3; and are shown in figure V-3. The N(z) values are close to the curve corresponding to the centrosymmetrical crystals; these results imply that the space group is $C_{2/c}$.

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Table V-3 : N(z) test for 2-nitro-4-methyl benzoic acid.

z	N(z) for centrosymmetrical structure	N(z) for non-centrosymmetrical structure	N(z) for present work
0.1	0.248	0.095	0.23
0.2	0.345	0.181	0.36
0.3	0.419	0.259	0.43
0.4	0.474	0.330	0.48
0.5	0.521	0.394	0.54
0.6	0.561	0.451	0.58
0.7	0.597	0.503	0.61
0.8	0.629	0.551	0.64
0.9	0.657	0.593	0.66
1.0	0.683	0.632	0.68

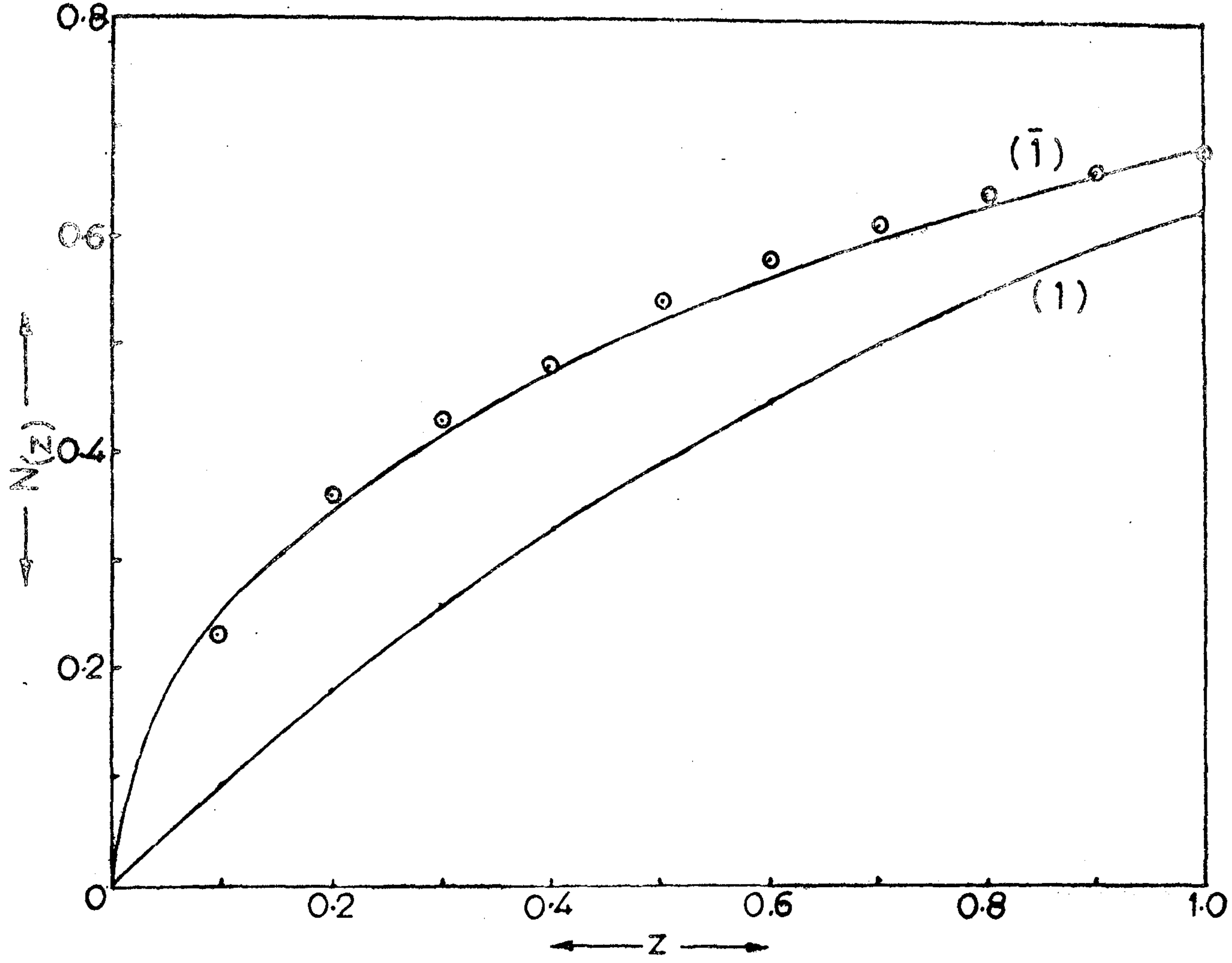


FIG. V-3: N(z) TEST FOR 2-nitro-4 methyl benzoic ACID.

CHAPTER - VI

STRUCTURE AND REFINEMENT

SECTION A : STRUCTURE DETERMINATION

An attempt was first made to solve the structure by using the Patterson projections. Meanwhile the listing and write-up of the Sayre's equation programme written by Long (1965) became available in the laboratory, hence the trial structure was determined by this method.

Sayre's Equations :

Sayre's equality relations (1952) are based on the fact that if all atoms in a structure are identical, and completely resolved from one another, the operation of squaring the electron density gives a distribution which is still a superposition of equal spherically symmetrical 'atoms' centred on the same points as before.

The electron density $\rho(\underline{r})$ at a point defined by vector $\underline{r}$ is given by

$$\rho(\underline{r}) = \frac{1}{V} \sum_{\underline{h}} F_{\underline{h}} \exp(-2\pi i \, \underline{h}.\underline{r}) \qquad \text{.....} \quad \text{VI-1.}$$

Similarly the squared electron density may be expressed as

$$\rho^2(\underline{r}) = \frac{1}{V} \cdot \sum_{\underline{h}} F^{sq}_{\underline{h}} \exp(-2\pi i\, \underline{h}.\underline{r}) \qquad \ldots\ldots \quad \text{VI-2.}$$

where $F^{sq}_{\underline{h}}$ is the $\underline{h}^{th}$ Fourier coefficient of the squared structure. From equation VI-1 we have

$$\rho^2(\underline{r}) = \rho(\underline{r}) \cdot \rho(\underline{r}) = \frac{1}{V^2} \cdot \sum_{\underline{h}'} \sum_{\underline{h}''} F_{\underline{h}'} \cdot F_{\underline{h}''} \exp(-2\pi i(\underline{h}'+\underline{h}'') \cdot \underline{r})$$

$$\ldots\ldots \quad \text{VI-3.}$$

If the terms for which $\underline{h}' + \underline{h}'' = \underline{h}$ are collected together, the equation VI-3 can be rearranged as

$$\rho^2(\underline{r}) = \frac{1}{V^2} \sum_{\underline{h}} \left[\sum_{\underline{h}'} F_{\underline{h}'} \cdot F_{\underline{h}-\underline{h}'} \exp(-2\pi i\, \underline{h}.\underline{r}) \right] \qquad \ldots\ldots \quad \text{VI-4.}$$

Comparing equations VI-2 and VI-4 we have

$$F^{sq}_{\underline{h}} = \frac{1}{V} \sum_{\underline{h}'} F_{\underline{h}'} \cdot F_{\underline{h}-\underline{h}'} \qquad \ldots\ldots \quad \text{VI-5.}$$

If f is the atomic scattering factor of an atom and g is the atomic scattering factor of the corresponding squared atom, then $F_{\underline{h}}$ and $F^{sq}_{\underline{h}}$ are given by

$$F_{\underline{h}} = \sum_{j=1}^{n} f \cdot \exp(2\pi i(\underline{h}.\underline{r}_j)) \qquad \ldots\ldots \quad \text{VI-6.}$$

and

$$F^{sq}_{\underline{h}} = \sum_{j=1}^{n} g \cdot \exp(2\pi i(\underline{h}.\underline{r}_j)) \qquad \ldots\ldots \quad \text{VI-7.}$$

For identical atoms, values of f and g for a reflection hkl will depend on the Bragg angle θ. From equations VI-5, VI-6 and VI-7 we have

$$F_{\underline{h}} = \phi_{\underline{h}} \sum_{\underline{h}'} F_{\underline{h}'} \cdot F_{\underline{h}-\underline{h}'} \qquad \ldots\ldots \quad \text{VI-8.}$$

where $\phi_{\underline{h}} = \frac{f}{g} \cdot \frac{1}{V}$.

The implication of equation VI-8 is that any structure factor F_{hkl} is determined by the sum of the products of all the pairs of structure factors whose indices add to give $\underline{h}$ (i.e. h k l). The equation VI-8 is not very useful for determining the phases directly because to determine one F it is necessary to know the magnitudes and phases of all the others. However, for centrosymmetrical structures for the case where F is very large, the series must tend strongly in one direction and the direction is generally determined by the agreement in signs among products between large F's. Thus for a case of three reflections of large F values, one can write

$$S(\underline{h}) \sim S(\underline{h}').S(\underline{h}-\underline{h}'), \qquad \ldots\ldots \quad \text{VI-9.}$$

where $S(\underline{h})$ means sign of the reflection $\underline{h}$ (i.e. hkl). The probability that the sign determined by the equation VI-9 is correct is given by (Cochran and Woolfson, 1955)

$$P = \frac{1}{2} + \frac{1}{2} \tanh \left[\frac{\sigma_3}{\sigma_2^{3/2}} \left| E_{\underline{h}} \cdot E_{\underline{h}'} \cdot E_{\underline{h}-\underline{h}'} \right| \right] \qquad \ldots\ldots \quad \text{VI-10.}$$

where $\sigma_3 = \sum_{i=1}^{N} n_i^3$ and $\sigma_2 = \sum_{i=1}^{N} n_i^2$

The value of n_i is given by

$$n_i = f_i \Big/ \sum_{j=1}^{N} f_j \, .$$

For N identical atoms in the unit cell, $n_i = \frac{1}{N}$. Therefore for a structure having identical atoms,

$$\frac{\sigma_3}{\sigma_2^{3/2}} = \frac{1}{\sqrt{N}}$$

The normalized structure factor $E_{\underline{n}}$ used in equation VI-10 is given by

$$E_{\underline{h}} = \frac{F_{\underline{h}}}{\epsilon \left[\sum_{j=1}^{N} f^2_{j\underline{h}} \right]^{1/2}} \, ,$$

where $F_{\underline{h}}$ is the structure factor for reflection $\underline{h}$. $f_{j\underline{h}}$ is the atomic scattering factor for j^{th} atom for the reflection $\underline{h}$ and ϵ is the multiplicity factor which is in general unity but may assume other values for special sets of reflections in certain space groups. For a given reflection, there may be a number of relationships in the form of equation VI-9, and the most probable sign of structure factor $\underline{h}$ is given by

$$S(\underline{h}) \approx s\left[\sum_{\underline{h}'} E(\underline{h}') \cdot E(\underline{h}-\underline{h}') \right] \, . \qquad \ldots\ldots \text{VI-11.}$$

The corresponding probability is given by

$$P = \frac{1}{2} + \frac{1}{2} \tanh \left[\frac{1}{\sqrt{N}} \, |E_{\underline{h}}| \cdot \sum_{\underline{h}'} E_{\underline{h}'} \cdot E_{\underline{h}-\underline{h}'} \right] \ldots\ldots \text{VI-12.}$$

The relation VI-11 can be effectively used if the signs of a few large structure factors are known in advance. Signs can be arbitrarily assigned to a few linearly independent reflections in order to fix the origin; for example, three linearly independent reflections, none of which has all the indices even, can be assigned signs arbitrarily for a structure with monoclinic primitive cell (Hauptman and Karle; 1953, 1959). Arbitrary signs are assigned to few more reflections (usually four) and on the basis of these, signs of other reflections are obtained. All permutations of signs can be assigned to the starting set of reflections (except the origin determining reflections) and obtain several solutions (e.g. sixteen solutions if there are four reflections in the starting set). One can assess the correctness of the solution by calculating the consistency index C, given by

$$C = \frac{\left\langle \left| E_{\underline{h}} \sum_{\underline{h}'} E_{\underline{h}'} \cdot E_{\underline{h}-\underline{h}'} \right| \right\rangle}{\left\langle \left| E_{\underline{h}} \right| \sum_{\underline{h}'} \left| E_{\underline{h}'} \right| \cdot \left| E_{\underline{h}-\underline{h}'} \right| \right\rangle}, \qquad \ldots\ldots \quad \text{VI-13.}$$

where $\langle \quad \rangle$ means the average over all values of $\underline{h}$. The true solution will usually have the highest consistency index; however, this is not always true as is also shown by the structure analysis discussed in this chapter.

The general procedure for sign determination adopted in the program is as follows: The reflections are arranged on the decreased order of magnitude of normalised structure factors. There is a provision in the program by means of which the computer selects the origin determining reflections and four other suitable reflections. The origin determining signs are arbitrarily assigned, and the other four signs may be + or - ; therefore 2^4 (=16) possible starting sets of signs are considered. Sayre's relation is reiteratively applied to each of these starting sign sets, yielding 16 solutions. When Sayre's relation is applied to a starting set of signs, additional signs are determined and these are used to determine more signs, and to redetermine those already predicted. The process is repeated until there are no new additions nor changes in the list. The program is written for structures having primitive cells. Therefore for non-primitive space groups, the Miller indices must be transformed to a primitive cell. The structure of 2.nitro-4-methyl benzoic acid belongs to the space group $C_{2/c}$. The Miller indices were transformed to the primitive cell using the matrix

$$\begin{array}{cccc} & h & k & l \\ H & \frac{1}{2} & \frac{1}{2} & 0 \\ K & -\frac{1}{2} & \frac{1}{2} & 0 \\ L & 0 & 0 & 1 \end{array} ,$$

where HKL are the Miller indices of the reflection with respect to the primitive cell.

The computer programme was run using 150 reflections (having $E > 1.2$) and signs of the structure factors for the sixteen sets were obtained. The highest consistency index was 0.79 (Table VI-1). Using the signs from this set, three dimensional Fourier sections were obtained with the help of the photosommatuer; normalised structure factors given in Table VI-1 were used for the Fourier synthesis. Six sections normal to the b axis were taken for $y = 0.00$ to $y = 0.25$ at intervals of 0.05 (Figures VI-2(a) and VI-2(b)). The expression for the electron density for space group $C_{2/c}$ is

$$(x,y,z) = \frac{4}{V}\left\{\left(\sum_{h=-\infty}^{\infty}\sum_{l=0}^{\infty}\left[\sum_{k=0}^{\infty}F_{hkl}\sin 2\pi ky\right].\cos\left(2\pi(hx+lz)+\pi/2\right)\right)^{l=2n+1} + \left(\sum_{h=-\infty}^{\infty}\sum_{l=0}^{\infty}\left[\sum_{k=0}^{\infty}F_{hkl}\cos 2\pi ky\right]\cos 2\pi(hx+lz)\right)^{l=2n}\right\}\ldots\ldots \quad \text{VI-14.}$$

The equation VI-14 was used to obtain the Fourier sections.

Interpretation of Fourier Sections :

The equivalent points for the space group $C_{2/c}$ to which 2-nitro-4-methyl benzoic acid crystals belong, are as follows:

x,y,z; $\bar{x},\bar{y},\bar{z}$; $x,\bar{y},\frac{1}{2}+z$; $\bar{x},y,\frac{1}{2}-z$; $\frac{1}{2}+x,\frac{1}{2}+y,z$;
$\frac{1}{2}-x,\frac{1}{2}-y,\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$.

The equivalent points and the symmetry elements are shown in Figure IV-1. The peaks appearing in the different Fourier sections are plotted in one composite diagram (Fig. VI-3);

the y parameters of the various peaks are also given in the diagram. From this figure, it is apparent that there are two overlapping molecules A and B related by a two fold axis, and two overlapping molecules C and D related by a centre of inversion; in the figure the other symmetry related molecules have not been shown for the sake of clarity. Fig. VI-3 shows that the molecular planes are almost normal to the (010) plane; for clarity of illustration, this diagram is shown again in Figure IV-4 after opening the molecules slightly. These results imply one of the following two possibilities: (1) either the structure is disordered with two half molecules A and C (or B and D) in the asymmetric unit, (2) or the signs of the structure factors used for Fourier summation are with respect to a false centre of symmetry which does not coincide with the crystallographic centre of symmetry. In such a case, the Fourier map will reveal the true structure approximately along with its inverted image. In the course of the structure analysis of 12-ethoxy-2,3-benzo-6,5 naphtho(b)(7,12)-thiaphosphorin-7,7,12-trioxide (Dhaneshwar, Kulkarni, Tavale, Pant; to be published) which crystallises in space group $P\frac{2_1}{n}$, the Fourier map obtained on the basis of the signs of E's corresponding to the set of highest consistency index revealed two half molecules; later analysis showed that the signs of E's were with respect to a false centre of symmetry; on shifting the origin to the correct centre, the structure refined normally.

Table VI-1 : Normalised structure factors with their phases corresponding to the consistency index 0.79 & 0.71.

h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index		h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index	
							0.79	0.71								0.79	0.71
- 2	4	9	1	3	9	3.19	-	-	4	C	8	2	-2	8	2.08	+	+
10	0	2	5	-5	2	2.67	-	+	-4	4	8	0	4	8	2.08	-	-
- 3	5	3	1	4	3	2.66	+	-	-5	3	4	-1	4	4	2.06	-	-
1	5	3	3	2	3	2.56	+	+	-4	6	8	1	5	8	2.04	+	+
- 7	5	7	-1	6	7	2.42	+	+	3	9	2	6	3	2	2.04	+	-
- 5	3	1	-1	4	1	2.39	+	+	3	3	0	3	0	0	2.03	-	-
- 5	5	7	0	5	7	2.39	+	-	1	9	0	5	4	0	2.02	-	-
- 3	3	2	0	3	2	2.36	+	+	-1	5	9	2	3	9	2.00	-	-
5	9	2	7	2	2	2.31	+	+	3	3	2	3	0	2	1.99	+	-
- 8	0	4	-4	4	4	2.30	+	+	-5	5	2	0	5	2	1.99	-	+
7	1	1	4	-3	1	2.26	+	-	4	4	1	4	0	1	1.97	-	+
1	3	10	2	1	10	2.24	+	+	-12	0	4	-6	6	4	1.97	+	-
- 7	3	8	-2	5	8	2.18	-	-	-5	1	5	-2	3	5	1.95	+	+
5	5	3	5	0	3	2.14	+	-	8	0	4	4	-4	4	1.92	+	-
- 7	3	6	-2	5	6	2.14	+	-	8	0	0	4	-4	0	1.91	+	+
-10	2	6	-4	6	6	2.13	+	-	-7	3	7	-2	5	7	1.89	-	-
0	4	5	2	2	5	2.11	-	-	-4	2	2	-1	3	2	1.89	+	+
3	5	2	4	1	2	2.10	-	+	-10	2	7	-4	6	7	1.88	-	-
6	0	2	3	-3	2	2.09	-	-	-2	6	7	2	4	7	1.88	-	+
- 3	3	7	0	3	7	2.09	-	+	2	4	5	3	1	5	1.86	-	+

continued.....

Table VI-1 (continued)

h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index		h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index	
							0.79	0.71								0.79	0.71
2	4	9	3	1	9	1.86	-	+	-5	7	7	1	6	7	1.71	-	+
-4	0	8	-2	2	8	1.86	+	+	-1	5	7	2	3	7	1.71	+	+
2	4	1	3	1	1	1.86	-	-	1	1	7	1	0	7	1.71	-	-
-8	2	2	-3	5	2	1.85	+	-	-7	3	4	-2	5	4	1.71	-	+
2	4	10	3	1	10	1.85	+	+	2	6	7	4	2	7	1.69	-	-
-3	3	8	0	3	8	1.84	-	+	3	1	1	2	-1	1	1.68	+	+
-9	5	6	-2	7	6	1.82	-	-	1	3	4	2	1	4	1.67	-	-
-5	5	8	0	5	8	1.81	+	+	5	9	0	7	2	0	1.67	-	+
12	0	4	6	-6	4	1.81	+	+	-7	1	2	-3	4	2	1.67	-	-
-10	4	6	-3	7	6	1.80	+	+	7	5	3	6	-1	3	1.62	+	+
-1	1	5	0	1	5	1.80	+	-	-9	3	2	-3	6	2	1.62	+	-
-1	5	2	2	3	2	1.79	-	-	-1	3	9	1	2	9	1.62	+	+
1	1	11	1	0	11	1.78	-	+	-2	4	2	1	3	2	1.60	+	+
5	7	1	6	1	1	1.77	+	+	1	9	1	5	4	1	1.59	+	-
-7	5	5	-1	6	5	1.77	-	-	-6	2	1	-2	4	1	1.59	+	+
6	4	3	5	-1	3	1.74	+	-	9	1	3	5	-4	3	1.58	-	-
3	5	9	4	1	9	1.73	-	+	4	2	4	3	-1	4	1.58	+	+
0	8	1	4	4	1	1.73	+	-	-13	3	5	-5	8	5	1.57	+	+
-4	0	4	-2	2	4	1.72	+	-	0	4	9	2	2	9	1.57	-	+
-5	1	2	-2	3	2	1.72	-	+	-8	4	3	-2	6	3	1.57	+	+

continued.....

Table VI-1 (continued)

h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index		h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index	
							0.79	0.71								0.79	0.71
-6	4	1	-1	5	1	1.56	-	-	-4	8	6	2	6	6	1.42	+	+
-2	6	8	2	4	8	1.55	+	-	-1	3	6	1	2	6	1.42	+	+
-2	0	6	-1	1	6	1.54	-	-	-4	4	7	0	4	7	1.42	+	-
6	2	1	4	-2	1	1.54	+	+	-3	9	1	3	6	1	1.42	+	-
0	4	3	2	2	3	1.53	+	+	8	8	1	8	0	1	1.41	+	-
1	5	8	3	2	8	1.51	+	-	3	3	9	3	0	9	1.41	+	-
1	5	9	3	2	9	1.51	-	+	-9	3	1	-3	6	1	1.41	+	-
6	0	6	3	-3	6	1.50	-	-	6	4	5	5	-1	5	1.41	-	-
-4	6	1	1	5	1	1.50	+	+	4	2	1	3	-1	1	1.41	+	-
0	2	8	1	1	8	1.49	-	-	3	9	0	6	3	0	1.40	-	+
-6	4	6	-1	5	6	1.49	+	-	1	9	6	5	4	6	1.40	+	-
5	3	2	4	-1	2	1.46	+	+	-3	7	5	2	5	5	1.40	+	+
10	2	2	6	-4	2	1.46	+	-	4	8	1	6	2	1	1.40	+	+
0	4	2	2	2	2	1.45	+	-	0	2	9	1	1	9	1.40	+	-
-11	1	3	-5	6	3	1.45	-	-	4	0	0	2	-2	0	1.40	+	-
0	2	5	1	1	5	1.44	+	+	3	3	1	3	0	1	1.39	-	-
0	4	8	2	2	8	1.43	-	+	-3	3	14	0	3	14	1.38	+	-
6	4	10	5	-11	10	1.43	+	-	3	1	6	2	-1	6	1.38	-	-
-8	6	5	-1	7	5	1.43	+	-	4	0	12	2	-2	12	1.38	+	-
6	2	2	4	-2	2	1.43	+	+	3	1	7	2	-1	7	1.38	-	+

continued.....

Table VI-1 (continued)

h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index		h	k	l	H	K	L	E_{hkl}	Phase corresponding to the consistency index	
							0.79	0.71								0.79	0.71
-6	6	7	0	6	7	1.37	-	-	3	5	4	4	1	4	1.33	+	+
0	6	1	3	3	1	1.37	+	-	-4	2	3	-1	3	3	1.32	-	-
10	4	5	7	-3	5	1.37	-	+	-3	3	9	0	3	9	1.32	-	-
5	1	3	3	-2	3	1.37	-	+	-3	5	1	1	4	1	1.32	-	+
2	4	2	3	1	2	1.36	+	-	-8	6	6	-1	7	6	1.32	-	+
-6	2	3	-2	4	3	1.35	-	+	5	3	10	4	-1	10	1.31	+	-
-8	4	4	-2	6	4	1.35	+	+	1	7	1	4	3	1	1.31	+	-
-2	0	4	-1	1	4	1.34	+	+	-3	5	1	1	4	1	1.31	-	+
2	0	10	1	-1	10	1.34	-	+	-6	6	1	0	6	1	1.30	+	+
7	7	3	7	0	3	1.34	-	-	5	5	7	5	0	7	1.30	+	+
9	7	1	8	-1	1	1.33	+	-	6	6	0	6	0	0	1.30	+	-
4	8	2	6	2	2	1.33	+	+	6	2	8	4	-2	8	1.29	-	+
-2	2	2	0	2	2	1.33	+	-	-4	6	6	1	5	6	1.29	-	-
-7	5	6	-1	6	6	1.33	-	+	0	0	6	0	0	6	1.28	-	+
13	1	3	7	-6	3	1.33	-	+	3	1	11	2	-1	11	1.28	-	-

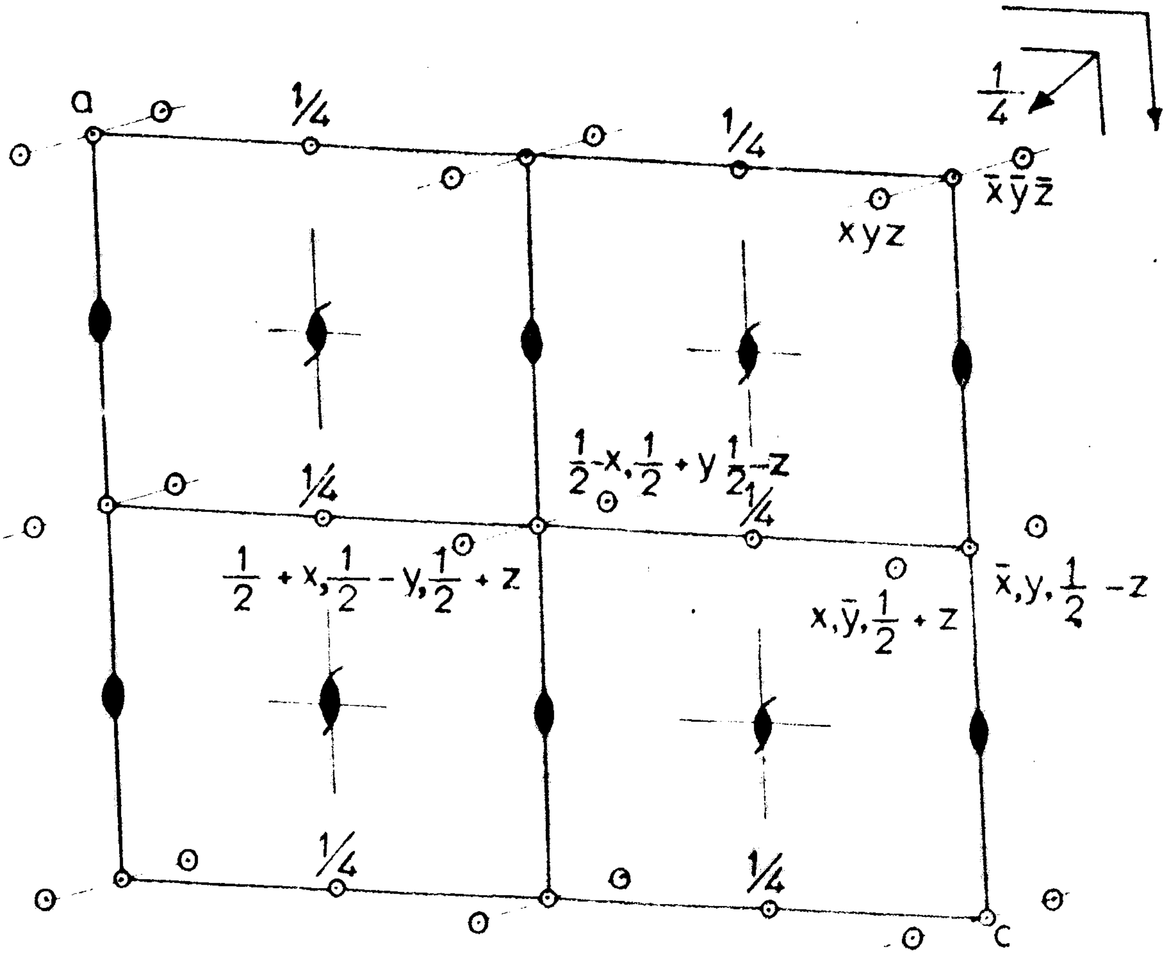
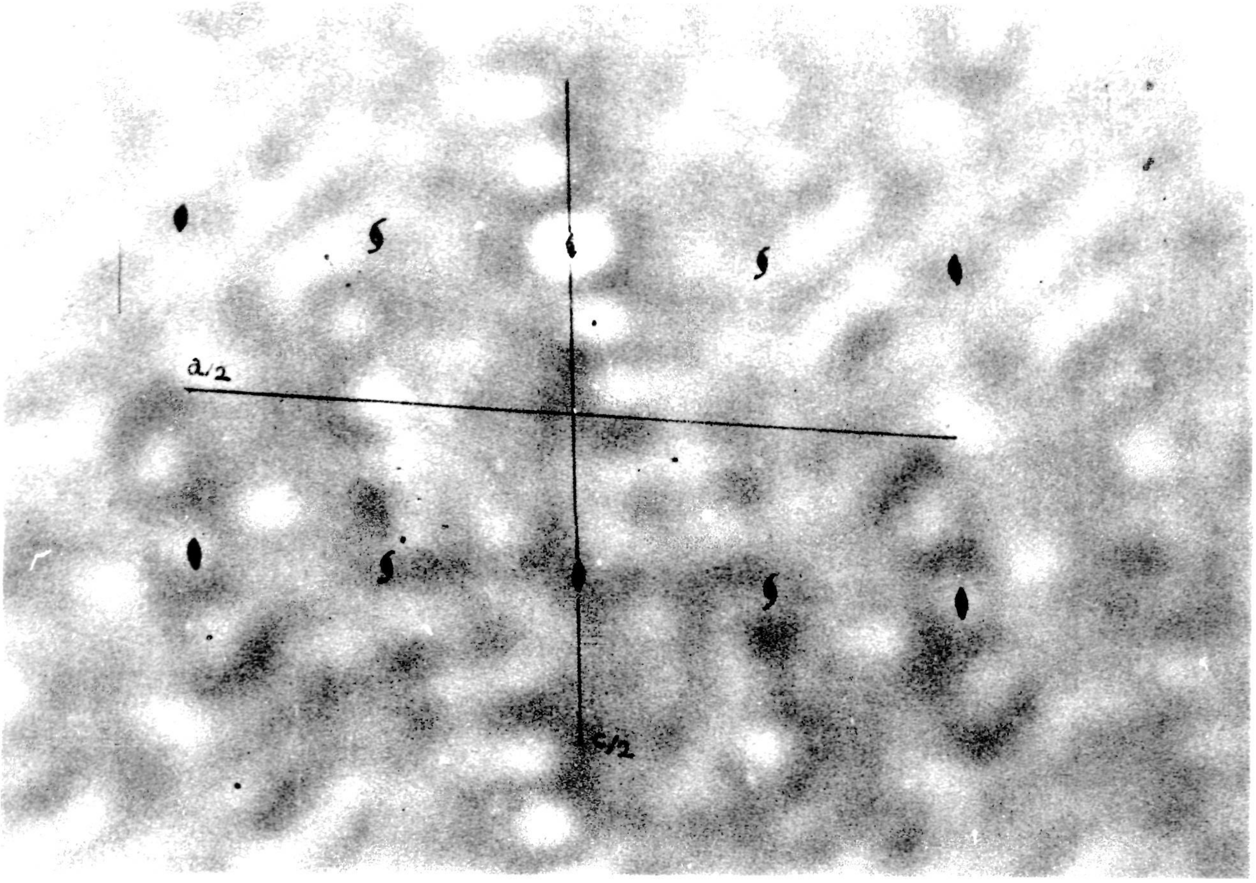
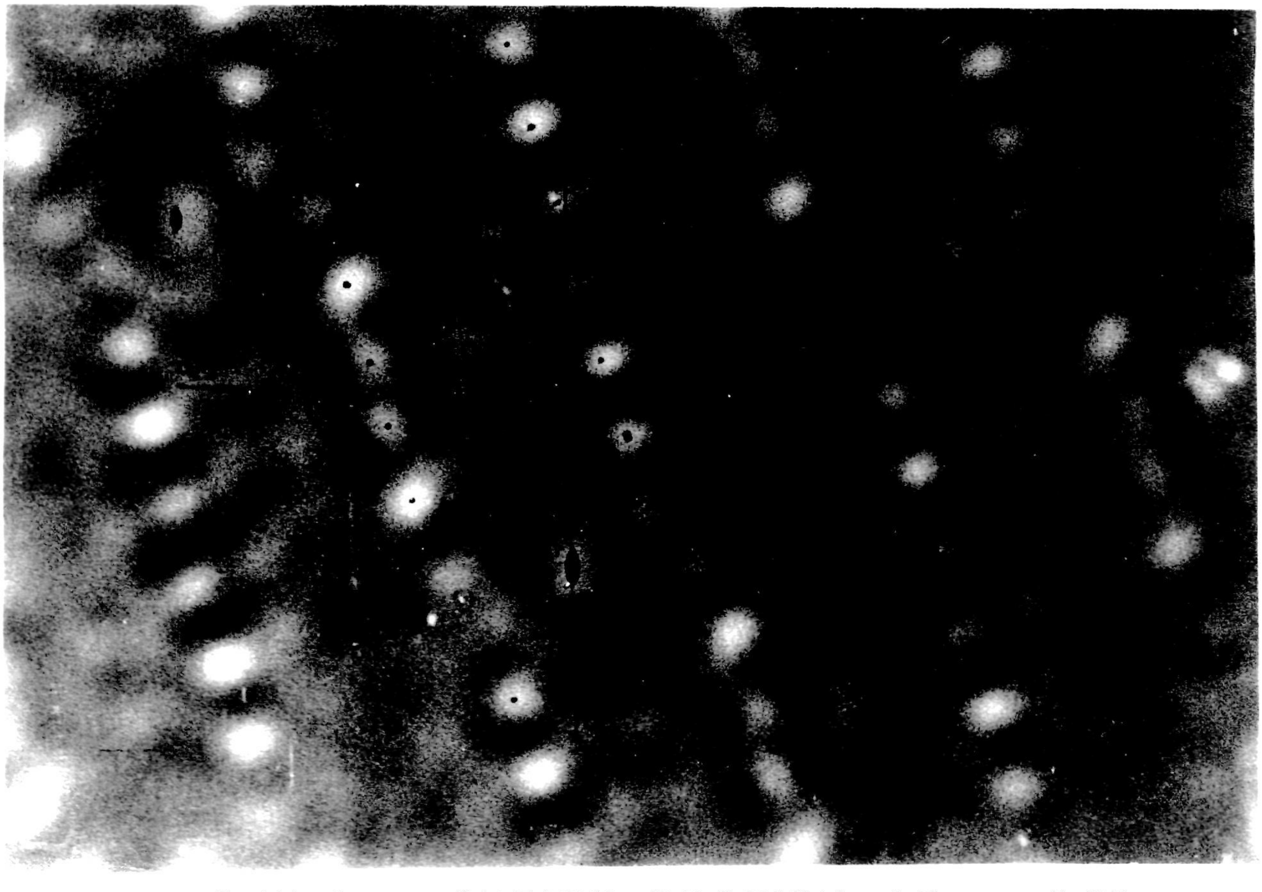


FIG VI-1. THE SYMMETRY ELEMENTS AND EQUIVALENT POINTS FOR SPACE GROUP C2/c, PROJECTED ON ac PLANE



FIG·VI-2 a: FOURIER SECTION AT $y = 0{\cdot}15$



FIG·VI-2 b: FOURIER SECTION AT $y = 0{\cdot}25$

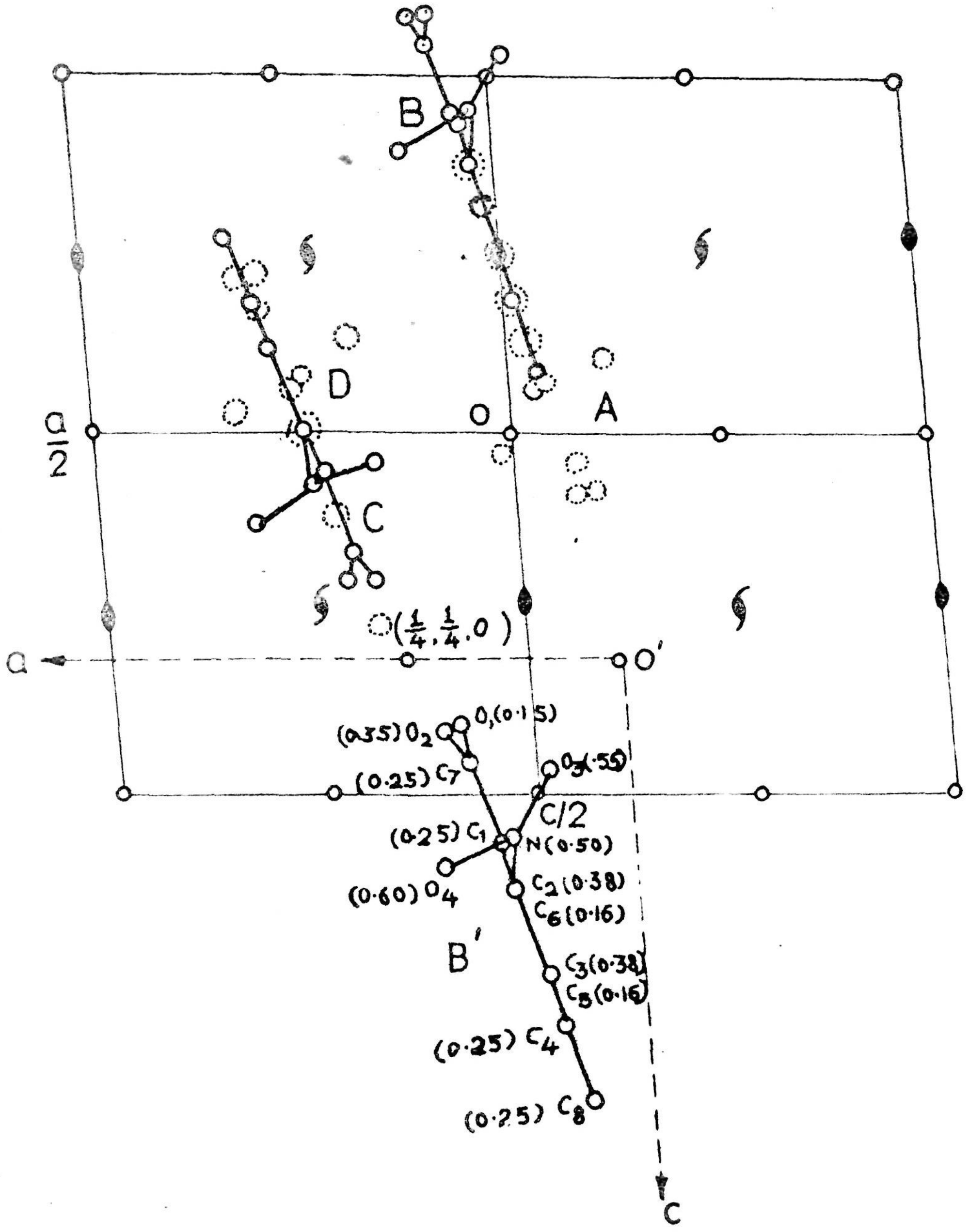
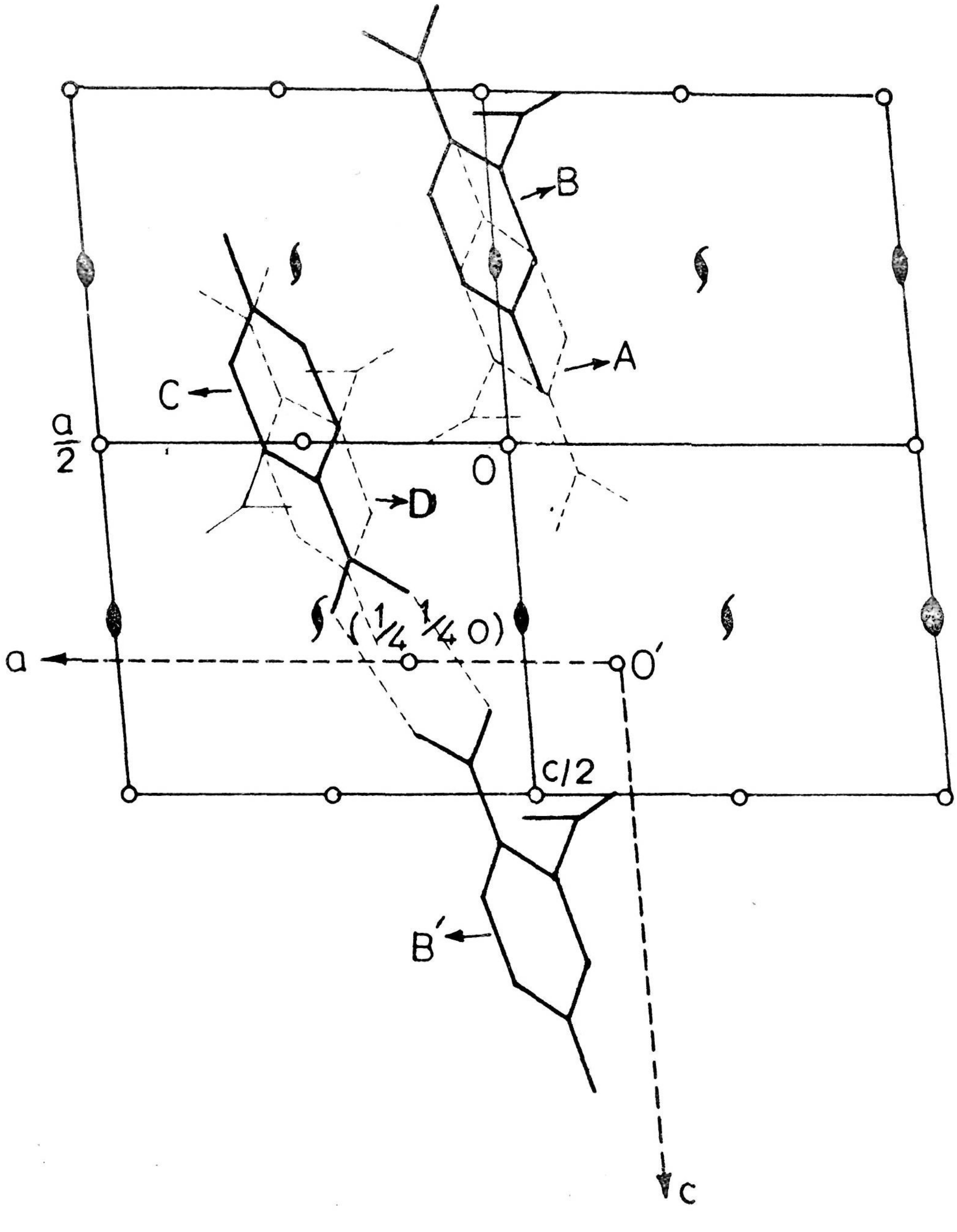


FIG-VI-3: THE POSITIONS OF THE PEAKS OBTAINED FROM THE FOURIER SECTIONS (FIG-VI-2) THE HEIGHTS OF THE PEAKS ARE ALSO GIVEN.



FIG·VI·4 - SAME AS FIG·VI·3 EXCEPT THAT THE MOLECULES ARE OPENED SLIGHTLY FOR CLARITY OF ILLUSTRATION

A careful look at Figure VI-4 suggests that the second alternative is probably the correct one. The molecule B' in Figure VI-4 which is obtained by translating the molecule B by vector distance c seems, as expected, to form a dimer with molecule C. The centre of this dimer is on the $(x,\frac{1}{4},z)$ plane, and the dimer appears to be approximately centrosymmetrical. It thus appears very likely that the molecule B' and C are in fact related by a centre of symmetry. The origin of the unit cell was therefore shifted to O' (Fig. VI-4) such that the dimer centre falls at $(\frac{1}{4},\frac{1}{4},0)$. The parameters of the atoms of molecule B' with respect to the new origin O' were used to calculate the structure factors. There was generally good agreement between F_o and F_c although there were some serious discrepancies and R was very high (0.79). Later refinement showed that the structure was basically correct and the high R value was due to large errors in the parameters of the oxygen atoms of carboxylic and nitro groups; these atoms do not appear clear in the Fourier map but were placed in the figure at the expected positions assuming structure of the compound to be similar to that of o-nitrobenzoic acid (Tavale and Pant, 1973).

It was found that the signs given by the set having consistency index 0.72 were generally agreeing with the signs obtained by the trial structure. Therefore this set of signs was chosen to obtain the Fourier sections again. As in the previous case, six sections normal to the b-axis were taken;

these are shown in Figures VI-5(a) to VI-5(f). These sections revealed all the non-hydrogen atoms clearly. The structure obtained on the basis of these Fourier sections is shown in (010) projection in Figure VI-6.

The atomic parameters obtained from the first and second trial structure are given in Table VI-2 for comparison; the table shows that the four oxygen atoms were placed at incorrect positions in the first trial. The structure factors on the basis of the atomic parameters of the second trial structure were calculated; the R factor for 1323 reflections was 0.35; this indicates that the second trial structure is correct. Further refinement of the structure was done by the method of least squares as discussed in Section B of this chapter.

SECTION B : REFINEMENT OF THE STRUCTURE

The refinement of atomic and thermal parameters was done with the help of 1315 observed reflections; eight reflections appear to be subject to extinction and these were omitted for the refinement.

Refinement using isotropic temperature factors :

The equation used to calculate the structure factor F(hkl) is given by

$$F(hkl) = \sum_{j=1}^{n} 8f_j \cos^2 2\pi(\frac{h+k}{2}) \cdot \cos 2\pi(hx_j+lz_j+\frac{1}{4}) . \cos 2\pi(ky_j-\frac{1}{4}), \qquad ..... \text{ VI-15.}$$

where $f_j = f_o \exp(-B \sin^2\theta/\lambda^2)$.

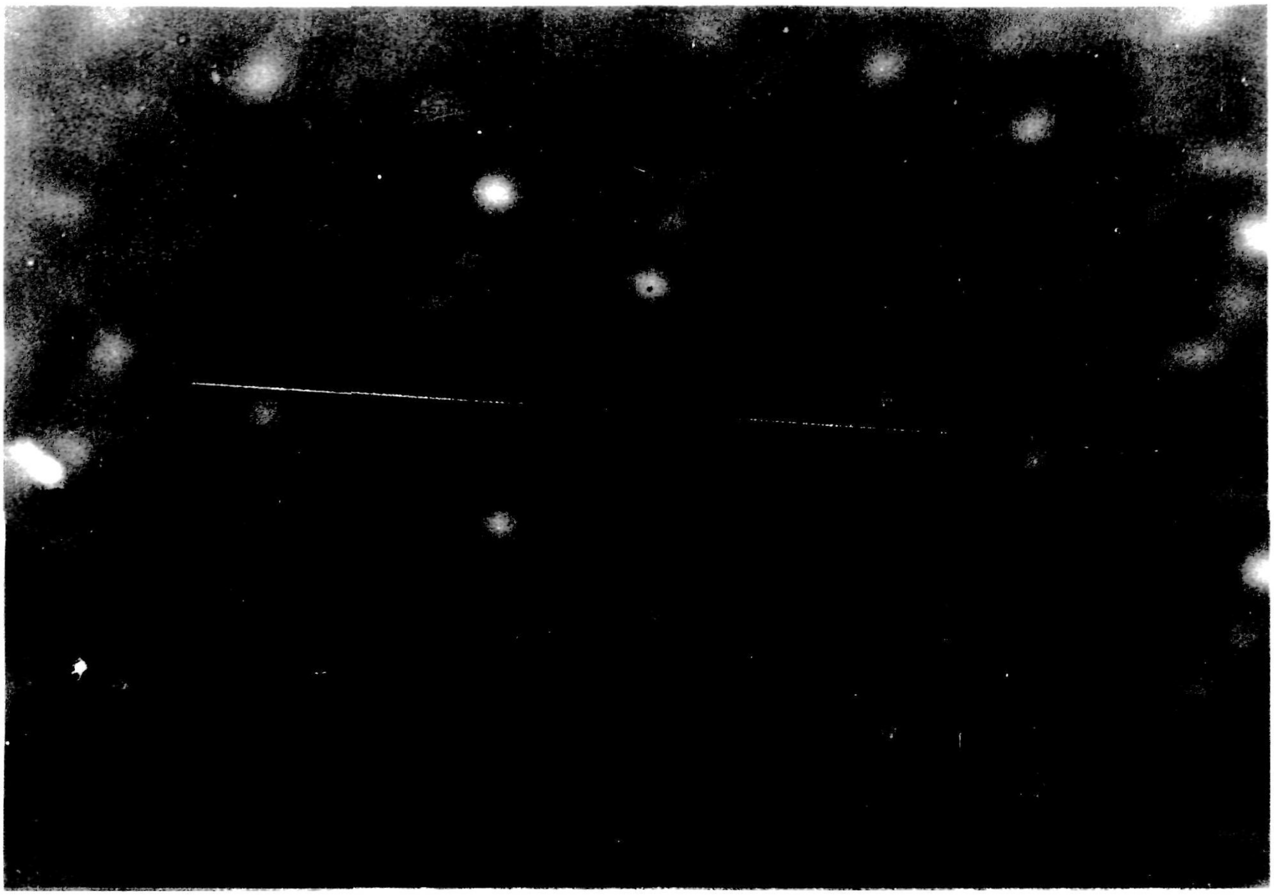


FIG-VI-5a: FOURIER SECTION AT y=0·00

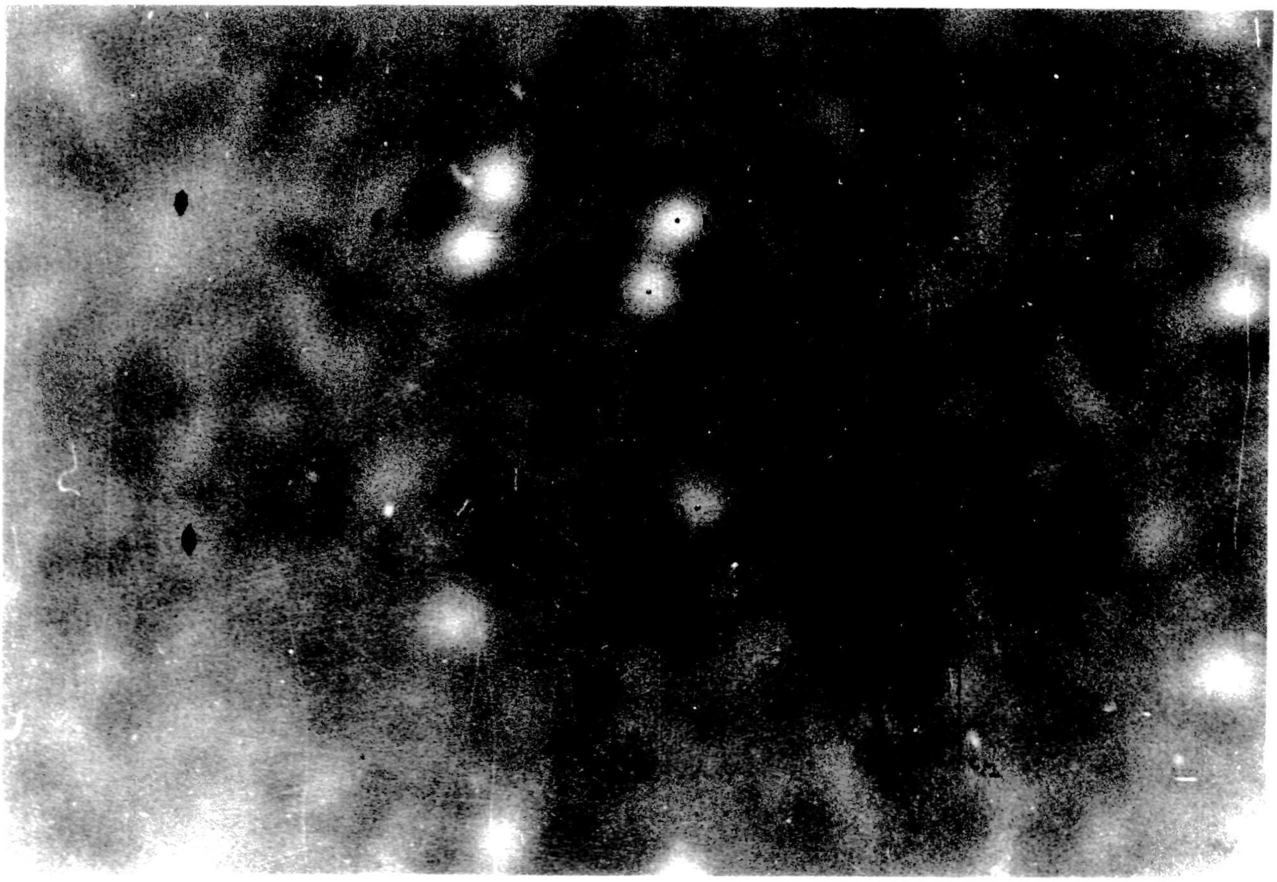


FIG-VI-5b: FOURIER SECTION AT y=0·05

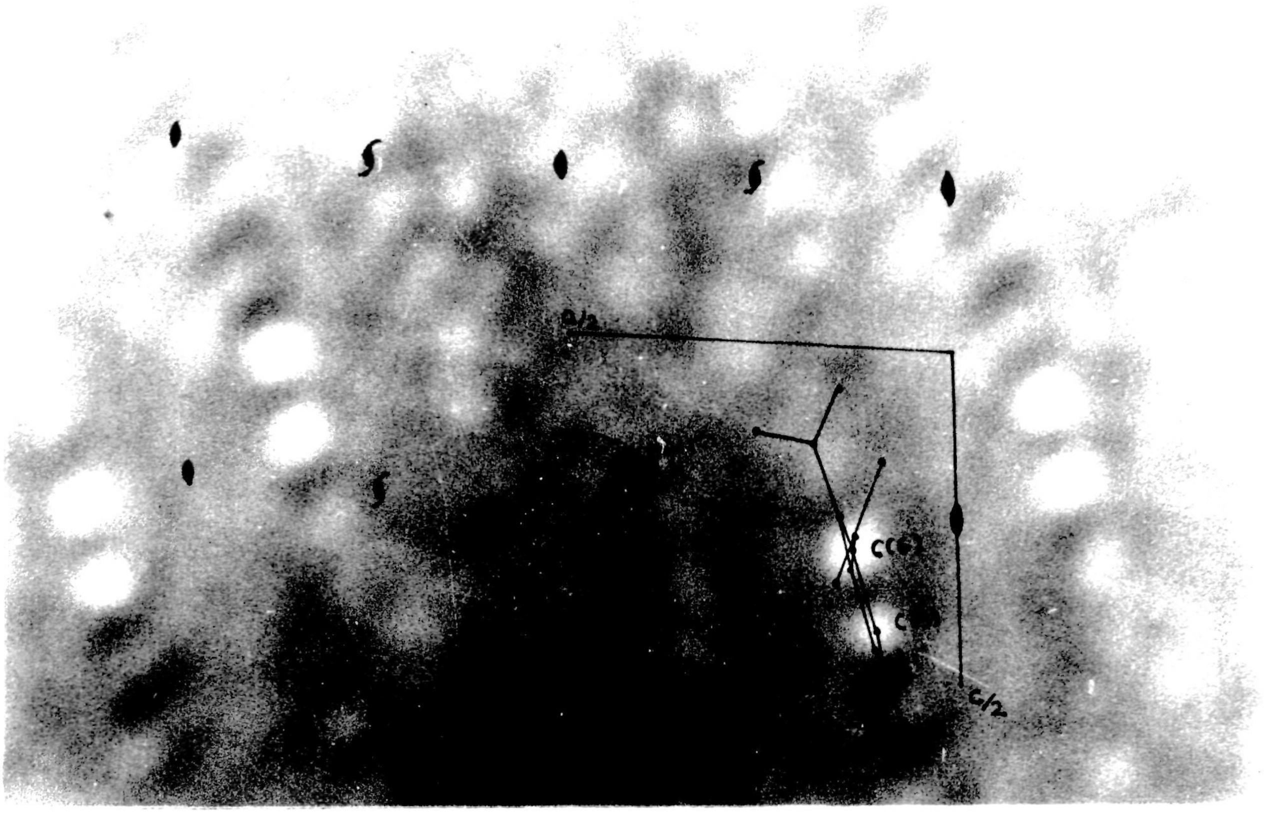


FIG-VI-5c: FOURIER SECTION AT y = 0·10

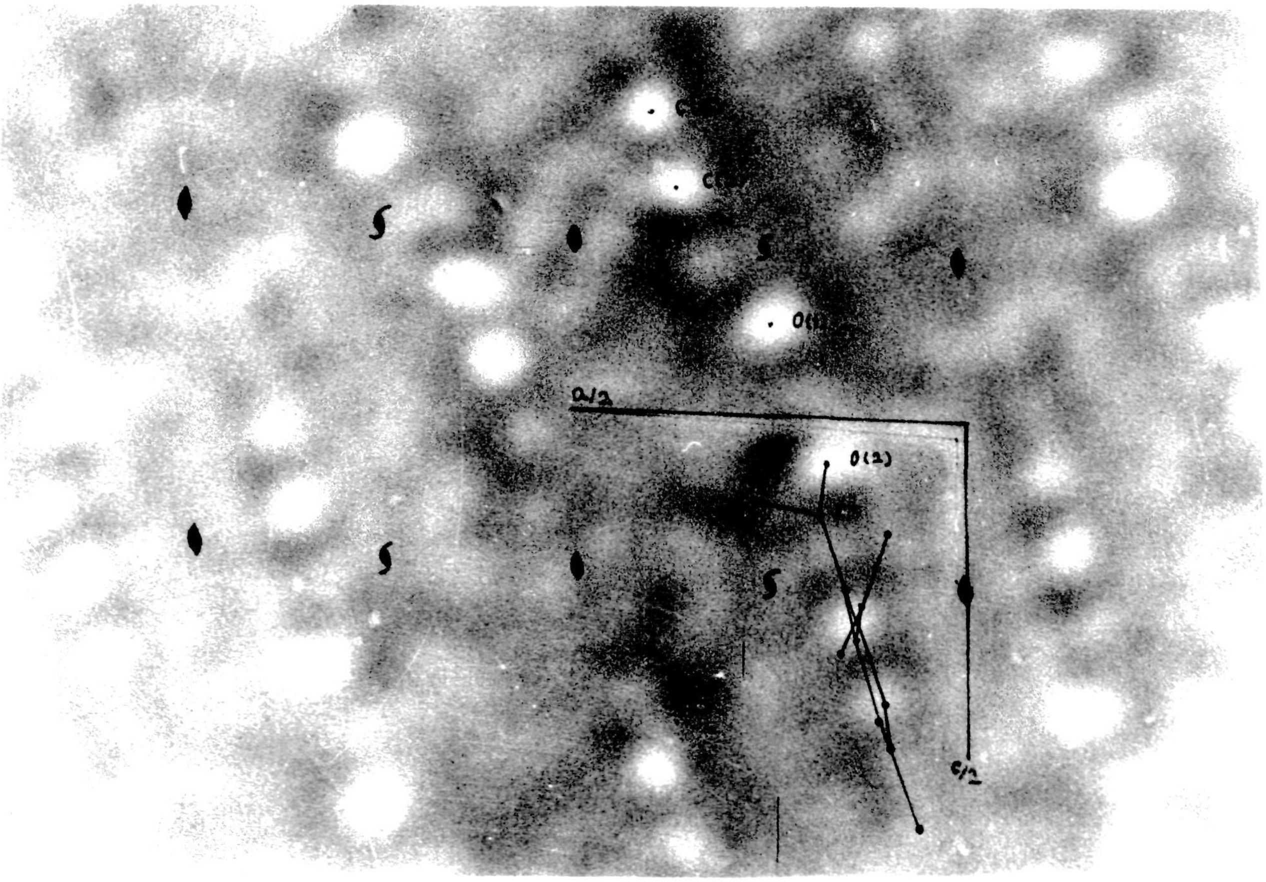


FIG-VI-5d: FOURIER SECTION AT y = 0·15

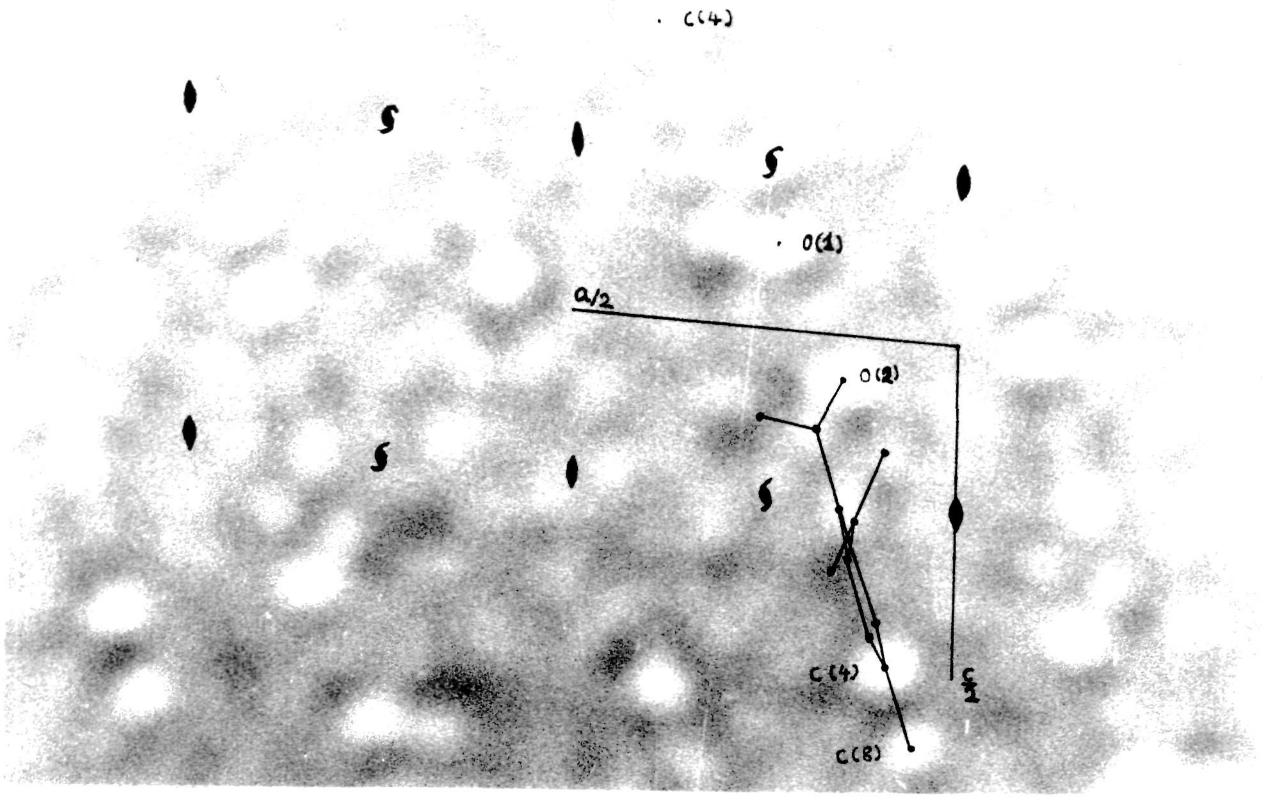


FIG-VI-5e: FOURIER SECTION AT y=0·20

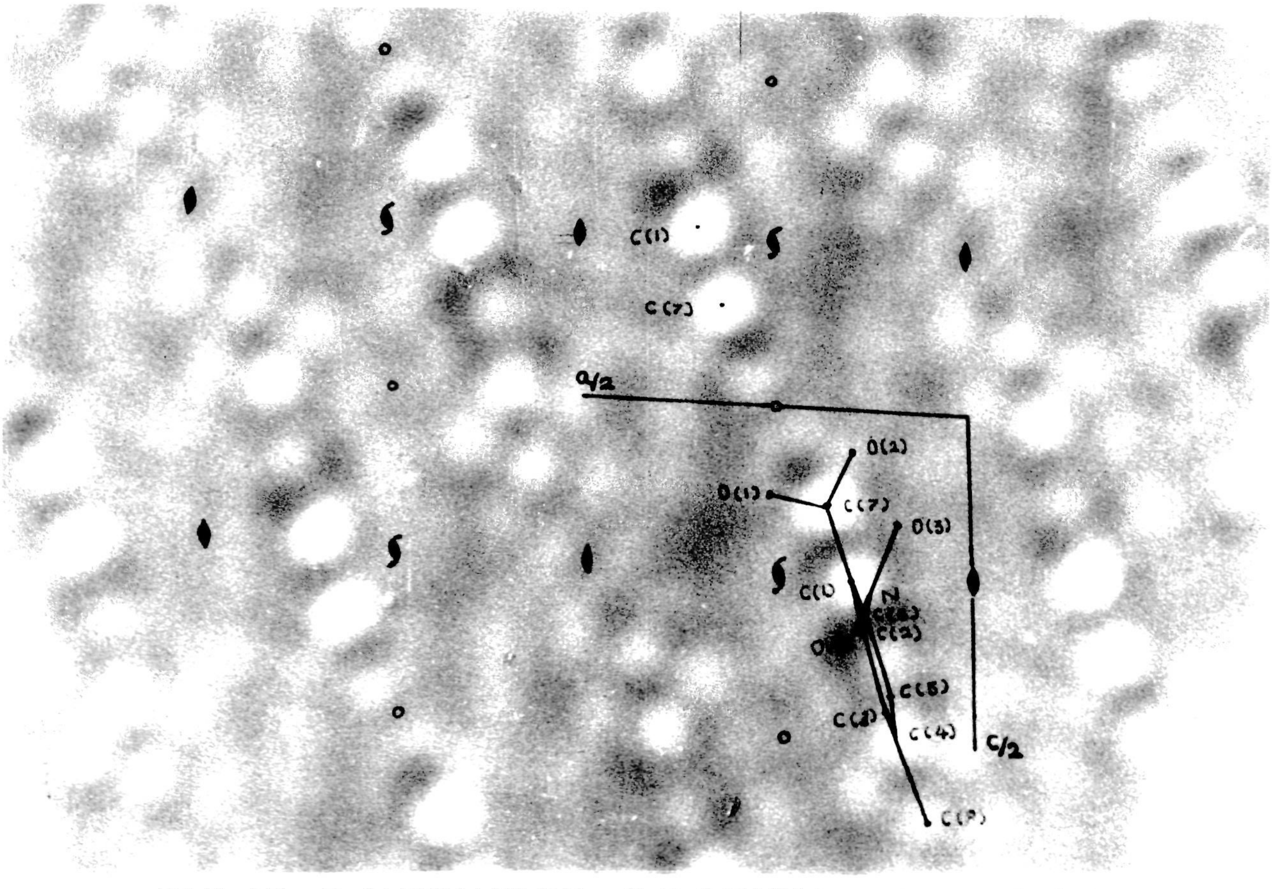


FIG-VI-5 f: FOURIER SECTION AT y=0·25

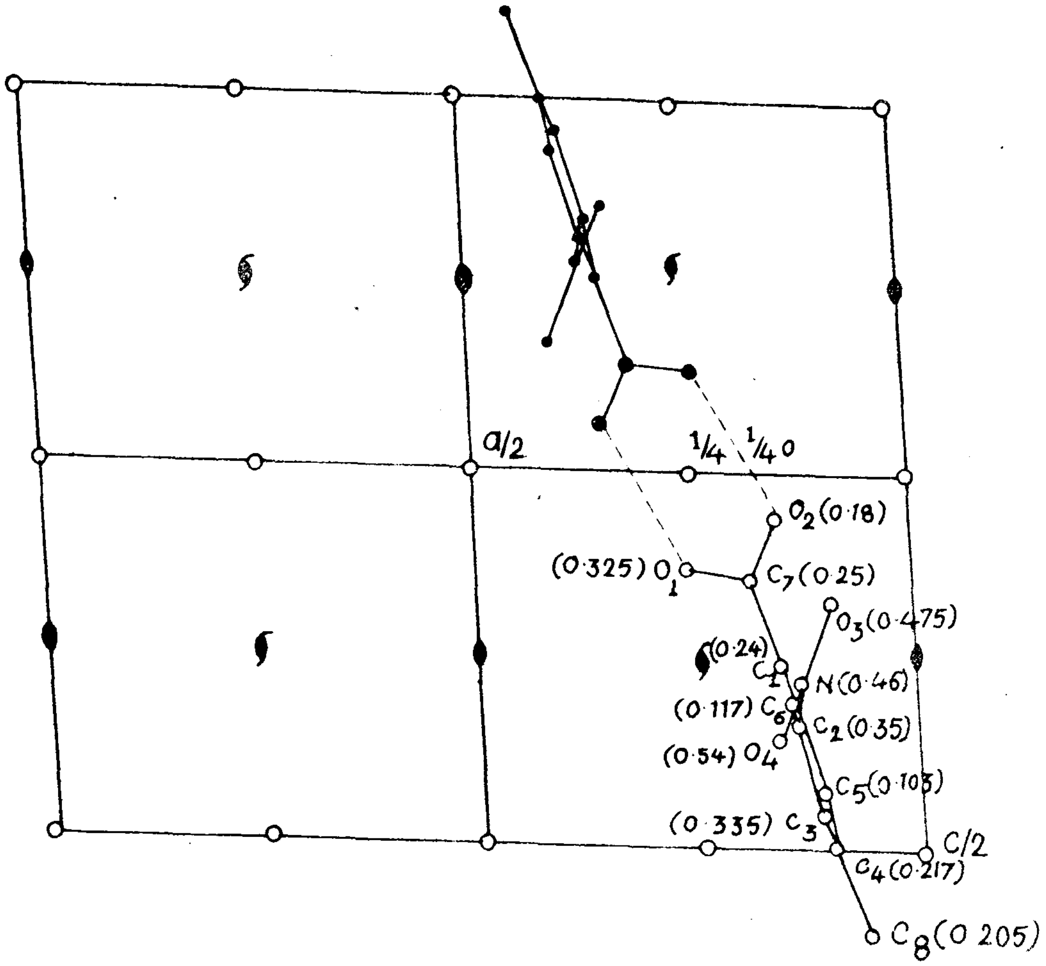


FIG-VI-6: TRIAL STRUCTURE OBTAINED FROM FOURIER SECTIONS SHOWN IN "FIGURE-VI 5"

Table VI-2

Atom	TRIAL I Consistency Index = 0.79			TRIAL II Consistency Index = 0.72		
	x	y	z	x	y	z
C(1)	0.156	0.250	0.255	0.154	0.240	0.260
C(2)	0.144	0.360	0.315	0.143	0.350	0.339
C(3)	0.115	0.360	0.438	0.107	0.335	0.453
C(4)	0.099	0.250	0.500	0.101	0.217	0.497
C(5)	0.115	0.140	0.438	0.112	0.105	0.430
C(6)	0.144	0.140	0.315	0.143	0.117	0.308
C(7)	0.185	0.250	0.146	0.188	0.250	0.149
C(8)	0.075	0.250	0.606	0.065	0.205	0.613
N	0.147	0.480	0.250	0.134	0.460	0.285
O(1)	0.195	0.150	0.091	0.261	0.325	0.135
O(2)	0.211	0.350	0.100	0.153	0.180	0.063
O(3)	0.093	0.500	0.156	0.096	0.475	0.173
O(4)	0.226	0.580	0.292	0.162	0.540	0.360

The atomic scattering factor f_o was calculated by using Moor's constants given in Table III-1. The refinement of the atomic parameters and the individual isotropic temperature factors was carried out by using the least squares method as discussed in Chapter III. The starting value of R, using overall temperature factor 2.9 Å obtained by Wilson's method, was 0.35; after six cycles of least squares refinement, it was reduced to 0.16. The individual isotropic temperature factors are given in Table V-3. At this stage of refinement, the anisotropic temperature factors were introduced.

The refinement of atomic and anisotropic thermal parameters :

For the space group $C_{2/c}$, the thermal vibration ellipsoids corresponding to the four atoms with equivalent points $\pm$ (x,y,z) and $\pm$ ($\frac{1}{2}$+x, $\frac{1}{2}$+y, z) are parallel; the ellipsoids corresponding to the other four atoms with equivalent points $\pm$ (x,$\bar{y}$,$\frac{1}{2}$+z) and $\pm$ ($\frac{1}{2}$+x, $\frac{1}{2}$-y, $\frac{1}{2}$+z) are parallel among themselves but are related to the first set of thermal vibration ellipsoids by a mirror plane perpendicular to the b axis. The atomic scattering factor for the atoms of the first set is given by

$$f_A = f_o \exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)\right] , \qquad \ldots\ldots \text{ VI-16.}$$

while for the atoms of the other set, it is given by

$$f_B = f_o \exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2-2b_{12}hk-2b_{23}kl+2b_{13}hl)\right] \quad \text{..... VI-17}$$

(Rollett, 1965)

When anisotropic temperature factors are used, the structure factor equation becomes:

$$F(hkl) = \sum_{j=1}^{n} 2f_{Aj}\left[\cos 2\pi(hx_j + ky_j + lz_j) + \cos 2\pi\left(hx_j + ky_j + lz_j + \frac{h+k}{2}\right)\right]$$

$$+ \sum_{j=1}^{n} 2f_{Bj}\left[\cos 2\pi(hx_j - ky_j + lz_j + 1/2) + \cos 2\pi\left(hx_j - ky_j + lz_j + \frac{h+k+1}{2}\right)\right] \quad \text{..... VI-18.}$$

The refinement was carried out as discussed in Chapter III, using 3x3 matrix for positional parameters and 6x6 matrix for thermal parameters of each atom. The starting values of b_{ij}'s given in Table VI-3 are obtained by using the following relations:

$$b_{11} = \frac{Ba^{*2}}{4}, \qquad b_{22} = \frac{Bb^{*2}}{4}, \qquad b_{33} = \frac{Bc^{*2}}{4},$$

$$b_{12} = 0, \qquad b_{23} = 0, \qquad b_{13} = \frac{Ba^*c^*\cos\beta^*}{4}.$$

The equations III-12 for triclinic crystals, given in Chapter III reduce to the above for monoclinic crystals. The value of R after four cycles of refinement was reduced to 0.106.

Table VI-3

Atom	B	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	2.61	0.0034	0.0048	0.0046	0.000	0.000	0.0005
C(2)	2.53	0.0034	0.0048	0.0046	0.000	0.000	0.0005
C(3)	3.09	0.0039	0.0056	0.0053	0.000	0.000	0.0005
C(4)	2.75	0.0038	0.0054	0.0051	0.000	0.000	0.0005
C(5)	3.92	0.0052	0.0074	0.0070	0.000	0.000	0.0005
C(6)	3.81	0.0050	0.0072	0.0068	0.000	0.000	0.0005
C(7)	2.80	0.0036	0.0052	0.0049	0.000	0.000	0.0005
C(8)	4.23	0.0056	0.0080	0.0076	0.000	0.000	0.0005
O(1)	3.36	0.0043	0.0062	0.0059	0.000	0.000	0.0005
O(2)	3.68	0.0048	0.0068	0.0065	0.000	0.000	0.0005
O(3)	5.18	0.0060	0.0086	0.0082	0.000	0.000	0.0005
O(4)	5.68	0.0088	0.0126	0.0120	0.000	0.000	0.0006
N	3.48	0.0048	0.0068	0.0065	0.000	0.000	0.0005

Table VI-4 : Final atomic and thermal parameters.
The anisotropic thermal parameters ($\times 10^4$) are of the form
$T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)\right]$.
The e.s.d.'s are given in parentheses and refer to last significant figures.

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	0.1512 (2)	0.2412 (3)	0.2649 (2)	53 (2)	44 (3)	53 (2)	1 (1)	3 (2)	16 (1)
C(2)	0.1297 (2)	0.3396 (3)	0.3346 (2)	50 (2)	47 (3)	58 (2)	-4 (1)	-5 (2)	15 (1)
C(3)	0.1031 (2)	0.3268 (3)	0.4481 (2)	61 (2)	56 (3)	58 (2)	-4 (2)	-12 (2)	17 (2)
C(4)	0.0949 (2)	0.2128 (3)	0.4962 (2)	56 (2)	74 (3)	50 (2)	0 (2)	3 (2)	10 (1)
C(5)	0.1159 (3)	0.1132 (3)	0.4279 (3)	88 (3)	61 (4)	79 (3)	8 (2)	22 (2)	28 (2)
C(6)	0.1435 (3)	0.1280 (3)	0.3146 (3)	88 (2)	49 (3)	79 (2)	5 (2)	-10 (2)	35 (2)
C(7)	0.1909 (2)	0.2508 (3)	0.1465 (2)	56 (2)	52 (3)	57 (2)	3 (2)	-6 (2)	18 (1)
C(8)	0.0626 (3)	0.1983 (4)	0.6188 (3)	89 (3)	115 (4)	50 (2)	-11 (2)	11 (2)	19 (2)
N	0.1281 (2)	0.4622 (2)	0.2850 (2)	70 (2)	47 (3)	88 (2)	-7 (1)	-4 (2)	32 (2)
O(1)	0.2611 (2)	0.3258 (2)	0.1344 (2)	67 (1)	88 (3)	60 (2)	-19 (1)	-13 (1)	28 (1)
O(2)	0.1553 (2)	0.1802 (2)	0.0673 (2)	68 (1)	113 (3)	58 (2)	-23 (1)	-26 (2)	21 (1)
O(3)	0.0981 (2)	0.4752 (2)	0.1819 (2)	97 (2)	80 (3)	87 (2)	13 (2)	34 (2)	24 (2)
O(4)	0.1527 (3)	0.5461 (3)	0.3509 (3)	175 (3)	62 (3)	135 (3)	-35 (2)	-16 (2)	35 (3)

Table VI-5 : Final atomic parameters. The e.s.d.'s are given in parentheses and refer to last significant figures.

Atom	x	y	z
H(1)	0.086 (3)	0.387 (4)	0.475 (3)
H(2)	0.110 (3)	0.038 (4)	0.454 (4)
H(3)	0.153 (3)	0.070 (4)	0.280 (4)
H(4)	0.062 (3)	0.108 (5)	0.634 (4)
H(5)	-0.001 (4)	0.238 (4)	0.639 (4)
H(6)	0.114 (3)	0.237 (4)	0.678 (4)
H(7)	0.293 (3)	0.309 (4)	0.071 (4)

The refinement was carried out using Cruickshank's weighting scheme $w = 1/(a + |F_o| + c\,|F_o|^2)$ where $a = 2F_{min}$ and $c = 2/F_{max}$.

Three hydrogen atoms which were attached to the ring were included in the refinement. Their positions were determined on stereochemical considerations. The layer-wise scaling was also applied at this stage. For the further refinement, the unobserved reflections having F_c greater than the minimum observable value were also used. Three more cycles of least squares refinement brought R factor to 0.097. The positions of hydrogen atoms attached to the methyl group carbon atom C(8) and the one attached to the carboxylic group were determined from the three difference Fourier projections. Three more cycles of refinement brought R value down to 0.089. The final atomic and thermal parameters of non-hydrogen atoms are given in Table VI-4; the atomic parameters of the hydrogen atoms are given in Table VI-5. The standard deviations given in these tables were obtained from the diagonal elements of the inverted matrix. The observed structure factors F_o and calculated structure factors F_c based on the final atomic and thermal parameters are given in Appendix B.

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CHAPTER - VII

RESULTS AND DISCUSSION

Crystal and Molecular Structure :

The bond lengths and bond angles are given in Table VII-1 and are also shown in Figure VII-1. The C(1)-C(7), C(4)-C(8), C(2)-N, C(7)-O(1), C(7)-O(2), N-O(3) and N-O(4) bond lengths have been corrected for the effect of librational motion by Cruickshank's method (1965) described in Chapter IV (page 56). The equations of planes with respect to a', b, c orthogonal axes, the angles between the planes and deviations of the atoms from these planes are given in Table VII-2. The equations of planes were obtained by the method of Schomaker, Waser, Marsh and Bergman (1959).

Discussion :

Aromatic ring

The aromatic ring is planar within 0.006 Å; the average C-C bond length in the ring is 1.388 Å; this agrees with the average C-C bond length in the aromatic ring in o-nitrobenzoic acid (1.380 Å; Tavale and Pant, 1973). The bond lengths and bond angles of o-nitrobenzoic acid are shown in Figure VII-2 for comparison. Within the benzene ring, the valency angle at the carbon atom C(1) bearing the carboxylic group is less than 120° (116.3 ± 0.3°) whereas the angle at the atom C(2) bearing the nitro group is more than

Table VII-1 : Intramolecular bond lengths and angles.

	Uncorrected	Corrected	E.s.d.	Angle	
C(1)-C(2)	1.394 Å		0.004 Å	C(6)-C(1)-C(2)	116.3 ± 0.3°
C(2)-C(3)	1.385		0.004	C(1)-C(2)-C(3)	122.8
C(3)-C(4)	1.383		0.004	C(2)-C(3)-C(4)	120.2
C(4)-C(5)	1.393		0.004	C(3)-C(4)-C(5)	118.0
C(5)-C(6)	1.389		0.004	C(4)-C(5)-C(6)	121.0
C(6)-C(1)	1.381		0.004	C(5)-C(6)-C(1)	121.8
C(1)-C(7)	1.504	1.507 Å	0.004	C(3)-C(4)-C(8)	120.3
C(4)-C(8)	1.514	1.529	0.005	C(5)-C(4)-C(8)	121.7
C(2)-N	1.467	1.478	0.004	C(2)-C(1)-C(7)	124.7
C(7)-O(1)	1.265	1.276	0.004	C(6)-C(1)-C(7)	118.7
C(7)-O(2)	1.250	1.265	0.004	C(1)-C(7)-O(1)	118.3
N-O(3)	1.212	1.230	0.004	C(1)-C(7)-O(2)	117.7
N-O(4)	1.217	1.250	0.004	O(1)-C(7)-O(2)	123.9
C(3)-H(1)	0.78		0.04	C(1)-C(2)-N	119.7
C(5)-H(2)	0.89		0.04	C(3)-C(2)-N	117.4
C(6)-H(3)	0.77		0.04	C(2)-N-O(3)	118.3
C(8)-H(4)	1.02		0.05	C(2)-N-O(4)	118.2
C(8)-H(5)	1.00		0.05	O(3)-N-O(4)	123.4
C(8)-H(6)	1.00		0.05		
O(1)-H(7)	0.90		0.04		

Table VII-2

Equations of planes

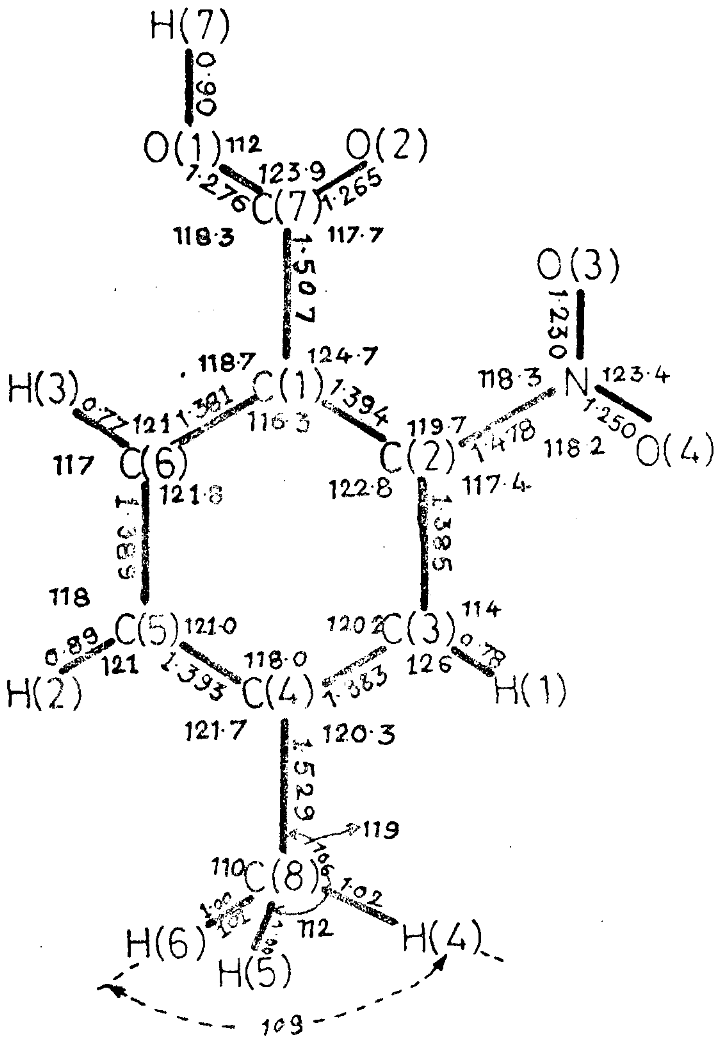
(1) Benzene ring	$0.9627\,x + 0.0438\,y + 0.2671\,z - 2.7915 = 0$
(2) Plane through O(1), O(2) and C(7)	$-0.6793\,x + 0.6884\,y - 0.2543\,z + 0.1644 = 0$
(3) Plane through O(3), O(4) and N	$0.9392\,x - 0.0685\,y - 0.3364\,z - 0.2042 = 0$

Angles between different planes

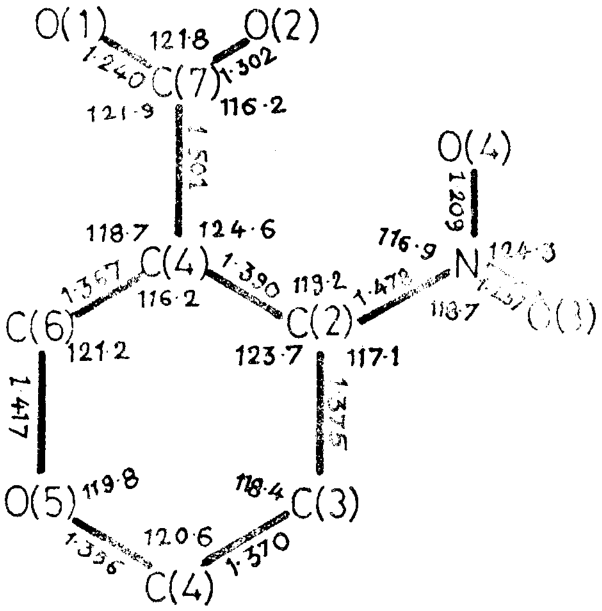
	(2)	(3)
(1)	46.2°	35.8°

Deviations of atoms from different planes(Å)

	Planes		
	(1)	(2)	(3)
C(1)	0.000	-0.074	
C(2)	-0.005		-0.077
C(3)	0.006		
C(4)	-0.004		
C(5)	-0.001		
C(6)	0.002		
C(7)	0.135	0.000	
C(8)	-0.036		
O(1)		0.000	
O(2)		0.000	
O(3)			0.000
O(4)			0.000
N	-0.116		0.000
H(1)	-0.096		
H(2)	-0.025		
H(3)	-0.020		



FIG·VII-1: BOND LENGTHS (A°) AND BOND ANGLES (°) IN 2-nitro-4-methyl benzoic ACID

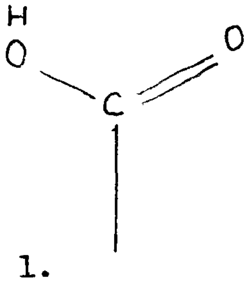


FIG·VII-2: BOND LENGTHS (A°) AND ANGLES (°) OF o-nitro-benzoic ACID

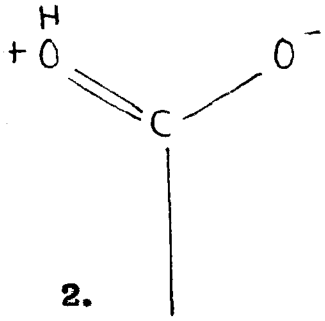
120° (122.8 ± 0.3°); similar result is observed in the structure of o-nitrobenzoic acid (Fig. VII-2) where the corresponding angles are 116.2 ± 0.9° and 123.7 ± 0.9° respectively. It may be mentioned that the increase in the valency angle within the benzene ring at the carbon atom bearing the nitro group is observed in most aromatic nitro compounds (e.g. p-nitrobenzoic acid, Tavale and Pant, 1971; m-nitrobenzoic acid, Dhaneshwar, Tavale and Pant, 1974; p-nitrotoluene, Barve and Pant, 1971).

Carboxylic group

The molecules form centrosymmetrical dimers with OH---O hydrogen bond of length 2.61 Å. The plane of the carboxylic group makes an angle of 46.2° with the aromatic plane (24.1° in o-nitrobenzoic acid); the atom C(1) of the aromatic ring is 0.074 Å away from the plane of the carboxylic group (Table VII-2). The C(1)-C(7) bond length, 1.507 ± 0.004 Å agrees with the corresponding bond length in o-nitrobenzoic acid, 1.501 ± 0.013 (Tavale and Pant, 1973). The C(7)-O(1) and C(7)-O(2) bond lengths are nearly equal (1.276 ± 0.004 and 1.265 ± 0.004 Å respectively). The equality of the two C-O bonds, as in the case of p-toluic acid structure, probably implies nearly equal contribution in the molecule from the following two structures :



1.



2.

It may be mentioned that the two C-O bonds are of unequal length in o-nitrobenzoic acid (Fig. VII-2). It is interesting to find that inspite of the near equality of the two C-O bonds, the hydrogen atom does not appear to be disordered.

Nitro group :

The atom N of the nitro group is 0.116 Å out of the aromatic plane; the C(7) and N atoms are displaced out of the aromatic plane in opposite directions. The N-O(3) bond length, 1.230 ± 0.004 Å and N-O(4) bond length, 1.250 ± 0.004 Å agree with the corresponding bond lengths in p-nitrobenzoic acid, 1.231 ± 0.005 and 1.246 ± 0.005 Å (Tavale and Pant, 1971), o-nitrobenzoic acid, 1.209 ± 0.013 Å and 1.237 ± 0.013 Å (Tavale and Pant, 1973) and in the two crystallographically independent molecules of m-nitrobenzoic acid, 1.232 ± 0.008 and 1.250 ± 0.007 Å and 1.233 ± 0.008 and 1.243 ± 0.008 Å respectively (Dhaneshwar, Tavale and Pant, 1974). The C(2)-N bond length, 1.478 ± 0.004 Å also agrees with the corresponding bond lengths in o-nitrobenzoic acid, 1.478 ± 0.013 Å, p-nitrobenzoic acid, 1.485 ± 0.005 Å and in the two independent molecules of m-nitrobenzoic acid, 1.474 ± 0.008 and 1.485 ± 0.008 Å respectively. The nitro group is out of the aromatic plane by 35.8° (54.3° in o-nitrobenzoic acid).

Methyl group :

The carbon atom C(8) of the methyl group is 0.036 Å away from the aromatic plane (0.034 Å in the case of p-toluic acid). The C(4)-C(8) bond length, 1.529 ± 0.005 Å agrees with the corresponding lengths in p-nitrotoluene, 1.528 ± 0.009 Å (Barve and Pant, 1971) and p-toluic acid, 1.514 ± 0.011 Å.

Crystal structure :

The (010) and (001) projections of the structure are shown in Figures VII-3(a) and (b) respectively; there is considerable overlapping of molecules in the(100) projection. The principal intermolecular distances ($<$ 3.60 Å) are also shown in these figures. As in p-toluic acid, infinite chains of molecules are held together by normal van der Waals interactions. The molecules in any chain are bonded to neighbouring molecules by double OH---O hydrogen bond of length 2.61 Å (2.63 Å in p-toluic acid structure) on one side and van der Waals bond between methyl group having C-C distance, 3.57 Å on the other side (C-C distance, 3.50 Å in p-toluic acid).

Thermal anisotropy :

Table VII-3 gives the direction cosines of the principal axes of the individual atomic vibration ellipsoids referred to a', b, c orthogonal axes, the root mean square amplitudes of maximum, medium and minimum vibrations and the angles between

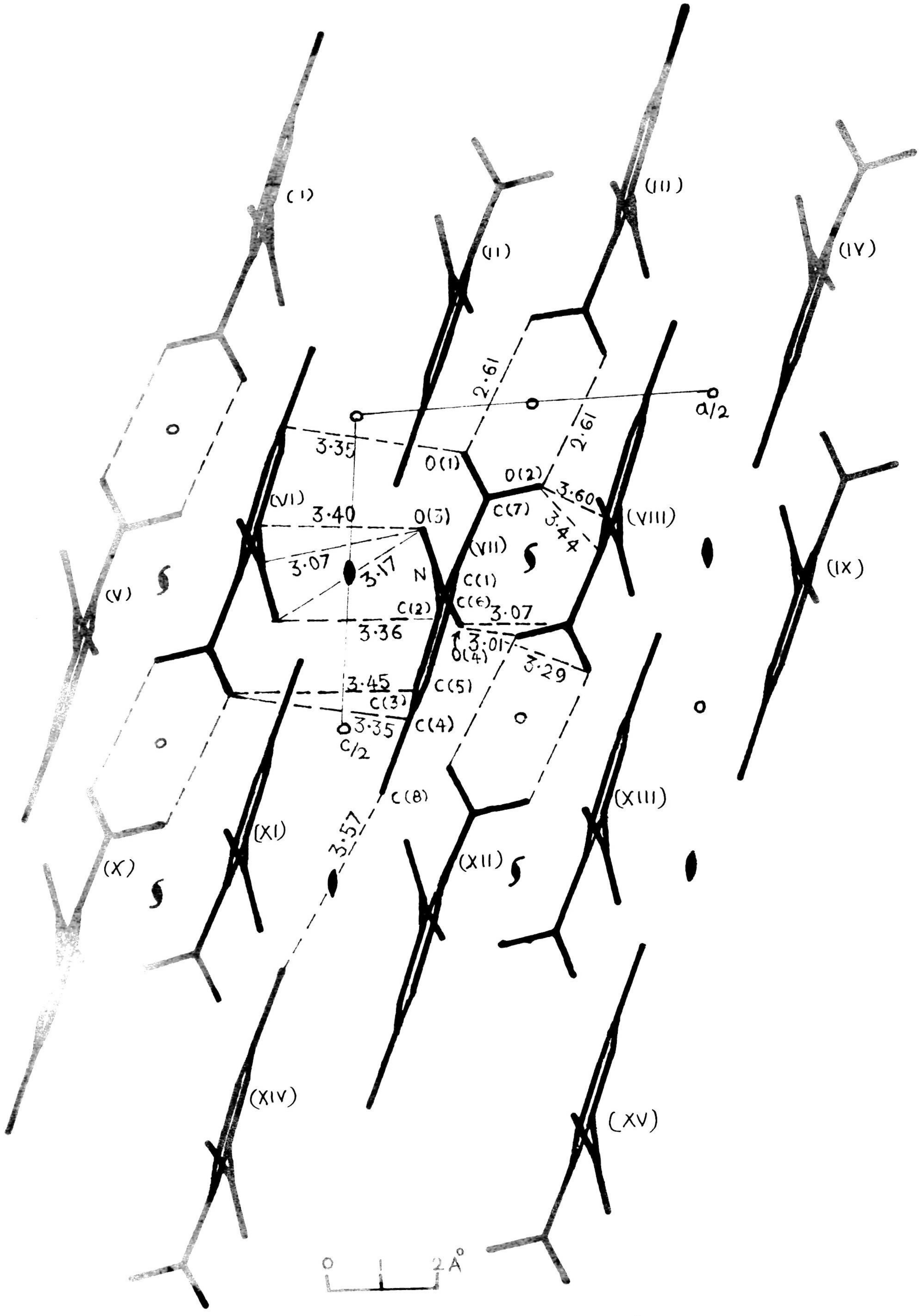


FIG. VII-3(a): THE STRUCTURE PROJECTED ALONG THE b-AXIS. SYMMETRY CODE:
I) $\bar{x}, \bar{y}, \bar{z}$; II) $x, \bar{y}, 1/2+z$; III) $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$; IV) $\frac{1}{2}+x, \frac{1}{2}-y, z-1/2$;
V) $-\frac{1}{2}+x, -1/2+y, z$; VI) $\bar{x}, y, \frac{1}{2}-z$; VII) x, y, z VIII) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$;
IX) $x+1/2, y+1/2, z$; X) $-1/2+x, 1/2-y, \frac{1}{2}+z$; XI) $\bar{x}, \bar{y}, 1-z$; XII) $x, \bar{y}, \frac{1}{2}+z$;
XIII) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$, XIV) $\bar{x}, y, 3/2-z$; XV) $\frac{1}{2}-x, \frac{1}{2}+y, 3/2-z$.

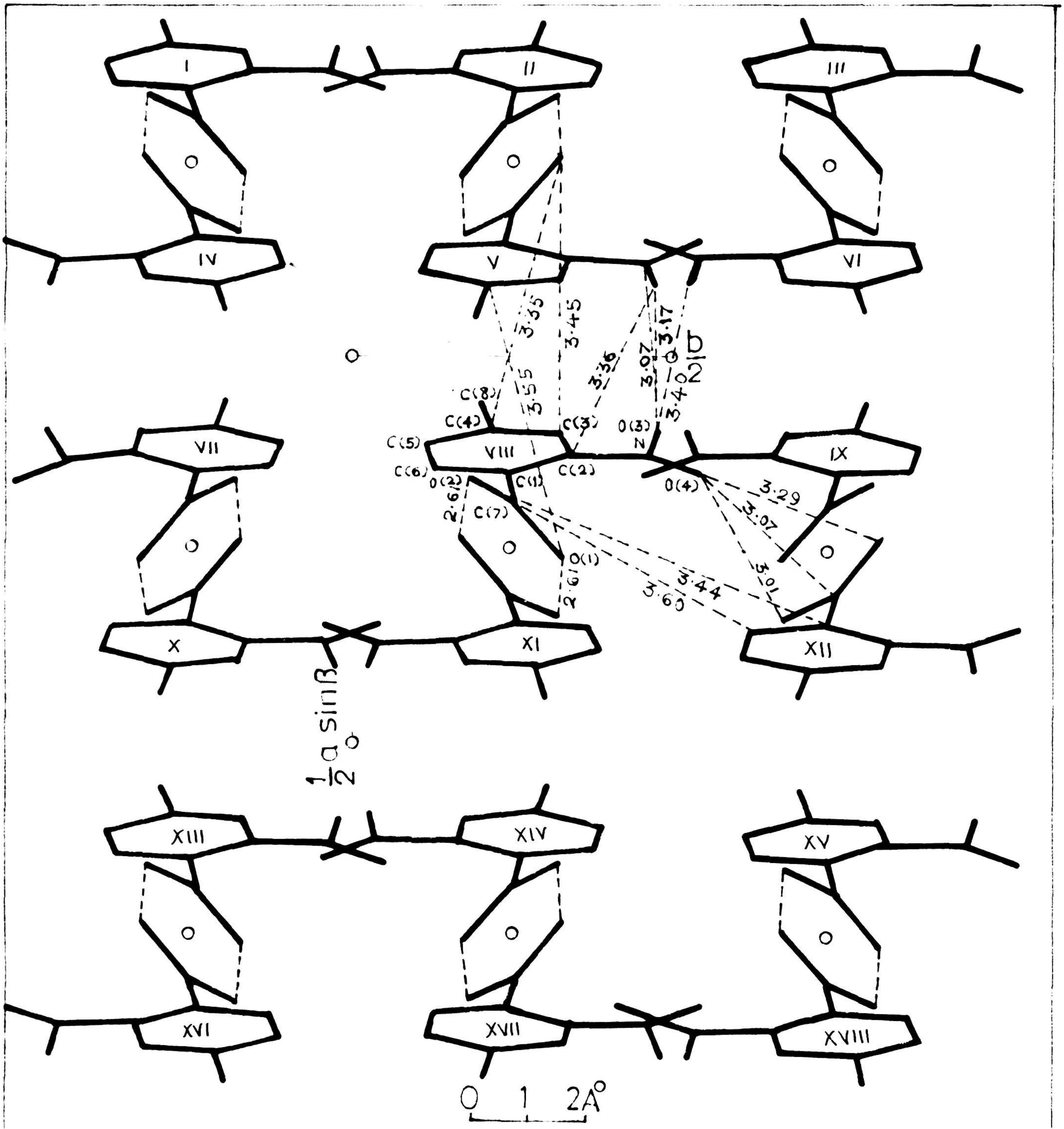


FIG. VII-3(b): THE STRUCTURE PROJECTED ALONG THE C-AXIS. SYMMETRY CODE: I) $X-1/2$, $Y-1/2$, Z; II) $X-1/2$, $\frac{1}{2}-Y$, $1/2+Z$; III) $X-1/2$, $\frac{1}{2}+Y$, Z IV) $\bar{X}$, $\bar{Y}$, $\bar{Z}$ V) $\bar{X}$, Y, $1/2-Z$; VI) $\bar{X}$, $1-Y$, $\bar{Z}$; VII) X, $\bar{Y}$, $1/2+Z$; VIII) X, Y, Z; IX) X, $1-Y$, $1/2+Z$; X) $\frac{1}{2}-X$, $Y-1/2$, $1/2-Z$; XI) $\frac{1}{2}-X$, $\frac{1}{2}-Y$, $\bar{Z}$; . XII) $\frac{1}{2}-X$, $\frac{1}{2}+Y$, $\frac{1}{2}-Z$; XIII) $\frac{1}{2}+X$, $Y-1/2$, Z, XIV) $\frac{1}{2}+X$, $\frac{1}{2}-Y$, $1/2+Z$; XV) $\frac{1}{2}+X$, $\frac{1}{2}+Y$, Z; XVI) $1-X$, $\bar{Y}$, $\bar{Z}$; XVII) $1-X$, Y, $1/2-Z$; XVIII) $1-X$, $1-Y$, $\bar{Z}$.

Table VII-3 : Magnitudes and direction cosines of the principal axes of the atomic vibration ellipsoids, the angles between the principal axes and the aromatic plane and those between the principal axes and the molecular axis (i.e. the C(1)-C(4) direction)

	Axis	$\sqrt{\bar{u}^2}$ (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with molecular axis
C(1)	1	0.287	0.988	0.012	0.152	83°	82°
	2	0.179	-0.135	-0.392	0.910	6	19
	3	0.162	-0.070	0.920	0.386	4	73
C(2)	1	0.280	0.981	-0.087	0.172	81	84
	2	0.188	-0.191	-0.296	0.936	3	12
	3	0.167	0.031	0.951	0.307	9	79
C(3)	1	0.308	0.988	-0.079	0.133	80	82
	2	0.201	-0.150	-0.689	0.708	1	38
	3	0.169	-0.036	0.720	0.693	11	54
C(4)	1	0.293	0.999	0.001	0.022	76	75
	2	0.214	0.004	-0.991	-0.133	4	89
	3	0.178	-0.022	-0.133	0.991	14	15
C(5)	1	0.372	0.981	0.098	0.169	84	83
	2	0.232	-0.195	0.568	0.799	2	41
	3	0.169	0.017	0.817	-0.577	6	50

continued.....

Table VII-3 (continued)

	Axis	$\sqrt{\bar{u}^2}$ (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with molecular axis
C(6)	1	0.374	0.975	0.029	0.219	87°	86°
	2	0.213	-0.182	-0.456	0.871	2	21
	3	0.162	-0.126	0.890	0.439	2	69
C(7)	1	0.296	0.985	0.039	0.169	85	83
	2	0.193	-0.101	-0.664	0.741	4	36
	3	0.167	-0.141	0.747	0.650	4	55
C(8)	1	0.372	0.988	-0.153	0.034	73	77
	2	0.267	-0.143	-0.967	-0.210	14	87
	3	0.169	-0.065	-0.203	0.977	11	14
N	1	0.339	0.943	-0.082	0.324	82	87
	2	0.214	-0.322	0.027	0.946	3	8
	3	0.171	0.087	0.996	0.001	7	83
O(1)	1	0.337	0.921	-0.314	0.231	69	90
	2	0.219	-0.328	-0.945	0.022	21	78
	3	0.174	-0.212	0.096	0.973	3	12
O(2)	1	0.344	0.869	-0.458	0.187	60	89
	2	0.247	-0.493	-0.830	0.260	26	62
	3	0.173	-0.036	0.318	0.947	13	28

continued.....

Table VII-3 (continued)

	Axis	$\sqrt{\bar{u}^2}$ (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with molecular axis
O(3)	1	0.356	0.953	0.215	0.212	80	85
	2	0.259	-0.301	0.635	0.712	4	46
	3	0.177	-0.018	0.742	-0.669	9	45
O(4)	1	0.523	0.989	-0.144	0.044	73	77
	2	0.291	-0.057	-0.088	0.994	12	13
	3	0.181	0.140	0.986	0.095	12	87

Table VII-4 : Some mean square displacements ($\mathring{A}^2 \times 10^3$)

Direction of displacement*

No.		Normal to the plane**		In the plane normal to the bond		Parallel to the bond	
1	O(1)	76		33		40	
2	C(7)	43	(a)	32	O(1)	42	O(1)
			(b)	36	O(2)	38	O(2)
3	O(2)	88		41		37	
4	O(3)	76		56		58	
5	N	50	(a)	29	O(3)	67	O(3)
			(b)	54	O(4)	42	O(4)
6	O(4)	143		86		50	
7	C(1)	50		27		30	
8	C(7)	53		31		32	
9	C(2)	47		31		32	
10	N	70		42		35	
11	C(4)	50		46		32	
12	C(8)	78		73		30	

* Values parallel and normal to the bond for C(1), C(2) and C(4) are given for the C(1)-C(7), C(2)-N and C(4)-C(8) bonds respectively. The atoms listed besides certain values in the Table indicate the direction of the bond in question.

** The values shown in this column are with respect to the plane of the carboxylic group for Nos. 1 to 3, with respect to the plane of the nitro group for Nos. 4 to 6, and are with respect to the aromatic plane for Nos. 7 to 12.

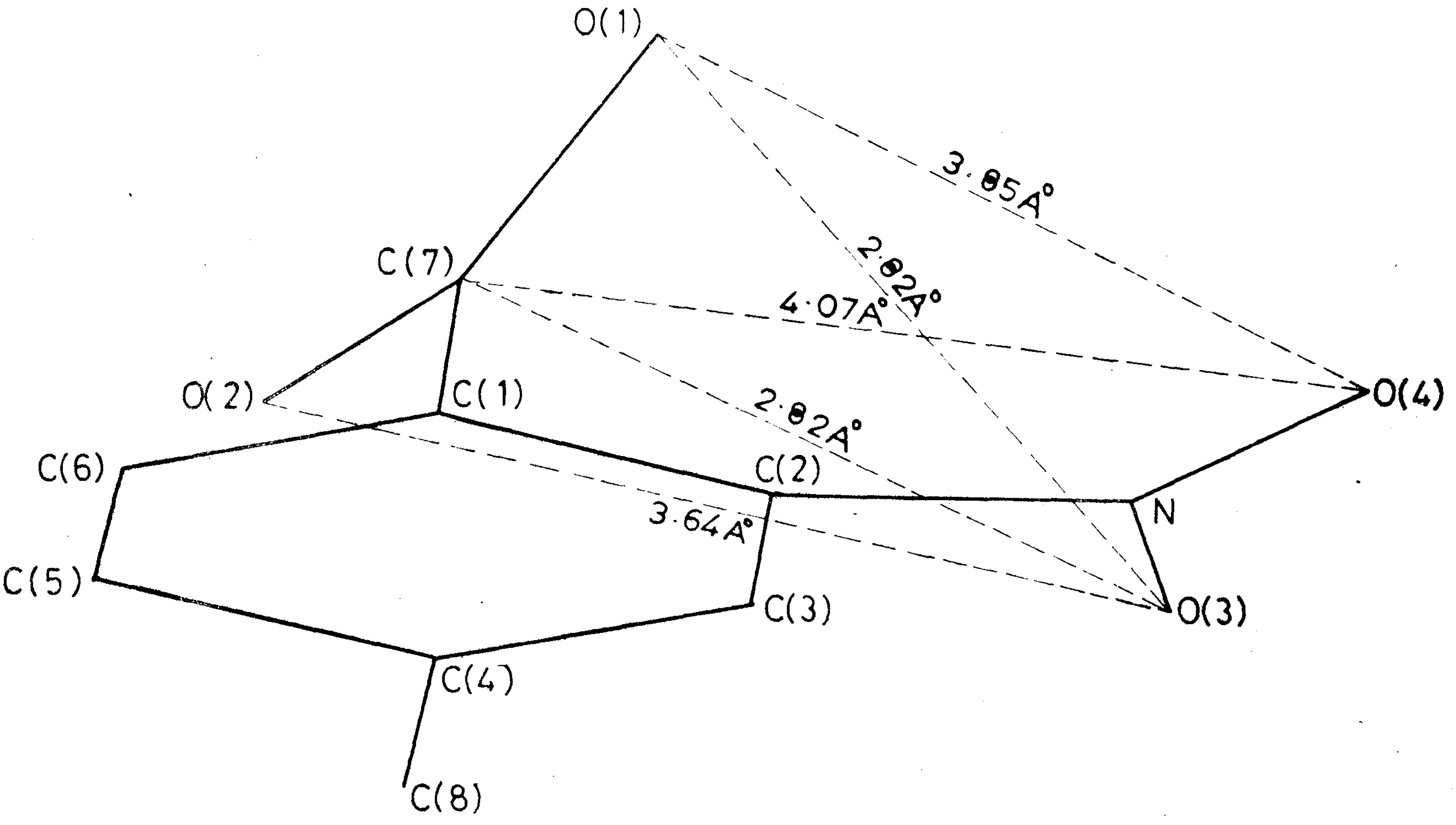


FIG-VII-4 SOME NON-BONDED INTRAMOLECULAR DISTANCES the principal axes of the vibration ellipsoids and the aromatic plane as well as those between the principal axes and the C(1)-C(4) direction (obtained as discussed in Chapter IV, Section B). Some mean square displacements required for the calculation of bond length corrections are given in Table VII-4.

It is seen from Table VII-3 that the oxygen atom O(4) of nitro group has a much larger root mean square amplitude of maximum vibration (0.523 Å) than that of atom O(3) (0.356 Å). As shown in Figure VII-4, atom O(3) has short contacts with the atoms of the carboxylic group whereas atom O(4) has none; therefore the vibration of O(3) is more restricted. The root mean square amplitude of torsional oscillation of the carboxylic group (calculated as shown in Chapter IV, page 55) is about 10°.

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APPENDIX -

Observed and calculated structure factors for p-toluic acid.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	0	0	15.9	-18.5	-9	5	0	2.7	- 3.2	-2	5	1	1.6	- 1.9	-3	-5	1	2.0	2.1
2	0	0	14.6	-14.7	2	6	0	1.2	1.2	-6	5	1	2.2	- 2.3	-4	-5	1	2.8	- 3.2
3	0	0	5.4	5.7	0	6	0	1.8	2.3	-9	5	1	1.7	- 1.5	6	-6	1	1.3	0.9
4	0	0	7.4	7.9	-1	6	0	4.7	- 4.5	1	6	1	1.8	- 1.8	5	-6	1	2.6	- 2.4
5	0	0	2.3	1.9	-3	6	0	5.4	5.5	-1	6	1	2.0	- 2.0	4	-6	1	4.6	- 3.9
6	0	0	4.9	5.3	-4	6	0	3.8	- 3.5	-5	6	1	1.4	- 1.9	3	-6	1	13.8	14.8
7	0	0	3.8	- 3.9	-7	6	0	1.8	- 1.8	-7	6	1	2.3	- 2.4	2	-6	1	3.9	- 3.9
8	0	0	8.1	- 1.9	-9	6	0	2.1	2.3	-8	6	1	2.2	2.1	1	-6	1	3.1	- 3.1
8	1	0	1.6	1.9	-2	8	0	1.4	- 1.7	-9	6	1	0.6	1.0	0	-6	1	1.8	2.3
7	1	0	4.1	- 3.8	-4	8	0	1.3	1.4	6	-1	1	1.6	1.7	-1	-6	1	1.3	1.4
6	1	0	3.2	3.1	-5	8	0	0.8	- 0.9	5	-1	1	5.6	5.2	-3	-6	1	2.9	2.9
5	1	0	8.6	8.2	7	0	1	2.6	3.0	4	-1	1	10.3	9.7	-4	-6	1	1.2	- 1.4
4	1	0	11.4	12.2	5	0	1	4.2	4.2	3	-1	1	9.4	9.5	3	-7	1	2.1	1.8
3	1	0	4.9	4.4	4	0	1	4.9	4.0	2	-1	1	7.2	- 6.6	-2	-7	1	1.2	1.2
2	1	0	2.5	1.9	3	0	1	16.0	15.0	1	-1	1	2.0	1.0	5	-8	1	1.8	- 2.1
0	1	0	15.5	17.3	2	0	1	21.6	-19.9	0	-1	1	14.2	15.7	4	-8	1	4.7	4.9
-1	1	0	16.0	17.6	1	0	1	8.3	9.5	-1	-1	1	9.9	7.9	3	-8	1	1.5	- 1.2
-2	1	0	5.1	4.8	0	0	1	41.7	50.1	-2	-1	1	11.0	-10.1	2	-8	1	1.7	- 1.8
-3	1	0	1.6	- 1.9	-1	0	1	20.0	-19.4	-3	-1	1	6.9	- 6.1	1	-8	1	1.2	1.1
-4	1	0	5.8	5.8	-2	0	1	3.7	- 2.9	-4	-1	1	4.3	4.4	5	0	2	3.2	3.2
-5	1	0	6.3	6.5	-3	0	1	20.4	-21.0	-5	-1	1	1.9	2.1	4	0	2	4.3	- 5.5
-6	1	0	2.8	2.6	-4	0	1	15.3	-13.9	-6	-1	1	11.0	-11.1	2	0	2	10.3	- 8.2
-7	1	0	6.0	- 6.4	-5	0	1	2.4	2.5	-7	-1	1	1.8	- 2.0	0	0	2	19.6	-17.4
-8	1	0	1.0	- 0.9	-6	0	1	10.1	9.6	8	-2	1	1.1	1.3	-1	0	2	8.3	8.2
-9	1	0	1.1	1.1	-7	0	1	15.1	-15.7	6	-2	1	3.0	2.8	-2	0	2	16.3	-17.4
7	2	0	1.4	- 1.1	6	1	1	1.4	2.0	5	-2	1	4.9	4.9	-3	0	2	18.1	-16.7
6	2	0	1.0	0.3	4	1	1	2.4	2.5	4	-2	1	13.0	11.9	-4	0	2	28.0	-31.5
5	2	0	3.5	3.5	3	1	1	6.9	6.7	3	-2	1	15.3	-15.3	-5	0	2	14.7	13.0
4	2	0	2.3	2.9	2	1	1	7.3	8.0	2	-2	1	3.4	3.2	-6	0	2	6.4	6.3
3	2	0	7.8	8.2	1	1	1	9.1	- 7.8	1	-2	1	57.2	69.6	-7	0	2	9.6	- 9.4
2	2	0	11.6	11.3	0	1	1	9.1	- 8.7	0	-2	1	19.4	-20.1	-10	0	2	0.8	1.0
1	2	0	15.7	-15.5	-1	1	1	4.6	3.3	-1	-2	1	3.4	- 2.9	3	1	2	3.4	- 3.5
0	2	0	6.7	- 6.4	-2	1	1	5.2	4.3	-2	-2	1	9.5	- 9.2	2	1	2	1.0	0.7
-1	2	0	64.6	81.5	-3	1	1	11.6	-11.6	-3	-2	1	1.8	- 1.9	1	1	2	6.4	- 5.2
-2	2	0	17.9	-19.4	-4	1	1	11.6	-12.3	-4	-2	1	2.0	2.3	0	1	2	12.8	-11.3
-3	2	0	6.4	- 6.3	-7	1	1	8.2	- 9.3	-5	-2	1	9.6	9.4	-1	1	2	12.7	-11.9
-4	2	0	2.3	- 2.7	6	2	1	1.8	2.2	-6	-2	1	11.5	-12.8	-2	1	2	4.3	- 3.7
-5	2	0	1.8	1.4	4	2	1	3.7	3.5	-7	-2	1	1.9	- 1.9	-3	1	2	1.1	- 0.8
-7	2	0	5.6	5.6	2	2	1	8.2	7.9	-8	-2	1	1.7	1.5	-4	1	2	12.8	-10.0
-8	2	0	5.9	- 6.6	1	2	1	14.6	-14.1	8	-3	1	0.7	- 1.2	-5	1	2	2.4	- 2.4
-9	2	0	1.4	- 1.6	0	2	1	3.4	3.7	7	-3	1	1.8	1.3	-10	1	2	1.6	1.6
4	3	0	2.4	2.3	-1	2	1	6.7	6.5	6	-3	1	3.8	4.0	4	2	2	1.7	1.7
3	3	0	4.7	4.2	-2	2	1	6.9	- 6.0	5	-3	1	5.8	5.3	3	2	2	5.2	- 5.8
2	3	0	8.1	8.1	-3	2	1	3.2	- 3.2	4	-3	1	3.8	4.0	2	2	2	2.4	- 2.1
1	3	0	3.0	3.5	-4	2	1	13.5	-13.2	3	-3	1	1.8	- 1.4	1	2	2	3.9	- 3.6
0	3	0	1.8	- 0.5	-5	2	1	15.1	-15.8	2	-3	1	7.3	6.9	-1	2	2	10.1	- 9.7
-1	3	0	6.7	5.8	-6	2	1	4.3	3.8	1	-3	1	18.5	17.3	-2	2	1	4.2	4.8
-2	3	0	8.0	7.7	-7	2	1	6.6	6.9	0	-3	1	6.0	4.8	-3	2	2	11.8	-10.9
-3	3	0	3.7	3.2	-8	2	1	10.9	-11.1	-1	-3	1	4.5	- 4.1	-4	2	2	1.4	- 1.1
-4	3	0	5.2	- 5.1	5	3	1	1.4	1.6	-2	-3	1	1.8	1.5	-5	2	2	14.7	-13.3
-5	3	0	1.6	- 1.5	2	3	1	1.0	1.0	-3	-3	1	5.9	5.9	-6	2	2	11.8	9.7
-6	3	0	2.4	2.3	1	3	1	2.2	2.8	-4	-3	1	2.4	2.6	-7	2	2	2.4	2.6
-7	3	0	2.0	1.7	0	3	1	4.6	- 4.1	-5	-3	1	7.0	- 7.5	-8	2	2	3.0	- 2.4
-8	3	0	5.3	- 5.7	-1	3	1	7.1	- 6.7	8	-4	1	1.6	1.8	2	3	2	3.0	- 3.2
5	4	0	1.1	1.6	-2	3	1	1.6	- 1.3	6	-4	1	1.6	2.0	0	3	2	2.1	- 1.8
4	4	0	1.0	1.2	-4	3	1	5.2	- 5.3	5	-4	1	4.4	4.3	-1	3	2	2.5	- 2.3
3	4	0	1.9	2.0	-5	3	1	8.1	- 7.7	4	-4	1	7.8	- 7.2	-2	3	2	4.8	- 5.0
2	4	0	2.7	2.9	-6	3	1	0.5	0.0	3	-4	1	4.9	- 3.7	-3	3	2	2.8	- 2.8
1	4	0	7.3	6.8	-7	3	1	0.7	0.7	2	-4	1	35.9	37.8	-4	3	2	2.4	2.0
0	4	0	10.2	- 9.6	-8	3	1	3.9	- 4.4	1	-4	1	10.0	- 9.4	-5	3	2	2.3	- 1.9
-1	4	0	1.6	- 1.7	3	4	1	2.0	2.1	0	-4	1	3.5	- 3.5	2	4	2	3.5	- 3.2
-2	4	0	18.5	22.8	2	4	1	2.4	- 2.6	-1	-4	1	1.4	1.4	1	4	2	1.7	- 1.4
-3	4	0	9.4	- 9.5	1	4	1	2.0	1.9	-2	-4	1	2.9	3.2	-3	4	2	2.3	2.1
-4	4	0	1.7	- 1.6	0	4	1	6.8	- 6.3	-3	-4	1	1.5	1.7	-4	4	2	5.8	- 5.4
-5	4	0	2.5	- 3.3	-1	4	1	1.8	1.5	-4	-4	1	6.2	6.4	-5	4	2	3.0	2.9
-6	4	0	1.9	- 2.1	-2	4	1	2.1	- 2.3	-5	-4	1	5.2	- 5.7	-6	4	2	3.6	- 3.6
-8	4	0	4.3	4.3	-3	4	1	0.9	- 0.5	-6	-4	1	0.8	- 1.5	-7	4	2	5.2	4.8
-9	4	0	4.6	- 5.3	-4	4	1	2.7	- 2.6	9	-5	1	1.3	- 1.7	1	5	2	1.4	- 1.4
3	5	0	1.2	1.2	-5	4	1	2.8	- 3.4	7	-5	1	1.2	1.7	-2	5	2	1.6	1.1
1	5	0	2.5	2.4	-6	4	1	6.5	- 6.8	3	-5	1	3.0	2.5	-3	6	2	1.8	1.4
-1	5	0	1.1	-0.8	-7	4	1	3.8	3.6	2	-5	1	7.5	7.2	-5	6	2	2.4	- 2.5
-5	5	0	2.2	- 2.9	-8	4	1	2.8	3.3	1	-5	1	2.8	1.4	-6	6	2	1.4	1.8
-6	5	0	1.9	- 1.9	-9	4	1	4.9	- 5.0	0	-5	1	1.2	- 1.2	-8	6	2	1.9	1.7
-7	5	0	1.1	1.0	-10	4	1	0.6	0.7	-1	-5	1	2.7	2.4	-3	7	2	1.8	1.0
-8	5	0	1.0	1.1	-1	5	1	1.4	- 1.5	-2	-5	1	2.7	3.3	7	-1	2	1.8	1.5

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	-1	2	3.5	3.6	-2	-8	2	2.7	2.8	6	-2	3	1.4	1.4	-2	0	4	6.9	- 6.0
2	-1	2	8.6	- 8.1	4	-9	2	1.4	1.2	5	-2	3	4.6	- 5.7	-3	0	4	14.0	12.9
1	-1	2	15.8	-15.1	4	0	3	4.5	- 5.4	4	-2	3	3.3	- 3.4	-4	0	4	7.8	7.7
0	-1	2	12.4	-11.1	3	0	3	4.1	- 4.1	3	-2	3	2.4	- 1.6	-5	0	4	2.0	1.6
-2	-1	2	9.1	- 7.4	1	0	3	4.3	- 3.8	2	-2	3	4.3	- 3.1	-6	0	4	6.3	6.6
-3	-1	2	19.0	-18.3	-2	0	3	20.1	-18.2	1	-2	3	10.0	- 8.9	-7	0	4	1.1	1.2
-4	-1	2	5.3	- 4.6	-3	0	3	11.6	10.6	0	-2	3	3.6	3.8	-8	0	4	2.7	- 2.6
-5	-1	2	1.3	- 1.6	-4	0	3	7.1	- 6.1	-1	-2	3	18.5	-23.1	-9	0	4	2.5	3.2
-6	-1	2	5.5	- 5.3	-5	0	3	11.6	11.4	-2	-2	3	0.7	- 0.7	-10	0	4	1.5	- 1.7
-7	-1	2	2.1	- 2.0	-6	0	3	2.4	2.5	-3	-2	3	20.1	-19.4	-11	0	4	1.8	1.6
-8	-1	2	2.3	- 2.4	-7	0	3	7.7	6.5	-4	-2	3	16.0	15.5	0	1	4	7.8	8.0
-9	-1	2	1.5	1.5	-8	0	3	1.3	- 1.4	-5	-2	3	3.7	3.1	-1	1	4	3.6	3.7
6	-2	2	3.7	3.9	-10	0	3	1.4	1.2	-6	-2	3	2.7	2.2	-2	1	4	1.6	- 1.6
5	-2	2	1.2	- 2.1	3	1	3	3.6	- 3.8	-9	-2	3	2.1	2.1	-3	1	4	1.9	2.5
4	-2	2	5.2	5.3	2	1	3	2.0	- 2.0	-10	-2	3	4.8	3.9	-4	1	4	7.3	7.0
3	-2	2	12.2	-10.3	1	1	3	1.1	- 0.3	5	-3	3	3.0	- 3.0	-6	1	4	4.7	4.6
2	-2	2	5.3	5.5	0	1	3	1.4	1.0	4	-3	3	1.1	- 0.7	-7	1	4	3.0	- 3.0
1	-2	2	7.1	- 5.4	-1	1	3	5.6	- 4.8	3	-3	3	3.5	- 3.2	-8	1	4	1.1	1.1
0	-2	2	3.7	3.4	-2	1	3	4.9	- 4.1	2	-3	3	8.1	- 8.1	-9	1	4	2.9	3.4
-1	-2	2	10.2	- 9.6	-3	1	3	8.1	8.1	1	-3	3	10.6	- 9.4	-10	1	4	1.3	- 1.5
-2	-2	2	21.4	-21.7	-4	1	3	6.8	6.2	0	-3	3	3.3	- 2.9	-1	2	4	10.5	11.1
-3	-2	2	29.3	-31.7	-5	1	3	1.7	1.6	-2	-3	3	9.7	- 7.8	-2	2	4	3.5	- 3.7
-4	-2	2	9.7	10.4	-6	1	3	1.7	- 0.9	-3	-3	3	6.9	- 5.5	-3	2	4	2.5	- 2.2
-5	-2	2	9.1	8.7	-7	1	3	4.2	4.3	-4	-3	3	2.7	- 2.6	-4	2	4	4.3	4.2
-6	-2	2	16.4	-16.0	-8	1	3	2.2	2.0	-5	-3	3	2.4	2.8	-5	2	4	2.4	2.3
6	-3	2	2.1	1.9	-9	1	3	2.4	2.4	-8	-3	3	2.2	1.9	-7	2	4	4.0	4.2
5	-3	2	2.6	2.5	-11	1	3	2.5	1.9	-9	-3	3	4.0	3.0	-8	2	4	3.5	- 3.6
4	-3	2	4.7	4.7	3	2	3	2.2	- 2.7	7	-4	3	1.7	2.0	-9	2	4	1.8	- 1.6
3	-3	2	6.3	- 5.3	2	2	3	1.8	- 2.1	6	-4	3	2.9	- 2.3	-10	2	4	1.8	2.2
2	-3	2	6.2	- 5.3	0	2	3	2.3	- 2.4	5	-4	3	1.1	- 0.6	-11	2	4	1.5	- 1.5
1	-3	2	1.6	0.6	-1	2	3	7.1	6.9	4	-4	3	3.5	- 2.9	-1	3	4	2.2	2.3
0	-3	2	4.0	3.6	-3	2	3	9.4	- 8.1	2	-4	3	7.0	- 7.2	-2	3	4	1.8	2.1
-1	-3	2	10.2	- 9.1	-4	2	3	10.6	9.7	1	-4	3	4.4	4.3	-3	3	4	0.8	- 0.9
-2	-3	2	15.3	-14.0	-5	2	3	1.0	0.8	0	-4	3	11.8	-11.7	-5	3	4	1.1	1.5
-3	-3	2	1.7	- 1.5	-6	2	3	5.2	4.8	-1	-4	3	5.8	- 5.6	-6	3	4	1.5	2.1
-5	-3	2	7.2	- 7.3	-8	2	3	3.5	3.6	-2	-4	3	19.8	-18.4	-7	3	4	0.6	1.1
-6	-3	2	2.8	- 2.7	-9	2	3	2.3	- 1.8	-3	-4	3	13.7	11.5	-8	3	4	3.2	- 3.4
-7	-3	2	2.1	- 2.3	-10	2	3	1.4	1.4	-4	-4	3	2.6	2.8	-10	3	4	1.2	1.4
7	-4	2	3.0	2.8	2	3	3	1.4	- 1.5	-5	-4	3	5.3	- 5.4	-2	4	4	4.3	4.7
5	-4	2	5.7	5.2	1	3	3	1.1	-1.1	-7	-4	3	1.1	- 1.1	-3	4	4	1.8	- 2.2
4	-4	2	9.0	- 8.1	-1	3	3	3.3	3.2	-8	-4	3	1.2	1.2	-8	4	4	2.1	2.4
3	-4	2	4.6	4.3	-3	3	3	1.9	- 1.7	4	-5	3	2.2	- 2.1	-9	4	4	3.0	- 3.3
2	-4	2	9.8	8.7	-4	3	3	3.1	3.0	3	-5	3	3.3	- 3.5	-9	5	4	1.8	- 1.9
1	-4	2	3.7	- 2.6	-5	3	3	3.6	3.5	2	-5	3	3.4	- 2.8	4	-1	4	1.4	- 1.5
0	-4	2	1.4	- 1.0	-6	3	3	1.8	1.9	0	-5	3	2.7	- 2.9	3	-1	4	1.4	- 1.5
-1	-4	2	9.8	- 8.6	-10	3	3	1.7	1.8	-1	-5	3	7.2	- 7.2	1	-1	4	5.4	4.8
-2	-4	2	13.9	-12.9	0	4	3	0.8	0.3	-5	-5	3	1.7	- 1.5	0	-1	4	2.7	2.9
-3	-4	2	5.6	5.6	-1	4	3	1.2	- 1.4	-7	-5	3	0.8	1.1	-1	-1	4	3.8	- 2.7
-4	-4	2	7.9	8.0	-2	4	3	6.2	5.9	7	-6	3	1.1	- 1.3	-2	-1	4	7.6	8.0
-5	-4	2	13.7	-14.0	-3	4	3	1.1	- 1.3	5	-6	3	2.7	- 2.8	-3	-1	4	14.1	13.5
7	-5	2	1.5	1.7	-4	4	3	4.0	- 3.3	4	-6	3	1.7	1.8	-4	-1	4	7.1	6.7
6	-5	2	1.4	1.6	-5	4	3	4.0	4.0	3	-6	3	1.1	- 1.1	-6	-1	4	1.3	1.5
5	-5	2	2.4	2.5	-7	4	3	1.7	1.4	2	-6	3	1.8	1.7	-7	-1	4	3.7	3.7
4	-5	2	2.5	- 2.3	-10	4	3	1.6	- 1.3	1	-6	3	3.5	- 3.6	-8	-1	4	4.0	5.2
2	-5	2	5.7	4.9	-2	5	3	2.1	1.8	0	-6	3	2.1	- 2.9	-9	-1	4	1.4	- 1.2
1	-5	2	2.3	2.1	-9	5	3	0.8	- 0.8	-1	-6	3	8.7	- 9.0	5	-2	4	1.4	- 2.1
0	-5	2	3.9	- 4.2	-3	6	3	3.6	2.9	-2	-6	3	6.4	6.2	4	-2	4	1.5	- 1.9
-1	-5	2	4.4	- 4.5	-4	6	3	1.0	- 1.1	-3	-6	3	2.7	2.9	2	-2	4	4.3	- 4.1
-2	-5	2	1.2	+ 1.7	-5	6	3	1.2	- 1.1	-4	-6	3	7.1	- 6.9	1	-2	4	13.7	13.6
-4	-5	2	4.5	- 4.8	-6	6	3	1.1	1.1	5	-7	3	1.4	- 1.2	0	-2	4	5.1	- 4.6
6	-6	2	2.7	2.6	4	-1	3	4.6	- 5.0	0	-7	3	2.1	- 2.7	-1	-2	4	15.6	-12.1
5	-6	2	4.4	- 4.5	3	-1	3	2.6	- 2.3	-2	-7	3	1.1	- 0.3	-2	-2	4	21.4	17.4
3	-6	2	9.7	9.4	2	-1	3	2.5	- 2.3	-3	-7	3	1.6	- 0.9	-3	-2	4	8.4	7.6
2	-6	2	3.7	- 3.5	1	-1	3	7.6	- 6.0	-4	-7	3	1.1	- 1.0	-4	-2	4	4.9	4.4
0	-6	2	1.3	- 1.2	0	-1	3	12.7	-10.8	6	-8	3	1.5	- 1.4	-5	-2	4	6.6	7.0
-1	-6	2	3.1	- 3.1	-1	-1	3	6.7	- 6.5	5	-8	3	0.8	1.1	-6	-2	4	7.6	7.9
-2	-6	2	2.0	2.2	-2	-1	3	8.7	8.8	4	-8	3	1.3	1.4	-7	-2	4	2.3	- 2.7
-3	-6	2	5.8	5.5	-3	-1	3	2.0	1.7	2	-8	3	1.0	- 1.0	-8	-2	4	2.2	3.2
-4	-6	2	6.9	- 7.3	-4	-1	3	2.7	- 2.3	0	-8	3	2.9	- 3.2	-9	-2	4	1.2	- 0.3
3	-7	2	2.9	3.0	-5	-1	3	0.8	- 2.6	-1	-8	3	2.4	2.5	-10	-2	4	3.6	3.4
-1	-7	2	1.7	1.6	-6	-1	3	5.7	6.0	-2	-8	3	2.3	2.4	5	-3	4	1.8	- 2.5
-3	-7	2	2.0	- 2.1	-7	-1	3	2.8	2.2	-3	-8	3	4.3	- 4.2	4	-3	4	1.3	- 1.7
6	-8	2	1.8	- 1.9	-8	-1	3	1.6	1.4	1	0	4	1.8	- 2.1	1	-3	4	0.9	- 0.7
4	-8	2	4.6	5.3	-9	-1	3	1.6	1.7	0	0	4	17.2	16.6	0	-3	4	4.3	- 3.4
3	-8	2	2.1	- 2.2	-10	-1	3	3.3	3.2	-1	0	4	4.9	- 4.7	-1	-3	4	6.9	7.8

Appendiz-A/cont./

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
-2	-3	4	10.9	9.8	-6	1	5	2.0	1.6	-1	-4	5	9.1	8.6	-5	-1	6	1.6	1.6
-3	-3	4	3.1	2.3	-7	1	5	7.2	-7.4	-2	-4	5	6.9	6.3	-6	-1	6	7.5	-7.6
-4	-3	4	1.4	-1.1	-1	2	5	3.2	3.5	-3	-4	5	2.4	1.5	-7	-1	6	2.0	-2.5
-5	-3	4	5.2	5.4	-2	2	5	1.8	-1.8	-4	-4	5	11.7	10.2	-9	-1	6	1.0	0.8
-6	-3	4	4.6	4.5	-4	2	5	2.2	-2.1	-5	-4	5	3.7	-3.8	1	-2	6	2.4	2.6
-7	-3	4	3.7	4.4	-5	2	5	1.3	-1.1	-6	-4	5	2.5	-2.5	-2	-2	6	4.3	-4.7
-9	-3	4	2.2	2.2	-6	2	5	1.7	1.3	-7	-4	5	3.4	4.5	-3	-2	6	2.4	-4.0
6	-4	4	1.5	-2.3	-7	2	5	3.6	3.7	-8	-4	5	2.2	-2.4	-4	-2	6	3.8	4.8
5	-4	4	1.7	-2.0	-8	2	5	8.1	-8.5	-9	-4	5	1.1	1.1	-5	-2	6	4.7	5.0
3	-4	4	3.8	-4.2	-2	3	5	1.1	1.4	3	-5	5	1.4	1.5	-6	-2	6	16.3	-18.7
2	-4	4	6.0	5.3	-3	3	5	0.8	-0.8	2	-5	5	3.5	3.5	2	-3	6	1.1	1.5
1	-4	4	1.4	-1.3	-4	3	5	1.1	-1.2	1	-5	5	1.5	-1.5	1	-3	6	3.0	3.4
0	-4	4	10.9	-10.8	-5	3	5	1.4	-1.3	0	-5	5	2.2	2.1	-1	-3	6	2.2	-1.8
-1	-4	4	11.9	10.0	-6	3	5	0.8	0.8	-1	-5	5	6.4	6.5	-2	-3	6	2.2	-3.2
-2	-4	4	0.8	0.2	-7	3	5	0.9	1.0	-2	-5	5	4.4	3.1	-3	-3	6	2.4	1.7
-3	-4	4	2.7	5.7	-8	3	5	3.1	-3.3	-5	-5	5	3.3	3.1	-4	-3	6	1.7	2.0
-4	-4	4	2.9	3.1	-5	4	5	0.8	-0.9	-6	-5	5	3.7	4.0	-5	-3	6	9.7	-10.5
-5	-4	4	7.0	6.6	-6	4	5	0.9	-0.9	-7	-5	5	1.1	-1.1	-6	-3	6	2.4	-2.6
-6	-4	4	2.7	-2.6	-7	4	5	0.9	0.8	4	-5	5	2.2	-2.6	-9	-3	6	1.6	-1.7
-7	-4	4	1.4	1.[illegible]	-8	4	5	1.2	1.6	3	-5	5	7.1	[illegible]	-10	-3	6	2.0	-2.4
-9	-4	4	4.9	4.2	-9	4	5	3.6	-3.6	2	-6	5	2.5	-2.7	-2	0	7	1.4	-1.6
6	-5	4	1.4	-1.9	1	-1	5	4.0	3.9	1	-6	5	4.3	-4.5	-4	0	7	2.1	-3.0
5	-5	4	1.1	-0.8	0	-1	5	6.2	6.2	0	-6	5	5.8	5.8	-5	0	7	2.6	2.7
3	-5	4	1.3	-1.9	-1	-1	5	0.9	-1.0	-1	-6	5	2.2	2.5	-10	0	7	1.0	1.6
2	-5	4	1.9	-1.8	-2	-1	5	0.8	-0.7	-2	-6	5	1.1	0.9	-3	-1	7	2.3	-2.6
1	-5	4	2.0	-2.1	-3	-1	5	4.0	3.6	-3	-6	5	5.3	5.4	-8	-1	7	1.2	-0.9
0	-5	4	0.7	1.4	-4	-1	5	6.5	5.1	-4	-6	5	1.1	0.3	-9	-1	7	1.8	1.8
-1	-5	4	1.4	1.3	-5	-1	5	1.4	1.8	-5	-6	5	2.6	-2.7	-10	-1	7	2.8	2.7
-2	-5	4	0.8	-0.9	-6	-1	5	9.8	-9.8	-6	-6	5	2.7	3.2	1	-2	7	1.0	-1.8
-4	-5	4	3.7	4.1	-8	-1	5	[illegible]	3.1	-8	-6	5	2.7	2.1	-1	-2	7	1.9	-2.2
-5	-5	4	1.9	1.9	-9	-1	5	1.9	-1.9	3	-7	5	1.8	1.4	-2	-2	7	1.3	-1.9
-6	-5	4	1.7	1.7	-10	-1	5	1.8	-1.6	0	-7	5	1.8	2.4	-3	-2	7	3.9	-5.3
-8	-5	4	2.5	2.4	-11	-1	5	2.3	-1.8	-1	-7	5	1.0	0.6	-4	-2	7	3.5	4.3
4	-6	4	1.8	-2.0	4	-2	5	1.0	1.2	-3	-7	5	0.8	1.0	-6	-2	7	3.8	-4.9
3	-6	4	1.3	1.0	3	-2	5	1.4	-1.3	-4	-7	5	1.1	1.5	-9	-2	7	1.9	2.3
2	-6	4	1.0	1.3	1	-2	5	14.9	14.9	-5	-7	5	1.9	1.7	-10	-2	7	2.2	2.8
1	-6	4	8.4	-8.0	0	-2	5	5.3	-5.0	5	-8	5	1.4	-1.7	-4	-3	7	1.1	0.9
0	-6	4	3.0	2.4	-1	-2	5	1.0	-1.2	4	-8	5	2.7	3.2	-1	-3	7	1.4	-1.7
-1	-6	4	4.2	-3.7	-2	-2	5	.5	4.9	2	-8	5	2.8	-3.4	-2	-3	7	3.4	-4.6
-2	-6	4	6.0	5.1	-3	-2	5	6.5	5.8	1	-8	5	2.0	2.2	-5	-3	7	2.8	-2.7
-4	-6	4	1.1	1.1	-4	-2	5	2.7	2.4	-1	-8	5	1.6	1.2	-6	-3	7	1.8	-2.2
-5	-6	4	1.6'	-1.7	-5	-2	5	10.9	10.2	-2	-8	5	1.5	1.2	-7	-3	7	1.4	-1.6
3	-8	4	1.2	1.2	-6	-2	5	12.1	-11.5	-4	-8	5	1.8	-1.8	-8	-3	7	1.9	1.9
2	-8	4	3.5	-3.5	-7	-2	5	2.0	-1.8	-5	-8	5	1.4	1.4	-9	-3	7	1.8	2.2
1	-8	4	0.8	0.3	-8	-2	5	3.9	3.9	-2	0	6	0.8	-1.0	0	-4	7	1.1	-1.6
0	-8	4	2.6	-2.4	-9	-2	5	5.3	-3.6	-3	0	6	3.3	-3.7	0	-5	7	1.2	-1.4
-1	-8	4	3.0	3.4	3	-3	5	1.2	-0.1	-4	0	6	3.7	-4.5	0	-6	7	1.2	-1.9
-3	-8	4	1.2	-1.5	2	-3	5	4.[illegible]	4.0	-5	0	6	3.7	3.7	0	-7	7	0.8	-1.7
2	0	5	1.6	-1.5	1	-3	5	0.7	6.3	-6	0	6	2.6	2.6	0	-8	7	1.1	-1.5
0	0	5	9.4	9.5	0	-3	5	1.9	-1.2	-7	0	6	10.3	-10.8	-5	0	8	0.7	-1.0
-1	0	5	3.7	-3.6	-1	-3	5	1.8	2.3	-8	0	6	1.1	0.9	-5	-1	8	1.3	1.7
-3	0	5	0.8	-0.9	-2	-3	5	7.8	8.3	-3	1	6	1.1	-1.2	-2	-2	8	0.8	1.8
-4	0	5	1.8	1.2	-4	-3	5	4.1	1.8	-4	1	6	2.8	-3.2	-4	-2	8	1.1	1.3
-5	0	5	2.3	1.9	-5	-3	5	6.5	-5.7	-7	1	6	2.8	-2.8	-6	-2	8	1.9	3.0
-6	0	5	8.1	7.0	-6	-3	5	2.2	2.1	-4	2	6	0.8	-1.1	-7	-2	8	1.7	-1.9
-7	0	5	14.0	-13.5	-7	-3	5	4.5	4.9	-5	2	6	2.0	-2.5	-3	-3	8	1.0	-1.0
-9	0	5	2.2	2.3	-8	-3	5	2.0	-2.1	-6	2	6	2.4	2.3	-4	-3	8	0.5	0.8
-10	0	5	2.1	-2.5	-9	-3	5	1.6	-1.4	-7	2	6	1.0	1.1	-5	-3	8	1.8	2.5
0	1	5	1.4	1.5	-10	-3	5	1.1	-1.3	-8	2	6	3.4	-3.9	-9	-3	8	2.7	3.3
-1	1	5	3.1	3.5	3	-4	5	1.9	-1.9	-5	3	6	0.9	-1.1	0	-4	8	1.7	-2.1
-2	1	5	1.0	-1.1	2	-4	5	12.8	13.5	0	-1	6	1.8	1.8	0	-8	8	1.8	-1.8
-3	1	5	2.4	-2.3	1	-4	5	4.9	-4.8	-2	-1	6	2.6	-2.6	-7	-3	9	1.0	1.7
-5	1	5	2.9	2.5	0	-4	5	3.6	-3.4	-3	-1	6	4.1	-4.9					

APPENDIX B

Observed and calculated structure factors for 2-nitro-[illegible]-methyl benzoic acid.

H	K	L	FOBS	FCAL
2	0	0	40.56	-67.91
4	0	0	66.09	-257.99
6	0	0	12.17	-11.91
8	0	0	53.83	58.06
10	0	0	13.96	-12.17
0	0	2	36.68	-59.63
0	0	4	47.54	-77.40
0	0	6	41.57	42.74
0	0	8	12.33	-10.98
0	0	10	21.34	-21.33
0	0	12	4.13	4.19
0	0	14	13.05	11.44
16	0	2	8.20	-6.94
14	0	2	8.16	-7.89
10	0	2	58.49	54.04
8	0	2	20.34	-19.25
6	0	2	70.87	-93.39
4	0	2	6.63	-5.20
2	0	2	50.88	100.55
-2	0	2	21.32	-22.20
-4	0	2	46.04	75.89
-6	0	2	27.76	28.64
-8	0	2	23.99	-19.43
-10	0	2	22.19	-20.71
-12	0	2	22.71	21.79
-14	0	2	10.38	-10.28
-16	0	2	2.94	-3.61
12	0	4	31.22	26.14
8	0	4	45.63	-45.75
6	0	4	27.62	24.54
4	0	4	23.09	18.01
2	0	4	10.16	9.08
-2	0	4	56.21	88.45
-4	0	4	64.92	-142.62
-6	0	4	17.19	-19.91
-8	0	4	58.88	84.87
-10	0	4	23.34	24.16
-12	0	4	35.28	-36.71
-14	0	4	3.22	3.30
-16	0	4	3.56	-3.68
14	0	6	9.89	-7.55
12	0	6	4.57	2.42
10	0	6	14.88	11.96
6	0	6	35.69	-30.03
4	0	6	11.58	12.19
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-10	0	6	16.87	16.30
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6	0	8	15.49	-14.06
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6	0	10	13.49	-12.94
4	0	10	8.83	-8.57
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0	2	11	10.33	10.22
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0	2	14	7.45	-7.52

H	K	L	FOBS	FCAL
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1	3	4	57.58	50.92
1	3	5	5.36	-6.16
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1	3	7	17.88	-17.65
1	3	9	4.43	4.04
1	3	10	37.92	-37.29
1	3	11	8.11	-8.01
1	3	14	3.48	-3.58
3	3	0	82.59	97.87
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3	3	3	8.02	5.26
3	3	4	5.86	-5.40
3	3	6	29.76	-26.96
3	3	7	20.99	-19.31
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3	3	9	25.44	-27.55
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5	3	1	28.44	27.05
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9	3	7	3.12	-3.32
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H	K	L	FOBS	FCAL
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11	3	1	10.86	10.66
11	3	2	3.18	3.98
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-13	3	7	4.95	-6.09
-13	3	8	7.10	6.99
-13	3	9	2.66	-3.33
-13	3	10	10.24	9.67
-15	3	0	3.75	5.01
-15	3	1	3.39	2.33
-15	3	2	3.36	-2.67
H	K	L	FOBS	FCAL
-15	3	4	8.52	-9.20
-15	3	6	7.56	8.17
15	3	1	2.21	-3.05
15	3	3	3.19	3.58
15	3	5	3.37	-4.02
0	4	1	40.37	-39.89
0	4	2	54.46	-60.46
0	4	3	52.71	-64.15
0	4	4	29.18	26.67
0	4	5	59.22	63.86
0	4	6	19.24	18.43
0	4	7	10.01	9.81
0	4	8	29.23	30.48
0	4	9	28.91	-29.36
0	4	13	4.73	4.53
0	4	14	3.99	3.11
2	4	0	3.70	2.53
2	4	1	69.54	89.04
2	4	2	47.98	-54.69
2	4	3	37.37	-34.65
2	4	4	17.90	15.96
2	4	5	50.02	-54.17
2	4	6	2.77	-1.48
2	4	7	4.53	-4.80
2	4	8	23.58	-22.89
2	4	9	32.78	-33.85
2	4	10	30.33	31.40
2	4	12	4.88	-5.94
2	4	13	2.52	2.27
4	4	0	19.98	-17.58
4	4	1	65.08	-66.29
4	4	2	25.21	25.05
4	4	3	11.03	11.53
4	4	4	32.95	-29.37
4	4	5	9.10	8.94
4	4	6	13.81	-14.34
4	4	8	9.09	-9.81
4	4	9	6.56	-6.27
4	4	10	4.46	-3.27
4	4	11	5.70	-5.43
4	4	12	4.15	3.36
6	4	0	11.13	9.31
6	4	1	11.73	-9.05
6	4	2	4.74	6.37
6	4	3	43.09	39.10
6	4	4	4.52	-4.98
6	4	5	28.78	28.27
6	4	6	3.86	-3.32
6	4	7	7.63	-7.37
6	4	8	13.92	-14.38
H	K	L	FOBS	FCAL
6	4	9	14.86	16.47
6	4	10	21.76	-26.27
6	4	11	2.51	-2.37
8	4	0	27.44	-23.68
8	4	1	2.93	3.60
8	4	2	10.27	10.65
8	4	4	21.83	20.69
8	4	5	9.57	8.94
8	4	6	4.64	-4.17
8	4	7	4.60	-4.01
8	4	8	3.13	-3.24
8	4	10	7.42	6.07
8	4	11	10.99	10.70
10	4	0	12.08	12.60
10	4	1	16.26	15.15
10	4	2	7.28	-6.69
10	4	3	11.03	-9.89
10	4	4	13.92	-12.63
10	4	5	22.41	-23.24
10	4	6	13.33	14.05
10	4	7	7.10	6.66
10	4	10	6.42	7.10
12	4	0	4.58	3.95
12	4	1	3.22	-2.65
12	4	2	5.03	-6.00
12	4	3	3.12	3.28
12	4	4	3.00	3.03
12	4	7	2.27	-1.18
-2	4	0	3.53	2.53
-2	4	1	36.07	-41.12
-2	4	2	57.53	69.67
-2	4	3	33.18	32.11
-2	4	4	21.61	-21.54
-2	4	5	16.22	-15.58
-2	4	6	10.41	11.17
-2	4	7	10.08	10.07
-2	4	8	20.13	20.86
-2	4	9	58.40	65.22
-2	4	10	14.19	-15.21
-2	4	12	3.92	4.59
-2	4	13	4.76	-4.84
-2	4	14	9.45	-9.52
-4	4	0	21.79	-17.58
-4	4	1	12.49	15.88
-4	4	2	41.47	42.02
-4	4	3	4.52	1.40
-4	4	4	21.15	-17.88
-4	4	5	26.21	-27.21
-4	4	6	12.66	10.86
-4	4	7	30.42	28.41
H	K	L	FOBS	FCAL
-4	4	8	40.58	-41.63
-4	4	9	11.03	10.61
-4	4	10	5.13	-4.82
-4	4	11	8.60	-8.72
-4	4	12	5.06	5.69
-4	4	13	10.62	10.55
-6	4	0	11.52	9.31
-6	4	1	42.51	41.56
-6	4	2	23.17	-18.35
-6	4	4	13.96	-13.44
-6	4	3	31.51	31.72
-6	4	5	4.57	4.77
-6	4	6	31.42	-33.15
-6	4	7	12.28	-11.91
-6	4	8	7.32	12.23
-6	4	9	20.61	-19.81
-6	4	10	3.85	4.63
-6	4	12	14.46	-14.33
-6	4	13	16.26	-16.36
-8	4	0	28.52	-23.68
-8	4	1	15.12	-11.63
-8	4	2	20.67	-22.36
-8	4	3	34.20	-30.57
-8	4	4	28.41	28.40
-8	4	5	15.56	15.04
-8	4	6	21.09	-19.46
-8	4	7	14.04	-13.64
-8	4	8	7.99	7.83
-8	4	9	8.31	-9.39
-8	4	10	8.18	8.12
-8	4	12	7.70	6.80
-10	4	0	12.74	12.60
-10	4	1	15.67	15.15
-10	4	2	5.10	5.97
-10	4	4	8.02	-8.02
-10	4	5	21.81	-23.98
-10	4	6	27.34	28.61
-10	4	7	19.96	-21.05
-10	4	9	13.45	12.96
-10	4	10	4.21	-3.71
-10	4	11	8.23	7.86
-12	4	0	3.97	3.95
-12	4	1	4.59	3.97
-12	4	2	5.61	7.24
-12	4	3	4.54	5.07
-12	4	4	4.48	2.99
-12	4	6	5.60	3.82
-12	4	7	16.53	15.76
-12	4	8	4.32	-4.11
-12	4	9	4.74	-4.25

Appendix-3 /cont.

H	K	L	FOBS	FCAL
-12	4	10	1.93	1.77
-14	4	1	2.76	-2.09
-14	4	2	3.87	-5.13
-14	4	3	6.56	8.53
-14	4	4	3.16	2.81
-14	4	5	13.12	12.90
-14	4	6	8.03	-7.88
-14	4	7	5.73	5.96
-16	4	3	3.15	-4.58
-16	4	4	4.79	-6.13
14	4	6	6.45	-6.89
14	4	2	5.17	6.03
14	4	1	3.79	4.95
16	4	1	3.53	-5.38
1	5	1	29.00	-26.47
1	5	2	14.78	14.86
1	5	3	75.50	84.92
1	5	4	25.24	-24.75
1	5	5	15.08	-14.16
1	5	6	20.74	-21.04
1	5	7	8.91	-9.33
1	5	8	28.36	31.73
1	5	9	25.10	25.63
1	5	10	14.65	15.53
1	5	11	13.01	-14.15
1	5	12	4.03	3.53
1	5	0	15.38	-13.23
3	5	0	19.72	15.83
3	5	1	36.67	-32.39
3	5	2	59.56	-66.05
3	5	3	11.43	-9.66
3	5	4	33.10	-31.46
3	5	5	20.79	19.75
3	5	6	18.68	20.98
3	5	7	22.17	-25.90
3	5	8	3.67	-3.17
3	5	9	28.05	31.52
3	5	11	4.07	5.01
3	5	12	4.77	5.86
3	5	13	2.48	2.81
5	5	0	32.46	31.35
5	5	1	19.70	17.81
5	5	2	17.55	16.93
5	5	3	50.83	-51.20
5	5	4	5.75	-5.62
5	5	5	3.37	1.92
5	5	7	23.19	24.60
5	5	8	14.13	-14.51
5	5	9	18.71	-20.25
5	5	10	13.39	-15.29
5	5	11	9.61	8.90
5	5	12	6.98	-7.68
7	5	0	19.82	-19.38
7	5	1	21.79	19.17
7	5	2	4.64	-5.88
7	5	3	33.41	35.49
7	5	4	18.79	19.54
7	5	5	23.82	-25.41
7	5	6	3.01	-3.37
7	5	7	3.00	-3.02
7	5	8	9.37	-11.69
7	5	9	10.88	-12.47
7	5	10	7.56	-6.65
9	5	0	18.20	-18.94
9	5	1	4.12	4.55
9	5	2	5.53	-6.21
9	5	3	8.62	-10.18
9	5	4	3.01	3.55
9	5	5	4.74	2.36
9	5	8	8.05	8.51
9	5	9	6.80	6.66
9	5	10	7.30	7.16
11	5	1	14.97	-15.75
11	5	4	6.88	6.15
11	5	5	13.92	15.67
11	5	6	2.53	3.87
11	5	7	6.79	-5.21
11	5	9	3.50	3.52
13	5	2	6.79	7.77
13	5	4	5.59	-5.38
13	5	5	2.90	-4.40
13	5	6	3.67	-3.72
-1	5	0	14.97	-13.23
-1	5	1	14.02	14.17
-1	5	2	56.54	55.45
-1	5	3	3.94	4.50
-1	5	4	34.67	31.98
-1	5	6	17.01	16.42
-1	5	7	35.24	39.20
-1	5	8	22.26	22.82
-1	5	9	33.69	-37.16
-1	5	10	8.26	-8.08
-1	5	13	3.91	-4.88
-3	5	0	18.62	15.83
-3	5	1	40.36	37.36
-3	5	2	23.31	24.19
-3	5	3	74.83	-80.86
-3	5	4	13.61	16.46
-3	5	5	6.93	6.41
-3	5	7	14.09	-14.75
-3	5	8	6.28	-5.42
-3	5	9	7.74	-7.13
-3	5	10	[illegible]	10.59
-3	5	11	9.14	8.26
-3	5	12	12.62	-12.19
-3	5	13	10.56	-10.08
-5	5	0	34.14	31.35
-5	5	1	28.44	-25.26
-5	5	2	51.09	-53.08
-5	5	3	16.10	13.81
-5	5	4	13.48	-12.69
-5	5	5	14.42	12.93
-5	5	6	23.32	-23.86
-5	5	7	45.52	-46.25
-5	5	8	31.24	-35.65
-5	5	9	6.34	5.61
-5	5	10	4.04	3.43
-5	5	11	5.77	7.64
-5	5	13	10.80	10.94
-7	5	0	19.45	-19.38
-7	5	1	13.97	16.67
-7	5	2	15.10	16.58
-7	5	3	17.49	16.98
-7	5	4	5.89	-4.58
-7	5	5	34.73	-38.38
-7	5	6	24.95	-27.78
-7	5	7	41.21	44.34
-7	5	8	6.89	-6.58
-7	5	9	13.88	14.50
-7	5	10	2.66	-2.80
-7	5	11	16.00	-15.60
-7	5	12	7.38	6.03
-9	5	0	18.66	-18.94
-9	5	1	11.49	-12.71
-9	5	2	4.12	4.95
-9	5	3	8.49	8.93
-9	5	5	13.93	13.16
-9	5	6	29.79	31.19
-9	5	7	2.95	4.20
-9	5	8	12.14	14.96
-9	5	9	2.61	-3.23
-9	5	10	7.45	-7.70
-9	5	11	11.07	11.43
-9	5	12	4.26	5.69
-11	5	1	7.36	8.34
-11	5	3	8.44	-8.97
-11	5	4	10.54	10.98
-11	5	5	12.67	13.16
-11	5	6	8.45	9.63
-11	5	7	10.56	-12.29
-11	5	9	3.83	-4.59
-11	5	10	9.05	9.42
13	5	7	4.64	5.85
13	5	6	3.67	-3.72
13	5	5	3.84	-4.40
13	5	4	5.10	-5.38
13	5	2	7.61	7.77
-13	5	0	12.28	13.92
-13	5	1	3.30	-3.72
-13	5	2	2.67	-2.88
-13	5	3	4.92	5.63
-13	5	4	3.60	4.83
-13	5	5	3.83	-3.96
-13	5	6	3.88	-4.46
-13	5	7	4.23	-4.79
15	5	1	3.58	3.19
-15	5	0	2.65	-3.38
-15	5	3	2.21	-2.64
-15	5	5	5.99	-6.68
-15	5	6	2.28	-5.18
0	6	1	42.37	42.25
0	6	2	20.29	18.51
0	6	3	8.67	-9.58
0	6	4	28.09	-25.71
0	6	5	3.28	-2.89
0	6	6	5.41	4.88
0	6	7	6.24	6.77
0	6	8	23.42	-23.75
0	6	9	16.55	-16.08
0	6	11	7.46	7.51
0	6	12	7.96	-7.23
0	6	13	3.04	-2.34
2	6	0	5.25	-7.92
2	6	1	23.17	20.39
2	6	2	9.85	-9.38
2	6	3	5.11	-6.83
2	6	4	5.99	5.24
2	6	5	5.73	3.45
2	6	6	10.47	-8.68
2	6	7	34.33	37.32
2	6	8	[illegible]	20.89
2	6	9	8.34	8.53
2	6	11	5.31	6.12
2	6	13	2.80	2.27
4	6	0	12.01	-9.99
4	6	1	2.88	1.24
4	6	2	23.31	-23.07
4	6	3	15.66	13.37
4	6	4	19.55	19.27
4	6	6	12.41	11.28
4	6	7	3.92	-3.35
4	6	8	16.57	15.96
4	6	9	16.05	16.61
4	6	12	4.40	-4.47
6	6	0	30.99	-30.87
6	6	1	14.89	-13.80
6	6	2	28.50	29.39
6	6	3	13.43	-12.64
6	6	6	10.26	-9.87
6	6	7	16.55	-16.43
6	6	8	11.58	-13.36
6	6	10	10.66	9.61
8	6	0	25.32	24.70
8	6	2	17.72	-17.30
8	6	3	11.61	-10.47
8	6	4	23.05	-24.09
8	6	5	7.74	-7.47
8	6	6	8.92	8.54
8	6	9	3.83	-3.70
8	6	10	8.79	-8.84
10	6	0	4.56	-5.75
10	6	1	7.68	-7.37
10	6	3	8.39	7.49
10	6	4	12.20	13.66
10	6	6	4.44	-4.68
10	6	7	3.12	3.41
10	6	9	2.80	-2.92
12	6	2	9.09	8.88
12	6	7	1.63	2.37
-2	6	0	5.70	-7.92
-2	6	1	6.08	3.22
-2	6	2	10.34	-13.67
-2	6	3	18.78	20.23
-2	6	4	25.12	24.80
-2	6	5	5.62	-5.87
-2	6	6	13.04	11.94
-2	6	7	38.82	-47.21
-2	6	8	28.96	-31.06
-2	6	9	8.94	-9.36
-2	6	11	6.18	-6.27
-2	6	12	3.99	4.23
-2	6	13	3.72	-3.13
-4	6	0	10.95	-9.99
-4	6	1	40.92	-41.60
-4	6	2	7.19	6.50
-4	6	3	17.72	19.64
-4	6	4	27.17	-29.25
-4	6	5	21.13	-20.79
-4	6	6	27.40	-29.41
-4	6	7	15.42	-15.19
-4	6	8	36.80	42.47
-4	6	9	16.76	16.87
-4	6	10	4.23	4.30
-4	6	11	13.03	-12.23
-4	6	13	4.89	3.37
-6	6	0	29.51	-30.87
-6	6	1	31.04	-33.06
-6	6	2	11.04	8.84
-6	6	3	13.81	-12.41
-6	6	4	13.36	11.42
-6	6	5	9.89	8.80
-6	6	7	24.79	26.12
-6	6	8	10.96	-10.80
-6	6	9	8.11	-7.81
-6	6	10	5.62	6.15
-6	6	11	11.51	10.38
-6	6	12	17.33	15.10
-8	6	0	24.32	24.70
-8	6	1	21.02	20.74
-8	6	2	6.83	6.10
-8	6	3	4.41	-4.44
-8	6	5	26.10	27.16
-8	6	6	23.35	24.42
-8	6	7	6.93	7.02
-8	6	9	9.47	-9.60
-8	6	10	6.76	-7.00
-8	6	11	12.39	11.67
-8	6	12	16.17	-15.73
-10	6	0	5.09	-5.75
-10	6	1	17.49	16.94
-10	6	2	17.03	-16.62
-10	6	4	19.37	23.43
-10	6	5	9.92	9.97
-10	6	6	8.87	-8.63
-10	6	7	4.08	-3.84
-10	6	8	5.62	-6.55
-10	6	9	6.98	6.13
-12	6	1	10.46	-10.39
-12	6	4	12.50	-13.23
-12	6	5	14.90	-16.06
-12	6	6	8.70	-9.13
-12	6	9	2.90	3.41
14	6	2	2.92	-3.47
-14	6	0	2.26	-3.09
-14	6	2	5.54	6.72
-14	6	3	4.09	-4.50
-14	6	4	10.13	-9.18
-14	6	5	11.57	-11.77
-14	6	6	5.60	6.19
1	7	0	26.13	-24.28

H	K	L	FOBS	FCAL
1	7	1	34.94	-33.17
1	7	2	7.20	7.84
1	7	3	22.52	21.20
1	7	4	14.31	-16.32
1	7	6	2.96	-3.75
1	7	7	16.69	-16.17
1	7	8	9.63	-7.25
1	7	9	9.35	9.89
1	7	10	2.79	-3.48
3	7	1	8.12	-8.70
3	7	2	11.14	10.03
3	7	3	8.62	6.64
3	7	4	6.24	3.67
3	7	5	14.08	13.71
3	7	6	3.04	2.05
3	7	7	13.01	13.96
3	7	9	5.08	-6.10
3	7	11	7.49	-7.67
3	7	12	3.70	4.43
5	7	0	20.18	21.84
5	7	1	41.17	42.92
5	7	2	9.05	6.69
5	7	3	6.47	5.57
5	7	4	9.11	7.65
5	7	5	18.01	-19.62
5	7	9	6.22	6.82
5	7	10	8.28	9.01
7	7	0	12.31	11.52
7	7	2	6.87	1.68
7	7	3	26.11	-26.61
7	7	6	3.06	3.09
7	7	7	10.26	11.48
7	7	8	5.45	5.12
7	7	10	3.46	4.69
9	7	0	8.06	-7.72
9	7	1	24.16	-25.91
9	7	2	3.12	3.10
9	7	3	12.85	12.76
9	7	5	7.13	9.15
9	7	6	4.79	-5.10
9	7	7	4.71	-5.36
9	7	9	2.85	-3.16
11	7	0	3.61	-3.64
11	7	1	6.53	9.08
11	7	2	7.53	-8.51
11	7	3	5.18	-6.91
11	7	4	3.71	-4.21
-1	7	0	27.01	-24.28
-1	7	1	24.44	21.99
-1	7	2	22.40	-21.61
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-3	7	9	21.77	-25.29
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-3	7	11	16.90	17.56
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-7	7	0	13.61	11.52
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-9	7	6	10.40	-11.36
-9	7	[illegible]	3.17	[illegible]
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13	7	2	3.10	-1.34
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