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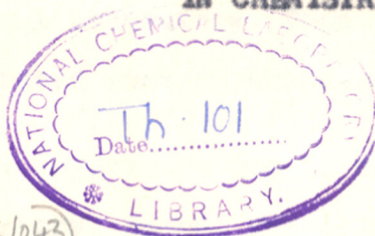
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THE CRYSTAL AND MOLECULAR STRUCTURES OF o-DIMETHYL
AMINO BENZOIC ACID AND RELATED COMPOUNDS
BY X-RAY DIFFRACTION

THESIS SUBMITTED
TO THE UNIVERSITY OF POONA
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by

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Poona
April, 1973.

N.N. Dhaneshwar-
(N.N. Dhaneshwar)

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ABSTRACT

In the present work, the crystal and molecular structures of (1) o-methyl amino benzoic acid and (2) o-dimethyl amino benzoic acid have been determined by X-ray diffraction.

o-Methyl amino benzoic acid crystallizes in the monoclinic system, space group $P2_1/c$ with

$$a = 8.15 \text{ \AA}; \quad b = 15.09 \text{ \AA}; \quad c = 7.03 \text{ \AA}; \quad \beta = 118.3^\circ; \\ \rho_o = 1.307 \text{ g.cm}^{-3}; \quad \rho_c \text{ for } Z = 4, 1.319 \text{ g.cm}^{-3}.$$

The structure was solved with the help of sharpened Patterson projections and the Harker line $P(o, y, \frac{1}{2})$ assuming plane centrosymmetrical dimers. Refinement was done with the help of 965 general reflections; final R was 0.101. Hydrogen atoms were located after isotropic refinement and the structure was further refined using anisotropic temperature factor. The molecules form strong dimers linked together by O-H---O hydrogen bonds across a centre of symmetry. There is a weak intramolecular hydrogen bond between the oxygen atom of the carboxylic group and the nitrogen atom of the methyl amino group. The structure of o-methyl amino benzoic acid was published under the title 'The structure of N-methyl anthranilic acid' in Acta Crystallographica. (1972). B28, 647.

o-Dimethyl amino benzoic acid crystallizes in the monoclinic system, space group $P2_1/n$ with

$a = 7.66 \text{ \AA}$; $b = 15.74 \text{ \AA}$; $c = 7.58 \text{ \AA}$; $\beta = 100^\circ$;
 ρ_c for $Z = 4$, 1.218 g.cm^{-3}

The structure was solved with the help of Sayre's equation programme written by R.E. Long (1965) and atomic positions were located by means of three dimensional Fourier sections between $y = 0$ and $y = 0.25$. Hydrogen atoms were located by three dimensional difference Fourier sections between $y = 0$ and $y = 0.175$. The structure was refined with the help of 1037 reflections; final R was 0.113.

The molecules of *o*-dimethyl amino benzoic acid exist as zwitterions in the crystal. There is a strong intramolecular hydrogen bond between the oxygen atom of the carboxylic group and the nitrogen atom of dimethyl amino group. The molecule probably forms a loose kind of dimer by means of a bifurcated hydrogen bond with the neighbouring molecule. As expected, the nitrogen atom is tetrahedral in *o*-dimethyl amino benzoic acid, while in *o*-methyl amino benzoic acid, it is planar.

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CHAPTER - I

INTRODUCTION

The science of X-ray crystallography started with Laue's suggestion in 1912 that a crystal may act as a diffraction grating and produce interference effects with X-rays since the interatomic distances in the crystal are of the order of the expected X-ray wavelengths. Friedrich and Knipping performed the experiment with zinc-blende $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystal and observed the expected diffraction effects. The diffraction spots in 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 as the crystal structure is essentially a repeating pattern in three dimensions, it can be expressed as the sum of a suitable Fourier series, the Fourier components being sinusoidal electron density distributions (electron density waves). The wave normal of each electron density wave is normal to a certain set of lattice planes and the wavelength of the electron density wave is equal to the spacing of that set of lattice planes. Each pair of spectra hkl and $\bar{h}\bar{k}\bar{l}$, given by the crystal can be considered as produced by the electron density wave corresponding to the hkl lattice planes; the whole array of spectra is thus produced by the total electron density distribution, which is a superposition of all the individual electron density

waves (Fourier components). It can be shown that the amplitude of an (hkl) electron density wave is proportional to the amplitude of the scattered radiation from the contents of one unit cell of the crystal in the direction of the hkl spectrum (called the structure amplitude).

In order to sum up the Fourier series, the knowledge of the phases of the structure amplitudes is necessary. The magnitudes of the structure amplitudes can be measured experimentally, but the knowledge about the relative phases is lost in recording the diffraction pattern of the crystal. The phases of the different structure amplitudes can sometimes be fixed by trial. A trial structure is postulated and if there is good agreement between observed and calculated structure amplitudes, the calculated phases are used along with observed structure amplitudes to sum the Fourier series.

An attempt to overcome the phase problem was made by Patterson (1935). He modified the 'Fourier series method' using the observed intensities as the coefficients of the series. By this one gets a map of interatomic vectors in the unit cell rather than the atomic positions themselves. One of the properties of the Patterson function of use in crystal structure analysis is the occurrence of peaks on certain planes (Harker sections) or lines (Harker lines) due to interaction between the symmetry related atoms.

The direct methods of structure determination are based on the fact that certain items of direct space

information of a completely general kind (for instance, that the electron density is always positive, or that it is a superposition of spherically-symmetric atoms of approximately the same shape) are sufficient to impose limitations on the magnitudes and phases of the structure factors. In some cases the restrictions are severe enough to determine the signs of most of the important structure factors. One of direct methods of structure analysis is by Sayre (1952). It is based on the fact that if all the atoms in the crystal are equal, and completely resolved from one another, the operation of squaring the electron density gives a distribution which is still a superposition of equal spherically symmetric 'atoms', centred on the same points as before. The relations between structure factors which hold when the above conditions are satisfied, as they are approximately in organic compounds, are unwieldy, but have proved to be of practical value. They have also led to the discovery of other less rigorous but more practically useful relations between the signs of the structure factors. R.E. Long (1965) has written a computer programme to solve the structure using Sayre's equation. One of the structures described in this thesis was solved by this method.

After getting the approximate atomic positions in the unit cell, the parameters defining these atoms must be refined. This can be done by difference synthesis or by the method of least squares. To obtain the difference Fourier

map, the differences between observed and calculated structure factors are used as 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 computed structure factors.

With the development of high speed computing facilities and of single crystal diffractometers for the accurate measurement of X-ray intensities, it has now become possible not only to make precise determination of molecular dimensions but also to obtain 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 analysis of triazine (Coppens, 1967), oxalic acid dihydrate (Coppens, Sabine, Delaplane and Ibers, 1969) and Cyanuric acid (Verschoor and Keulen, 1971). The structure analysis of cyanuric acid was done at liquid nitrogen temperature in order to increase the resolution in electron density difference maps and to obtain still more accurate atomic parameters. In all these studies, the final difference maps show the bonding effects clearly.

In the present work, the structures of ortho methyl amino benzoic acid (N-methyl anthranilic acid) and ortho dimethyl amino benzoic acid (N,N-dimethyl anthranilic acid) have been determined. These structure analyses were undertaken in order to compare them with the structure of the

parent compound (anthranilic acid) and to study the effect of methyl group substitution on the molecular structure. The structure of anthranilic acid was determined by Brown (1968); it consists of two molecules per asymmetric unit, one of which is a neutral molecule and the other a zwitterion.

In the determination of the preliminary structures, von Eller photoscanner was frequently used. For three dimensional refinement of the structures and for all other later computations the CDC-3600 computer of the Tata Institute of Fundamental Research, Bombay was used.

Part - I : Crystal and molecular structure
of o-methyl amino benzoic acid.

CHAPTER - II

EXPERIMENTAL

(A) Preparation of the compound :-

o-Methyl amino benzoic acid (also known as N-methyl anthranilic acid) was prepared by the method of Wilstatter and Kahn (1904). 1.14 gms. of anthranilic acid dissolved in 4.2 ml. of 8% sodium hydroxide solution was treated with 0.14 ml. of dimethyl sulphate at about 0°C. After about an hour the solution was filtered and the precipitate was crystallised from alcohol to give o-methyl amino benzoic acid (m.p. 178-9°C). Purity was also checked by infrared spectrum and mass spectrum. Crystals suitable for X-ray work were obtained by crystallizing the compound from toluene at 5°C.

(1) The determination of unit cell dimensions :-

The preliminary values of the unit cell dimensions were obtained from the rotation photographs taken with $\text{CuK}\alpha$ radiation and the crystal oscillated about the three crystallographic axes in turn. Accurate determination of the axial lengths was done with the help of high angle reflections in equatorial Weissenberg photographs. The values of spacings d_{100} , d_{010} and d_{001} obtained from high angle reflections were plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$. 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 value of angle β (118.3°) was obtained from equatorial Weissenberg photograph taken with 'b' as the oscillation axis.

Length of axis 'a' :- 'a' was measured from eight reflections of the type hko (Table II-1a and graph shown in Fig. II-1) using the formula

$$d_{100} = \frac{\lambda}{2} \left[h^2 + \left(\frac{a \sin \beta}{b} \right)^2 k^2 \right]^{\frac{1}{2}} \operatorname{cosec} \theta_{hko}$$

Table II-1a

Reflection used	θ	$\sin \theta$	$\sin^2 \theta$	d_{100}
7,0,0	48.6°	0.7494	0.5616	$7.210 \text{ \AA}$
7,2,0	49.1	0.7559	0.5714	7.206
7,4,0	50.8	0.7749	0.6005	7.216
8,0,0	58.8	0.8554	0.7317	7.211
8,4,0	61.8	0.8813	0.7767	7.193
α_1 8,7,0	68.1	0.9278	0.8608	7.188
α_2	68.3	0.9291	0.8632	7.196
α_1 8,8,0	71.6	0.9435	0.8996	7.188
α_2	72.2	0.9521	0.9065	7.178
α_1 9,4,0	80.8	0.9871	0.9744	7.174
α_2	81.8	0.9898	0.9797	7.174

The extrapolated value of d_{100} from the graph is $7.179 \pm 0.008 \text{ \AA}$. $\therefore a = 0.15 \text{ \AA} (= d_{100}/\sin \theta)$.

Length of axis 'b' :- 'b' was measured from 1st reflection of the types hky and chl (Table II-1b and graph shown in Fig. II-3) using the formulae

$$d_{010} = \frac{1}{b} \left[\frac{a^2}{a^2 \sin^2 \theta} + h^2 + k^2 \right]^{-1/2} \quad \text{cases 1 for hky}$$

Reflections; and

$$d_{010} = \frac{1}{b} \left[h^2 + \left(\frac{a}{a \sin \theta} \right)^2 + l^2 \right]^{-1/2} \quad \text{cases 2 for chl}$$

Reflections.

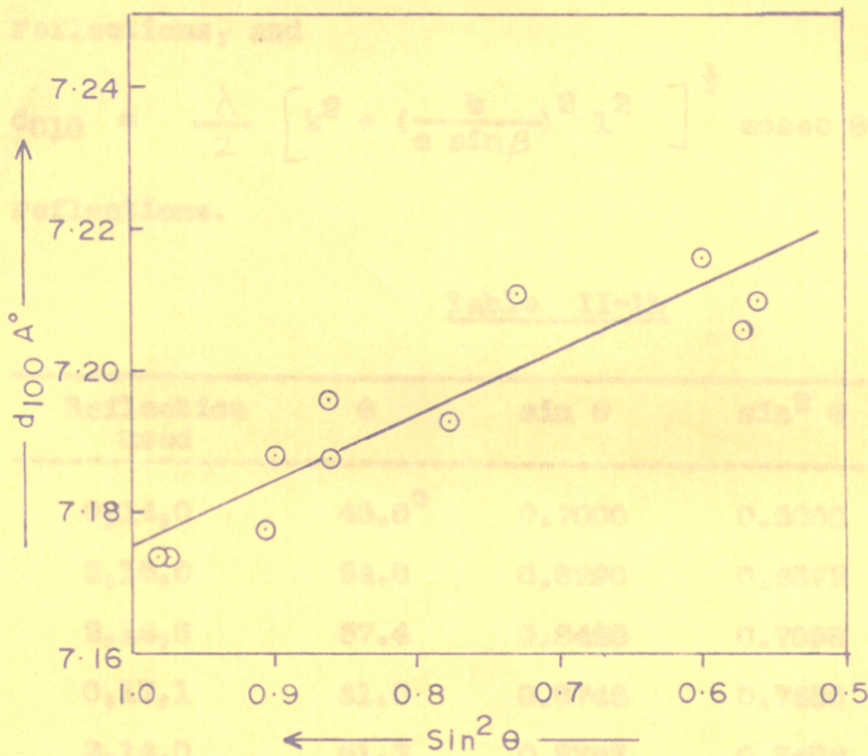


FIG. II-1 - GRAPH OF d_{100} Vs. $\sin^2 \theta$

The extrapolated value of d_{100} from the graph is 7.175
 $\pm 0.005 \text{ \AA}$ $\therefore a = 8.15 \text{ \AA} (= d_{100}/\sin\beta)$.

Length of axis 'b' :- 'b' was measured from ten reflections
of the types hko and okl (Table II-1b and graph shown in
Fig. II-2) using the formulae

$$d_{010} = \frac{\lambda}{2} \left[\left(\frac{b}{a \sin\beta} \right)^2 h^2 + k^2 \right]^{\frac{1}{2}} \operatorname{cosec} \theta \text{ for hko}$$

reflections, and

$$d_{010} = \frac{\lambda}{2} \left[k^2 + \left(\frac{b}{c \sin\beta} \right)^2 l^2 \right]^{\frac{1}{2}} \operatorname{cosec} \theta \text{ for okl}$$

reflections.

Table II-1b

Reflection used	θ	$\sin \theta$	$\sin^2 \theta$	d_{010}
0,14,0	45.0°	0.7000	0.5000	15.260 $\text{\AA}$
3,15,0	56.0	0.8290	0.6872	15.141
2,16,0	57.4	0.8425	0.7098	15.136
0,17,1	61.0	0.8746	0.7650	15.145
3,16,0	61.3	0.8767	0.7686	15.126
0,15,4	65.8	0.9121	0.8319	15.122
0,17,3	70.4	0.9421	0.8876	15.148
0,18,2	71.8	0.9500	0.9025	15.136
0,16,4	72.8	0.9553	0.9126	15.132
α_1 6,14,0	74.0	0.9610	0.9235	15.111
α_2	74.6	0.9638	0.9289	15.107

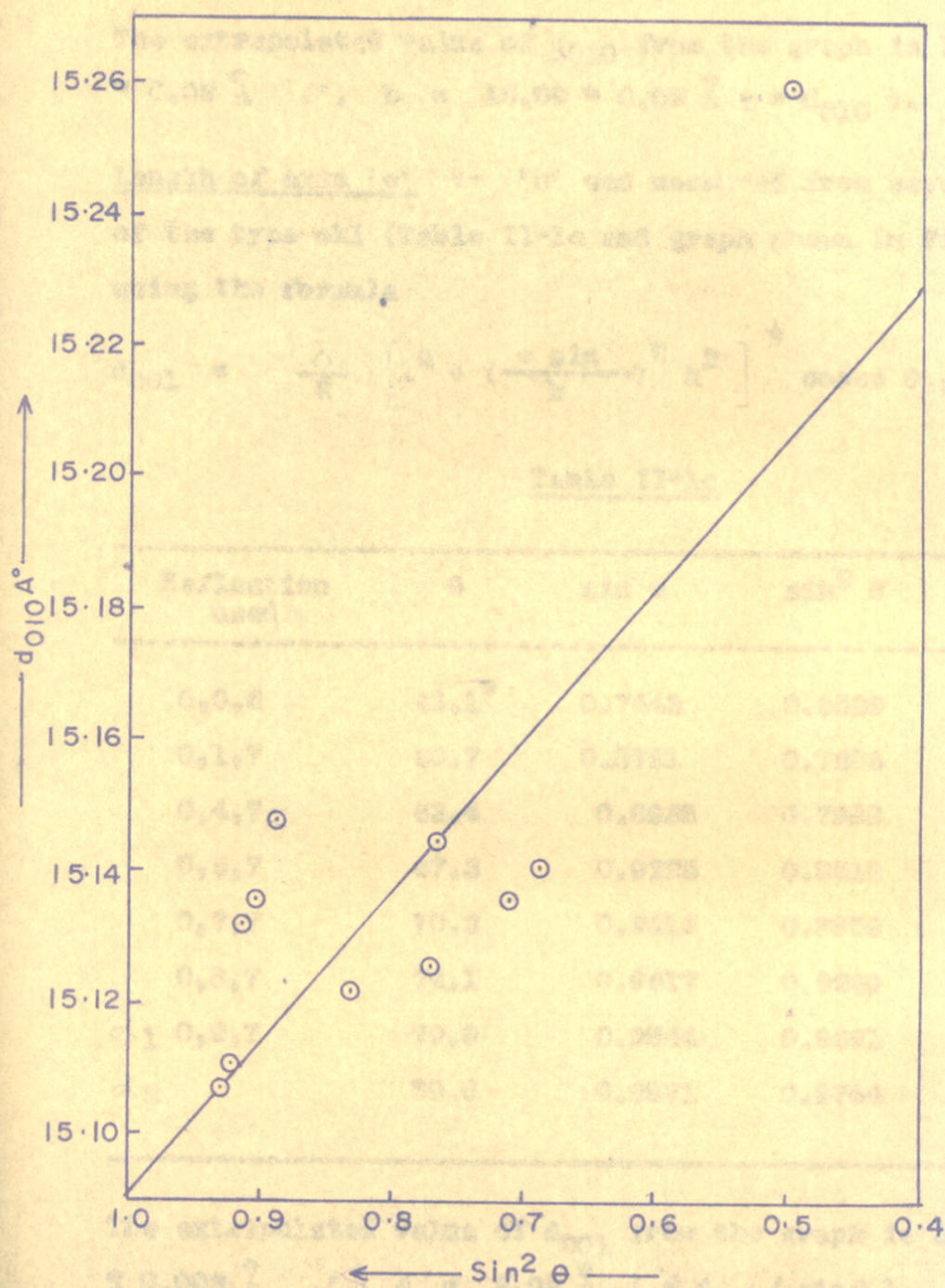


FIG.II-2 GRAPH OF d_{010} Vs. $\sin^2 \theta$

The extrapolated value of d_{010} from the graph is 15.091
 $\pm 0.02 \text{ \AA}$ $\therefore b = 15.09 \pm 0.02 \text{ \AA} (= d_{010})$.

Length of axis 'c' :- 'c' was measured from seven reflections
of the type okl (Table II-1c and graph shown in Fig. II-3)
using the formula

$$d_{001} = \frac{\lambda}{2} \left[1^2 + \left(\frac{c \sin \theta}{b} \right)^2 k^2 \right]^{\frac{1}{2}} \operatorname{cosec} \theta_{okl}$$

Table II-1c

Reflection used	θ	$\sin \theta$	$\sin^2 \theta$	d_{001}
0,0,6	48.1°	0.7443	0.5539	6.210 $\text{\AA}$
0,1,7	60.7	0.8721	0.7606	6.198
0,4,7	63.4	0.8938	0.7988	6.201
0,6,7	67.3	0.9225	0.8510	6.198
0,7,7	70.3	0.9412	0.8859	6.194
0,8,7	74.1	0.9617	0.9249	6.193
α_1 0,9,7	79.9	0.9844	0.9691	6.184
α_2	80.8	0.9871	0.9744	6.183

The extrapolated value of d_{001} from the graph is 6.185
 $\pm 0.003 \text{ \AA}$ $\therefore c = 7.03 \text{ \AA} (= d_{001} / \sin \beta)$. The final
cell dimensions are thus :

$$a = 8.15 \text{ \AA}; \quad b = 15.09 \text{ \AA}; \quad c = 7.03 \text{ \AA}; \quad \beta = 118.3^\circ.$$

± 0.005
 ± 0.02
 ± 0.003

(iii) The crystal density determination :- The density was measured by the flotation method using a solution of lithium bromide in water. The average observed density is 1.307 g./cc.

(iii) Number of molecules per unit cell :- The number of molecules per unit cell was obtained from the formula $n = (V \cdot d \cdot N_A) / M$ where

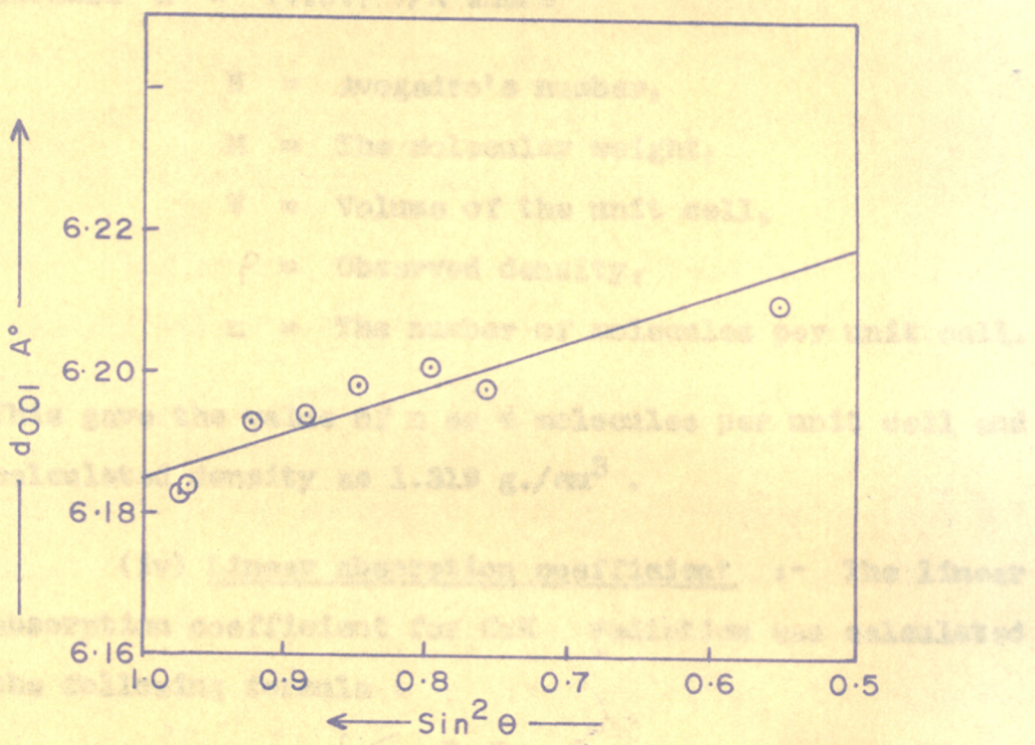


FIG. II-3- GRAPH OF d_{001} Vs. $\sin^2 \theta$

(ii) The crystal density determination :- The density was measured by the flotation method using a solution of Lithium bromide in water. The average observed density is 1.307 g./ml.

(iii) Number of molecules per unit cell :- The number of molecules per unit cell n was obtained from the formula $n = (V.M.\rho)/M$ where

- N = Avogadro's number,
- M = The molecular weight,
- V = Volume of the unit cell,
- ρ = Observed density,
- n = The number of molecules per unit cell.

This gave the value of n as 4 molecules per unit cell and calculated density as 1.319 g./cm³.

(iv) Linear absorption coefficient :- The linear absorption coefficient for CuK radiation was calculated by the following formula :

$$\mu = \frac{\rho \sum n \mu_g}{nW}$$

where ρ is the density in gm./cm³, 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 the atoms present. μ calculated is 9.7 cm⁻¹.

(B) Collection of data and estimation of intensity :-

Three dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with unfiltered Cu radiation. Data were collected from zero to sixth layer Weissenberg photographs about the a axis, the cross section of the crystal used being $1.5 \times 1.3 \text{ mm}^2$. Data were also collected from zero to fifth layer Weissenberg photographs about the c axis, the cross section of the crystal used being $1.0 \times 1.4 \text{ mm}^2$ of the 972 observed reflections, 560 were present in both sets of photographs.

The intensities of the reflections were measured visually with the help of an intensity scale prepared in the following way. From the zero layer Weissenberg photograph, a strong reflection with a good spot shape was chosen which was sufficiently separated from other reflections and the crystal was oscillated through 10° about the angular position of this reflection. The film cassette was kept stationary. The exposure was given for one oscillation. The cassette was shifted by 5 mm. and the next exposure was given for two oscillations. Thus by shifting the cassette and increasing the number of oscillations each time, a set of diffraction spots of known relative intensities was obtained. X-rays were generated by a stabilized X-ray generator (Phillips PW 1010), and 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.

(1) Lorentz and Polarization (Lp) factor :- The Lorentz factor arises from the variable time opportunity for reflection, which is offered to the various planes by the geometry of rotation. The reciprocal points near the origin, obviously move more slowly, while those away from the origin move faster. The polarization factor arises on account of the uneven loss of intensity of different reflections due to different degree of polarization of the diffracted X-ray beam. The relative intensities I of diffracted spots on equi-inclination Weissenberg photographs are given by $|F|^2 \propto D I$ where F is the structure factor and $D = (\xi \cos \theta) / (1 + \cos^2 2\theta)$.

(11) Effect of spot extension :- In the higher layer photographs, the reflections get extended on one side and contracted on the other side. Suppose the crystal consists of small mosaics having slightly different orientations. As the crystal rotates, the different mosaics giving rise to the same reflection do not reflect the incident beam at the same time. When the film movement and spot growth are in the same direction, the spots get extended and when they are in opposite directions they are contracted. The correction for spot extension was applied by the expression $I = W \cdot I_e$ where $W = (A + \Delta A) / A$ and I_e is the intensity of extended spot; A is the area of spot when cassette is not moving.

The intensities of higher layer photographs were measured from extended spots. Both the corrections for Lp factor as well as for the effect of spot extension depend on the Bragg angle θ and the reciprocal coordinates (ξ, ζ) .

The combined correction factors for both the effects are tabulated in "International tables for X-ray crystallography" (Volume III). These tables were used to correct the intensities. Absorption correction was neglected.

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

(iii) Scale and temperature factor :- The relative intensities were put on an ^{approximately} absolute scale and an overall temperature factor B was determined by Wilson's (1942) statistical method. The reflections from three dimensional data were divided into zones lying between certain values of $\sin \theta$. The mean value of the observed intensities $\langle I \rangle$ ($= \frac{\sum I}{n}$ where $\sum I$ denotes the sum of the intensities in a certain range and n, the number of reflections in that range) was evaluated over each zone. The constant C which makes the average equal to $\sum f_n^2$; i.e. $C = (\sum f_n^2) / \langle I \rangle$ was found; f_n is the scattering factor of an atom at rest, the summation being done over all the atoms in the unit cell. McWeeny's (1951) values of scattering factors were used. $\log_e C$ was plotted against the mean value of $\sin^2 \theta / \lambda^2$ for each zone. The slope of the line drawn through the plotted points gives the value of $2B$. The intercept at $\sin \theta = 0$ gives the value of $\log_e C_0$ and hence C_0 , the scale factor. The graph of $\log_e C$ against $\sin^2 \theta / \lambda^2$ is given in Figure II-4 and the corresponding data are given in Table II-2.

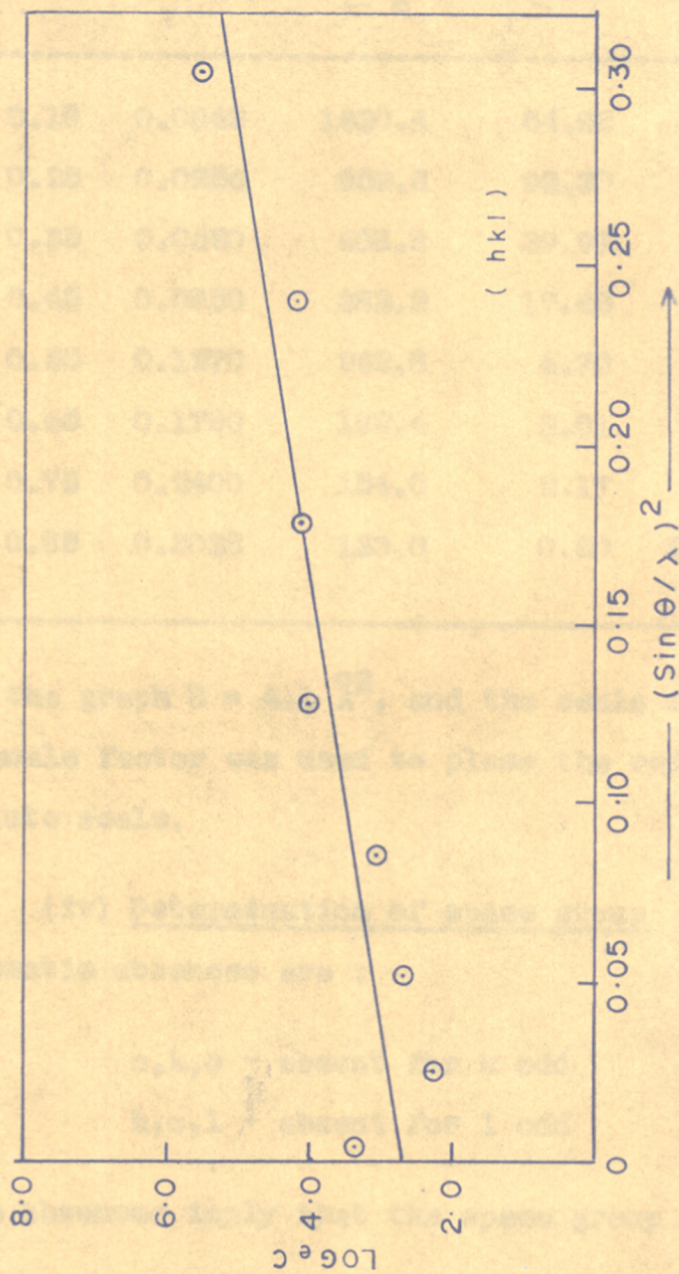


FIG 11-4-4- DETERMINATION OF PRELIMINARY SCALE AND TEMP.
FACTOR BY WILSON'S METHOD USING 3 DIMENSIONAL DATA

Table II-2

No.	$\sin \theta$	$\sin^2 \theta / \lambda^2$	$\sum f_n^2$	$\langle I \rangle$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1.	0.10	0.0042	1630.4	54.95	29.66	3.38
2.	0.25	0.0256	952.8	93.30	10.21	2.32
3.	0.35	0.0520	608.8	39.97	15.23	2.72
4.	0.45	0.0850	383.2	17.40	22.03	3.09
5.	0.55	0.1270	262.8	4.70	55.81	4.02
6.	0.65	0.1780	192.4	3.01	63.92	4.16
7.	0.75	0.2400	154.0	2.17	71.10	4.26
8.	0.85	0.3038	133.0	0.50	266.00	5.58

From the graph $B = 4.1 \text{ \AA}^2$, and the scale factor is 14.9.
This scale factor was used to place the reflections on the absolute scale.

(iv) Determination of space group :- The observed systematic absences are :

$0, k, 0$ - absent for k odd

$h, 0, l$ - absent for l odd

These absences imply that the space group is $P2_1/C$.

CHAPTER - III

PRELIMINARY STRUCTURE

A crystal can be considered as a continuous distribution of electron density. The electron density reaches to a maximum at the atomic centre and falls off asymptotically to zero in the space between the atoms. This distribution is triply periodic and can be represented by the Fourier series

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_{l=-\infty}^{\infty} F(hkl) \exp. \{-2\pi i (hx+ky+lz)\}$$

..... (III-1)

In this equation $\rho(x,y,z)$ is the electron density at the point (x,y,z) and V is the volume of the unit cell. The term $F(hkl)$, called structure factor is the expression which gives the amplitude and the phase of the wave diffracted by the contents of the unit cell in the direction of (hkl) reflection. By summing up the Fourier series one can get the electron density distribution in the crystal and hence the crystal structure. The magnitudes of the structure factor can be measured experimentally but in recording the diffraction patterns of the crystal, the knowledge about the relative phases of the diffracted beams is lost.

A general method of overcoming this difficulty is the method of 'Trial and error'. In this method, an atomic arrangement that conforms to the space group symmetry and the chemical formula is postulated and the phases of the structure factors are determined. The success of the crystal structure determination depends on the fixing up of the correct trial structure. The trial structure of o-methyl amino benzoic acid was fixed on (0,0,1) projection from the combined information, obtained by the methods described below :

Patterson function :

Patterson function $P(u,v,w)$ at the point (u,v,w) in the unit cell is defined by the relation

$$P(u,v,w) = \frac{1}{V} \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \rho(x+u, y+v, z+w) dx dy dz$$

..... (III-2)

where $\rho(x,y,z)$ and $\rho(x+u, y+v, z+w)$ are the electron densities at the points (x,y,z) and $(x+u, y+v, z+w)$ respectively. It can be shown that expression (III-2) simplifies to

$$P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi (hx + ky + lz)$$

..... (III-3)

For the Patterson projections $P(u,0,w)$ and $P(0,v,w)$ the expression reduces to

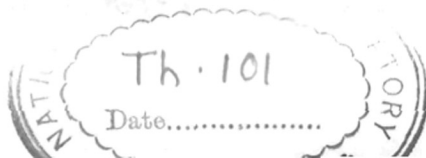
$$P(u,0,w) = \frac{1}{A} \sum_h \sum_l |F(h0l)|^2 \cos 2\pi (hu + lw)$$

..... (III-4)

$$P(o,v,w) = \frac{1}{A} \sum_k \sum_l |F(okl)|^2 \cos 2\pi (kv + lw) \dots\dots (III-5)$$

The $|F(hkl)|^2$ values are experimentally available, so the series can be summed up without the knowledge of phase angles. A peak in the Patterson function implies the presence of two atoms separated by a vector distance equal to the vector distance of the peak from the origin. The height of this peak depends on the product of the atomic numbers of the two atoms involved. In a structure of N atoms there are N^2 Patterson peaks. Out of these N^2 peaks, N peaks will occur at the origin since they correspond to the interactions of the atoms with themselves. The remaining $N(N-1)$ peaks are distributed over the unit cell. Half of these peaks are related by centre of symmetry to the other half. So there are only $N(N-1)/2$ independent peaks. For crystal structures, containing several atoms of almost equal diffracting power, these peaks are not all resolved, and overlapping of the peaks complicates the derivation of the original set of atoms which give rise to the particular vector set.

The chances of the interpretation of the Patterson map are greatest when individual peaks are resolved to the greatest possible extent. This will be so if the intensities used as coefficients of the Fourier series correspond to the intensities given by the point atoms. But if the Patterson function is modified for this only, then each peak will be surrounded by diffraction rings due to series termination error. Some of



548.73:547.466 (043)

DHA

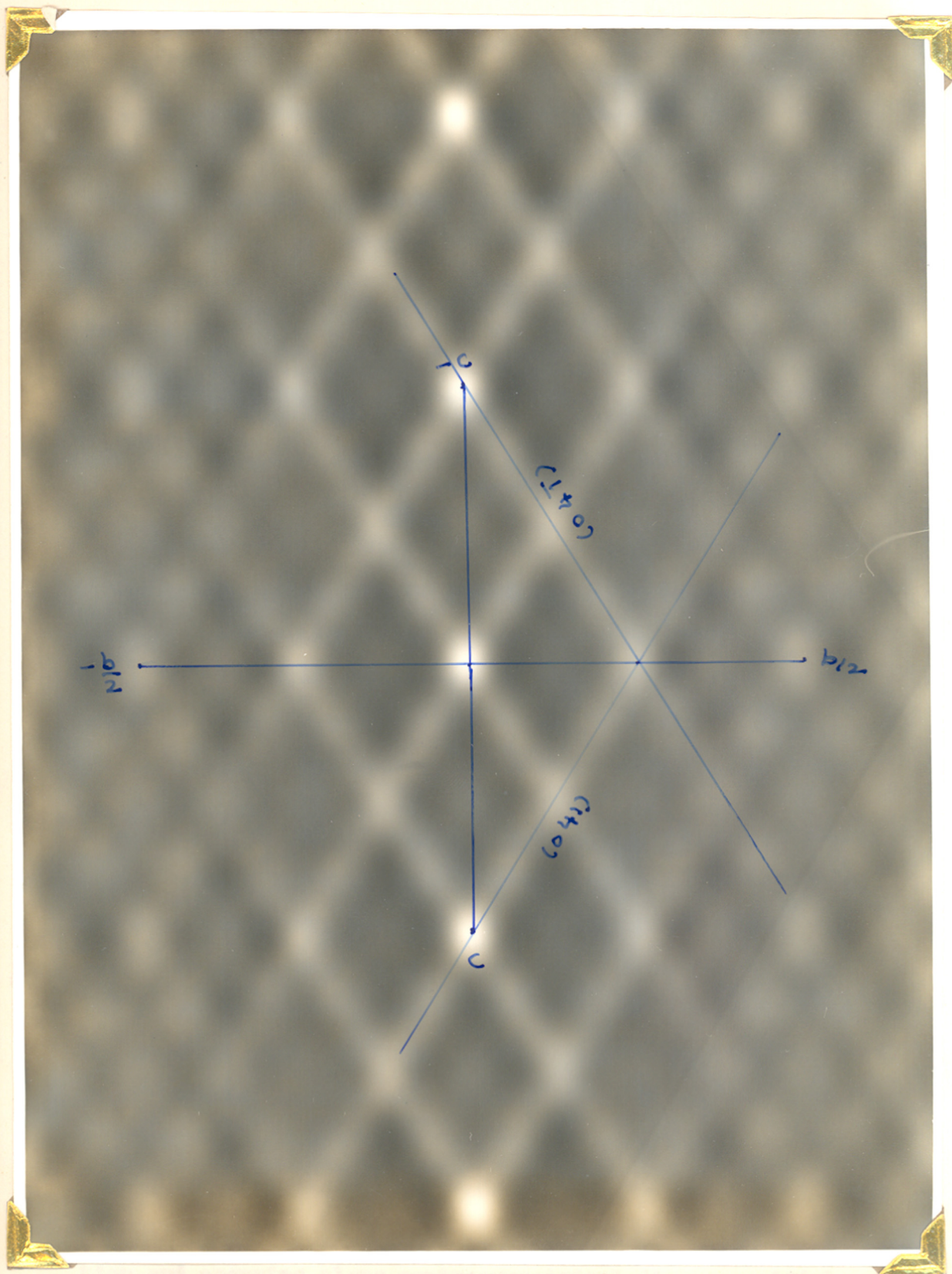


Figure III-1 : (100) Patterson map.

the suggested modifications therefore include both the factors, one of which will sharpen the Patterson peaks while the other will reduce the effect of series termination to a certain extent. Schomaker and Shoemaker (unpublished) suggested the following :

$$M(S) = \frac{1}{\sum f^2} S^2 \exp. (-\pi^2 S^2 / P)$$

This 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.

In the present work the sharpening of the Patterson function was done by multiplying the corrected intensities of each reflection by S^2 , where S is the reciprocal lattice vector from the origin. The (1,0,0) and (0,1,0) sharpened Patterson projections of o-methyl amino benzoic acid were obtained optically with the help of von Eller photosommateur. They are shown in Figures III-1 and III-2.

In the (1,0,0) Patterson map, the peaks fall on (0,4,1) and (0,4, $\bar{1}$). No other prominent peaks are seen. It can be inferred that the molecules lie near the (0,4,1) and (0,4, $\bar{1}$) planes.

The (0,1,0) Patterson map shown in Figure III-2 was obtained with 45 reflections. (5,0,2) and ($\bar{3}$,0,4) are very strong reflections and in the (0,1,0) Patterson map all the peaks lie near these planes. With the help of this information and assuming plane centrosymmetrical dimers, a trial

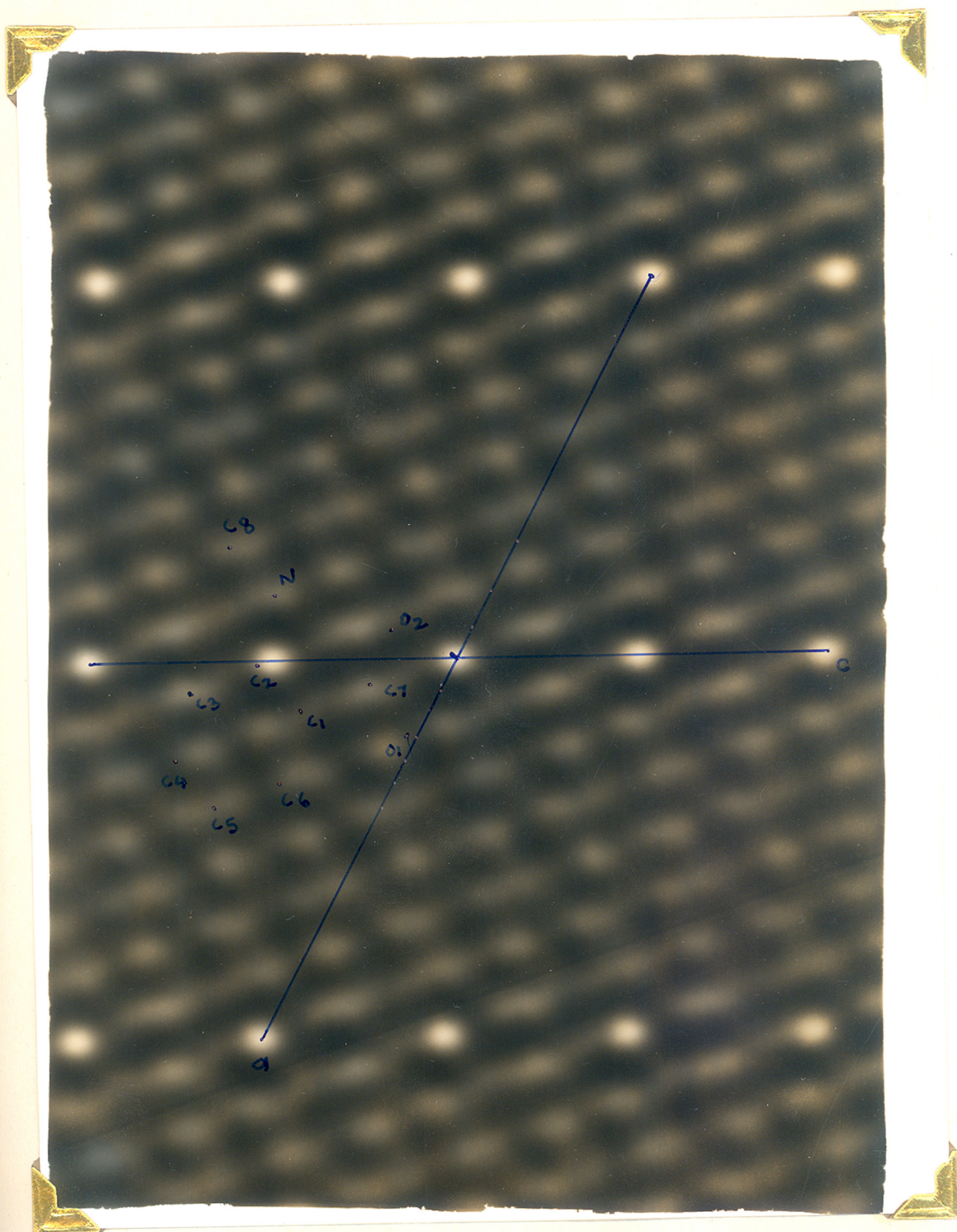


Figure III-2 : (010) Patterson map.

structure in this projection could be postulated as shown in Figure III-2. This projection could not be refined due to intense overlapping. However, with the help of this projection and bearing in mind that the molecules lie near $(0,4,1)$ and $(0,4,\bar{1})$ planes a model of the structure was set up and its projection on the $(X,Y,0)$ plane was plotted as shown in Figure III-3. $F(h,0,0)$ computed on the basis of this trial structure gave reasonable agreements with F_0 ; however, the agreement for $F(0,k,0)$ was not satisfactory, thus implying that y parameters required improvement. In order to improve the y parameters, the Harker line $P(0,v,\frac{1}{2})$ was plotted.

For the space group $P2_1/C$ (to which this structure belongs) the Harker line $P(0,v,\frac{1}{2})$ contains peaks at $(0, \frac{1}{2}-2y, \frac{1}{2})$ due to interaction between the symmetry related atoms (x,y,z) and $(x,\frac{1}{2}-y,\frac{1}{2}+z)$ and is given by

$$\begin{aligned}
 P(0,v,\frac{1}{2}) &= \sum \sum_{-\infty}^{\infty} |F(hk1)|^2 \cos 2\pi (kv + \frac{1}{2}) \\
 &= \sum_k \left\{ \sum \sum (-1)^l |F(hk1)|^2 \right\} \cos 2\pi kv
 \end{aligned}
 \qquad \text{..... (III-6)}$$

$P(0,v,\frac{1}{2})$ line is shown in Figure III-4. The distances of the peaks from the origin give us the values of $\frac{1}{2}-2y$ for different atoms. Although there is overlapping of peaks in the Harker line, y parameters could be improved with its help and a better trial structure in the $(X,Y,0)$ projection could be set up.

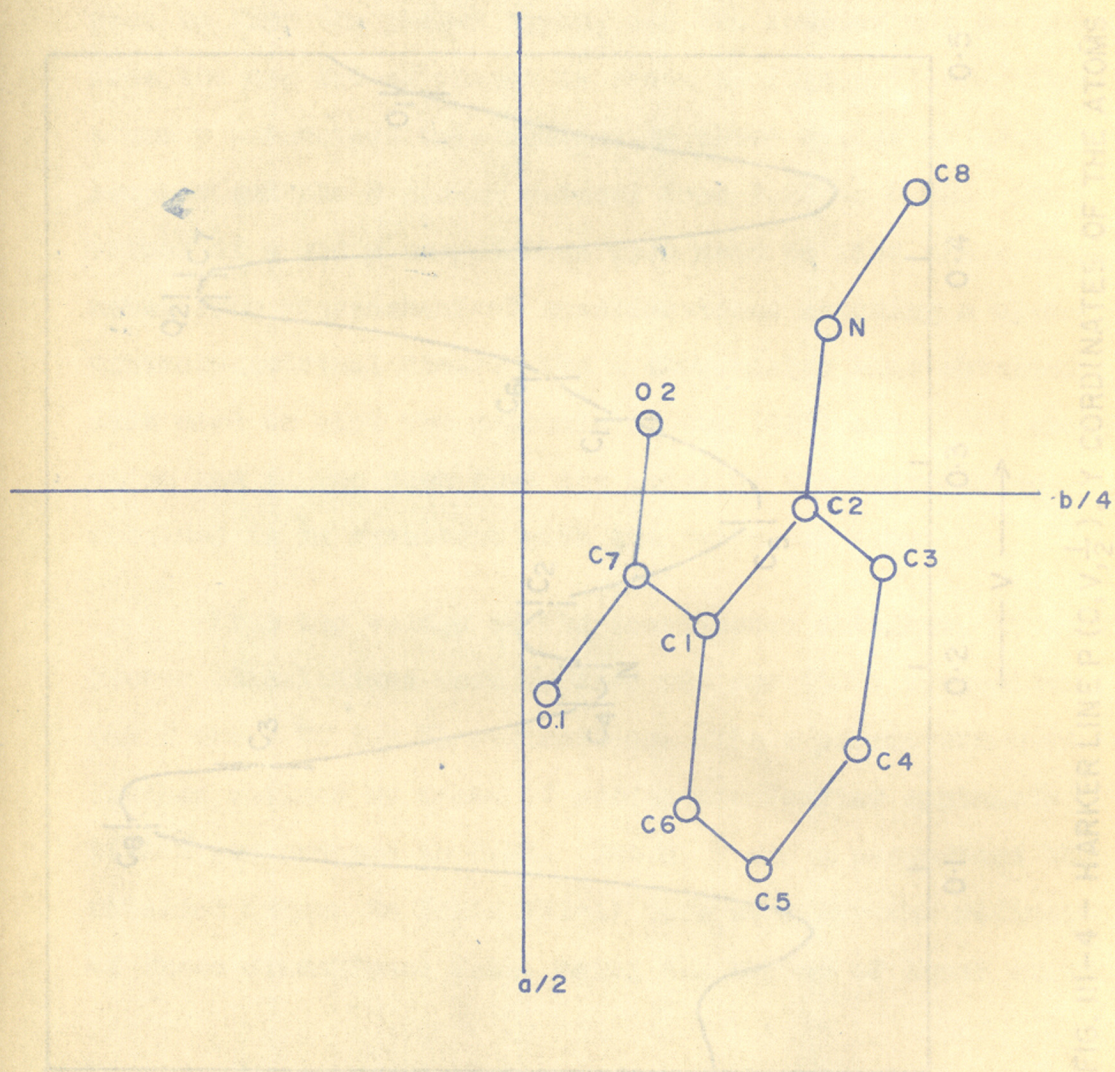


FIG-III-3 TRIAL STRUCTURE ON (001) PLANE, O-METHYL AMINO
BENZOIC ACID

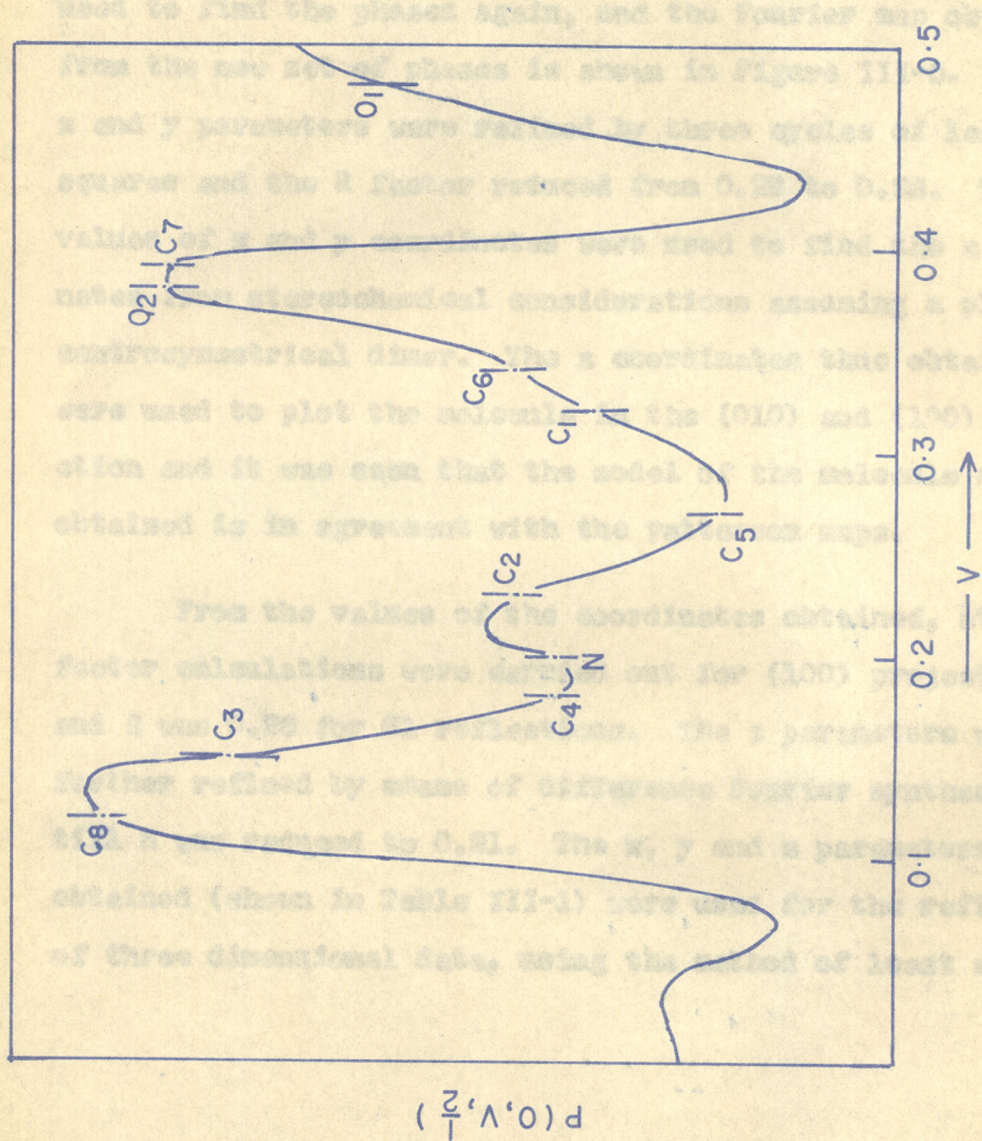


FIG. III-4 - HARKER LINE $P(0, V, \frac{1}{2})$. Y COORDINATES OF THE ATOMS ARE TAKEN FROM FINAL REFINEMENT.

With the help of this trial structure, the phases of the $F(hko)$ structure factors were obtained and a Fourier map taken. The x and y parameters obtained from this map were used to find the phases again, and the Fourier map obtained from the new set of phases is shown in Figure III-5. The x and y parameters were refined by three cycles of least squares and the R factor reduced from 0.28 to 0.23. The values of x and y coordinates were used to find the z coordinates from stereochemical considerations assuming a plane centrosymmetrical dimer. The z coordinates thus obtained were used to plot the molecule in the (010) and (100) projection and it was seen that the model of the molecule so obtained is in agreement with the Patterson maps.

From the values of the coordinates obtained, structure factor calculations were carried out for (100) projection and R was 0.26 for 81 reflections. The z parameters were further refined by means of difference Fourier synthesis till R was reduced to 0.21. The x , y and z parameters thus obtained (shown in Table III-1) were used for the refinement of three dimensional data, using the method of least squares.

Figure III-5 : (001) Fourier map.

Table III-1

Fractional coordinates and temperature factors

Sr. No.	Atom	x	y	z	$B \text{ \AA}^2$

1.	C ₁	0.1436	0.0919	-0.3505	4.1
2.	C ₂	0.0106	0.1310	-0.5355	4.1
3.	C ₃	0.0860	0.1741	-0.6706	4.1
4.	C ₄	0.2686	0.1639	-0.6260	4.1
5.	C ₅	0.3912	0.1189	-0.4464	4.1
6.	C ₆	0.3280	0.0755	-0.2952	4.1
7.	C ₇	0.0834	0.0569	-0.1907	4.1
8.	C ₈	-0.3057	0.2020	-0.7845	4.1
9.	O ₁	0.2114	0.0044	-0.0245	4.1
10.	O ₂	-0.0758	0.0649	-0.2183	4.1
11.	N	-0.1731	0.1494	-0.5370	4.1

CHAPTER - IV

THREE DIMENSIONAL REFINEMENT

For the three dimensional 'Least Squares' refinement of atomic parameters and individual isotropic temperature factors all the 965 observed general reflections were used. Parameters from Table III-1 were used as starting parameters. The refinement was done on CDC-3600-160A computer at Tata Institute of Fundamental Research, Bombay. The following expressions were used :

$$F_o(hkl) = \sum_1^n 4 \text{ (Atomic scattering factor part) } \times \text{ (geometrical structure factor part).}$$

For space group $P2_1/C$, the geometrical structure factor part is given by

$$A = \cos 2\pi \left(hx + lz + \frac{k+1}{4} \right) \cos 2\pi \left(ky - \frac{k+1}{4} \right) \text{ and } B = 0$$

..... (IV-1)

The atomic scattering factor $E(J)$ for each reflection was taken as $E(J) = \text{Scat } J \times W(J)$ where J indicates the type of atom (i.e. O, N, C or H). $\text{Scat}(J) = A \exp.(-aP^2) + B \exp.(-bP^2) + C$ and $W(J) = \exp.B(J) \times (-P^2)$. In these equations A , a , B , b and C are the analytical constants for atomic scattering factors and

$$p^2 = \left(\frac{\sin \theta}{\lambda} \right)^2 = \frac{1}{4} s^2 = \frac{1}{4} (h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hla^*c^* \cos \beta^*)$$

..... (IV-2)

Throughout this work unity has been taken as the reciprocal constant, so that $a^* = 1/a \sin \beta$, $b^* = 1/b$, $c^* = 1/c \sin \beta$ and $s = 2 \sin \theta / \lambda$.

The values of the analytical constants used were taken from F.H. Moore's table (1963) and are tabulated in table IV-1.

Table IV-1

Analytical constants for atomic
scattering factors
for Cu range.

Atom	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 atomic parameters were refined first by using isotropic temperature factor by the least squares programme using block diagonal approximation. Initial value of R was 0.184. In five cycles it became 0.143. At this stage difference Fourier maps were taken for (001) and (010) projections and the hydrogen atom of the carboxylic group

was located. The hydrogen atoms of the aromatic ring were also included in the least squares refinement at this stage; their positions were fixed from stereochemical considerations.

During the isotropic refinement a weight of unity was given to all the structure factors, so the convergence was rapid. An overall scale factor was used in the programme. At this stage, anisotropic temperature factors were introduced for the further refinement of the structure.

Method of least squares and
block diagonal approximation

In the least squares refinement applied to all the three coordinates of n atoms simultaneously and using the anisotropic temperature factor, the normal equations may be written in the form

$$\begin{pmatrix}
 A_{1j} & L_{1j} & M_{1j} & N_{1j} & O_{1j} & P_{1j} & Q_{1j} & R_{1j} & S_{1j} \\
 & B_{1j} & M_{1j}^1 & N_{1j}^1 & O_{1j}^1 & P_{1j}^1 & Q_{1j}^1 & R_{1j}^1 & S_{1j}^1 \\
 & & C_{1j} & N_{1j}^2 & O_{1j}^2 & P_{1j}^2 & Q_{1j}^2 & R_{1j}^2 & S_{1j}^2 \\
 & & & D_{1j} & O_{1j}^3 & P_{1j}^3 & Q_{1j}^3 & R_{1j}^3 & S_{1j}^3 \\
 & & & & E_{1j} & P_{1j}^4 & Q_{1j}^4 & R_{1j}^4 & S_{1j}^4 \\
 & & & & & F_{1j} & Q_{1j}^5 & R_{1j}^5 & S_{1j}^5 \\
 & & & & & & G_{1j} & R_{1j}^6 & S_{1j}^6 \\
 & & & & & & & H_{1j} & S_{1j}^7 \\
 & & & & & & & & I_{1j}
 \end{pmatrix}
 \times
 \begin{pmatrix}
 \Delta x_1 \\
 \Delta y_1 \\
 \Delta z_1 \\
 \Delta b_{11_1} \\
 \Delta b_{22_1} \\
 \Delta b_{33_1} \\
 \Delta b_{12_1} \\
 \Delta b_{23_1} \\
 \Delta b_{13_1}
 \end{pmatrix}
 =
 \begin{pmatrix}
 U_1^1 \\
 U_1^2 \\
 U_1^3 \\
 U_1^4 \\
 U_1^5 \\
 U_1^6 \\
 U_1^7 \\
 U_1^8 \\
 U_1^9
 \end{pmatrix}$$

$(1, j = 1, 2, 3, \dots, n)$

.... (IV-3)

where the matrix coefficients consist of eighty one blocks (A_{1j} , L_{1j} , M_{1j} etc.) and each of these blocks has n^2 terms with following typical elements. A weight of unity is assumed.

$$a_{1j} = \sum \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial x_j} ;$$

$$b_{1j} = \sum \frac{\partial F}{\partial y_1} \cdot \frac{\partial F}{\partial y_j} ;$$

$$c_{1j} = \sum \frac{\partial F}{\partial z_1} \cdot \frac{\partial F}{\partial z_j} ;$$

$$d_{1j} = \sum \frac{\partial F}{\partial b_{11_1}} \cdot \frac{\partial F}{\partial b_{11_j}} ;$$

$$e_{1j} = \sum \frac{\partial F}{\partial b_{22_1}} \cdot \frac{\partial F}{\partial b_{22_j}} ;$$

$$f_{1j} = \sum \frac{\partial F}{\partial b_{33_1}} \cdot \frac{\partial F}{\partial b_{33_j}} ;$$

and so on upto

$$i_{1j} = \sum \frac{\partial F}{\partial b_{13_1}} \cdot \frac{\partial F}{\partial b_{13_j}} ;$$

$$l_{1j} = \sum \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial y_j} ;$$

$$m_{1j} = \sum \frac{\partial F}{\partial x_1} \cdot \frac{\partial F}{\partial z_j} ;$$

and so on.

$$n_{1j}^1 = \sum \frac{\partial F}{\partial y_1} \cdot \frac{\partial F}{\partial z_j} ;$$

$$n_{1j}^1 = \sum \frac{\partial F}{\partial y_1} \cdot \frac{\partial F}{\partial b_{11_j}} ;$$

and so on.

$$n_{1j}^2 = \sum \frac{\partial F}{\partial z_1} \cdot \frac{\partial F}{\partial b_{11_j}} ;$$

$$o_{1j}^2 = \sum \frac{\partial F}{\partial z_1} \cdot \frac{\partial F}{\partial b_{22_j}} ;$$

and so on.

The column matrices in equation (IV-3) have been written for brevity in terms of submatrices. Thus Δx_1 stands for the column submatrix $(\Delta x_1, \Delta x_2, \Delta x_3, \dots, \Delta x_n)$, and similarly for $\Delta y_1, \Delta z_1, \Delta b_{11_1}, \Delta b_{22_1}$ etc.

$$U_1^1 = \sum \frac{\partial F}{\partial x_1} (F_o - F_c) ; \quad U_1^2 = \sum \frac{\partial F}{\partial y_1} (F_o - F_c) ;$$

$$U_1^3 = \sum \frac{\partial F}{\partial z_1} (F_o - F_c) ; \quad U_1^4 = \sum \frac{\partial F}{\partial b_{11_1}} (F_o - F_c)$$

and so on upto

$$U_1^8 = \sum \frac{\partial F}{\partial b_{23_1}} (F_o - F_c) ; \quad U_1^9 = \sum \frac{\partial F}{\partial b_{13_1}} (F_o - F_c) .$$

..... (IV-5)

The summations in equations (IV-4) and (IV-5) are over all the structure factors used and unit weight has been assumed.

The lower and upper triangular parts of the matrix separated by the diagonal coefficients are symmetric.

The totals to be stored during structure factor calculation occupy q locations for the right hand side matrix and $q(q+1)/2$ for the left hand side matrix, where q is the number of parameters refined.

For the refinement of a structure containing twenty atoms, $q = 181$. This gives $q(q+1)/2 = 16,471$ and a computer with a large storage is necessary. Even for the largest

computers available the term in q^2 leads to difficulty for relatively small q and it may become necessary to leave out some of the off diagonal terms of the left hand side matrix which are known to be small. A commonly used approximation is that of omitting all off-diagonal terms except for those between x, y and z of the same atom and those between B_{ij} of the same atom

Standard deviations of atomic and thermal parameters

The general equation for calculating σ , the standard deviation for any parameter p_i is (Stout and Jensen, 1968)

$$\sigma_{p_i} = \sqrt{b_{ii} \left(\sum_{r=1}^m w_r \cdot \Delta F_r^2 \right) / (m - n)} \quad \dots (IV-6)$$

where b_{ii} is the i th diagonal element of the least squares inverse matrix, w_r the weight of the r th ΔF , m the number of observations and n the number of parameters.

Anisotropic temperature factor

For the space group $P2_1/C$, the equivalent points are $\pm (x, y, z)$; $\pm (x, \frac{1}{2}-y, \frac{1}{2}+z)$. When the vibrations of the atoms are anisotropic, the thermal vibration ellipsoids of the pair of atoms (x, y, z) and $(\bar{x}, \bar{y}, \bar{z})$ are parallel whereas the ellipsoids of the pair of atoms $\pm (x, \frac{1}{2}-y, \frac{1}{2}+z)$ are

related to the first pair by mirror symmetry normal to the 'b' axis. Let the atomic scattering factor for atoms $\pm (x, y, z)$ be

$$f(x, y, z) = f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \dots\dots (IV-7)$$

The atomic scattering factor for the pair of atoms $\pm (x, \frac{1}{2}-y, \frac{1}{2}+z)$ will then be given by

$$f(x, \frac{1}{2}-y, \frac{1}{2}+z) = f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \dots\dots (IV-8)$$

(Rollet and Davies, 1955)

Therefore the expression for $F(hkl)$ becomes

$$F(hkl) = \sum 2f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \cdot \cos 2\pi (hx + ky + lz) + \sum 2f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \cdot \cos 2\pi (hx - ky + lz + (\frac{k+1}{2})) \dots\dots (IV-9)$$

For convenience write

$$C = a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl$$

$$D = a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl$$

Differentiating expressions for the structure factors with respect to different a_{ij} 's, we get the following expressions

for $\partial F / \partial a_{1j}$

$$\begin{aligned} \frac{\partial F}{\partial a_{11}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-h^2) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (-h^2) \\ &\dots\dots (IV-10) \end{aligned}$$

$$\begin{aligned} \frac{\partial F}{\partial a_{22}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-k^2) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (-k^2) \\ &\dots\dots (IV-11) \end{aligned}$$

$$\begin{aligned} \frac{\partial F}{\partial a_{33}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-l^2) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (-l^2) \\ &\dots\dots (IV-12) \end{aligned}$$

$$\begin{aligned} \frac{\partial F}{\partial a_{12}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-2hk) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (2hk) \\ &\dots\dots (IV-13) \end{aligned}$$

$$\begin{aligned} \frac{\partial F}{\partial a_{23}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-2kl) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (2kl) \\ &\dots\dots (IV-14) \end{aligned}$$

$$\begin{aligned} \frac{\partial F}{\partial a_{13}} &= 2f_0 \exp. (-C) \cos 2\pi (hx + ky + lz) (-2kl) \\ &\quad + 2f_0 \exp. (-D) \cos 2\pi (hx - ky + lz + \frac{k+1}{2}) (-2kl) \\ &\dots\dots (IV-15) \end{aligned}$$

The values of a_{1j} 's used to start the least squares refinement are those corresponding to the individual isotropic

temperature factors obtained by refinement.

The values of a_{1j} 's given in Table IV-2 were obtained from the B values (isotropic temperature factors) as shown below :

The atomic scattering factor 'f' is given by

$$f = f_0 \exp. (-B \sin^2 \theta / \lambda^2) \quad \dots\dots (IV-16)$$

The expression for f in terms of a_{1j} 's is given by

$$f = f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \quad \dots\dots (IV-17)$$

From equation (IV-16)

$$f = f_0 \exp. -B/4 (2\sin\theta/\lambda)^2 = f_0 \exp. (-\frac{BS^2}{4}) \quad \dots\dots (IV-18)$$

Here $S = ha^* + kb^* + lc^*$ where a^* , b^* and c^* are the axial lengths of the reciprocal cell.

$$S^2 = (ha^*)^2 + (kb^*)^2 + (lc^*)^2 + 2(ha^*)(lc^*)(\cos\beta^*) \quad \dots\dots (IV-19)$$

Substituting the value of S^2 from (IV-19) in (IV-7)

$$f = f_0 \exp. -(\frac{B}{4} a^{*2}h^2 + \frac{B}{4} b^{*2}k^2 + \frac{B}{4} c^{*2}l^2 + 2.\frac{B}{4} a^*c^*\cos\beta^*hl) \quad \dots\dots (IV-20)$$

Comparing equations (IV-19) and (IV-20) and putting
 $a^* = 1/a \sin \beta$; $b^* = 1/b$ and $c^* = 1/c \sin \beta$; we get
 $a_{11} = B/4 a^2 \sin^2 \beta$; $a_{22} = B/4 b^2$; $a_{33} = B/4 c^2 \sin^2 \beta$;
 $a_{13} = B \cos \beta^*/4 ac \sin^2 \beta$; $a_{12} = 0$; $a_{23} = 0$.

Table IV-2

Atom	B	a_{11}	a_{22}	a_{33}	a_{13}
C ₁	4.1250	0.0200	0.0045	0.0269	0.0110
C ₂	4.4700	0.0217	0.0049	0.0292	0.0119
C ₃	4.9314	0.0244	0.0055	0.0328	0.0134
C ₄	5.3972	0.0265	0.0060	0.0357	0.0146
C ₅	5.4950	0.0270	0.0061	0.0364	0.0149
C ₆	4.9675	0.0244	0.0055	0.0328	0.0134
C ₇	4.5249	0.0221	0.0050	0.0298	0.0122
C ₈	5.5913	0.0275	0.0062	0.0371	0.0152
O ₁	5.0404	0.0244	0.0055	0.0328	0.0134
O ₂	4.7952	0.0234	0.0052	0.0315	0.0129
N	4.4642	0.0217	0.0049	0.0292	0.0119

$$a_{23} = 0$$

$$a_{12} = 0$$

Refinement using anisotropic temperature factor

Using a_{ij} 's given in Table IV-2, least squares refinement of both positional and thermal parameters was carried out

for carbon, oxygen and nitrogen atoms. For the hydrogen atoms, the thermal parameters of the atoms to which they are attached were used and only positional parameters were refined. The refinement was carried out using Cruickshank's weighting scheme $w = 1/a + |F_o| + c |F_o|^2$ where $a = 2F_{\min}$ and $c = 2/F_{\max}$. In the present work $a = 2.4$ and $c = 0.019$. Initial value of R was 0.142. In 5 cycles the value of R became 0.106.

At this stage the difference Fourier maps were taken for the three projections with the help of Eller photosommateur and the positions of the hydrogen atoms of the methyl group as well as the hydrogen atom of the NH group were determined. These hydrogen atoms were then included in the structure refinement; in three cycles R factor became 0.101. The thermal parameters were refined for heavy atoms only; for hydrogen atoms only positional parameters were refined. The final atomic and thermal parameters are listed in Table IV-3 and Table IV-4.

Table IV-3

Final atomic parameters with standard deviations.

Atom	x	y	z
C ₁	0.1420 ± 0.0007	0.0905 ± 0.0003	-0.3482 ± 0.0008
C ₂	0.0126 ± 0.0007	0.1372 ± 0.0003	-0.5352 ± 0.0009
C ₃	0.0871 ± 0.0008	0.1737 ± 0.0004	-0.6675 ± 0.0010
C ₄	0.2667 ± 0.0010	0.1627 ± 0.0005	-0.6200 ± 0.0011
C ₅	0.3907 ± 0.0009	0.1142 ± 0.0005	-0.4442 ± 0.0012
C ₆	0.3259 ± 0.0008	0.0785 ± 0.0004	-0.3060 ± 0.0010
C ₇	0.0808 ± 0.0008	0.0541 ± 0.0004	-0.1945 ± 0.0008
C ₈	-0.3052 ± 0.0010	0.1922 ± 0.0005	-0.7799 ± 0.0011
O ₁	0.2113 ± 0.0006	0.0112 ± 0.0003	-0.0274 ± 0.0006
O ₂	-0.0779 ± 0.0006	0.0618 ± 0.0003	-0.2180 ± 0.0006
N	-0.1695 ± 0.0006	0.1493 ± 0.0003	-0.5855 ± 0.0007
H ₁	0.401 ± 0.009	0.044 ± 0.005	-0.184 ± 0.011
H ₂	0.543 ± 0.010	0.105 ± 0.005	-0.421 ± 0.012
H ₃	0.280 ± 0.010	0.191 ± 0.005	-0.707 ± 0.013
H ₄	0.025 ± 0.009	0.205 ± 0.005	-0.775 ± 0.012
H ₅	0.207 ± 0.010	-0.024 ± 0.005	0.044 ± 0.011
H ₆	-0.266 ± 0.010	0.259 ± 0.005	-0.812 ± 0.012
H ₇	-0.359 ± 0.011	0.140 ± 0.005	-0.903 ± 0.012
H ₈	-0.426 ± 0.010	0.192 ± 0.006	-0.759 ± 0.012
H ₉	-0.227 ± 0.009	0.121 ± 0.005	-0.508 ± 0.011

Table IV-4

Final thermal parameters.

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

Atom	a_{11}	a_{22}	a_{33}	a_{12}	a_{23}	a_{13}
C ₁	223 ± 11	43 ± 2	269 ± 13	-3 ± 4	-1 ± 5	114 ± 10
C ₂	229 ± 11	42 ± 2	294 ± 15	-3 ± 4	-6 ± 5	120 ± 11
C ₃	267 ± 13	60 ± 3	333 ± 16	8 ± 5	23 ± 6	153 ± 13
C ₄	331 ± 17	68 ± 4	437 ± 22	-10 ± 6	20 ± 8	218 ± 17
C ₅	263 ± 14	69 ± 4	439 ± 21	-11 ± 6	7 ± 7	182 ± 15
C ₆	230 ± 12	58 ± 3	355 ± 18	5 ± 5	14 ± 6	109 ± 13
C ₇	244 ± 12	51 ± 3	251 ± 13	3 ± 4	2 ± 5	98 ± 11
C ₈	312 ± 16	84 ± 4	383 ± 21	39 ± 7	48 ± 8	169 ± 16
O ₁	274 ± 10	73 ± 2	305 ± 11	22 ± 4	36 ± 4	132 ± 9
O ₂	267 ± 9	67 ± 2	291 ± 11	15 ± 4	32 ± 4	133 ± 9
N	239 ± 10	60 ± 2	290 ± 13	15 ± 4	24 ± 5	124 ± 10

CHAPTER - V

RESULTS AND DISCUSSION

This chapter is divided into two portions (a) Crystal and molecular structure, (b) Thermal anisotropy.

(a) Crystal and molecular structure

The bond lengths and bond angles are given in Table V-1 and are also shown in Figure V-1. The C_7-O_1 , C_7-O_2 , C_2-N and $N-C_8$ bond lengths have been corrected for the effect of librational motion; the method of applying the correction is given in the next section (page 56).

The standard deviations in the bond lengths are given by

$$\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2) \quad \dots\dots (V-1)$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the deviations in the atomic positions of atom 1 and atom 2 respectively and $\sigma(d_{12})$ is the standard deviation of the length between them.

The standard deviation $\sigma(\theta)$ in bond angles is given by

$$\sigma^2(\theta) = \frac{\sigma^2(r_1)}{(d_{12})^2} + \frac{\sigma^2(r_2)(d_{13})^2}{(d_{12})^2 (d_{23})^2} + \frac{\sigma^2(r_3)}{(d_{23})^2} \quad \dots\dots (V-2)$$

where θ is the angle subtended at atom 2 by the bonds from

Table V-1

Intramolecular bond lengths and angles.

Bond	Bond lengths ($\text{\AA}$)			Bond angles	
	Uncor- rected	Corre- cted	s.s.d.		
C ₁ -C ₂	1.422		0.008	C ₆ -C ₁ -C ₂	120.8 $\pm$ 0.5°
C ₂ -C ₃	1.439		0.008	C ₁ -C ₂ -C ₃	115.6 $\pm$ 0.5
C ₃ -C ₄	1.348		0.010	C ₂ -C ₃ -C ₄	122.3 $\pm$ 0.6
C ₄ -C ₅	1.378		0.011	C ₃ -C ₄ -C ₅	122.4 $\pm$ 0.7
C ₅ -C ₆	1.414		0.010	C ₄ -C ₅ -C ₆	117.7 $\pm$ 0.7
C ₆ -C ₁	1.395		0.008	C ₅ -C ₆ -C ₁	121.2 $\pm$ 0.6
C ₁ -C ₇	1.492		0.008	C ₁ -C ₂ -N	123.0 $\pm$ 0.5
C ₇ -O ₁	1.321	1.332	0.007	C ₃ -C ₂ -N	121.4 $\pm$ 0.5
C ₇ -O ₂	1.229	1.238	0.007	C ₂ -N-C ₈	123.9 $\pm$ 0.6
C ₂ -N	1.365	1.373	0.008	O ₁ -C ₇ -O ₂	121.2 $\pm$ 0.5
N-C ₈	1.441	1.456	0.009	C ₁ -C ₇ -O ₂	124.0 $\pm$ 0.5
O ₁ - O ₂	2.673		0.006	C - C - O	114.8 $\pm$ 0.5
(x,y,z) ($\bar{x},\bar{y},\bar{z}$)					
O ₂ -N	2.672		0.007		

continued.....

Table V-1 (contd.)

Bond	Bond lengths ($\text{\AA}$)			Bond angles
	Uncor- rected	Corre- cted	e.s.d.	
C ₆ -H ₁	0.94		0.08	
C ₅ -H ₂	1.18		0.08	
C ₄ -H ₃	0.79		0.08	
C ₃ -H ₄	0.83		0.08	
N-H ₉	0.97		0.07	
O ₁ -H ₅	0.74		0.08	
C ₈ -H ₆	1.11		0.08	
C ₈ -H ₇	1.09		0.09	
C ₈ -H ₈	1.07		0.08	
O ₂ -H ₉	2.02		0.07	

atoms 1 and 3. $\sigma(r_1)$, $\sigma(r_2)$ and $\sigma(r_3)$ are the standard deviations for the coordinates of the atoms 1, 2 and 3 respectively. d_{12} , d_{13} and d_{23} are the bond lengths.

Table V-2 gives the equations of different planes with respect to a' , b , c orthogonal axes, and the angles between the planes. Table V-3 gives the deviations of the atoms from different planes. The equations of the planes were obtained by the method of Schomaker, Waser, Marsh and Bergman (1959).

Table V-2

Equations of planes

Plane	Equations
1. Benzene ring	$0.2530 x + 0.8410 y + 0.4783 z + 0.0419 = 0$
2. Carboxylic group	$0.2651 x + 0.8515 y + 0.4526 z - 0.0890 = 0$
3. Plane through C_2 , N and C_3	$0.2330 x + 0.8822 y + 0.4092 z - 0.2892 = 0$

Angles between different planes

Plane	(2)	(3)
(1)	1.3°	4.8°
(2)	-	3.4°

Table V-3

Deviations of atoms from different planes ($\text{\AA}$)

Atom	Planes		
	(1)	(2)	(3)
	Benzene ring	Carboxylic group	Plane through C_2, N and C_8
C_1	0.016	-0.012	-0.072
C_2	-0.016	-	0.000
C_3	0.001	-	0.112
C_4	0.015	-	-
C_5	-0.014	-	-
C_6	-0.001	-	-
C_7	0.072	0.000	-
C_8	-0.129	-	0.000
O_1	0.085	0.000	-
O_2	0.096	0.000	-
N	-0.025	-	0.000
H_1	-0.03	-	-
H_2	-0.06	-	-
H_3	0.08	-	-
H_4	0.04	-	-
H_5	-0.12	-0.22	-
H_6	0.61	-	0.79
H_7	-1.20	-	-1.05
H_8	-0.06	-	0.04
H_9	-0.12	-	-0.15

DISCUSSION

The aromatic ring

The estimated standard deviations (e.s.d.) of the carbon-carbon bond lengths are from $\pm 0.008 \text{ \AA}$ to $\pm 0.011 \text{ \AA}$. The individual bond lengths of the aromatic ring deviate significantly from the normal value ($1.393 \text{ \AA}$); the deviations are however, comparable with those observed in the structures of anthranilic acid (Brown, 1968), 2-amino 3-methyl benzoic acid (Brown and Marsh, 1963) and 3-5 dichloro anthranilic acid (Arora and Pant, 1969). Figures V-2 and V-3 give the molecular dimensions of the two crystallographically independent molecules of anthranilic acid, and of 2-amino 3-methyl benzoic acid and 3-5 dichloro anthranilic acid respectively.

The aromatic ring is planar within $0.02 \text{ \AA}$; the parallel bonds C_1-C_2 and C_4-C_5 of the ring are bent out of the plane by about 1° in opposite directions (Table V-3).

Methyl amino group

The $C-NHCH_3$ distance in o-methyl amino benzoic acid is given in Table V-4 along with C-N bonds in similar structures for comparison. Some of the bond lengths are corrected for the effect of librational motion. It may be of interest to mention that while in p-nitro aniline the amino group is coplanar with the attached carbon atom

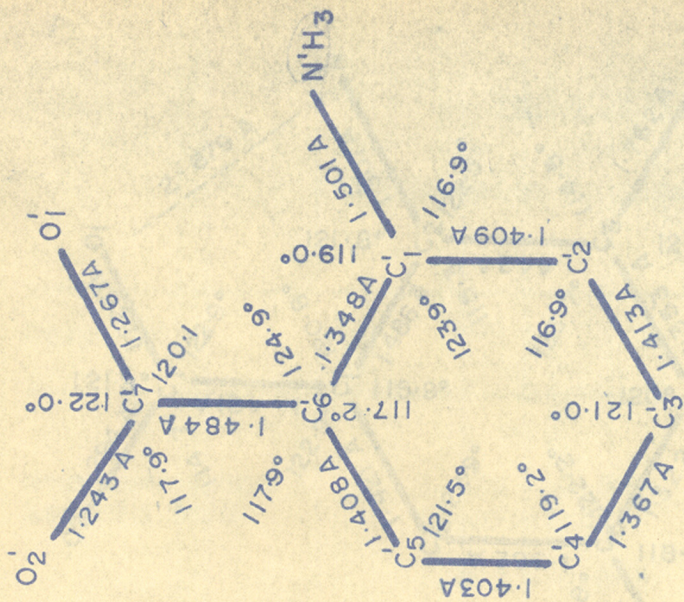
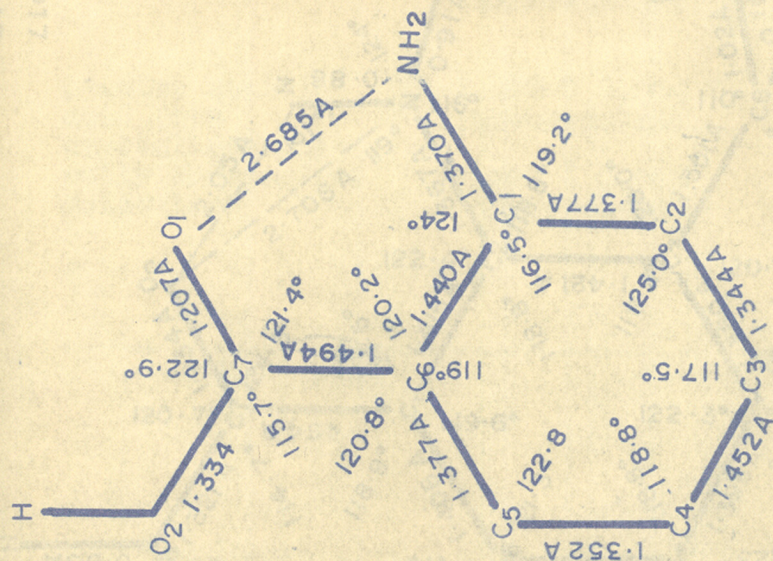
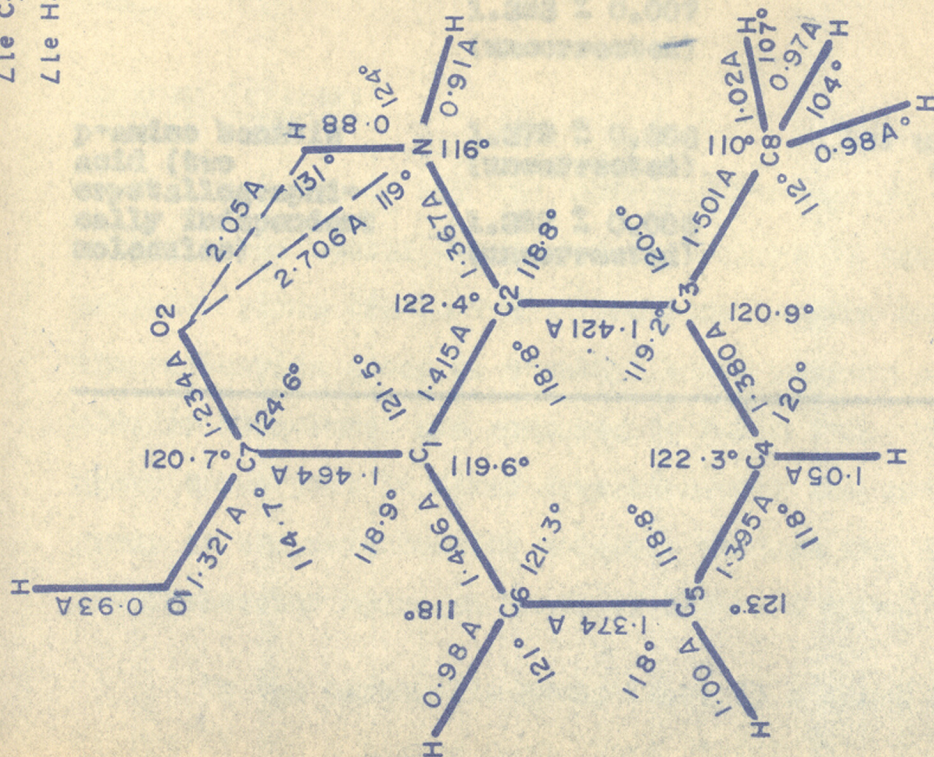


FIG V-2- BOND LENGTHS AND ANGLES IN THE TWO FORMS OF ANTHRANILIC ACID

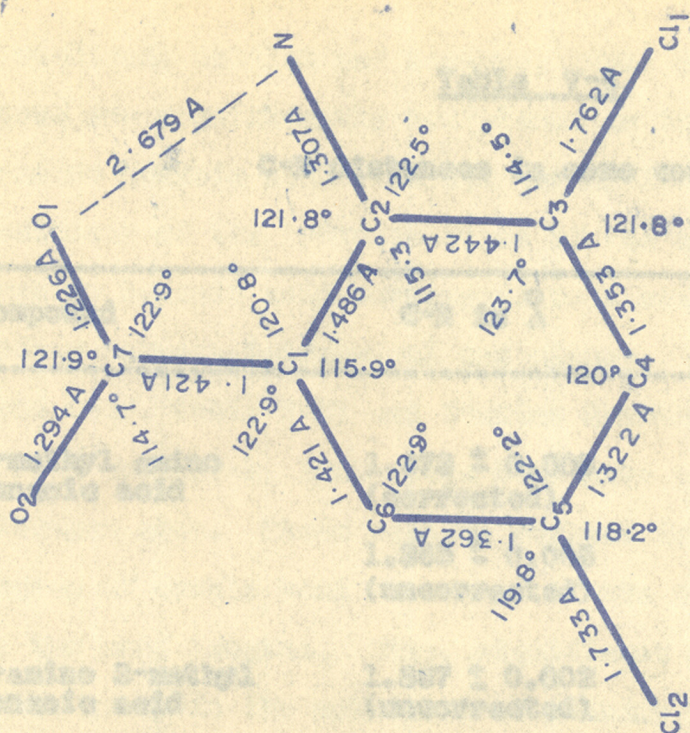
(BROWN, 1968)

$\angle \text{le } \text{C}_3\text{C}_8\text{H}_6 = 114^\circ$
 $\angle \text{le } \text{H}_7\text{C}_8\text{H}_8 = 109^\circ$



2-amino 3-methyl benzoic acid

Brown and Marsh (1963)



3-5 dichloroanthranilic acid

Arora and Pant (1969)

FIG V-3- BOND LENGTHS AND ANGLES IN 2-AMINO 3-METHYL BENZOIC ACID AND 3-5 DICHLORO-ANTHRANILIC ACID

Table V-4

C-N distances in some compounds

Compound	C-N in Å	Reference
o-methyl amino benzoic acid	1.373 ± 0.008 (corrected)	Present work
	1.365 ± 0.008 (uncorrected)	
2-amino 3-methyl benzoic acid	1.367 ± 0.002 (uncorrected)	Brown and Marsh (1963)
p-nitro aniline	1.371 ± 0.007 (corrected)	Trueblood, Goldish and Donohue (1961)
	1.353 ± 0.007 (uncorrected)	
p-amino benzoic acid (two crystallographically independent molecules)	1.378 ± 0.006 (uncorrected)	Lai and Marsh (1967)
	1.382 ± 0.006 (uncorrected)	

(Trueblood, Goldish and Donohue, 1961; page 1014), nitrogen atoms are significantly non-planar in the molecules of p-amino benzoic acid (Lai and Marsh, 1967; page 889); the positions of the hydrogen atoms of the amino group in p-amino benzoic acid correspond to a configuration about midway between tetrahedral and planar. o-methyl amino benzoic acid (ref. Table V-3) and 2-amino 3-methyl benzoic acid (Brown and Marsh, 1963; page 201) have a more nearly planar nitrogen atom. These results reflect in a general way the degree of double bond character of the C-N bonds as revealed by the bond lengths. Thus, significant non-planarity of the amino group in the molecules of p-amino benzoic acid suggests lesser double bond character of the C-N bond; the C-N bond in these molecules is therefore a little longer (ref. Table V-4).

Carboxylic group

The atom C₁ and the carboxylic group are coplanar within experimental error, but this plane is bent out of the aromatic plane (Table V-3). The bond lengths and angles of the carboxylic group in o-methyl amino benzoic acid and in similar structures are compared in Table V-5. The carboxylic group takes part in dimer formation with the carboxylic group of the neighbouring molecule through the formation of intermolecular hydrogen bonds of O-H---O type.

In the carboxylic group there is a short C₇-O₂ bond (1.238 Å) and a longer C₇-O₁ bond (1.332 Å). The short bond

Table V-5

Bond distances and angles in some carboxylic acids

Compound	Exocyclic C-C bond	C-OH	C=O	RC-OH	R-C=O	O=C-OH	Reference
p-nitro benzoic acid (dimer)	1.487 Å ±0.006 Å	1.317 Å ±0.005 Å	1.252 Å ±0.005 Å	115.8° ± 0.3°	121.0° ±0.4°	123.2° ±0.4°	Tavale and Pant (1971)
p-nitro benzoic acid (dimer)	1.439 ±0.010	1.295 ±0.009	1.223 ±0.009	117.4° ± 0.6°	121.4° ±0.6°	121.1° ±0.6°	Sakore, Tavale and Pant (1967)
3-5 dichloro- anthranilic acid (dimer)	1.421 ±0.011	1.294 ±0.010	1.226 ±0.010	114.7° ± 0.9°	122.9° ±0.9°	121.9° ±0.9°	Arora and Pant (1969)
o-methyl amino benzoic acid (dimer)	1.492 ±0.008	1.332 ±0.007	1.238 ±0.007	114.8° ± 0.5°	124.0° ±0.5°	121.2° ±0.5°	Present work
m-nitro benzoic acid (two crystallogra- phically ind- ependent molecules) (dimer)	1.494 ±0.009	1.297 ±0.008	1.260 ±0.007	115.7° ± 0.5°	120.4° ±0.5°	123.9° ±0.5°	Dhaneshwar, Tavale & Pant (To be publi- shed).
	1.498 ±0.008	1.298 ±0.008	1.258 ±0.008	116.9° ± 0.5°	119.6° ±0.5°	123.4° ±0.6°	

is associated with $C_1-C_7-O_2$ angle of 124.0° and longer bond with an angle $C_1-C_7-O_1$ of 114.8° ; the angle $O_2-C_7-O_1$ is 121.2° . The obtuse angle O-C-O may be attributed to the charge repulsion between strongly electronegative oxygen atoms. The dimensions of the carboxylic group reveal a significant distinction between the two C-O bonds, both in bond lengths and valency angles. This feature is observed in many carboxylic acids.

Hydrogen distances

By looking at Table V-1, the distances of the hydrogen atoms from the non-hydrogen atoms to which they are attached are from $0.8 \text{ \AA}$ to $1.18 \text{ \AA}$. According to P. Coppens (1972) the X-H bond lengths ($X = C, N, O$) as determined by X-ray diffraction are shortened because an appreciable part of the charge on the hydrogen atom is displaced towards the bond centre. The shortening of the X-H bond is, to a large extent, the result of an incorrect scattering formalism rather than an inherent property of the X-ray data. Use of an improved non-spherical formalism can correct the effect. A one centre model in which a hydrogen atom is polarized towards the X atom may be adequate for a correction of the bond length. Equations for the hydrogen wave function have been described as a mixing of $1s$ and $2p$ orbitals, the positive lobe of the p orbital being directed along the X-H bond.

However the variations of the X-H distances in the present work are no doubt due to the limited accuracy of

visual intensity estimations.

Intramolecular hydrogen bond

The hydrogen atom H_D attached to the nitrogen atom appears to be involved in an intramolecular N-H---O hydrogen bond of length $2.672 \pm 0.007 \text{ \AA}$. However, the infrared studies of Jose et al. (private communication) in this laboratory shows that the hydrogen bond is very weak. The short N-O distance (i.e. $2.672 \text{ \AA}$) appears to be due to intramolecular overcrowding rather than due to a strong hydrogen bond. The large O-N-H angle (39°) seems to confirm that the hydrogen bond is weak.

Crystal structure

The projections of the structure on (001), (010) and (100) planes are shown in Figures V-4, V-5 and V-6 respectively. The short intermolecular contacts are shown in Figure V-4. In these figures, all symmetry related molecules in the unit cell and few neighbouring molecules are shown. The principal intermolecular contacts are between the oxygen atoms of the carboxyl groups of the neighbouring molecules (x,y,z) and ($\bar{x},\bar{y},\bar{z}$) forming dimers, the distance between the oxygen atoms being $2.67 \text{ \AA}$. These dimers are held in the structure by normal van der Waal's interactions.

(b) Thermal anisotropy

The atomic scattering factor when the atom is in the

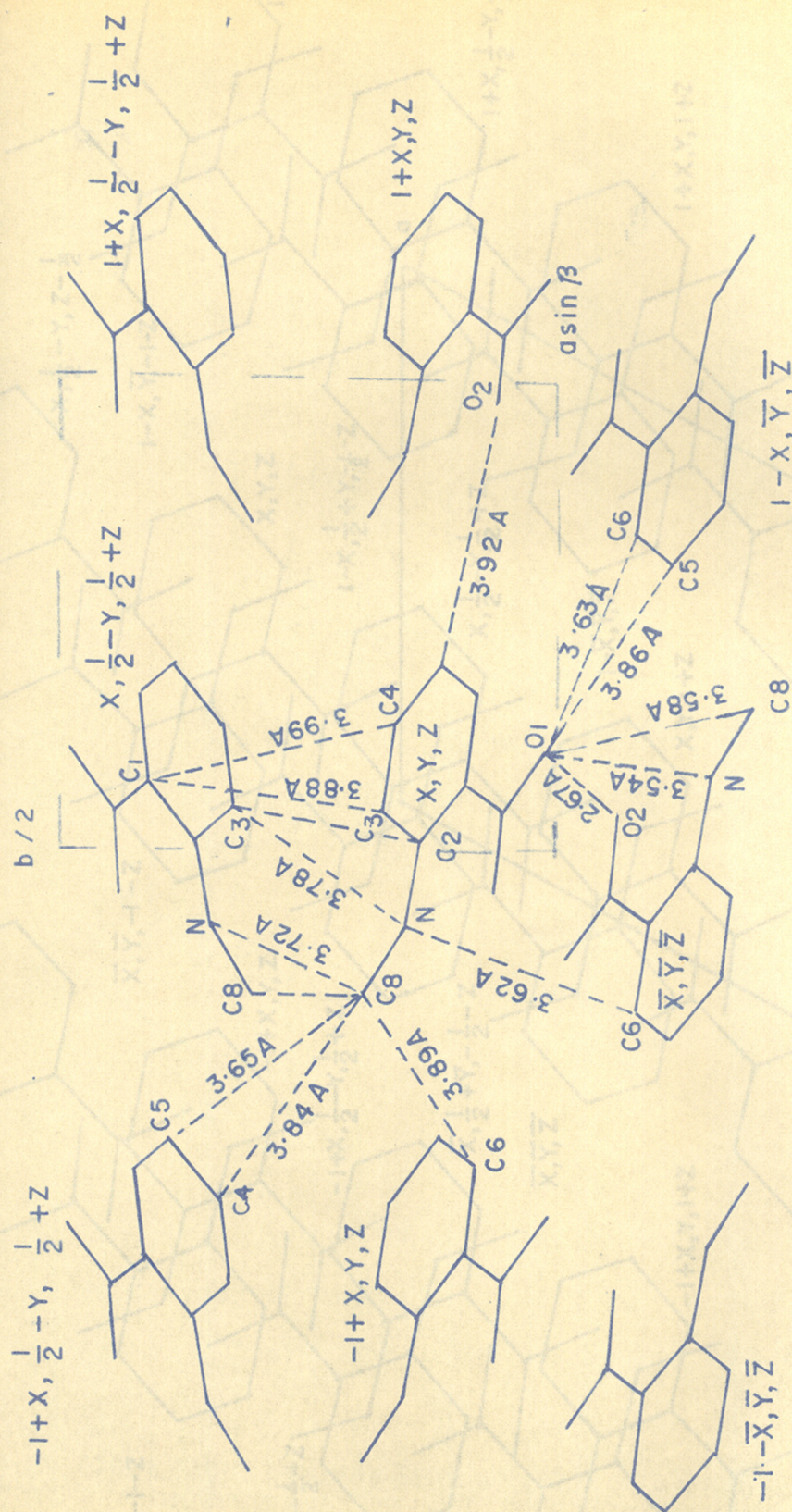


FIG V-4- STRUCTURE ON (001) PLANE. O-METHYL AMINO BENZOIC ACID

FIG V-5- STRUCTURE OF O-METHYL AMINO BENZOIC ACID PROJECTED ON (010) PROJECTION

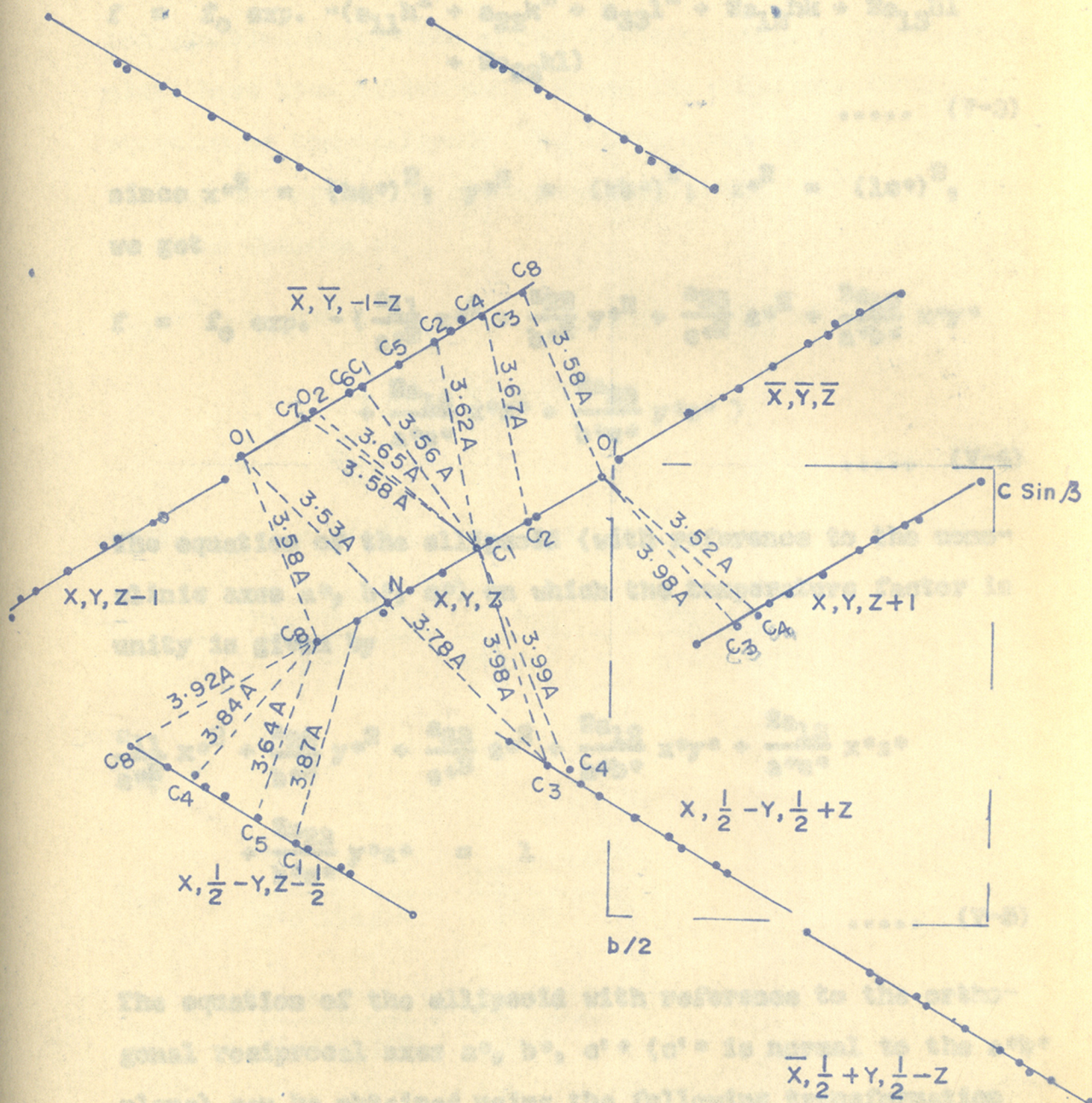


FIG V-6- STRUCTURE PROJECTED ON (100) PLANE O-METHYL AMINO
BENZOIC ACID

thermal motion is given by

$$f = f_0 \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{13}hl + 2a_{23}kl) \quad \dots (V-3)$$

since $x^{*2} = (ha^*)^2$; $y^{*2} = (kb^*)^2$; $z^{*2} = (lc^*)^2$,
we get

$$f = f_0 \exp. - \left(\frac{a_{11}}{a^{*2}} x^{*2} + \frac{a_{22}}{b^{*2}} y^{*2} + \frac{a_{33}}{c^{*2}} z^{*2} + \frac{2a_{12}}{a^*b^*} x^*y^* + \frac{2a_{13}}{a^*c^*} x^*z^* + \frac{2a_{23}}{b^*c^*} y^*z^* \right) \quad \dots (V-4)$$

The equation of the ellipsoid (with reference to the monoclinic axes a^* , b^* , c^*) on which the temperature factor is unity is given by

$$\frac{a_{11}}{a^{*2}} x^{*2} + \frac{a_{22}}{b^{*2}} y^{*2} + \frac{a_{33}}{c^{*2}} z^{*2} + \frac{2a_{12}}{a^*b^*} x^*y^* + \frac{2a_{13}}{a^*c^*} x^*z^* + \frac{2a_{23}}{b^*c^*} y^*z^* = 1 \quad \dots (V-5)$$

The equation of the ellipsoid with reference to the orthogonal reciprocal axes a^* , b^* , c'^* (c'^* is normal to the a^*b^* plane) can be obtained using the following transformation relations :

$$\begin{aligned} X^* &= x^* + z^* \cos \beta^* \\ Y^* &= y^* \\ Z^* &= z^* \sin \beta^* \end{aligned} \quad \dots (V-6)$$

The orthogonal reciprocal axes a^* , b^* , c^* coincide with the orthogonal axes a' , b , c respectively with respect to which the equation of various planes (benzene ring, carboxyl group etc.) have been determined. Using the relations (V-6), the equation of the ellipsoid (for temperature factor, unity) with reference to the orthogonal axes a^* , b^* , c^* comes out to be as follows :

$$b_{11}X^{*2} + b_{22}Y^{*2} + b_{33}Z^{*2} + 2b_{12}X^*Y^* + 2b_{13}X^*Z^* + 2b_{23}Y^*Z^* = 1$$

..... (V-7)

where $b_{11} = a_{11}/a^{*2}$, $b_{22} = a_{22}/b^{*2}$,

$$b_{33} = \frac{a_{11}\cot^2\beta^*}{a^{*2}} + \frac{a_{33}}{c^{*2}\sin^2\beta^*} - \frac{2a_{13}\cot\beta^*}{a^*c^*\sin\beta^*},$$

$$b_{12} = \frac{a_{12}}{a^*b^*},$$

$$b_{23} = \frac{a_{23}}{b^*c^*\sin\beta^*} - \frac{a_{12}\cot\beta^*}{a^*b^*},$$

$$b_{13} = \frac{a_{13}}{a^*c^*\sin\beta^*} - \frac{a_{11}\cot\beta^*}{a^{*2}}$$

Direction cosines of the maximum, medium and minimum vibration directions

The major, medium and minor axes of the ellipsoid (given by equation (V-7)) are parallel to the directions of

minimum, medium and maximum vibration of the atom respectively. The direction cosines of the axes of the ellipsoid are obtained from the matrices formed with the six b_{ij} in the following way (Nye, 1957).

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

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

The largest column of the matrix is multiplied by the matrix. Successive multiplication of the matrix by the product is done till the convergence takes place. The final column reduced to unity gives the required direction cosines. The direction cosines of the minimum vibration direction are obtained by performing the same operation on the α^{-1} matrix.

If (a, b, c) and (a', b', c') are the direction cosines of the maximum and minimum vibration directions respectively, the direction cosines of the medium vibration direction are given by $(bc' - b'c)$, $(a'c - ac')$, $(ab' - a'b)$.

Let the equation of the ellipsoid (for temperature factor, unity) with respect to its axes be

$$B_{11}x^2 + B_{22}y^2 + B_{33}z^2 = 1 \quad \dots\dots (V-8)$$

B_{11} , B_{22} and B_{33} are obtained by successively multiplying

the matrix by the direction cosines of the three axes of the ellipsoid.

Root mean square amplitude

Since the value of the temperature factor for a reciprocal point on the surface of the ellipsoid is unity, the atomic scattering factor for the corresponding reflection is given by

$$f = f_0 e^{-B(\sin\theta/\lambda)^2} = f_0 e^{-1}$$

$$\text{Therefore } B(\sin\theta/\lambda)^2 = 1$$

$$\text{or } \frac{1}{4} B(2\sin\theta/\lambda)^2 = 1$$

$$\text{or } \frac{B}{4} s^2 = 1 \quad (\because s = 2\sin\theta/\lambda) \dots\dots (V-9)$$

Let B_{11} correspond to the maximum vibration direction. It is clear from equation (V-8) that s corresponding to the maximum vibration direction is $1/\sqrt{B_{11}}$. Therefore,

$$\frac{B}{4} \cdot s^2 = \frac{B}{4 B_{11}} = 1$$

$$\text{So, } B = 4 B_{11} = 8\pi^2 \bar{u}_{11}^2$$

where $\bar{u}_{11}^2$ is the mean square amplitude of maximum vibration. The values of the root mean square amplitudes of the maximum, medium and minimum vibrations ($\sqrt{\bar{u}_{11}^2}$, $\sqrt{\bar{u}_{22}^2}$, $\sqrt{\bar{u}_{33}^2}$ respectively) for different atoms were calculated from the corresponding values of B_{11} , B_{22} and B_{33} .

Angles between vibration
and lines or planes

The angle between a vibration direction and a plane is given by

$$\sin\theta = p.e + q.d + r.f$$

where p, q, r are the direction cosines of the vibration direction and e, d, f are the direction cosines of the normal to the plane.

The angle between a vibration direction and a line is given by $\cos\theta = p.e' + q.d' + r.f'$ where e', d', f' are the direction cosines of the line. Table V-6 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 C₁-C₄ direction.

Discussion of thermal anisotropy

It is seen from the Table V-6 that the atoms of the side groups (carboxylic group and methyl amino group) are as expected having a large root mean square amplitude perpendicular to the aromatic plane. In order to see whether the carboxylic group is oscillating about the C₁-C₇ bond as a rigid group, the amplitude of torsional oscillation of the C₇-O₁ and C₇-O₂ bond about the C₁-C₇ bond was calculated as follows :

Table V-6

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 C₁-C₄ direction.

Atom	Axis	$\sqrt{U^2}(\text{\AA})$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with C ₁ -C ₄ dire- ction
C ₁	1	0.243	0.930	-0.170	-0.326	4°	59°
	2	0.228	0.317	-0.079	0.945	28	42
	3	0.222	0.157	0.982	0.020	62	65
C ₂	1	0.246	0.886	-0.031	-0.462	1	48
	2	0.240	0.435	-0.288	0.853	16	45
	3	0.218	0.160	0.957	0.241	74	77
C ₃	1	0.283	0.385	0.753	0.533	80	88
	2	0.260	0.920	-0.264	-0.291	7	64
	3	0.228	0.079	-0.603	0.794	6	27
C ₄	1	0.303	0.675	0.370	0.638	52	79
	2	0.298	0.646	-0.714	-0.270	34	81
	3	0.242	-0.356	-0.595	0.721	14	14
C ₅	1	0.295	0.232	0.552	0.801	65	67
	2	0.285	-0.596	0.732	-0.331	18	68
	3	0.243	0.769	0.401	-0.499	17	33
C ₆	1	0.282	-0.151	0.398	0.905	47	48
	2	0.258	0.518	0.811	-0.270	43	44
	3	0.238	0.842	-0.428	0.328	1	80

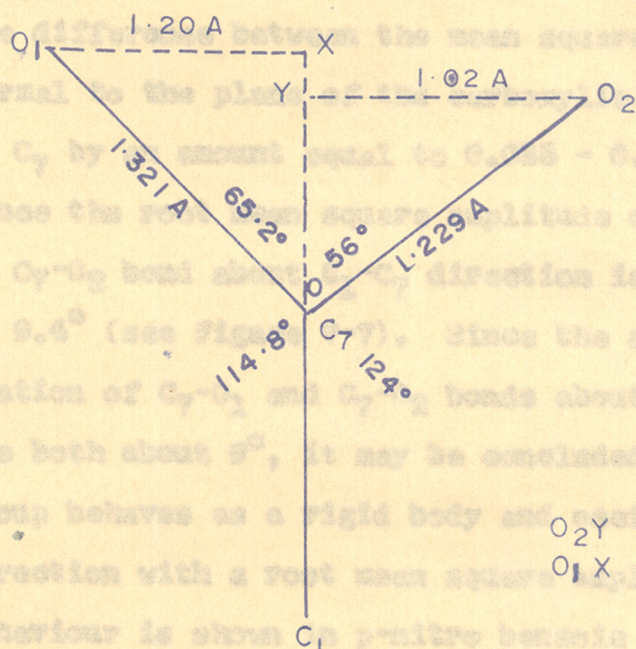
continued.....

Table V-6 (contd.)

Atom	Axis	$\sqrt{u^2}(\text{\AA})$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$	Angle with benzene plane	Angle with C ₁ -C ₄ dire- ction
C ₇	1	0.264	0.849	0.122	-0.514	4	40
	2	0.242	0.052	-0.988	-0.148	63	76
	3	0.220	0.526	-0.099	0.845	27	53
C ₈	1	0.339	0.513	0.815	0.268	71	75
	2	0.277	0.651	-0.166	-0.741	19	38
	3	0.244	0.559	-0.555	0.616	2	55
O ₁	1	0.306	0.408	0.870	0.277	75	76
	2	0.268	0.801	-0.196	-0.566	13	48
	3	0.225	0.438	-0.453	0.777	6	45
O ₂	1	0.293	0.371	0.867	0.333	79	80
	2	0.263	0.875	-0.207	-0.438	9	55
	3	0.219	0.311	-0.454	0.835	6	37
N	1	0.277	0.442	0.841	0.311	75	78
	2	0.248	0.783	-0.193	-0.592	14	47
	3	0.223	0.438	-0.505	0.744	2	46

From Table V-7, it is seen that the root mean square amplitude of atom O_1 normal to the plane of the carboxylic group is more than that of O_2 by an amount equal to $0.036 - 0.037$ i.e. $0.036 \text{ \AA}^2$. Hence the root mean square amplitude of torsional oscillation of C_7-O_1 bond about the C_1-C_7 direction is $\sqrt{0.036/1.8}$ radians, or 0.1° (see Figure V-7). Similarly

the difference between the root mean square amplitude of atom O_2 normal to the plane of the carboxylic group is more than that of O_1 by an amount equal to $0.036 - 0.037$ i.e. $0.036 \text{ \AA}^2$. Hence the root mean square amplitude of torsional oscillation of C_7-O_2 bond about the C_1-C_7 direction is $\sqrt{0.036/1.8}$ radians or 0.1° (see Figure V-7). Since the angle of torsional oscillation of C_7-O_1 and C_7-O_2 bonds about the C_1-C_7 direction are both about 0° , it may be concluded that the carboxylic group behaves as a rigid body and oscillates about the C_1-C_7 direction with a root mean square amplitude of 0.1° . Similar behaviour is shown in nitro benzoic acid (Ghosh and Pant, 1971) where the angle of torsional oscillation of the carboxylic group is 0° and in p-toluic acid (Ghosh and Pant, 1971)



$$O_2Y = 1.229 \sin 56^\circ$$

$$O_1X = 1.321 \sin 65.2^\circ$$

FIG-V-7 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

Equation (V-7) gives the equation of ellipsoid for temperature factor unity as

$$h_{11}x^2 + h_{22}y^2 + h_{33}z^2 + 2h_{12}xy + 2h_{23}yz + 2h_{13}xz = 1$$

From Table V-7, it is seen that the mean square amplitude of atom O_1 normal to the plane of the carboxylic group is more than that of C_7 by an amount equal to $0.093 - 0.057$ i.e. $0.036 \text{ \AA}^2$. Hence the root mean square amplitude of torsional oscillation of C_7-O_1 bond about the C_1-C_7 direction is $\sqrt{0.036/1.2}$ radians, or 9.1° (see Figure V-7). Similarly the difference between the mean square amplitude of atom O_2 normal to the plane of the carboxylic group is more than that of C_7 by an amount equal to $0.085 - 0.057$ i.e. $0.028 \text{ \AA}^2$. Hence the root mean square amplitude of torsional oscillation of C_7-O_2 bond about C_1-C_7 direction is $\sqrt{0.028/1.02}$ radians or 9.4° (see Figure V-7). Since the angle of torsional oscillation of C_7-O_1 and C_7-O_2 bonds about the C_1-C_7 direction are both about 9° , it may be concluded that the carboxylic group behaves as a rigid body and oscillates about the C_1-C_7 direction with a root mean square amplitude of 9° . Similar behaviour is shown in p-nitro benzoic acid (Tavale and Pant, 1971) where the angle of torsional oscillation of the carboxylic group is 9° and in p-toluic acid (Takawale and Pant, 1971) where the angle is 12° .

Some mean square displacements for correcting bond lengths for librational motion

Equation (V-7) gives the equation of ellipsoid for temperature factor unity as

$$b_{11}x^{*2} + b_{22}y^{*2} + b_{33}z^{*2} + 2b_{12}x^*y^* + 2b_{23}y^*z^* + 2b_{13}x^*z^* = 1$$

Table V-7

Some mean square displacements ($\text{\AA}^2 \times 10^3$)

Atom	Direction of displacement**		
	Normal to the plane*	In the plane normal to the bond	Parallel to the bond
O ₁	93	70	57
C ₇	57	a) 68 O ₁	52 O ₁
	57	b) 51 O ₂	68 O ₂
O ₂	85	48	70
C ₂	48	57	60
N	76	51 C ₂	61 C ₂
N	76	61 C ₈	51 C ₈
C ₈	111	79	60

* The vibration directions of O₁, O₂ and C₇ are with respect to the plane through O₁, C₇ and O₂, the vibration directions of C₂ and N are with respect to the benzene plane, and the vibration directions of N and C₈ are with respect to the plane through C₂, N and C₈.

** The atoms listed besides certain values in the table indicate the direction of the bond in question.

Equation (V-9) shows that $Bs^2/4 = 1$. Let α, β, γ be the direction cosines of any direction. Now since $\alpha = x^*/s$, $\beta = y^*/s$ and $\gamma = z^*/s$,

$$\therefore x^* = \alpha s ; \quad y^* = \beta s ; \quad z^* = \gamma s .$$

After substituting for x^*, y^* and z^* the expression (V-9) becomes

$$\begin{aligned} b_{11} \alpha^2 s^2 + b_{22} \beta^2 s^2 + b_{33} \gamma^2 s^2 + 2b_{12} \alpha \beta s^2 + 2b_{23} \beta \gamma s^2 \\ + 2b_{13} \alpha \gamma s^2 = 1 \end{aligned}$$

..... (V-10)

Taking s^2 common and rearranging

$$\frac{1}{s^2} = (b_{11} \alpha^2 + b_{22} \beta^2 + b_{33} \gamma^2 + 2b_{12} \alpha \beta + 2b_{23} \beta \gamma + 2b_{13} \alpha \gamma)$$

..... (V-11)

Substituting the value $B = 8\pi^2 \bar{u}^2$ in expression (V-9) and rearranging we get

$$8\pi^2 \bar{u}^2 = 1/s^2 .$$

Substituting this in expression (V-11) we get

$$\begin{aligned} \bar{u}^2 = \frac{1}{8\pi^2} (b_{11} \alpha^2 + b_{22} \beta^2 + b_{33} \gamma^2 + 2b_{12} \alpha \beta + 2b_{23} \beta \gamma \\ + 2b_{13} \alpha \gamma) \end{aligned}$$

..... (V-12)

Using the expression (V-12), mean square displacements along

required directions were obtained which are shown in Table V-7.

Correction of bond lengths
for librational effects

Cruickshank (1956) showed that angular oscillations of the molecules cause displacements of the electron density peaks. He gave a formula for relating the displacements to the amplitudes of small angular oscillations. The error in the atomic position with the amplitude of the angular oscillation is given by

$$y = \frac{1}{2r} \left(\frac{s^2}{1 + s^2/q^2} + \frac{t^2}{1 + t^2/q^2} \right)$$

where s^2 and t^2 are the mean square amplitudes of oscillation of the atom perpendicular to the plane and perpendicular to the bond in the plane. q^2 is the breadth parameter which for carbon atom is taken as $0.13 \text{ \AA}^2$ (Cruickshank, 1956). It is several times larger than s^2 or t^2 , hence it is sufficient to have an approximate value of q^2 ; a value of $0.13 \text{ \AA}^2$ has been taken in these calculations.

The corrections were calculated for the side groups and are shown in Table V-8. For the other atoms, the libration corrections are insignificant.

Table V-8

Corrections for bond lengths due to
librational motion

Bond	Uncorrected bond length	Correction	Corrected bond length
C ₇ -O ₁	1.321 Å	0.011 Å	1.332 Å
C ₇ -O ₂	1.229	0.009	1.238
C ₂ -N	1.365	0.008	1.373
N-C ₈	1.441	0.015	1.456

Part - II : Crystal and molecular structure
of
o-dimethyl amino benzoic acid

CHAPTER - VI

EXPERIMENTAL

Preparation of the compound

o-Dimethyl amino benzoic acid (also known as N,N-dimethyl anthranilic acid) was prepared in the following way. To 3.4 gms. of anthranilic acid in 5 ml. water, 16 gms. of dimethyl sulphate was added with stirring during two and half hours, maintaining mild alkalinity with slow addition of 40% potassium hydroxide solution. A temperature of 10°C during the first half hour and 65°C later on was maintained. The oily layer of methyl ester was extracted with ether and after removal of ether, distilled under reduced pressure (b.p. 139°C at 16 mm.). The ester was hydrolysed by refluxing for 8 hrs. with excess water to give the desired product, which was twice crystallised from ether. Melting point was found to be 70°C which is in agreement with the reported value (72°C). The crystals for crystallographic work were obtained by crystallizing the compound from carbon tetrachloride in which it gives needle shaped crystals. The needles are thin and the axis along the needle is called as 'a' axis.

Cell dimensions

The crystal belongs to the monoclinic system. The preliminary values of cell dimensions were determined from

rotation photographs. More accurate determination of cell dimensions was done from the high angle reflections in equatorial Weissenberg photographs along the three axes. The values of d_{100} , d_{010} and d_{001} obtained were plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$. The angle β was measured from equatorial Weissenberg photograph with 'b' as the oscillation axis.

For precision work the accurate values of cell dimensions are required. ^{CuK α radiation was used} For this the finite thickness of the film and wrapper has to be taken into consideration as it decreases the effective radius of the camera and thereby affects θ . Film shrinkage during processing also reduces the value of θ . In order to account for the above sources of error Levins and Straumanis (1936) devised the method known as asymmetric method. In this method on the same film the positions corresponding to $\theta = 0^\circ$ and $\theta = 90^\circ$ can be located. The collimator enters through a long slit cut in the film. Although the 180° position lies within this slit, it is accurately bracketed half way between equivalent reflections of coordinates $+r'_2$ and $+r''_2$. This permits the zero and 180° positions for r to be accurately located.

$$\frac{r'_2 + r''_2}{2} = r_3 \text{ in mm. (distance from the position } \theta=0^\circ)$$

This distance in millimeters should be 90 but is always found to be less. $90/r_3$ gives the factor with which θ for every

high angle reflection has to be multiplied to get correct θ .

The general expression used for calculating the cell dimensions is given below :

$$\sin^2 \theta = \frac{\lambda^2}{4 a^2 \sin^2 \beta} h^2 - \frac{2 \lambda^2 \cos \beta}{4 a c \sin^2 \beta} h l + \frac{\lambda^2}{4 c^2 \sin^2 \beta} l^2 + \frac{\lambda^2}{4 b^2} k^2$$

High angle reflections were used for the determination of cell dimensions and repeated calculations gave the accurate values of cell dimensions; these are shown in Table VI-1. The method of extrapolating the values of spacings to $\sin^2 \theta = 1$ was not used, since the number of reflections used were few.

Table VI-1
Cell dimensions in Å

Spacing	h	k	l	θ	d	Mean
d_{100}	9	0	5 $\angle_1$	76.7°	7.537 Å	7.54 Å
			$\angle_2$	77.4	7.536	
d_{010}	0	18	4 $\angle_1$	76.2	15.76	15.74 Å
			$\angle_2$	76.9	15.76	
	0	15	6 $\angle_1$	73.8	15.72	
			$\angle_2$	74.3	15.72	
d_{001}	0	7	8	63.6	7.46	7.47 Å
	0	6	9 $\angle_1$	76.7	7.46	
			$\angle_2$	77.4	7.47	

For 'a' axis d_{100} ($a \sin \beta$) is $7.54 \text{ \AA}$

$$\therefore a = 7.66 \text{ \AA}$$

For 'c' axis d_{001} ($c \sin \beta$) is $7.47 \text{ \AA}$

$$\therefore c = 7.58 \text{ \AA}$$

Angle β was measured from (010) Weissenberg photograph by measuring the angle between a^* and c^* which is 100° . β^* was also obtained by the method of triangulation using high angle $h0l$ reflection (Jeffrey^{ery}, 1971). The highest angle $h0l$ reflection for which $h a^*$ and $l c^*$ are not too unequal is chosen and d_{h0l}^* measured. This, together with $h a^*$ and $l c^*$, form a triangle with β^* between the two axes. The cosine rule gives an accurate value of β^* . $\bar{9} 0 5$ was the highest angle reflection used for this calculation and a value of $\beta^* = 80^\circ 2'$ was obtained which gave $\beta = 100.0^\circ$. This agrees well with the value mentioned above.

Crystal density

The crystals are highly soluble in water and all common organic solvents and hence density could not be determined by flotation method. The calculated density from cell dimensions and assuming 4 molecules per unit cell (an assumption based on space group consideration) gives a value of 1.218 g./ml.

Linear absorption coefficient

It was calculated as described in Chapter II using $\rho = 1.218 \text{ g./ml.}$ and found to be 8.8 cm^{-1} . for $\text{CuK}\alpha$ radiation

Scale and temperature factor

Three dimensional data were collected with unfiltered Cu radiation from zero to fourth layer around a axis and from zero to fifth layer around c axis; the crystals used for the two sets of photographs had cross sections $0.5 \times 0.57 \text{ mm.}$ and $0.61 \times 1.15 \text{ mm.}$ respectively. Of the 1037 reflections, 442 were present in both sets of photographs. The data were processed for Lorentz and polarization factor and spot extension factor, by methods described in Chapter II. Absorption was neglected. The data from the two axes was brought to the same scale with the help of the common reflections.

Intensities of the reflections were put on the ^{approximately} absolute scale by the application of Wilson's statistical method to three dimensional data as described in Chapter II. Table VI-2 gives $\log_e C$ values for three dimensional data, and Figure VI-1 gives the plot of $\log_e C$ against $\sin^2 \theta / \lambda^2$ for all the reflections.

Space group

The observed systematic absences are :

hol for $h + 1$, odd

oko for k odd.

This implies that the space group is $P2_1/n$.

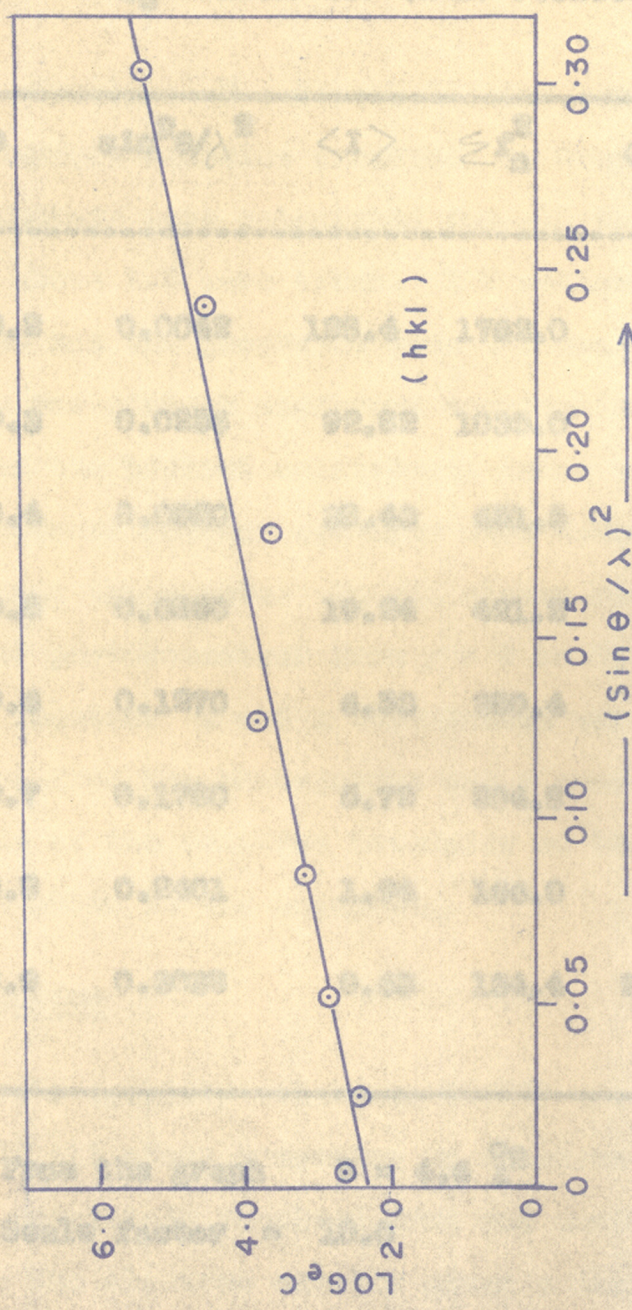


FIG. VI-1 DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTOR BY WILSON'S METHOD USING 3 DIMENSIONAL DATA.

Table VI-2

$\log_e C$ values for (hkl) reflections

No.	$\sin\theta$	$\sin^2\theta/\lambda^2$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1.	0.0-0.2	0.0042	128.4	1762.0	13.73	2.6196
2.	0.2-0.3	0.0256	92.82	1035.0	11.15	2.4114
3.	0.3-0.4	0.0520	38.43	651.5	16.95	2.8303
4.	0.4-0.5	0.0850	19.24	421.2	21.90	3.0865
5.	0.5-0.6	0.1270	6.53	280.4	42.94	3.7598
6.	0.6-0.7	0.1780	5.72	204.8	35.80	3.5780
7.	0.7-0.8	0.2401	1.94	166.0	85.57	4.4493
8.	0.8-0.9	0.3038	0.63	134.4	213.30	5.3627

From the graph $B = 4.6 \text{ \AA}^2$

Scale factor = 10.0

CHAPTER - VII

STRUCTURE AND REFINEMENT

The structure of o-dimethyl amino benzoic acid was solved by Sayre's equation programme on computer. Normalised structure factors were calculated for all the reflections and values above 1.5 were taken. 157 reflections were used in programme and the programme gave the phases of these reflections for sixteen different combinations of phases. The set with the highest consistency index was taken and three dimensional Fourier sections were taken at the intervals of $0.4 \text{ \AA}$ along the b axis. In all eleven sections were taken on Von Eller photosommateur from $y = 0$ to 0.25 and all the atoms were located. x and z coordinates were obtained by measurements from the photographs and y coordinate was fixed on the basis of the relative intensity of the peak in the sections in which it was occurring.

Sayre's equation

Sayre's equality relations (1952) are based on the fact that if all atoms composing an electron distribution are equal, and completely resolved from one another, the operation of squaring the electron density gives a distribution which is still a superposition of equal spherically symmetric 'atoms', centred on the same points as before. This led to a fruitful new development in the determination of phases from a set of

intensities.

The electron density at location x is given by

$$\rho(x) = \frac{1}{V} \sum_H F_H e^{-i 2\pi Hx} \quad \dots\dots (VII-1)$$

Let the density at each point be squared. This squared density can also be represented by a Fourier series

$$\rho(x)^2 = \frac{1}{V} \sum_H \text{sq } F_H e^{-i 2\pi Hx} \quad \dots\dots (VII-2)$$

The new Fourier series has different F 's but, provided that all atoms are equal and resolved, the F 's of VII-1 and VII-2 must be related by some factor g which takes account of the change in shape; that is

$$\text{sq } F_H = g_H F_H \quad \dots\dots (VII-3)$$

For centrosymmetric crystals, $F_H = F_{-H}$, so the square of electron density can be written

$$\begin{aligned} \rho(x)^2 &= \rho(x) \rho(x) = \left(\frac{1}{V} \sum_H e^{-i 2\pi Hx} \right) \left(\frac{1}{V} \sum_H e^{-i 2\pi (-H)x} \right) \\ &= \frac{1}{V^2} \sum_{H_1} \sum_{H_2} F_{H_1} F_{H_2} e^{-i 2\pi (H_1 - H_2)x} \\ &= \frac{1}{V} \sum_{H_1} \left(\frac{1}{V} \sum_{H_2} F_{H_1} F_{H_2} \right) e^{-i 2\pi (H_1 - H_2)x} \\ &\quad \dots\dots (VII-4) \end{aligned}$$

Now let $H_1 - H_2 = H$ and let $H_2 = H'$. Then, since the summations run over all integers, VII-4 can be rewritten

$$P(x)^2 = \frac{1}{V} \sum_H \left(\frac{1}{V} \sum_{H'} F_{H'} F_{H+H'} \right) e^{-12WHx} \quad \text{..... (VII-5)}$$

If VII-2, VII-3 and VII-5 are compared, it is found

$$\text{sq } F_H = S_H F_H = \frac{1}{V} \sum_{H'} F_{H'} F_{H+H'} \quad \text{..... (VII-6)}$$

$$\text{so, } F_H = \frac{1}{S_H V} \sum_{H'} F_{H'} F_{H+H'} \quad \text{..... (VII-7)}$$

This is a general relation which must be obeyed by crystals composed of equal, resolved atoms. For such a crystal, the signs can only be correct if VII-7 holds.

In using the method it became obvious that in a sum of products, such as occur on the right of VII-7, if one term is so large that it dominates the sum, the sign of the sum is controlled by that product. If S_H is used to indicate the sign of F_H , then this conclusion can be expressed by

$$S_H = S_{H'} S_{H+H'} \quad \text{..... (VII-8)}$$

That is, the sign of F_H tends to be the same as the product of the signs of two other F 's, related as in VII-8. This can be rewritten

$$S_{H+H'} = S_H S_{H'} \quad \text{..... (VII-9)}$$

This rule certainly holds when F_H , $F_{H'}$ and $F_{H+H'}$ are all large. But it appears to express a deeper principle, perhaps that, if F_H and $F_{H'}$ are both large, they impose a characteristic

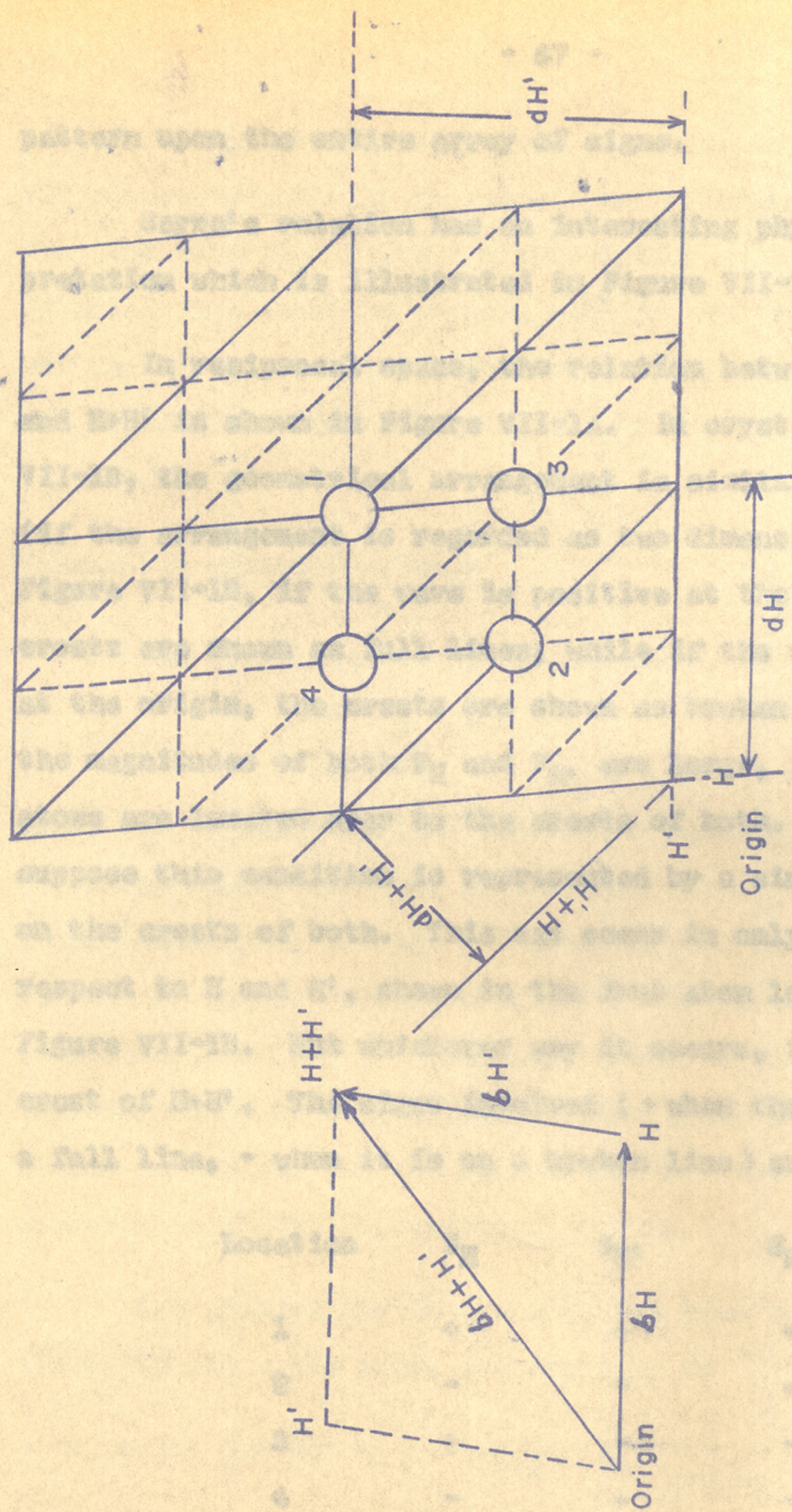


FIG VII-1 - GEOMETRICAL INTERPRETATION OF SAYRE'S SIGN RELATIONSHIP

pattern upon the entire array of signs.

Sayre's relation has an interesting physical interpretation which is illustrated in Figure VII-1.

In reciprocal space, the relation between points H , H' and $H+H'$ is shown in Figure VII-1A. In crystal space, Figure VII-1B, the geometrical arrangement is similar but rotated 90° (if the arrangement is regarded as two dimensional). In Figure VII-1B, if the wave is positive at the origin, the crests are shown as full lines, while if the wave is negative at the origin, the crests are shown as broken lines. Now if the magnitudes of both F_H and $F_{H'}$ are large, it is because atoms are located near to the crests of both. For clearness, suppose this condition is represented by a single atom exactly on the crests of both. This can occur in only four ways with respect to H and H' , shown in the four atom locations in Figure VII-1B. But whichever way it occurs, it is also on a crest of $H+H'$. The signs involved (+ when the circle is on a full line, - when it is on a broken line) are

Location	S_H	$S_{H'}$	$S_{H+H'}$
1	+	+	+
2	-	-	+
3	+	-	-
4	-	+	-

It will be seen that, in every case, VII-9 is satisfied.

Cochran (1952) and others investigated Sayre's squaring method, especially in respect to a limited set of large F 's, and justified Sayre's sign relation on more rigorous grounds. The computer program used in the present work was written by R.E. Long, University of California (1965). It was modified for CDC-3600 computer by S.S. Tavale of this laboratory.

Normalised structure factor

The normalised structure factor $E_{\vec{h}}$, is defined by

$$E_{\vec{h}} = F_{\vec{h}} / \left(\sum_{j=1}^N f_{j\vec{h}}^2 \right)^{1/2} \quad \text{..... (VII-10)}$$

where $F_{\vec{h}}$ is the structure factor for reflection $\vec{h}$, and N is the total number of atoms in the unit cell. $f_{j\vec{h}}$ is the atomic scattering for the j^{th} atom for the value of θ (the scattering angle) associated with $\vec{h}$, and is corrected by the temperature factor. ϵ is usually equal to one, except for certain groups of reflections in some space groups. The factor ϵ adjusts for the degeneracy in F for reflections at symmetry locations in reciprocal space.

The probability that a sign has been correctly determined, if all other signs are correct, is

$$P = 0.5 + 0.5 \tanh \left| \frac{\epsilon}{2} \frac{3}{3/2} E_A \sum_{\vec{A}=\vec{B}+\vec{C}} E_B E_C \right| \quad \text{..... (VII-11)}$$

where $\epsilon_m = \sum_{j=1}^N f_o^m$, f_o is the atomic scattering factor for the j^{th} atom, and N is the total number of atoms in the unit cell (Cochran and Woolfson, 1955; Woolfson, 1961). The quantity $(\epsilon_3/\epsilon_2^{3/2})$ is called PROBK in the program. It is equal to $N^{-1/2}$ for an equal atom structure with N atoms in the unit cell.

The consistency index, C , is defined as

$$C = \frac{\langle |E_A| \sum_{A=B+C} |E_B| |E_C| \rangle}{\langle |E_A| \sum_{A=B+C} |E_B| |E_C| \rangle}$$

where the sums are over all pairs of B and C for which $B+C = A$, and where $\langle \rangle$ means the average over all values of A . If C is equal to one, then for each reflection all of the terms in the sum in Sayre's equation have the same sign as all other terms in that particular sum. In that case the solution is said to be completely consistent. The true solution usually has the highest consistency index.

In order to determine origin, the signs of certain reflections may be specified (Hauptman and Karle, 1953, 1956, 1959) once the functional form for the structure factor has been chosen. The 92 centrosymmetric spacegroups may be divided into seven groups or types, each having a particular semivariant vector, h_s , and semivariant modulus, w_s . These tables were prepared by Hauptman and Karle (1953, 1959).

From the tables, one can find out the number of signs which must be specified in order to fix the origin. For the origin determining reflections the values of h_s must be linearly independent modulo w_s .

For space group $P2_1/n$ which falls in group 1, three signs may be arbitrarily assigned. If the values of h_s for these three reflections are called h_{s_1} , h_{s_2} and h_{s_3} , then these three origin determining reflections must be chosen such that the following six vectors are not (even, even, even): h_{s_1} , h_{s_2} , h_{s_3} , $(h_{s_1}+h_{s_2})$, $(h_{s_1}+h_{s_3})$ and $(h_{s_2}+h_{s_3})$. This may be accomplished by choosing the three reflections as follows: None may have the parity (even, even, even). The parity of the second reflection chosen must be different from the parity of the first reflection. The parity of the third must be different from the parities of the first, the second and the sum of the first two.

The general procedure for sign determination is as follows. The reflections are arranged on the decreased order of magnitude of normalised structure factors. Values above 1.5 are only taken. There is a provision in the program by means of which the computer selects the three origin determining reflections and four other reflections, which are not structure seminvariants. The origin determining signs are arbitrarily assigned, and the other four signs may be + or -; therefore 2^4 possible starting sign sets are considered. Sayre's equation is reiteratively applied to each of these

starting sign sets, yielding 2^4 solutions. When Sayre's equation 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. This process is reiterated until there are no new additions nor changes in the list.

The program was run on the computer and phases for sixteen different combinations were obtained. The highest consistency index was 0.85. The reflections with phases from this set which are given in Table VII-1 were used for a three dimensional Fourier along b axis. 11 sections were taken along b axis for $y = 0$ to 0.25 at intervals of 0.025 by means of the Eller photosommateur.

Three dimensional Fourier sections

The structure factor formula for hkl type reflections for the space group $P2_1/n$ is given below. The space group has the following four equivalent positions.

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

$$F(hkl) = 2f_1 \cos 2\pi (hx + ky + lz) + 2f_2 \cos 2\pi (hx - ky + lz) + \pi (h + k + l) \dots (VII-12)$$

The expression for electron density is

Table VII-1

Normalised structure factors with their phases
obtained by Sayre's equation

h	k	l	E_h	h	k	l	E_h	h	k	l	E_h
6	2	1	4.25	6	7	4	-2.84	2	9	3	-2.38
$\bar{7}$	1	4	-4.28	$\bar{4}$	9	3	2.82	2	10	3	-2.37
$\bar{6}$	7	2	4.56	$\bar{8}$	6	2	2.79	2	4	6	2.36
0	2	1	-2.04	1	11	3	2.78	$\bar{4}$	8	3	2.34
0	4	1	-2.46	$\bar{5}$	11	3	-2.74	$\bar{7}$	1	5	2.34
0	7	2	-2.63	$\bar{7}$	0	1	-2.70	6	2	4	2.33
$\bar{7}$	6	2	-3.21	1	10	4	-2.66	2	5	6	2.32
$\bar{8}$	1	4	4.05	$\bar{6}$	4	1	2.63	$\bar{1}$	5	7	2.32
7	9	3	-3.90	6	0	0	-2.60	$\bar{4}$	6	5	-2.28
2	7	4	-3.68	2	10	4	2.60	$\bar{6}$	4	5	-2.27
$\bar{5}$	7	4	-3.62	7	8	0	-2.57	$\bar{1}$	4	3	2.26
$\bar{7}$	5	4	3.57	$\bar{5}$	12	3	2.56	0	3	1	2.25
$\bar{9}$	0	1	-3.55	$\bar{4}$	11	2	2.54	0	5	3	-2.25
2	2	7	3.40	$\bar{5}$	10	4	2.52	$\bar{6}$	5	1	-2.24
7	1	0	3.30	$\bar{6}$	0	4	2.51	$\bar{4}$	5	4	2.23
2	1	8	-3.28	1	7	2	-2.51	2	3	6	2.22
$\bar{7}$	3	5	3.24	1	13	4	-2.48	6	7	3	-2.22
$\bar{7}$	6	2	-3.21	6	5	2	2.44	0	2	2	-2.17
0	9	3	3.18	0	6	3	2.43	2	0	2	2.14
$\bar{7}$	3	3	-3.07	1	9	4	2.42	0	12	4	2.14
$\bar{5}$	13	2	-3.03	5	12	1	-2.39	$\bar{2}$	11	4	2.14
6	5	3	3.00	0	9	4	2.39	$\bar{1}$	1	6	-2.14
5	6	4	3.00	$\bar{4}$	12	2	2.38	$\bar{5}$	9	3	-2.10
2	7	5	2.92	$\bar{6}$	8	2	-2.38	$\bar{4}$	3	5	2.08

continued...

Table VII-1 (contd.)

h	k	l	E_h	h	k	l	E_h	h	k	l	E_h
0	5	2	-2.08	6	1	0	-1.84	5	6	5	1.72
$\bar{6}$	9	3	-2.06	$\bar{3}$	8	1	-1.84	2	4	1	1.71
$\bar{2}$	13	4	2.06	$\bar{4}$	5	5	-1.84	2	12	2	-1.71
$\bar{5}$	3	5	-2.05	3	5	3	1.83	6	6	2	-1.71
1	3	1	2.05	$\bar{4}$	9	4	-1.82	$\bar{2}$	13	2	-1.71
2	6	4	-2.04	2	13	2	-1.82	$\bar{3}$	11	2	-1.71
2	6	0	2.00	6	7	2	1.81	$\bar{4}$	13	2	1.70
6	4	2	-2.00	$\bar{3}$	5	3	-1.81	$\bar{4}$	5	3	-1.70
1	5	6	-2.00	$\bar{7}$	3	1	-1.80	3	7	4	-1.68
$\bar{2}$	9	6	-2.00	$\bar{2}$	10	1	-1.80	6	4	0	1.68
2	11	4	1.98	1	14	0	-1.80	$\bar{2}$	1	7	1.67
2	4	5	-1.97	$\bar{3}$	5	4	-1.78	4	9	1	-1.67
$\bar{5}$	8	5	1.97	3	3	1	-1.75	4	6	0	-1.66
4	5	0	1.96	3	6	1	1.74	$\bar{3}$	3	2	1.66
0	7	4	1.95	6	4	1	1.74	$\bar{2}$	3	6	1.64
3	7	5	-1.95	5	4	2	-1.74	$\bar{4}$	1	5	1.64
0	13	4	-1.94	3	4	0	-1.73	4	8	1	1.64
3	1	2	-1.93	$\bar{1}$	10	1	1.73	$\bar{1}$	1	4	1.64
0	3	2	1.92	$\bar{7}$	4	1	1.73	3	0	3	1.64
$\bar{1}$	1	5	-1.92	3	2	2	1.73	$\bar{1}$	8	3	-1.61
6	6	0	1.91	$\bar{2}$	12	2	1.73	$\bar{4}$	1	2	1.61
$\bar{6}$	6	2	-1.90	3	3	3	1.73	3	6	0	-1.60
$\bar{7}$	3	4	1.89	6	2	0	-1.72	3	9	4	-1.60
0	0	4	-1.84	$\bar{2}$	3	3	1.72	4	0	4	-1.59

continued...

Table VII-1 (contd.)

h	k	l	E_h	h	k	l	E_h	h	k	l	E_h
$\bar{1}$	7	2	1.59	$\bar{4}$	0	2	-1.57	2	12	3	1.56
$\bar{3}$	1	4	-1.53	$\bar{1}$	4	6	-1.57	0	4	2	-1.54
0	10	3	-1.53	3	5	5	-1.56	$\bar{3}$	10	1	-1.50
$\bar{1}$	8	2	1.53	$\bar{2}$	1	1	-1.56	$\bar{1}$	12	2	-1.50

$$\begin{aligned} \rho(x,y,z) = & \sum_{h=-\infty, k=0, l=0}^{\infty} F(hkl) \left[\cos 2\pi (hx + ky + lz) \right. \\ & \left. + \cos 2\pi (hx - ky + lz) \right] + \sum_{h=-\infty, k=0, l=0}^{\infty} F(hkl) \\ & \left[\cos 2\pi (hx + ky + lz) - \cos 2\pi (hx - ky + lz) \right] \\ & \text{..... (VII-13)} \end{aligned}$$

$$\begin{aligned} \rho(x,y,z) = & \sum_{h=-\infty, k, l=0}^{\infty} F(hkl) \cos 2\pi (hx + lz) \cos 2\pi ky \\ & - \sum_{h=-\infty, k, l=0}^{\infty} F(hkl) \sin 2\pi (hx + lz) \sin 2\pi ky \\ & \text{..... (VII-14)} \end{aligned}$$

Rearranging

$$\begin{aligned} \rho(x,y,z) = & \sum_{h=-\infty, l=0}^{\infty} \left\{ \sum_{k=0}^{\infty} F(hkl) \cos 2\pi ky \cos 2\pi (hx+lz) \right. \\ & + \sum_{h=-\infty, l=0}^{\infty} \left\{ \sum_{k=0}^{\infty} F(hkl) \sin 2\pi ky \cos 2\pi (hx+lz) + \frac{\pi}{2} \right. \\ & \text{..... (VII-15)} \end{aligned}$$

Equation VII-15 is used for obtaining the Fourier sections. A weight of $\frac{1}{2}$ was given to $h0l$ and $0k0$ type reflections and a weight of unity was given to hkl and $\bar{h}kl$ type of reflections.

All the non-hydrogen atoms were revealed from these 11 sections and the molecular model was fitted. The fractional coordinates of the atoms are given in Table VII-2.

Table VII-2

Fractional coordinates of atoms

Atom	x	y	z
C ₁	0.577	0.125	0.380
C ₂	0.731	0.106	0.362
C ₃	0.835	0.153	0.433
C ₄	0.871	0.205	0.581
C ₅	0.709	0.220	0.614
C ₆	0.548	0.180	0.529
C ₇	0.412	0.088	0.307
C ₈	0.849	-0.008	0.244
C ₉	0.810	0.098	0.052
O ₁	0.258	0.090	0.331
O ₂	0.424	0.037	0.150
N	0.747	0.060	0.189

These coordinates were used for least squares refinement using isotropic temperature factor for three dimensional data. The initial value of R was 0.30 and in 5 cycles of least squares refinement it was reduced to R = 0.19. The

starting value of temperature factor was 4.6 which was obtained by Wilson's method. The positional parameters and individual temperature factors are shown in Table VII-3.

Table VII-3

Atom	x	y	z	B
C ₁	0.5650	0.1217	0.3932	4.10
C ₂	0.7312	0.1116	0.3486	3.75
C ₃	0.8848	0.1523	0.4359	4.66
C ₄	0.8666	0.2064	0.5859	4.99
C ₅	0.6955	0.2177	0.6292	5.15
C ₆	0.5478	0.1764	0.5375	4.55
C ₇	0.3997	0.0795	0.2901	4.66
C ₈	0.8469	-0.0209	0.2460	4.64
C ₉	0.8229	0.1060	0.0451	5.05
O ₁	0.2590	0.0909	0.3493	5.26
O ₂	0.4180	0.0389	0.1522	5.18
N	0.7453	0.0565	0.1928	4.01

The thermal parameters for anisotropic refinement were calculated with the aid of the equations for a_{1j} given in Chapter IV. The values of a_{1j} for all the atoms are given in Table VII-4.

Table VII-4

Atom	B	a_{11}	a_{22}	a_{33}	a_{13}	
C ₁	4.10	0.0176	0.0040	0.0180	0.0040	
C ₂	3.75	0.0164	0.0037	0.0165	0.0037	
C ₃	4.66	0.0208	0.0047	0.0210	0.0047	
C ₄	5.00	0.0220	0.0050	0.0225	0.0050	
C ₅	5.15	0.0220	0.0050	0.0225	0.0050	$a_{12} = 0$
C ₆	4.55	0.0198	0.0045	0.0202	0.0045	$a_{23} = 0$
C ₇	4.66	0.0208	0.0047	0.0210	0.0047	
C ₈	4.64	0.0198	0.0045	0.0202	0.0045	
C ₉	5.05	0.0220	0.0050	0.0225	0.0050	
O ₁	5.26	0.0232	0.0053	0.0240	0.0053	
O ₂	5.18	0.0232	0.0053	0.0240	0.0053	
N	4.01	0.0176	0.0040	0.0180	0.0040	

Anisotropic temperature factor

For space group $P2_1/n$, the expression for structure factor is given by equation VII-12.

$$f(hkl) = 2f_1 \cos 2\pi (hx + ky + lz) + 2f_2 \cos \left\{ 2\pi (hx - ky + lz) + \pi (h+k+l) \right\}$$

..... (VII-12)

Now,

$$f_1 = f_0 \exp. - (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \quad \dots\dots (VII-16)$$

$$f_2 = f_0 \exp. - (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \quad \dots\dots (VII-17)$$

where f_1 and f_2 are the anisotropic temperature factors. The expression for structure factor becomes

$$\begin{aligned} F(hkl) = & 2f_0 \exp. - (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk \\ & + 2a_{23}kl + 2a_{13}hl) \cos 2\pi (hx+ky+lz) \\ & + 2f_0 \exp. - (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk \\ & - 2a_{23}kl + 2a_{13}hl) \cos 2\pi \{(hx-ky+lz) + \pi (h+k+l)\} \end{aligned} \quad \dots\dots (VII-18)$$

For the sake of brevity the first and the second terms on the right hand side of equation VII-18 are denoted by A and B.

Hence,

$$F(hkl) = A + B \quad \dots\dots (VII-19)$$

After proceeding in the same way as in Chapter IV, we obtain the following expressions :

$$\frac{\partial F}{\partial a_{11}} = (-h^2) F(hkl)$$

$$\frac{\partial F}{\partial a_{22}} = (-k^2) F(hkl)$$

$$\frac{\partial F}{\partial a_{33}} = (-1^2) F(hkl)$$

$$\frac{\partial F}{\partial a_{12}} = (-2hk) A + (2hk) B$$

$$\frac{\partial F}{\partial a_{23}} = (-2kl) A + (2kl) B$$

$$\frac{\partial F}{\partial a_{13}} = (-2hl) F(hkl)$$

These expressions were used for the anisotropic refinement of temperature factors.

Refinement using anisotropic temperature factor

The positional parameters from Table VII-3 and thermal parameters from Table VII-4 were used for least squares refinement using anisotropic temperature factor. The value of R after the first cycle was 0.18 and in four cycles of least squares refinement the value of R was reduced to 0.13. Four hydrogen atoms which were attached to the ring were included in the refinement. Their positions were determined on stereochemical considerations and shown in Table VII-5.

Table VII-5

Positional parameters of the hydrogen atoms
attached to the ring carbon atoms

Atom	x	y	z
H ₁	1.000	0.146	0.402
H ₂	0.967	0.235	0.649
H ₃	0.688	0.254	0.744
H ₄	0.430	0.184	0.567

The hydrogen atoms were considered to have the same anisotropic temperature factor as the non-hydrogen atoms to which they were attached.

After this three dimensional difference Fourier sections were taken along b axis, 8 sections were taken from $y = 0$ to $y = 0.175$ at intervals of 0.025 by means of the Eller photo-sommateur. The positions of the six hydrogen atoms which were attached to C_8 and C_9 to form two methyl groups and the position of the hydrogen atom which lies near the nitrogen atom were located. The parameters of these hydrogen atoms thus located are given in Table VII-6.

After the inclusion of all the hydrogen atoms, anisotropic refinement was further carried out using Cruickshank's weighting scheme and giving a weight of zero for those structure factors where $F_o - F_c$ was greater than 5. After 5 cycles of least squares refinement, the final value of R became 0.113. The final positional parameters of the atoms are shown in Table VII-7 and thermal parameters are shown in Table VII-8.

Table VII-6

Positional parameters of the hydrogen atoms of the methyl groups and the one attached to nitrogen atom

Atom	x	y	z
H ₅	0.596	0.052	0.131
H ₆	0.994	0.001	0.301
H ₇	0.739	-0.032	0.352
H ₈	0.810	-0.059	0.111
H ₉	0.923	0.117	0.082
H ₁₀	0.781	0.052	-0.055
H ₁₁	0.740	0.161	0.032

Table VII-7

Positional parameters of the atoms,
and their standard deviations.

Atom	x	y	z
C ₁	0.5638 ± 0.0007	0.1227 ± 0.0003	0.3938 ± 0.0008
C ₂	0.7313 ± 0.0006	0.1132 ± 0.0003	0.3455 ± 0.0007
C ₃	0.8792 ± 0.0007	0.1526 ± 0.0004	0.4358 ± 0.0008
C ₄	0.8615 ± 0.0009	0.2051 ± 0.0004	0.5824 ± 0.0009
C ₅	0.6977 ± 0.0009	0.2155 ± 0.0004	0.6292 ± 0.0009
C ₆	0.5529 ± 0.0008	0.1743 ± 0.0004	0.5380 ± 0.0008
C ₇	0.3990 ± 0.0007	0.0797 ± 0.0004	0.2896 ± 0.0008
C ₈	0.8457 ± 0.0008	-0.0202 ± 0.0004	0.2484 ± 0.0009
C ₉	0.8202 ± 0.0010	0.1044 ± 0.0005	0.0475 ± 0.0010
O ₁	0.2586 ± 0.0005	0.0898 ± 0.0003	0.3482 ± 0.0006
O ₂	0.4167 ± 0.0005	0.0398 ± 0.0003	0.1515 ± 0.0006
N	0.7449 ± 0.0005	0.0583 ± 0.0003	0.1919 ± 0.0005
H ₁	0.992 ± 0.009	0.146 ± 0.005	0.418 ± 0.009
H ₂	1.009 ± 0.010	0.238 ± 0.005	0.633 ± 0.010
H ₃	0.691 ± 0.010	0.261 ± 0.005	0.729 ± 0.010
H ₄	0.433 ± 0.009	0.175 ± 0.005	0.575 ± 0.008
H ₅	0.595 ± 0.008	0.058 ± 0.004	0.136 ± 0.008
H ₆	0.973 ± 0.010	-0.001 ± 0.005	0.306 ± 0.010
H ₇	0.779 ± 0.009	-0.045 ± 0.005	0.340 ± 0.009
H ₈	0.827 ± 0.010	-0.059 ± 0.005	0.132 ± 0.010
H ₉	0.939 ± 0.011	0.106 ± 0.005	0.089 ± 0.010
H ₁₀	0.788 ± 0.011	0.069 ± 0.005	-0.049 ± 0.010
H ₁₁	0.741 ± 0.010	0.153 ± 0.005	0.035 ± 0.009

Table VII-8

Final thermal parameters and their standard deviations.

Anisotropic thermal parameters are of the form

$$T = \exp. -(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{13}hl + 2a_{23}kl)$$

Non hydrogen atoms ($\times 10^4$)

Atom	a_{11}	a_{22}	a_{33}	a_{12}	a_{23}	a_{13}
C ₁	147 ± 9	44 ± 2	203 ± 12	12 ± 3	15 ± 4	34 ± 9
C ₂	141 ± 9	47 ± 2	133 ± 10	7 ± 3	3 ± 4	26 ± 8
C ₃	161 ± 10	56 ± 3	242 ± 15	- 9 ± 4	-20 ± 5	39 ± 10
C ₄	244 ± 14	62 ± 3	233 ± 14	- 2 ± 5	-37 ± 6	18 ± 11
C ₅	295 ± 15	53 ± 3	248 ± 15	9 ± 5	-28 ± 6	47 ± 12
C ₆	236 ± 12	53 ± 3	200 ± 12	30 ± 5	- 3 ± 5	76 ± 10
C ₇	116 ± 9	56 ± 3	261 ± 15	6 ± 4	20 ± 5	48 ± 9
C ₈	204 ± 12	51 ± 3	255 ± 15	15 ± 5	-14 ± 5	59 ± 11
C ₉	291 ± 16	69 ± 4	232 ± 16	-33 ± 6	2 ± 6	114 ± 14
O ₁	155 ± 7	87 ± 3	315 ± 12	0 ± 3	2 ± 5	92 ± 8
O ₂	155 ± 7	89 ± 3	279 ± 11	-19 ± 4	-57 ± 5	28 ± 7
N	143 ± 7	49 ± 2	153 ± 9	- 5 ± 3	-13 ± 4	51 ± 6

CHAPTER - VIII

RESULTS AND DISCUSSION

(I) Molecular Structure

The final bond lengths and angles are given in Table VIII-1 and are also shown in Figure VIII-1. Some of the bonds (belonging to side groups) have been corrected for librational motion by Cruickshank's method (1956) described in Chapter V.

Table VIII-2 gives equations with respect to a' , b , c orthogonal axes, of the least squares planes and the angle between the plane of the benzene ring and the plane of the carboxylic group. Table VIII-3 gives deviations of the atoms from the plane of benzene ring and the plane of the carboxylic group.

Table VIII-4 gives some mean square displacements for the atoms of the side groups, which were used to calculate the corrections to the bond lengths of the side groups for librational motion.

The thermal parameters b_{1j} were used to calculate the direction cosines of the principal axes of the individual atomic vibration ellipsoids referred to a' , b , c orthogonal axes; these are given in Table VIII-5 along with the angles between the principal axes of the vibration ellipsoids and the aromatic plane.

Table VIII-1

Intramolecular bond lengths and angles

Bond	Bond lengths (Å)			Bond angles	
	Uncor- rected	Corre- cted	e.s.d.		
C ₁ -C ₂	1.402 ^o Å		0.007 ^o Å	C ₁ -C ₂ -C ₃	122.5 ± 0.5 ^o
C ₂ -C ₃	1.367		0.008	C ₂ -C ₃ -C ₄	118.4 ± 0.5
C ₃ -C ₄	1.409		0.009	C ₃ -C ₄ -C ₅	119.4 ± 0.6
C ₄ -C ₅	1.372		0.009	C ₄ -C ₅ -C ₆	120.9 ± 0.6
C ₅ -C ₆	1.361		0.009	C ₅ -C ₆ -C ₁	121.7 ± 0.6
C ₆ -C ₁	1.381		0.008	C ₆ -C ₁ -C ₂	117.0 ± 0.5
C ₁ -C ₇	1.526	1.530 ^o Å	0.008	C ₇ -C ₁ -C ₂	122.0 ± 0.5
C ₇ -O ₁	1.243	1.262	0.007	C ₇ -C ₁ -C ₆	121.0 ± 0.5
C ₇ -O ₂	1.248	1.267	0.007	O ₁ -C ₇ -C ₁	116.6 ± 0.5
C ₂ -N	1.464	1.467	0.006	O ₂ -C ₇ -C ₁	117.2 ± 0.5
C ₈ -N	1.487	1.501	0.008	O ₁ -C ₇ -O ₂	126.2 ± 0.6
C ₉ -N	1.505	1.526	0.009	N-C ₂ -C ₁	117.7 ± 0.4
C ₃ -H ₁	0.90		0.07	N-C ₂ -C ₃	119.8 ± 0.5
C ₄ -H ₂	1.24		0.08	C ₈ -N-C ₂	111.4 ± 0.4
C ₅ -H ₃	1.06		0.08	C ₉ -N-C ₂	112.9 ± 0.4
C ₆ -H ₄	1.01		0.07	C ₈ -N-C ₉	111.3 ± 0.5
N-H ₅	1.15		0.06	C ₂ -N-H ₅	95.5 ± 3.0

continued...

Table VIII-1 (contd.)

Bond	Bond lengths (Å)			Bond angles	
	Uncor- rected	Corre- cted	e.s.d.		
C ₈ -H ₆	1.04		0.08	O ₂ -N-H ₅	15.6 ± 3.0
C ₈ -H ₇	1.01		0.07	N-H ₅ -O ₂	151.8 ± 5.4
C ₈ -H ₈	1.06		0.08		
C ₉ -H ₉	0.91		0.08		
C ₉ -H ₁₀	0.91		0.08		
C ₉ -H ₁₁	1.03		0.08		
N-O ₂	2.497		0.006		
O ₂ -H ₅	1.481		0.06		

Table VIII-2

Equations of planes

Plane	Equations
1. Benzene ring	0.1801 x - 0.7837 y + 0.5945 z - 0.5794 = 0
2. Carboxylic group	0.2004 x - 0.8281 y + 0.5236 z - 0.4258 = 0

Angle between benzene ring and carboxylic group is 4.8°

Table VIII-3

Deviations of atoms from different
planes (Å)

Atom	Planes	
	Benzene ring	Carboxylic group
C ₁	0.002	-0.003
C ₂	-0.003	0.066
C ₃	0.000	-
C ₄	0.004	-
C ₅	-0.006	-
C ₆	0.003	-0.118
C ₇	-0.031	0.010
C ₈	1.270	-
C ₉	-1.187	-
O ₁	0.029	-0.004
O ₂	-0.151	-0.004
N	-0.017	0.177
H ₁	0.07	-
H ₂	-0.09	-
H ₃	-0.13	-
H ₄	0.09	-0.08
H ₅	-0.34	-0.16
H ₆	1.36	-
H ₇	1.95	-
H ₈	1.22	-
H ₉	-0.95	-
H ₁₀	-1.21	-
H ₁₁	-1.95	-

Table VIII-4

Some mean square displacements ($\text{\AA}^2 \times 10^3$)

Atom	Direction of displacement**		
	Normal to the plane*	In the plane normal to the bond	Parallel to the bond
C ₁	47	52	56
O ₁	103	96	40
O ₂	132	43	61
C ₇	60 (a)	59 (C ₁)	57 (C ₁)
	60 (b)	78 (O ₁)	38 (O ₁)
	60 (c)	37 (O ₂)	79 (O ₂)
C ₂	52	43	42
C ₈	67	66	60
C ₉	100	82	47
N	63 (a)	40 (C ₂)	40 (C ₂)
	42 (b)	40 (C ₈)	62 (C ₈)
	49 (c)	49 (C ₉)	45 (C ₉)

* The vibration directions of C₁, O₁, O₂ and C₇ are with respect to the plane through C₁, C₇, O₁ and O₂. The vibration direction of C₂ and N is with respect to benzene plane. The vibration directions of C₈ and N and C₉ and N are with respect to the planes through C₂, N, C₈ and C₂, N, C₉.

** The atoms listed besides certain values in the table indicate the direction of the bond in question.

Table VIII-5

Magnitudes and direction cosines of the principal axes of the atomic vibration ellipsoids and the angles between the principal axes and the aromatic plane.

Atom	Axis	$\sqrt{u^2}(\text{\AA})$	$\cos \alpha_1$	$\cos \alpha_2$	$\cos \alpha_3$	Angle with benzene plane
C ₁	1	0.257	0.277	0.634	0.675	5°
	2	0.223	0.335	0.589	-0.735	57
	3	0.197	0.900	-0.430	0.067	33
C ₂	1	0.245	0.206	0.973	-0.105	52
	2	0.260	0.937	-0.165	0.307	21
	3	0.192	-0.281	0.162	0.946	22
C ₃	1	0.285	-0.171	0.739	-0.651	85
	2	0.241	0.095	-0.646	-0.758	4
	3	0.212	0.981	0.192	-0.041	0
C ₄	1	0.310	0.139	0.759	-0.636	72
	2	0.267	0.949	-0.286	-0.134	18
	3	0.220	0.284	0.584	0.760	2
C ₅	1	0.300	0.660	0.543	-0.519	38
	2	0.284	0.746	-0.391	0.539	50
	3	0.223	-0.090	0.743	0.663	12
C ₆	1	0.293	0.738	0.664	0.124	18
	2	0.248	0.370	-0.551	0.748	71
	3	0.200	-0.565	0.506	0.652	6

continued....

Table VIII-5 (contd.)

Atom	Axis	$\sqrt{u^2}(\text{\AA})$	$\cos\chi_1$	$\cos\chi_2$	$\cos\chi_3$	Angle with benzene plane
C ₇	1	0.290	0.163	0.656	0.737	3°
	2	0.245	-0.093	0.754	-0.650	85
	3	0.178	0.982	-0.037	-0.183	5
C ₈	1	0.279	0.002	-0.597	0.803	71
	2	0.262	0.738	0.542	0.402	3
	3	0.215	0.875	-0.592	-0.441	19
C ₉	1	0.327	-0.723	0.659	-0.208	55
	2	0.279	0.445	0.674	0.589	6
	3	0.210	-0.529	-0.333	0.780	39
O ₁	1	0.365	-0.111	0.849	-0.517	84
	2	0.248	0.303	-0.467	-0.831	5
	3	0.204	0.947	0.249	0.205	5
O ₂ N	1	0.255	-0.222	0.913	-0.343	74
	2	0.213	0.728	0.389	0.564	9
	3	0.182	-0.648	0.124	0.751	13
#O ₁	1	0.331	0.017	0.998	0.060	48
	2	0.302	-0.372	0.062	-0.926	42
	3	0.192	0.928	0.006	-0.372	3

Aromatic ring

The C-C bond lengths of the aromatic ring deviate appreciably from the normal value, 1.393 Å. The estimated standard deviations of the C-C bond lengths are from 0.007 Å to 0.009 Å. The deviations of the carbon atoms of the aromatic ring from the least squares plane are within experimental error.

Carboxylic group

The hydrogen atom of the carboxylic group has migrated and attached itself to the nitrogen atom of the dimethyl amino group. The two C-O bond lengths have become almost equal.

Some examples of the carboxylic acids where the two C-O bonds are almost equal and the molecule exists in the zwitterion form are shown in Table VIII-6. The O-C-O angle is in general more than 125°; in the case of anthranilic acid, however, it is only 122°. The two oxygen atoms of the carboxylic group are negatively charged due to the loss of proton and hence repel each other.

The exocyclic C-C bond in all these compounds is more than 1.52 Å in length except in anthranilic acid.

Dimethyl amino group

The nitrogen atom of this group acquires positive charge due to the acquisition of a proton from the carboxylic

Carboxylic groups where the two CO bonds are nearly equal.

Compound	exocyclic C-C bond	C-O	C=O	Angle OCO	Form	Reference
Anthranilic acid (zwitterion)	1.494 Å	1.267 Å	1.243 Å	122.0°	Zwitterion	Brown (1968)
α -Glycine	1.523 $\pm$ 0.005	1.265 $\pm$ 0.005	1.261 $\pm$ 0.005	125.5 $\pm$ 0.3	Zwitterion	Marsh (1953)
β -Glycine	1.521 $\pm$ 0.015	1.257 $\pm$ 0.015	1.233 $\pm$ 0.015	126.2 $\pm$ 0.9	Zwitterion	Iitaka (1960)
γ -Glycine	1.527 $\pm$ 0.011	1.254 $\pm$ 0.011	1.237 $\pm$ 0.011	125.4 $\pm$ 0.7	Zwitterion	Iitaka (1961)
β -Alanine	1.553 $\pm$ 0.010	1.292 $\pm$ 0.009	1.237 $\pm$ 0.009	127.0 $\pm$ 0.7	Zwitterion	Jose and Pant (1965)
o-dimethyl amino benzoic acid	1.530 $\pm$ 0.008	1.267 $\pm$ 0.007	1.262 $\pm$ 0.007	126.2 $\pm$ 0.6	Zwitterion	Present work.

group. The two methyl groups attached to the nitrogen atom are symmetrically placed on either side of the benzene plane, the distances being $1.270 \text{ \AA}$ and $-1.187 \text{ \AA}$. The deviation of the hydrogen atom H_5 is only $-0.34 \text{ \AA}$ from the plane of the benzene ring. The bonds around the nitrogen atom are as expected disposed approximately tetrahedrally.

The C_2-N distance is $1.467 \pm 0.006 \text{ \AA}$ (corrected) which is a little shorter than the corresponding value in the zwitterionic form of anthranilic acid which is $1.501 \text{ \AA}$. The $N-C_8$ and $N-C_9$ bond lengths are $1.501 \pm 0.008 \text{ \AA}$ and $1.526 \pm 0.009 \text{ \AA}$ (both corrected for librational motion); these bonds are longer than $N-C_8$ distance, $1.456 \pm 0.009 \text{ \AA}$ in o-methyl amino benzoic acid.

Intramolecular hydrogen bond

There is a strong intramolecular hydrogen bond between the oxygen of the carboxyl group and the nitrogen atom of length $2.497 \pm 0.006 \text{ \AA}$. The infrared studies of Jose et al. (private communication) confirm that the $NH\cdots O$ hydrogen bond is strong. The small value of the ONH angle (16°) further confirms the result.

(II) Crystal Structure

The structure projected on (100), (010) and (001) projections is shown in Figures VIII-2, VIII-3 and VIII-4. Intermolecular distances are shown in Figures VIII-2 and VIII-4.

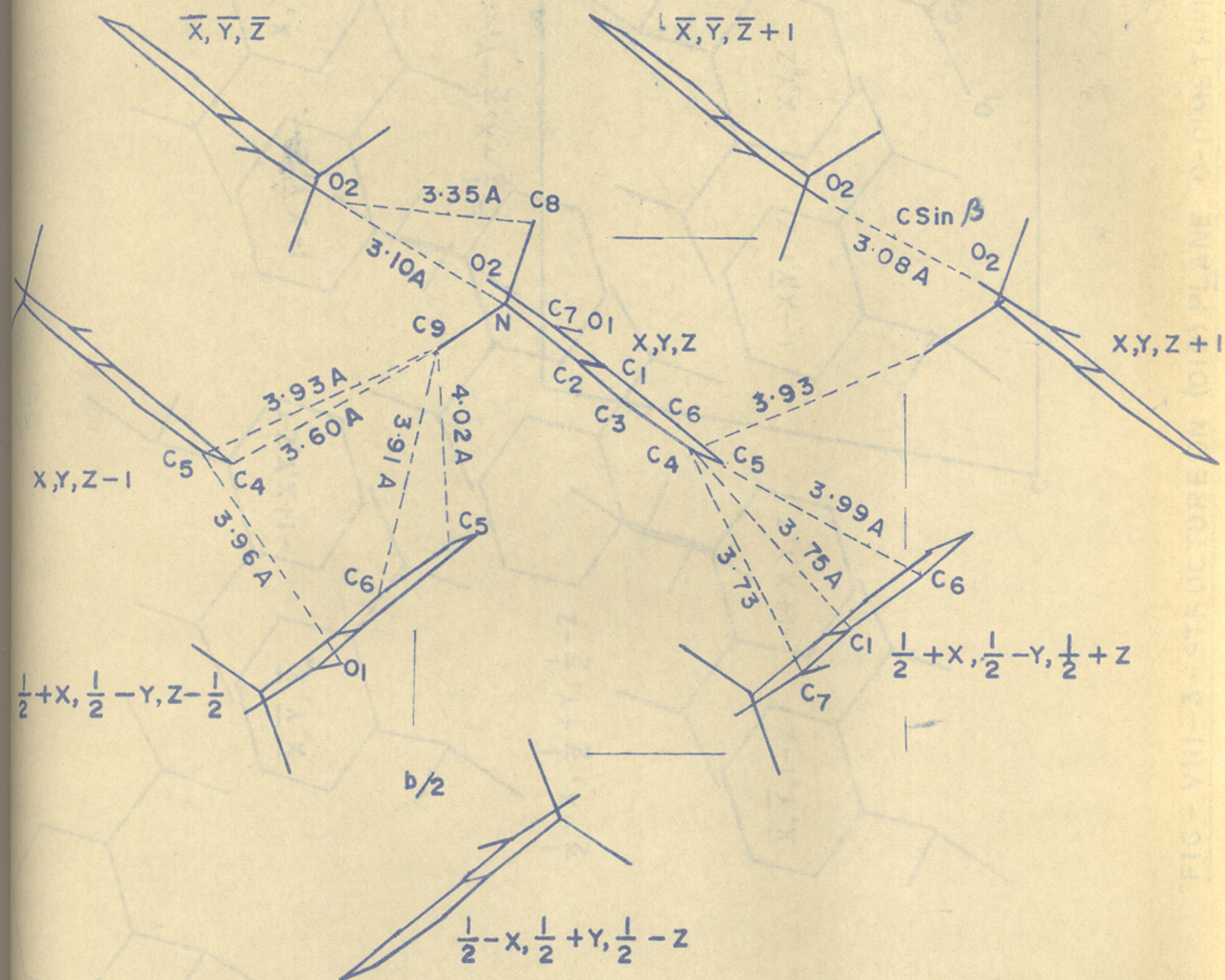


FIG VIII-2- STRUCTURE PROJECTED ON (100) PLANE. O-DIMETHYL
AMINO BENZOIC ACID

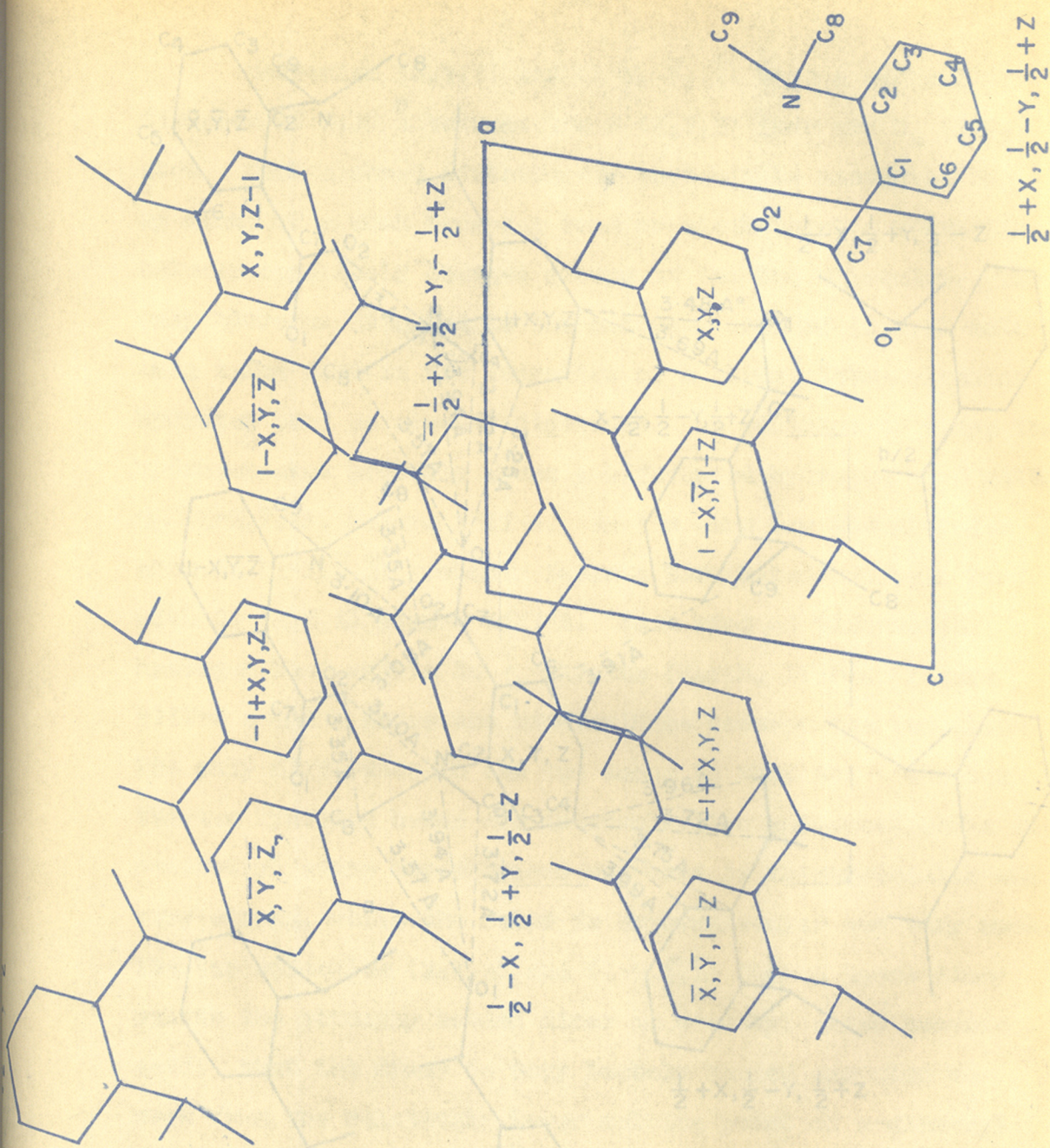
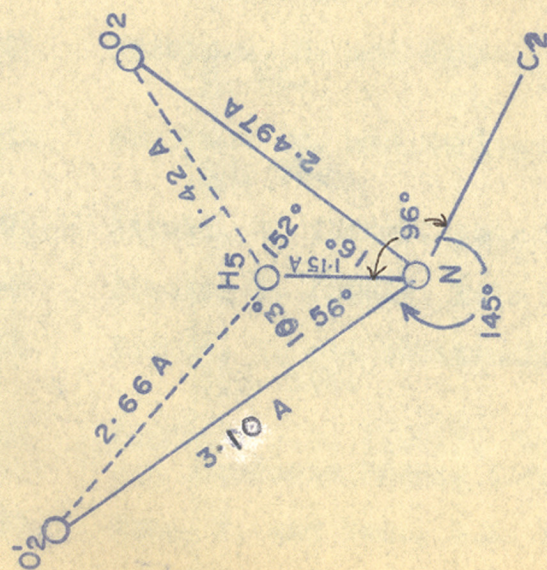
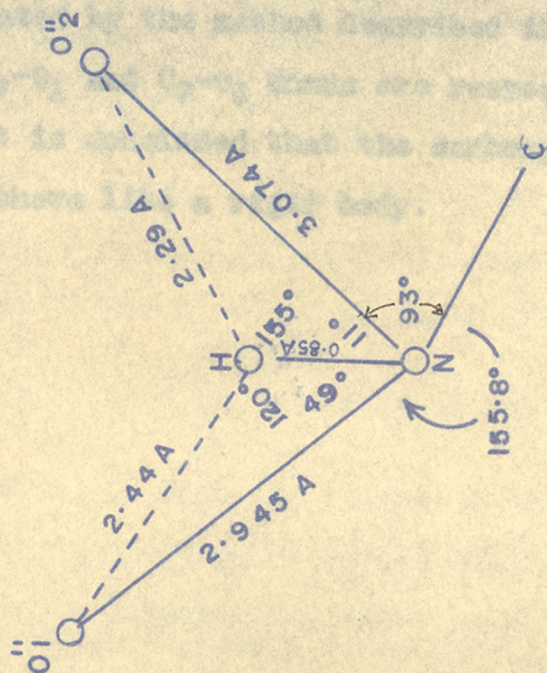


FIG- VIII-3- STRUCTURE ON (010) PLANE. O-DIMETHYL AMINO BENZOIC ACID

Molecules (X,Y,Z) and $(1-X, \bar{Y}, \bar{Z})$ have a contact distance of $3.10 \text{ \AA}$ between the N (X,Y,Z) atom and O_2 $(1-X, \bar{Y}, \bar{Z})$ atom. Such a short distance can probably be accounted for by means of a weak hydrogen bond or electrostatic attraction between oppositely charged groups of the two molecules. The only hydrogen attached to the nitrogen atom of (X,Y,Z) molecule takes part in the formation of a strong intramolecular hydrogen bond as already discussed. In addition to this, the hydrogen atom probably forms a bifurcated hydrogen bond with O_2 $(1-X, \bar{Y}, \bar{Z})$, Figure VIII-4. In the same way the nitrogen atom of $(1-X, \bar{Y}, \bar{Z})$ probably forms a bifurcated hydrogen bond with O_2 (X,Y,Z) Figure VIII-4. Such kind of bifurcated hydrogen bond exists in α -Glycine (Marsh, 1958). Figure VIII-5 a and b shows the similarities between the two cases. The only difference in the two cases is that in α -Glycine the two hydrogen bonds are intermolecular and weak, while in o-dimethyl amino benzoic acid one bond is intramolecular and very strong, while the other is intermolecular and very weak. The two molecules (X,Y,Z) and $(1-X, \bar{Y}, \bar{Z})$ form a loose dimer unlike the strongly bonded dimer in o-methyl amino benzoic acid. That the dimer is very loosely bonded can also be seen from the relatively lower melting point of o-dimethyl amino benzoic acid (72°C) in comparison with o-methyl amino benzoic acid (melting point 178°). There is also a rather short contact between $O(X,Y,Z)$ and $C_3(-1+X,Y,Z)$ of length $3.25 \text{ \AA}$. All other contacts are of the usual van der Waals type.



a) O-DIMETHYL AMINO BENZOIC ACID
(PRESENT WORK)



b) α -GLYCINE (MARSH, 1958)

FIG-VIII-5-BIFURCATED HYDROGEN BONDS IN α GLYCINE AND O-DIMETHYL AMINO BENZOIC ACID

The angle of torsional oscillation of the two C-O bonds of the carboxylic group about the C_1-C_7 bond were calculated by the method described in Chapter V. Their values for C_7-O_1 and C_7-O_2 bonds are respectively 10.5° and 13.6° . Hence it is concluded that the carboxylic group does not quite behave like a rigid body.

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A P P E N D I X

Observed and calculated structure factors
(o-methyl amino benzoic acid)

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	2	0	40.8	37.3	2	0	4	2.6	2.3
0	4	0	51.5	-53.6	4	0	4	3.7	3.3
0	6	0	13.5	17.0	1	0	6	5.7	4.1
0	8	0	12.1	-14.2	2	0	6	2.6	3.5
0	10	0	6.9	- 6.7	1	1	0	17.6	-13.6
0	12	0	8.0	7.7	1	2	0	25.8	23.3
0	14	0	6.3	5.2	1	3	0	41.1	-41.2
0	0	2	15.3	-17.0	1	4	0	7.7	- 7.2
0	0	4	8.0	9.1	1	5	0	10.4	-11.2
0	0	6	3.5	3.1	1	6	0	5.8	6.8
1	0	0	74.3	74.6	1	7	0	2.8	2.2
2	0	0	28.1	-26.7	1	8	0	9.9	-11.1
3	0	0	4.9	6.2	1	9	0	4.3	5.0
4	0	0	9.4	- 9.5	1	10	0	15.3	-15.1
5	0	0	4.0	- 3.9	1	13	0	8.9	- 8.9
7	0	0	1.6	- 1.9	1	14	0	3.9	4.7
8	0	0	1.1	- 2.2	2	1	0	2.6	- 0.5
1	0	2	12.9	-12.8	2	2	0	2.6	1.7
2	0	2	14.4	-13.4	2	3	0	25.1	23.4
3	0	2	19.8	-16.9	2	4	0	15.8	-15.2
4	0	2	18.6	17.8	2	6	0	22.1	-20.5
5	0	2	33.9	27.3	2	7	0	9.4	- 9.8
6	0	2	4.6	4.4	2	8	0	4.6	- 5.4
1	0	4	3.3	2.3	2	9	0	6.1	6.9

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	10	0	8.1	- 9.6	4	5	0	12.9	13.1
2	11	0	3.7	- 4.9	4	6	0	15.0	14.5
2	12	0	8.9	- 8.5	4	7	0	2.3	- 2.5
2	13	0	5.1	- 5.7	4	8	0	6.7	8.0
2	15	0	1.6	1.4	4	9	0	3.5	- 4.4
2	16	0	2.6	2.8	4	11	0	6.3	6.7
3	1	0	14.9	-13.1	4	12	0	1.6	- 2.1
3	2	0	10.5	-14.1	4	13	0	1.6	1.8
3	4	0	10.1	-10.7	4	14	0	2.4	2.5
3	5	0	11.2	9.2	5	1	0	4.3	- 4.3
3	6	0	7.0	- 7.9	5	2	0	2.8	2.8
3	7	0	7.0	7.3	5	3	0	7.8	7.5
3	8	0	7.6	- 7.5	5	5	0	11.7	11.8
3	9	0	2.8	2.7	5	6	0	7.5	7.8
3	10	0	1.7	- 2.2	5	7	0	10.4	-10.1
3	11	0	5.1	- 4.2	5	8	0	20.9	18.6
3	12	0	6.3	- 4.7	5	9	0	8.6	- 9.0
3	15	0	3.3	3.2	5	10	0	2.4	2.0
3	16	0	2.8	3.0	5	12	0	2.4	- 2.4
3	18	0	1.1	- 0.9	5	14	0	1.6	1.8
4	1	0	7.2	- 8.8	6	1	0	1.9	- 1.1
4	2	0	5.6	- 6.5	6	2	0	2.8	- 3.4
4	3	0	2.6	- 2.3	6	3	0	1.6	2.1
4	4	0	9.1	9.9	6	4	0	4.9	- 5.8

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	7	0	1.6	1.5	0	10	1	3.0	- 4.3
6	8	0	4.9	5.2	0	11	1	3.3	3.9
6	9	0	3.3	- 3.3	0	12	1	5.8	- 5.7
6	10	0	1.1	1.7	0	13	1	2.5	- 2.1
6	11	0	2.8	- 3.6	0	14	1	2.0	- 1.8
6	12	0	2.0	1.5	0	15	1	1.6	1.7
6	14	0	3.0	2.7	0	17	1	3.0	2.6
7	1	0	3.7	4.1	0	1	2	28.1	21.9
7	2	0	4.9	- 6.0	0	2	2	2.7	4.9
7	4	0	4.8	- 5.2	0	3	2	3.7	- 2.5
7	5	0	4.6	- 4.3	0	4	2	7.1	- 7.0
7	8	0	2.0	2.1	0	5	2	19.3	-17.9
8	4	0	2.8	- 1.9	0	6	2	31.7	28.8
8	7	0	4.0	2.6	0	7	2	26.6	26.9
8	8	0	3.7	2.6	0	8	2	40.3	40.1
0	1	1	27.2	-25.6	0	9	2	15.3	14.1
0	2	1	9.4	9.0	0	10	2	3.3	3.4
0	3	1	88.5	91.7	0	11	2	10.3	- 9.9
0	4	1	96.4	109.7	0	13	2	4.9	- 4.4
0	5	1	35.9	38.8	0	18	2	2.3	- 1.2
0	6	1	13.5	14.2	0	1	3	8.1	8.0
0	7	1	11.8	-11.7	0	2	3	24.5	-20.8
0	8	1	22.1	-20.1	0	3	3	4.6	3.7
0	9	1	5.8	5.3	0	4	3	7.6	- 8.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	5	3	9.0	9.3	0	11	5	2.6	- 2.1
0	7	3	7.2	5.2	0	12	5	2.0	1.7
0	8	3	13.5	-13.3	0	2	6	4.9	3.5
0	9	3	4.6	4.7	0	3	6	6.1	5.5
0	10	3	4.6	5.1	0	5	6	4.6	4.5
0	11	3	14.0	12.8	0	6	6	2.5	- 2.0
0	12	3	12.0	11.4	0	8	6	2.3	- 1.5
0	13	3	4.8	5.1	0	9	6	3.5	2.1
0	15	3	4.3	- 4.2	0	10	6	2.6	1.7
0	17	3	2.3	- 2.0	0	11	6	2.3	- 1.5
0	1	4	5.6	4.9	0	12	6	2.6	2.0
0	2	4	11.5	11.6	0	1	7	3.0	- 2.6
0	4	4	11.8	11.8	0	2	7	2.1	1.9
0	5	4	10.0	-10.1	0	4	7	2.9	2.9
0	7	4	3.3	- 3.1	0	6	7	1.4	1.4
0	12	4	4.6	- 4.7	0	7	7	3.5	3.7
0	15	4	6.4	5.2	0	8	7	2.2	- 1.2
0	16	4	2.3	2.6	0	9	7	2.6	1.5
0	1	5	11.7	11.7	1	1	1	27.6	29.6
0	2	5	1.1	- 2.3	1	2	1	24.8	24.3
0	5	5	4.9	4.4	1	3	1	24.3	23.6
0	6	5	3.7	3.0	1	4	1	31.1	30.2
0	8	5	3.5	3.3	1	5	1	10.9	-12.0
0	9	5	4.3	- 4.6	1	6	1	15.4	15.0

h	k	l	$ P_o $	P_c	h	k	l	$ P_o $	P_c
1	7	1	16.8	-19.0	3	2	1	8.9	10.6
1	8	1	15.0	-15.0	3	3	1	9.4	- 8.6
1	9	1	10.3	11.1	3	4	1	13.4	12.6
1	10	1	13.0	-12.8	3	5	1	8.0	- 8.7
1	11	1	5.9	6.4	3	6	1	7.4	- 6.2
1	12	1	2.6	- 1.8	3	7	1	3.0	- 2.5
1	14	1	3.0	- 3.6	3	9	1	2.8	- 2.6
1	16	1	3.3	- 2.7	3	10	1	3.5	3.2
2	1	1	23.5	-23.3	3	15	1	4.1	- 4.3
2	2	1	1.1	- 1.5	3	16	1	1.6	1.3
2	3	1	5.7	- 5.7	3	17	1	1.6	- 1.6
2	4	1	1.6	- 1.6	4	1	1	2.1	1.5
2	5	1	14.1	-14.9	4	3	1	7.7	8.3
2	6	1	16.3	14.5	4	4	1	15.2	-14.2
2	7	1	3.0	- 2.7	4	16	1	3.3	- 2.4
2	8	1	5.8	- 1.1	4	17	1	5.9	- 6.7
2	9	1	3.3	- 4.7	4	18	1	8.5	9.7
2	10	1	5.1	- 6.4	4	9	1	8.9	5.3
2	11	1	3.0	- 2.8	4	11	1	4.3	4.9
2	13	1	2.0	2.6	4	13	1	2.0	- 2.2
2	14	1	2.6	- 2.2	4	14	1	2.0	1.6
2	15	1	3.3	- 3.8	4	16	1	1.1	1.2
2	17	1	2.3	- 2.1	5	1	1	10.5	- 9.4
3	1	1	14.8	-12.6	5	3	1	15.5	14.0

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
5	4	1	22.0	-19.4	1	2	2	23.5	-23.1
5	5	1	11.3	11.7	1	3	2	21.4	21.5
5	6	1	4.8	- 3.8	1	4	2	15.8	14.4
5	8	1	4.9	4.8	1	5	2	14.9	-11.2
5	9	1	3.0	2.6	1	6	2	33.3	34.1
5	11	1	2.0	2.0	1	8	2	8.2	9.6
5	12	1	1.6	1.8	1	11	2	11.9	-11.6
5	13	1	1.6	- 1.5	1	13	2	3.7	- 3.6
6	1	1	5.5	- 5.7	2	1	2	11.0	12.0
6	2	1	1.1	- 1.3	2	2	2	15.9	-16.4
6	3	1	1.1	1.4	2	4	2	7.6	- 7.1
6	4	1	3.3	- 3.4	2	5	2	3.3	- 3.4
6	5	1	3.3	3.7	2	6	2	3.7	- 3.6
6	6	1	4.6	- 4.7	2	9	2	4.6	- 4.8
6	7	1	2.8	2.5	2	10	2	3.0	2.7
6	8	1	3.0	- 3.2	2	12	2	3.7	- 4.5
6	12	1	1.9	1.3	2	15	2	3.0	- 2.7
6	13	1	2.0	- 1.9	2	16	2	2.3	2.5
7	2	1	3.9	3.5	3	1	2	2.8	- 3.6
7	3	1	3.0	- 2.4	3	2	2	6.3	- 6.1
7	7	1	2.3	- 2.0	3	3	2	5.7	- 5.9
7	8	1	1.6	1.8	3	4	2	5.3	- 5.7
7	9	1	2.0	- 1.8	3	5	2	4.4	3.6
1	1	2	20.7	21.5	3	6	2	1.6	- 1.7

n	k	l	$ F_o $	F_c	n	k	l	$ F_o $	F_c
3	7	2	3.5	3.2	5	12	2	1.6	1.6
3	10	2	4.9	- 5.5	6	1	2	2.3	- 2.5
3	11	2	2.6	2.6	6	2	2	2.8	2.8
3	12	2	4.8	- 5.3	6	3	2	5.6	- 5.6
3	13	2	3.3	3.5	6	5	2	3.7	- 3.7
4	3	2	5.8	6.5	6	9	2	2.3	2.4
4	4	2	5.9	- 5.8	6	10	2	3.3	- 2.8
4	6	2	6.1	6.2	6	11	2	1.6	1.1
4	7	2	4.9	- 4.9	1	1	3	4.3	4.5
4	8	2	1.6	- 1.3	1	2	3	34.5	-35.8
4	10	2	4.8	- 4.7	1	4	3	5.7	- 5.2
4	11	2	2.0	1.8	1	5	3	2.8	2.6
4	13	2	3.5	3.2	1	6	3	4.8	- 5.3
4	15	2	1.1	1.5	1	7	3	12.5	12.7
5	1	2	2.3	- 3.0	1	8	3	5.3	- 4.6
5	2	2	5.9	5.5	1	9	3	7.2	7.8
5	3	2	4.1	- 4.1	1	10	3	4.8	5.1
5	4	2	5.9	- 6.3	1	11	3	6.1	5.8
5	5	2	2.3	- 2.5	1	15	3	3.9	- 3.4
5	6	2	1.6	1.7	2	1	3	9.8	- 8.0
5	7	2	1.1	- 1.3	2	2	3	5.3	- 5.9
5	8	2	1.1	- 1.2	2	3	3	7.7	- 8.6
5	10	2	1.1	- 1.4	2	4	3	4.6	- 5.0
5	11	2	1.1	1.2	2	5	3	5.7	5.1

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	6	3	3.9	- 3.7	4	9	3	1.6	- 1.5
2	7	3	1.6	- 2.7	4	10	3	3.0	2.6
2	8	3	2.0	2.7	4	11	3	2.0	- 1.8
2	9	3	3.7	- 4.2	4	12	3	1.1	- 0.4
2	11	3	3.7	3.4	4	13	3	2.3	- 1.4
2	12	3	3.5	- 2.3	5	2	3	2.3	2.3
3	1	3	3.5	- 3.6	5	3	3	9.8	8.6
3	2	3	2.3	1.9	5	4	3	7.9	7.2
3	3	3	3.0	- 2.8	5	5	3	3.0	2.7
3	4	3	3.5	- 4.1	5	7	3	3.5	- 3.3
3	5	3	3.5	- 3.7	5	8	3	2.8	- 2.9
3	7	3	7.0	- 6.8	5	10	3	2.3	- 1.7
3	8	3	4.9	5.0	6	3	3	3.0	2.7
3	9	3	4.9	- 4.5	6	4	3	1.6	1.6
3	10	3	4.8	4.4	6	5	3	2.3	- 2.0
3	15	3	1.1	- 0.9	6	6	3	2.3	1.9
4	1	3	4.4	- 4.8	6	7	3	4.1	- 3.3
4	2	3	4.4	- 4.6	6	8	3	2.0	- 1.5
4	3	3	8.8	8.8	1	1	4	5.2	5.3
4	4	3	4.4	3.9	1	2	4	15.2	16.1
4	5	3	2.6	1.8	1	3	4	2.6	- 2.4
4	6	3	3.5	4.0	1	4	4	5.8	7.2
4	7	3	2.6	- 2.3	1	5	4	11.6	-10.6
4	8	3	2.3	1.7	1	6	4	6.2	- 6.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
1	7	4	7.5	- 6.5	2	1	5	3.5	- 3.2
1	14	4	3.3	3.5	2	3	5	3.5	3.5
2	1	4	4.3	- 4.9	2	7	5	2.3	- 2.2
2	4	4	6.5	- 6.3	2	9	5	2.0	- 2.2
3	4	4	4.9	- 6.3	2	10	5	1.6	- 1.8
3	5	4	3.5	4.2	3	1	5	5.8	- 5.7
3	6	4	3.5	- 4.5	3	2	5	1.6	1.8
3	7	4	1.4	1.6	3	3	5	1.6	- 2.0
4	1	4	4.1	4.1	4	1	5	2.3	- 2.2
4	4	4	4.6	- 4.3	4	3	5	1.6	- 1.3
4	6	4	3.0	- 2.2	4	4	5	2.3	2.0
4	7	4	3.9	3.8	4	6	5	1.1	1.4
4	8	4	2.3	1.9	4	7	5	1.1	- 1.1
4	9	4	2.6	2.3	1	3	6	2.3	2.3
5	6	4	4.0	3.5	1	6	6	2.3	1.8
5	7	4	4.6	2.8	1	10	6	2.8	2.5
5	8	4	3.0	2.8	2	4	6	2.3	- 2.4
5	10	4	2.0	- 0.2	3	2	6	1.1	- 1.1
1	1	5	9.0	8.4	3	4	6	2.3	- 1.9
1	3	5	2.0	2.1	3	5	6	2.3	- 1.4
1	4	5	2.3	- 2.2	3	6	6	1.1	0.8
1	5	5	3.3	4.2	I	0	2	12.7	-13.3
1	6	5	3.3	4.3	$\bar{2}$	0	2	8.2	- 8.3
1	10	5	4.8	- 4.8	$\bar{3}$	0	2	9.5	- 9.7

h	k	l	$ F_o $	F_o	h	k	l	$ F_o $	F_o
$\bar{5}$	0	2	18.7	17.9	$\bar{8}$	0	8	3.3	3.5
$\bar{6}$	0	2	12.2	9.1	$\bar{1}$	1	1	29.1	-30.1
$\bar{7}$	0	2	8.1	7.8	$\bar{1}$	2	1	14.8	-16.0
$\bar{8}$	0	2	10.4	9.3	$\bar{1}$	3	1	27.9	35.3
$\bar{10}$	0	2	1.1	1.1	$\bar{1}$	4	1	37.8	39.6
$\bar{1}$	0	4	6.7	6.0	$\bar{1}$	5	1	9.4	9.3
$\bar{2}$	0	4	5.6	4.8	$\bar{1}$	6	1	25.4	27.3
$\bar{3}$	0	4	21.3	22.2	$\bar{1}$	7	1	3.5	-4.1
$\bar{4}$	0	4	5.6	6.7	$\bar{1}$	8	1	8.5	8.9
$\bar{7}$	0	4	11.7	-11.5	$\bar{1}$	9	1	2.0	-2.4
$\bar{1}$	0	6	1.6	2.1	$\bar{1}$	10	1	4.4	5.0
$\bar{2}$	0	6	3.7	-4.2	$\bar{1}$	12	1	4.9	-5.8
$\bar{3}$	0	6	2.6	3.0	$\bar{1}$	13	1	3.7	-3.5
$\bar{4}$	0	6	3.7	4.1	$\bar{1}$	14	1	3.7	-3.1
$\bar{6}$	0	6	3.5	-2.9	$\bar{1}$	15	1	2.6	-2.4
$\bar{7}$	0	6	4.8	-6.0	$\bar{1}$	17	1	4.6	4.9
$\bar{9}$	0	6	2.8	2.9	$\bar{1}$	18	1	1.1	-0.7
$\bar{10}$	0	6	1.6	-1.8	$\bar{1}$	19	1	1.6	2.0
$\bar{1}$	0	8	2.0	-2.7	$\bar{2}$	2	1	34.9	41.2
$\bar{2}$	0	8	5.1	-4.5	$\bar{2}$	3	1	29.1	-29.8
$\bar{3}$	0	8	2.0	-2.1	$\bar{2}$	4	1	4.8	-5.4
$\bar{4}$	0	8	2.6	2.8	$\bar{2}$	5	1	5.3	-5.0
$\bar{5}$	0	8	2.0	-1.8	$\bar{2}$	7	1	29.9	-25.6
$\bar{6}$	0	8	3.3	-3.8	$\bar{2}$	8	1	13.8	14.3

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{2}$	9	1	21.1	-18.7	$\bar{4}$	9	1	3.5	3.5
$\bar{2}$	10	1	3.3	3.6	$\bar{4}$	10	1	3.0	2.5
$\bar{2}$	11	1	2.6	2.8	$\bar{4}$	11	1	6.3	5.7
$\bar{2}$	12	1	4.4	- 5.0	$\bar{4}$	12	1	3.7	3.3
$\bar{2}$	14	1	3.7	- 3.9	$\bar{4}$	15	1	3.0	- 3.2
$\bar{2}$	17	1	2.8	2.1	$\bar{4}$	16	1	2.6	- 2.4
$\bar{3}$	1	1	8.2	- 8.8	$\bar{5}$	1	1	13.9	14.8
$\bar{3}$	2	1	15.3	-15.8	$\bar{5}$	2	1	7.1	- 7.3
$\bar{3}$	3	1	12.7	-14.2	$\bar{5}$	3	1	4.4	3.4
$\bar{3}$	4	1	4.7	5.0	$\bar{5}$	4	1	8.8	- 8.1
$\bar{3}$	5	1	3.7	2.1	$\bar{5}$	5	1	4.6	5.6
$\bar{3}$	7	1	15.2	-13.1	$\bar{5}$	7	1	3.3	- 3.5
$\bar{3}$	8	1	4.3	4.4	$\bar{5}$	8	1	4.9	- 5.3
$\bar{3}$	9	1	11.3	-10.0	$\bar{5}$	9	1	2.6	- 2.9
$\bar{3}$	10	1	6.7	- 6.8	$\bar{5}$	10	1	2.3	1.9
$\bar{3}$	11	1	3.5	3.7	$\bar{5}$	11	1	10.3	10.4
$\bar{3}$	12	1	10.2	- 8.6	$\bar{5}$	12	1	8.8	9.0
$\bar{4}$	1	1	21.7	18.1	$\bar{5}$	13	1	6.4	5.1
$\bar{4}$	2	1	33.7	-32.9	$\bar{5}$	14	1	1.1	1.3
$\bar{4}$	4	1	4.8	- 4.9	$\bar{5}$	15	1	2.0	- 2.3
$\bar{4}$	5	1	1.1	- 0.9	$\bar{6}$	1	1	4.3	- 4.2
$\bar{4}$	6	1	2.0	- 1.6	$\bar{6}$	2	1	1.6	- 2.1
$\bar{4}$	7	1	6.3	5.6	$\bar{6}$	3	1	1.1	- 0.9
$\bar{4}$	8	1	4.4	- 4.5	$\bar{6}$	4	1	4.9	- 4.0

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{6}$	5	1	2.0	1.9	$\bar{1}$	3	2	11.3	9.3
$\bar{6}$	7	1	7.2	- 6.1	$\bar{1}$	4	2	21.4	-22.3
$\bar{6}$	8	1	2.3	- 2.4	$\bar{1}$	6	2	6.7	- 6.2
$\bar{6}$	9	1	1.1	1.5	$\bar{1}$	7	2	14.4	15.2
$\bar{6}$	10	1	4.8	- 4.0	$\bar{1}$	8	2	21.5	13.8
$\bar{6}$	11	1	5.3	5.2	$\bar{1}$	9	2	5.7	6.6
$\bar{6}$	12	1	3.3	4.2	$\bar{1}$	10	2	3.5	4.1
$\bar{6}$	13	1	1.1	- 1.6	$\bar{1}$	11	2	4.8	3.8
$\bar{7}$	1	1	11.1	-11.0	$\bar{1}$	13	2	5.1	- 3.4
$\bar{7}$	4	1	5.1	- 4.8	$\bar{1}$	14	2	7.2	6.3
$\bar{7}$	6	1	7.0	- 5.8	$\bar{1}$	15	2	4.1	- 3.6
$\bar{7}$	9	1	1.6	2.3	$\bar{1}$	16	2	3.3	- 3.0
$\bar{7}$	12	1	3.3	2.9	$\bar{1}$	17	2	2.6	2.2
$\bar{7}$	13	1	3.0	- 2.7	$\bar{1}$	18	2	5.3	- 5.5
$\bar{8}$	1	1	3.3	- 3.5	$\bar{2}$	1	2	23.3	- 21.6
$\bar{8}$	2	1	1.1	- 2.0	$\bar{2}$	2	2	35.6	-37.0
$\bar{8}$	3	1	1.1	2.4	$\bar{2}$	3	2	16.9	17.4
$\bar{8}$	4	1	4.4	- 5.1	$\bar{2}$	4	2	33.6	-33.7
$\bar{9}$	1	1	1.1	1.2	$\bar{2}$	5	2	40.4	37.9
$\bar{9}$	5	1	1.1	1.3	$\bar{2}$	6	2	8.5	- 9.6
$\bar{9}$	6	1	1.1	0.9	$\bar{2}$	7	2	4.6	- 2.7
$\bar{9}$	7	1	2.0	1.4	$\bar{2}$	8	2	3.6	3.0
$\bar{1}$	1	2	35.6	35.4	$\bar{2}$	9	2	5.8	- 7.0
$\bar{1}$	2	2	3.7	- 3.4	$\bar{2}$	11	2	3.3	- 3.5

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{2}$	13	2	4.0	- 4.2	$\bar{4}$	15	2	2.3	1.8
$\bar{2}$	14	2	3.5	3.0	$\bar{4}$	16	2	2.0	1.8
$\bar{2}$	16	2	4.0	- 3.7	$\bar{5}$	1	2	4.1	3.6
$\bar{2}$	17	2	3.5	3.6	$\bar{5}$	2	2	12.0	11.6
$\bar{2}$	18	2	3.9	- 4.6	$\bar{5}$	3	2	9.6	7.7
$\bar{3}$	1	2	8.0	- 9.4	$\bar{5}$	4	2	8.9	7.1
$\bar{3}$	3	2	17.5	15.7	$\bar{5}$	7	2	4.8	- 4.0
$\bar{3}$	4	2	20.9	-21.0	$\bar{5}$	12	2	3.5	- 4.0
$\bar{3}$	5	2	5.1	5.5	$\bar{5}$	13	2	2.3	- 0.7
$\bar{3}$	6	2	8.9	- 8.7	$\bar{5}$	14	2	1.6	1.5
$\bar{3}$	7	2	15.5	-16.3	$\bar{5}$	16	2	4.3	3.7
$\bar{3}$	8	2	12.4	11.7	$\bar{5}$	17	2	3.1	2.3
$\bar{3}$	9	2	3.5	- 4.2	$\bar{6}$	2	2	1.6	- 3.4
$\bar{3}$	11	2	3.5	- 0.7	$\bar{6}$	3	2	1.6	2.6
$\bar{3}$	13	2	2.6	- 2.5	$\bar{6}$	4	2	4.8	- 3.8
$\bar{3}$	16	2	1.6	- 1.3	$\bar{6}$	5	2	7.0	- 6.1
$\bar{4}$	1	2	16.3	14.9	$\bar{6}$	6	2	6.1	5.7
$\bar{4}$	2	2	27.5	29.1	$\bar{6}$	7	2	8.9	- 7.3
$\bar{4}$	3	2	8.6	10.1	$\bar{6}$	8	2	1.6	- 2.2
$\bar{4}$	4	2	15.7	15.7	$\bar{6}$	9	2	8.1	8.5
$\bar{4}$	5	2	8.7	- 9.6	$\bar{6}$	10	2	8.0	- 8.8
$\bar{4}$	6	2	9.8	- 9.0	$\bar{6}$	11	2	3.3	3.5
$\bar{4}$	7	2	6.5	- 6.9	$\bar{6}$	12	2	2.8	- 3.3
$\bar{4}$	14	2	4.4	3.8	$\bar{6}$	13	2	1.1	- 1.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{6}$	15	2	2.8	1.6	$\bar{1}$	13	3	3.7	- 3.9
$\bar{7}$	3	2	7.2	- 7.4	$\bar{1}$	14	3	10.3	9.7
$\bar{7}$	4	2	6.3	- 6.4	$\bar{1}$	15	3	5.6	- 5.2
$\bar{7}$	5	2	7.2	- 6.8	$\bar{2}$	1	3	62.7	-55.1
$\bar{7}$	8	2	5.8	- 5.9	$\bar{2}$	2	3	13.4	12.4
$\bar{7}$	9	2	4.6	3.8	$\bar{2}$	3	3	6.3	- 5.3
$\bar{7}$	10	2	7.7	- 7.5	$\bar{2}$	4	3	8.7	- 8.3
$\bar{7}$	15	2	1.1	- 0.1	$\bar{2}$	6	3	14.8	-13.4
$\bar{8}$	3	2	1.1	- 1.8	$\bar{2}$	7	3	2.6	- 2.0
$\bar{8}$	4	2	3.5	- 3.7	$\bar{2}$	8	3	2.3	- 1.4
$\bar{8}$	5	2	1.6	- 2.0	$\bar{2}$	9	3	8.3	7.0
$\bar{8}$	8	2	1.1	- 1.8	$\bar{2}$	10	3	3.9	- 4.0
$\bar{9}$	4	2	1.6	1.9	$\bar{2}$	11	3	1.1	0.9
$\bar{9}$	7	2	1.1	- 0.9	$\bar{2}$	12	3	5.2	5.2
$\bar{1}$	1	3	18.4	-20.7	$\bar{2}$	13	3	10.6	- 9.3
$\bar{1}$	3	3	12.5	-13.7	$\bar{2}$	14	3	8.0	7.5
$\bar{1}$	4	3	4.9	- 5.1	$\bar{2}$	15	3	3.3	- 3.3
$\bar{1}$	5	3	13.8	14.4	$\bar{2}$	16	3	2.0	- 1.8
$\bar{1}$	6	3	6.4	6.0	$\bar{2}$	17	3	2.6	2.3
$\bar{1}$	7	3	4.6	- 5.2	$\bar{3}$	1	3	32.4	-29.8
$\bar{1}$	8	3	4.9	- 4.7	$\bar{3}$	3	3	14.5	14.3
$\bar{1}$	10	3	8.8	- 8.9	$\bar{3}$	4	3	18.1	-17.8
$\bar{1}$	11	3	14.0	12.1	$\bar{3}$	5	3	4.6	4.2
$\bar{1}$	12	3	8.8	8.3	$\bar{3}$	7	3	3.0	- 1.7

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{3}$	8	3	3.3	- 2.5	$\bar{6}$	6	3	11.9	12.5
$\bar{3}$	10	3	6.4	- 6.5	$\bar{6}$	7	3	10.1	-11.3
$\bar{3}$	16	3	1.1	- 1.3	$\bar{6}$	8	3	2.3	1.8
$\bar{4}$	1	3	16.4	15.0	$\bar{6}$	9	3	1.1	- 1.0
$\bar{4}$	2	3	4.1	5.3	$\bar{6}$	10	3	1.1	- 1.7
$\bar{4}$	4	3	3.7	- 1.7	$\bar{6}$	11	3	1.1	- 1.0
$\bar{4}$	5	3	13.6	12.2	$\bar{6}$	14	3	1.6	- 1.4
$\bar{4}$	6	3	12.5	11.7	$\bar{7}$	1	3	1.1	2.9
$\bar{4}$	7	3	12.3	10.8	$\bar{7}$	4	3	11.7	9.6
$\bar{4}$	10	3	12.1	- 9.4	$\bar{7}$	5	3	8.6	- 9.6
$\bar{4}$	12	3	1.6	- 1.8	$\bar{7}$	6	3	6.7	5.9
$\bar{5}$	1	3	5.6	5.6	$\bar{7}$	7	3	8.6	- 8.9
$\bar{5}$	3	3	5.8	6.0	$\bar{7}$	8	3	6.6	- 6.7
$\bar{5}$	4	3	6.1	6.4	$\bar{7}$	10	3	3.0	- 2.6
$\bar{5}$	5	3	8.1	7.4	$\bar{7}$	14	3	2.0	- 1.5
$\bar{5}$	6	3	7.1	6.0	$\bar{8}$	3	3	1.6	2.4
$\bar{5}$	7	3	4.4	4.7	$\bar{8}$	4	3	6.0	4.9
$\bar{5}$	8	3	4.0	4.2	$\bar{8}$	5	3	3.5	2.7
$\bar{5}$	11	3	3.0	- 2.6	$\bar{8}$	7	3	2.3	- 2.5
$\bar{5}$	16	3	3.3	- 2.7	$\bar{8}$	8	3	2.8	- 2.3
$\bar{6}$	2	3	11.3	-11.4	$\bar{8}$	9	3	2.0	- 1.6
$\bar{6}$	3	3	14.8	12.7	$\bar{9}$	1	3	3.7	2.7
$\bar{6}$	4	3	6.7	6.0	$\bar{9}$	3	3	2.8	2.0
$\bar{6}$	5	3	13.8	-11.8	$\bar{9}$	8	3	1.1	0.7

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\overline{10}$	1	3	0.9	0.3	$\overline{2}$	10	4	16.5	-15.9
$\overline{10}$	3	3	0.7	- 0.4	$\overline{2}$	11	4	4.8	4.7
$\overline{10}$	5	3	1.6	0.7	$\overline{2}$	13	4	4.6	- 3.8
$\overline{1}$	1	4	8.8	- 8.1	$\overline{2}$	14	4	2.0	2.2
$\overline{1}$	2	4	8.4	- 7.4	$\overline{2}$	15	4	1.6	1.2
$\overline{1}$	4	4	4.4	- 4.6	$\overline{3}$	2	4	2.8	- 2.7
$\overline{1}$	5	4	14.3	-13.3	$\overline{3}$	3	4	11.6	-10.5
$\overline{1}$	6	4	8.5	8.1	$\overline{3}$	4	4	11.9	-11.6
$\overline{1}$	7	4	12.9	-12.1	$\overline{3}$	5	4	7.6	- 8.9
$\overline{1}$	9	4	13.6	14.7	$\overline{3}$	6	4	3.5	3.4
$\overline{1}$	10	4	12.7	-10.7	$\overline{3}$	13	4	2.8	- 2.7
$\overline{1}$	11	4	7.4	8.0	$\overline{3}$	17	4	1.1	0.9
$\overline{1}$	12	4	7.2	- 6.9	$\overline{4}$	4	4	10.8	10.1
$\overline{1}$	15	4	3.9	3.6	$\overline{4}$	6	4	8.4	8.6
$\overline{1}$	16	4	1.6	1.6	$\overline{4}$	7	4	6.3	- 5.6
$\overline{2}$	1	4	14.9	-12.8	$\overline{4}$	8	4	3.3	3.1
$\overline{2}$	2	4	11.5	-10.5	$\overline{4}$	9	4	1.6	2.7
$\overline{2}$	3	4	21.2	-20.4	$\overline{4}$	10	4	8.4	6.8
$\overline{2}$	4	4	15.2	-16.3	$\overline{4}$	11	4	2.6	2.2
$\overline{2}$	5	4	15.8	-15.2	$\overline{4}$	13	4	1.6	- 2.1
$\overline{2}$	6	4	3.5	4.5	$\overline{4}$	14	4	1.6	- 1.9
$\overline{2}$	7	4	3.0	- 3.1	$\overline{4}$	15	4	2.6	- 2.1
$\overline{2}$	8	4	5.2	- 6.6	$\overline{5}$	3	4	3.5	4.1
$\overline{2}$	9	4	12.6	11.4	$\overline{5}$	5	4	4.3	3.9

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{5}$	7	4	3.3	3.6	$\bar{8}$	11	4	2.0	- 1.5
$\bar{5}$	9	4	3.5	3.8	$\bar{9}$	1	4	1.1	1.5
$\bar{5}$	10	4	3.5	4.2	$\bar{9}$	2	4	1.1	1.6
$\bar{5}$	12	4	3.3	3.3	$\bar{9}$	3	4	2.0	1.9
$\bar{5}$	13	4	2.0	- 1.4	$\bar{9}$	8	4	1.6	1.6
$\bar{5}$	14	4	1.1	- 1.3	$\bar{1}$	1	5	4.3	5.2
$\bar{5}$	16	4	1.1	- 1.0	$\bar{1}$	2	5	11.3	-11.6
$\bar{6}$	2	4	5.4	- 6.3	$\bar{1}$	3	5	11.3	11.1
$\bar{6}$	3	4	18.0	16.5	$\bar{1}$	5	5	11.9	-11.9
$\bar{6}$	4	4	7.7	- 7.0	$\bar{1}$	6	5	9.7	10.4
$\bar{6}$	7	4	3.3	3.8	$\bar{1}$	7	5	13.6	-13.5
$\bar{6}$	11	4	3.3	- 3.3	$\bar{1}$	8	5	3.9	4.3
$\bar{6}$	14	4	2.0	- 1.8	$\bar{1}$	9	5	4.6	- 5.2
$\bar{6}$	15	4	1.6	1.3	$\bar{1}$	11	5	3.3	- 2.8.
$\bar{7}$	1	4	10.1	11.3	$\bar{1}$	12	5	3.0	2.7
$\bar{7}$	2	4	9.3	- 9.5	$\bar{2}$	1	5	4.4	4.2
$\bar{7}$	3	4	8.3	7.8	$\bar{2}$	2	5	4.9	- 4.3
$\bar{7}$	5	4	3.5	- 3.5	$\bar{2}$	3	5	8.8	8.0
$\bar{7}$	6	4	4.8	4.8	$\bar{2}$	4	5	5.2	5.4
$\bar{7}$	7	4	3.5	3.0	$\bar{2}$	5	5	19.7	-17.7
$\bar{7}$	11	4	4.0	- 4.2	$\bar{2}$	6	5	10.4	9.4
$\bar{7}$	12	4	2.6	- 2.0	$\bar{2}$	7	5	19.8	-17.0
$\bar{7}$	13	4	1.1	- 1.5	$\bar{2}$	8	5	7.7	- 6.9
$\bar{8}$	8	4	4.1	3.8	$\bar{2}$	10	5	3.5	- 3.3

$\bar{h}$	k	l	$ F_o $	F_c	$\bar{h}$	k	l	$ F_o $	F_c
$\bar{2}$	12	5	3.7	3.6	$\bar{5}$	14	5	1.6	1.5
$\bar{2}$	14	5	1.1	- 1.3	$\bar{5}$	15	5	1.1	0.3
$\bar{3}$	2	5	3.7	- 2.8	$\bar{6}$	2	5	12.0	-11.7
$\bar{3}$	3	5	9.7	- 7.1	$\bar{6}$	3	5	11.2	-10.0
$\bar{3}$	4	5	4.6	4.1	$\bar{6}$	4	5	2.3	1.8
$\bar{3}$	5	5	4.6	4.6	$\bar{6}$	5	5	7.7	7.0
$\bar{3}$	6	5	2.6	- 2.5	$\bar{6}$	6	5	4.6	4.2
$\bar{3}$	7	5	5.2	- 5.4	$\bar{6}$	7	5	5.2	5.6
$\bar{3}$	8	5	6.4	- 5.3	$\bar{6}$	8	5	2.3	- 2.5
$\bar{4}$	2	5	7.0	- 6.1	$\bar{6}$	10	5	2.0	2.2
$\bar{4}$	3	5	7.4	7.0	$\bar{6}$	11	5	2.0	- 1.6
$\bar{4}$	5	5	3.5	3.9	$\bar{6}$	12	5	2.3	2.3
$\bar{4}$	6	5	3.0	- 2.5	$\bar{7}$	2	5	13.3	-13.2
$\bar{4}$	7	5	4.3	4.0	$\bar{7}$	3	5	9.3	- 9.6
$\bar{4}$	8	5	3.1	2.0	$\bar{7}$	7	5	3.0	3.2
$\bar{4}$	13	5	1.6	1.7	$\bar{7}$	11	5	2.3	1.7
$\bar{4}$	14	5	4.1	2.8	$\bar{8}$	9	5	2.3	1.4
$\bar{5}$	2	5	2.6	2.3	$\bar{8}$	10	5	1.6	- 1.7
$\bar{5}$	4	5	3.0	2.6	$\bar{8}$	11	5	4.4	3.0
$\bar{5}$	7	5	7.7	6.6	$\bar{9}$	3	5	1.1	0.8
$\bar{5}$	8	5	2.0	- 2.5	$\bar{9}$	4	5	1.1	- 1.5
$\bar{5}$	9	5	2.3	2.3	$\bar{9}$	5	5	1.6	1.4
$\bar{5}$	11	5	1.6	- 1.8	$\bar{9}$	6	5	2.3	2.1
$\bar{5}$	12	5	3.0	2.9	$\bar{10}$	1	5	3.3	1.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\overline{10}$	3	5	3.0	- 1.3	$\overline{4}$	8	6	3.5	4.0
$\overline{1}$	1	6	12.5	12.4	$\overline{4}$	11	6	2.3	2.2
$\overline{1}$	3	6	11.3	13.4	$\overline{4}$	13	6	2.3	- 2.2
$\overline{1}$	4	6	5.3	- 5.5	$\overline{4}$	14	6	2.3	2.5
$\overline{1}$	5	6	3.9	3.0	$\overline{5}$	4	6	2.3	3.3
$\overline{1}$	6	6	3.9	- 3.2	$\overline{5}$	5	6	3.5	- 2.9
$\overline{1}$	7	6	3.5	3.2	$\overline{5}$	7	6	3.5	3.7
$\overline{1}$	8	6	3.5	- 2.4	$\overline{5}$	9	6	3.0	2.6
$\overline{1}$	11	6	3.5	2.9	$\overline{5}$	11	6	2.3	2.1
$\overline{2}$	1	6	14.4	13.8	$\overline{6}$	4	6	2.3	- 1.7
$\overline{2}$	2	6	8.9	- 8.6	$\overline{6}$	5	6	6.3	- 7.0
$\overline{2}$	3	6	9.1	10.6	$\overline{6}$	6	6	8.2	- 8.9
$\overline{2}$	5	6	3.9	- 3.4	$\overline{6}$	8	6	1.1	- 1.7
$\overline{2}$	6	6	3.9	3.7	$\overline{6}$	9	6	4.1	4.7
$\overline{2}$	7	6	3.9	4.1	$\overline{6}$	10	6	2.3	3.4
$\overline{2}$	8	6	3.5	- 4.0	$\overline{6}$	11	6	1.6	1.5
$\overline{2}$	11	6	4.1	- 4.6	$\overline{6}$	13	6	1.1	0.8
$\overline{3}$	5	6	2.0	- 2.2	$\overline{1}$	1	7	8.2	- 8.0
$\overline{3}$	6	6	1.6	1.6	$\overline{1}$	2	7	2.3	- 2.6
$\overline{3}$	7	6	2.0	2.3	$\overline{1}$	3	7	4.6	- 4.6
$\overline{3}$	9	6	2.3	2.5	$\overline{1}$	4	7	3.0	3.3
$\overline{3}$	11	6	3.0	- 3.1	$\overline{1}$	5	7	2.3	2.3
$\overline{3}$	13	6	2.6	- 2.7	$\overline{1}$	6	7	3.0	3.4
$\overline{3}$	14	6	2.0	1.8	$\overline{1}$	7	7	3.5	3.8

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{2}$	1	7	2.6	- 3.5	$\bar{5}$	12	7	2.3	1.5
$\bar{2}$	2	7	8.6	- 9.1	$\bar{6}$	2	7	2.3	2.2
$\bar{2}$	3	7	7.5	- 6.7	$\bar{6}$	3	7	3.0	- 3.3
$\bar{2}$	4	7	3.5	3.3	$\bar{6}$	4	7	1.1	1.8
$\bar{2}$	6	7	3.0	2.5	$\bar{6}$	5	7	2.3	- 2.0
$\bar{2}$	7	7	3.0	2.6	$\bar{6}$	7	7	1.1	- 1.0
$\bar{2}$	10	7	1.6	0.4	$\bar{6}$	8	7	1.1	- 0.9
$\bar{3}$	2	7	2.0	- 2.1	$\bar{6}$	9	7	5.6	- 5.2
$\bar{3}$	4	7	2.0	2.0	$\bar{6}$	11	7	2.8	- 1.9
$\bar{3}$	8	7	3.0	- 2.1	$\bar{1}$	2	8	1.6	- 1.2
$\bar{3}$	9	7	2.6	1.8	$\bar{1}$	3	8	2.3	2.4
$\bar{3}$	10	7	2.3	- 1.9	$\bar{1}$	6	8	2.8	- 3.3
$\bar{3}$	11	7	3.5	3.8	$\bar{2}$	5	8	3.0	- 3.5
$\bar{3}$	12	7	1.1	- 1.1	$\bar{2}$	7	8	2.6	- 2.4
$\bar{4}$	3	7	2.3	2.7	$\bar{3}$	1	8	1.6	1.5
$\bar{4}$	4	7	1.6	- 1.7	$\bar{3}$	4	8	1.6	1.4
$\bar{4}$	5	7	2.3	1.9	$\bar{3}$	5	8	2.3	- 2.4
$\bar{4}$	6	7	4.5	2.8	$\bar{3}$	8	8	2.6	2.5
$\bar{4}$	9	7	2.3	2.3	$\bar{3}$	9	8	1.1	- 1.2
$\bar{4}$	10	7	3.0	- 3.4	$\bar{4}$	3	8	2.3	1.7
$\bar{4}$	11	7	2.8	3.3	$\bar{4}$	5	8	1.6	- 1.3
$\bar{5}$	3	7	2.3	- 2.6	$\bar{4}$	6	8	5.1	3.6
$\bar{5}$	5	7	2.3	- 1.5	$\bar{4}$	7	8	2.8	- 2.8
$\bar{5}$	7	7	2.3	- 2.1	$\bar{5}$	3	8	2.8	2.5

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{5}$	5	8	2.3	2.0	$\bar{6}$	6	8	1.6	- 1.8
$\bar{5}$	8	8	1.6	- 1.2	$\bar{6}$	8	8	1.1	- 0.7
$\bar{6}$	5	8	2.8	3.0					

A P P E N D I X

Observed and calculated structure factors
(o-dimethyl amino benzoic acid)

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	0	0	37.0	-50.5	1	12	0	5.3	- 5.4
4	0	0	3.6	2.2	1	13	0	5.4	4.1
6	0	0	19.3	-23.9	1	14	0	8.1	- 9.2
8	0	0	5.7	4.7	1	16	0	3.8	- 4.3
0	2	0	35.0	45.4	1	17	0	3.4	- 3.5
0	4	0	37.0	-39.7	1	20	0	1.3	3.1
0	6	0	21.4	-23.9	2	1	0	14.3	18.8
0	8	0	12.3	-11.0	2	2	0	14.1	-17.5
0	10	0	8.3	6.7	2	3	0	25.3	25.5
0	12	0	6.6	- 5.8	2	4	0	10.0	9.0
0	18	0	2.6	2.7	2	5	0	7.6	7.1
0	0	2	12.6	-14.9	2	6	0	36.2	35.7
0	0	4	21.9	-25.4	2	7	0	3.0	2.0
0	0	6	3.0	2.9	2	8	0	4.4	3.8
0	0	8	2.6	- 2.6	2	9	0	11.7	- 8.3
1	1	0	29.1	-30.0	2	10	0	8.8	- 7.9
1	2	0	45.3	52.4	2	11	0	9.3	- 7.4
1	4	0	39.7	-45.7	2	12	0	3.8	3.3
1	5	0	12.3	12.9	2	15	0	3.8	3.4
1	6	0	8.8	- 8.6	2	19	0	2.8	- 3.4
1	7	0	9.7	10.4	3	1	0	20.5	-20.3
1	8	0	10.3	-10.1	3	3	0	7.7	7.3
1	9	0	7.0	8.0	3	4	0	31.1	-35.9
1	10	0	8.6	6.9	3	5	0	10.2	- 8.9

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
3	6	0	22.9	-23.3	5	7	0	2.8	- 2.5
3	7	0	11.7	-12.0	5	8	0	7.0	6.6
3	9	0	1.3	0.6	5	9	0	3.6	- 3.3
3	10	0	4.3	- 3.8	5	10	0	3.6	3.2
3	11	0	3.2	- 2.3	5	14	0	3.2	- 3.7
3	12	0	3.2	3.0	5	16	0	1.6	- 2.6
3	13	0	3.2	2.3	6	1	0	11.9	-15.3
4	1	0	2.0	- 2.2	6	2	0	11.1	-12.6
4	2	0	5.9	4.7	6	4	0	10.1	10.6
4	4	0	12.5	-12.8	6	5	0	5.1	4.4
4	5	0	23.5	22.5	6	6	0	10.2	9.7
4	6	0	17.6	-16.2	6	8	0	5.1	4.4
4	7	0	10.8	-9.7	7	1	0	14.3	16.2
4	9	0	4.7	4.5	7	2	0	5.1	4.6
4	14	0	3.6	- 3.1	7	3	0	3.6	- 3.5
4	15	0	4.5	4.5	7	4	0	3.6	3.6
4	16	0	2.8	- 2.7	7	8	0	6.6	- 6.3
4	18	0	2.8	3.5	7	9	0	3.2	2.3
5	1	0	10.6	-11.4	7	10	0	3.2	- 2.9
5	2	0	3.2	3.4	8	2	0	2.2	2.4
5	3	0	11.6	12.6	8	3	0	4.5	- 4.7
5	4	0	3.2	2.8	8	4	0	2.2	- 2.1
5	5	0	5.3	- 5.4	8	5	0	3.9	- 3.6
5	6	0	3.6	- 2.7	8	6	0	3.9	- 3.2

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
8	7	0	3.9	- 3.1	3	0	1	16.8	-18.4
8	8	0	2.2	- 2.9	1	1	1	11.3	-11.6
9	1	0	3.2	- 3.3	1	2	1	18.4	24.7
9	2	0	3.2	2.5	1	3	1	60.5	70.7
9	3	0	3.6	- 3.1	1	4	1	29.1	-32.9
9	4	0	1.6	2.1	1	5	1	34.1	39.3
9	5	0	2.8	3.3	1	6	1	8.0	9.0
9	6	0	2.8	3.0	1	7	1	6.9	- 7.9
9	7	0	4.5	4.1	1	8	1	12.4	13.7
0	2	1	71.7	-84.4	1	9	1	4.7	- 4.1
0	3	1	72.6	78.9	1	12	1	1.8	- 1.5
0	4	1	70.6	-74.6	1	13	1	4.2	4.8
0	5	1	17.8	-17.6	1	14	1	7.1	- 7.3
0	6	1	26.3	22.8	1	16	1	5.5	6.1
0	7	1	3.9	- 4.4	1	17	1	2.6	3.0
0	8	1	9.2	7.8	1	18	1	3.2	3.7
0	9	1	10.2	- 9.3	2	1	1	34.1	38.6
0	10	1	9.1	8.3	2	2	1	31.8	30.7
0	11	1	2.6	- 2.5	2	3	1	28.4	34.3
0	12	1	3.9	4.2	2	4	1	27.7	32.5
0	13	1	2.2	- 1.6	2	5	1	6.1	6.0
0	14	1	4.2	4.0	2	6	1	15.5	-12.7
0	16	1	3.9	3.8	2	7	1	15.8	-13.0
1	0	1	14.8	18.3	2	8	1	12.8	-10.6

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	9	1	4.5	3.6	4	4	1	10.4	- 9.2
2	10	1	5.2	- 4.1	4	5	1	8.0	8.1
2	12	1	5.1	4.5	4	6	1	2.4	3.1
2	13	1	5.1	4.1	4	7	1	2.6	- 1.8
2	14	1	4.2	- 4.1	4	8	1	12.1	11.7
2	15	1	3.0	- 2.9	4	9	1	10.3	-10.5
2	16	1	5.4	- 6.7	4	10	1	3.0	- 3.9
2	17	1	3.8	- 4.9	4	12	1	3.0	- 2.7
2	18	1	1.8	2.2	4	13	1	3.0	2.8
3	1	1	25.0	-25.6	4	15	1	1.8	2.1
3	2	1	26.7	-30.9	5	1	1	5.3	- 4.3
3	3	1	30.6	-32.3	5	2	1	5.3	- 5.2
3	4	1	7.6	- 7.4	5	3	1	5.4	- 5.8
3	5	1	5.5	- 5.1	5	4	1	7.7	- 6.8
3	6	1	22.5	19.6	5	5	1	3.9	- 2.6
3	7	1	17.0	-16.2	5	6	1	5.7	- 5.0
3	8	1	9.6	7.9	5	9	1	1.8	- 1.7
3	9	1	1.8	- 1.7	5	10	1	1.8	- 1.8
3	12	1	2.2	3.0	5	11	1	4.2	- 3.5
3	13	1	2.2	- 1.9	5	12	1	6.8	- 6.4
3	14	1	2.2	2.2	6	2	1	25.5	28.9
3	17	1	1.8	- 2.2	6	3	1	7.2	- 7.2
4	2	1	5.6	- 5.5	6	4	1	9.3	8.1
4	3	1	1.6	- 1.6	6	5	1	3.0	- 2.5

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	6	1	4.2	3.5	1	4	2	2.4	- 1.9
6	9	1	3.9	4.5	1	5	2	10.9	-12.5
6	10	1	3.9	3.6	1	6	2	17.2	18.0
6	11	1	2.6	2.7	1	7	2	35.2	-40.0
7	6	1	5.5	- 4.0	1	8	2	17.0	17.3
7	7	1	2.6	2.3	1	9	2	3.4	3.6
7	8	1	1.8	- 2.2	1	10	2	1.8	- 0.9
7	9	1	1.8	2.0	1	11	2	2.8	2.7
0	1	2	10.2	-11.4	1	12	2	2.0	2.0
0	2	2	51.0	-60.5	1	13	2	8.2	7.0
0	3	2	40.9	39.8	1	14	2	9.7	9.2
0	4	2	29.8	-30.0	1	15	2	3.0	3.2
0	5	2	35.9	-39.8	1	16	2	1.6	1.5
0	6	2	19.6	19.7	1	17	2	3.8	- 4.3
0	7	2	32.7	-36.4	1	18	2	1.3	- 1.5
0	8	2	5.1	3.6	2	1	2	8.4	7.8
0	9	2	3.4	2.5	2	2	2	14.9	15.8
0	13	2	6.4	5.9	2	3	2	19.2	-18.6
0	17	2	1.3	1.9	2	4	2	3.7	- 2.9
2	0	2	35.3	37.7	2	5	2	1.8	- 2.1
4	0	2	3.6	3.4	2	6	2	2.3	- 1.9
1	1	2	26.3	25.4	2	7	2	3.4	2.8
1	2	2	26.2	25.3	2	8	2	2.6	- 2.1
1	3	2	5.9	- 5.9	2	9	2	8.9	7.8

h	k	l	$ F_o $	F_o	h	k	l	$ F_o $	F_o
2	11	2	4.2	4.5	4	6	2	1.6	2.3
2	12	2	9.1	- 8.7	4	7	2	8.5	- 8.8
2	13	2	8.2	- 7.3	4	8	2	3.0	3.2
2	14	2	4.5	- 4.4	4	9	2	3.2	- 3.4
2	15	2	3.9	- 3.3	4	10	2	1.3	- 1.0
2	16	2	3.7	4.2	4	11	2	5.7	5.0
3	1	2	29.3	-33.4	4	12	2	3.0	- 2.5
3	2	2	25.5	25.3	4	15	2	0.9	- 1.6
3	3	2	12.1	11.3	5	1	2	5.4	- 5.6
3	4	2	7.6	7.6	5	2	2	6.7	- 7.6
3	5	2	11.2	11.5	5	4	2	11.3	-11.0
3	6	2	6.1	6.5	5	5	2	3.4	- 3.0
3	7	2	9.4	7.7	5	6	2	3.0	- 2.5
3	8	2	1.8	1.9	5	7	2	3.6	- 2.8
3	9	2	6.7	5.4	5	8	2	5.1	- 5.6
3	10	2	4.8	- 4.1	5	9	2	5.1	- 5.2
3	11	2	6.5	5.8	5	10	2	3.6	- 2.8
3	12	2	3.0	2.9	5	11	2	2.8	2.9
3	13	2	2.0	- 1.4	5	13	2	2.4	2.5
4	1	2	6.7	- 6.4	6	4	2	9.2	-10.2
4	2	2	7.8	9.0	6	5	2	10.1	10.6
4	3	2	2.4	- 2.4	6	6	2	7.1	- 6.9
4	4	2	11.3	10.7	6	7	2	6.4	6.5
4	5	2	1.3	- 0.8	6	11	2	3.4	- 3.5

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	1	3	6.1	6.4	1	10	3	5.5	- 5.4
0	2	3	17.4	-16.0	1	11	3	15.9	17.5
0	3	3	25.4	-23.0	1	12	3	3.0	3.7
0	4	3	17.2	-16.7	1	13	3	4.6	- 5.5
0	5	3	30.7	-29.7	1	14	3	4.5	- 5.4
0	6	3	25.9	23.5	1	15	3	4.2	- 5.5
0	7	3	6.3	- 5.1	2	1	3	20.0	-21.3
0	8	3	11.8	-11.5	2	2	3	1.8	- 1.1
0	9	3	27.2	25.9	2	3	3	3.6	4.0
0	10	3	11.6	-10.6	2	4	3	1.3	- 0.8
0	11	3	8.1	8.1	2	5	3	6.7	0.3
0	12	3	4.6	- 5.1	2	6	3	9.5	- 9.3
1	0	3	2.6	- 0.6	2	7	3	1.8	1.7
3	0	3	19.6	20.1	2	8	3	5.3	- 5.3
5	0	3	3.4	- 2.8	2	9	3	16.5	-15.0
1	1	3	2.0	- 2.4	2	10	3	14.2	-13.1
1	2	3	4.4	6.4	2	11	3	4.6	- 4.9
1	3	3	17.6	-17.3	2	12	3	6.5	6.9
1	4	3	14.8	-14.6	2	13	3	5.7	5.2
1	5	3	5.5	- 4.8	2	14	3	5.5	5.6
1	6	3	7.4	7.0	3	3	3	19.9	22.2
1	7	3	11.8	-11.5	3	4	3	9.1	- 7.8
1	8	3	3.6	3.4	3	5	3	17.4	17.5
1	9	3	7.9	7.7	3	6	3	4.5	- 4.0

h	k	l	$ F_O $	F_C	h	k	l	$ F_O $	F_C
3	7	3	4.6	4.9	6	5	3	9.7	9.9
3	8	3	1.8	1.6	6	6	3	1.6	- 1.9
3	9	3	7.0	7.5	6	7	3	6.6	- 6.3
3	10	3	3.0	- 2.5	6	8	3	2.6	1.7
3	14	3	3.2	4.1	6	9	3	4.2	- 4.4
4	1	3	3.8	4.3	6	12	3	1.8	- 2.2
4	4	3	9.0	- 7.4	7	5	3	4.9	4.1
4	5	3	6.6	5.1	7	6	3	4.7	- 4.5
4	7	3	4.9	4.6	7	8	3	2.0	2.2
4	8	3	4.9	5.3	7	9	3	7.2	- 5.7
4	12	3	1.8	- 2.3	7	10	3	3.3	3.0
4	14	3	2.3	2.4	0	1	4	13.6	-12.2
4	15	3	2.0	- 2.7	0	2	4	5.3	4.4
5	1	3	3.0	- 2.4	0	4	4	13.7	9.5
5	2	3	3.0	- 2.2	0	5	4	10.3	7.2
5	5	3	5.0	- 5.7	0	6	4	14.5	11.8
5	7	3	3.0	- 2.7	0	7	4	17.1	15.1
5	8	3	5.7	5.7	0	9	4	15.9	14.6
5	9	3	4.8	4.3	0	10	4	3.3	- 3.3
5	10	3	3.8	3.6	0	11	4	5.7	-5.9
5	14	3	1.3	1.8	0	12	4	8.5	8.5
6	1	3	3.0	2.4	0	13	4	6.8	- 6.6
6	3	3	5.7	6.5	0	18	4	1.3	- 1.7
6	4	3	4.9	- 4.3	2	0	4	8.9	8.8

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
4	0	4	10.2	-10.8	2	10	4	12.3	11.5
1	1	4	4.3	4.4	2	11	4	7.3	6.9
1	2	4	1.8	1.9	2	14	4	2.4	2.7
1	3	4	2.0	2.2	3	2	4	2.6	- 2.1
1	4	4	3.8	3.8	3	3	4	8.6	7.4
1	5	4	3.0	3.0	3	4	4	6.5	- 6.1
1	6	4	5.4	- 5.3	3	5	4	5.7	5.3
1	7	4	9.4	7.8	3	6	4	9.1	8.9
1	8	4	6.8	5.6	3	7	4	9.3	- 8.3
1	9	4	14.5	15.5	3	9	4	6.9	- 8.3
1	10	4	14.0	-15.5	3	15	4	0.9	1.6
1	11	4	4.1	- 4.2	4	1	4	3.8	- 3.3
1	12	4	4.4	- 3.8	4	2	4	2.8	- 3.3
1	13	4	8.0	- 8.4	4	3	4	1.6	1.0
1	14	4	3.2	3.3	4	5	4	6.8	6.3
1	15	4	3.0	- 2.9	4	9	4	4.5	- 3.6
2	1	4	4.9	4.2	4	10	4	3.0	- 3.3
2	2	4	8.6	- 8.2	4	13	4	2.0	- 2.4
2	3	4	6.9	5.8	5	3	4	4.8	- 4.8
2	4	4	7.1	- 6.4	5	5	4	2.8	2.1
2	5	4	11.4	-10.4	5	6	4	10.5	8.8
2	6	4	16.2	-15.7	5	7	4	3.8	3.4
2	7	4	24.1	-22.8	5	8	4	3.7	3.6
2	8	4	4.1	- 3.6	5	9	4	2.4	2.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
5	11	4	3.0	3.1	0	16	5	1.8	- 2.0
5	12	4	1.8	1.8	1	0	5	11.1	12.3
6	2	4	6.5	5.0	1	1	5	2.3	3.2
6	4	4	3.6	- 3.5	1	2	5	2.8	2.5
6	5	4	3.6	- 3.3	1	3	5	2.3	- 1.1
6	6	4	1.3	0.5	1	4	5	3.4	3.0
6	7	4	6.6	- 4.8	1	5	5	7.8	10.1
6	8	4	5.7	4.1	1	8	5	6.1	- 6.6
6	9	4	2.0	- 1.7	1	9	5	5.5	- 4.8
6	10	4	1.8	- 2.1	1	12	5	3.3	4.3
6	11	4	2.4	3.1	1	13	5	3.9	- 5.7
0	1	5	9.2	8.3	1	14	5	1.8	1.6
0	2	5	11.5	12.0	1	15	5	1.3	2.3
0	3	5	5.3	- 4.8	1	16	5	2.3	- 3.6
0	4	5	12.0	11.0	2	2	5	5.7	- 5.9
0	5	5	6.6	5.6	2	3	5	4.8	- 6.8
0	6	5	7.0	6.1	2	4	5	12.7	-14.0
0	8	5	3.7	2.4	2	5	5	7.0	- 6.5
0	9	5	2.4	2.1	2	6	5	8.9	8.9
0	10	5	1.3	1.7	2	7	5	14.0	13.8
0	11	5	5.5	- 5.7	2	8	5	6.6	7.0
0	12	5	5.1	5.7	2	9	5	4.3	4.1
0	13	5	2.6	- 1.6	2	11	5	4.2	4.0
0	15	5	2.3	1.9	3	2	5	5.1	6.2

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
3	3	5	7.1	7.2	1	4	6	3.0	- 2.8
3	5	5	7.2	- 8.6	1	5	6	9.2	-10.8
3	7	5	7.6	- 9.2	1	6	6	3.0	- 4.6
3	8	5	2.6	2.8	1	8	6	3.0	3.9
3	10	5	4.2	- 5.0	2	1	6	4.2	- 3.5
4	2	5	3.3	3.6	2	2	6	4.2	- 3.4
4	6	5	3.3	- 3.3	2	3	6	10.9	11.6
4	7	5	4.9	- 5.9	2	4	6	10.9	11.4
4	9	5	3.0	- 3.3	2	5	6	9.2	8.3
4	10	5	3.2	- 3.0	2	6	6	3.0	3.6
4	14	5	2.6	1.7	2	9	6	2.6	3.7
5	3	5	3.7	3.0	3	1	6	5.0	6.2
5	4	5	3.4	2.9	3	2	6	3.0	- 4.2
5	5	5	3.4	2.8	3	3	6	3.0	- 3.7
5	7	5	3.2	2.7	3	8	6	2.6	- 3.5
5	9	5	3.0	3.1	3	9	6	1.6	2.7
0	1	6	3.9	- 4.4	4	3	6	2.6	- 4.0
0	2	6	8.0	7.7	4	7	6	1.6	- 1.7
0	3	6	9.0	- 7.9	4	11	6	2.6	3.5
0	5	6	3.0	3.4	0	2	7	4.2	- 4.4
0	6	6	7.1	- 7.1	0	4	7	5.8	- 6.2
0	7	6	3.0	2.9	0	5	7	3.0	4.7
0	8	6	2.3	- 2.5	0	6	7	3.0	- 3.6
0	15	6	4.5	4.1	0	9	7	3.4	- 4.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
0	13	7	1.3	2.0	$\bar{7}$	0	1	12.5	-13.6
1	1	7	4.2	- 5.9	$\bar{9}$	0	1	6.6	- 7.0
1	2	7	4.2	- 4.7	$\bar{1}$	2	1	40.0	-40.5
1	3	7	4.2	- 6.3	$\bar{1}$	3	1	3.0	- 2.5
2	1	7	9.7	8.7	$\bar{1}$	4	1	16.2	-15.7
2	2	7	10.3	11.7	$\bar{1}$	5	1	15.1	13.3
2	3	7	5.5	- 4.7	$\bar{1}$	6	1	20.2	-18.9
2	5	7	3.7	- 3.9	$\bar{1}$	7	1	16.9	17.0
2	6	7	2.6	2.4	$\bar{1}$	8	1	7.5	- 6.7
4	8	7	0.9	2.1	$\bar{1}$	9	1	10.4	11.7
4	9	7	0.9	0.9	$\bar{1}$	10	1	15.8	16.9
0	4	8	2.6	1.9	$\bar{1}$	11	1	11.3	11.6
0	7	8	1.8	- 2.6	$\bar{1}$	12	1	5.5	6.5
0	8	8	1.8	2.3	$\bar{1}$	13	1	4.2	- 4.5
0	11	8	0.9	1.4	$\bar{2}$	1	1	44.6	-51.1
2	1	8	6.4	- 6.1	$\bar{2}$	2	1	12.6	12.2
2	2	8	4.5	4.6	$\bar{2}$	3	1	9.6	- 9.3
2	3	8	4.3	- 3.9	$\bar{2}$	4	1	3.0	2.9
2	6	8	3.7	- 3.5	$\bar{2}$	5	1	7.5	- 7.6
3	5	8	3.0	- 0.9	$\bar{2}$	6	1	7.2	- 8.2
3	6	8	2.6	- 1.9	$\bar{2}$	7	1	6.8	- 7.6
0	6	9	1.8	2.1	$\bar{2}$	8	1	7.8	- 6.9
$\bar{3}$	0	1	19.1	21.9	$\bar{2}$	9	1	14.5	13.3
$\bar{5}$	0	1	16.1	18.5	$\bar{2}$	10	1	15.4	-14.8

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{2}$	11	1	3.9	- 3.1	$\bar{4}$	6	1	4.2	- 4.6
$\bar{2}$	12	1	5.6	- 6.4	$\bar{4}$	7	1	4.7	5.2
$\bar{2}$	13	1	4.2	- 3.8	$\bar{4}$	8	1	4.7	- 4.4
$\bar{2}$	15	1	2.3	1.9	$\bar{4}$	9	1	2.2	2.2
$\bar{3}$	1	1	25.9	28.9	$\bar{4}$	11	1	4.2	- 4.6
$\bar{3}$	2	1	11.9	12.4	$\bar{4}$	12	1	4.2	- 4.5
$\bar{3}$	3	1	7.2	7.7	$\bar{4}$	14	1	3.9	4.5
$\bar{3}$	4	1	7.0	7.2	$\bar{4}$	15	1	2.6	3.3
$\bar{3}$	5	1	10.1	-11.0	$\bar{5}$	1	1	4.9	- 5.7
$\bar{3}$	6	1	8.6	9.8	$\bar{5}$	2	1	6.1	7.6
$\bar{3}$	7	1	3.0	3.1	$\bar{5}$	4	1	3.7	3.7
$\bar{3}$	8	1	19.6	-19.3	$\bar{5}$	5	1	12.0	-14.1
$\bar{3}$	9	1	1.8	2.0	$\bar{5}$	6	1	2.6	3.8
$\bar{3}$	10	1	11.1	-12.1	$\bar{5}$	7	1	3.9	- 4.2
$\bar{3}$	11	1	4.1	- 3.9	$\bar{5}$	9	1	5.8	5.4
$\bar{3}$	12	1	2.0	- 2.0	$\bar{5}$	11	1	3.0	3.3
$\bar{3}$	13	1	4.2	- 3.7	$\bar{5}$	12	1	4.2	4.0
$\bar{3}$	15	1	2.2	- 2.6	$\bar{5}$	13	1	3.9	4.3
$\bar{3}$	16	1	2.6	2.7	$\bar{5}$	15	1	4.5	- 5.0
$\bar{4}$	1	1	8.9	-10.4	$\bar{5}$	16	1	4.7	- 6.1
$\bar{4}$	2	1	19.4	-19.5	$\bar{6}$	1	1	8.0	10.5
$\bar{4}$	3	1	11.7	-12.6	$\bar{6}$	2	1	7.0	7.8
$\bar{4}$	4	1	8.2	- 8.0	$\bar{6}$	3	1	5.8	- 6.8
$\bar{4}$	5	1	10.8	12.2	$\bar{6}$	4	1	22.2	24.5

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	5	1	12.4	-15.8	2	0	2	11.1	12.6
6	6	1	7.2	8.0	4	0	2	21.8	-22.6
6	7	1	4.2	6.0	6	0	2	8.9	8.9
6	9	1	4.2	4.8	8	0	2	5.5	- 6.0
6	11	1	3.9	3.9	1	1	2	8.0	- 8.6
7	1	1	3.0	- 2.6	1	2	2	32.4	-34.4
7	3	1	8.3	- 8.7	1	3	2	5.1	5.3
7	4	1	7.2	7.0	1	5	2	18.5	-18.4
7	5	1	2.3	2.6	1	6	2	22.6	20.3
7	6	1	3.0	3.2	1	7	2	24.3	23.6
7	7	1	3.0	3.5	1	8	2	19.6	19.7
7	9	1	2.6	- 3.4	1	10	2	7.6	- 7.1
7	10	1	5.1	- 5.5	1	11	2	7.8	- 7.8
8	2	1	5.5	- 5.6	1	12	2	8.9	- 9.4
8	4	1	3.7	- 4.1	1	13	2	3.3	- 2.6
8	7	1	3.4	- 4.4	1	14	2	3.3	- 3.7
8	8	1	1.8	1.8	1	16	2	3.4	- 3.8
8	9	1	1.3	- 2.2	2	1	2	11.2	-10.2
8	10	1	3.7	5.5	2	2	2	12.1	-10.4
9	1	1	1.8	1.8	2	3	2	20.0	-16.6
9	2	1	2.3	- 2.4	2	4	2	5.0	- 4.4
9	6	1	1.3	- 2.0	2	5	2	4.4	4.2
9	7	1	1.3	- 2.3	2	6	2	4.2	4.0
9	8	1	1.3	1.5	2	7	2	5.3	4.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
2	8	2	14.9	-11.9	4	9	2	4.9	- 5.5
2	9	2	6.1	- 4.7	4	10	2	5.0	5.3
2	10	2	8.3	- 7.4	4	11	2	11.7	12.8
2	11	2	6.7	- 6.6	4	12	2	9.2	9.3
2	12	2	9.9	8.7	4	13	2	5.8	6.0
2	13	2	8.2	- 8.5	4	14	2	2.8	- 2.4
2	14	2	2.4	2.8	4	15	2	1.8	- 2.1
3	1	2	23.5	24.2	4	18	2	0.9	- 1.6
3	2	2	20.6	-20.8	5	1	2	5.1	- 5.3
3	3	2	29.1	29.0	5	2	2	2.0	- 2.2
3	4	2	2.0	- 2.3	5	3	2	4.4	- 4.8
3	5	2	2.0	3.4	5	4	2	1.3	- 0.3
3	6	2	13.8	-12.5	5	6	2	6.6	6.7
3	7	2	2.3	1.6	5	7	2	6.1	6.0
3	8	2	11.1	- 9.6	5	8	2	5.0	- 5.1
3	9	2	3.7	- 3.4	5	9	2	13.0	13.7
3	11	2	9.8	- 9.7	5	10	2	3.0	3.3
3	12	2	6.5	6.9	5	11	2	3.0	- 2.2
3	18	2	0.9	- 1.3	5	12	2	4.1	- 3.4
4	1	2	22.3	23.0	5	13	2	8.1	- 9.4
4	3	2	20.1	22.4	5	16	2	3.0	3.4
4	5	2	5.9	5.8	5	17	2	1.6	2.3
4	6	2	7.0	6.5	6	1	2	3.9	- 4.9
4	7	2	5.3	- 4.9	6	2	2	2.8	2.3

h	k	l	$ F_0 $	F_0	h	k	l	$ F_0 $	F_0
$\bar{6}$	3	2	8.9	-9.2	$\bar{8}$	10	2	1.8	-2.4
$\bar{6}$	4	2	4.1	4.2	$\bar{9}$	1	2	1.3	0.7
$\bar{6}$	5	2	2.0	2.9	$\bar{9}$	3	2	3.6	-3.4
$\bar{6}$	6	2	10.1	-11.1	$\bar{9}$	4	2	2.0	1.7
$\bar{6}$	7	2	20.2	19.0	$\bar{9}$	7	2	1.8	1.6
$\bar{6}$	8	2	9.2	-10.6	$\bar{3}$	0	3	2.0	-4.0
$\bar{6}$	9	2	5.8	6.5	$\bar{5}$	0	3	5.7	-4.7
$\bar{6}$	11	2	4.7	-4.7	$\bar{7}$	0	3	2.0	2.5
$\bar{6}$	14	2	2.0	2.6	$\bar{9}$	0	3	1.3	-1.0
$\bar{7}$	1	2	2.0	-1.5	$\bar{1}$	1	3	10.6	-10.9
$\bar{7}$	2	2	5.1	4.5	$\bar{1}$	2	3	9.9	10.9
$\bar{7}$	3	2	3.0	-3.1	$\bar{1}$	3	3	9.2	9.3
$\bar{7}$	5	2	3.0	-3.3	$\bar{1}$	4	3	40.2	40.8
$\bar{7}$	6	2	11.5	-12.1	$\bar{1}$	5	3	15.9	16.6
$\bar{7}$	7	2	4.9	-5.5	$\bar{1}$	6	3	13.0	11.5
$\bar{7}$	8	2	3.9	-3.8	$\bar{1}$	8	3	16.3	-16.7
$\bar{7}$	9	2	2.6	-2.5	$\bar{1}$	9	3	6.4	-6.9
$\bar{7}$	11	2	1.3	1.3	$\bar{1}$	10	3	3.3	-2.0
$\bar{8}$	1	2	2.8	2.3	$\bar{1}$	11	3	7.3	-8.0
$\bar{8}$	2	2	2.0	-1.7	$\bar{1}$	12	3	3.4	-3.4
$\bar{8}$	4	2	2.6	2.2	$\bar{1}$	13	3	6.2	-6.7
$\bar{8}$	5	2	4.5	-4.6	$\bar{1}$	17	3	1.3	2.1
$\bar{8}$	6	2	6.2	5.8	$\bar{2}$	1	3	13.3	-14.8
$\bar{8}$	8	2	2.8	3.5	$\bar{2}$	2	3	2.3	0.6

$\bar{h}$	k	l	$\{F_0\}$	F_c	$\bar{h}$	k	l	$\{F_0\}$	F_c
$\bar{2}$	3	3	30.1	29.0	$\bar{4}$	3	3	11.3	-11.5
$\bar{2}$	4	3	3.0	- 2.6	$\bar{4}$	4	3	14.4	15.7
$\bar{2}$	5	3	11.7	11.5	$\bar{4}$	5	3	15.7	-17.7
$\bar{2}$	7	3	3.3	- 2.4	$\bar{4}$	8	3	15.1	15.3
$\bar{2}$	8	3	7.8	7.6	$\bar{4}$	9	3	15.6	16.3
$\bar{2}$	10	3	5.4	6.2	$\bar{4}$	10	3	4.1	5.2
$\bar{2}$	11	3	4.2	- 3.6	$\bar{4}$	11	3	2.3	- 1.6
$\bar{2}$	12	3	4.2	4.5	$\bar{4}$	12	3	1.6	- 2.2
$\bar{2}$	15	3	5.4	7.7	$\bar{4}$	13	3	1.6	- 2.2
$\bar{3}$	1	3	9.4	8.3	$\bar{5}$	1	3	3.2	3.9
$\bar{3}$	2	3	13.3	-13.0	$\bar{5}$	3	3	9.8	8.9
$\bar{3}$	3	3	8.8	- 8.0	$\bar{5}$	4	3	11.3	-10.4
$\bar{3}$	4	3	15.0	14.8	$\bar{5}$	5	3	3.9	4.1
$\bar{3}$	5	3	21.7	-19.7	$\bar{5}$	6	3	3.4	- 4.1
$\bar{3}$	6	3	12.7	11.5	$\bar{5}$	7	3	4.1	3.8
$\bar{3}$	7	3	12.4	-10.3	$\bar{5}$	8	3	7.0	- 6.4
$\bar{3}$	8	3	2.6	- 2.7	$\bar{5}$	9	3	9.1	-10.2
$\bar{3}$	9	3	3.8	4.2	$\bar{5}$	10	3	5.0	- 6.0
$\bar{3}$	10	3	4.9	4.5	$\bar{5}$	11	3	8.9	-10.6
$\bar{3}$	11	3	5.0	5.4	$\bar{5}$	12	3	7.1	8.3
$\bar{3}$	13	3	4.1	4.8	$\bar{5}$	13	3	2.6	2.8
$\bar{3}$	15	3	2.6	3.2	$\bar{5}$	15	3	1.6	1.8
$\bar{4}$	1	3	12.2	12.4	$\bar{6}$	3	3	5.0	4.9
$\bar{4}$	2	3	3.6	4.5	$\bar{6}$	4	3	3.4	- 3.4

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
6	5	3	5.7	5.5	9	4	3	1.8	2.2
6	6	3	4.2	- 4.7	9	5	3	4.3	4.1
6	7	3	4.1	4.4	9	7	3	3.4	2.8
6	8	3	4.1	- 5.1	2	0	4	3.4	4.3
6	9	3	6.9	- 7.9	4	0	4	2.3	- 1.8
6	10	3	5.4	5.9	6	0	4	12.7	11.5
6	11	3	4.9	- 5.8	1	1	4	24.2	22.0
6	14	3	1.8	- 3.0	1	2	4	8.9	6.8
7	1	3	4.1	- 4.7	1	3	4	17.6	14.9
7	2	3	3.0	- 3.7	1	4	4	20.3	-18.1
7	3	3	12.2	-13.8	1	5	4	10.0	- 9.8
7	4	3	4.1	- 4.9	1	6	4	3.0	- 1.8
7	5	3	2.8	- 3.8	1	7	4	3.0	- 2.6
7	7	3	3.3	3.7	1	9	4	5.6	- 6.0
7	8	3	3.2	2.9	1	11	4	7.0	- 6.9
7	12	3	1.3	1.8	1	13	4	2.6	3.0
8	1	3	2.6	2.5	1	14	4	3.0	3.0
8	4	3	4.8	5.5	1	15	4	3.0	3.0
8	5	3	1.8	2.4	2	1	4	1.6	1.9
8	8	3	3.0	- 4.0	2	2	4	6.1	- 6.5
8	9	3	0.9	1.7	2	3	4	5.5	4.2
9	1	3	0.9	1.3	2	6	4	11.2	9.2
9	2	3	0.9	1.5	2	8	4	1.8	- 2.0
9	3	3	2.0	2.2	2	9	4	6.6	6.6

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{2}$	10	4	3.0	- 2.2	$\bar{4}$	7	4	6.6	6.7
$\bar{2}$	11	4	9.9	9.5	$\bar{4}$	8	4	8.2	- 8.8
$\bar{2}$	12	4	4.1	4.5	$\bar{4}$	9	4	8.4	- 9.2
$\bar{2}$	13	4	6.8	6.1	$\bar{4}$	10	4	4.9	- 4.8
$\bar{2}$	16	4	1.3	- 1.7	$\bar{4}$	11	4	1.6	- 2.1
$\bar{2}$	18	4	0.9	1.6	$\bar{4}$	13	4	3.6	- 3.9
$\bar{3}$	1	4	19.0	-17.8	$\bar{4}$	14	4	1.3	- 2.1
$\bar{3}$	2	4	9.8	8.9	$\bar{5}$	1	4	8.1	7.7
$\bar{3}$	3	4	13.4	-12.6	$\bar{5}$	2	4	9.0	- 7.4
$\bar{3}$	4	4	3.0	3.3	$\bar{5}$	4	4	1.8	- 1.7
$\bar{3}$	5	4	16.4	-13.2	$\bar{5}$	5	4	8.1	- 7.9
$\bar{3}$	6	4	2.6	- 2.6	$\bar{5}$	6	4	8.2	- 8.5
$\bar{3}$	7	4	9.7	11.1	$\bar{5}$	7	4	16.7	-14.8
$\bar{3}$	8	4	8.5	- 8.3	$\bar{5}$	9	4	4.8	4.9
$\bar{3}$	9	4	4.9	3.6	$\bar{5}$	10	4	8.1	7.4
$\bar{3}$	10	4	2.8	- 2.4	$\bar{5}$	14	4	3.3	- 3.8
$\bar{3}$	12	4	2.8	2.5	$\bar{5}$	16	4	1.3	- 2.4
$\bar{3}$	16	4	1.3	1.9	$\bar{6}$	1	4	3.4	- 3.2
$\bar{4}$	1	4	3.2	2.7	$\bar{6}$	2	4	8.4	6.7
$\bar{4}$	2	4	5.7	- 6.1	$\bar{6}$	5	4	3.9	- 3.7
$\bar{4}$	3	4	6.3	- 4.7	$\bar{6}$	6	4	2.8	- 3.1
$\bar{4}$	4	4	8.5	7.2	$\bar{6}$	7	4	1.6	- 1.7
$\bar{4}$	5	4	16.4	15.0	$\bar{6}$	8	4	2.8	2.1
$\bar{4}$	6	4	9.7	10.6	$\bar{6}$	9	4	5.9	- 5.6

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{6}$	10	4	3.0	3.4	$\bar{1}$	1	5	19.5	-21.2
$\bar{6}$	11	4	4.2	- 4.5	$\bar{1}$	2	5	7.2	- 8.3
$\bar{6}$	13	4	3.3	3.8	$\bar{1}$	3	5	13.2	-15.7
$\bar{6}$	14	4	2.6	- 2.9	$\bar{1}$	5	5	3.7	- 3.3
$\bar{7}$	1	4	15.0	-13.0	$\bar{1}$	6	5	3.2	- 2.0
$\bar{7}$	3	4	6.6	5.2	$\bar{1}$	7	5	5.8	- 5.5
$\bar{7}$	4	4	4.6	3.6	$\bar{1}$	8	5	7.9	- 8.4
$\bar{7}$	5	4	9.9	8.6	$\bar{1}$	11	5	3.3	4.0
$\bar{7}$	6	4	1.8	1.9	$\bar{1}$	12	5	2.4	2.7
$\bar{7}$	7	4	5.1	5.1	$\bar{1}$	13	5	1.8	2.1
$\bar{7}$	8	4	3.4	4.2	$\bar{1}$	15	5	2.3	2.4
$\bar{7}$	9	4	1.3	1.5	$\bar{1}$	16	5	1.8	2.3
$\bar{7}$	10	4	3.0	3.6	$\bar{2}$	1	5	13.3	-13.7
$\bar{7}$	12	4	1.6	- 1.8	$\bar{2}$	2	5	2.6	- 1.4
$\bar{8}$	1	4	3.0	2.7	$\bar{2}$	3	5	3.4	2.9
$\bar{8}$	5	4	2.3	- 1.4	$\bar{2}$	4	5	2.3	- 1.9
$\bar{8}$	7	4	3.0	3.1	$\bar{2}$	5	5	2.3	2.6
$\bar{9}$	1	4	3.0	2.3	$\bar{2}$	9	5	5.5	5.5
$\bar{9}$	2	4	3.0	2.9	$\bar{2}$	11	5	3.7	- 3.7
$\bar{9}$	4	4	2.8	1.6	$\bar{2}$	12	5	2.6	- 2.5
$\bar{1}$	0	5	4.9	- 8.5	$\bar{2}$	13	5	3.4	- 3.2
$\bar{3}$	0	5	5.7	- 5.3	$\bar{3}$	1	5	4.5	- 3.4
$\bar{7}$	0	5	5.1	4.5	$\bar{3}$	2	5	8.9	- 8.9
$\bar{9}$	0	5	4.2	2.8	$\bar{3}$	3	5	7.5	7.3

h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c
$\bar{3}$	5	5	2.6	3.0	$\bar{6}$	2	5	7.5	- 8.6
$\bar{3}$	6	5	3.7	- 3.7	$\bar{6}$	4	5	8.4	- 7.7
$\bar{3}$	8	5	5.3	- 4.6	$\bar{6}$	5	5	3.7	2.9
$\bar{3}$	10	5	3.7	2.7	$\bar{6}$	8	5	3.4	4.2
$\bar{3}$	11	5	4.5	- 4.2	$\bar{6}$	10	5	3.2	3.2
$\bar{3}$	12	5	3.7	3.1	$\bar{6}$	11	5	2.3	2.2
$\bar{3}$	15	5	2.6	- 2.6	$\bar{6}$	12	5	2.6	- 2.7
$\bar{4}$	1	5	11.3	12.1	$\bar{6}$	13	5	3.7	3.8
$\bar{4}$	2	5	16.3	17.9	$\bar{7}$	1	5	6.3	6.1
$\bar{4}$	3	5	13.5	14.7	$\bar{7}$	3	5	8.7	9.3
$\bar{4}$	4	5	6.9	8.3	$\bar{7}$	5	5	4.9	5.1
$\bar{4}$	5	5	10.1	-10.9	$\bar{7}$	6	5	3.2	3.1
$\bar{4}$	6	5	12.6	-15.1	$\bar{7}$	7	5	3.2	2.8
$\bar{4}$	7	5	3.7	- 3.2	$\bar{7}$	9	5	1.8	- 1.5
$\bar{4}$	8	5	5.3	- 6.1	$\bar{7}$	10	5	2.6	- 2.1
$\bar{4}$	10	5	3.7	- 3.6	$\bar{8}$	1	5	2.3	- 1.6
$\bar{4}$	11	5	3.7	- 2.6	$\bar{8}$	3	5	2.3	- 1.4
$\bar{5}$	3	5	11.0	-11.9	$\bar{8}$	4	5	2.3	1.9
$\bar{5}$	4	5	5.3	- 4.4	$\bar{8}$	6	5	2.6	- 2.6
$\bar{5}$	6	5	7.5	8.4	$\bar{8}$	7	5	2.3	- 1.9
$\bar{5}$	7	5	9.1	9.6	$\bar{8}$	9	5	3.4	- 2.5
$\bar{5}$	8	5	6.4	6.8	$\bar{9}$	3	5	3.2	- 2.2
$\bar{5}$	15	5	2.3	2.6	$\bar{1}$	1	6	13.8	-15.4
$\bar{6}$	1	5	2.6	- 2.1	$\bar{1}$	2	6	4.2	3.1

h	k	l	$ F_o $	F_o	h	k	l	$ F_o $	F_o
$\bar{1}$	3	6	4.2	- 3.1	$\bar{1}$	2	7	3.0	- 3.7
$\bar{1}$	4	6	9.1	-11.7	$\bar{1}$	3	7	3.0	3.1
$\bar{1}$	5	6	2.3	1.6	$\bar{1}$	5	7	8.1	7.0
$\bar{1}$	6	6	5.8	- 4.3	$\bar{1}$	6	7	5.7	6.5
$\bar{2}$	1	6	5.7	5.3	$\bar{1}$	7	7	2.3	- 2.0
$\bar{2}$	3	6	10.0	8.4	$\bar{2}$	1	7	7.1	6.8
$\bar{2}$	4	6	3.0	4.6	$\bar{2}$	2	7	5.8	5.4
$\bar{2}$	5	6	2.3	2.3	$\bar{2}$	3	7	5.8	4.2
$\bar{2}$	6	6	7.1	8.2	$\bar{2}$	4	7	3.0	3.0
$\bar{2}$	7	6	3.0	- 3.6	$\bar{2}$	6	7	4.2	- 3.9
$\bar{2}$	8	6	3.0	- 3.4	$\bar{2}$	7	7	3.9	- 3.6
$\bar{2}$	9	6	7.0	- 6.1	$\bar{3}$	1	7	3.0	- 4.1
$\bar{2}$	10	6	4.9	- 4.4	$\bar{3}$	2	7	3.0	5.6
$\bar{3}$	1	6	4.9	4.9	$\bar{1}$	4	8	1.8	2.6
$\bar{3}$	2	6	13.9	13.2					