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THE STRUCTURES OF SOME SUBSTITUTED BENZOIC ACIDS

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A THESIS
SUBMITTED TO
THE UNIVERSITY OF POONA
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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JANUARY - 1968

A B S T R A C T 14
A C K N O W L E D G E M E N T
I N T R O D U C T I O N

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Poona
January 1968

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(S.K. Arora)

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A B S T R A C T

In the present work the crystal and molecular structures of (i) 3:5 dichloro-2-aminobenzoic acid, and (ii) m-aminobenzoic acid hydrochloride have been determined by X-ray diffraction.

3:5 dichloro-2-aminobenzoic acid crystallizes in the monoclinic system, space group $P2_1/a$ with

$$a = 12.49 \text{ \AA}; \quad b = 17.02 \text{ \AA}; \quad c = 3.80 \text{ \AA}; \\ \beta = 92.7^\circ; \quad Z = 4.$$

The structure was determined with the help of Patterson projections and refined by three dimensional data. The molecules form dimers; these dimers are held in stable structure by normal van der Waals interactions. It is shown that one chlorine atom in the molecule is slightly deviated from the aromatic plane; this deviation appears to be due to intermolecular interactions.

m-aminobenzoic acid hydrochloride crystallizes in triclinic system, space group $P\bar{1}$ with

$$a = 14.78 \text{ \AA}; \quad b = 5.83 \text{ \AA}; \quad c = 4.58 \text{ \AA}; \\ \alpha = 96.9^\circ; \quad \beta = 91.3^\circ; \quad \gamma = 98.6^\circ; \quad Z = 2.$$

The structure was determined with the help of Patterson projections and refined by three dimensional data. The

molecules form dimers; these dimers are held in stable structure by strong N-Cl bonds as well as by van der Waals bonds. The N-Cl bonds around the nitrogen atom are roughly tetrahedral.

CHAPTER - I

INTRODUCTION

The discovery of the diffraction of X-rays by crystals by Laue, Friedrich and Knipping in 1912 had consequences in two main directions. The first concerned the nature of the radiation itself, and with the development of X-ray spectroscopy, this led to the fundamental advances in the theory of atomic structure. In the second place a powerful new tool became available for investigating the structure of the matter on an atomic scale. It was found that a great range of substances, from metals to the most complex biological structures, display a sufficient degree of order in their atomic arrangement to give diffraction effects, and so lie within this field of study. W.L. Bragg explained the diffraction spots in X-ray photographs as arising due to the reflection of X-rays by various sets of crystal lattice planes.

W.H. Bragg (1915) suggested that since a crystal is periodic in three dimensions, it can be represented by 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 wave length 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 the 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 scattered radiation from the contents of the unit cell of the crystal in the direction of (hkl) spectrum (called the structure amplitude).

Ewald in 1921 showed how to express Fourier series for crystal in terms of reciprocal lattice vectors. The vector $r^*(hkl)$ to the point (hkl) of the reciprocal lattice is perpendicular to the planes (hkl) of the crystal lattice and its magnitude is proportional to the reciprocal of the spacings of these planes. The direction of the reciprocal vector $r^*(hkl)$ is also the direction of the wave normal of the corresponding Fourier wave and the length of the reciprocal vector is proportional to the wave number of the Fourier wave.

Without the knowledge of the phases of the reflections, it is not possible to get the summation of the Fourier series. The magnitudes of the structure amplitudes can be obtained experimentally, but the knowledge of the relative phases is lost in recording the diffraction pattern of the

crystal. Determination of the phases remains the main problem in crystal structure analysis. Once a set of fairly reliable phases have been derived, the process of arriving at the true structure is automatic. Generally the phases are 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.

The two dimensional Fourier series employing reflexions from a certain zone of lattice planes only took form in 1925. The series represents the projection of the structure on a plane normal to the zone axis (of the lattice planes). The first two dimensional Fourier maps to be obtained were the three principal plane projections of diopside (Bragg, 1929). In the next few years the two dimensional Fourier series played an important role in determining the structures of simple organic compounds and improving the accuracy in the observed molecular dimensions.

A.L. Patterson, in 1934, modified the 'Fourier series method' using the observed intensities as the coefficients of the series instead of the observed amplitudes. From the Patterson map one gets various interatomic vectors rather than the atomic parameters. Patterson function has proved to be particularly useful in the determination of structures containing a small number of relatively heavy atoms.

In 1948, Harker and Kasper derived some inequality relationships, based on the physical condition that the electron density in the crystal is everywhere positive. Using these inequality relationships, Harker, Lucht and Kasper (1950) were able to solve the structure of decaborane. Since then, direct methods have been developed and have sometimes been used to solve crystal structures.

After getting the approximate atomic positions in the unit cell, the parameters defining these atoms must be refined. There are a number of methods of refining a crystal structure. In Fourier synthesis, the maxima of the electron density will occur away from the assumed atomic positions in the direction of the true one. The new atomic positions are used to recalculate the phases and the Fourier map is computed again. The process is repeated till the structure factors stop changing phases. The structure can be further refined by difference synthesis or by the method of 'Least Squares'. To obtain the difference Fourier map, the difference 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 of a weighted sum of squares of discrepancies between the observed and the computed structure factors. Because of the great versatility of the method, the least square refinement has become a usual technique in crystallography.

With the development of high speed computing facilities in recent years, it has become possible to determine complicated structures and to make detailed study of simple ones. Mention may be made of the structures of vitamin B₁₂ (Hodgkin et al. 1957) and the proteins myoglobin (Kendrew, 1961), haemoglobin (Perutz, 1964) and hen egg white lysozyme (Philips, 1966) as examples of complicated structures which have been solved by X-ray diffraction. The detailed study of simple structures implies not only the determination of precise molecular dimensions but also the study of thermal anisotropy and, if possible, of bond anisotropy as well. As examples of the precise determination of the molecular dimensions, mention may be made of the structure analyses of anthracene (Cruickshank, 1956), naphthalene (Cruickshank, 1957) and p-nitro aniline (Trueblood, 1961). In case of p-nitro aniline, the accuracy is such that the influence of electron donating amino-group on the molecular dimensions could be detected; the results are in accord with theoretical ideas. In the case of anthracene as well, the accuracy is such that slight deviation from planarity of the molecule of the order of 0.005 Å could be detected; this deviation is interpreted as arising from intermolecular interactions. In these structures, a thorough study of the thermal anisotropy has also been made. In anthracene and naphthalene, the r.m.s. amplitude of translational vibration along the principal molecular axes and of the librations about them have been determined; in p-nitro aniline, the principal movement is shown to be the

torsional oscillation of the nitro group. In recent years, such detailed study has become a usual feature in crystallography.

In the present work, the structures of 3:5 dichloro-2-aminobenzoic acid and m-aminobenzoic acid hydrochloride have been determined. In the former structure, thermal anisotropy has also been studied; the results clearly show the influence of intermolecular bonds on the vibration pattern of the atoms. An attempt has also been made to determine the structure of m-nitrobenzoic acid. This work forms part of a programme to study the structures of substituted benzoic acids in order to study the effect of the substituted groups on the molecular geometry. The structures of p-nitrobenzoic acid (Sakore and Pant, 1966) and o-nitrobenzoic acid (Sakore, Tavale and Pant, 1967) have already been determined in this laboratory.

In the determination of the preliminary structures, Von Eller photosommateur was frequently used. The refinement of the projections of the structures was done with the help of a desk calculating machine. For three dimensional refinement of the structures, the CDC 3600 computer of the Tata Institute of Fundamental Research, Bombay was used.

P A R T - I

CRYSTAL AND MOLECULAR STRUCTURE OF
3:5 DICHLORO-2-AMINO BENZOIC ACID

CHAPTER - II

EXPERIMENTAL

(A) 3:5 dichloro-2-aminobenzoic acid ($C_7H_5NO_2Cl_2$) was prepared by the chlorination of 2-aminobenzoic acid. The crystals obtained by the slow evaporation of a saturated solution of 3:5 dichloro-2-aminobenzoic acid in acetic acid grow along (001) face in the form of parallelepipeds. The preliminary X-ray photographs show that these crystals belong to the monoclinic system.

(1) The determination of unit cell dimensions :-

The preliminary values of the unit cell dimensions were obtained from the rotation photographs taken with $CuK\alpha$ radiation and the crystal oscillated about the three crystallographic axes in turn. The crystal was first set visually and then accurately by the method of double oscillation (Davies, 1950). Accurate determination of the axial lengths was done from the high angle reflexions in equatorial Weissenberg photographs taken along 'a' and 'c' axes. The angle β was obtained from equatorial Weissenberg photograph taken with 'b' as the oscillation axis.

Length of axis 'a'

Reflections used:	8,0,0	10,0,0
d100	12.50 Å	12.47 Å
Mean d100 =	12.485 Å	
a =	12.490 Å	(= d100/sin β)

Length of axis 'b'

Reflexions used:	0,14,0	0,18,0	1,20,0(₁)
d010	17.01 Å	17.03 Å	17.03 Å
Mean d010 =	17.02 Å		
b =	17.02 Å		

Length of axis 'c'

Reflexions used:	0,0,4	0,1,3
d001	3.80 Å	3.80 Å
Mean d001 =	3.80 Å	
c =	3.80 Å	(= d001/sin β)

For the measurement of 'b' and 'c' axes, reflexions 1,20,0(₁) and 0,1,3 respectively were used; the formulae are

$$\sin^2 \theta = \frac{\lambda^2}{4a^2 \sin^2} h^2 + \frac{\lambda^2}{4b^2} k^2$$

and

$$\sin^2 \theta = \frac{\lambda^2}{4c^2 \sin^2 \beta} l^2 + \frac{\lambda^2}{4b^2} k^2 \text{ respectively.}$$

The final cell dimensions are:

$$a = 12.49 \text{ Å}; \quad b = 17.02 \text{ Å}; \quad c = 3.80 \text{ Å} \quad \text{and} \quad \beta = 92.7^\circ.$$

(ii) The crystal density determination :- The density was measured by the flotation method using dioxan and ethylene dibromide mixture. The average observed density is 1.700 gm/cm³.

(iii) Number of molecules per unit cell :- The number of molecules per unit cell (n) were obtained from the formula

$$n = \frac{V.N.P}{M}$$

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 1.705 gm/cm³.

(iv) Linear absorption coefficient :- The linear absorption coefficient for CuK α 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 70.4 cm⁻¹.

(B) Collection of data and estimation of intensity

Three dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with CuK radiation. The cross-section of the crystal mounted along 'c' axis (3.80 Å) was 0.6 x 0.3 mm². With the 'c' as the oscillation axis, zero to third layers were taken with the usual multiple film technique. Scaling was done with the help of common reflexions in zero layer Weissenberg photographs, taken with 'a' and 'b' as oscillation axes.

In all 92, 231, 140 and 46 reflections of the type hko, hkl, hk2 and hk3 respectively were observed out of 340, 448, 328 and 258 possible reflexions.

The intensities of reflexions were measured visually with the help of an intensity scale prepared in the following way. From the zero layer Weissenberg photograph, a strong and well shaped reflexion was chosen which was sufficiently separated from the other reflexions and the crystal was oscillated through 10° about the angle giving this reflexion. The camera was kept stationary. The exposure was given for one oscillation. The camera was shifted by 3 mm and the second exposure was given for two oscillations. Thus by shifting the camera and increasing the number of oscillations each time, a set of diffraction spots of known relative intensities were obtained. X-rays were generated by a stabilized X-ray unit (Phillips P.W.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 (L_p) factor :- The relative intensities, I, of diffracted spots on the equi-inclination Weissenberg photographs are given by

$$I \propto D I$$

where

$$D = \frac{\int \cos \theta}{1 + \cos^2 2\theta}$$

All the intensities were corrected for the L_p factor with the help of curves given by Cochran (1948).

(ii) Correction for spot extension :- In the higher layers, the reflexions get extended on one side and contracted on the other side. Suppose the crystal consists of small elements having slightly different orientations. As the crystal rotates, the different elements giving the same reflexion 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 direction they are contracted. The correction for spot extension was applied by the expression

$$I = W \cdot I_0$$

where $W = (A + A) / A$ and I_0 is the intensity of extended spot; A is the area of spot when camera is not moving.

The intensities of higher layer photographs were measured from extended spots and correction 'W' was applied. The curves for constant W, given by Phillips (1956) were used to get the required correction factors.

(iii) Scale and temperature factors :- The relative intensities were put on an absolute scale and the overall temperature factor B was determined by Wilson's (1942) statistical method. The reflexions were divided into groups

lying between certain values of $\sin^2\theta$. The mean value of the observed intensities $\langle I \rangle$ ($= \frac{\sum I}{n}$ where $\sum I$ denotes the sum of intensities in a certain range and n the number of reflexions in that range) was evaluated over each range. The constant C which makes the average equal to $\sum f_n^2$ i.e. $C = \frac{\sum f_n^2}{\langle I \rangle}$ was found; $\sum f_n^2$ is the sum of the squares of the scattering factors of atoms (at rest), the summation being done over all the atoms in the unit cell. McWeeny's (1951) values of the scattering factors were used. $\log_e C$ was plotted against the mean value $\sin^2\theta/\lambda^2$ for each range. 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 $\sin^2\theta/\lambda^2$ for hko , okl and hol type reflexions are given in figs. II-1, II-2 and the corresponding data are given in table II-1(a,b,c).

TABLE - II-1(a)

$\log_e C$ values for (hko) reflexions

No.	$\sin\theta$	$\frac{\sin^2\theta}{\lambda^2}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.3 to 0.4	0.051	1.00	587.0	587.0	6.34
2	0.4 to 0.5	0.085	0.76	422.0	555.0	6.32
3	0.5 to 0.6	0.128	0.39	314.0	804.0	6.69
4	0.6 to 0.7	0.178	0.30	241.0	815.0	6.70

From the graph $B = 2.0 \text{ \AA}^2$; Scale factor = 493.0

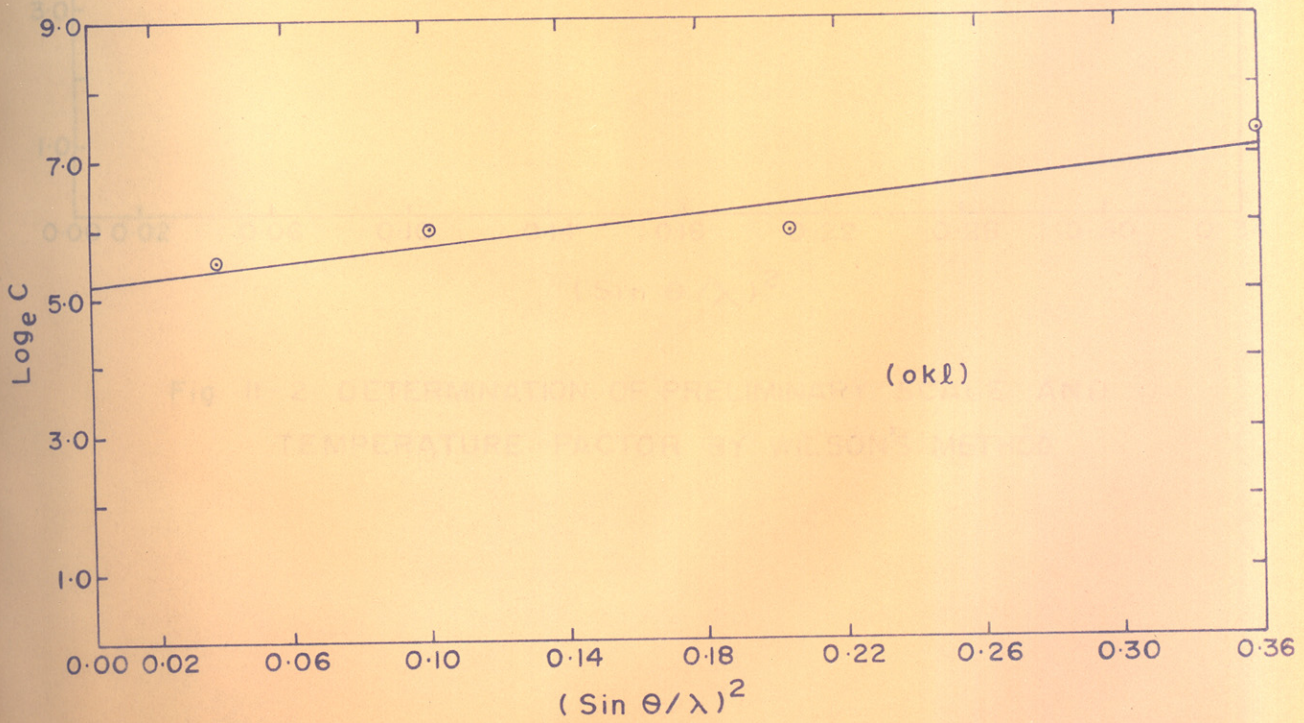
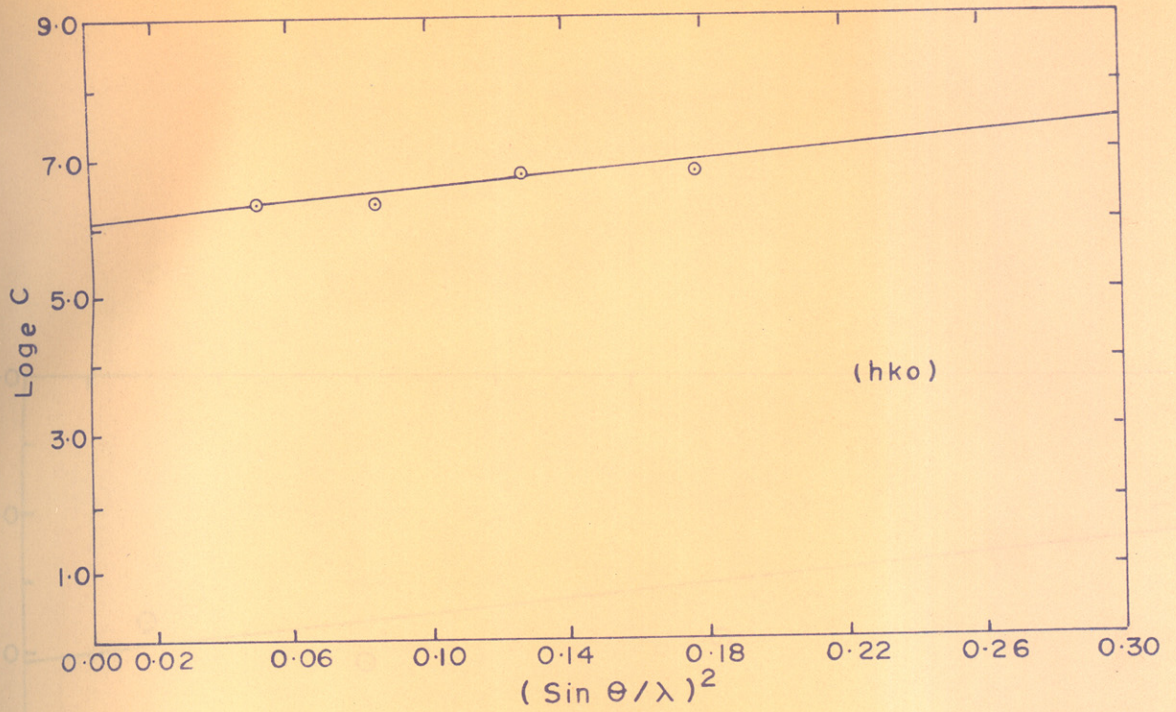


Fig. II-1 DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTOR BY WILSON'S METHOD

TABLE 11-12

log₁₀ S values for (100) reflections

h	k	l	h ²	k ²	l ²	h ² +k ² +l ²
1	0	0	1	0	0	1
2	0	0	4	0	0	4
3	0	0	9	0	0	9
4	0	0	16	0	0	16
5	0	0	25	0	0	25
6	0	0	36	0	0	36
7	0	0	49	0	0	49
8	0	0	64	0	0	64
9	0	0	81	0	0	81
10	0	0	100	0	0	100
11	0	0	121	0	0	121
12	0	0	144	0	0	144
13	0	0	169	0	0	169
14	0	0	196	0	0	196
15	0	0	225	0	0	225
16	0	0	256	0	0	256
17	0	0	289	0	0	289
18	0	0	324	0	0	324
19	0	0	361	0	0	361
20	0	0	400	0	0	400
21	0	0	441	0	0	441
22	0	0	484	0	0	484
23	0	0	529	0	0	529
24	0	0	576	0	0	576
25	0	0	625	0	0	625
26	0	0	676	0	0	676
27	0	0	729	0	0	729
28	0	0	784	0	0	784
29	0	0	841	0	0	841
30	0	0	900	0	0	900
31	0	0	961	0	0	961
32	0	0	1024	0	0	1024
33	0	0	1089	0	0	1089
34	0	0	1156	0	0	1156
35	0	0	1225	0	0	1225
36	0	0	1296	0	0	1296
37	0	0	1369	0	0	1369
38	0	0	1444	0	0	1444
39	0	0	1521	0	0	1521
40	0	0	1600	0	0	1600
41	0	0	1681	0	0	1681
42	0	0	1764	0	0	1764
43	0	0	1849	0	0	1849
44	0	0	1936	0	0	1936
45	0	0	2025	0	0	2025
46	0	0	2116	0	0	2116
47	0	0	2209	0	0	2209
48	0	0	2304	0	0	2304
49	0	0	2401	0	0	2401
50	0	0	2500	0	0	2500
51	0	0	2601	0	0	2601
52	0	0	2704	0	0	2704
53	0	0	2809	0	0	2809
54	0	0	2916	0	0	2916
55	0	0	3025	0	0	3025
56	0	0	3136	0	0	3136
57	0	0	3249	0	0	3249
58	0	0	3364	0	0	3364
59	0	0	3481	0	0	3481
60	0	0	3600	0	0	3600
61	0	0	3721	0	0	3721
62	0	0	3844	0	0	3844
63	0	0	3969	0	0	3969
64	0	0	4096	0	0	4096
65	0	0	4225	0	0	4225
66	0	0	4356	0	0	4356
67	0	0	4489	0	0	4489
68	0	0	4624	0	0	4624
69	0	0	4761	0	0	4761
70	0	0	4900	0	0	4900
71	0	0	5041	0	0	5041
72	0	0	5184	0	0	5184
73	0	0	5329	0	0	5329
74	0	0	5476	0	0	5476
75	0	0	5625	0	0	5625
76	0	0	5776	0	0	5776
77	0	0	5929	0	0	5929
78	0	0	6084	0	0	6084
79	0	0	6241	0	0	6241
80	0	0	6400	0	0	6400
81	0	0	6561	0	0	6561
82	0	0	6724	0	0	6724
83	0	0	6889	0	0	6889
84	0	0	7056	0	0	7056
85	0	0	7225	0	0	7225
86	0	0	7396	0	0	7396
87	0	0	7569	0	0	7569
88	0	0	7744	0	0	7744
89	0	0	7921	0	0	7921
90	0	0	8100	0	0	8100
91	0	0	8281	0	0	8281
92	0	0	8464	0	0	8464
93	0	0	8649	0	0	8649
94	0	0	8836	0	0	8836
95	0	0	9025	0	0	9025
96	0	0	9216	0	0	9216
97	0	0	9409	0	0	9409
98	0	0	9604	0	0	9604
99	0	0	9801	0	0	9801
100	0	0	10000	0	0	10000

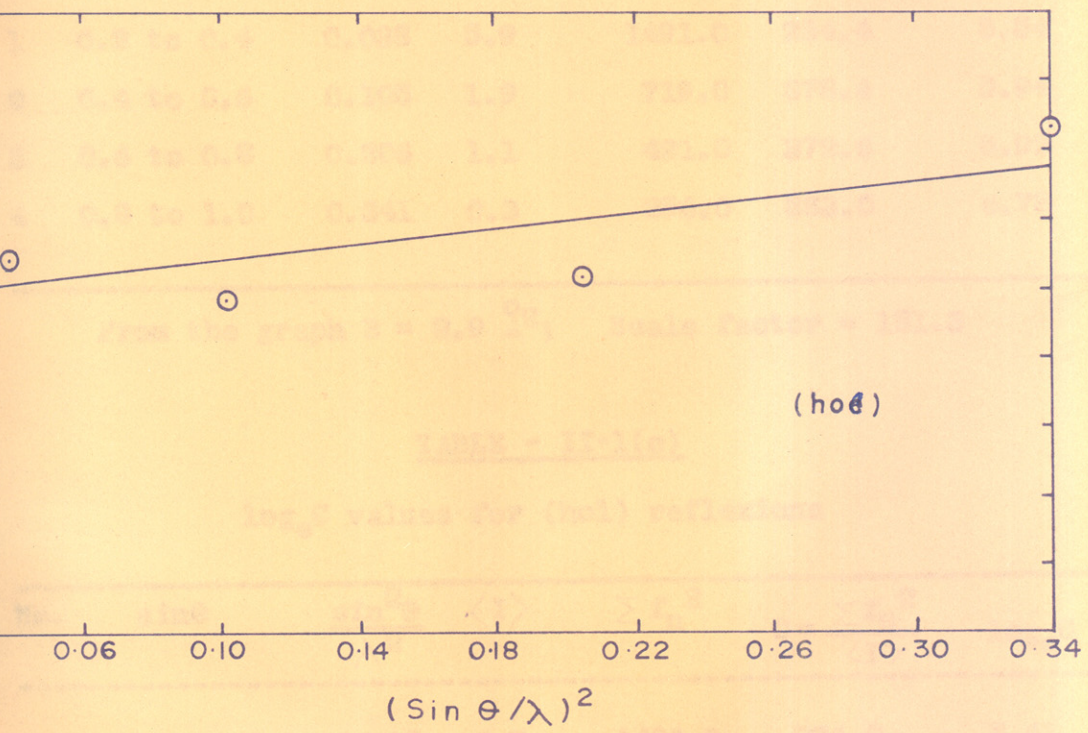


Fig. 11-2 DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTOR BY WILSON'S METHOD.

Space group

The observed systematic absences are:

hkl for h odd

and hkl for h odd

This implies that the space group is P2₁

TABLE - II-1(b)

$\log_e C$ values for (okl) reflexions

No.	$\sin\theta$	$\frac{\sin^2\theta}{\lambda^2}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.2 to 0.4	0.038	5.9	1491.0	254.4	5.54
2	0.4 to 0.6	0.105	1.9	719.0	378.4	5.94
3	0.6 to 0.8	0.206	1.1	421.0	372.6	5.92
4	0.8 to 1.0	0.341	0.3	286.0	883.0	6.78

From the graph $B = 2.9 \text{ \AA}^2$; Scale factor = 181.3

TABLE - II-1(c)

$\log_e C$ values for (hol) reflexions

No.	$\sin\theta$	$\frac{\sin^2\theta}{\lambda^2}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.2 to 0.4	0.033	6.7	1491.0	224.0	5.41
2	0.4 to 0.6	0.105	5.9	719.0	122.3	4.81
3	0.6 to 0.8	0.206	2.5	421.0	168.4	5.13
4	0.8 to 1.0	0.341	0.2	286.0	1588.0	7.37

From the graph $B = 2.8 \text{ \AA}^2$; Scale factor = 125.2

Space group

The observed systematic absences are:

oko for k odd
and hol for h odd

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

C H A P T E R - I I I

PRELIMINARY STRUCTURE AND PROJECTIONAL REFINEMENT

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

$$P(u,v,w) = V \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \rho(x+u, y+v, z+w) dx.dy.dz \quad \dots (III-1)$$

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-1 simplifies to

$$P(u,v,w) = \frac{1}{V} \sum \sum \sum |F(hk1)|^2 \cos 2\pi(hx + ky + lz) \quad \dots (III-2)$$

where V is the volume of the unit cell.

For Patterson projection $P(u,v,0)$, this expression reduces to

$$P(u,v,0) = \frac{1}{A} \sum \sum |F(hko)|^2 \cos 2\pi(hx + ky) \quad \dots (III-3)$$

The Patterson map consists of several peaks, any peak occurring at a distance from the origin equal to the vector distance between two atoms in the crystal. In a structure of N atoms, there are N^2 Patterson peaks; out of these, N peaks 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 are related to the other half by centre of symmetry. For a crystal having atoms of almost equal diffracting power, these peaks are not all resolved. Overlapping of the peaks complicates the derivation of the original set of atoms which gives rise to a particular set of Patterson peaks. But when the crystal contains a relatively small number of heavy atoms per unit cell, the Patterson function can be used to solve the structure fairly directly. The Patterson peaks due to interaction between the heavy atoms then stand out against a background of overlapping smaller peaks and give immediately the coordinates of heavy atoms. The phase angles that would result from the contribution of the heavy atoms alone can be deduced. The assumption that these phase angles are those of various reflexions should then give a Fourier synthesis which is a close approximation to the complete structure.

Sharpened Patterson Function

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 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. Patterson (1935) used the following modifications in his two dimensional Patterson function of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

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

In this equation $M(S)$ is the modifying factor and \hat{f} is the unitary scattering factor taking account of the temperature factor and P is the constant given by Costain's equation (1941) and $S = 2\sin\theta/\lambda$. Another modification suggested by Schomaker and Shoemaker (unpublished) is as follows:

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

This modification reduces greatly the influence of low angle terms on the Patterson function, which is very useful when they are likely to be in error through extinction.

In the present work, no sharpening of Patterson function was done.

(001) Patterson and Fourier Projections

The four equivalent points for space group $P2_1/a$ in (001) projection are:

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

The structure contains two heavy atoms i.e. Cl_1 and Cl_2 in a molecule. Let their co-ordinates be (x_1, y_1) and (x_2, y_2) .

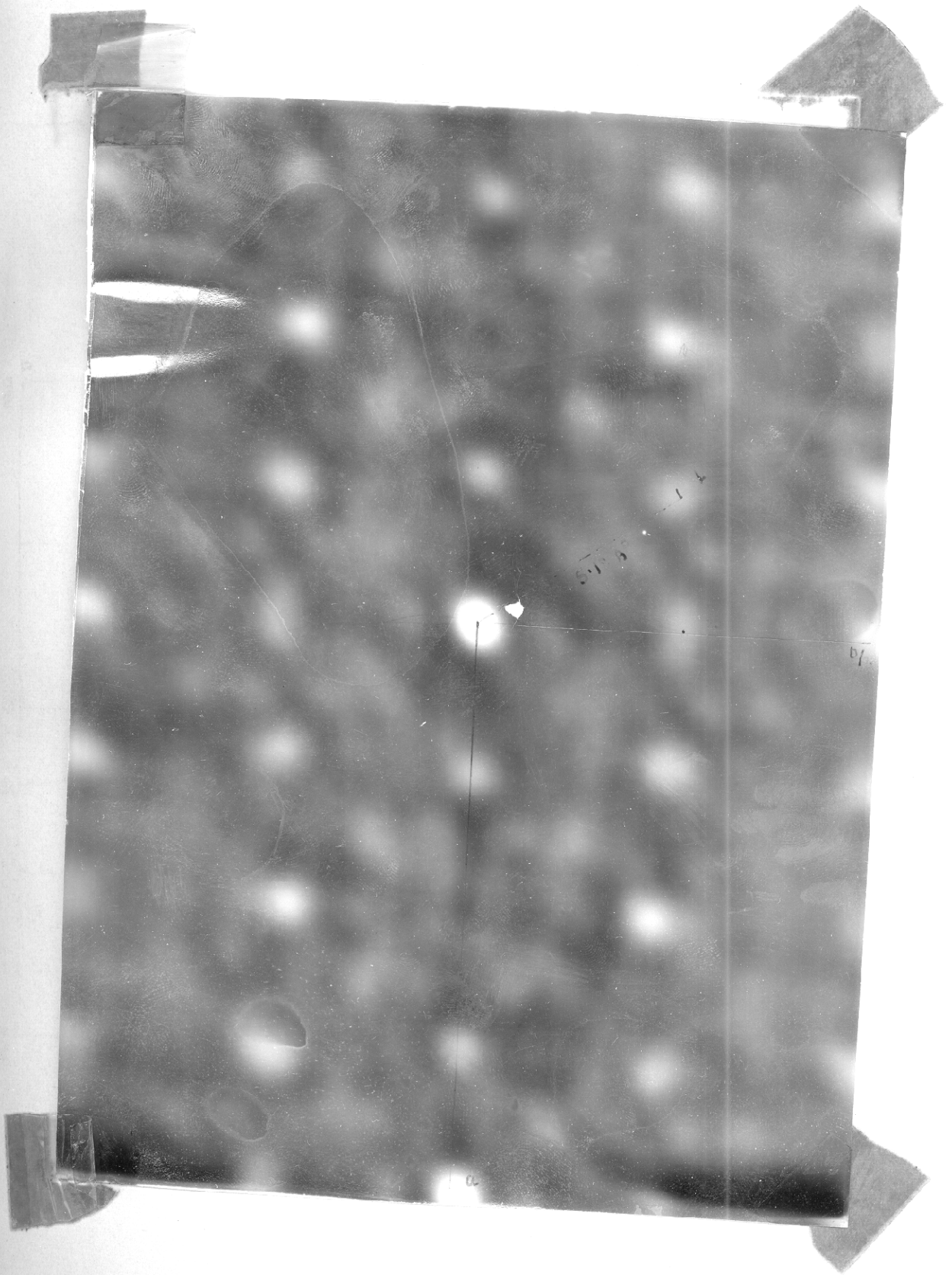


FIGURE III-1 : (001) PATTERSON MAP

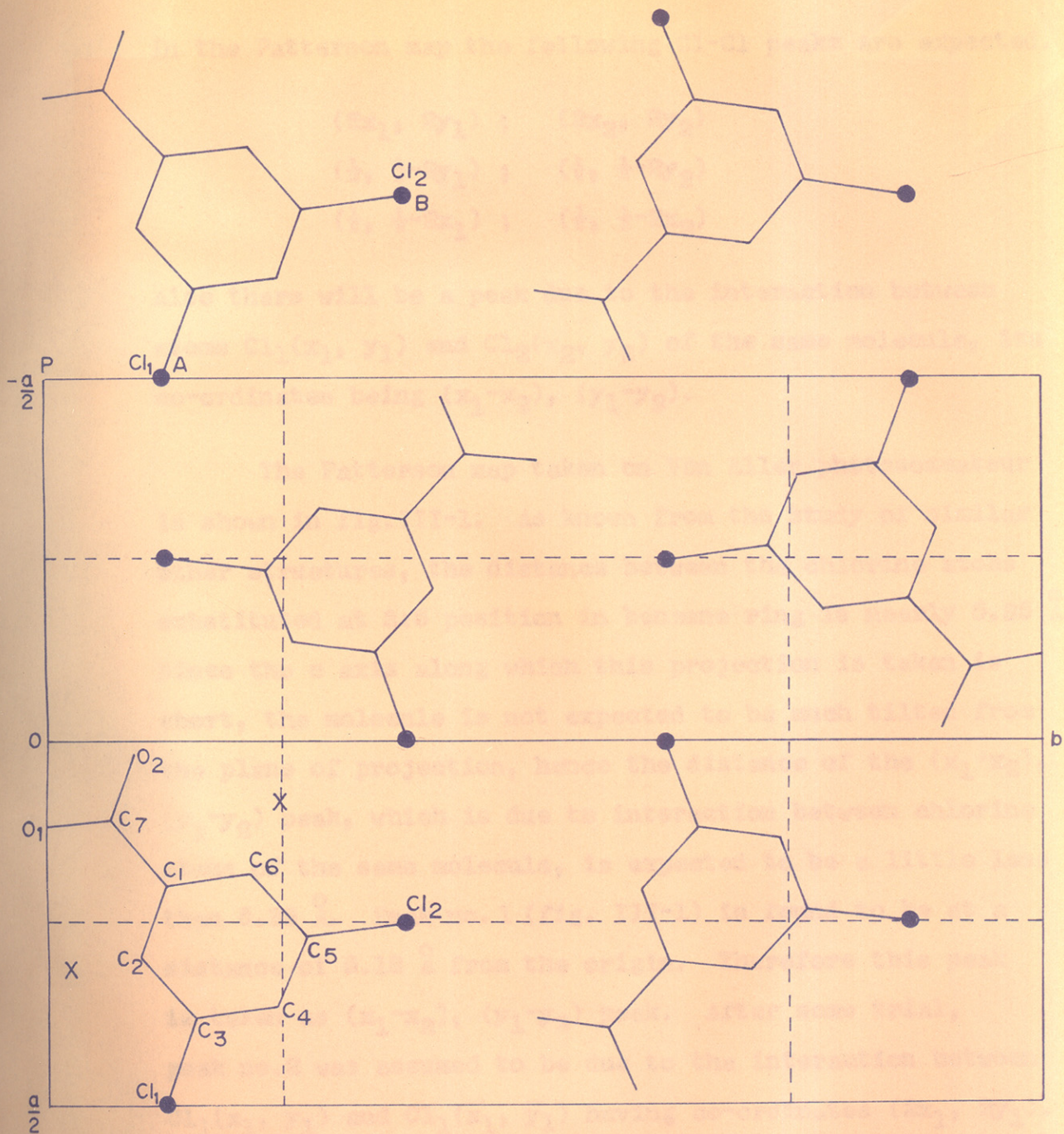


Fig. III-2 SYMMETRY RELATED ATOMS IN THE UNIT CELL

In the Patterson map the following Cl-Cl peaks are expected.

$$(2x_1, 2y_1) ; (2x_2, 2y_2)$$

$$\left(\frac{1}{2}, \frac{1}{2}-2y_1\right) ; \left(\frac{1}{2}, \frac{1}{2}-2y_2\right)$$

$$\left(\frac{1}{2}, \frac{1}{2}-2x_1\right) ; \left(\frac{1}{2}, \frac{1}{2}-2x_2\right)$$

Also there will be a peak due to the interaction between atoms $Cl_1(x_1, y_1)$ and $Cl_2(x_2, y_2)$ of the same molecule, its co-ordinates being $(x_1-x_2), (y_1-y_2)$.

The Patterson map taken on Von Eller photosommateur is shown in fig. III-1. As known from the study of similar other structures, the distance between the chlorine atoms substituted at 3:5 position in benzene ring is nearly 5.35 Å. Since the c axis along which this projection is taken is short, the molecule is not expected to be much tilted from the plane of projection, hence the distance of the $(x_1-x_2), (y_1-y_2)$ peak, which is due to interaction between chlorine atoms of the same molecule, is expected to be a little less than 5.35 Å. Peak no. 1 (fig. III-1) is found to be at a distance of 5.18 Å from the origin. Therefore this peak is taken as $(x_1-x_2), (y_1-y_2)$ peak. After some trial, peak no. 2 was assumed to be due to the interaction between $Cl_1(x_1, y_1)$ and $Cl_1(\bar{x}_1, \bar{y}_1)$ having co-ordinates $(2x_1, 2y_1)$. This gave the (x_1, y_1) co-ordinates of Cl_1 atom. This is marked as atom A in fig. III-2, which shows the symmetry related atoms in the unit cell.

Since the vector distance between Cl_1 and Cl_2 in the projection is 5.18 Å, the Cl_2 peak in fig. III-2 is

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fixed at B, at a distance of 5.18 \AA from A and such that AB is parallel to the line joining the Cl_1 - Cl_2 peak in the Patterson map to the origin. It is clear that all the strong Patterson peaks in fig. III-1 are explained by chlorine positions shown in fig. III-2.

Assuming that molecules form dimers, the only way in which the other atoms of the molecule could be fixed is shown in fig. III-2. The origin was now shifted to the centre of the dimer. The approximate co-ordinates of all the atoms of the molecule except the N atom, whose position could not, at this stage, be fixed, were measured from fig. III-2; the nitrogen atom could be in one of the two positions marked by crosses (x) in the figure.

With these parameters, structure factors were calculated using the expressions:

$$F(hko) = 4 \sum_1^N f_n \cos 2\pi h x_n \cos 2\pi k y_n \quad \text{for } h + k = 2n \quad \dots\dots \text{(III-4a)}$$

and

$$F(hko) = -4 \sum_1^N f_n \sin 2\pi h x_n \sin 2\pi k y_n \quad \text{for } h + k = 2n + 1 \quad \dots\dots \text{(III-4b)}$$

With the signs obtained, a direct Fourier map was obtained. The map shows all the atoms of the molecule; it was possible to fix the position of nitrogen atom as well. The structure was refined by direct Fourier synthesis and the parameters obtained from the third Fourier map are given

in table III-1. The value of R at this stage calculated by the expression

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

was 22.5%. The F_o values were scaled by the expression

$$K = \sum |F_c| / \sum |F_o|.$$

Even at this stage of refinement the calculated structure factors of reflexions 0,6,0 and 0,12,0 were very small as compared to their observed values. On carefully observing these reflexions in the Weissenberg photograph, it was found that the shape of these two reflexions is different from the others; so it is expected that these are Renninger reflexions. These reflexions were left out for the refinement of the structure.

(001) Electron Density Projection

The electron density on (001) projection for a crystal belonging to space group $P2_1/a$ is given by

$$\rho(xy_0) = \frac{1}{A} \left[F(000) + 2 \sum_0^{\infty} F(h00) \cos 2\pi hx + 2 \sum_0^{\infty} F(0k0) \cos 2\pi ky + 4 \left\{ \sum_0^{\infty} \sum_0^{\infty} F(hko)^{h+k=2n} \cos 2\pi hx \cos 2\pi ky - \sum_0^{\infty} \sum_0^{\infty} F(hko)^{h+k=2n+1} \sin 2\pi hx \sin 2\pi ky \right\} \right],$$

..... (III-6)

where A is the area of the projection.

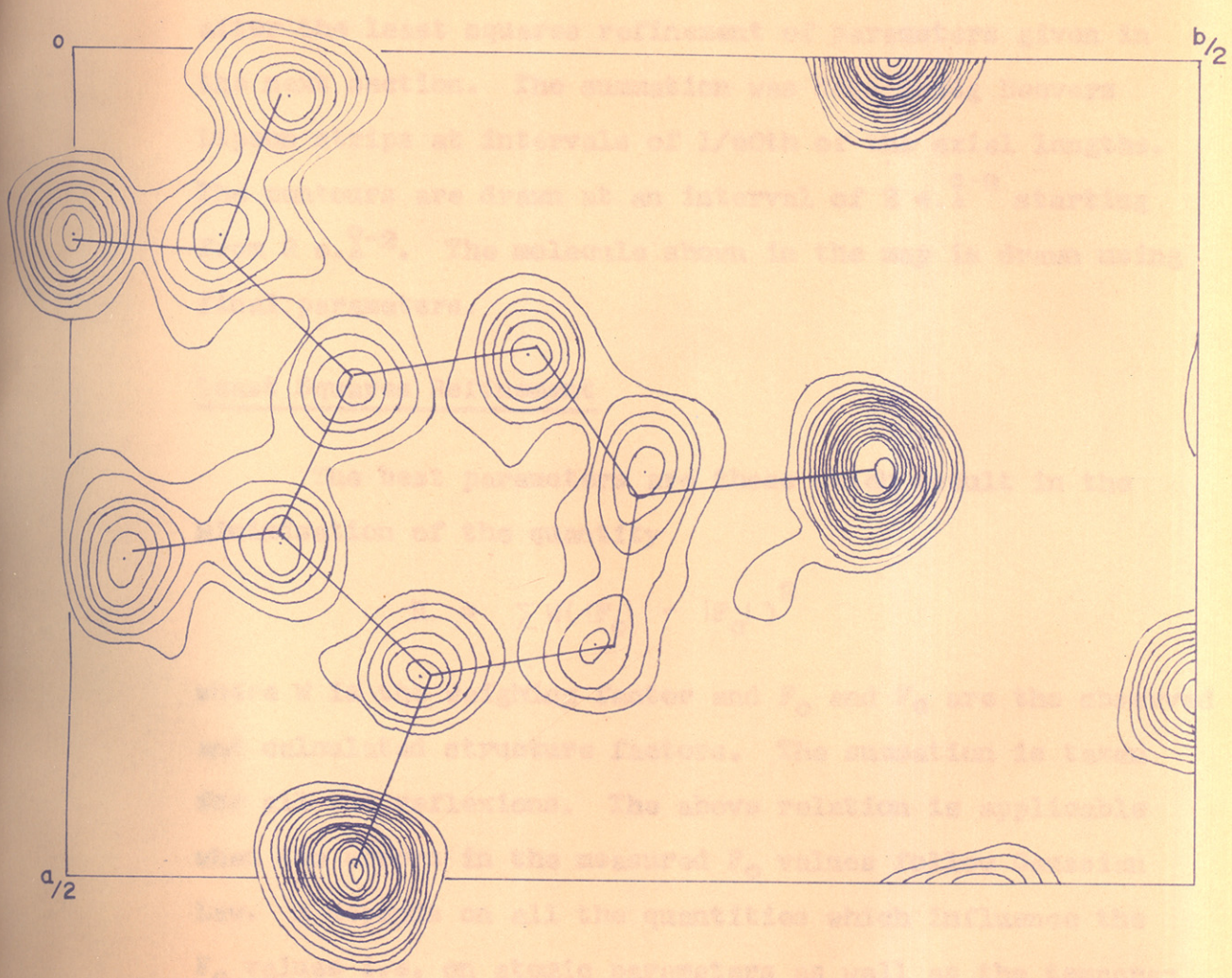


Fig. III-3 ELECTRON DENSITY PROJECTED ON (001) PLANE
 CONTOURS DRAWN AT INTERVALS OF $2eA^{-2}$ STARTING FROM $2eA^{-2}$

$$\Delta F_0 = \sum_{hkl} \left[\frac{\partial F_0}{\partial x_h} \Delta x_h + \frac{\partial F_0}{\partial y_k} \Delta y_k + \frac{\partial F_0}{\partial z_l} \Delta z_l \right]$$

The (001) electron density map shown in fig. III-3 was computed with the signs of the structure factors obtained after the least squares refinement of parameters given in the next section. The summation was done using Beevers Lipson strips at intervals of 1/60th of the axial lengths. The contours are drawn at an interval of $2 \text{ e.}\text{\AA}^{-2}$ starting from $2 \text{ e.}\text{\AA}^{-2}$. The molecule shown in the map is drawn using final parameters.

Least Squares Refinement

The best parameters are those which result in the minimisation of the quantity

$$R = \sum W(|F_o| - |F_c|)^2$$

where W is the weighting factor and F_o and F_c are the observed and calculated structure factors. The summation is taken for all the reflexions. The above relation is applicable when the errors in the measured F_o values follow Gaussian Law. R depends on all the quantities which influence the F_c values i.e. on atomic parameters as well as the temperature factor. Here only atomic parameters are considered.

A small change Δx_n in the x co-ordinate of the n^{th} atom of a structure changes F_c by ΔF_c amount $(\partial F_c / \partial x_n) \Delta x_n$; changes to all the co-ordinates simultaneously result in a change in F_c of the amount

$$\Delta F_c = \sum_{n=1}^N \left[\frac{\partial F_c}{\partial x_n} \Delta x_n + \frac{\partial F_c}{\partial y_n} \Delta y_n + \frac{\partial F_c}{\partial z_n} \Delta z_n \right]$$

The correct values of x_n etc. are those which most nearly equate ΔF_c to $F_o - F_c$ for all equations of this type that can be set up corresponding to all measured values of F_o 's.

Multiplying both sides of the equation (III-7) by $W \cdot F_c / x_n$ and adding all the equations, we have

$$\begin{aligned} \sum_q W(F_o - F_c) \frac{\partial F_c}{\partial x_n} &= \sum_m W \left[\left(\frac{\partial F_c}{\partial x_n} \right) \Delta x_n + \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial y_n} \Delta y_n \right. \\ &+ \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial z_n} z_n + \sum_m \frac{\partial F_c}{\partial x_n} \left(\frac{\partial F_c}{\partial x_m} \Delta x_m \right. \\ &\left. \left. + \frac{\partial F_c}{\partial y_m} \Delta y_m + \frac{\partial F_c}{\partial z_m} \Delta z_m \right) \right] \end{aligned} \quad \dots\dots (III-8)$$

\sum_m denotes the sum over all the reflexions.

If the atoms are well resolved from one another, the quantities such as $\sum_q W \frac{F_c}{x_n} \frac{F_c}{x_m}$ are very small compared to $\sum_q W (\partial F_c / \partial x_n)^2$ and hence can be neglected. If the axes are orthogonal or nearly so, $\sum_q W \frac{\partial F_c}{\partial x_n} \frac{\partial F_c}{\partial y_n}$ can also be neglected so that expression (III-8) takes the form

$$\Delta x_n = \frac{\sum_q W (F_o - F_c) \partial F_c / \partial x_n}{\sum_q W (\partial F_c / \partial x_n)^2} \quad \dots\dots (III-9)$$

For the refinement of x and y parameters, all the $F(hko)$ (including those unobserved F 's whose calculated

values were more than the minimum observable values) were used. The expressions for Δx and Δy are given below:

$$\Delta x = -\frac{1}{2\pi} \left[\frac{\sum_{h+k=2n} \Delta F(4f_n \cdot h) (A) + \sum_{h+k=2n+1} \Delta F(4f_n \cdot h) (B)}{\sum_{h+k=2n} (4f_n \cdot h)^2 (A)^2 + \sum_{h+k=2n+1} (4f_n \cdot h)^2 (B)^2} \right] \dots (III-10)$$

$$\Delta y = -\frac{1}{2\pi} \left[\frac{\sum_{h+k=2n} \Delta F(4f_n \cdot k) (P) + \sum_{h+k=2n+1} \Delta F(4f_n \cdot k) (Q)}{\sum_{h+k=2n} (4f_n \cdot k)^2 (P)^2 + \sum_{h+k=2n+1} (4f_n \cdot k)^2 (Q)^2} \right] \dots (III-11)$$

where

$$A = \sin 2\pi h x \cos 2\pi k y$$

$$B = \cos 2\pi h x \sin 2\pi k y$$

$$P = \cos 2\pi h x \sin 2\pi k y$$

$$Q = \sin 2\pi h x \cos 2\pi k y$$

$$\Delta F = (F_o - F_c)$$

Using the expressions (III-10, III-11), Δx and Δy for all the twelve atoms of the molecule were obtained. Three least squares refinement were given. The x and y parameters and R value after each cycle of refinement are given in table III-1.

TABLE - III-1

x and y parameters during the stages of refinements

Atom	From third direct Fourier synthesis		From first cycle of Least Square refinement		From second cycle of Least Square refinement		From third cycle of Least Square refinement	
	x	y	x	y	x	y	x	y
C ₁	0.194	0.128	0.185	0.128	0.191	0.127	0.195	0.129
C ₂	0.299	0.103	0.297	0.100	0.291	0.099	0.291	0.098
C ₃	0.376	0.160	0.377	0.165	0.374	0.164	0.378	0.165
C ₄	0.363	0.241	0.355	0.245	0.359	0.245	0.359	0.246
C ₅	0.258	0.257	0.266	0.255	0.262	0.255	0.266	0.255
C ₆	0.184	0.208	0.179	0.208	0.181	0.210	0.177	0.210
C ₇	0.109	0.074	0.122	0.070	0.116	0.069	0.121	0.071
O ₁	0.119	0.000	0.118	0.998	0.113	0.002	0.116	0.000
O ₂	0.030	0.095	0.026	0.096	0.024	0.095	0.024	0.097
Cl ₁	0.496	0.132	0.495	0.132	0.499	0.131	0.500	0.131
Cl ₂	0.254	0.358	0.253	0.359	0.253	0.360	0.252	0.359
N	0.306	0.027	0.306	0.030	0.303	0.029	0.304	0.030
	B = 2.0 Å ²		B = 2.0 Å ²		B = 2.0 Å ²		B = 2.0 Å ²	
	R = 22.5 %		R = 18.9 %		R = 16.8 %		R = 15.8 %	

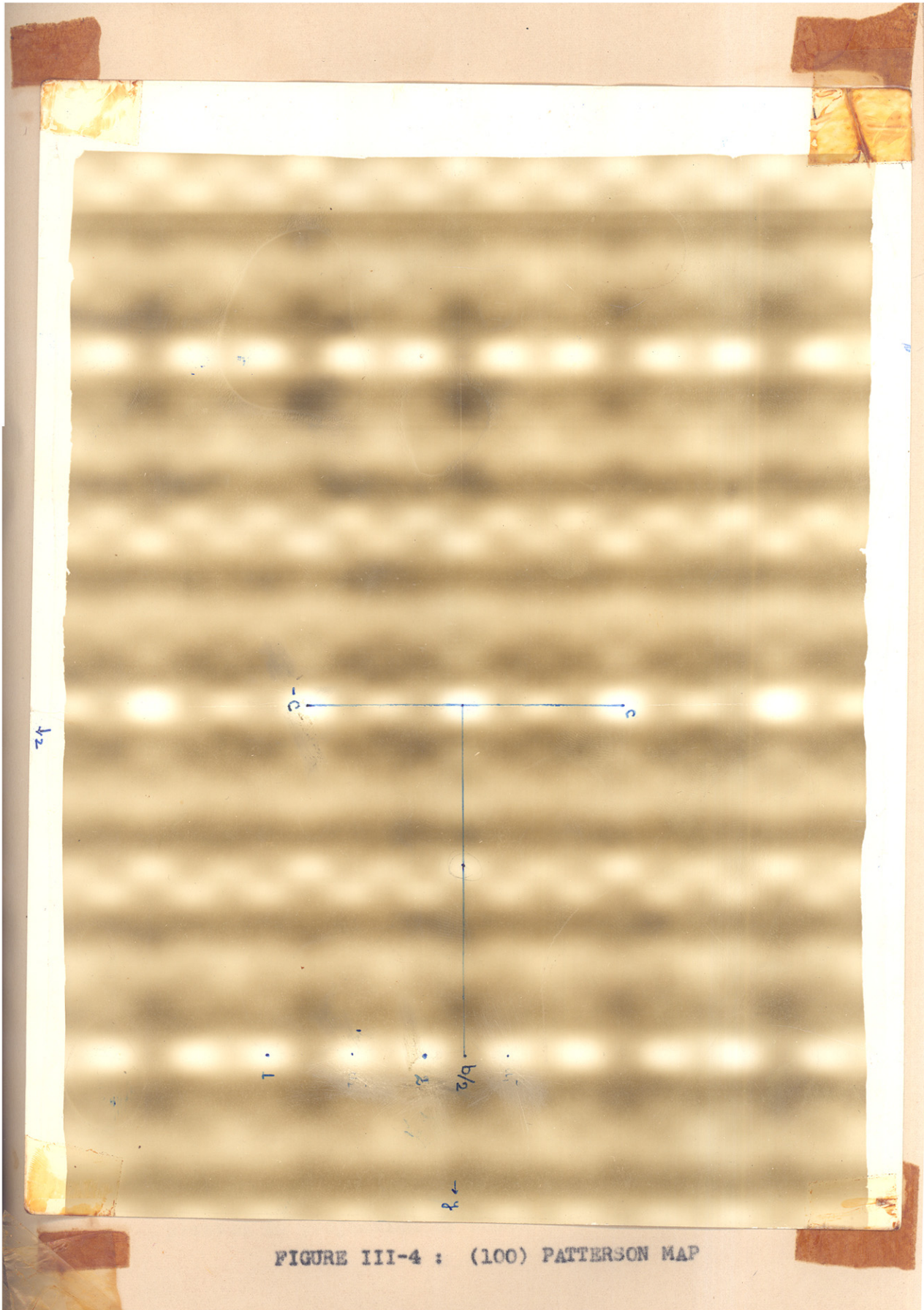


FIGURE III-4 : (100) PATTERSON MAP

(100) Patterson and Fourier Projections

The equivalent points for this projection are:

$$y, x_1 \quad \bar{y}, \bar{x}_1; \quad \frac{1}{2} - y, x_1; \quad \frac{1}{2} - y, \bar{x}_1;$$

The following peaks due to the interaction between symmetry related chlorine atoms are expected to occur

$$(2y_1, 2x_1); \quad (2y_2, 2x_2)$$

$$(2y_1 - \frac{1}{2}, 0); \quad (2y_2 - \frac{1}{2}, 0)$$

$$(\frac{1}{2}, 2x_1); \quad (\frac{1}{2}, 2x_2)$$

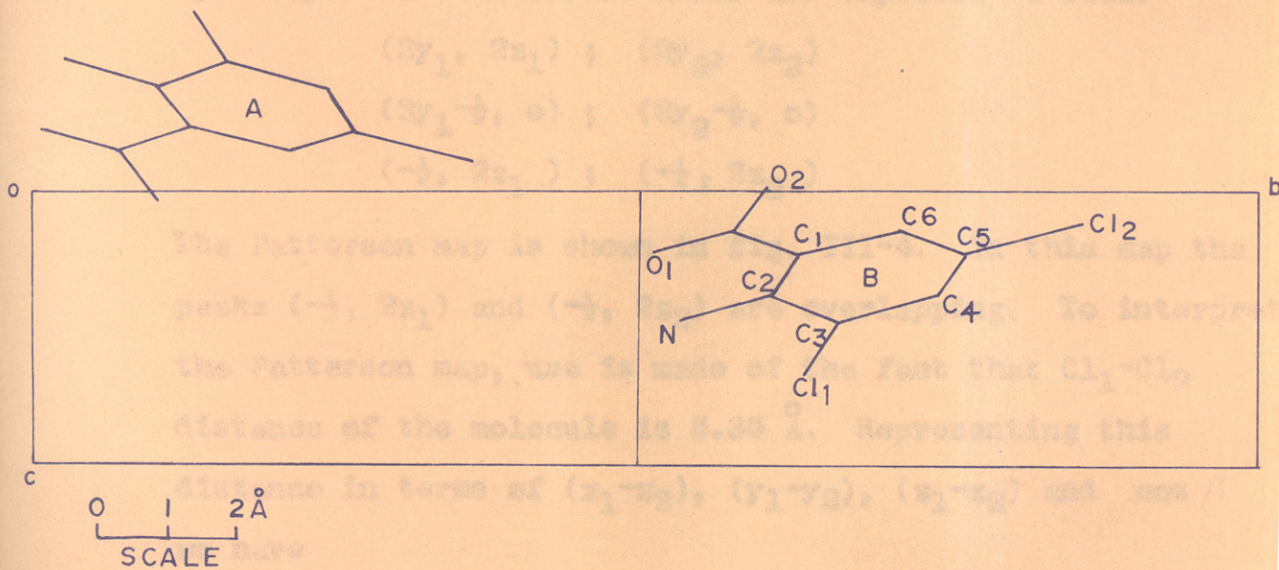


Fig. III-5, SYMMETRY RELATED ATOMS IN THE UNIT CELL (100)

Putting the values of d , $(x_1 - x_2)$, $(y_1 - y_2)$ and $\cos \beta$ in the above equation we get

$$(x_1 - x_2) = 2.023 \text{ \AA} \text{ or } -2.231 \text{ \AA}$$

The x_1 parameter is obtained from peak no. 1 ($x_1 = -0.140$), fig. III-4 and x_2 parameter from peak no. 9 ($x_2 = 0.380$). This way, we get $x_1 - x_2 = 0.380 - (-0.140) = 0.520$ ($\approx 2.0 \text{ \AA}$) this is close to the expected value. With the knowledge of y and approximate x parameters, Cl_1 and Cl_2 atoms are plotted in projection as shown in fig. III-5; the other

(100) Patterson and Fourier Projections

The equivalent points for this projection are:

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

The following peaks due to the interaction between symmetry related chlorine atoms are expected to occur

$$(2y_1, 2z_1); (2y_2, 2z_2)$$

$$(2y_1 - \frac{1}{2}, 0); (2y_2 - \frac{1}{2}, 0)$$

$$(-\frac{1}{2}, 2z_1); (-\frac{1}{2}, 2z_2)$$

The Patterson map is shown in fig. III-4. In this map the peaks $(-\frac{1}{2}, 2z_1)$ and $(-\frac{1}{2}, 2z_2)$ are overlapping. To interpret the Patterson map, use is made of the fact that Cl_1-Cl_2 distance of the molecule is 5.35 \AA . Representing this distance in terms of (x_1-x_2) , (y_1-y_2) , (z_1-z_2) and $\cos \beta$ we have

$$d^2 = (x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2 + 2(x_1-x_2)(z_1-z_2)\cos\beta$$

Putting the values of d , (x_1-x_2) , (y_1-y_2) and $\cos \beta$ in the above equation we get

$$(z_1-z_2) = 2.023 \text{ \AA} \text{ or } -2.231 \text{ \AA}$$

The z_1 parameter is obtained from peak no.1 ($z_1 = -0.140$),
 fig. III-4 and z_2 parameter from peak no.2 ($z_2 = 0.380$).
 This way, we get $z_1-z_2 = -0.380 - (-0.140) = -0.520$ ($\approx -2.0 \text{ \AA}$)
 this is close to the expected value. With the knowledge of y and approximate z parameters, Cl_1 and Cl_2 atoms are plotted in projection as shown in fig. III-5; the other

atoms of the molecule could be fixed from stereochemical considerations. Since most of the z parameters are coming negative, the origin is shifted by a distance of $\frac{1}{2} b$, and the parameters measured from molecule B instead of molecule A (fig. III-5).

With the y parameters obtained from (001) projection and these z parameters, $F(okl)$ are calculated using the expressions,

$$F(okl) = 4 \sum f_n \cos 2\pi ky \cos 2\pi lz \quad \text{for } k = 2n$$

and

$$F(okl) = -4 \sum f_n \sin 2\pi ky \sin 2\pi lz \quad \text{for } k = 2n+1.$$

The parameters were first refined by direct Fourier synthesis and then by the method of Least Squares using the expression

$$\Delta z = - \frac{1}{2\pi} \left[\frac{\sum_{k=2n} \Delta F(4f_n \cdot 1) (G) + \sum_{k=2n+1} (4f_n \cdot 1) \Delta F (H)}{\sum_{k=2n} (4f_n \cdot 1)^2 (G)^2 + \sum_{k=2n+1} (4f_n \cdot 1)^2 (H)^2} \right] \dots (III-12)$$

where $G = \cos 2\pi ky \sin 2\pi lz$

$H = \sin 2\pi ky \cos 2\pi lz$

$\Delta F = (F_o - F_c).$

The z parameters from second direct Fourier map and from first and second Least Square refinement and corresponding R values are given in table III-2.

TABLE - III-2

Atom	From second direct Fourier synthesis	From first Least Square refinement	From second Least Square refinement
	z	z	z
C ₁	0.212	0.224	0.203
C ₂	0.370	0.404	0.400
C ₃	0.456	0.464	0.462
C ₄	0.385	0.399	0.432
C ₅	0.218	0.189	0.208
C ₆	0.127	0.110	0.099
C ₇	0.119	0.120	0.101
O ₁	0.188	0.186	0.181
O ₂	0.973	0.957	0.963
Cl ₁	0.660	0.659	0.659
Cl ₂	0.105	0.088	0.088
N	0.438	0.452	0.485
	R = 26.5 %	R = 22.5 %	R = 17.6 %

(100) Electron Density Projection

The expression for electron density on (100) projection for P2_{1/a} is

$$\rho(\text{oyz}) = \frac{1}{A} \left[F(\text{ooo}) + 2 \sum_0^{\infty} F(\text{oko}) \cos 2\pi ky + 2 \sum_0^{\infty} F(\text{ool}) \cos 2\pi lz \right. \\ \left. + 4 \left\{ \sum_0^{\infty} \sum_0^{\infty} F(\text{okl}) \cos 2\pi ky \cos 2\pi lz - \sum_0^{\infty} \sum_0^{\infty} F(\text{okl}) \sin 2\pi ky \sin 2\pi lz \right\} \right]$$

where A is the area of the projection.



Fig. III - 3 ELECTRON DENSITY PROJECTED ON (100.) PLANE
CONTOURS DRAWN AT INTERVALS OF $1eA^{-2}$
STARTING FROM $3eA^{-2}$

Using observed structure factors and signs obtained from the Least Squares refinement, the (100) electron density projection shown in fig. III-6 was computed; the summation was done using Beever's Lipson strips at interval of 1/60 along b and 1/60 along c. The contours are drawn at an interval of 1 e.Å⁻² starting from 3 e.Å².

(010) Projection

The x parameters from (001) projection and z parameters from (100) projection were used to calculate F(hol). The expression used is

$$F(hol) = \sum_1^n 4f_n \cos 2\pi (hx_n + lz_n) .$$

Directly one least square refinement was given. Further least square refinement did not give sufficient change in z. The parameters after least square refinement are given in table III-3. The expression for Δz is

$$\Delta z = - \frac{1}{2\pi} \frac{\sum \Delta F \cdot 4f_n \cdot l (\sin 2\pi hx \cos 2\pi lz + \cos 2\pi hx \sin 2\pi lz)}{\sum (4f_n l)^2 (\sin 2\pi hx \cos 2\pi lz + \cos 2\pi hx \sin 2\pi lz)^2}$$

TABLE - III-3

z parameters after least square refinement

Atom	z	Atom	z	Atom	z	Atom	z
C ₁	0.221	C ₄	0.400	C ₇	0.073	Cl ₁	0.667
C ₂	0.352	C ₅	0.251	C ₁	0.217	Cl ₂	0.097
C ₃	0.448	C ₆	0.101	C ₂	0.964	N	0.467
R = 17.5 %							

The z parameters used for the three dimensional refinement are the average of the z parameters from (100) and (010) projections.

CHAPTER - IV

THREE DIMENSIONAL REFINEMENT

For the three dimensional 'Least Squares' refinement of atomic parameters and individual isotropic temperature factors, all the observed structure factors of the type hko, hkl, hk2 and hk3 numbering 90, 231, 140 and 46 respectively and totalling 507 were used. The refinement was done with the help of the CDC 3600-160A computer at the Tata Institute of Fundamental Research, Bombay. The following expressions were used:

$$F_c(hkl) = \sum_1^{12} 4 \text{ (Atomic scattering factor part) (Geometric structure factor part)}$$

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

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

The atomic scattering factor $E(J)$ for each reflexion was taken as

$$E(J) = \text{Scat.}(J) \times W(J)$$

'J' indicates the type of atom (i.e. O, N, C, H or Cl).

$$\text{Scat.}(J) = A \exp.(-aP^2) + B \exp.(-bP^2) + C$$

$$\text{and} \quad W(J) = \exp. B(J) \times (-P^2)$$

In these equations A, a, B, b and C are the analytical constants for atomic scattering factors and

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

Throughout this work unity is 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 (1961) 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
Cl	7.239	1.138	7.937	22.203	1.819

Refinement of Parameters

All the four parameters (x_j , y_j , z_j and B_j) were refined simultaneously by the method of Least Squares on computer. The parameters at different stages of refinement and corresponding R values are given in table IV-2. At this stage layerwise scaling was determined and came out to be 1.00, 1.03, 1.07 and 0.89 for zero, first, second and third

layers respectively. After applying layerwise scaling and removing punching errors, the value of R came down to 12.2 % and no further refinement took place. It was therefore decided to refine the anisotropic temperature factors of the atoms along with the atomic parameters.

Atomic parameters at different stages of refinement

Cycle of refinement	Parameters	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
1st cycle R = 20.7%	x	0.1387	0.3011	0.3767	0.3580	0.2678	0.1846
	y	0.1285	0.0982	0.1641	0.2412	0.2605	0.2116
	z	0.2210	0.3768	0.4557	0.4160	0.2291	0.1002
	B*	2.06	2.07	1.83	2.13	1.93	1.94
2nd cycle R = 17.3%	x	0.1928	0.3000	0.3777	0.3629	0.2684	0.1870
	y	0.1287	0.1018	0.1626	0.2410	0.2618	0.2110
	z	0.2282	0.3762	0.4589	0.3740	0.2222	0.1402
	B*	2.08	2.10	1.82	2.14	1.93	1.97
3rd cycle R = 16.8%	x	0.1921	0.2993	0.3762	0.3611	0.2684	0.1866
	y	0.1293	0.1021	0.1631	0.2405	0.2628	0.2097
	z	0.2292	0.3815	0.4610	0.3702	0.2224	0.1458
	B*	2.11	2.12	1.81	2.16	1.93	1.99
4th cycle R = 16.6%	x	0.1926	0.2991	0.3765	0.3610	0.2679	0.1867
	y	0.1294	0.1018	0.1636	0.2402	0.2628	0.2098
	z	0.2283	0.3822	0.4612	0.3676	0.2203	0.1472
	B*	2.13	2.13	1.80	2.17	1.92	2.00

* B in Å²

contd.....

TABLE - IV-2 (contd..)

Cycle of refinement	Parameters	C ₇	C ₁	O ₂	C ₁	C ₁₂	N
1st cycle R = 20.7%	x	0.1155	0.1120	0.0285	0.4999	0.2542	0.3094
	y	0.0745	0.0049	0.0999	0.1296	0.3595	0.0277
	z	0.0873	0.1990	0.9640	0.6632	0.0934	0.4763
	B*	2.01	2.03	2.04	2.06	2.00	2.08
2nd cycle R = 17.3%	x	0.1139	0.1133	0.0275	0.4980	0.2527	0.3123
	y	0.0753	0.0061	0.1040	0.1300	0.3596	0.0289
	z	0.1179	0.2239	0.9735	0.6604	0.1002	0.4778
	B*	2.02	2.07	2.06	2.07	2.01	2.11
3rd cycle R = 16.8%	x	0.1133	0.1136	0.0279	0.4982	0.2527	0.3131
	y	0.0750	0.0062	0.1045	0.1300	0.3598	0.0292
	z	0.1261	0.2242	0.9720	0.6585	0.1023	0.4787
	B*	2.01	2.10	2.08	2.08	2.02	2.14
4th cycle R = 16.6%	x	0.1132	0.1134	0.0280	0.4982	0.2528	0.3134
	y	0.0751	0.0060	0.1049	0.1301	0.3600	0.0296
	z	0.1281	0.2232	0.9711	0.6585	0.1027	0.4790
	B*	1.99	2.13	2.11	2.10	2.03	2.16

* B in Å²

CHAPTER - V

REFINEMENT OF TEMPERATURE FACTOR

The use of average isotropic temperature factor (determined by Wilson's statistical method) for all atoms of the crystal in order to account for the diminution of the intensities of X-ray reflexions with increasing angle is only an approximation. In the later stages of crystal structure refinement, the use of proper anisotropic temperature factor becomes necessary to determine accurate atomic parameters and to remove the discrepancies between observed and calculated structure factors. Hughes (1941) for the first time applied anisotropic temperature factors while refining the structure of melamine; he found a marked improvement in the observed and calculated F 's for $\sin\theta/\lambda$ less than 0.60. Beyond this, however, the discrepancies remained very bad and it became clear that an adjustment of atomic parameters to remove these discrepancies would spoil the agreement already obtained for $\sin\theta/\lambda < 0.60$. An inspection of $h0l$ reflexions showed that in general the F 's which calculated high were of the type $(h0l)$ and those which calculated low were of the type $(h0\bar{l})$. This would mean that thermal vibrations are anisotropic and the larger displacements (which are most likely to be normal to the molecular plane) are generally across $(h0l)$ planes. Hughes used an anisotropic temperature factor of the form

$e^{-B' \sin^2 \theta / \lambda^2}$ where $B' = A + B \cos^2 \theta$, A and $(A+B)$ are the temperature factors for planes parallel and perpendicular respectively to the direction of maximum vibration, and θ is the angle between the normal to the reflecting plane and the direction of maximum vibration.

For the space group $P2_{1/a}$, the equivalent points are $\pm (x, y, z)$; $\pm (\frac{1}{2}+x, \frac{1}{2}-y, z)$. 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 $\pm (\frac{1}{2}+x, \frac{1}{2}-y, z)$ are related to the first pair by mirror symmetry normal to 'b' axis. Let the atomic scattering factors for atoms $\pm (x, y, z)$ be

$$f_{(x,y,z)} = f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right]$$

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

$$f_{(\frac{1}{2}+x, \frac{1}{2}-y, z)} = f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right]$$

(Rollet and Davies, 1955).

Therefore the expression for $F(hkl)$ becomes,

$$F(hkl) = \sum 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi (hx+ky+lz) + \sum 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos \pi \left\{ 2\pi (hx-ky+lz) + \pi (h+k) \right\}$$

As in the case of refinement of atomic parameters, it can be shown that the correction Δa_{1j} in the thermal parameter a_{1j} is given by

$$a_{1j} = \frac{\sum \Delta F (\partial F / \partial a_{1j})}{\sum (\partial F / \partial a_{1j})^2}$$

Differentiating expressions for the structure factors with respect to different a_{1j} 's, we get the following expressions for $\partial F / \partial a_{1j}$:

$$\frac{\partial F}{\partial a_{11}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi(hx+ky+lz) \times (-h^2) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx-ky+lz+\frac{h+k}{2} \right) \times (-h^2)$$

$$\frac{\partial F}{\partial a_{22}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi(hx+ky+lz) \times (-k^2) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx-ky+lz+\frac{h+k}{2} \right) \times (-k^2)$$

$$\frac{\partial F}{\partial a_{33}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi(hx+ky+lz) \times (-l^2) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx + ky + lz + \frac{h+k}{2} \right) \times (-l^2)$$

$$\frac{\partial F}{\partial a_{12}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi (hx+ky+lz) \times (-2hk) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx + ky + lz + \frac{h+k}{2} \right) \times (+2hk)$$

$$\frac{\partial F}{\partial a_{23}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi (hx+ky+lz) \times (-2kl) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx + ky + lz + \frac{h+k}{2} \right) \times (2kl)$$

$$\frac{\partial F}{\partial a_{13}} = 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{23}kl + 2a_{13}hl) \right] \cos 2\pi (hx+ky+lz) \times (-2hl) + 2f_0 \exp. \left[- (a_{11}h^2 + a_{22}k^2 + a_{33}l^2 - 2a_{12}hk - 2a_{23}kl + 2a_{13}hl) \right] \times \cos 2\pi \left(hx + ky + lz + \frac{h+k}{2} \right) \times (-2hl)$$

The values of a_{1j} 's used to start the least square refinement are those corresponding to the isotropic temperature factors obtained after the refinement shown in chapter IV. These values of a_{1j} 's given in table V-1 were obtained from the B^* values (isotropic temperature factors) as shown below.

The atomic scattering factor 'f' is given by

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

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

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

From equation (V-1)

$$f = f_0 e^{-B/4 (2\sin\theta/\lambda)^2} = f_0 e^{-\frac{B}{4} S^2} \quad \dots (V-3)$$

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

$$S^2 = (ha^*)^2 + (kb^*)^2 + (lc^*)^2 + 2(ha^*)(lc^*)(\cos\beta^*) \quad \dots (V-4)$$

Substituting the values of S^2 from (V-4) in (V-3), we have

$$f = f_0 \exp. - \left(\frac{B}{4} a^{*2} h^2 + \frac{B}{4} b^{*2} k^2 + \frac{B}{4} c^{*2} l^2 + 2 \frac{B}{4} a^* c^* \cos\beta^* hl \right) \quad \dots (V-5)$$

Comparing the equations (V-2) and (V-5) and putting

$a^* = 1/a \sin \beta$, $b^* = 1/b$ and $c^* = 1/c \sin \beta$, we get

$$\begin{aligned} a_{11} &= B/4a^2 \sin^2 \beta; & a_{22} &= B/4b^2; & a_{33} &= B/4c^2 \sin^2 \beta; \\ a_{13} &= B \cos\beta^*/4a c \sin^2 \beta; & a_{12} &= 0; & a_{23} &= 0. \end{aligned}$$

TABLE - V-1

Atom	B	a_{11}	a_{22}	a_{33}	a_{13}	
C ₁	2.15	0.0035	0.0018	0.0377	0.0005	
C ₂	2.14	0.0035	0.0018	0.0375	0.0005	
C ₃	1.79	0.0029	0.0015	0.0313	0.0005	
C ₄	2.18	0.0035	0.0019	0.0382	0.0006	$a_{23} = 0$
C ₅	1.91	0.0031	0.0016	0.0334	0.0005	$a_{12} = 0$
C ₆	2.01	0.0033	0.0017	0.0353	0.0005	
C ₇	1.98	0.0032	0.0017	0.0346	0.0005	
O ₁	2.16	0.0035	0.0018	0.0379	0.0005	
O ₂	2.13	0.0034	0.0018	0.0373	0.0005	
N	2.18	0.0035	0.0019	0.0382	0.0005	
Cl ₁	2.11	0.0034	0.0018	0.0371	0.0005	
Cl ₂	2.03	0.0033	0.0017	0.0357	0.0005	

Using a_{ij} 's given in table V-1, least squares refinement of both positional and thermal parameters was carried out. After one cycle of refinement, R came down to 11.3%. It started increasing on further refinement. So, thermal parameters of only Cl₁, Cl₂, N, O₁ and O₂ and positional parameters of all the atoms were refined. The refinement proceeded normally. After two more cycles of refinement, R came down to 10.5%. The positional and thermal parameters at different stages of refinement and corresponding R values are given in table V-2.

Atomic and thermal parameters at different stages of refinement

Cycle of refinement	Parameters	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	
Starting cycle R = 12.2%	x	0.1926	0.2991	0.3765	0.3610	0.2679	0.1867	
	y	0.1295	0.1018	0.1636	0.2402	0.2628	0.2099	
	z	0.2283	0.3822	0.4612	0.3677	0.2204	0.1472	
	a ₁₁	0.0035	0.0035	0.0029	0.0035	0.0031	0.0033	
	a ₂₂	0.0018	0.0018	0.0015	0.0019	0.0016	0.0017	
	a ₃₃	0.0377	0.0375	0.0313	0.0382	0.0334	0.0353	
	a ₁₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
	a ₂₃	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
	a ₁₃	0.0005	0.0005	0.0006	0.0006	0.0005	0.0005	
	1st cycle R = 11.3%	x	0.1931	0.2987	0.3764	0.3613	0.2680	0.1865
		y	0.1295	0.1020	0.1636	0.2401	0.2626	0.2100
		z	0.2283	0.3818	0.4592	0.3665	0.2217	0.1463
		a ₁₁	0.0033	0.0022	- 0.0001*	0.0025	0.0027	0.0040
a ₂₂		0.0033	0.0031	0.0021	0.0023	0.0014	0.0018	
a ₃₃		0.0505	0.0392	0.0226	0.0366	- 0.0019*	0.0446	
a ₁₂		0.0003	0.0007	0.0013	- 0.0003	0.0001	- 0.0007	
a ₂₃		0.0037	0.0003	- 0.0007	0.0019	0.0006	- 0.0018	
a ₁₃		0.0105	- 0.0003	- 0.0017	0.0112	0.0047	0.0048	

TABLE - V-2 (contd..)

Cycle of refinement	Parameters	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
2nd cycle R = 10.6%	x	0.1931	0.2987	0.3764	0.3612	0.2680	0.1865
	y	0.1295	0.1021	0.1636	0.2400	0.2626	0.2100
	z	0.2283	0.3818	0.4592	0.3665	0.2219	0.1463
	a ₁₁	0.0033	0.0022	- 0.0001*	0.0025	0.0027	0.0040
	a ₂₂	0.0033	0.0031	0.0021	0.0023	0.0014	0.0018
	a ₃₃	0.0505	0.0392	0.0226	0.0366	- 0.0019*	0.0446
	a ₁₂	0.0003	0.0007	0.0018	- 0.0003	0.0001	- 0.0007
	a ₂₃	0.0037	0.0003	- 0.0007	0.0019	0.0006	- 0.0018
	a ₁₃	0.0105	- 0.0003	- 0.0017	0.0112	0.0047	0.0048
	3rd cycle R = 10.5%	x	0.1937	0.2988	0.3763	0.3606	0.2678
y		0.1295	0.1023	0.1635	0.2398	0.2624	0.2108
z		0.2283	0.3821	0.4593	0.3703	0.2218	0.1454
a ₁₁		0.0033	0.0021	- 0.0001*	0.0025	0.0027	0.0040
a ₂₂		0.0033	0.0030	0.0021	0.0023	0.0014	0.0018
a ₃₃		0.0505	0.0392	0.0226	0.0366	- 0.0019*	0.0446
a ₁₂		0.0003	0.0007	0.0018	- 0.0003	0.0001	- 0.0007
a ₂₃		0.0036	0.0003	- 0.0007	0.0019	0.0006	- 0.0018
a ₁₃		0.0105	- 0.0003	- 0.0017	0.0112	0.0047	0.0048

TABLE - V-2 (contd...)

Cycle of Refinement	Parameters	C ₇	O ₁	O ₂	N	Cl ₁	Cl ₂
Starting cycle R = 12.2%	x	0.1132	0.1135	0.0280	0.3134	0.4982	0.2528
	y	0.0751	0.0060	0.1050	0.0296	0.1301	0.3600
	z	0.1281	0.2232	0.9712	0.4790	0.6585	0.1027
	a ₁₁	0.0032	0.0035	0.0034	0.0035	0.0034	0.0033
	a ₂₂	0.0017	0.0018	0.0018	0.0019	0.0018	0.0017
	a ₃₃	0.0346	0.0379	0.0373	0.0382	0.0371	0.0357
	a ₁₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	a ₂₃	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	a ₁₃	0.0005	0.0005	0.0005	0.0006	0.0005	0.0005
1st cycle R = 11.3%	x	0.1127	0.1135	0.0279	0.3136	0.4982	0.2527
	y	0.0750	0.0062	0.1054	0.0297	0.1302	0.3600
	z	0.1275	0.2233	0.9704	0.4806	0.6589	0.1026
	a ₁₁	0.0029	0.0047	0.0029	0.0046	0.0036	0.0042
	a ₂₂	0.0016	0.0022	0.0026	0.0027	0.0025	0.0017
	a ₃₃	0.0081	0.0676	0.0620	0.0512	0.0482	0.0428
	a ₁₂	- 0.0006	0.0002	- 0.0003	- 0.0002	0.0003	- 0.0005
	a ₂₃	- 0.0025	0.0002	- 0.0009	- 0.0008	0.0002	- 0.0006
	a ₁₃	- 0.0018	- 0.0044	0.0014	0.0001	- 0.0033	- 0.0015

TABLE - V-2 (contd..)

Cycle of refinement	Parameters	C ₇	C ₁	O ₂	N	Cl ₁	Cl ₂	
2nd cycle R = 10.6%	x	0.1128	0.1135	0.0279	0.3136	0.4983	0.2528	
	y	0.0750	0.0062	0.1054	0.0297	0.1302	0.3600	
	z	0.1275	0.2233	0.9704	0.4806	0.6588	0.1026	
	a ₁₁	0.0029	0.0047	0.0029	0.0046	0.0036	0.0041	
	a ₂₂	0.0016	0.0022	0.0026	0.0027	0.0025	0.0017	
	a ₃₃	0.0081	0.0676	0.0620	0.0512	0.0482	0.0427	
	a ₁₂	- 0.0006	0.0002	- 0.0003	- 0.0002	0.0003	- 0.0005	
	a ₂₃	- 0.0025	0.0002	- 0.0009	- 0.0008	0.0002	- 0.0006	
	a ₁₃	0.0018	- 0.0044	0.0014	0.0001	- 0.0038	- 0.0015	
	3rd cycle R = 10.5%	x	0.1118	0.1137	0.0280	0.3144	0.4982	0.2529
		y	0.0748	0.0060	0.1053	0.0295	0.1304	0.3602
		z	0.1297	0.2254	0.9691	0.4826	0.6586	0.1026
		a ₁₁	0.0029	0.0027	0.0014	0.0037	0.0030	0.0041
a ₂₂		0.0016	0.0010	0.0017	0.0019	0.0021	0.0012	
a ₃₃		0.0081	0.0554	0.0421	0.0241	0.0353	0.0294	
a ₁₂		- 0.0006	- 0.0002	- 0.0006	- 0.0003	0.0004	- 0.0004	
a ₂₃		- 0.0025	0.0009	- 0.0022	- 0.0002	- 0.0004	0.0006	
a ₁₃		- 0.0018	- 0.0048	0.0017	0.0005	- 0.0025	0.0001	

* These a_{ij} values for carbon atoms have small negative values. Since negative value for a₁₁ is not possible, thermal parameters of carbons are not meaningful.

CHAPTER - VI

RESULTS AND DISCUSSION

The present chapter is divided into two portions:

(a) crystal and molecular structure, (b) thermal anisotropy.

(a) Crystal and Molecular Structure

Results

The final atomic co-ordinates and standard deviations are given in table VI-1, and the bond lengths and bond angles in table VI-2; the bond lengths and angles are also shown in fig. VI-1.

TABLE - VI-1

Atom	x Å	y Å	z Å
C ₁	2.419 ± 0.007	2.204 ± 0.007	0.869 ± 0.008
C ₂	3.733 ± 0.007	1.741 ± 0.007	1.452 ± 0.008
C ₃	4.700 ± 0.007	2.783 ± 0.007	1.745 ± 0.008
C ₄	4.504 ± 0.007	4.081 ± 0.007	1.407 ± 0.008
C ₅	3.345 ± 0.007	4.466 ± 0.007	0.843 ± 0.008
C ₆	2.331 ± 0.007	3.588 ± 0.007	0.553 ± 0.008
C ₇	1.396 ± 0.007	1.273 ± 0.007	0.493 ± 0.008
O ₁	1.420 ± 0.006	0.102 ± 0.005	0.857 ± 0.006
O ₂	0.350 ± 0.006	1.792 ± 0.005	0.117 ± 0.006
N	3.927 ± 0.006	0.502 ± 0.007	1.834 ± 0.007
Cl ₁	6.223 ± 0.002	2.219 ± 0.003	2.503 ± 0.001
Cl ₂	3.159 ± 0.002	6.131 ± 0.003	0.390 ± 0.001

TABLE - VI-2

Final bond lengths and angles along with their estimated standard deviations

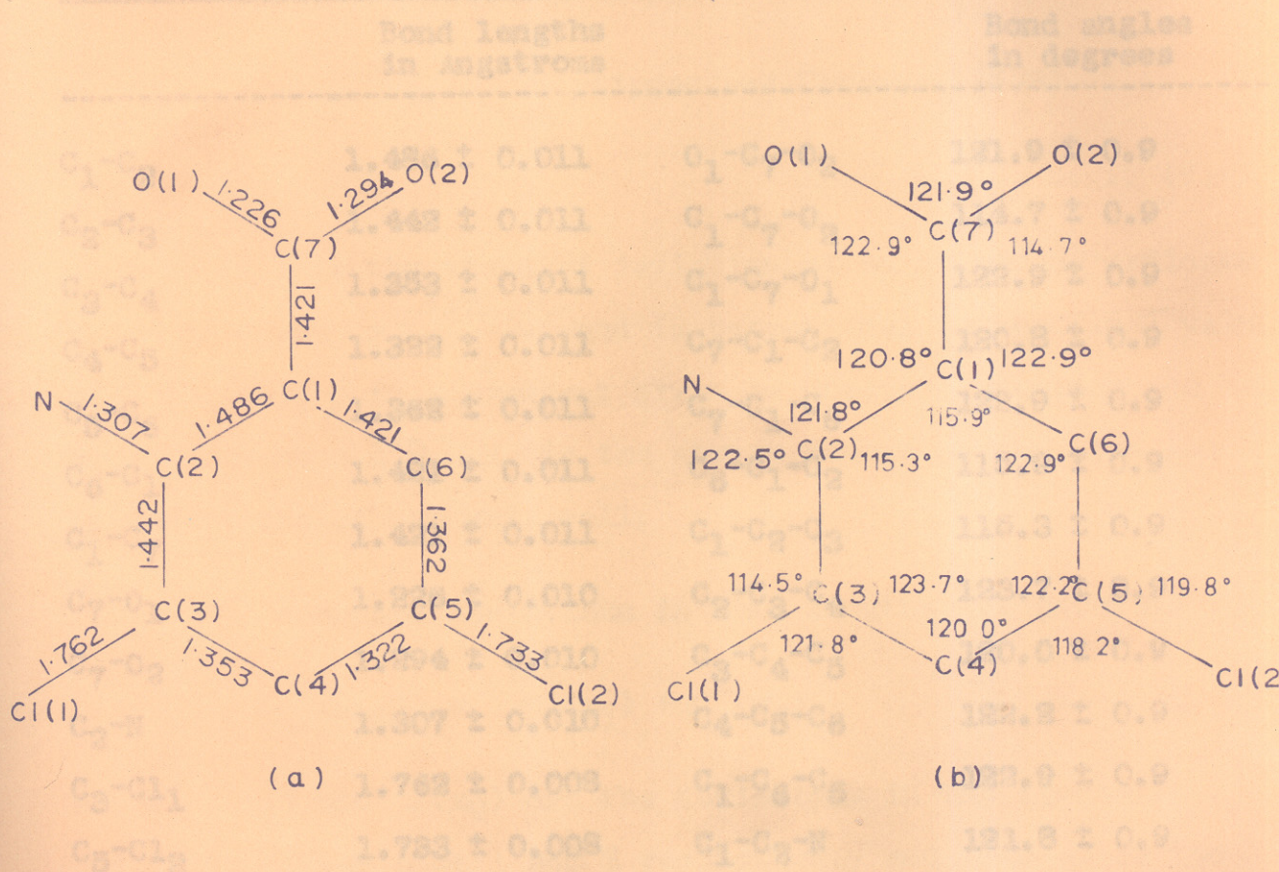


Fig. VI-1 (a) BOND LENGTHS (A°) AND (b) BOND ANGLES IN 3:5 DICHLORO-2-AMINO BENZOIC ACID

TABLE - VI-2

Final bond lengths and angles along with their
estimated standard deviations

	Bond lengths in Angstroms		Bond angles in degrees
C ₁ -C ₂	1.436 ± 0.011	O ₁ -C ₇ -O ₂	121.9 ± 0.9
C ₂ -C ₃	1.442 ± 0.011	C ₁ -C ₇ -O ₂	114.7 ± 0.9
C ₃ -C ₄	1.353 ± 0.011	C ₁ -C ₇ -O ₁	122.9 ± 0.9
C ₄ -C ₅	1.322 ± 0.011	C ₇ -C ₁ -C ₂	120.8 ± 0.9
C ₅ -C ₆	1.362 ± 0.011	C ₇ -C ₁ -C ₆	122.9 ± 0.9
C ₆ -C ₁	1.421 ± 0.011	C ₆ -C ₁ -C ₂	115.9 ± 0.9
C ₁ -C ₇	1.421 ± 0.011	C ₁ -C ₂ -C ₃	115.3 ± 0.9
C ₇ -O ₁	1.226 ± 0.010	C ₂ -C ₃ -C ₄	123.7 ± 0.9
C ₇ -O ₂	1.294 ± 0.010	C ₃ -C ₄ -C ₅	120.0 ± 0.9
C ₂ -N	1.307 ± 0.010	C ₄ -C ₅ -C ₆	122.2 ± 0.9
C ₃ -Cl ₁	1.762 ± 0.008	C ₁ -C ₆ -C ₅	122.9 ± 0.9
C ₅ -Cl ₂	1.733 ± 0.008	C ₁ -C ₂ -N	121.8 ± 0.9
		C ₃ -C ₂ -N	122.5 ± 0.9
		C ₂ -C ₃ -Cl ₁	114.5 ± 0.8
		C ₄ -C ₃ -Cl ₁	121.8 ± 0.9
		C ₄ -C ₅ -Cl ₂	118.2 ± 0.9
		C ₆ -C ₅ -Cl ₂	119.8 ± 0.9

The standard deviations in atomic co-ordinates have been calculated using the formula,

$$\sigma(x_n) = \left(\frac{K}{\sqrt{2} Z_n} \right) \left(\frac{\bar{F}}{2p} \right)^{5/4} \left(\frac{1}{V} \sum_{n=1}^N Z_n^2 \right)^{1/2}$$

(Lipson and Cochran, 1953)

..... (VI-1)

where $\sigma(x_n)$ is the standard deviation of an atomic co-ordinate x_n , K is given by $\left(\frac{\sigma(F_0)}{F_0} \right)$ and is taken equal to the final value of R (0.105), p is a constant given by Costán's equation and has been taken as 5 \AA^{-2} . Z_n is the atomic number of the atom and V is the volume of the unit cell.

The standard deviations in bond lengths are given by

$$\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2), \quad \text{..... (VI-2)}$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the deviations in the atomic positions of the atom 1 and 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

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

..... (VI-3)

Here θ is the angle subtended at atom 2 by the bonds from atoms 1 and 3. $\sigma(r_1)$, $\sigma(r_2)$ and $\sigma(r_3)$ are the standard deviations for the co-ordinates of the atoms 1, 2 and 3 respectively. d_{12} , d_{13} and d_{23} are the bond lengths.

Orthogonal co-ordinates

The atomic coordinates (x', y, z') in Å units as referred to orthogonal axes a' , b and c (a' axis is normal to bc plane) are given in table VI-3 and are calculated using the relations,

$$x' = x \sin \beta; \quad y' = y; \quad z' = z + x \cos \beta.$$

TABLE - VI-3

Orthogonal coordinates in Å units

Atom	x'	y	z'
C ₁	2.416	2.204	0.755
C ₂	3.729	1.741	1.276
C ₃	4.695	2.783	1.524
C ₄	4.500	4.081	1.195
C ₅	3.341	4.466	0.685
C ₆	2.328	3.588	0.443
C ₇	1.394	1.273	0.427
O ₁	1.418	0.102	0.790
O ₂	0.350	1.792	0.133
N	3.923	0.502	1.649
Cl ₁	6.216	2.219	2.210
Cl ₂	3.156	6.131	0.241

The tables VI-4, VI-5 and VI-6 give equations of different planes (with respect to the orthogonal coordinate angles between different planes and deviation of atoms from different planes respectively.

TABLE - VI-4

Equations of planes.

No.	Plane	Equation
(1)	Benzene ring	$0.3537 x' - 0.1605 y - 0.9215 z' + 0.1674 = 0$
(2)	Carboxylic group	$0.3469 x' - 0.2714 y - 0.8984 z' + 0.2454 = 0$
(3)	Plane through O_1 , O_2 and dimer	$-0.4893 x' + 0.1592 y + 0.8577 z' = 0$
(4)	Plane through O_1 , O_2 and C_4^1	$0.4216 x' - 0.2148 y - 0.8811 z' + 0.1203 = 0$
(5)	Plane through O_1 , C_1^1 and N	$-0.3440 x' + 0.1790 y + 0.9218 z' - 0.2587 = 0$

TABLE - VI-5

Angles between different planes.

	(2)	(3)
(1)	6.0°	10.4°
(2)	-	3.5°

TABLE - VI-6

Deviation in Å units of atoms
from different planes

Atom	(1)	(2)	(3)	(4)	(5)
C ₁	-0.028	-	-0.184	-	-
C ₂	0.031	-	-	0.194	-0.542
C ₃	-0.023	-	-	-	-
C ₄	0.003	-	-	-	-
C ₅	0.001	-	-	-	-
C ₆	0.007	-	-	-	-
C ₇	0.063	-0.193	-0.109	-	-0.117
O ₁	-0.076	-	-	-	-
O ₂	0.126	-	-	-	-
N	-0.045	-	-	0.213	-
Cl ₁	-0.027	-	-	-	-
Cl ₂	0.078	-	-	-	-
N($\frac{1}{2}$ -x, $\frac{1}{2}$ +y, 1-z)	-2.170	-	-	-	-
O ₁ ($\frac{1}{2}$ -x, $\frac{1}{2}$ +y, \bar{z})	1.490	-	-	-	-

Discussion

(i) Molecular structure

The estimated standard deviations (e.s.d.) of the measured carbon-carbon bond lengths are ± 0.011 Å. The bond lengths of the benzene ring (average value 1.391 Å)

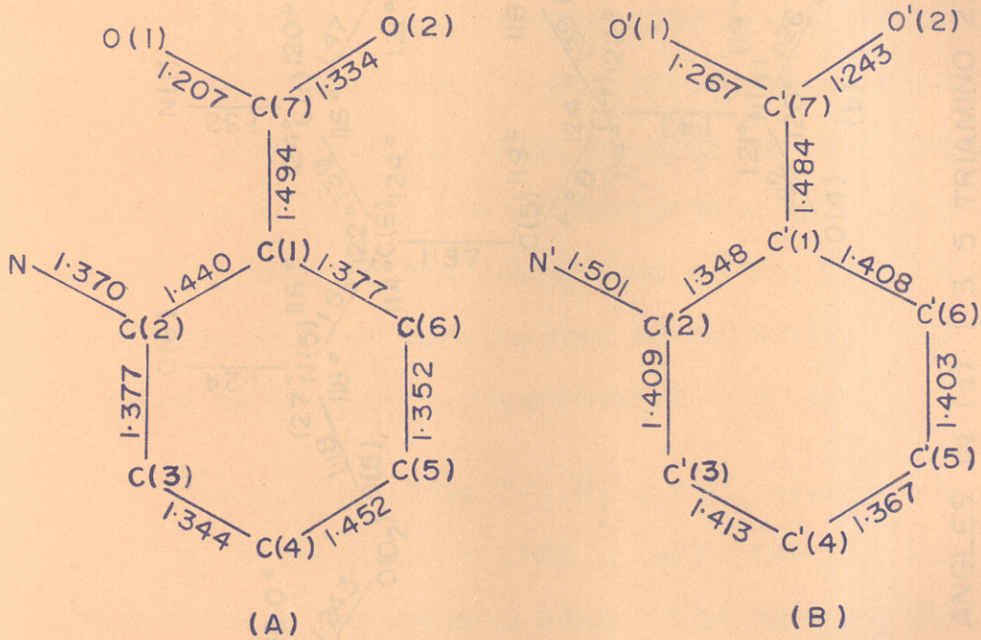


Fig. VI-2 BOND LENGTHS IN 2-AMINOBENZOIC ACID

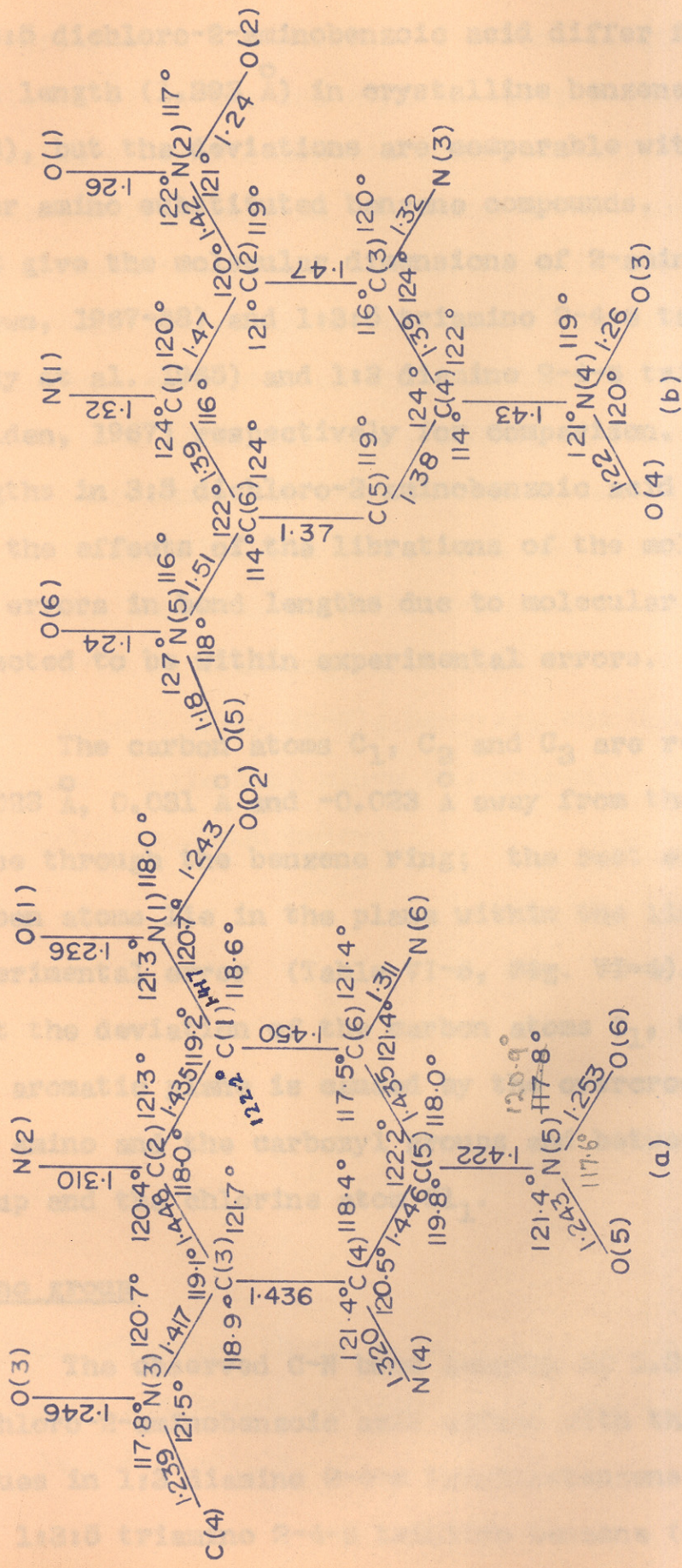


Fig. VI-3 BOND LENGTHS AND BOND ANGLES IN (a) 1:3:5 TRIAMINO 2:4:6 TRINITRO BENZENE
 (b) 1:3 DIAMINO 2:4:6 TRINITRO BENZENE.

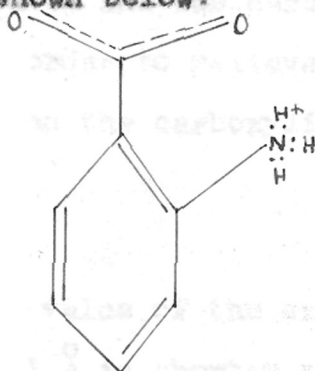
in 3:5 dichloro-2-aminobenzoic acid differ from the C-C bond length (1.393 \AA) in crystalline benzene (Cox et al., 1958), but the deviations are comparable with those in other amino substituted benzene compounds. Figs. VI-2 and VI-3 give the molecular dimensions of 2-aminobenzoic acid (Brown, 1967-68) and 1:3:5 triamino 2-4-6 trinitrobenzene (Cady et al. 1965) and 1:3 diamino 2-4-6 trinitrobenzene (Holden, 1967) respectively for comparison. The bond lengths in 3:5 dichloro-2-aminobenzoic acid are not corrected for the effects of the librations of the molecule; however, the errors in bond lengths due to molecular oscillation are expected to be within experimental errors.

The carbon atoms C_1 , C_2 and C_3 are respectively -0.023 \AA , 0.031 \AA and -0.023 \AA away from the least square plane through the benzene ring; the rest of the aromatic carbon atoms lie in the plane within the limit of experimental error (Table VI-6, ~~Fig. VI-4~~). It appears that the deviation of the carbon atoms C_1 , C_2 and C_3 from the aromatic plane is caused by the overcrowding between the amino and the carboxyl groups and between the amino group and the chlorine atom Cl_1 .

Amino group

The observed C-N bond length of 1.307 \AA in 3:5 dichloro-2-aminobenzoic acid agrees with the corresponding values in 1:3 diamino 2-4-6 trinitrobenzene (Holden, 1967) and 1:3:5 triamino 2-4-6 trinitro benzene (Cady, 1965) but

is shorter than the observed C-N bond lengths (1.370 Å and 1.501 Å) in the two crystallographically independent molecules of 2-aminobenzoic acid (table VI-7). There is a free electron pair in the amino group, and the electron-displacement toward the C-N bond can impart a large double bond character to this bond. Owing to the large double bond character of the C₂-N bond in 3:5 dichloro-2-aminobenzoic acid, the C₂-C₁ and C₂-C₃ bonds show lesser double bond character than in benzene and have increased in length from 1.393 Å to 1.486 Å and 1.442 Å respectively. The double bond character in C-N bond is lesser in molecule A (fig. VI-2) of 2-aminobenzoic acid (C-N bond length, 1.370 Å); in molecule B (fig. VI-2), however, the C-N bond (1.501 Å) is a pure single bond since the molecule exists as a zwitterion as shown below:



In this molecule, there is no free electron pair in the NH₃⁺ group and hence electron displacement towards the C-N bond is not possible.

TABLE - VI-7

No.	Compound	C-N bond lengths in Å	Reference
1	1:3:5 triamino-2:4:6 trinitrobenzene	1.310, 1.320, 1.311	Cady et al., 1965
2	1:3 diamino-2:4:6-trinitrobenzene	1.320, 1.320	Holden, 1967
3	2-aminobenzoic acid (A)	1.37	Brown, 1967-68
4	2-aminobenzoic acid (B)	1.50	Brown, 1967-68

The nitrogen atom of the amino group is -0.045 \AA away from the benzene plane. The C_7 atom of the carboxyl group is deviated to the other direction to the extent of $+0.063 \text{ \AA}$. This shows that the nitrogen atom and the carbon atom C_7 are moving away from each other in order to relieve intramolecular overcrowding between the amino and the carboxylic groups.

Carboxylic group

The observed value of the exocyclic C-C (i.e. C_1-C_7) bond length of 1.421 \AA is shorter than that usually observed in substituted benzoic acids (table VI-8). This indicates a sufficient degree of conjugation across this bond. The fact that inspite of sufficient conjugation across this bond, the plane of the carboxylic group makes an angle of 6.0° with the aromatic plane (table VI-5) suggests that departure from coplanarity of the carboxylic group and the aromatic plane is due probably to the intramolecular overcrowding between the carboxylic and the amino groups.

TABLE - VI-3

Bond distances and angles in various carboxylic acids

Compound	exocyclic C-C bond	C-OH	C=O	R-C-OH	R-C-O	O=C-OH	Reference
Salicylic acid (dimer)	1.457 Å	1.307 Å	1.234 Å	116.0°	122.8°	121.2°	Sundaralingam and Jensen (1965)
*Benzoic acid (dimer)	1.480	1.290	1.240	118.0	122.0	122.0	Sim, Robertson and Goodwin (1955)
p-nitrobenzoic acid (dimer)	1.480	1.319	1.222	115.0	121.1	123.9	Sakore, Pant (1966)
o-nitrobenzoic acid (dimer)	1.489	1.295	1.223	117.0	121.0	121.0	Sakore, Tavale and Pant (1967)
3:5 dichloro-2- aminobenzoic acid (dimer)	1.421	1.294	1.226	114.7	122.9	121.9	Present work.

* Two dimensional work

In the carboxylic group, there is a short C₇-O₁ bond (1.226 Å) and a large C₇-O₂ bond (1.294 Å). The short bond is associated with C₁-C₇-O₁ angle of 122.9° and longer bond with an angle C₁-C₇-O₂ of 114.7°; the angle O₂-C₇-O₁ is ^{121.9°}122.0°. The obtuse value of O-C-O angle 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 most of the carboxylic acids (table VI-8).

Chlorine atoms

The two chlorine atoms are substituted at 3 and 5 positions. The C₃-Cl₁ distance is 1.762 Å and C₅-Cl₂ distance is 1.733 Å. The C-Cl bond lengths in some other chlorosubstituted benzene compounds are given in table VI-9 for comparison.

TABLE - VI-9

No.	Compound	C-Cl bond lengths in Å	Reference
1.	2:5 dichloroaniline	1.744, 1.743	Jeffery et al., 1963
2.	2-chloro-4-nitro-aniline	1.760	McPhail et al., 1965
3.	3:5 dichloro-2-aminobenzoic acid	1.762, 1.733	Present work.

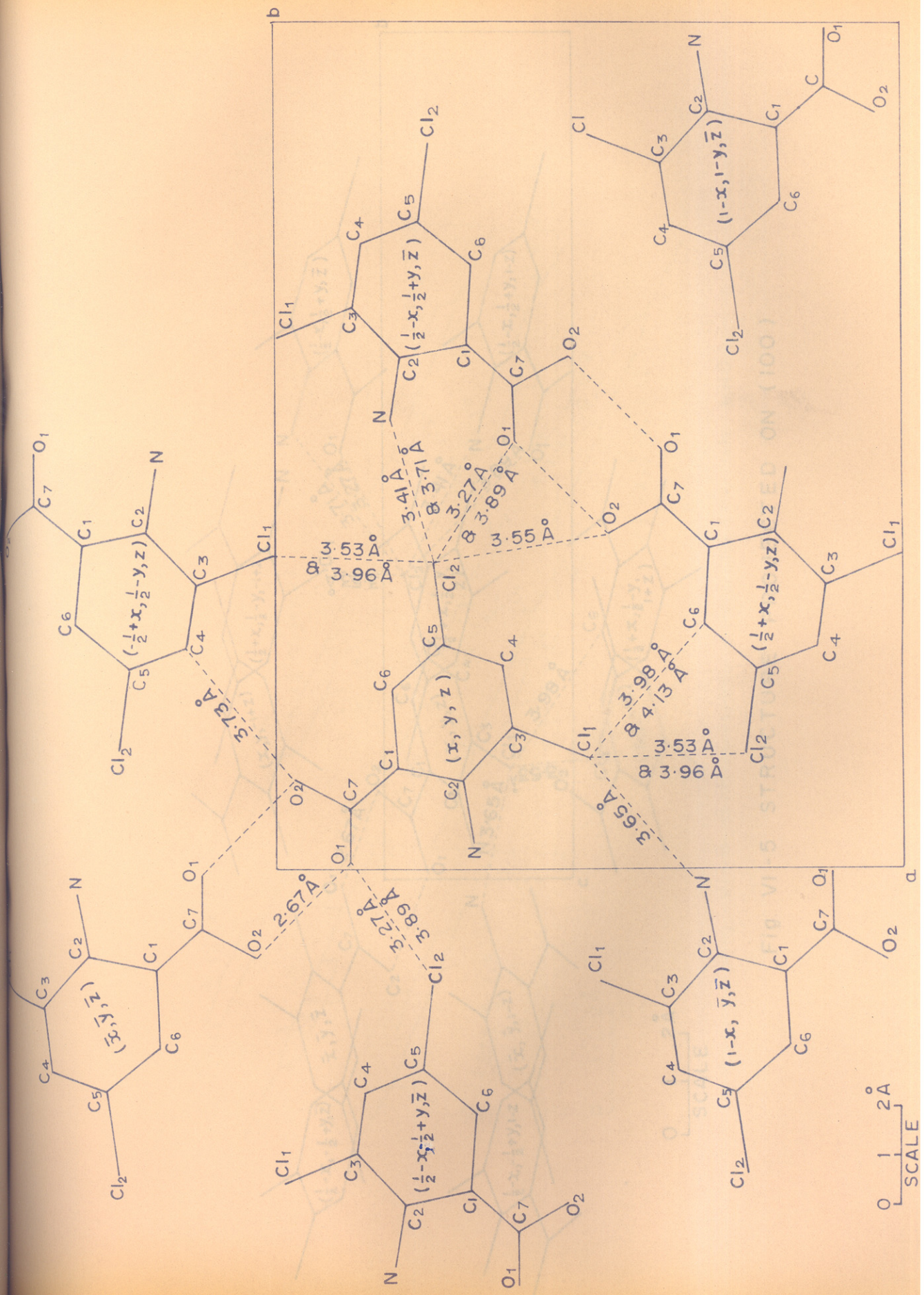
The two chlorine atoms Cl_1 and Cl_2 are respectively -0.027 \AA and $+0.078 \text{ \AA}$ away from the benzene plane (table - VI-6). The large deviation of the Cl_2 atom from the benzene plane appears to be due to intermolecular interaction and is discussed in the following section.

(11) Crystal structure

The projections of the structure on (001), (010)⁽¹⁰⁰⁾ and (100) planes are shown in fig. VI-4, VI-5 and VI-6. The short intermolecular contacts are listed in table VI-10. In these figures, all the symmetry related molecules in the unit cell and few neighbouring molecules are shown. The intermolecular contacts are indicated by broken lines. The principal intermolecular contacts are between the oxygen atoms of the carboxyl groups of the neighbouring molecules forming dimers, the distance between the oxygen atoms being 2.67 \AA . These dimers are packed in the unit cell in such a way that the axis of any dimer A is across the axes of the neighbouring dimers B (fig. VI-7).

The chlorine atom Cl_1 has the following short contacts with the neighbouring molecules

$Cl_1(x, y, z) - N(1-x, \bar{y}, 1-z)$	3.65 \AA
$Cl_1(x, y, z) - Cl_2(\frac{1}{2}+x, \frac{1}{2}-y, 1+z)$	3.53 \AA
$Cl_1(x, y, z) - Cl_2(\frac{1}{2}+x, \frac{1}{2}-y, z)$	3.96 \AA



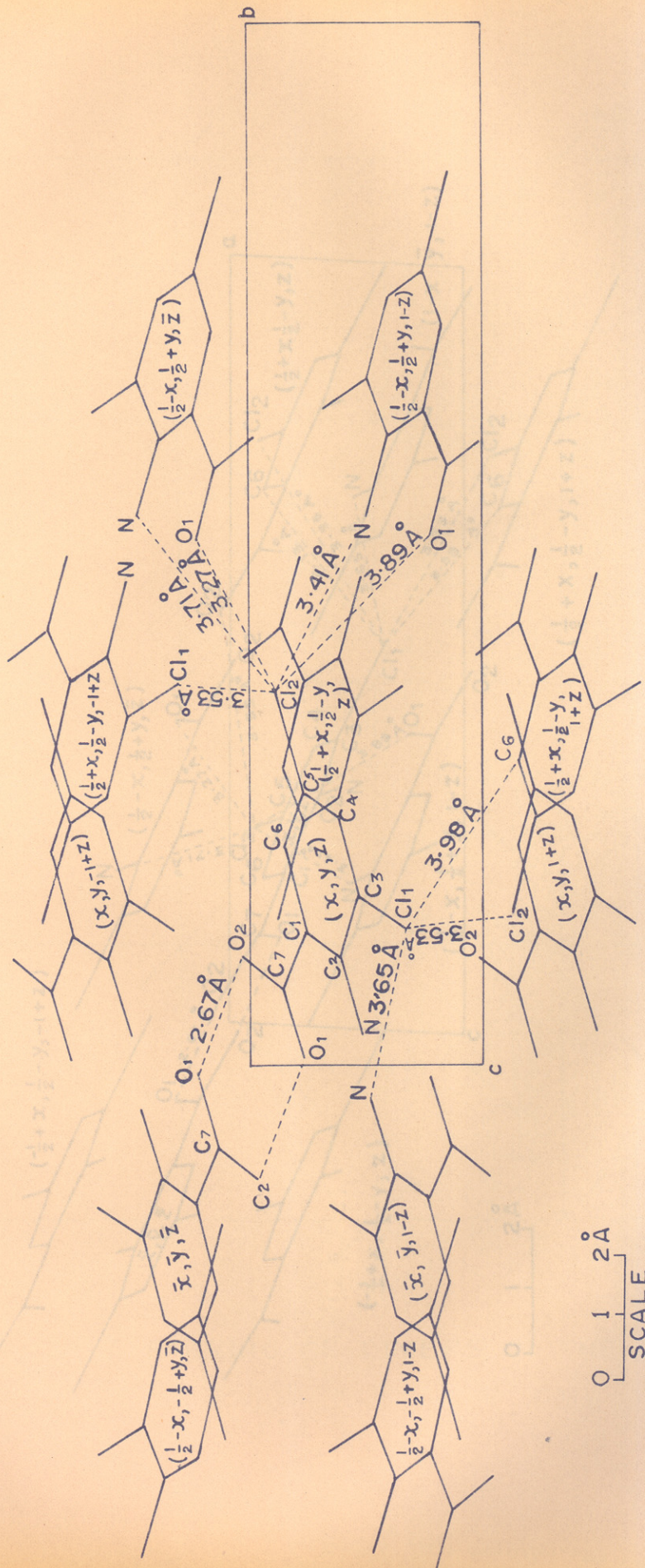


FIG. VI-5 STRUCTURE PROJECTED ON (100)

Fig. VI-5 STRUCTURE PROJECTED ON (100)

0 1 2 Å
SCALE

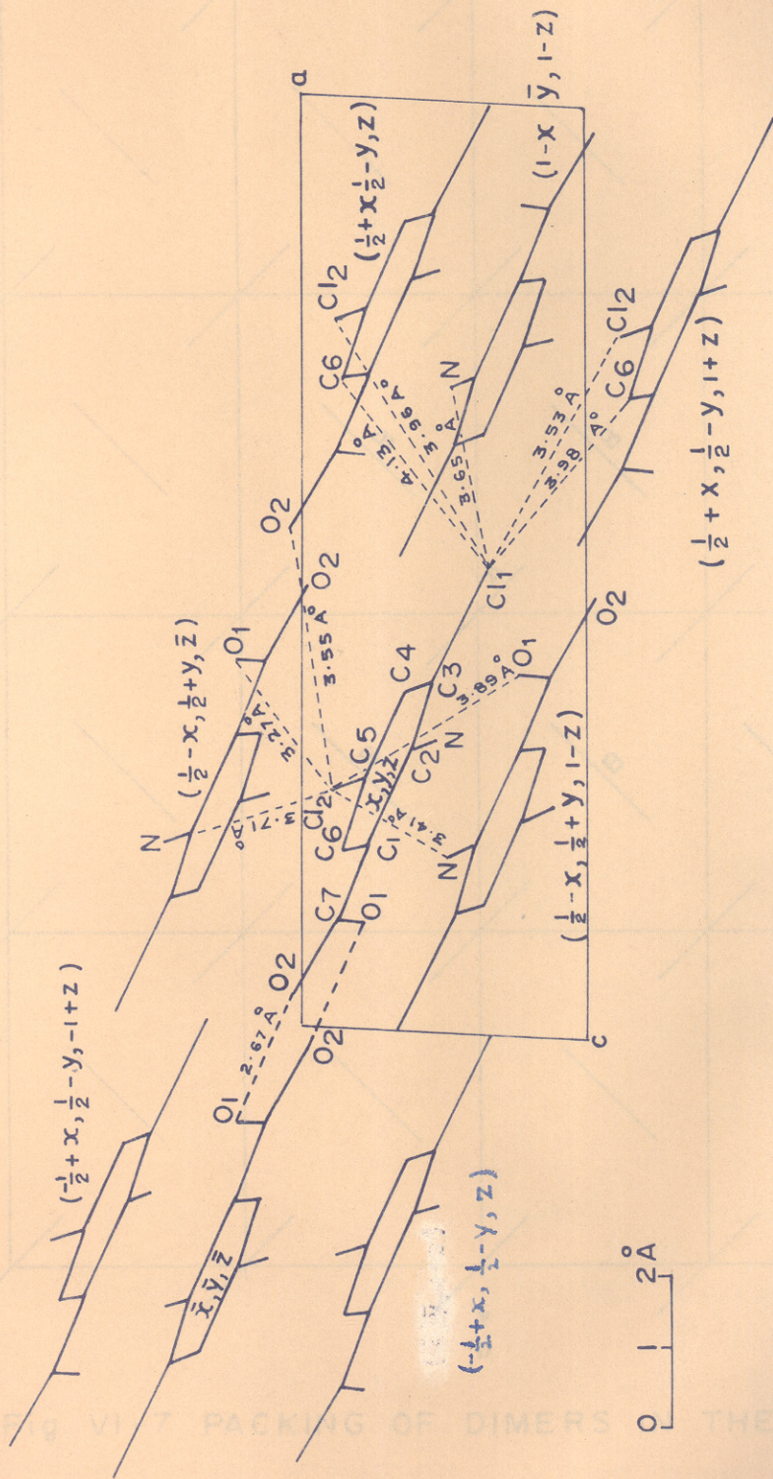


Fig. VI-6 STRUCTURE PROJECTED ON (010)

Fig. VI-7 PACKING OF DIMERS IN THE UNIT CELLS

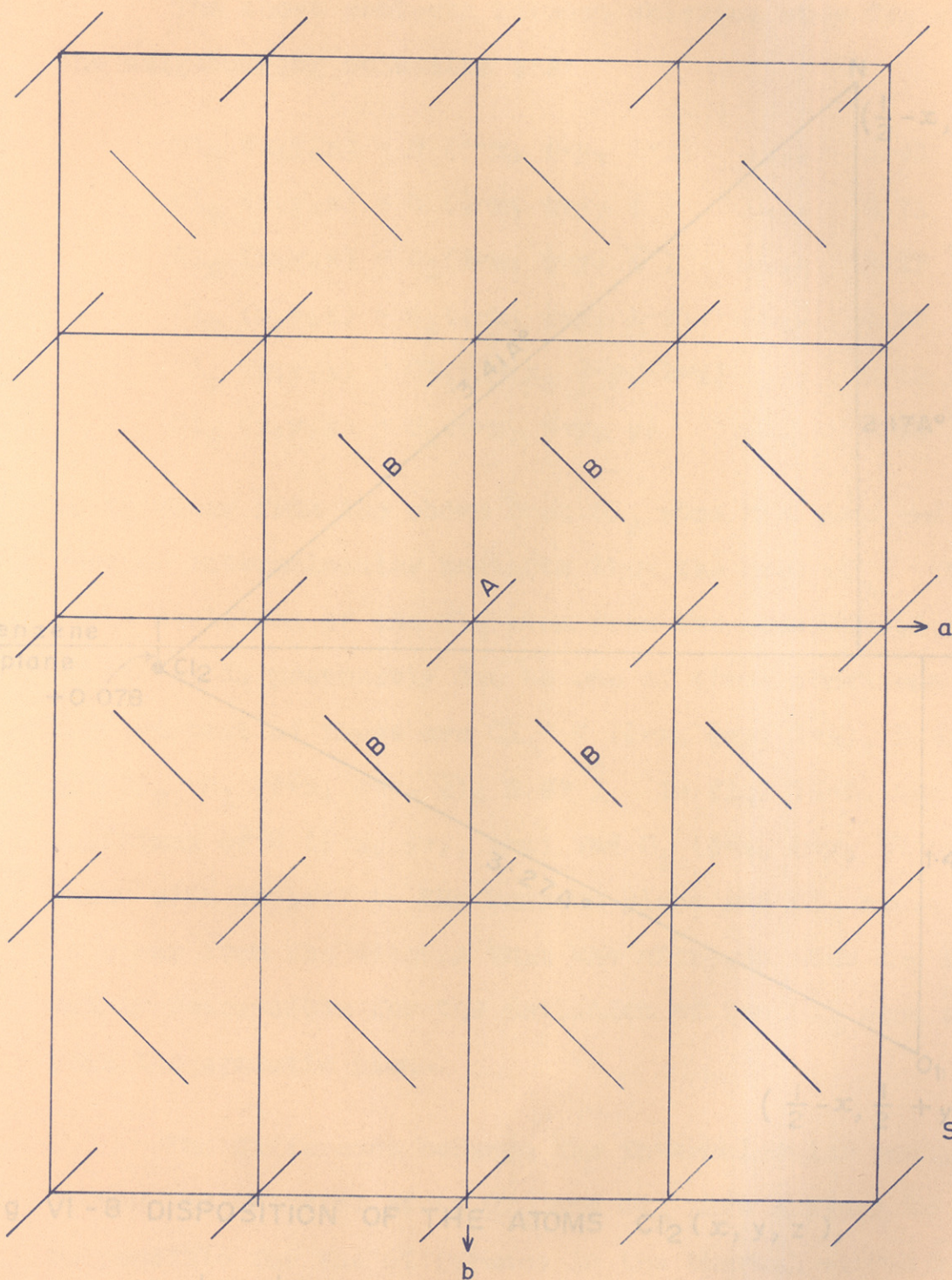


Fig. VI-7 PACKING OF DIMERS IN THE UNIT CELLS

TO THE PLANE OF BENZENE RING

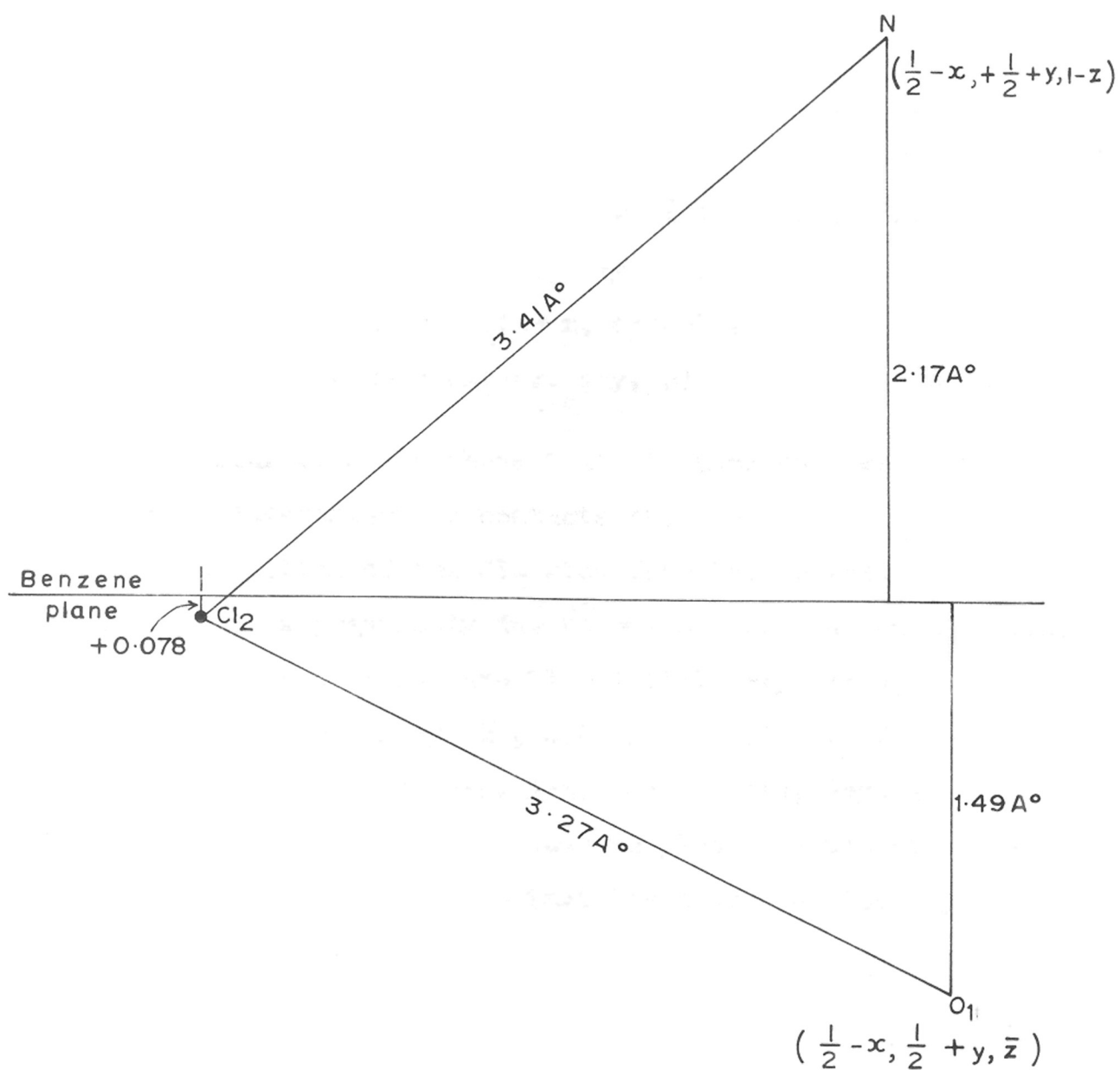


Fig. VI - 8 DISPOSITION OF THE ATOMS Cl₂(x, y, z),
 N($\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$) AND O₁($\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$) WITH RESPECT
 TO THE PLANE OF BENZENE RING.

The short contacts between chlorine atom Cl₂ and the neighbouring molecules are:

Cl ₂ (x,y,z) - N (½-x, ½+y, 1-z)	3.41 Å
Cl ₂ (x,y,z) - N (½-x, ½+y, ½)	3.71 Å
Cl ₂ (x,y,z) - O ₁ (½-x, ½+y, ½)	3.27 Å
Cl ₂ (x,y,z) - O ₁ (½-x, ½+y, 1-z)	3.89 Å
Cl ₂ (x,y,z) - Cl ₁ (½+x, ½-y, -1+z)	3.53 Å
Cl ₂ (x,y,z) - O ₂ (½+x, ½-y, z)	3.55 Å

It is clear from the above that Cl₂ atom has more and shorter intermolecular contacts than the atom Cl₁; the large deviation of the Cl₂ atom from the aromatic plane (0.078 Å) is presumably due to one of these short contacts. The shortest of these are Cl₂ - N (½-x, ½+y, 1-z), 3.41 Å and Cl₂ - O₁ (½-x, ½+y, ½), 3.27 Å. In fig. VI-8, the positions of N (½-x, ½+y, 1-z) and O₁ (½-x, ½+y, ½) are shown with respect to the benzene plane and Cl₂ atom; it is clear from the diagram that the nitrogen atom may be mainly responsible for the deviation of the Cl₂ atom away from the aromatic plane.

The difference between the intermolecular contacts around the chlorine atoms Cl₁ and Cl₂ also appears to be responsible for the difference in the thermal vibration patterns of the two atoms. This is discussed in the next section.

TABLE - VI-10

Intermolecular distances

Contact	Distance in Å
$O_1(x,y,z) \dots O_2(\bar{x}, \bar{y}, \bar{z})$	2.67 ± 0.008
$Cl_2(x,y,z) \dots O_1(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$	3.27 ± 0.009
$Cl_2(x,y,z) \dots O_1(\frac{1}{2}-x, \frac{1}{2}+y, 1-z)$	3.89 ± 0.009
$Cl_2(x,y,z) \dots N(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$	3.71 ± 0.009
$Cl_2(x,y,z) \dots N(\frac{1}{2}-x, \frac{1}{2}+y, 1-z)$	3.41 ± 0.009
$Cl_1(x,y,z) \dots Cl_2(\frac{1}{2}+x, \frac{1}{2}-y, 1+z)$	3.53 ± 0.008
$Cl_1(x,y,z) \dots Cl_2(\frac{1}{2}+x, \frac{1}{2}-y, z)$	3.96 ± 0.008
$Cl_1(x,y,z) \dots N_1(1-x, \bar{y}, 1-\bar{z})$	3.65 ± 0.009
$Cl_2(x,y,z) \dots O_2(\frac{1}{2}+x, \frac{1}{2}-y, z)$	3.55 ± 0.009
$C_4(x,y,z) \dots O_2(\frac{1}{2}+x, \frac{1}{2}-y, z)$	3.73 ± 0.010
$C_4(x,y,z) \dots O_2(\frac{1}{2}+x, \frac{1}{2}-y, 1+z)$	4.01 ± 0.010
$Cl_1(x,y,z) \dots C_6(\frac{1}{2}+x, \frac{1}{2}-y, 1+z)$	3.98 ± 0.008
$Cl_1(x,y,z) \dots C_6(\frac{1}{2}+x, \frac{1}{2}-y, z)$	4.13 ± 0.008

(b) Thermal Anisotropy

The atomic scattering factor when the atom is in thermal motion is given by

$$f = f_0 e^{-(a_{11}h^2 + a_{22}k^2 + a_{33}l^2 + 2a_{12}hk + 2a_{13}hl + 2a_{23}kl)}$$

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

$$f = f_0 e^{-\left\{ \frac{a_{11}}{a^{*2}} x^{*2} + \frac{a_{22}}{b^{*2}} y^{*2} + \frac{a_{33}}{c^{*2}} z^{*2} + \frac{2a_{12}}{a^*b^*} x^*y^* + \frac{2a_{13}}{a^*c^*} x^*z^* + \frac{2a_{23}}{b^*c^*} y^*z^* \right\}}$$

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

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

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:

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

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 (VI-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:

$$b_{11} X^{*2} + b_{22} Y^{*2} + b_{33} Z^{*2} + 2b_{12} X^*Y^* + 2b_{13} X^*Z^* + 2b_{23} Y^*Z^* = 1 \quad \dots (VI-7)$$

where

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

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

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

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

Direction cosines of the maximum, medium and minimum vibration directions :-

The major, medium and minor axes of the ellipsoid (given by equation VI-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

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

B_{11} , B_{22} and B_{33} are obtained by successively multiplying the α 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 reflexion is given by

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

Therefore,

$$B(\sin\theta/\lambda)^2 = 1$$

or

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

or

$$\frac{B}{4} \cdot S^2 = 1 \quad (\because S = 2\sin\theta/\lambda)$$

Let B_{11} correspond to the maximum vibration direction. S corresponding to the maximum vibration direction is $1/\sqrt{B_{11}}$.

Therefore,

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

so,

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

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 directions and lines or planes

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

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

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

$$\cos\theta = p \cdot e' + q \cdot d' + r \cdot f'$$

where e' , d' , f' are the direction cosines of the line.

The angles which the maximum, medium and minimum vibration directions of the atoms Cl_1 , Cl_2 , O_1 , O_2 and N make with different planes or lines are given in tables (VI-11, 12, 13, 14 and 15) along with the root mean square displacements. Calculations were not made for the carbon atoms as some of the a_{ij} for some of the atoms were found to be negative. It was thus clear that the results for carbon atoms are not significant.

Discussion of the thermal anisotropy results

In order to assess the accuracy of the results, two sets of values of different angles and r.m.s. displacements are given in the tables; one set of values is obtained from the thermal parameters after the last cycle of refinement ($R = 10.5\%$) and the other set from the parameters after the last but one cycle ($R = 10.6\%$). Since the R values at the two stages of refinement are nearly equal, the differences between the two values of angles and r.m.s. displacements must be insignificant. In general, the angles from the two sets agree within about 20° or so; however, in

TABLE - VI-11

(Cl₁)

Plane or Line	Cl ₁ (max.)		Cl ₁ (med.)		Cl ₁ (min.)				
	R=10.5%	R=10.6%	Mean	R=10.5%	R=10.6%	Mean	R=10.5%	R=10.6%	Mean
Benzene plane	32°	66°	49°	54°	22°	38°	13°	1°	7°
C ₃ -Cl ₁ bond	88°	82°	85°	76°	84°	80°	14°	6°	10°
Cl ₁ (x,y,z)...	73°	80°	77°	89°	75°	82°	17°	15°	16°
..Cl ₂ ($\frac{1}{2}x, \frac{1}{2}y, 1+z$)									
$\sqrt{u^2}$ in Å	0.191	0.207	0.199	0.167	0.191	0.179	0.131	0.146	0.138

TABLE - VI-12

(Cl₂)

Plane Or Line	Cl ₂ (max.)		Cl ₂ (med.)		Cl ₂ (min.)				
	R=10.5%	Mean	R=10.5%	Mean	R=10.5%	Mean			
Benzene plane	29°	51°	40°	59°	33°	46°	10°	12°	11°
Cl ₂ -C ₅ bond	71°	75°	73°	86°	42°	64°	20°	62°	41°
Cl ₂ (x,y,z).....	58°	54°	56°	54°	82°	68°	53°	57°	55°
..N($\frac{1}{2}$ -x, $\frac{1}{2}$ y, 1-z)									
Cl ₂ (x,y,z).....	71°	67°	69°	82°	54°	68°	20°	56°	38°
..O ₁ ($\frac{1}{2}$ -x, $\frac{1}{2}$ y, \bar{z})									
Cl ₂ (x,y,z).....	35°	57°	46°	55°	55°	55°	85°	63°	74°
..Cl ₁ ($-\frac{1}{2}$ +x, $\frac{1}{2}$ y, -1+z)									
$\sqrt{u^2}$ in Å	0.190	0.194	0.192	0.145	0.174	0.160	0.128	0.144	0.136

TABLE - VI-13

(O_1)

Plane OR Line	O_1 (max.)		O_1 (med.)		O_1 (min.)				
	R=10.5%	R=10.6%	Mean	R=10.5%	R=10.6%	Mean	R=10.5%	R=10.6%	Mean
Carboxyl plane	79°	71°	75°	10°	20°	15°	1°	1°	1°
C7-O1 bond	81°	75°	78°	50°	38°	44°	31°	57°	44°
$O_1(x,y,z)$	48°	54°	51°	56°	52°	54°	64°	57°	61°
..Cl ₂ (-1/2-x, -1/2+y, z)									
$O_1(x,y,z)$	84°	90°	87°	77°	22°	50°	28°	70°	49°
..O ₂ (x̄,ȳ,z̄)									
$\sqrt{u^2}$ in Å	0.241	0.222	0.232	0.182	0.122	0.152	0.170	0.120	0.145

TABLE - VI-14

(O₂)

Plane of Line	O ₂ (max.)		O ₂ (med.)		O ₂ (min.)		Mean		
	R=10.5%	R=10.6%	R=10.5%	R=10.6%	R=10.5%	R=10.6%			
Carboxyl plane	27°	45°	36°	58°	38°	48°	15°	21°	18°
C7-O ₂ bond	40°	50°	45°	68°	70°	69°	27°	47°	37°
O ₂ (x,y,z)...	68°	85°	77°	60°	50°	55°	30°	41°	36°
••O ₁ ($\bar{x}, \bar{y}, \bar{z}$)									
$\sqrt{u^2}$ in Å	0.191	0.214	0.202	0.147	0.194	0.218 ₁₇₁	0.093	0.150	0.119 ₁₂₂

TABLE - VI-15

(N)

Plane or Line	N (max.)		N (med.)		N (min.)	
	R=10.5%	Mean	R=10.5%	Mean	R=10.5%	Mean
	R=10.6%	R=10.6%	R=10.6%	R=10.6%	R=10.6%	R=10.6%
Benzene plane	22°	15°	7°	42°	66°	39°
C ₂ -N bond	45°	27°	76°	79°	50°	69°
$\sqrt{u^2}$ in Å	0.179	0.192	0.159	0.178	0.132	0.157
	8°		77°		88°	
	9°		82°			

some cases there are larger differences. As expected, these large differences occur only when the thermal anisotropy is slight. For example, the differences between the two sets of angles are large in case of nitrogen atom; in this case, the thermal anisotropy is small, the maximum, medium and minimum r.m.s. displacements being 0.192 \AA , 0.178 \AA and 0.157 \AA respectively (table VI-15). In the case of oxygen atom O_1 , the anisotropy is marked along the maximum vibration direction while it is very small in the plane normal to it, the max., med. and min. r.m.s. displacements being 0.232 \AA , 0.152 \AA and 0.145 \AA respectively. It is therefore found that the angles (in the two sets) which involve the maximum vibration direction agree with in 10° while those which involve medium and minimum vibration directions show larger differences (table VI-13).

The chlorine atom Cl_1 has only one moderately short intermolecular contact $Cl_1(x,y,z) \dots Cl_2(\frac{1}{2}+x, \frac{1}{2}-y, 1+z)$, 3.53 \AA . The maximum and medium vibration directions of Cl_1 make, as expected large angles (77° and 82° respectively, table VI-11) with this bond. However, the maximum and medium vibration directions of Cl_2 make smaller angles (46° and 55° respectively) (Table VI-12) with this bond. The reason becomes clear when one notices that the atom Cl_2 has two shorter intermolecular contacts as well (fig. VI-4); these are $Cl_2(x,y,z) \dots N(\frac{1}{2}-x, \frac{1}{2}+y, 1-z)$, 3.41 \AA and $Cl_2(x,y,z) \dots O_1(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$, 3.27 \AA . The vibration directions of the

atom Cl_2 are naturally influenced to a great extent by these shorter bonds. The maximum and medium vibration directions of Cl_2 make angles of 56° and 68° respectively with the $\text{Cl}_2\text{-N}$ bond (3.41 \AA) and 69° and 68° respectively with $\text{Cl}_2\text{-O}_1$ bond (3.27 \AA).

It is seen from table VI-13 and table VI-14 that there are differences between the vibration patterns of the oxygen atoms O_1 and O_2 . It is possible that these differences are also related with the differences in the surroundings of the two oxygen atoms. Both atoms are involved in $\text{OH}\dots\text{O}$ hydrogen bonds; however, atom O_1 has one short intermolecular contact $\text{O}_1(x,y,z) \dots \text{Cl}_2(-\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$, 3.27 \AA as well. The nearness of the amino group can also influence the vibration pattern of the atom O_1 , if this atom makes appreciable intramolecular vibration.

P A R T - I I

CRYSTAL AND MOLECULAR STRUCTURE OF
m-AMINOBENZOIC ACID HYDROCHLORIDE

CHAPTER - VII

EXPERIMENTAL

m-aminobenzoic acid hydrochloride was prepared by adding pure HCl to the m-aminobenzoic acid. The filtrate on slow evaporation gave, colourless, needle shaped crystals. The preliminary X-ray photographs showed that the crystals belong to the triclinic system.

For the collection of the data along the needle axis (c axis), a crystal having cross-section 0.4 mm x 0.2 mm was used. The crystal was first set visually and then accurately by the method of double oscillation (Davies, 1950) Preliminary values of the axial lengths were obtained from the rotation photographs taken around all the three axes in turn using CuK radiation. Accurate values of the unit cell dimensions were determined from high angle spots in zero layer Weissenberg photographs. The angle α , β and γ were calculated from the measured α^* , β^* and γ^* .

The expression for calculating the angles α , β and γ in triclinic system are

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

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

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

and the relations used for axial lengths are,

$$a = \frac{b^*c^*}{V^*} \sin\alpha^*$$

$$b = \frac{c^*a^*}{V^*} \sin\beta^*$$

$$c = \frac{a^*b^*}{V^*} \sin\gamma^*$$

where $V^* = a^* b^* c^* \sqrt{(1+2 \cos\alpha^* \cos\beta^* \cos\gamma^* - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^*)}$

a^* was determined from reflexions 12,0,0; 15,0,0 and 17,0,0;
 b^* from 0,4,0; 0,5,0; 0,7,0; and 1,7,0 and c^* from
 0,0,3; 0,0,4; 2,0,5; 3,0,5.

The b^* value from reflexion 1,7,0 and c^* value from
 2,0,5; 3,0,5 were determined by using the general formula:

$$\frac{4 \sin^2 \theta}{\lambda^2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos\gamma^* + 2klb^*c^* \cos\alpha^* + 2hla^*c^* \cos\beta^*$$

In all these expressions, reciprocal constant is unity, so
 that $a^* = 1/d100$, $b^* = 1/d010$ and $c^* = 1/d001$. The unit
 cell dimensions are,

$$a = 14.78 \text{ \AA} ; \quad b = 5.83 \text{ \AA} ; \quad c = 4.58 \text{ \AA}$$

$$\alpha = 96.9^\circ ; \quad \beta = 91.3^\circ ; \quad \gamma = 98.6^\circ$$

The density measured by the flotation method using
 carbon tetrachloride and benzene mixture at room temperature
 was found to be 1.480 gm/cm^3 ; while the calculated density

for two molecules per unit cell comes out to be 1.489 gm/cm³. The linear absorption coefficient, as calculated by the expression given in chapter-II is 42.5 cm⁻¹.

The three dimensional data were collected from zero and higher layers equi-inclination Weissenberg photographs taken with CuK radiation around the c axis, using the multiple film technique. In all 130, 218, 117 and 125 reflexions of the type hko, hkl, hk2 and hk3 respectively were observed out of 226, 418, 372 and 320 possible reflexions. The intensities were measured with the help of intensity scales. The observed intensities were corrected for (i) Lorentz and Polarization factor, (ii) spot extension factors; by method described in chapter-II. No absorption correction was applied. Temperature factors and scale factors for hko and hol zones were obtained by Wilson's method (1942) described in chapter-II. The plot of log_e C against sin²θ/λ² for hko and hol type reflexions are shown in fig. VII-1. The corresponding data are given in table VII-1a,b.

TABLE - VII-1a

log_e C values for (hko) reflexions

No.	sinθ	$\frac{\sin^2 \theta}{\lambda^2}$	< I >	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	log _e C
1	0.2 to 0.3	0.025	79.1	690.0	104.5	4.65
2	0.3 to 0.4	0.051	55.1	443.0	112.7	4.73
3	0.4 to 0.5	0.085	42.8	311.0	138.2	4.93
4	0.5 to 0.6	0.128	38.4	196.0	132.7	4.89
5	0.6 to 0.7	0.178	37.0	165.0	134.0	4.90
6	0.7 to 0.8	0.237	21.4	116.0	166.0	5.11
7	0.8 to 0.9	0.303	11.5	101.0	336.0	5.82

From the graph $B = 1.8 \text{ \AA}^2$ Scale factor = 90.0

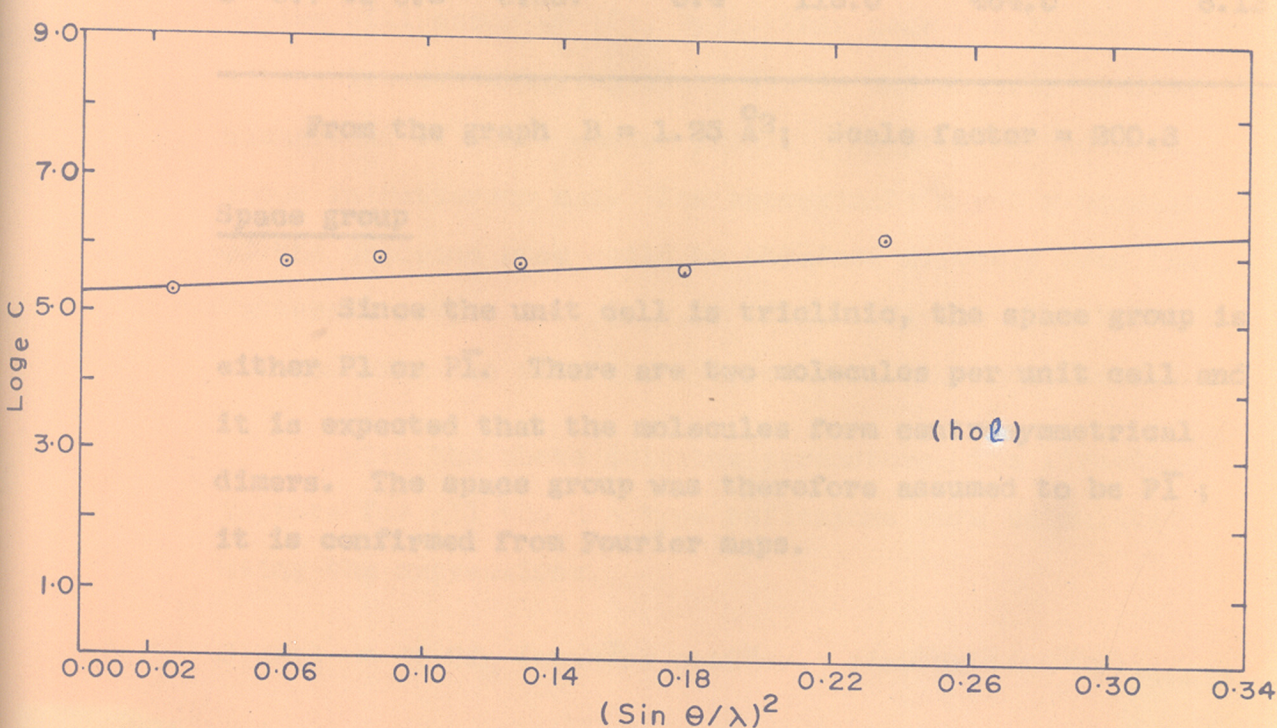
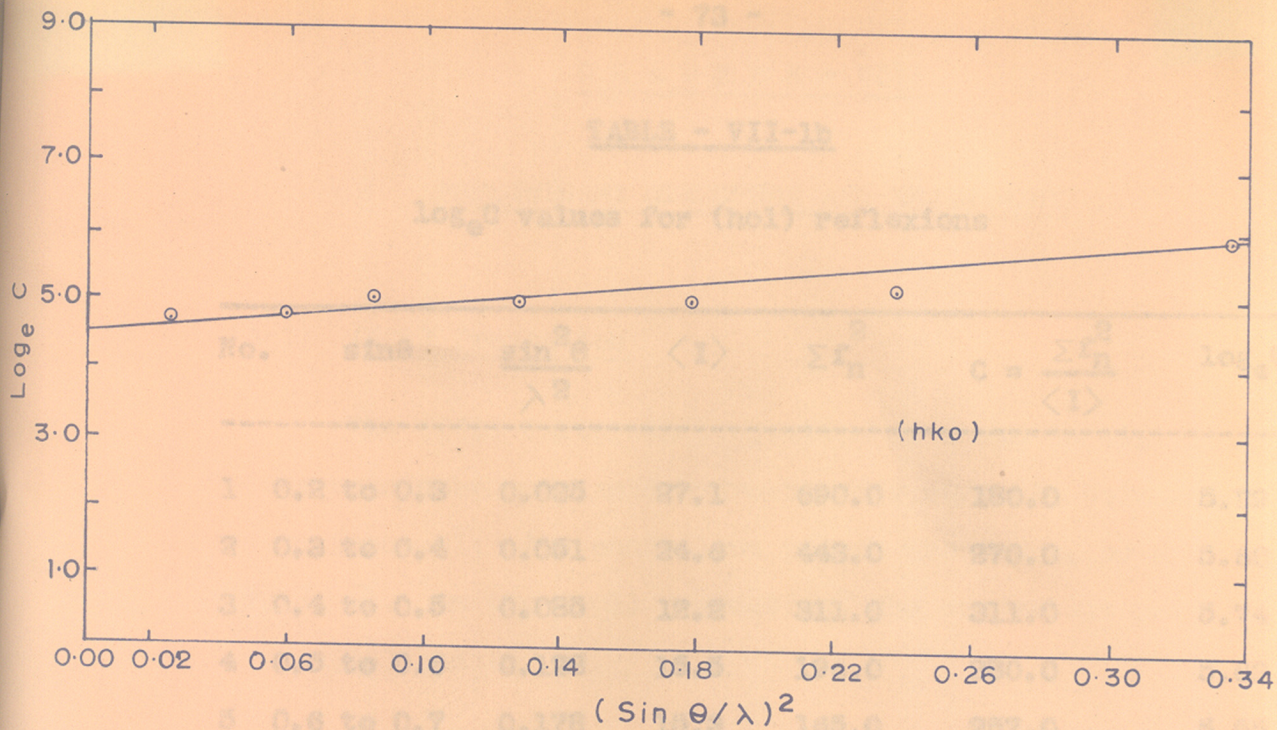


Fig. VII-1 DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTOR BY WILSON'S METHOD

TABLE - VII-1b

$\log_e C$ values for (hol) reflexions

No.	$\sin\theta$	$\frac{\sin^2\theta}{\lambda^2}$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.2 to 0.3	0.025	27.1	690.0	180.0	5.29
2	0.3 to 0.4	0.051	24.6	443.0	270.0	5.60
3	0.4 to 0.5	0.085	12.2	311.0	311.0	5.74
4	0.5 to 0.6	0.128	15.5	196.0	280.0	5.63
5	0.6 to 0.7	0.178	15.3	165.0	257.0	5.55
6	0.7 to 0.8	0.237	6.4	116.0	464.0	6.13

From the graph $B = 1.25 \text{ \AA}^2$; Scale factor = 200.3

Space group

Since the unit cell is triclinic, the space group is either $P1$ or $P\bar{1}$. There are two molecules per unit cell and it is expected that the molecules form centrosymmetrical dimers. The space group was therefore assumed to be $P\bar{1}$; it is confirmed from Fourier maps.

CHAPTER - VIII

PRELIMINARY STRUCTURE AND REFINEMENT

(A-1) (001) Projection

The (001) Patterson projection is shown in fig. VIII-1. Since *m*-aminobenzoic acid hydrochloride crystals belong to space group $P\bar{1}$; the equivalent points are (x, y, z) and $(\bar{x}, \bar{y}, \bar{z})$. In the (001) projection, the equivalent points are (x, y) and (\bar{x}, \bar{y}) .

Therefore, in the Patterson map (fig. VIII-1), the maxima will occur at $(2x, 2y)$. This peak due to the interaction between chlorine atoms stands out clearly against the background of other weaker peaks. The peak marked A is shown in Patterson map. The approximate *x* and *y* coordinates of the chlorine atom could be obtained directly from the Patterson projection $P(u, v, 0)$ (fig. VIII-1). The Patterson map was obtained with the help of Von Eller photosommateur.

With the above chlorine parameters, the structure factors for all the *hko* type reflexions were calculated using the expressions,

$$F(hko) = \sum 2f_n (\cos 2\pi hx \cos 2\pi ky - \sin 2\pi hx \sin 2\pi ky)$$

and

$$F(h\bar{k}o) = \sum 2f_n (\cos 2\pi hx \cos 2\pi ky + \sin 2\pi hx \sin 2\pi ky)$$

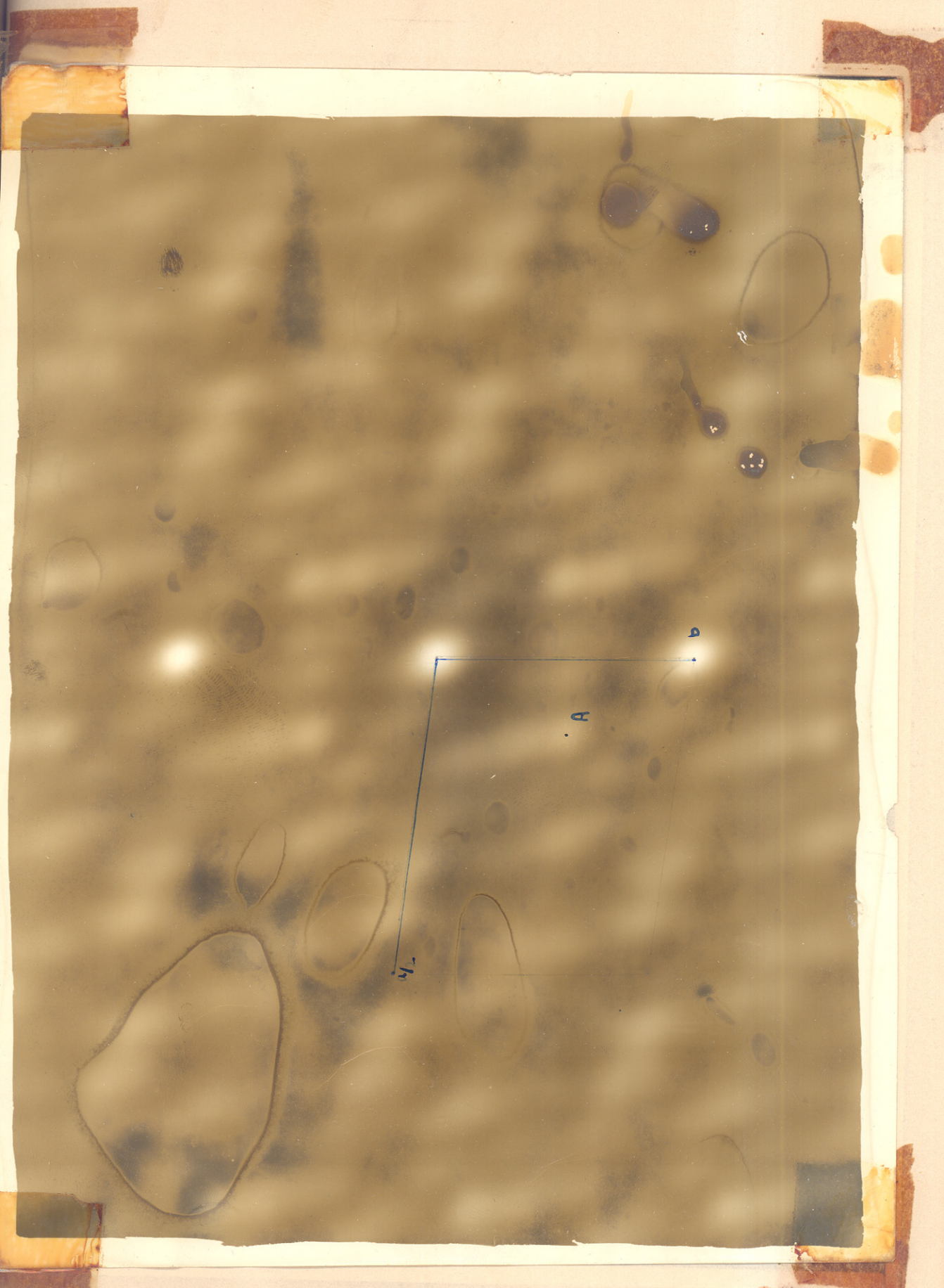


FIGURE VIII-1 : (OC1) PATTERSON MAP

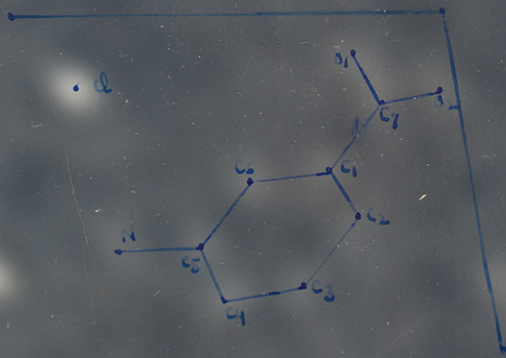


FIGURE VIII-2 : (001) FOURIER MAP

With the signs of the structure factors, a Fourier summation was done. The Fourier map contained bright peaks of chlorine atom and faint peaks of the light atoms. The unit cell was drawn and the parameters of all the atoms of the molecule were determined. With these approximate parameters structure factors were calculated. The value of R at this stage was 43.0%. After one direct Fourier refinement the value of R came down to 27.5%. The molecule had become clear. Further direct Fourier refinements ^{were} done till there was no change in the signs of the structure factors. The Fourier map obtained at this stage is shown in fig. (VIII-2). The atomic parameters at different stages of refinement by direct Fourier synthesis are given in table-VIII-1. The parameters were further refined by least squares method using the expressions

$$\Delta x = - \frac{1}{2\pi} \frac{\sum \Delta F(2f_n \cdot h) (\cos 2\pi hx \sin 2\pi ky + \sin 2\pi hx \cos 2\pi ky)}{\sum (2f_n \cdot h)^2 (\cos 2\pi hx \sin 2\pi ky + \sin 2\pi hx \cos 2\pi ky)^2}$$

and

$$\Delta y = - \frac{1}{2\pi} \frac{\sum \Delta F(2f_n \cdot k) (\cos 2\pi hx \sin 2\pi ky + \sin 2\pi hx \cos 2\pi ky)}{\sum (2f_n \cdot k)^2 (\cos 2\pi hx \sin 2\pi ky + \sin 2\pi hx \cos 2\pi ky)^2}$$

The number of reflexions used were 130. The parameters after I and II least squares refinement are given in table VIII-1.

x and y parameters during the stages of refinement

Atom	From first direct Fourier synthesis	From second direct Fourier synthesis	From third direct Fourier synthesis	After first Least Square refinement	After second Least Square refinement
C ₁	0.165	0.163	0.164	0.165	0.162
C ₂	0.150	0.148	0.144	0.141	0.144
C ₃	0.216	0.213	0.212	0.207	0.203
C ₄	0.290	0.293	0.300	0.299	0.302
C ₅	0.310	0.313	0.320	0.320	0.319
C ₆	0.244	0.246	0.252	0.252	0.248
C ₇	0.092	0.094	0.094	0.094	0.091
O ₁	0.101	0.102	0.104	0.102	0.107
O ₂	0.018	0.018	0.018	0.018	0.015
N	0.403	0.406	0.412	0.411	0.407
Cl	0.430	0.429	0.436	0.434	0.433

Value of R	43.0%	27.5%	24.8%	21.0%	17.1%
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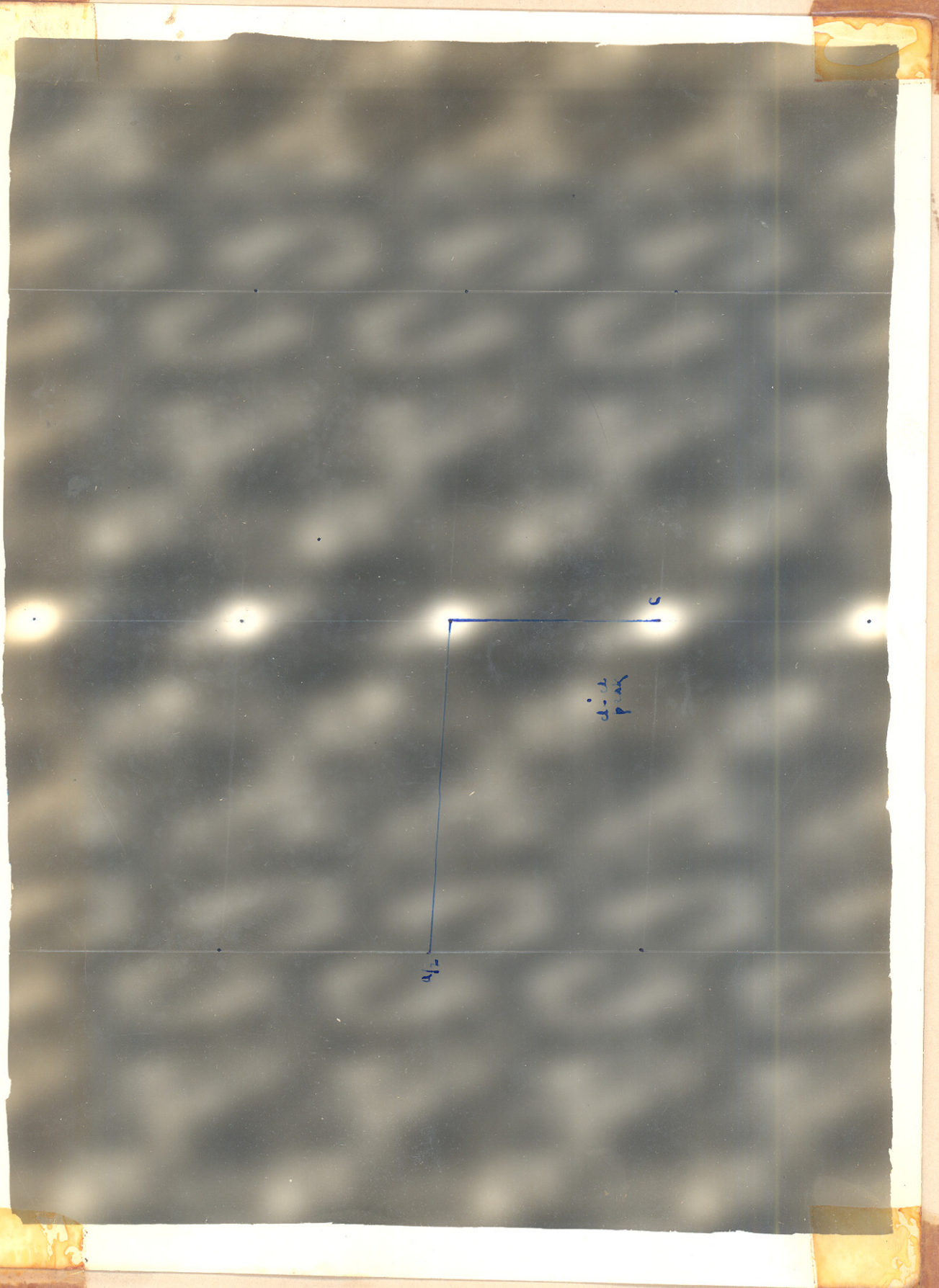


FIGURE VIII-3 : (010) PATTERSON MAP

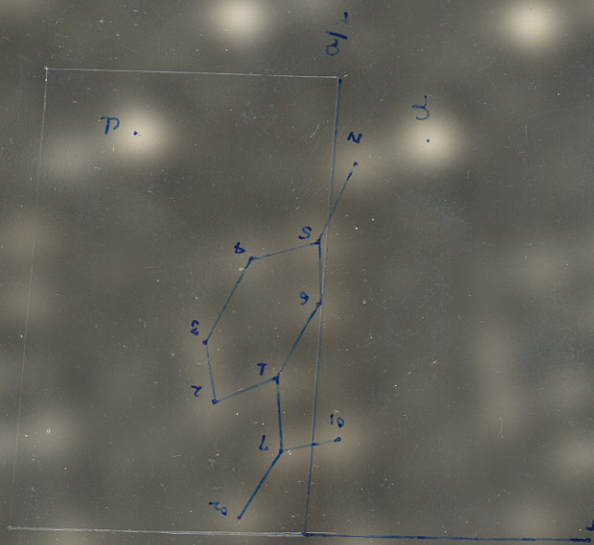


FIGURE VIII-4 : (010) FOURIER MAP

(A-11) (010) Projection

The (010) Patterson projection is shown in fig. VIII-3. The equivalent points in this projection are (x, z) and (\bar{x}, \bar{z}) . In the Patterson map there will be a bright peak at $(2x, 2z)$. This gives directly the parameters of chlorine atom. With these parameters $F(h0l)$ were calculated for all $(h0l)$ type reflexions. With the calculated signs and observed F 's, a (010) Fourier summation was done on photosommateur. The molecule could be seen in the Fourier map. The x and z parameters were measured; as expected, the x parameters agreed with those obtained from (001) Projection. The z parameters were refined both by direct Fourier maps and by the method of Least Squares. These parameters are given in table VIII-2. The expression used for Least Squares refinement is,

$$\Delta z = - \frac{1}{2\pi} \frac{\sum \Delta F(2f_n \cdot 1) (\cos 2\pi h x \sin 2\pi l z + \sin 2\pi h x \cos 2\pi l z)}{\sum (2f_n \cdot 1)^2 (\cos 2\pi h x \sin 2\pi l z + \sin 2\pi h x \cos 2\pi l z)^2}$$

The final direct Fourier map is shown in figure VIII-4.

(B) Three dimensional refinement

For the three dimensional least squares refinement of positional parameters and individual isotropic temperature factors, all the observed structure factors (and also those unobserved whose calculated values were more than minimum observable value) of the type hko , $hk1$, $hk2$ and $hk3$ numbering 130, 218, 117 and 125 respectively were used. The scaling of $F_o(hko)$, $F_o(hk1)$, $F_o(hk2)$ and $F_o(hk3)$ was done by the common reflexions from (hol) Weissenberg photograph.

TABLE - VIII-2

z parameters during stages of refinement

Atom	From first direct Fourier synthesis	From second direct Fourier synthesis	From third direct Fourier synthesis	After Least Square refinement
C ₁	0.148	0.143	0.146	0.137
C ₂	0.354	0.340	0.328	0.338
C ₃	0.405	0.388	0.392	0.387
C ₄	0.230	0.250	0.264	0.257
C ₅	0.018	0.038	0.072	0.052
C ₆	0.021	0.015	0.015	0.015
C ₇	0.077	0.100	0.077	0.058
O ₁	0.090	0.093	0.103	0.130
O ₂	0.179	0.230	0.220	0.222
N	0.128	0.085	0.069	0.100
Cl	0.661	0.675	0.616	0.649
Value of R	29.3%	28.4%	25.7%	18.2%

The structure factors were calculated on the electronic computer using the following scheme:

$$F(hkl) = \sum_{n=1}^{11} \left(\begin{array}{l} \text{Atomic scattering factor part} \\ \text{Geometrical structure factor part} \end{array} \right)$$

For the space group $P\bar{1}$, the geometrical structure factor part is given by,

$$\begin{aligned} A &= \cos 2\pi (hx + ky + lz) \\ B &= 0 \end{aligned}$$

The atomic scattering factor for each reflexion was calculated by,

$$E(J) = \text{scat.}(J) \times w(J)$$

J indicates the type of atom (i.e. O, N, C, H or Cl)

$$\begin{aligned} \text{Scat.}(J) &= A \exp. (-ap^2) + B \exp. (-bp^2) + C \\ \text{and } w(J) &= \exp. B(J) \times (-p^2) \end{aligned}$$

In these equations A, a, B, b and C are analytical constants for atomic scattering factors and

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

The values of the analytical constants used were taken from F.H. Moor's tables (1961). The values are given in chapter IV.

The starting parameters from two dimensional refinement gave R value 42.1%. All the x_j , y_j , z_j and B_j were refined simultaneously by 'Least Squares'. After second cycle when R

was 23.3 %, the layer-wise scaling was done again; scaling factors came out to be 1.05, 1.05, 1.03 and 1.10 for hko, hk1, hk2 and hk3 type reflexions respectively. Also card punching errors were removed and further refinement on computer was carried on. The third and fourth cycles gave R values 15.6 % and 15.5 % respectively. The parameters at different stages of refinement and corresponding R values are given in table VIII-3.

TABLE - VIII-3

Atomic parameters at different stages of refinement

Cycle of refinement	Parameters	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
After first cycle R = 38.9 %	x	0.1633	0.1461	0.2043	0.3013	0.3178	0.2502
	y	0.4573	0.6087	0.8057	0.8299	0.6555	0.4732
	z	0.8690	0.6711	0.6299	0.7420	0.9437	0.0114
	B*	2.57	3.72	2.66	2.54	1.98	2.63
After second cycle R = 23.3 %	x	0.1645	0.1436	0.2037	0.2976	0.3174	0.2514
	y	0.4581	0.6171	0.8050	0.8275	0.6514	0.4705
	z	0.8690	0.6930	0.6438	0.7643	0.9263	0.0027
	B*	2.84	3.42	2.92	2.56	2.71	2.92
After third cycle R = 15.6 %	x	0.1635	0.1414	0.2063	0.2973	0.3182	0.2511
	y	0.4549	0.6162	0.8035	0.8300	0.6580	0.4711
	z	0.8671	0.6871	0.6348	0.7622	0.9309	0.0057
	B*	2.55	3.24	3.27	2.50	2.64	2.51
After fourth cycle R = 15.5 %	x	0.1635	0.1415	0.2065	0.2972	0.3180	0.2508
	y	0.4569	0.6172	0.8032	0.8299	0.6570	0.4717
	z	0.8706	0.6887	0.6344	0.7635	0.9303	0.0042
	B*	2.54	3.27	3.20	2.48	2.58	2.50

* B in Å²

contd....

TABLE - VIII-3 (contd....)

Cycle of refinement	Parameters	C ₇	O ₁	O ₂	N	C ₁
After first cycle R = 38.9 %	x	0.0922	0.1073	0.0137	0.4078	0.4333
	y	0.2523	0.1263	0.2249	0.6919	0.2277
	z	0.9362	0.1330	0.7849	0.0883	0.3543
	B*	3.66	3.67	3.69	2.63	1.16
After second cycle R = 23.3 %	x	0.0926	0.1083	0.0135	0.4082	0.4328
	y	0.2584	0.1333	0.2293	0.6925	0.2266
	z	0.9345	0.1320	0.7910	0.0873	0.3564
	B*	3.76	3.72	3.21	2.75	0.72
After third cycle R = 15.6 %	x	0.0922	0.1078	0.0145	0.4090	0.4329
	y	0.2561	0.1301	0.2267	0.6905	0.2259
	z	0.9266	0.1273	0.7835	0.0880	0.3572
	B*	2.77	3.26	3.08	2.57	1.05
After fourth cycle R = 15.5 %	x	0.0924	0.1078	0.0145	0.4088	0.4329
	y	0.2544	0.1305	0.2267	0.6909	0.2260
	z	0.9268	0.1268	0.7834	0.0900	0.3571
	B*	2.70	3.26	3.02	2.59	1.01

* B in A₂

CHAPTER - IX

RESULTS AND DISCUSSION

Results

The final atomic coordinates and their standard deviations in Å units are given in table IX-1. The standard deviations are calculated by the expression given in chapter VI.

TABLE - IX-1

Atom	x Å	y Å	z Å
C ₁	2.417 ± 0.008	2.663 ± 0.008	0.594 ± 0.008
C ₂	2.090 ± 0.008	2.599 ± 0.008	1.428 ± 0.008
C ₃	3.052 ± 0.008	4.683 ± 0.008	1.674 ± 0.008
C ₄	4.393 ± 0.008	4.839 ± 0.008	1.083 ± 0.008
C ₅	4.702 ± 0.008	3.832 ± 0.008	0.320 ± 0.008
C ₆	3.708 ± 0.008	2.749 ± 0.008	0.021 ± 0.008
C ₇	1.366 ± 0.008	1.485 ± 0.008	0.338 ± 0.008
O ₁	1.595 ± 0.006	0.760 ± 0.006	0.583 ± 0.006
O ₂	0.214 ± 0.006	1.321 ± 0.006	0.993 ± 0.006
N	6.044 ± 0.007	4.028 ± 0.007	0.411 ± 0.007
Cl	6.398 ± 0.003	1.318 ± 0.003	1.635 ± 0.003

Bond lengths and bond angles

The bond lengths and bond angles with the standard deviations are listed in the table IX-2, and shown in fig. IX-1.

TABLE - 11-3

Final bond lengths and bond angles with their standard deviations

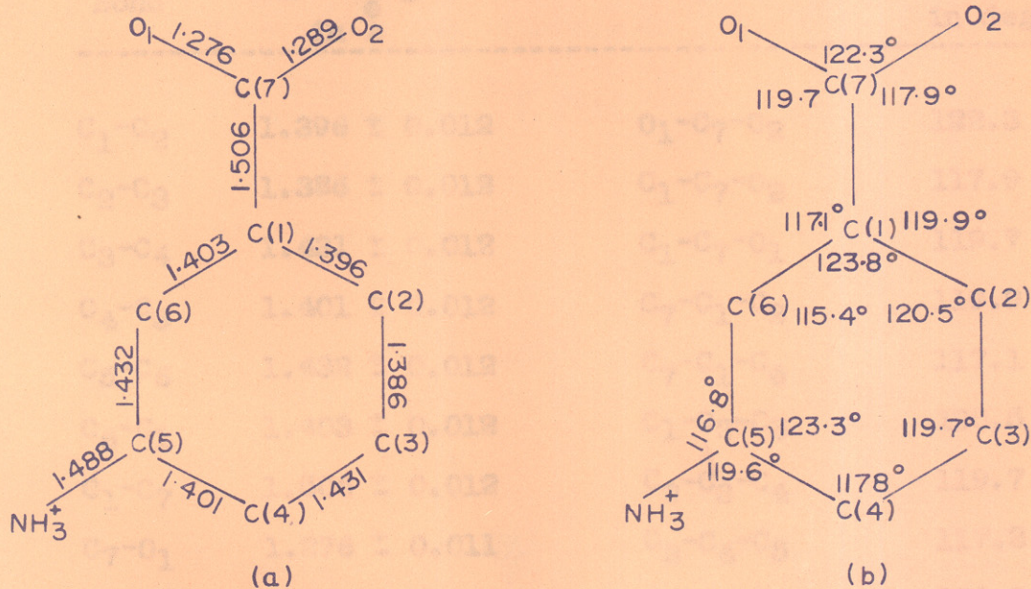


Fig. IX 1 (a) BOND LENGTHS (Å) AND (b) BOND-ANGLES IN m-AMINOBENZOIC ACID HYDROCHLORIDE.

TABLE - IX-2

Final bond lengths and bond angles with
their standard deviations

Bond	Bond lengths in Å	Angle	Bond angles in degree
C ₁ -C ₂	1.396 ± 0.012	O ₁ -C ₇ -O ₂	122.3 ± 0.6
C ₂ -C ₃	1.386 ± 0.012	C ₁ -C ₇ -O ₂	117.9 ± 0.6
C ₃ -C ₄	1.431 ± 0.012	C ₁ -C ₇ -O ₁	119.7 ± 0.6
C ₄ -C ₅	1.401 ± 0.012	C ₇ -C ₁ -C ₂	119.9 ± 0.6
C ₅ -C ₆	1.432 ± 0.012	C ₇ -C ₁ -C ₆	117.1 ± 0.6
C ₆ -C ₁	1.403 ± 0.012	C ₁ -C ₂ -C ₃	120.5 ± 0.6
C ₁ -C ₇	1.506 ± 0.012	C ₂ -C ₃ -C ₄	119.7 ± 0.6
C ₇ -O ₁	1.276 ± 0.011	C ₃ -C ₄ -C ₅	117.8 ± 0.6
C ₇ -O ₂	1.289 ± 0.011	C ₄ -C ₅ -C ₆	123.3 ± 0.6
C ₅ -N	1.488 ± 0.011	C ₅ -C ₆ -C ₁	115.4 ± 0.6
N-C ₁	3.050 ± 0.008	C ₆ -C ₁ -C ₂	123.8 ± 0.6
O ₁ (x,y,z)		C ₄ -C ₅ -N	119.6 ± 0.6
O ₂ (\bar{x},\bar{y},\bar{z})	2.53 ± 0.010	C ₆ -C ₅ -N	116.8 ± 0.6

Orthogonal coordinates

The atomic coordinates (x', y', z') in Å units referred to the orthogonal axes a, b' and c' (such that ab and ab' planes are the same) are given in table IX-3 and are calculated using the expressions,

$$x' = x + y \cos \gamma + z \cos \beta$$

$$y' = y \sin \gamma + z \left\{ \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \gamma} \right\}$$

$$z' = \pm z \left\{ \frac{(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}}}{\sin \gamma} \right\}$$

TABLE - IX-3
Orthogonal coordinates in Å units

Atom	x' Å	y' Å	z Å
C ₁	2.027	2.708	0.589
C ₂	1.576	3.739	1.416
C ₃	2.383	4.841	1.661
C ₄	3.636	4.920	1.074
C ₅	4.129	3.828	0.317
C ₆	3.292	2.715	0.021
C ₇	1.489	1.512	0.335
O ₁	1.466	0.677	0.578
O ₂	0.038	1.431	0.985
N	5.425	3.929	0.408
Cl	6.161	1.095	1.622

The equations of the planes passing through different atoms (with respect to the orthogonal axes), deviations of the different atoms from these planes and angles between different planes are given in table IX-4(a,b,c).

TABLE - IX-4(a)

Equations of different planes

Plane	Equations
1. Benzene ring	$-0.3706 x' + 0.4702 y' + 0.8014 z' - 0.0543 = 0$
2. Plane through C ₁ , C ₂ , C ₃ , C ₄ and C ₆	$-0.3811 x' + 0.4591 y' + 0.8018 z' + 0.0075 = 0$
3. Carboxyl plane	$+0.4426 x' - 0.5794 y' - 0.6843 z' + 0.1395 = 0$
4. Dimer plane	$-0.5071 x' + 0.4977 y' + 0.7038 z' = 0$

TABLE - IX-4(b)

Deviations in Å of atoms from the different planes

Atom	(1)	(2)	(3)
C ₁	-0.004	+0.006	0.134
C ₂	-0.016	-0.014	-
C ₃	+0.007	-0.010	-
C ₄	+0.033	0.000	-
C ₅	-0.039	-0.063	-
C ₆	+0.019	+0.016	-
C ₇	-0.038	-0.005	-
O ₁	-	+0.223	-
O ₂	-	-0.139	-
N	-	+0.080	-

TABLE - IX-4(c)

Angle between different planes

Planes	(2)	(3)	(4)
(1)	-	10.0°	9.6°
(2)	-	10.5°	9.6°
(3)	-	-	6.1°

DISCUSSION

Molecular structure

The estimated standard deviation (e.s.d.) of the measured C-C bond lengths in m-aminobenzoic acid hydrochloride is $\pm 0.012 \text{ \AA}$. Some of the bond lengths of the benzene ring (average, 1.408 \AA) differ from the C-C bond lengths (1.393 \AA) in crystalline benzene; specially C₃-C₄ (1.431 \AA) and C₅-C₆ (1.432 \AA). The deviations of the atoms C₄ and C₅, from the benzene ring plane are appreciable (table IX-4(b)). Because of the possibility that atom C₅ may be deviated from the aromatic plane due to the substitution of the amino group, the equations of the plane through the atoms C₁, C₂, C₃, C₄ and C₆ of the benzene ring was obtained and the deviation of different atoms from this plane were determined (table IX-4(b)); it is seen that except C₅, all other carbon atoms of the benzene ring as well as the exocyclic carbon atom C₇ lie in this plane within the limits of experimental error. It is possible that atom C₅ is significantly out of the benzene plane.

Structure of carboxylic group

In the carboxylic group the two C-O bonds are C₇-O₁ (1.276 Å) and C₇-O₂ (1.289 Å). The angle C₁-C₇-O₁ is 119.7° while angle C₁-C₇-O₂ is 117.9°. The angle O₂-C₇-O₁, 122.3° is close to the values observed in various carboxylic acids given in tables VI-8, chapter VI. It is seen from this table that for all the carboxylic acids listed there, the C=O and C-OH bonds are of unequal lengths and the angle C-C=O and C-C-OH are also unequal, the C-C-OH angle being less than 120° and C-C=O angle being greater than 120°. In the present case, the two C-O bonds are nearly of the same length (1.276 Å and 1.289 Å) and the two angles C-C-O are also nearly equal (119.7° and 117.9°). It is possible that this effect is connected with the shortening of the OH...O hydrogen bonds, linking the two molecules of the dimer. The OH...O hydrogen bond length in the present case is 2.53 Å (table IX-7); in benzoic acid (Sim et al., 1955), salicylic acid (Sundaralingam, 1955), p-nitrobenzoic acid (Sakore and Pant, 1966), o-nitrobenzoic acid (Sakore, Tavale and Pant, 1967), ^{Masayasu, (1967)} 3:5 dichloro-2-amino benzoic acid (present thesis, chapter VI, table VI-10), The values of the corresponding bond lengths are, 2.64 Å, 2.66 Å, 2.65 Å, 2.65 Å and 2.67 Å respectively. It is possible that in case of dimers with short OH...O hydrogen bonds, tautomerism of the type OH...O ⇌ O...HO may be occurring (Robertson, 1953). Results similar to the present one have been reported by Pant (1965) in the structure of

3:5 dibromo-p-aminobenzoic acid. In this structure there are two sets of crystallographically independent molecules. One set of molecules has mirror symmetry while the other set has diad symmetry. The molecules in each set form dimers and the O...OH bond length in each case is 2.56 Å (at -150°C). In the molecules of the first set, the two C-O bonds are each 1.275 Å and the two C-C-O angles, 119.6° each (at -150°C); the corresponding values for the other set of molecules are 1.300 Å and 120.5° respectively. It may be that tautomerism of the type $\text{OH}\dots\text{O} \rightleftharpoons \text{O}\dots\text{OH}$ may be occurring in both sets of molecules in 3:5 dibromo-p-aminobenzoic acid; Pant has, however, suggested that it is most likely that OH...O bonds are statistically symmetrical.

Structure of amino group

The C-N bond in m-aminobenzoic acid hydrochloride is 1.488 ± 0.011 Å. This is close to the value 1.475 Å usually quoted for single C-N bond distance (Trotter, 1960). This is to be expected since the nitrogen atom in the hydrochloride has no free pair of electrons which could impart double bond character to the C-N bond. In o-aminophenol hydrochloride, the C-N bond length is 1.474 Å (Richard and Cesur, 1965).

The arrangement of $\text{NH}\dots\text{Cl}$ bonds about the NH_3^+ group is nearly tetrahedral; the lengths of different

bonds around the nitrogen atom and the interbond angles about it are listed in table IX-6 and shown in fig. below. The NH...Cl hydrogen bond lengths, observed in other hydrochlorides are given in table IX-5.

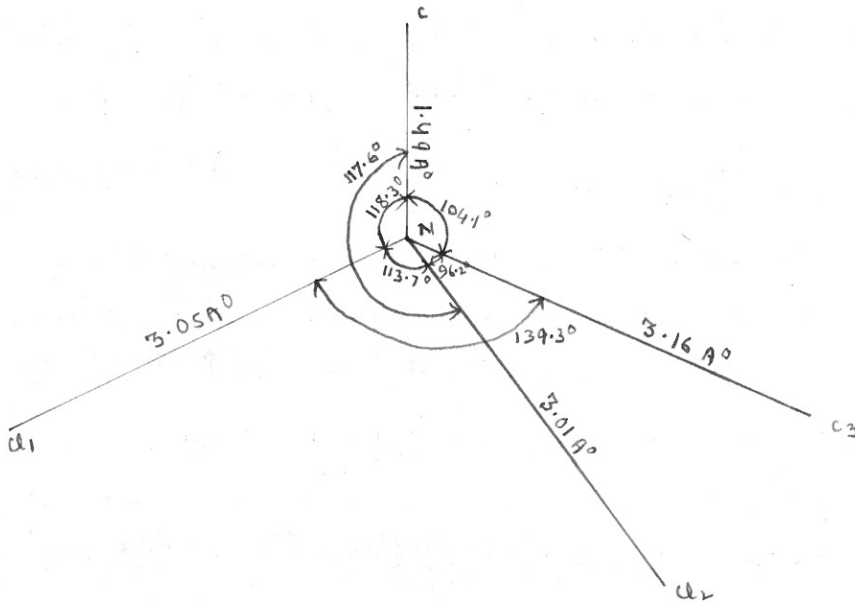


TABLE - IX-5

NH...Cl hydrogen bonds in various hydrochlorides

Hydrochloride	NH...Cl distance in Å	Reference
m-Toluidine 2HCl	3.10, 3.22, 3.26	Fow weather and Hargreaves, (1950)
Hydrazine 2HCl	3.10 ± 0.02	Donohue and Lipscomb, (1947)
Hexamethylene-diamine 2HCl	3.01, 3.07	Donohue, (1952)
Adenine HCl½H ₂ O	3.11, 3.21	Broomhead, (1948)
Hydrazine HCl	3.12, 3.12, 3.41	Sakurai, Tomiic, (1952)
o-aminophenol HCl	3.24, 3.17, 3.13, 3.20, 3.19, 3.18.	Cesur and Richards, (1965)

TABLE - IX-6

Bond	Length	Angle	
N-C	1.49 Å	Cl ₁ -N-Cl ₂	113.7°
N-Cl ₁	3.05 Å	Cl ₂ -N-Cl ₃	96.2°
N-Cl ₂	3.01 Å	Cl ₃ -N-C	104.1°
N-Cl ₃	3.16 Å	Cl ₁ -N-C	118.3°
		Cl ₁ -N-Cl ₃	139.3°
		Cl ₂ -N-C	117.6°

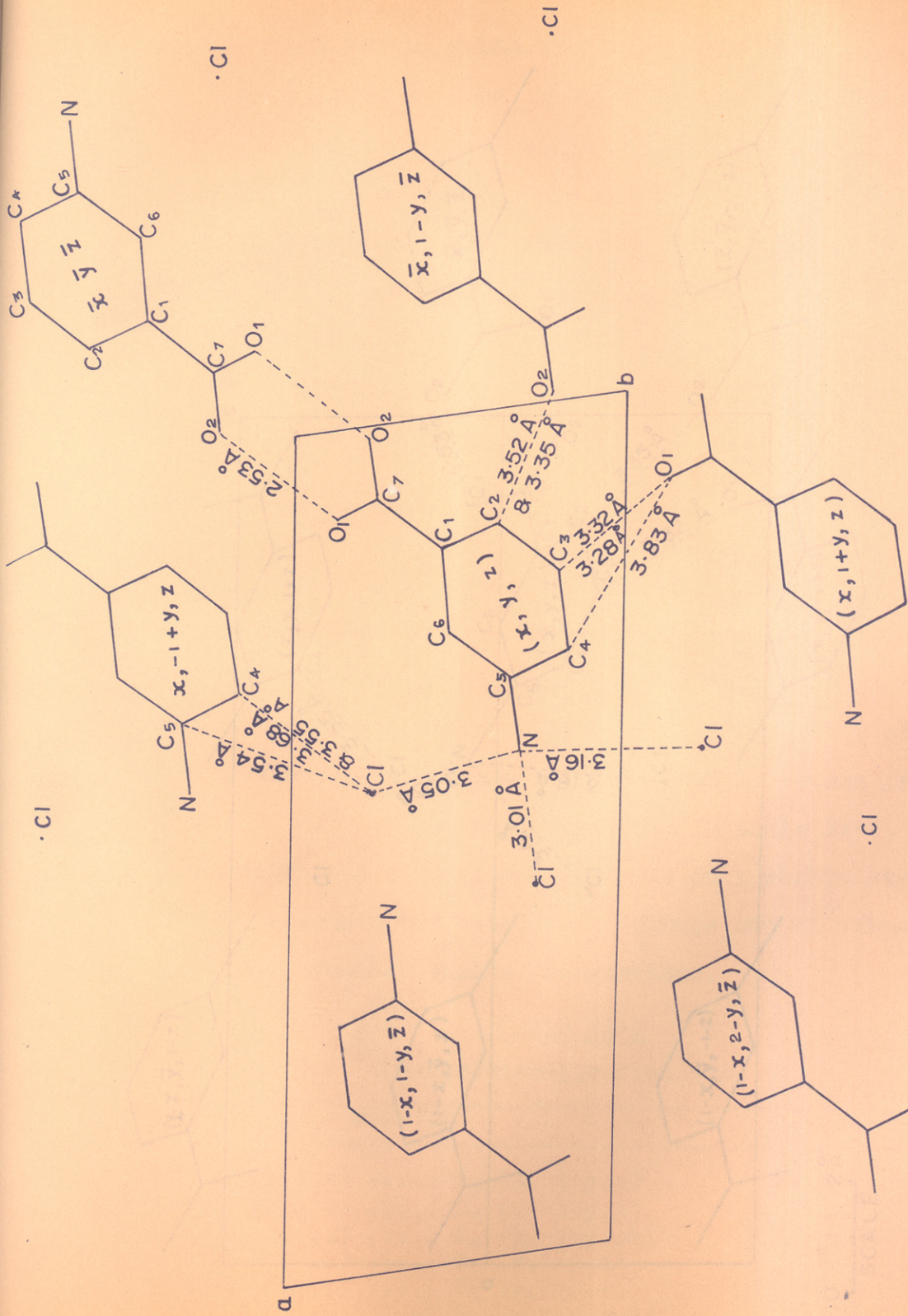


Fig. IX - 2 STRUCTURE PROJECTED ON (001)

It is found in the table IX-6 that all angles except $\text{Cl}_2\text{-N-Cl}_3$ (96.2°) and $\text{Cl}_1\text{-N-Cl}_3$ (139.3°) have values near to the tetrahedral value (110°). Both these angles involve N-Cl₃ contact. This indicates that N....Cl₃ bond may be away from the direction of N-H bond; this would imply that the NH....Cl₃ bond should be weaker than the other two NH....Cl bonds. This appears to be the case since the N-Cl₃ bond (3.16 \AA) is longer than the other two N-Cl bond distances (3.05 \AA and 3.01 \AA).

Crystal structure

The projection of the structure along the c and b axes are shown in figures IX-2 and 3. In these figures all the symmetry related molecules in the unit cell and a few neighbouring molecules are shown. The short intermolecular distances are indicated by broken lines in figures IX-2 and 3, and are listed in table IX-7. The m-aminobenzoic acid dimers are held in a stable structure by the strong bonds between NH_3^+ groups and Cl^- ions and by normal van der Waal's interactions.

TABLE IX-7
Intermolecular distances

Contact	Distance in \AA
$\text{Cl} (x,y,z) \dots\dots \text{Cl}_5 (x,-1+y,z)$	3.54 ± 0.010
$\text{Cl} (x,y,z) \dots\dots \text{Cl}_4 (x,-1+y,z)$	3.68 ± 0.010
$\text{Cl} (x,y,z) \dots\dots \text{Cl}_4 (x,-1+y,z+1)$	3.55 ± 0.010
$\text{Cl}_4 (x,y,z) \dots\dots \text{O}_1 (x,1+y,z)$	3.83 ± 0.011
$\text{Cl}_3 (x,y,z) \dots\dots \text{O}_1 (x,1+y,z)$	3.28 ± 0.011
$\text{Cl}_3 (x,y,z) \dots\dots \text{O}_1 (x,1+y,z-1)$	3.32 ± 0.011
$\text{Cl}_2 (x,y,z) \dots\dots \text{O}_2 (\bar{x},1-y,\bar{z})$	3.52 ± 0.011
$\text{Cl}_2 (x,y,z) \dots\dots \text{O}_2 (\bar{x},1-y,1-z)$	3.35 ± 0.011
$\text{O}_1 (x,y,z) \dots\dots \text{O}_2 (\bar{x},\bar{y},\bar{z})$	2.53 ± 0.011

P A R T - I I I

AN ATTEMPT TO SOLVE THE STRUCTURE OF
m-NITROBENZOIC ACID BY
DIRECT METHODS

CHAPTER - X

(A) EXPERIMENTAL

m-nitrobenzoic acid ($C_7H_5NO_4$) crystals were obtained by dissolving the acid in a mixture of alcohol and water and evaporating the saturated solution. The preliminary photographs showed that the crystals belong to the monoclinic system.

The unit cell dimensions obtained from the rotation photographs around the three axes are,

$$a = 10.38 \text{ \AA}; \quad b = 10.72 \text{ \AA}; \quad c = 13.38 \text{ \AA}; \quad \beta = 91.0^\circ$$

The values given by Thakar, Prasad and Kapadia (1940) are,

$$a = 10.41 \text{ \AA}; \quad b = 10.60 \text{ \AA}; \quad c = 13.22 \text{ \AA}; \quad \beta = 91.2^\circ$$

The density measured by flotation method using carbon tetrachloride and ethylene dibromide, at room temperature, was 1.501 gm./cm^3 , while the calculated density for eight molecules per unit cell comes out to be 1.490 gm./cm^3 . The linear absorption coefficient calculated by expression given in chapter-II is 14.7 cm^{-1} .

The three dimensional data were collected from zero and higher layer equi-inclination Weissenberg photographs taken with CuK radiation around the b axis, using the multiple film technique. The intensities were measured visually with the help of intensity scales. The visually estimated intensities were corrected for the (i) Lorentz

and Polarisation (L_p) factor (and spot extension factor, which are described in chapter-II.

Temperature factors and scale factors for (h0l) and (okl) zones were obtained by Wilson's method (1942). The plots of $\log_e C$ against $\sin^2 \theta / \lambda^2$ are shown in fig. X-1 and the corresponding values are given in table X-1(a,b).

Space group

The observed systematic absences are,

h k l	no condition
h o l	for h odd
o k l	for k odd.

The above systematic absences confirm the conclusion of Thakar, Prasad and Kapadia (1940) that the space group is $P2_1/a$. This space group has four equivalent positions and since there are eight molecules/unit cell, it is clear that there are two molecules per asymmetric unit.

(B) TRIAL STRUCTURE

The Patterson maps for all the three projections were taken with the help of the photosommateur. However these maps could not be interpreted. It was therefore decided to solve the structure by direct methods.

The following inequities given by Harker and Kasper (1948) were used.

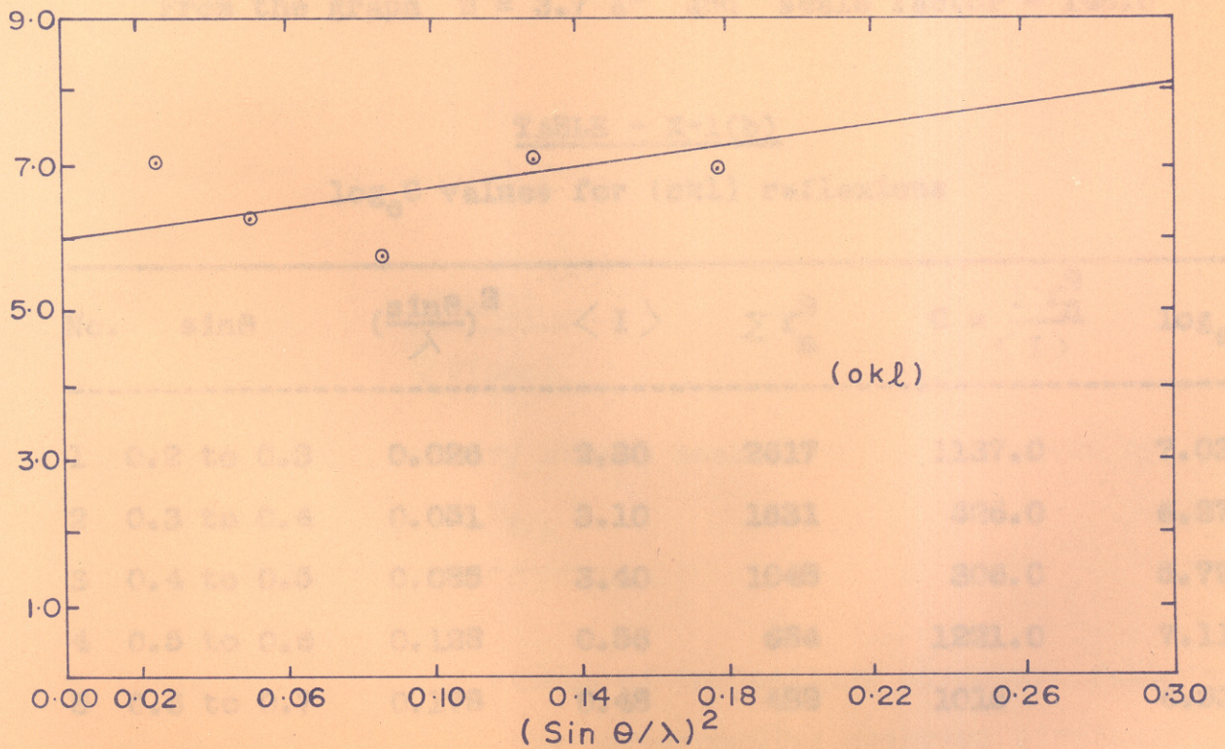
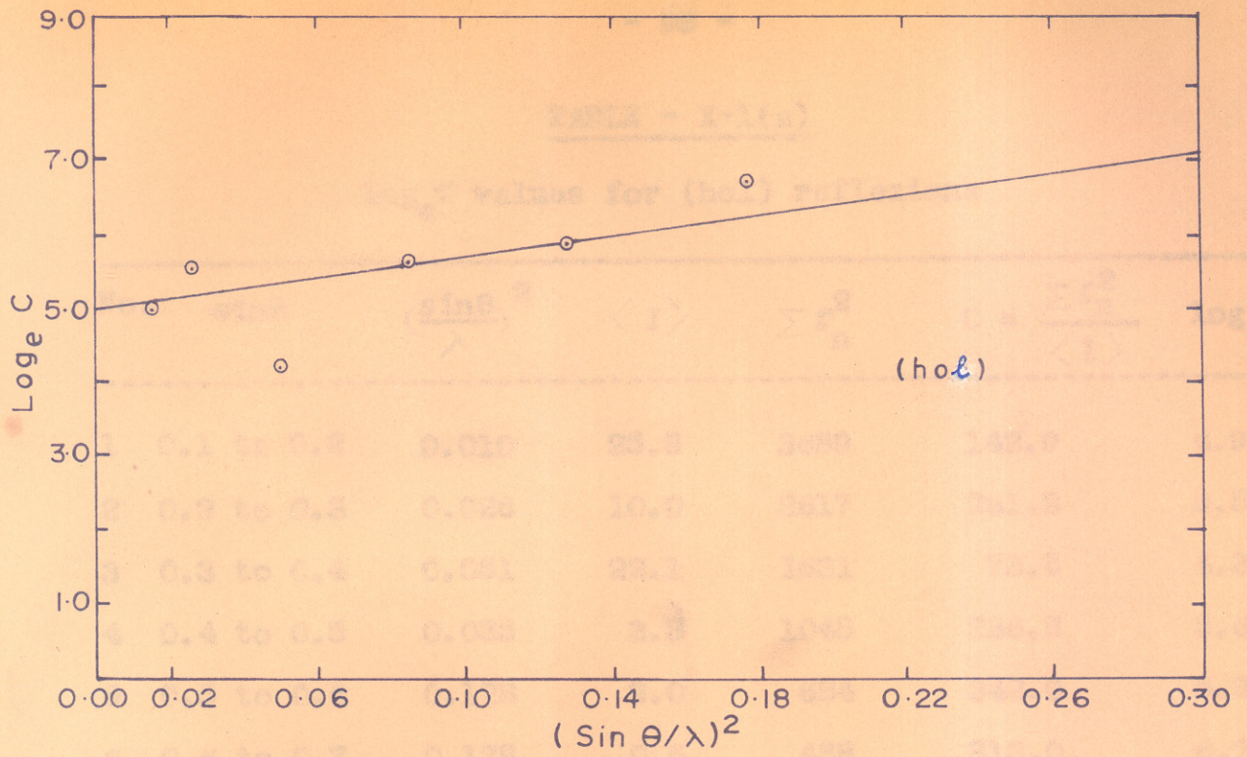


Fig. X-1 DETERMINATION OF PRELIMINARY SCALE AND TEMPERATURE FACTOR BY WILSON'S METHOD

TABLE - X-1(a)

$\log_e C$ values for (hol) reflexions

No.	$\sin\theta$	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.1 to 0.2	0.010	25.8	3689	142.9	4.96
2	0.2 to 0.3	0.026	10.0	2617	261.2	5.57
3	0.3 to 0.4	0.051	22.1	1631	73.8	4.30
4	0.4 to 0.5	0.085	3.8	1048	236.8	5.63
5	0.5 to 0.6	0.128	2.0	684	342.0	5.84
6	0.6 to 0.7	0.178	0.6	488	813.0	6.70

From the graph $B = 3.7 \text{ \AA}^2$ and scale factor = 148.0

TABLE - X-1(b)

$\log_e C$ values for (okl) reflexions

No.	$\sin\theta$	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$\langle I \rangle$	$\sum f_n^2$	$C = \frac{\sum f_n^2}{\langle I \rangle}$	$\log_e C$
1	0.2 to 0.3	0.026	2.30	2617	1137.0	7.03
2	0.3 to 0.4	0.051	3.10	1631	526.0	6.27
3	0.4 to 0.5	0.085	3.40	1048	306.0	5.72
4	0.5 to 0.6	0.128	0.56	684	1221.0	7.11
5	0.6 to 0.7	0.178	0.48	488	1016	6.93

From the graph $B = 3.7 \text{ \AA}^2$ and scale factor = 403.0

$$|U(H) + U(H')|^2 \leq [1 + U(H+H')] [1 + U(H-H')] \quad \dots (X-1)$$

$$|U(H) - U(H')|^2 \leq [1 - U(H+H')] [1 - U(H-H')] \quad \dots (X-2)$$

where $U(H)$, $U(H')$, $U(H+H')$, $U(H-H')$ are the unitary structure factors for reflexions (h,k,l) , (h',k',l') , $(h+h', k+k', l+l')$ and $(h-h', k-k', l-l')$ respectively.

These inequilities can also be written in the form

$$|a U(H) + b U(H')|^2 \leq [1 + ab U(H+H')] [1 + ab U(H-H')] \quad \dots (X-3)$$

where a and b are the signs of the structure factors $U(H)$ and $U(H')$ where a or b could be positive. If a and b are of same sign, the inequality reduces to X-1 and if a and b are of opposite sign, this reduces to X-2.

First of all the values of the unitary structure factor for the general reflexions were determined by the formula,

$$U(hkl) = \frac{F(hkl)}{\hat{f} F(000)}$$

where f is the unitary atomic scattering factor given by,

$$\hat{f} = \frac{f \cdot e^{-B \sin^2 \theta / \lambda^2}}{Z}$$

Table X-1 gives the values of the unitary structure factors greater than 0.2 and the corresponding observed structure factors.

TABLE - X-1

h	k	l	F _o	U	h	k	l	F _o	U
4	0	0	110	0.25	2	0	5	34	0.44
10	0	0	42	0.42	2	0	12	37	0.36
0	0	7	69	0.29	4	0	1	102	0.24
0	0	11	26	0.26	4	0	2	63	0.50
0	0	12	22	0.22	4	0	3	156	0.40
0	0	15	30	0.39	4	0	6	62	0.27
1	3	0	46	0.26	4	0	7	86	0.43
1	9	0	12	0.25	6	0	2	22	0.28
1	10	0	86	0.84	6	0	3	57	0.27
2	9	0	17	0.42	8	0	9	56	0.58
4	4	0	58	0.31	$\bar{2}$	0	3	120	0.22
6	2	0	45	0.38	$\bar{2}$	0	4	110	0.24
10	3	0	8	0.33	$\bar{2}$	0	12	37	0.39
0	1	12	27	0.23	$\bar{4}$	0	3	105	0.29
0	1	14	43	0.62	$\bar{4}$	0	4	83	0.23
0	1	15	16	0.39	$\bar{4}$	0	9	45	0.30
0	2	8	72	0.39	$\bar{4}$	0	10	56	0.42
0	3	6	83	0.38	$\bar{6}$	0	4	57	0.28
0	5	3	62	0.25	$\bar{6}$	0	6	39	0.24
0	9	8	42	0.25	$\bar{8}$	0	7	26	0.27
2	0	1	160	0.24	$\bar{10}$	0	2	26	0.27
2	0	2	173	0.23	$\bar{10}$	0	7	22	0.33

TABLE - X-1 (contd..)

h	k	l	F _o	U	h	k	l	F _o	U
2̄	0	15	23	0.45	6̄	2	2	52	0.28
2̄	0	16	15	0.30	6̄	2	4	42	0.25
1	1	6	74	0.26	1	3	5	124	0.44
1	1	8	34	0.27	7	3	4	48	0.39
2	1	5	95	0.29	1̄	3	3	161	0.43
4	1	3	77	0.26	1̄	3	4	101	0.29
4	1	5	66	0.28	3̄	3	4	129	0.43
2̄	1	2	191	0.37	6̄	3	2	39	0.25
3̄	1	2	130	0.30	1	4	7	45	0.25
3̄	1	3	126	0.33	2	4	6	50	0.25
4̄	1	3	76	0.27	3	4	1	72	0.27
7̄	1	4	50	0.37	3	4	8	29	0.25
11̄	1	1	22	0.35	4	4	9	59	0.57
12̄	1	2	24	0.60	5	4	8	35	0.33
3	2	10	31	0.28	2̄	4	6	74	0.38
4	2	6	72	0.39	3̄	4	4	66	0.29
1̄	2	2	176	0.34	3̄	4	5	93	0.47
2̄	2	2	155	0.33	4̄	4	6	50	0.30
2̄	2	3	178	0.38	5̄	4	5	39	0.30
2̄	2	4	105	0.29	6̄	4	6	31	0.28
2̄	2	7	57	0.25	6̄	4	8	22	0.23
3̄	2	8	73	0.46	1	5	3	74	0.30
4̄	2	5	100	0.44	2	5	3	71	0.30
4̄	2	6	55	0.30	2	5	9	30	0.27

TABLE - X-1 (contd..)

h	k	l	F ₀	U	h	k	l	F ₀	U
4	5	8	32	0.30	3	6	4	55	0.35
5	5	7	54	0.53	5	6	7	74	0.77
4	5	10	24	0.28	5	6	8	47	0.53
7	5	5	24	0.25	6	6	7	27	0.32
7	5	6	30	0.34	6	6	8	32	0.39
1	5	12	23	0.30	7	6	10	16	0.32
2	5	10	24	0.25	8	6	8	16	0.34
4	5	6	63	0.46	9	6	5	17	0.28
7	5	10	16	0.29	3	6	9	36	0.40
8	5	9	16	0.28	1	7	10	24	0.29
8	5	10	14	0.28	4	7	8	28	0.31
1	6	2	65	0.30	2	7	4	41	0.29
1	6	9	30	0.31	1	8	8	35	0.39
2	6	3	57	0.32	1	8	2	85	0.65
4	6	1	46	0.28	4	8	6	43	0.48
4	6	8	47	0.49	3	8	4	30	0.27
5	6	8	23	0.26	3	8	5	79	0.84
8	6	4	27	0.35	5	8	5	25	0.29
7	6	4	25	0.28					
7	6	5	23	0.26					
1	6	1	67	0.30					
1	6	5	42	0.25					
1	6	9	47	0.55					
2	6	2	59	0.39					

Out of these reflexions (table X-1), there are three having fairly large values of U. These are,

$$U(1,10,0) = 0.84$$

$$U(0,1,14) = 0.62$$

$$U(\bar{3}, 3, 5) = 0.84$$

These reflexions are linearly independent and hence have been assigned positive signs in order to fix the origin. The signs of other reflexions were obtained using inequality relations X-1 and X-2. The signs of the following reflexions were given alphabetical symbols as shown below:

$$S(\bar{5}, 6, 7) = a; \quad S(\bar{5}, 6, 8) = b; \quad S(2, 0, 5) = c;$$

$$S(1, 2, \bar{2}) = d; \quad S(\bar{2}, 1, 2) = e; \quad S(4, 6, 8) = f;$$

$$S(1, 3, 5) = g.$$

Also the following relations were used.

$$\text{For } h+k = 2n, \quad F(hk1) = F(h\bar{k}1) \neq F(hk\bar{1}); \quad F(hk\bar{1}) = F(\bar{h}k1)$$

$$\text{For } h+k = 2n+1, \quad F(hk1) = -F(h\bar{k}1) \neq F(hk\bar{1}); \quad F(hk\bar{1}) = -F(\bar{h}k1)$$

Inequalities

$$(1) \left| U(\bar{3}, 3, 5) + U(1, 10, 0) \right|^2 \leq \left[1 + U(4, 2, \bar{5}) \right] \left[1 + U(\bar{2}, 13, 5) \right]$$

$$\text{i.e. } \left| 0.84 + 0.84 \right|^2 \leq \left[1 + S(4, 2, \bar{5}) (0.44) \right] \left[1 + U(\bar{2}, 13, 5) \right]$$

The above inequality is satisfied when $U(\bar{2}, 13, 5)$ (beyond the Cu reflecting sphere) is large and $S(4, 2, \bar{5}) = +$, hence $S(4, 2, \bar{5}) = +$.

(2)

$$|U(\bar{3}, 3, 5) + U(4, 2, \bar{5})|^2 \leq [1 + U(\bar{7}, 6, 10)] [1 + U(1, 10, 0)]$$

i.e. $|0.84 + 0.44|^2 \leq [1 + S(\bar{7}, 6, 10) (0.32)] [1 + 0.84]$

i.e. $1.66 \leq [1 + S(\bar{7}, 6, 10) (0.32)] [(1.84)]$

This is possible when $S(\bar{7}, 6, 10) = +$

(3)

$$|U(\bar{3}, 3, 5) + aU(\bar{5}, 6, 7)|^2 \leq [1 + aU(2, 2, \bar{2})] [1 + aU(\bar{8}, 14, 12)]$$

i.e. $|0.84 + a(0.77a)|^2 \leq [1 + a.S(2, 2, \bar{2})(0.33)] [1 + aU(\bar{8}, 14, 12)]$

i.e. $2.6 \leq [1 + aS(2, 2, \bar{2})(0.33)] [1 + aU(\bar{8}, 14, 12)]$

This is possible when $S(2, 2, \bar{2}) = S(\bar{2}, \bar{2}, 2) = a$

(4)

$$|aU(2, 2, \bar{2}) + U(1, 10, 0)|^2 \leq [1 + aU(\bar{1}, 8, 2)] [1 + aU(3, 12, \bar{2})^*]$$

i.e. $|a(0.33a) + 0.84|^2 \leq [1 + aS(\bar{1}, 8, 2)(0.65)] [1 + aU(3, 12, \bar{2})]$

i.e. $1.3 \leq [1 + aS(\bar{1}, 8, 2) (0.65)] [1 + aU(3, 12, \bar{2})]$

This is possible when $S(\bar{1}, 8, 2) = a$

(5)

$$|U(\bar{3}, 3, 5) + bU(\bar{5}, 6, 8)|^2 \leq [1 + bU(\bar{2}, \bar{2}, 3)] [1 + bU(\bar{8}, 14, 13)]$$

i.e. $|0.84 + b(0.53b)|^2 \leq [1 + bS(\bar{2}, \bar{2}, 3)(0.38)] [1 + bU(\bar{8}, 14, 13)]$

i.e. $1.85 \leq [1 + bS(\bar{2}, \bar{2}, 3)(0.38)] [1 + bU(\bar{8}, 14, 13)]$

This is possible when $S(\bar{2}, \bar{2}, 3) = b$

(6)

$$|bU(\bar{2}, \bar{2}, 3) + aU(\bar{5}, 6, 7)|^2 \leq [1 + baU(\bar{3}, 8, 4)] [1 + baU(\bar{7}, 4, 10)^*]$$

$$\text{i.e. } |b(0.38b) + a(0.77a)|^2 \leq [1 + baS(\bar{3}, 8, 4)(0.27)] [1 + baU(\bar{7}, 4, 10)]$$

$$\text{i.e. } 1.30 \leq [1 + abS(\bar{3}, 8, 4)(0.27)] [1 + baU(\bar{7}, 4, 10)]$$

Since $U(\bar{7}, 4, 10)$ is small, this is possible when

$$S(\bar{3}, 8, 4) = ab.$$

(7)

$$|bU(\bar{2}, 2, 3) + bU(\bar{5}, 6, 8)|^2 \leq [1 + bbU(\bar{3}, 4, 5)] [1 + bU(\bar{7}, 8, 11)^*]$$

$$\text{i.e. } |b(0.380) + b(0.53b)|^2 \leq [1 + b^2S(\bar{3}, 4, 5)(0.47)] [1 + bU(\bar{7}, 8, 11)]$$

$$\text{i.e. } 0.81 \leq [1 + b^2S(\bar{3}, 4, 5)(0.47)] [1 + bU(\bar{7}, 8, 11)]$$

This is possible when $S(\bar{3}, 4, 5) = b^2 = +$.

(8)

$$|U(\bar{3}, 8, 5) + aU(\bar{1}, 8, 2)|^2 \leq [1 + aU(\bar{2}, 0, 3)] [1 + aU(\bar{4}, 16, 8)]$$

$$\text{i.e. } |0.84 + a(0.65a)|^2 \leq [1 + aS(\bar{2}, 0, 3)(0.22)] [1 + aU(\bar{4}, 16, 8)]$$

$$\text{i.e. } 2.25 \leq [1 + aS(\bar{2}, 0, 3)(0.22)] [1 + aU(\bar{4}, 16, 8)]$$

This is possible when $S(\bar{2}, 0, 3) = a$

(9)

$$|aU(\bar{2}, 0, 3) + aU(\bar{5}, 6, 7)|^2 \leq [1 + a^2U(\bar{3}, 6, 4)] [1 + a^2U(\bar{7}, 6, 10)]$$

$$\text{i.e. } 0.98 \leq [1 + a^2S(\bar{3}, 6, 4)(0.35)] [1.32]$$

This is possible when $S(\bar{3}, 6, 4) = +$.

(10)

$$|U(4, 2, \bar{5}) + aU(\bar{5}, 6, 7)|^2 \leq [1 + aU(\bar{1}, 8, 2)] [1 + aU(\bar{9}, 14, 12)^*]$$

$$\text{i.e. } |0.44 + a(0.77a)|^2 \leq [1 + aS(\bar{1}, 8, 2)(0.65)] [1 + aU(\bar{9}, 14, 12)^*]$$

$$\text{i.e. } 1.22 \leq [1 + aS(\bar{1}, 8, 2)(0.65)] [1 + aU(\bar{9}, 14, 12)^*]$$

This is possible when $S(\bar{1}, 8, 2) = a$.

This confirms no (4)

(11)

$$|U(\bar{4}, 2, 5) + cU(2, 0, 5)|^2 \leq [1 + cU(6, \bar{2}, 0)] [1 + cU(\bar{2}, 2, 10)^*]$$

$$\text{i.e. } |0.44 + c(0.44c)|^2 \leq [1 + cS(6, \bar{2}, 0)(0.38)] [1 + cU(\bar{2}, 2, 10)^*]$$

$$\text{i.e. } 0.8 \leq [1 + cS(6, \bar{2}, 0)(0.38)] [1 + cU(\bar{2}, 2, 10)^*]$$

This is possible when $S(6, \bar{2}, 0) = c$.

(12)

$$|aU(\bar{5}, 6, 7) + cU(6, \bar{2}, 0)|^2 \leq [1 + acU(1, 4, 7)] [1 + acU(\bar{1}\bar{1}, 8, 7)^*]$$

$$\text{i.e. } |a(0.77a) + c(0.38c)|^2 \leq [1 + acS(1, 4, 7)(0.25)] [1 + acU(\bar{1}\bar{1}, 8, 7)^*]$$

$$\text{i.e. } 1.3 \leq [1 + acS(1, 4, 7)(0.25)] [1 + acU(\bar{1}\bar{1}, 8, 7)^*]$$

This is possible when $S(1, 4, 7) = ac$.

(13)

$$|U(\bar{3}, 6, 4) + cU(205)|^2 \leq [1 + cU(\bar{1}, 6, 9)] [1 + cU(\bar{5}, 6, \bar{1})^*]$$

$$\text{i.e. } |0.35 + c(0.44c)|^2 \leq [1 + cS(\bar{1}, 6, 9)(0.55)] [1 + cU(\bar{5}, 6, \bar{1})^*]$$

$$\text{i.e. } 0.64 \leq [1 + cS(\bar{1}, 6, 9)(0.55)] [1 + cU(\bar{5}, 6, \bar{1})^*]$$

This is possible when $S(\bar{1}, 6, 9) = c$.

(14)

$$|aU(\bar{5}, 6, 7) + cU(\bar{1}, 6, 9)|^2 \leq [1 + ac(4, 0, 2)] [1 + acU(\bar{6}, 12, 16)]$$

$$\text{i.e. } |a(0.77a) + c(0.55c)|^2 \leq [1 + acS(4, 0, 2)(0.50)] [(1 + acU(\bar{6}, 12, 16))]$$

$$\text{i.e. } 1.70 \leq [1 + acS(4, 0, 2)(0.50)] [1 + acU(\bar{6}, 12, 16)]$$

This is possible when $S(4, 0, 2) = ac$, and $S(\bar{6}, 12, 16)$ (which is beyond Cu reflecting sphere) is large. > 0.2

(15)

$$|U(0, 1, 14) + eU(\bar{2}, 1, 2)|^2 \leq [1 + eU(2, 0, 12)] [1 + eU(\bar{2}, 2, 16)]$$

$$\text{i.e. } |0.62 + e(0.37e)|^2 \leq [1 + eS(2, 0, 12)(0.36)] [1 + eU(\bar{2}, 2, 16)]$$

$$\text{i.e. } 1.0 \leq [1 + eS(2, 0, 12)(0.36)] [1 + eU(\bar{2}, 2, 16)]$$

This is possible when $S(2, 0, 12) = +$. (Uncertain)

(16)

$$|aU(\bar{5}, 6, 7) + acU(4, 0, 2)|^2 \leq [1 + aacU(\bar{9}, 6, 5)] [1 + a^2cU(\bar{1}, 6, 9)]$$

$$\text{i.e. } |a(0.77a) + ac(0.50ac)|^2 \leq [1 + a^2cS(\bar{9}, 6, 5)(0.25)] [1 + a^2c(0.55)]$$

$$\text{i.e. } 1.65 \leq [1 + a^2cS(\bar{9}, 6, 5)(0.25)] [1 + a^2c(0.55)]$$

This is possible when $S(\bar{9}, 6, 5) = a^2c = c$.

(17)

$$|bU(\bar{5}, 6, 8) + cU(6, 2, 0)|^2 \leq [1 + bcU(1, 8, 8)] [1 + bcU(\bar{11}, 4, 8)^*]$$

$$\text{i.e. } |b(0.53b) + (0.39c)|^2 \leq [1 + bcS(1, 8, 8)(0.39)] [1 + bcU(\bar{11}, 4, 8)]$$

$$\text{i.e. } 0.88 \leq [1 + bcS(1, 8, 8)(0.39)] [1 + bcU(\bar{11}, 4, 8)]$$

This is possible when $S(1, 8, 8) = bc$.

(18)

$$|U(\bar{3}, 8, 5) + bcU(1, 8, 8)|^2 \leq [1 + bcU(4, 0, 3)] [1 + bcU(\bar{2}, 16, 13)]$$

i.e. $|0.84 + bc(0.39)|^2 \leq [1 + bcS(4, 0, 3)(0.40)] [1 + bcU(\bar{2}, 16, 13)]$

i.e. $1.50 \leq 1 + bcS(4, 0, 3)(0.40) + bcU(\bar{2}, 16, 13)$

This is possible when $S(4, 0, 3) = bc$.

(19)

$$|U(1, 10, 0) + bcU(1, 8, 8)|^2 \leq [1 + bcU(0, \bar{2}, 8)] [1 + bcU(2, 18, 8)]$$

i.e. $|0.84 + bc(0.39 bc)|^2 \leq [1 + bcS(0, 2, 8)] [1 + bcU(2, 18, 8)]$

i.e. $1.50 \leq [1 + bcS(0, \bar{2}, 8)(0.39)] [1 + bcU(2, 18, 8)]$

This is possible when $S(0, \bar{2}, 8) = bc$.

(20)

$$|U(0, 1, 14) + bcU(0, \bar{2}, 8)|^2 \leq [1 + bcU(0, 3, 6)] [1 + bcU(0, \bar{1}, 22)]$$

i.e. $|0.64 + bc(0.39bc)|^2 \leq [1 + bcS(0, 3, 6)(0.33)] [1 + bcU(0, \bar{1}, 22)]$

i.e. $1.50 \leq [1 + bcS(0, 3, 6)(0.33)] [1 + bcU(0, \bar{1}, 22)]$

This is possible when $S(0, 3, 6) = bc$. (Uncertain)

(21)

$$|U(0, 1, 14) + aU(\bar{5}, 6, 7)|^2 \leq [1 + aU(\bar{5}, 5, \bar{7})] [1 + aU(\bar{10}, \bar{11}, 0)^*]$$

i.e. $|0.64 + a(0.77a)|^2 \leq [1 + aS(\bar{5}, 5, \bar{7})(0.53)] [1 + aU(\bar{10}, \bar{11}, 0)^*]$

i.e. $1.90 \leq [1 + aS(\bar{5}, 5, \bar{7})(0.53)] [1 + aU(\bar{10}, \bar{11}, 0)^*]$

This is possible when $S(\bar{5}, 5, \bar{7}) = S(5, 5, 7) = a$.

Relation $(\bar{10}, \bar{11}, 0)$ must be cut off; its value must be fairly large in order to prove the inequality.

Reflexion $\bar{5}, 7, 21$ may be cut off; its value must be or small

(22)

$$|bU(\bar{5}, 6, 8) + dU(1, 2, \bar{2})|^2 \leq [1 + bdU(\bar{4}, 8, 6)] [1 + bdU(\bar{6}, 4, 10)]^2$$

$$\text{i.e. } |b(0.65b) + d(0.34d)|^2 \leq [1 + bdS(\bar{4}, 8, 6)(0.48)] [1 + bdU(\bar{6}, 4, 10)]^2$$

$$\text{i.e. } 1.0 \leq [1 + bdS(\bar{4}, 8, 6)(0.48)] [1 + bdU(\bar{6}, 4, 10)]^2$$

This is possible when $S(\bar{4}, 8, 6) = bd$.

(23)

$$|aU(\bar{1}, 8, 2) + dU(1, 2, \bar{2})|^2 \leq [1 + adU(\bar{2}, 6, 4)] [1 + adU(0, 10, 0)]^2$$

$$\text{i.e. } |a(0.65a) + d(0.34d)|^2 \leq [1 + adS(\bar{2}, 6, 4)(0.39)] [1 + adU(0, 10, 0)]^2$$

$$\text{i.e. } 1.0 \leq [1 + adS(\bar{2}, 6, 4)(0.39)] [1 + adU(0, 10, 0)]^2$$

This is possible when $S(\bar{2}, 6, 4) = ad$.

(24)

$$|fU(4, \bar{6}, 8) + aU(\bar{1}, 8, 2)|^2 \leq [1 + afU(3, 2, 10)] [1 + afU(5, \bar{14}, 6)]^2$$

$$\text{i.e. } |f(0.49f) + a(0.65a)|^2 \leq [1 + afS(3, 2, 10)(0.39)] [1 + afU(5, \bar{14}, 6)]^2$$

$$\text{i.e. } 1.30 \leq [1 + afS(3, 2, 10)(0.39)] [1 + afU(5, \bar{14}, 6)]^2$$

This is possible when $S(3, 2, 10) = af$.

(25)

$$|U(0, 1, 14) + fU(4, 6, 8)|^2 \leq [1 + fU(\bar{4}, \bar{5}, 6)] [1 + fU(4, 7, 22)]^2$$

$$\text{i.e. } |0.62 + f(0.49f)|^2 \leq [1 + fS(\bar{4}, \bar{5}, 6)(0.46)] [1 + fU(4, 7, 22)]^2$$

$$\text{i.e. } 1.21 \leq [1 + fS(\bar{4}, \bar{5}, 6)(0.46)] [1 + fU(4, 7, 22)]^2$$

This is possible when $S(\bar{4}, \bar{5}, 6) = f$.

(26)

$$| -a \cdot U(1, 8, \bar{2}) + rU(\bar{4}, \bar{5}, 6) |^2 \leq [1 + (-af)U(\bar{3}, 3, 4)] [(1 + (-af)U(\bar{5}, \bar{13}, 8))]$$

$$\text{i.e. } | -a(0.65\bar{a}) + r(0.46\bar{r}) |^2 \leq [1 + (-af)S(\bar{3}, 3, 4)(0.43)] \times [1 + (-af)U(\bar{5}, \bar{13}, 8)]$$

$$\text{i.e. } 1.23 \leq [1 + (-af)S(\bar{3}, 3, 4)(0.43)] [1 + (-af)U(\bar{5}, \bar{13}, 8)]$$

This is possible when $S(\bar{3}, 3, 4) = -af$.

(27)

$$| rU(4, 6, 8) + (-af)U(\bar{3}, 3, 4) |^2 \leq [1 + (-af^2)U(7, 3, 4)] \times [1 + (-af^2)U(1, 9, \bar{12}^*)]$$

$$\text{i.e. } | r(0.49\bar{r}) + (-af)(0.46\bar{a}\bar{r}) |^2 \leq [1 + (-af^2)S(7, 3, 4)(0.39)] \times [1 + (-af^2)U(1, 9, \bar{12}^*)]$$

$$\text{i.e. } 0.90 \leq [1 + (-af^2)S(7, 3, 4)(0.39)] [1 + (-af^2)U(1, 9, \bar{12}^*)]$$

This is possible when $S(7, 3, 4) = -af^2 = -a$.

(28)

$$| gU(1, 3, 5) + (-a)U(7, \bar{3}, 4) |^2 \leq [1 + (-a)gU(8, 0, 9)] \times [1 + (-a)gU(6, \bar{6}, \bar{1})^*]$$

$$\text{i.e. } | g(0.44g) + (-a)(0.48\bar{a}) |^2 \leq [1 + (-a)gS(8, 0, 9)(0.58)] \times [1 + (-a)gU(6, \bar{6}, \bar{1})]$$

$$\text{i.e. } 0.85 \leq [1 + (-a)gS(8, 0, 9)(0.58)] [1 + (-a)gU(6, \bar{6}, \bar{1})]$$

This is possible when $S(8, 0, 9) = -ag$.

(29)

$$|gU(1,3,5)+aU(\bar{1},8,2)|^2 \leq [1+a.gU(2,\bar{5},3)][1+a.gU(0,11,7)^*]$$

$$\text{i.e. } |g(0.44g)+a(0.65a)|^2 \leq [1+a.gS(2,5,3)(0.36)] \times [1+a.gU(0,11,7)]$$

$$\text{i.e. } 1.20 \leq [1+a.gS(2,\bar{5},3)(0.36)] [1+a.gU(0,11,7)]$$

This is possible when $S(2,5,3) = -S(2,\bar{5},3) = -ag$.

(30)

$$|aU(\bar{5},6,7)+(-ag)U(2,5,3)|^2 \leq [1+(-ag)aU(\bar{7},1,4)] \times [1+(-ag)aU(\bar{3},11,\bar{7})^*]$$

$$\text{i.e. } |a(0.77a)+(-ag)(0.36\bar{a}g)|^2 \leq [1+(-ag)aS(\bar{7},1,4)(0.37)] \times [1+(-ag)aU(\bar{3},11,\bar{7})]$$

$$\text{i.e. } 1.26 \leq [1+(-ag)aS(\bar{7},1,4)(0.37)] [1+(-ag)aU(\bar{3},11,\bar{7})]$$

This is possible when $S(\bar{7},1,4) = (-ag)a = -g$

(31)

$$|aU(\bar{1},8,2)+(-a)U(\bar{1},\bar{8},2)|^2 \leq [1+(-a)aU(\bar{2},0,4)] \times [1+(-a)aU(0,16,4)]$$

$$\text{i.e. } |a(0.65a)+(-a)(0.65\bar{a})|^2 \leq [1+(-a)aS(\bar{2},0,4)(0.24)] \times [1+(-a)aU(0,16,4)]$$

$$\text{i.e. } 1.69 \leq [1+(-a)aS(\bar{2},0,4)(0.24)] [1+(-a)aU(0,16,4)]$$

This is possible when $S(\bar{2},0,4) = (-a)a = -a^2 = -$

In many of the above inequalities one of the reflexions is either cut off or is unobserved. The reflexions marked '*' are unobserved (within the limiting sphere), while other with unknown U are beyond reflecting sphere. The U 's for unobserved reflexions (i.e. those within the reflecting sphere) are taken to be small.

Therefore we have the following signs certain :

$S(1, 10, 0) = +$	$S(\bar{5}, 6, 8) = b$	$S(\bar{3}, 8, 4) = ab$
$S(\bar{3}, 8, 5) = +$	$S(2, 0, 1) = c$	$S(4, 0, 2) = ac$
$S(0, 1, 14) = +$	$S(6, 2, 0) = c$	$S(1, 4, 7) = ac$
$S(4, 2, \bar{5}) = +$	$S(\bar{1}, 6, 9) = c$	$S(4, 0, 3) = bc$
$S(\bar{7}, 6, 10) = +$	$S(\bar{9}, 6, 5) = c$	$S(1, 8, 8) = bc$
$S(\bar{3}, 4, 5) = +$	$S(1, 2, \bar{2}) = d$	$S(0, \bar{2}, 8) = bc$
$S(\bar{3}, 6, 4) = +$	$S(\bar{2}, 1, 2) = e$	$S(0, 3, 6) = bc$
$S(\bar{2}, 0, 4) = -$	$S(2, 0, 12) = e$	$S(\bar{4}, 8, 6) = bd$
$S(2, 2, \bar{2}) = a$	$S(4, 6, 8) = f$	$S(\bar{2}, 6, 4) = ad$
$S(\bar{1}, 8, 2) = a$	$S(4, 5, \bar{6}) = f$	$S(3, 2, 10) = af$
$S(\bar{5}, 6, 7) = a$	$S(\bar{3}, \bar{4}, 8) = f$	$S(\bar{3}, 3, 4) = -af$
$S(2, 0, \bar{3}) = a$	$S(1, 3, 5) = g$	$S(8, 0, 9) = -ag$
$S(7, 3, 4) = -a$	$S(7, 1, \bar{4}) = -g$	$S(2, 5, 3) = -ag$
$S(2, 2, \bar{3}) = b$	$S(5, 5, 7) = +ab$	

Now using the relationship $S(H) S(H') \sim S(H+H')$ statistically we get following relations between different symbols.

$$a = -gc; \quad b = -; \quad e = +; \quad f = - \quad \text{and} \quad d = -a.$$

This gives four combinations, two when a is + and two when a is - . The four cases are,

- (i) a +, d -, g +, c -, b -, e +, f -,
- (ii) a +, d -, g -, c +, b -, e +, f -,
- (iii) a -, d +, g -, c -, b -, e +, f -,
- (iv) a -, d +, g +, c +, b -, e +, f -.

Three dimensional Fourier sections were taken using signs from all the combinations turn by turn with the help of the photosomaateur. However, the molecule could not be fixed.

The following reasons may be attributed for the failure of the structure determination.

(1) Due to imperfect scaling of structure factors and the errors in temperature factors, the values of unitary structure factors may be in error, and in some cases these errors may be large enough to give wrong conclusions.

(2) Many observed reflexions which have large structure factors i.e. above 50.0 e.g. 0,0,7; 0,5,3; 2,0,1; 2,0,2; 4,0,6; 4,0,7; $\bar{6}$,0,4; 1,1,6; 2,1,5; 4,1,3; 4,1,5; $\bar{3}$,1,2; $\bar{4}$,1,3; $\bar{2}$,2,4; $\bar{2}$,2,7; $\bar{3}$,2,8; $\bar{4}$,2,6; $\bar{6}$,2,2; $\bar{1}$,3,3; 3,4,1; 4,4,9; $\bar{2}$,4,6; $\bar{3}$,4,4; 1,5,3; 1,6,2; 2,6,3; $\bar{2}$,6,2; could not be assigned any definite sign and were therefore not included in the Fourier summation.

(3) The statistical relation $S(H) S(H') \sim S(H+H')$, used to find the relation between the different symbols may not give the correct answer, since many structure factors have small values of U.

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OBSERVED AND CALCULATED STRUCTURE FACTORS

(3:5 dichloro-2-aminobenzoic acid)

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	4	0	90.4	-95.0	2	4	0	33.7	-32.5
0	8	0	105.4	110.9	2	6	0	18.6	-10.8
0	10	0	20.0	-22.7	2	8	0	1.0	- 3.2
0	14	0	29.5	31.9	2	9	0	28.4	22.8
0	18	0	20.5	-26.4	2	10	0	32.7	29.4
4	0	0	67.0	71.4	2	13	0	17.4	14.8
6	0	0	23.8	21.9	3	1	0	19.1	-20.3
10	0	0	26.9	23.2	3	2	0	64.5	-72.7
1	4	0	34.6	-35.3	3	3	0	40.0	39.9
1	6	0	43.0	-47.2	3	4	0	17.0	16.2
1	7	0	40.0	-37.7	11	0	0	0.0	0.0
1	8	0	26.0	24.9	3	6	0	31.2	30.5
1	9	0	17.6	11.7	3	7	0	30.0	-32.2
1	10	0	7.0	7.8	3	8	0	22.9	-18.2
1	11	0	40.6	39.8	3	9	0	22.4	-16.1
1	12	0	38.6	-37.8	3	10	0	17.8	-14.1
1	16	0	17.0	16.7	3	11	0	30.3	30.5
1	20	0	23.2	-24.6	3	12	0	31.2	32.0
2	2	0	27.0	35.1	3	15	0	42.0	-43.8
2	3	0	25.7	-28.4	4	1	0	13.4	-11.7

h	k	l	F _o	F _c	h	k	l	F _o	F _c
4	2	0	25.7	-29.5	6	12	0	26.0	-24.0
4	3	0	33.8	-30.9	6	14	0	15.6	-16.8
4	4	0	109.4	-114.8	7	1	0	16.0	-17.1
4	5	0	27.7	-24.9	7	2	0	47.0	-52.3
4	8	0	58.4	62.4	7	3	0	42.0	47.9
4	10	0	49.9	-28.5	7	6	0	31.0	31.9
4	12	0	49.0	-52.8	7	7	0	27.7	-27.1
4	13	0	30.3	-21.9	7	10	0	41.2	-42.1
4	18	0	27.6	-29.6	7	11	0	36.8	36.5
5	1	0	48.0	-54.1	8	3	0	13.5	-5.7
5	2	0	43.0	46.4	8	4	0	37.0	-42.0
5	3	0	30.5	-29.3	8	6	0	18.1	20.4
5	4	0	30.0	-28.5	8	8	0	41.0	44.0
5	5	0	14.0	17.6	8	10	0	28.3	-34.0
5	7	0	27.6	-31.7	8	14	0	22.0	28.2
5	8	0	26.7	30.1	8	16	0	17.0	20.4
5	9	0	15.0	-13.0	8	17	0	10.2	9.5
5	10	0	27.5	23.8	9	3	0	31.5	37.4
5	12	0	36.7	-37.4	9	10	0	21.4	18.9
5	16	0	17.1	20.4	9	11	0	17.4	15.2
6	1	0	18.3	-18.4	9	12	0	14.1	-14.7
6	3	0	15.2	15.1	9	16	0	20.0	21.6
6	4	0	18.0	-14.1	10	2	0	19.3	17.0
6	5	0	25.4	21.6	10	3	0	19.6	-19.8

h	k	l	F _O	F _C	h	k	l	F _O	F _C
11	2	0	43.7	-47.4	2	7	1	38.2	-38.7
11	5	0	17.1	15.3	2	8	1	30.0	-31.9
4	0	1	30.8	26.4	2	9	1	40.7	48.0
6	0	1	36.7	-38.4	2	10	1	18.5	18.6
8	0	1	9.8	10.6	2	12	1	18.5	23.0
10	0	1	23.0	-26.7	2	13	1	37.6	-41.3
12	0	1	13.9	-12.7	2	14	1	50.3	-52.2
14	0	1	21.0	-22.3	2	16	1	16.5	-21.2
0	5	1	30.5	-28.8	2	17	1	20.6	23.6
0	6	1	15.1	-11.6	2	18	1	18.6	19.4
0	7	1	8.0	3.7	2	21	1	9.8	-12.9
0	8	1	5.0	2.6	3	1	1	38.5	-40.6
0	9	1	15.0	-9.0	3	2	1	68.3	-73.5
0	14	1	19.6	24.8	3	3	1	25.0	-18.7
1	5	1	34.0	-37.5	3	4	1	14.4	-14.6
1	6	1	6.1	4.2	3	5	1	59.0	-51.0
1	7	1	30.2	29.8	3	6	1	57.8	62.4
1	8	1	27.1	27.0	3	7	1	6.3	-5.0
1	11	1	25.0	-31.5	3	8	1	13.3	-16.4
1	19	1	13.2	-16.1	3	9	1	11.5	9.7
1	20	1	13.0	-11.9	3	10	1	27.5	-32.0
2	4	1	32.0	33.1	3	13	1	33.8	-35.3
2	5	1	62.6	-59.8	3	20	1	20.6	23.6
2	6	1	48.5	-50.8	4	1	1	16.4	-14.2

h	k	l	F _o	F _c	h	k	l	F _o	F _c
4	2	1	34.3	-33.4	6	6	1	16.4	-17.1
4	3	1	17.8	17.0	6	8	1	25.4	-28.2
4	4	1	29.2	-24.4	6	9	1	36.5	39.8
4	5	1	17.0	13.7	6	10	1	35.5	35.5
4	6	1	19.1	19.6	6	11	1	30.5	-27.5
4	7	1	10.7	6.5	6	12	1	27.8	29.0
4	10	1	17.9	-15.6	6	13	1	21.8	-23.9
4	11	1	16.4	19.4	6	14	1	14.0	-16.6
5	1	1	59.2	63.6	6	17	1	27.4	26.6
5	2	1	23.4	-21.0	6	18	1	27.0	27.5
5	3	1	39.1	-36.8	7	1	1	11.3	12.5
5	4	1	19.8	17.6	7	2	1	48.4	-52.0
5	5	1	16.4	-16.4	7	3	1	11.7	14.2
5	6	1	10.7	10.1	7	4	1	16.4	16.6
5	7	1	27.9	31.2	7	6	1	48.7	50.0
5	9	1	35.6	34.9	7	10	1	17.0	-21.1
5	10	1	18.7	-18.9	7	11	1	17.0	15.5
5	11	1	33.2	-36.5	7	16	1	14.0	-15.3
5	16	1	13.2	16.4	7	17	1	18.1	16.9
6	1	1	35.7	37.4	8	2	1	27.9	28.1
6	2	1	26.1	20.7	8	3	1	12.5	11.8
6	3	1	8.8	10.3	8	5	1	14.9	-12.8
6	4	1	39.5	40.5	8	11	1	13.9	18.7
6	5	1	28.9	-37.7	8	13	1	9.9	-11.3

h	k	l	F _o	F _c	h	k	l	F _o	F _c
9	1	1	32.0	35.9	13	3	1	17.7	-17.6
9	2	1	15.6	-14.4	13	5	1	9.8	-11.5
9	3	1	37.5	-41.8	13	7	1	22.2	21.4
9	4	1	22.3	-23.8	14	1	1	26.2	26.4
9	5	1	21.6	-23.0	14	3	1	11.5	15.4
9	7	1	23.8	24.9	14	4	1	24.8	27.7
9	11	1	19.2	-19.4	14	5	1	14.7	-21.6
9	12	1	16.4	-13.2	14	8	1	11.8	-16.2
9	15	1	16.4	16.4	15	1	1	11.6	10.3
10	2	1	19.6	-18.2	15	2	1	20.5	-20.1
10	4	1	31.0	31.5	4	0	1	47.0	42.1
10	5	1	15.3	-18.2	5	0	1	68.8	-64.4
10	6	1	14.0	-17.4	10	0	1	33.3	-39.1
10	8	1	19.5	-21.3	14	0	1	31.4	-34.4
10	9	1	29.2	37.2	1	2	1	98.4	-104.9
10	12	1	13.9	16.5	1	3	1	20.0	-15.7
10	13	1	22.9	-26.4	1	4	1	12.7	9.9
11	2	1	31.2	-35.5	1	5	1	13.5	-15.3
11	6	1	27.5	28.5	1	6	1	47.8	51.9
11	10	1	22.0	-22.9	1	8	1	44.2	-46.2
11	12	1	15.3	16.2	1	9	1	29.4	31.4
11	13	1	22.0	-21.2	1	10	1	40.0	-45.3
11	14	1	20.0	17.5	1	11	1	12.5	16.5
13	2	1	8.0	-11.9	1	12	1	22.3	25.7

h	k	l	F _o	F _c	h	k	l	F _o	F _c
1̄	20	1	18.5	20.7	3̄	9	1	12.5	15.7
1̄	21	1	10.0	-14.7	3̄	11	1	14.0	-17.1
2̄	1	1	139.5	148.4	3̄	13	1	17.2	13.8
2̄	2	1	80.0	72.6	3̄	15	1	19.5	22.8
2̄	3	1	58.7	52.3	3̄	16	1	20.0	20.3
2̄	4	1	50.6	47.0	4̄	2	1	14.6	-15.1
2̄	5	1	34.9	-34.4	4̄	3	1	25.7	26.9
2̄	6	1	16.0	-14.7	4̄	5	1	13.4	-14.6
2̄	7	1	43.5	-40.1	4̄	7	1	15.3	-15.8
2̄	8	1	20.6	-26.0	4̄	8	1	19.5	18.7
2̄	9	1	49.7	53.7	4̄	9	1	8.0	-8.0
2̄	10	1	45.0	50.6	4̄	10	1	22.9	-20.7
2̄	11	1	10.5	9.5	4̄	11	1	7.0	4.8
2̄	12	1	22.8	21.5	4̄	12	1	18.5	18.8
2̄	13	1	19.2	-21.3	5̄	6	1	41.2	43.2
2̄	14	1	15.3	-18.5	5̄	8	1	20.3	-20.0
2̄	18	1	19.2	22.3	5̄	10	1	33.0	-39.8
3̄	1	1	24.5	24.9	5̄	12	1	38.9	40.2
3̄	2	1	32.5	28.3	5̄	13	1	31.0	-29.2
3̄	3	1	21.9	-21.4	5̄	14	1	26.2	29.4
3̄	4	1	16.5	17.5	5̄	16	1	18.6	-23.9
3̄	5	1	27.5	-22.6	4̄	20	1	8.0	10.5
3̄	7	1	35.2	37.1	5̄	2	1	48.8	-47.4
3̄	8	1	6.0	-4.3	5̄	4	1	46.0	42.0

h	k	l	F _o	F _c	h	k	l	F _o	F _c
$\bar{6}$	1	1	28.5	30.8	$\bar{9}$	6	1	19.3	25.1
$\bar{6}$	2	1	26.8	-26.2	$\bar{9}$	8	1	15.0	-19.6
$\bar{6}$	3	1	48.2	47.0	$\bar{9}$	10	1	19.7	-23.8
$\bar{6}$	4	1	16.4	18.8	$\bar{9}$	12	1	35.5	37.3
$\bar{6}$	5	1	28.8	-27.7	$\bar{9}$	16	1	25.1	-21.6
$\bar{6}$	6	1	15.8	-14.4	$\bar{10}$	4	1	27.4	30.2
$\bar{6}$	7	1	24.1	-26.7	$\bar{10}$	5	1	22.0	-23.6
$\bar{6}$	8	1	28.0	-34.8	$\bar{10}$	7	1	15.0	-19.4
$\bar{6}$	9	1	24.5	27.7	$\bar{10}$	8	1	20.7	-24.3
$\bar{6}$	10	1	13.5	17.7	$\bar{10}$	9	1	19.7	24.3
$\bar{6}$	11	1	23.7	23.9	$\bar{11}$	7	1	13.9	14.4
$\bar{6}$	18	1	17.2	21.6	$\bar{11}$	15	1	17.2	18.1
$\bar{5}$	20	1	13.7	17.5	$\bar{12}$	3	1	19.6	23.0
$\bar{7}$	3	1	45.3	-48.9	$\bar{13}$	6	1	17.7	19.8
$\bar{7}$	4	1	28.1	-33.2	$\bar{13}$	8	1	15.8	-14.8
$\bar{7}$	7	1	17.6	20.3	$\bar{13}$	10	1	17.2	-16.9
$\bar{7}$	11	1	33.7	-36.1	$\bar{14}$	8	1	20.8	-21.4
$\bar{7}$	12	1	15.3	-19.1	2	0	2	45.9	-42.5
$\bar{8}$	1	1	15.3	16.3	4	0	2	18.6	15.4
$\bar{8}$	2	1	14.0	11.5	0	3	2	32.4	-32.8
$\bar{8}$	5	1	20.0	-19.2	0	4	2	15.5	-18.0
$\bar{8}$	11	1	19.6	24.4	0	5	2	44.2	46.4
$\bar{9}$	2	1	31.4	-36.0	0	8	2	18.6	-19.1
$\bar{9}$	4	1	18.6	22.2	0	9	2	33.7	-38.1

h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	13	2	43.7	50.6	3	1	2	16.6	12.4
0	15	2	13.2	-15.8	3	3	2	29.3	22.7
0	16	2	16.6	-17.8	3	5	2	10.3	13.4
0	17	2	27.8	-32.9	3	10	2	22.2	23.8
1	1	2	19.1	21.7	3	15	2	16.6	-16.9
1	2	2	22.8	26.1	3	18	2	8.9	11.4
1	3	2	47.6	-53.5	4	1	2	50.8	-56.2
1	4	2	8.1	-9.2	4	2	2	18.6	18.0
1	5	2	43.1	-45.8	4	3	2	25.5	-23.5
1	6	2	48.6	-53.3	4	5	2	45.8	51.5
1	7	2	32.4	32.2	4	7	2	19.4	16.2
1	8	2	13.3	11.9	4	9	2	45.5	-52.4
1	9	2	12.6	10.6	4	10	2	24.9	23.9
1	10	2	23.4	26.3	4	13	2	23.2	32.2
1	11	2	34.9	-33.0	4	17	2	22.7	-21.1
1	14	2	24.9	-30.6	5	1	2	31.5	35.9
1	16	2	18.6	18.7	5	2	2	26.8	30.5
2	1	2	18.7	18.3	5	3	2	25.5	-29.8
2	2	2	10.5	-12.1	5	5	2	15.3	-15.6
2	3	2	5.9	-5.9	5	6	2	23.2	-27.4
2	6	2	14.3	-12.8	5	7	2	30.8	35.5
2	7	2	26.0	24.6	5	8	2	26.1	26.5
2	9	2	18.6	16.0	5	12	2	13.2	-15.9
2	15	2	14.3	13.4	5	15	2	23.5	25.7

h	k	l	F _o	F _c	h	k	l	F _o	F _c
5	16	2	16.6	14.8	12	3	2	22.0	-20.7
6	4	2	27.5	27.4	12	4	2	9.9	10.1
6	12	2	24.1	22.7	12	5	2	33.1	33.3
6	18	2	5.8	4.3	12	7	2	20.4	15.7
7	2	2	22.0	23.0	12	9	2	18.6	-20.0
7	3	2	20.4	20.7	13	1	2	13.2	14.0
7	4	2	16.6	-14.0	13	2	2	26.4	24.3
7	5	2	17.6	-13.5	13	6	2	7.5	-13.0
7	6	2	22.0	-23.4	13	7	2	30.0	23.2
7	10	2	13.2	12.1	$\bar{1}$	2	2	16.0	12.8
8	1	2	26.0	-30.2	$\bar{1}$	3	2	14.3	12.9
8	3	2	39.2	-47.0	$\bar{1}$	6	2	16.6	-16.0
8	4	2	24.9	-23.1	$\bar{1}$	7	2	37.1	-35.4
8	5	2	31.1	35.9	$\bar{1}$	13	2	13.2	-17.7
8	7	2	17.6	17.5	$\bar{2}$	2	2	22.5	-19.4
8	13	2	23.4	22.9	$\bar{2}$	3	2	24.9	-20.4
9	3	2	25.5	-27.2	$\bar{2}$	4	2	20.4	17.3
9	8	2	17.6	11.4	$\bar{2}$	6	2	30.4	-33.4
9	10	2	20.4	24.3	$\bar{2}$	13	2	13.2	-9.9
9	11	2	32.7	-27.4	$\bar{3}$	1	2	63.3	73.4
9	14	2	17.6	-18.7	$\bar{3}$	2	2	75.3	75.0
11	10	2	18.6	14.7	$\bar{3}$	3	2	33.7	-30.0
11	12	2	14.3	-11.7	$\bar{3}$	4	2	16.6	-11.7
12	1	2	22.0	-23.5	$\bar{3}$	5	2	24.0	23.7

h	k	l	F _o	F _c	h	k	l	F _o	F _c
3̄	6	2	37.5	-41.8	7̄	7	2	19.3	22.7
3̄	7	2	41.9	41.9	7̄	10	2	19.6	22.0
3̄	9	2	16.6	14.0	7̄	11	2	32.0	-37.4
3̄	10	2	21.1	21.3	8̄	1	2	14.3	-18.4
3̄	11	2	22.0	-24.7	8̄	2	2	18.6	-22.9
3̄	15	2	21.4	19.6	8̄	3	2	18.6	-23.7
4̄	1	2	43.4	-40.2	8̄	5	2	17.6	23.0
4̄	2	2	32.2	28.0	8̄	9	2	22.6	-28.4
4̄	3	2	18.6	14.0	2̄	0	2	43.3	37.2
4̄	5	2	37.1	39.5	4̄	0	2	22.3	-22.2
4̄	6	2	11.7	12.2	6̄	0	2	16.6	-18.9
4̄	7	2	15.3	15.2	14̄	0	2	31.4	-28.0
4̄	9	2	37.5	45.6	14̄	1	2	22.0	22.7
4̄	11	2	17.6	15.8	2	0	3	55.5	58.5
4̄	13	2	24.9	26.6	1	7	3	18.3	21.8
5̄	1	2	11.6	-11.7	2	1	3	19.4	22.0
5̄	2	2	13.2	12.0	2	3	3	21.6	20.9
5̄	3	2	15.3	15.2	2	4	3	32.1	-26.0
5̄	6	2	15.3	-15.7	2	6	3	20.4	17.1
6̄	4	2	24.9	23.4	2	8	3	36.2	38.4
7̄	1	2	13.2	15.9	3	3	3	26.6	34.0
7̄	2	2	31.5	33.5	3	7	3	33.6	-42.0
7̄	3	2	32.0	-39.5	6	4	3	35.5	-43.0
7̄	6	2	24.1	-26.8	6	5	3	29.5	-35.6

h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	3	3	16.0	-13.5	5	1	3	23.7	-23.3
0	4	3	29.3	-24.4	5	2	3	29.0	24.6
0	5	3	18.3	16.4	5	3	2	47.4	49.1
0	8	3	22.2	18.7	5	7	3	25.5	-32.1
2	0	3	27.3	29.2	5	11	3	23.7	28.3
4	0	3	31.0	26.5	6	3	3	25.5	21.4
6	0	3	23.7	29.0	6	10	3	16.8	-16.3
1	1	3	30.2	-26.9	9	1	3	25.5	-24.8
1	3	3	33.5	23.0	9	5	3	13.7	17.6
1	5	3	18.5	16.6	10	4	3	21.6	-17.4
1	6	3	16.8	-14.5	10	5	3	16.8	-24.0
1	7	3	42.2	-44.0					
1	11	3	25.5	31.5					
1	15	3	43.2	-39.5					
2	1	3	11.6	10.4					
2	3	3	29.0	23.6					
2	4	3	31.0	-25.1					
2	5	3	36.2	-33.9					
2	9	3	19.3	20.5					
2	12	3	20.9	-23.1					
3	2	3	23.7	-18.8					
3	3	3	19.4	-16.6					
4	2	3	16.8	17.2					
4	4	3	33.5	-35.3					

OBSERVED AND CALCULATED STRUCTURE FACTORS

(m-aminobenzoic acid hydrochloride)

h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	0	0	12.6	-10.2	6	1	0	8.1	4.8
4	0	0	16.0	-13.8	9	1	0	9.4	8.7
5	0	0	13.2	8.2	10	1	0	3.0	- 2.3
6	0	0	22.9	-19.0	11	1	0	16.7	17.2
7	0	0	38.4	37.1	12	1	0	28.3	-29.6
8	0	0	20.8	-13.3	13	1	0	5.7	- 3.4
10	0	0	10.6	5.6	14	1	0	7.5	- 6.0
12	0	0	15.0	10.2	1	2	0	9.9	6.7
15	0	0	10.4	-12.5	2	2	0	32.1	-29.3
17	0	0	8.1	- 6.6	3	2	0	41.3	-37.9
0	1	0	14.2	-13.6	5	2	0	11.2	-11.2
0	2	0	42.2	-49.3	6	2	0	21.5	24.4
0	3	0	22.0	-20.2	7	2	0	10.9	-11.7
0	4	0	13.5	13.7	8	2	0	16.7	16.7
0	5	0	7.1	8.9	9	2	0	21.5	-18.4
1	1	0	10.8	7.9	10	2	0	23.8	-19.0
2	1	0	5.8	6.0	14	2	0	10.0	-10.7
3	1	0	37.0	-37.4	15	2	0	7.3	9.0
4	1	0	13.2	12.3	1	3	0	7.1	- 5.4
5	1	0	37.5	-31.4	2	3	0	11.0	- 8.8

h	k	l	F _O	F _C	h	k	l	F _O	F _C
3	3	0	30.6	25.8	7	6	0	5.9	- 6.4
4	3	0	16.6	-14.7	1	7	0	7.8	9.6
5	3	0	13.2	11.3	2	7	0	9.6	- 9.6
7	3	0	3.1	1.3	1	$\bar{1}$	0	9.9	- 6.8
9	3	0	10.7	-10.4	2	$\bar{1}$	0	9.9	- 6.5
10	3	0	13.2	12.6	3	$\bar{1}$	0	46.7	52.6
11	3	0	15.4	-15.0	4	$\bar{1}$	0	9.8	- 9.9
12	3	0	12.9	10.5	5	$\bar{1}$	0	22.3	22.3
3	4	0	14.5	12.0	6	$\bar{1}$	0	17.5	-18.8
5	4	0	21.2	20.3	7	$\bar{1}$	0	12.8	- 9.4
6	4	0	13.2	-14.0	8	$\bar{1}$	0	11.5	- 8.6
7	4	0	10.7	8.5	9	$\bar{1}$	0	15.2	12.6
12	4	0	8.1	11.3	10	$\bar{1}$	0	23.5	20.5
1	5	0	17.0	-16.7	11	$\bar{1}$	0	8.6	- 8.5
2	5	0	13.3	12.1	12	$\bar{1}$	0	18.3	17.5
3	5	0	10.8	- 9.1	13	$\bar{1}$	0	7.7	- 6.4
4	5	0	9.2	9.2	14	$\bar{1}$	0	14.7	13.5
6	5	0	7.6	5.2	1	$\bar{2}$	0	26.3	24.0
8	5	0	13.8	-12.5	2	$\bar{2}$	0	33.3	-32.5
9	5	0	12.9	11.2	3	$\bar{2}$	0	26.4	22.1
10	5	0	9.8	- 8.9	5	$\bar{2}$	0	13.2	-17.6
11	5	0	9.1	8.5	6	$\bar{2}$	0	3.5	4.0
4	6	0	9.4	8.8	7	$\bar{2}$	0	21.3	-25.6
5	6	0	12.2	-13.0	8	$\bar{2}$	0	18.3	20.0

h	k	l	F _O	F _C	h	k	l	F _O	F _C
9	$\bar{2}$	0	17.7	-22.6	10	$\bar{4}$	0	13.2	-14.0
13	$\bar{2}$	0	8.4	9.7	11	$\bar{4}$	0	15.5	17.3
14	$\bar{2}$	0	13.3	-13.8	13	$\bar{4}$	0	11.0	- 8.9
17	$\bar{2}$	0	5.4	7.6	5	$\bar{5}$	0	13.2	14.2
1	$\bar{3}$	0	9.4	- 7.5	6	$\bar{5}$	0	7.7	- 6.5
2	$\bar{3}$	0	14.0	12.6	7	$\bar{5}$	0	14.6	14.4
3	$\bar{3}$	0	17.6	-14.3	11	$\bar{5}$	0	7.1	- 8.0
4	$\bar{3}$	0	5.1	- 2.0	14	$\bar{5}$	0	11.2	15.4
5	$\bar{3}$	0	17.7	-15.9	2	$\bar{6}$	0	18.5	-22.3
6	$\bar{3}$	0	16.3	15.0	3	$\bar{6}$	0	13.4	14.2
7	$\bar{3}$	0	13.0	-13.4	8	$\bar{6}$	0	6.4	7.4
10	$\bar{3}$	0	8.9	-11.9	9	$\bar{6}$	0	8.1	-11.4
12	$\bar{3}$	0	8.4	-10.5	10	$\bar{6}$	0	9.1	11.5
13	$\bar{3}$	0	10.9	11.5	11	$\bar{6}$	0	6.6	- 8.8
14	$\bar{3}$	0	8.9	-11.5	4	$\bar{7}$	0	2.3	- 0.4
17	$\bar{3}$	0	6.1	- 7.3	6	$\bar{7}$	0	5.8	6.6
1	$\bar{4}$	0	16.3	-15.5	7	$\bar{7}$	0	7.3	- 8.1
2	$\bar{4}$	0	21.4	21.8	8	$\bar{7}$	0	6.3	7.8
3	$\bar{4}$	0	16.6	-15.1	5	0	1	42.7	-40.9
4	$\bar{4}$	0	17.6	18.9	6	0	1	9.8	8.9
5	$\bar{4}$	0	10.2	8.9	7	0	1	13.2	9.9
6	$\bar{4}$	0	10.3	- 7.6	8	0	1	22.9	18.1
8	$\bar{4}$	0	15.2	-16.4	9	0	1	6.9	4.5
9	$\bar{4}$	0	7.6	9.0	11	0	1	16.3	13.0

h	k	l	F _o	F _c	h	k	l	F _o	F _c
13	0	1	11.3	11.3	11	2	1	23.8	-21.7
14	0	1	9.8	-10.6	12	2	1	8.2	9.3
15	0	1	12.5	10.5	13	2	1	9.1	-10.3
3	1	1	16.4	16.2	14	2	1	8.7	6.9
4	1	1	9.1	-7.5	0	3	1	7.1	5.7
5	1	1	22.4	18.9	1	3	1	35.7	-41.3
6	1	1	18.3	15.6	2	3	1	9.4	11.2
7	1	1	10.2	-7.6	4	3	1	8.9	8.2
8	1	1	35.0	30.0	5	3	1	8.5	7.9
9	1	1	19.3	-18.0	6	3	1	9.8	-9.7
10	1	1	17.9	16.8	8	3	1	30.2	-32.4
14	1	1	9.8	-8.4	14	3	1	10.2	8.4
16	1	1	12.2	-11.7	15	3	1	9.6	-8.3
17	1	1	10.4	10.7	0	4	1	3.3	4.0
0	2	1	6.9	-4.1	2	4	1	8.9	9.6
1	2	1	4.9	-7.0	3	4	1	10.9	-11.3
2	2	1	13.3	-15.8	4	4	1	13.2	12.2
3	2	1	7.5	6.4	5	4	1	7.5	-8.6
4	2	1	15.0	-19.1	11	4	1	13.6	10.5
5	2	1	16.3	18.9	13	4	1	14.9	11.6
6	2	1	6.1	-6.1	0	5	1	9.9	-9.9
7	2	1	6.4	6.3	1	5	1	11.2	15.6
8	2	1	9.7	8.0	5	5	1	11.1	-10.1
10	2	1	15.7	-10.9	6	5	1	13.9	14.2

h	k	l	F _o	F _c	h	k	l	F _o	F _c
7	5	1	10.0	- 8.8	2	$\bar{2}$	1	23.9	-23.9
8	5	1	10.7	9.8	3	$\bar{2}$	1	8.1	6.2
10	5	1	9.1	6.6	4	$\bar{2}$	1	14.6	-13.6
0	6	1	4.2	- 2.6	5	$\bar{2}$	1	11.0	11.5
1	6	1	7.4	8.1	6	$\bar{2}$	1	30.7	-27.3
2	6	1	7.4	- 7.7	7	$\bar{2}$	1	6.1	6.1
3	6	1	7.1	10.1	8	$\bar{2}$	1	12.7	-13.5
4	6	1	6.5	- 4.4	9	$\bar{2}$	1	6.5	- 5.4
7	6	1	3.5	1.5	13	$\bar{2}$	1	12.9	-11.7
0	7	1	6.9	8.4	15	$\bar{2}$	1	13.3	-13.9
1	7	1	6.3	- 6.3	0	$\bar{3}$	1	5.7	3.6
5	$\bar{1}$	1	23.7	-19.5	1	$\bar{3}$	1	14.9	13.7
6	$\bar{1}$	1	5.6	3.0	3	$\bar{3}$	1	34.6	34.9
8	$\bar{1}$	1	30.4	-26.8	4	$\bar{3}$	1	22.0	-19.7
9	$\bar{1}$	1	21.6	19.2	6	$\bar{3}$	1	11.8	- 9.4
10	$\bar{1}$	1	13.6	-13.0	7	$\bar{3}$	1	8.8	- 7.9
11	$\bar{1}$	1	14.9	14.4	8	$\bar{3}$	1	7.1	6.6
12	$\bar{1}$	1	12.3	-12.4	10	$\bar{3}$	1	23.3	23.9
14	$\bar{1}$	1	9.7	8.9	11	$\bar{3}$	1	19.3	-21.0
16	$\bar{1}$	1	9.9	10.4	16	$\bar{3}$	1	7.4	- 9.3
17	$\bar{1}$	1	7.3	- 8.8	0	$\bar{4}$	1	17.9	-14.7
18	$\bar{1}$	1	6.8	8.4	1	$\bar{4}$	1	10.0	9.2
0	$\bar{2}$	1	26.5	26.4	4	$\bar{4}$	1	14.5	14.8
1	$\bar{2}$	1	9.6	-10.1	6	$\bar{4}$	1	16.3	18.1

h	k	l	F _o	F _c	h	k	l	F _o	F _c
7	$\bar{4}$	1	12.8	-13.6	$\bar{11}$	0	1	11.9	-14.0
8	$\bar{4}$	1	7.6	10.2	$\bar{12}$	0	1	17.3	13.3
9	$\bar{4}$	1	7.6	- 7.8	$\bar{14}$	0	1	19.3	-16.8
10	$\bar{4}$	1	7.6	- 6.2	$\bar{16}$	0	1	10.8	-12.7
11	$\bar{4}$	1	9.8	10.2	$\bar{2}$	1	1	76.2	83.2
12	$\bar{4}$	1	8.6	7.1	$\bar{3}$	1	1	15.4	17.0
13	$\bar{4}$	1	8.9	12.5	$\bar{4}$	1	1	11.0	13.0
14	$\bar{4}$	1	7.5	- 8.4	$\bar{5}$	1	1	15.4	-13.1
0	$\bar{5}$	1	19.3	-15.7	$\bar{6}$	1	1	13.1	13.1
2	$\bar{5}$	1	16.3	14.0	$\bar{7}$	1	1	21.9	-22.0
3	$\bar{5}$	1	13.9	-11.0	$\bar{8}$	1	1	10.2	11.2
4	$\bar{5}$	1	16.3	16.4	$\bar{9}$	1	1	6.8	3.8
5	$\bar{5}$	1	10.8	- 7.8	$\bar{11}$	1	1	10.2	11.5
6	$\bar{5}$	1	7.1	5.0	$\bar{2}$	2	1	6.9	8.8
7	$\bar{5}$	1	5.3	- 4.2	$\bar{3}$	2	1	20.4	-23.0
10	$\bar{5}$	1	10.0	-11.8	$\bar{4}$	2	1	37.7	45.1
11	$\bar{5}$	1	10.9	12.0	$\bar{6}$	2	1	14.3	17.2
12	$\bar{5}$	1	11.5	-11.6	$\bar{8}$	2	1	7.5	-10.0
$\bar{4}$	0	1	32.5	-32.9	$\bar{10}$	2	1	16.3	-20.0
$\bar{6}$	0	1	12.8	-10.4	$\bar{11}$	2	1	20.8	23.5
$\bar{7}$	0	1	13.9	-21.0	$\bar{16}$	2	1	10.9	13.3
$\bar{8}$	0	1	8.6	8.2	$\bar{1}$	3	1	19.2	-24.1
$\bar{9}$	0	1	13.3	-15.8	$\bar{4}$	3	1	12.4	-13.6
$\bar{10}$	0	1	17.9	13.0	$\bar{5}$	3	1	14.7	19.2

h	k	l	F _o	F _c	h	k	l	F _o	F _c
$\bar{6}$	3	1	8.8	-11.1	$\bar{9}$	$\bar{1}$	1	7.9	6.2
$\bar{7}$	3	1	9.3	10.1	$\bar{10}$	$\bar{1}$	1	10.2	10.7
$\bar{8}$	3	1	15.2	-16.2	$\bar{11}$	$\bar{1}$	1	16.2	-16.4
$\bar{1}$	4	1	3.9	- 3.9	$\bar{12}$	$\bar{1}$	1	8.7	- 6.5
$\bar{2}$	4	1	16.8	-19.3	$\bar{13}$	$\bar{1}$	1	14.7	-11.9
$\bar{3}$	4	1	7.7	7.2	$\bar{14}$	$\bar{1}$	1	13.7	11.2
$\bar{4}$	4	1	8.1	-11.0	$\bar{1}$	$\bar{2}$	1	27.7	-26.7
$\bar{5}$	4	1	7.9	9.4	$\bar{2}$	$\bar{2}$	1	10.8	8.3
$\bar{6}$	4	1	17.4	-18.6	$\bar{3}$	$\bar{2}$	1	42.8	-39.0
$\bar{1}$	5	1	14.9	16.9	$\bar{4}$	$\bar{2}$	1	24.7	21.4
$\bar{2}$	5	1	7.5	- 9.8	$\bar{5}$	$\bar{2}$	1	9.8	6.3
$\bar{5}$	5	1	9.8	9.4	$\bar{6}$	$\bar{2}$	1	8.9	- 6.9
$\bar{6}$	5	1	12.6	15.7	$\bar{7}$	$\bar{2}$	1	17.1	14.2
$\bar{4}$	6	1	7.5	9.4	$\bar{8}$	$\bar{2}$	1	13.9	-13.4
$\bar{5}$	6	1	9.6	-10.3	$\bar{9}$	$\bar{2}$	1	21.5	17.7
$\bar{1}$	7	1	11.0	- 8.0	$\bar{10}$	$\bar{2}$	1	17.9	-14.1
$\bar{2}$	7	1	13.0	10.4	$\bar{11}$	$\bar{2}$	1	13.8	11.9
$\bar{3}$	7	1	7.8	-11.7	$\bar{13}$	$\bar{2}$	1	11.2	- 8.8
$\bar{2}$	$\bar{1}$	1	31.5	-23.8	$\bar{14}$	$\bar{2}$	1	10.2	8.5
$\bar{3}$	$\bar{1}$	1	5.4	4.1	$\bar{2}$	$\bar{3}$	1	13.8	11.9
$\bar{4}$	$\bar{1}$	1	41.0	-39.4	$\bar{3}$	$\bar{3}$	1	11.5	- 7.8
$\bar{5}$	$\bar{1}$	1	20.3	-15.4	$\bar{4}$	$\bar{3}$	1	16.3	14.2
$\bar{6}$	$\bar{1}$	1	30.4	-25.0	$\bar{6}$	$\bar{3}$	1	26.3	21.6
$\bar{7}$	$\bar{1}$	1	17.3	14.6	$\bar{11}$	$\bar{3}$	1	10.2	10.7

h	k	l	F _o	F _c	h	k	l	F _o	F _c
12	3	1	9.7	-9.5	3	1	2	7.3	-6.2
13	3	1	10.8	8.9	4	1	2	15.3	-16.3
15	3	1	11.4	9.5	5	1	2	29.0	33.0
1	4	1	25.9	30.5	7	1	2	17.8	16.4
2	4	1	15.3	-15.0	9	1	2	8.4	8.4
6	4	1	10.5	9.1	14	1	2	14.4	12.5
16	2	1	11.0	11.4	1	2	2	10.7	-12.8
7	4	1	10.5	-8.7	2	2	2	13.8	18.5
8	4	1	18.9	20.0	4	2	2	14.4	19.7
9	4	1	15.1	-13.8	6	2	2	11.8	12.6
14	4	1	7.5	-9.3	9	2	2	16.3	17.9
1	5	1	13.5	-11.4	10	2	2	11.6	-13.5
3	5	1	13.7	11.8	0	3	2	9.1	-13.3
4	5	1	10.5	-10.4	1	3	2	7.1	4.7
5	5	1	11.8	11.3	5	3	2	12.7	-13.4
11	5	1	7.5	-8.6	6	3	2	14.0	18.8
1	6	1	14.3	-13.4	7	3	2	11.1	-7.8
4	0	2	14.0	-11.7	9	3	2	11.6	-11.9
5	0	2	5.8	7.7	10	3	2	6.3	-2.8
6	0	2	24.3	-19.8	14	3	2	8.8	-6.7
8	0	2	14.0	10.5	0	4	2	8.7	-10.2
9	0	2	8.3	-9.4	1	4	2	10.5	16.4
11	0	2	16.3	-17.7	2	4	2	13.3	-9.2
12	0	2	15.0	14.8	4	4	2	8.8	-8.9

h	k	l	F_o	F_c	h	k	l	F_o	F_c
7	4	2	14.0	- 9.3	12	$\bar{2}$	2	9.3	-13.7
8	4	2	8.7	11.9	0	$\bar{3}$	2	30.8	30.0
9	4	2	10.8	-12.6	1	$\bar{3}$	2	14.2	-10.2
10	4	2	12.2	9.7	2	$\bar{3}$	2	22.8	22.9
11	4	2	8.3	- 6.8	4	$\bar{3}$	2	7.5	6.0
5	5	2	11.1	7.5	6	$\bar{3}$	2	15.4	-11.8
4	$\bar{1}$	2	5.8	- 4.8	7	$\bar{3}$	2	18.0	14.5
5	$\bar{1}$	2	24.7	-21.4	8	$\bar{3}$	2	29.9	-22.7
6	$\bar{1}$	2	16.4	15.3	9	$\bar{3}$	2	26.4	21.4
7	$\bar{1}$	2	26.9	-23.3	10	$\bar{3}$	2	16.8	11.1
8	$\bar{1}$	2	16.4	14.4	11	$\bar{3}$	2	9.4	8.0
9	$\bar{1}$	2	12.7	- 9.3	16	$\bar{3}$	2	7.5	9.1
12	$\bar{1}$	2	14.8	-11.9	3	$\bar{4}$	2	14.8	13.8
14	$\bar{1}$	2	13.1	-12.1	4	$\bar{4}$	2	14.4	-14.2
0	$\bar{2}$	2	18.9	16.3	5	$\bar{4}$	2	9.3	7.1
1	$\bar{2}$	2	16.0	12.3	6	$\bar{4}$	2	11.6	- 9.5
3	$\bar{2}$	2	24.6	-22.0	12	$\bar{4}$	2	14.5	15.1
4	$\bar{2}$	2	15.0	11.5	14	$\bar{4}$	2	9.7	9.0
5	$\bar{2}$	2	16.3	-17.4	8	$\bar{5}$	2	12.2	9.4
6	$\bar{2}$	2	13.2	9.8	10	$\bar{5}$	2	10.0	6.8
7	$\bar{2}$	2	15.2	10.2	$\bar{3}$	0	2	10.1	-14.0
8	$\bar{2}$	2	15.1	12.2	$\bar{5}$	0	2	16.2	-19.6
10	$\bar{2}$	2	12.3	-12.2	$\bar{7}$	0	2	26.9	-22.7
11	$\bar{2}$	2	14.8	15.0	$\bar{11}$	0	2	12.7	16.0

h	k	l	F _c	F _c	h	k	l	F _c	F _c
$\overline{14}$	0	2	14.9	-18.6	$\overline{1}$	$\overline{2}$	2	14.2	11.7
$\overline{2}$	1	2	37.1	41.9	$\overline{2}$	$\overline{2}$	2	14.5	12.2
$\overline{3}$	1	2	19.4	-24.7	$\overline{4}$	$\overline{2}$	2	10.7	- 8.3
$\overline{5}$	1	2	12.5	12.6	$\overline{5}$	$\overline{2}$	2	17.2	16.5
$\overline{7}$	1	2	8.6	11.4	$\overline{6}$	$\overline{2}$	2	11.6	-11.3
$\overline{8}$	1	2	18.1	-22.3	$\overline{7}$	$\overline{2}$	2	9.9	8.1
$\overline{10}$	1	2	18.0	20.2	$\overline{8}$	$\overline{2}$	2	10.3	10.0
$\overline{14}$	1	2	13.8	16.3	$\overline{12}$	$\overline{2}$	2	14.3	14.7
$\overline{3}$	2	2	20.9	25.0	$\overline{1}$	$\overline{3}$	2	16.2	-15.6
$\overline{4}$	2	2	21.5	24.8	$\overline{2}$	$\overline{3}$	2	11.6	9.6
$\overline{5}$	2	2	22.0	26.3	$\overline{3}$	$\overline{3}$	2	11.8	12.8
$\overline{6}$	2	2	10.1	-11.4	$\overline{7}$	$\overline{3}$	2	14.8	13.3
$\overline{1}$	3	2	13.1	10.2	$\overline{8}$	$\overline{3}$	2	13.1	-11.4
$\overline{2}$	3	2	13.1	-17.4	$\overline{3}$	$\overline{4}$	2	24.4	-29.6
$\overline{3}$	3	2	14.2	18.4	$\overline{6}$	$\overline{6}$	1	7.9	- 7.5
$\overline{4}$	3	2	11.7	14.6	$\overline{7}$	$\overline{6}$	1	6.8	8.8
$\overline{6}$	3	2	16.6	16.2	$\overline{8}$	$\overline{6}$	1	8.1	-11.3
$\overline{8}$	3	2	12.5	17.2	2	0	3	8.2	9.7
$\overline{2}$	$\overline{1}$	2	12.0	- 9.2	3	0	3	17.6	-18.2
$\overline{3}$	$\overline{1}$	2	8.6	9.4	4	0	3	7.5	7.9
$\overline{4}$	$\overline{1}$	2	11.8	- 8.5	6	0	3	9.3	- 8.2
$\overline{5}$	$\overline{1}$	2	24.0	-23.8	7	0	3	10.2	11.3
$\overline{6}$	$\overline{1}$	2	21.7	23.8	8	0	3	23.7	-19.1
$\overline{8}$	$\overline{1}$	2	11.6	14.1	9	0	3	10.1	10.0

h	k	l	F _o	F _c	h	k	l	F _o	F _c
10	0	3	21.6	-15.8	13	2	3	9.8	8.3
11	0	3	4.1	- 1.1	1	3	3	11.2	12.8
14	0	3	12.4	8.5	3	3	3	10.1	12.8
0	1	3	7.1	- 9.4	7	3	3	12.5	8.5
1	1	3	7.3	- 8.3	9	3	3	8.6	- 7.8
2	1	3	10.4	12.1	10	3	3	8.3	7.5
3	1	3	12.4	-13.7	11	3	3	10.3	- 7.6
5	1	3	10.2	-11.1	0	4	3	6.9	11.0
6	1	3	9.9	11.1	2	4	3	6.9	9.6
7	1	3	7.3	- 6.3	5	4	3	12.5	9.8
8	1	3	6.1	- 5.3	6	4	3	21.1	-19.0
11	1	3	14.9	11.5	8	4	3	7.9	- 7.8
12	1	3	10.6	- 8.6	4	5	3	3.5	0.5
13	1	3	10.6	8.5	2	$\bar{1}$	3	13.5	- 9.8
0	2	3	13.7	-16.1	3	$\bar{1}$	3	10.7	9.4
2	2	3	11.0	-15.6	4	$\bar{1}$	3	12.9	-10.8
4	2	3	5.9	6.0	5	$\bar{1}$	3	33.1	36.1
3	2	3	12.7	17.8	6	$\bar{1}$	3	3.1	1.4
5	2	3	5.9	- 5.8	8	$\bar{1}$	3	7.4	- 6.6
6	2	3	11.2	12.2	11	$\bar{1}$	3	12.2	-10.7
7	2	3	10.2	-10.7	13	$\bar{1}$	3	15.2	-10.9
8	2	3	15.2	14.8	0	$\bar{2}$	3	5.9	- 4.2
9	2	3	8.7	- 8.6	1	$\bar{2}$	3	25.1	19.9
10	2	3	6.5	6.7	2	$\bar{2}$	3	14.2	-12.5

h	k	l	F _o	F _c	h	k	l	F _o	F _c
3	$\bar{2}$	3	14.2	11.9	9	$\bar{4}$	3	8.0	7.4
4	$\bar{2}$	3	14.5	-11.7	10	$\bar{4}$	3	13.6	-12.6
5	$\bar{2}$	3	6.3	4.5	11	$\bar{4}$	3	13.0	11.7
6	$\bar{2}$	3	8.9	- 5.4	12	$\bar{4}$	3	4.7	- 5.7
7	$\bar{2}$	3	3.2	1.6	$\bar{2}$	0	3	10.2	- 8.1
8	$\bar{2}$	3	38.9	32.8	$\bar{5}$	0	3	18.4	16.4
10	$\bar{2}$	3	12.1	10.5	$\bar{6}$	0	3	18.3	-19.3
11	$\bar{2}$	3	11.7	- 8.9	$\bar{9}$	0	3	11.7	7.9
0	$\bar{3}$	3	6.5	- 7.3	$\bar{2}$	1	3	15.2	-17.5
1	$\bar{3}$	3	12.1	8.4	$\bar{3}$	1	3	8.1	-11.0
3	$\bar{3}$	3	13.8	-12.5	$\bar{4}$	1	3	11.4	-14.8
4	$\bar{3}$	3	10.6	9.7	$\bar{5}$	1	3	9.9	11.6
5	$\bar{3}$	3	18.3	-16.6	$\bar{6}$	1	3	10.3	-11.8
6	$\bar{3}$	3	11.1	8.9	$\bar{9}$	1	3	18.0	-21.3
7	$\bar{3}$	3	6.4	- 6.5	$\bar{16}$	1	3	10.1	-13.2
10	$\bar{3}$	3	4.1	3.9	$\bar{1}$	2	3	7.1	7.2
11	$\bar{3}$	3	13.8	9.9	$\bar{2}$	2	3	7.5	- 8.4
13	$\bar{3}$	3	9.8	10.1	$\bar{3}$	2	3	12.2	11.7
14	$\bar{3}$	3	7.1	- 7.8	$\bar{4}$	2	3	12.7	14.4
2	$\bar{4}$	3	17.6	14.2	$\bar{5}$	2	3	15.6	-18.0
3	$\bar{4}$	3	8.7	- 6.8	$\bar{3}$	3	3	11.0	-13.4
4	$\bar{4}$	3	10.2	7.2	$\bar{5}$	3	3	25.3	21.3
5	$\bar{4}$	3	17.3	-17.9	$\bar{6}$	3	3	17.6	25.4
8	$\bar{4}$	3	13.2	-10.9	$\bar{12}$	3	3	14.5	- 9.8

h	k	l	F _o	F _c	h	k	l	F _o	F _c
$\bar{1}$	4	3	9.4	-12.7	$\bar{1}$	$\bar{2}$	3	12.1	10.9
$\bar{2}$	4	3	6.8	9.0	$\bar{2}$	$\bar{2}$	3	16.2	12.0
$\bar{6}$	4	3	7.1	-11.8	$\bar{3}$	$\bar{2}$	3	11.1	-8.3
$\bar{2}$	$\bar{1}$	3	26.6	27.2	$\bar{4}$	$\bar{2}$	3	16.0	14.2
$\bar{3}$	$\bar{1}$	3	14.8	10.5	$\bar{6}$	$\bar{2}$	3	9.8	8.5
$\bar{4}$	$\bar{1}$	3	21.2	19.8	$\bar{7}$	$\bar{2}$	3	15.2	-13.8
$\bar{6}$	$\bar{1}$	3	9.1	8.7	$\bar{14}$	$\bar{2}$	3	7.1	10.4
$\bar{7}$	$\bar{1}$	3	9.2	6.4	$\bar{1}$	$\bar{3}$	3	14.9	13.9
$\bar{8}$	$\bar{1}$	3	11.6	12.8	$\bar{3}$	$\bar{3}$	3	18.1	16.8
$\bar{9}$	$\bar{1}$	3	15.2	15.2	$\bar{4}$	$\bar{3}$	3	23.2	-26.4
$\bar{11}$	$\bar{1}$	3	11.17	14.50	$\bar{5}$	$\bar{3}$	3	15.0	-11.6