

CHAPTER 2

CRYSTAL AND MOLECULAR STRUCTURE OF N-p-METHOXY BENZYLIDENE p-PHENYL AZOANILINE (MBPAA)

2.1 Introduction

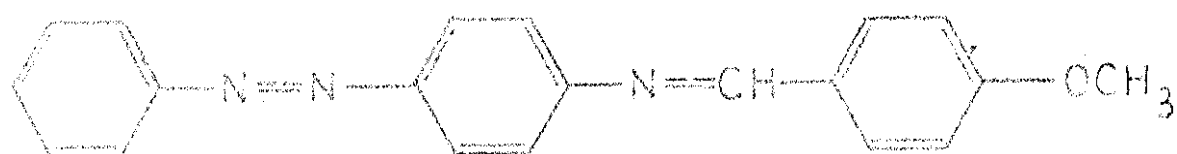
The first compound to be studied in this series of X-ray investigations on liquid crystalline materials was n-p-methoxy benzylidene p-phenyl azoaniline, i.e., MBPAA, $C_{20}H_{17}ON_3$ (I). The compound is also known as anisal-p-amino azobenzene and is the first member of the homologous series of compounds 4-n-alkoxy benzylidene-4'-phenyl azoaniline, $C_nH_{2n+1} \cdot O \cdot C_6H_4 \cdot CH=N \cdot C_6H_4 \cdot N=N \cdot C_6H_5$. While the higher homologues in this series exhibit a smectic A phase [1], MBPAA is nematogenic and exhibits the following phase transitions:



Some of the physical properties of MBPAA in its liquid crystalline and isotropic phases have been investigated [2-8]. However, no X-ray studies are reported in the literature.

2.2 Experimental

Orange coloured needles of MBPAA were obtained



(I)

by slow evaporation of a solution in toluene. Oscillation and Weissenberg photographs were recorded with crystals mounted along and perpendicular to the needle axis. The diffraction pattern showed the crystals to be monoclinic. The space group was determined to be $P2_1/c$ based on the systematic extinctions of the type $h0l, l$ odd and $0k0, k$ odd.

The unit cell dimensions a , b^* and c^* were measured from rotation and Weissenberg photographs. The axial dimensions of the unit cell were refined by minimising the quantity $|(\sin^2 \theta)_{\text{measured}} - (\sin^2 \theta)_{\text{calculated}}|$ [10], using 22 high angle projection reflections. A comparison of the values of $(\sin^2 \theta)_{\text{measured}}$ and $(\sin^2 \theta)_{\text{calculated}}$ at the end of the refinement procedure is given in Table 2.1. The monoclinic angle β was determined by the method of angular lag [9] using ten high angle reflections and the refined values of the cell parameters a and b . As it was not possible to cut the crystal to record the $h0l$ Weissenberg photograph, the monoclinic angle β could not be refined by the least-squares methods. However, the value of β as obtained above was found to have quite low standard deviation.

The density of the crystal, measured by flotation in aqueous potassium iodide solution, showed that the unit cell contained eight molecules of MBPAA. The

TABLE 2.1

A comparison of the measured and the calculated values of $\sin^2\theta$ for the reflections used in the least-squares refinement of the unit cell parameters

h	k	l	$\sin^2\theta_{\text{measured}}$	$\sin^2\theta_{\text{calculated}}$
2	13	0	0.2088	0.2088
4	4	0	0.1329	0.1337
3	9	0	0.1519	0.1517
5	3	0	0.1925	0.1919
2	10	0	0.1350	0.1354
2	9	0	0.1144	0.1152
1	10	0	0.1129	0.1136
4	2	0	0.1209	0.1210
3	6	0	0.1041	0.1039
0	9	5	0.1576	0.1572
0	10	4	0.1525	0.1518
0	8	5	0.1398	0.1391
0	4	7	0.1570	0.1563
0	6	6	0.1414	0.1406
0	5	6	0.1297	0.1289
0	8	4	0.1134	0.1135
0	9	1	0.0889	0.0889
0	1	6	0.1032	0.1034
0	2	8	0.1846	0.1862
0	1	8	0.1828	0.1831
0	5	3	0.0524	0.0522
0	4	5	0.0885	0.0881

preliminary crystal data are listed in Table 2.2.

Intensity data

Three-dimensional intensity data were collected from the reciprocal levels Hkl , $H = 0$ to 5, using a nearly cylindrical crystal of mean radius = 0.024 cm ($\mu_r = 0.15$) mounted along the needle axis (a -axis). Multifilm equi-inclination Weissenberg technique was used with nickel filtered copper radiation ($\lambda = 1.5418 \text{ \AA}$). Intensity data from the hko reciprocal level were also recorded using a crystal of mean radius = 0.042 cm ($\mu_r = 0.26$). Though the crystals used for data collection were optically clear, the diffraction patterns were generally weak and faded off rapidly with increasing Bragg angle, leading to the conspicuous absence of high angle data. In spite of very long exposures (of the order of 200-300 hours, using a rotating anode generator run at an average rating of 55 mA and 55 KV), only 1071 independent observable reflections could be recorded out of a total of 7717 possible reflections in the $CuK\alpha$ sphere. The highest θ value recorded was only $57^\circ 45'$.

The intensities were estimated visually by comparison with a standard calibrated strip prepared from the crystal used for data collection. The intensities

TABLE 2.2

Crystal Data for MBPAA

Unit cell dimensions	$a = 9.77 \pm 0.01 \text{ \AA}$ $b = 23.65 \pm 0.02 \text{ \AA}$ $c = 15.64 \pm 0.01 \text{ \AA}$ $\beta = 112.4 \pm 0.3^\circ$
Space group	$P2_1/c$
Volume of the unit cell	$U = 3340.22 \text{ \AA}^3$
Molecular weight	$= 315.38$
Number of molecules per unit cell	$Z = 8$
Calculated density	$\rho_c = 1.25 \text{ gm. cm}^{-3}$
Measured density	$\rho_m = 1.26 \text{ gm. cm}^{-3}$
Linear absorption coefficient for CuK α radiation	$= 6.356 \text{ cm}^{-1}$
Total number of electrons per unit cell	$F(000) = 1328$

of most of the **reflections** were measured twice **and** averaged. The intensities were corrected for L_p [11] and spot shape [12] **effects**. Palm's [13] absorption correction for **cylindrical** specimens was **applied**. The intensity data from the reciprocal **levels** Hkl , $H = 0$ to 5, were scaled using **the** common reflections from the hko level. **The** three-dimensional intensity data were scaled to an absolute **value** using **Wilson's statistics** [14].

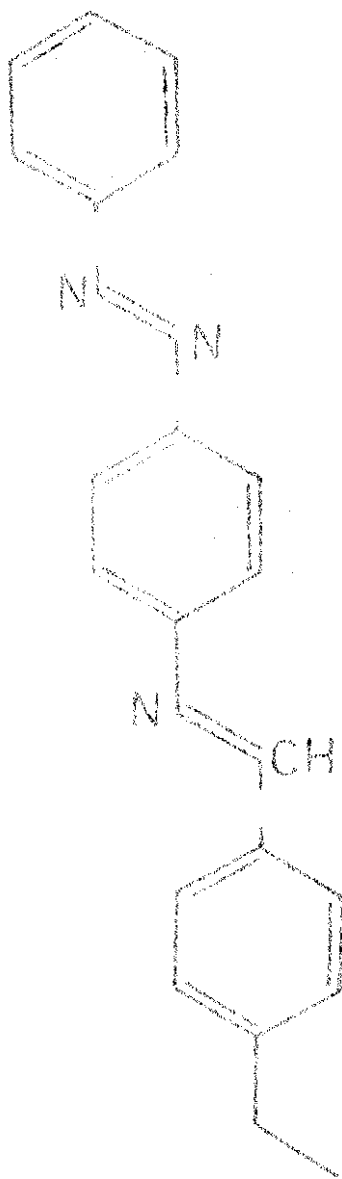
2.3 Structure determination

With eight molecules in the unit cell of space group $P2_1/c$, there were two **independent** molecules in the **asymmetric part** of the cell. In addition to the hydrogen atoms, **each** molecule had 24 light **atoms** and hence the problem was one of 48 **nearly** equal, non-hydrogen atoms in the **asymmetric** unit. With the **advancement** of the well-known 'direct methods' this might not be considered formidable under normal **circumstances**. However, when a great deal of high **angle data** were **not** available, **the** **successful** application of **the direct** methods did not appear to be very certain. Hence, the **structure** analysis was started with the combination of trial and error and Patterson techniques.

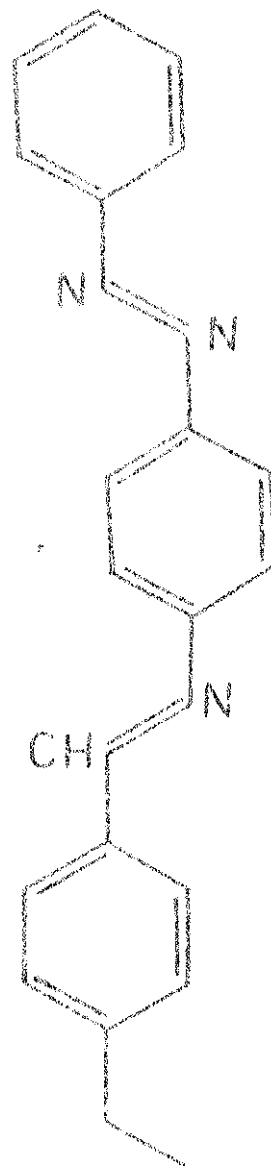
The structural **formula** of MBPAA **has** been presented **earlier** in this chapter. As could be seen in (I), the

molecule is geometrically anisotropic and the terminal methyl group has freedom of rotation, In addition, the relative orientation of the two benzene rings could correspond to either of the two configurations shown in Fig. 21 In the initial stages of the structure analysis the configuration in Fig. 21 (b) was ignored and the rod-Like molecule was treated as nearly rigid and in the configuration shown in Fig. 2.1(a).

The three-dimensional Patterson map was computed with 999 coefficients. The vector density distribution in this map was highly directional. There were continuous bands of vector density which were inclined to the cell axes in the bc-plane, In each section perpendicular to the a-axis, the adjacent parallel bands were clearly separated and were $b/2$ apart along the b-direction and $c/2$ along the c-direction. The sections of the Patterson map presented in Fig. 2.2 are examples of the vector distribution. The orientation of the vector density with respect to the b- and c-axes suggested that the molecules were more likely to have a similar, inclined orientation in the cell and not lie parallel to any cell edge. As could be seen from Fig. 2.2(b) and 2.2(e), the vector distribution had clear breaks along the a-direction near $x = 24/120$ and $x = 96/120$, or approximately near $x = \frac{1}{4}$ and $x = \frac{3}{4}$. This feature suggested that along the a-direction the crystallographi-



(a)



(b)

Figure 2.1: The two possible configurations of the MBPAA molecule.

(a)

$\chi = 0$

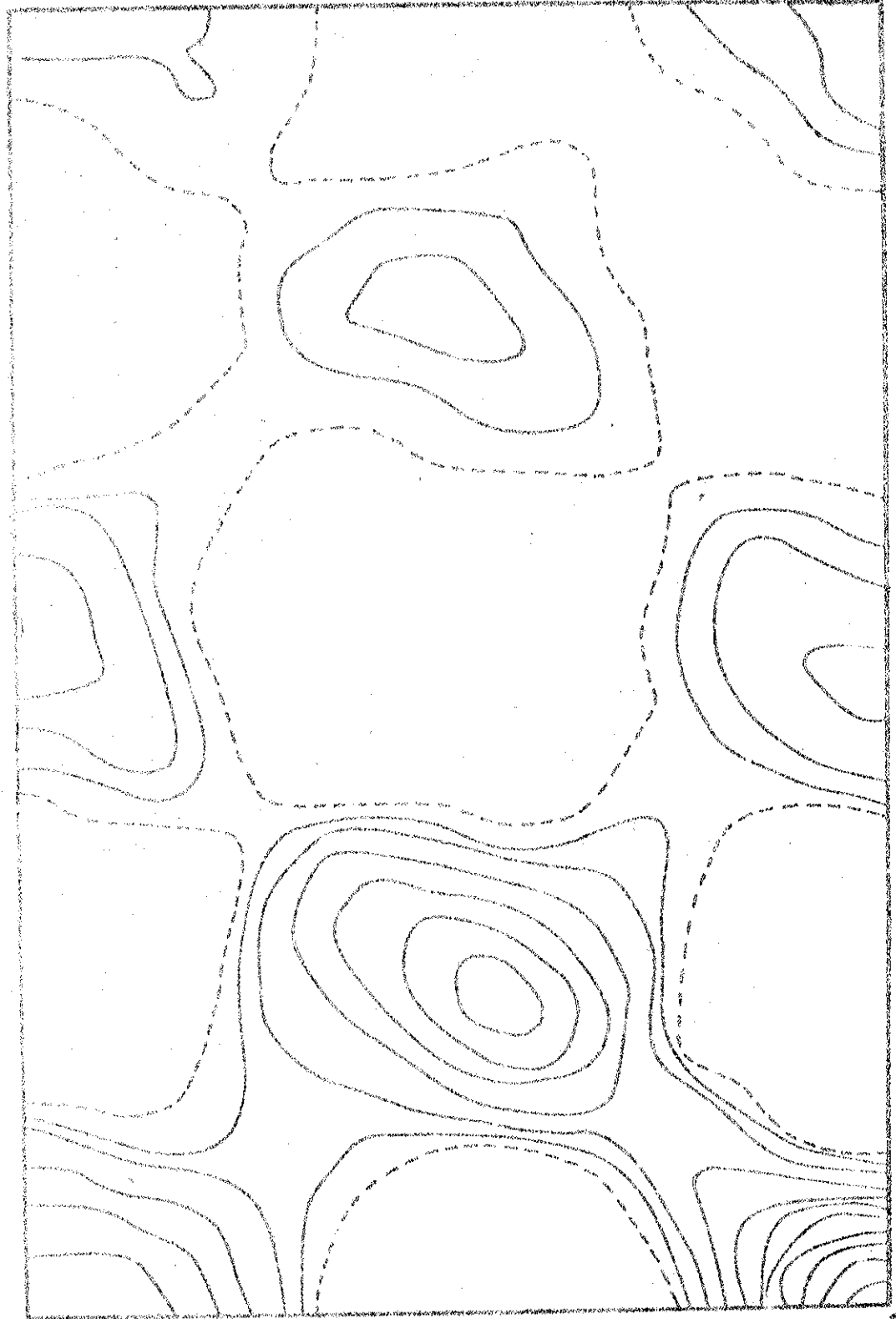
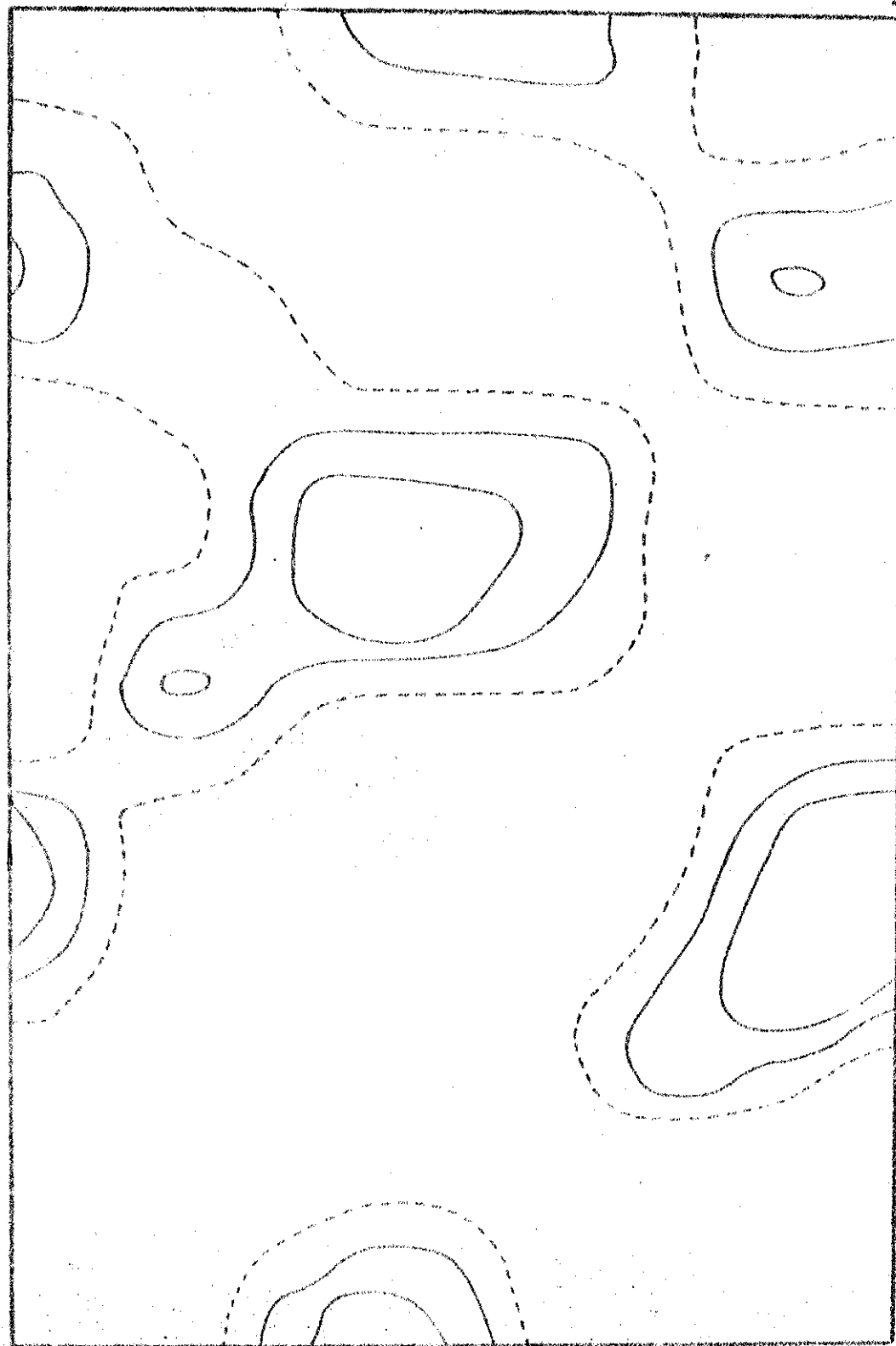


Figure 2.2: Three-dimensional Patterson map of MBPAA

$x = 24/120$

c/2



0

b/2

Figure 2.2(b)

$\lambda = 48/120$

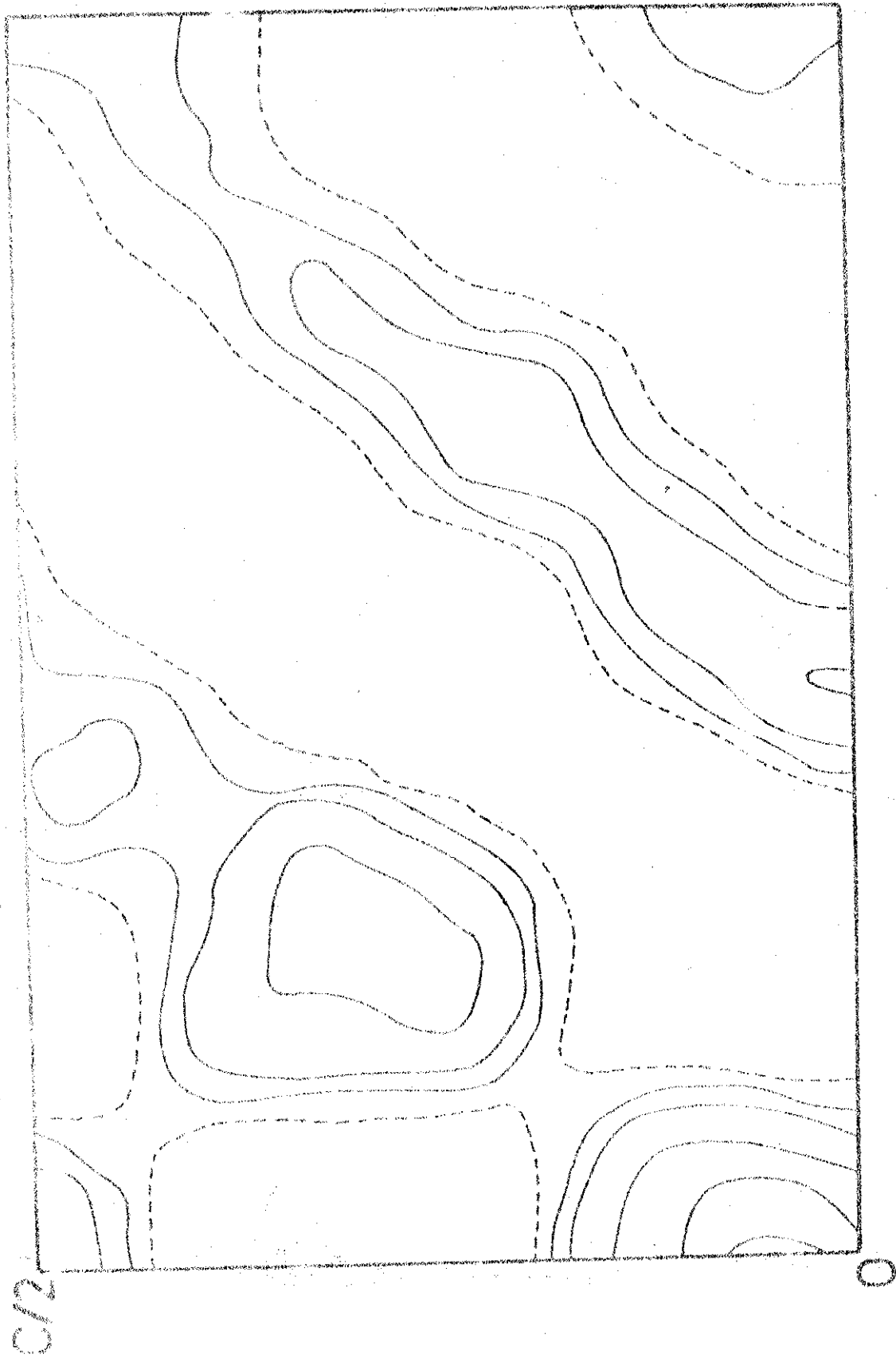
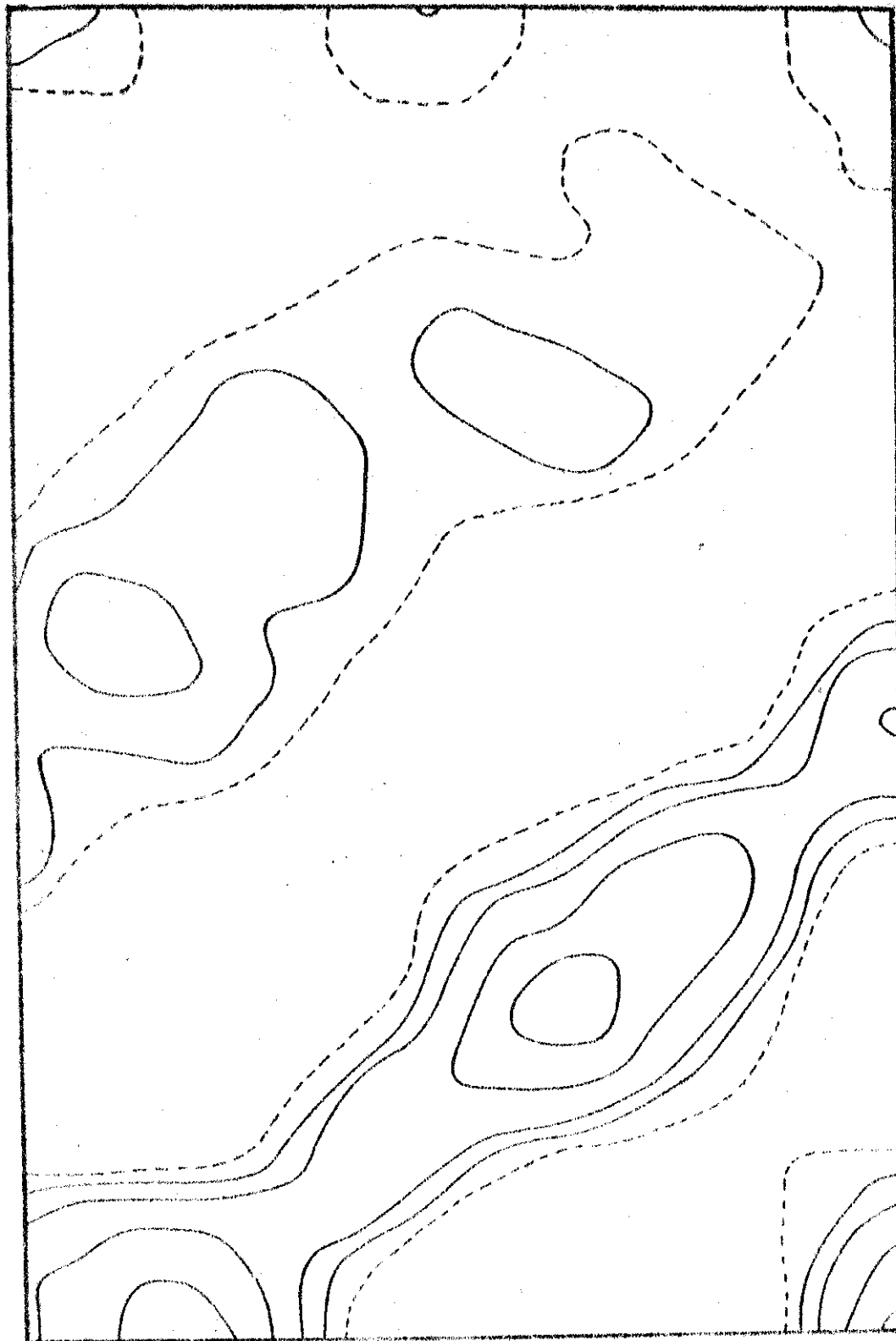


Figure 2.2(c)

$x = 72/120$

$c/2$



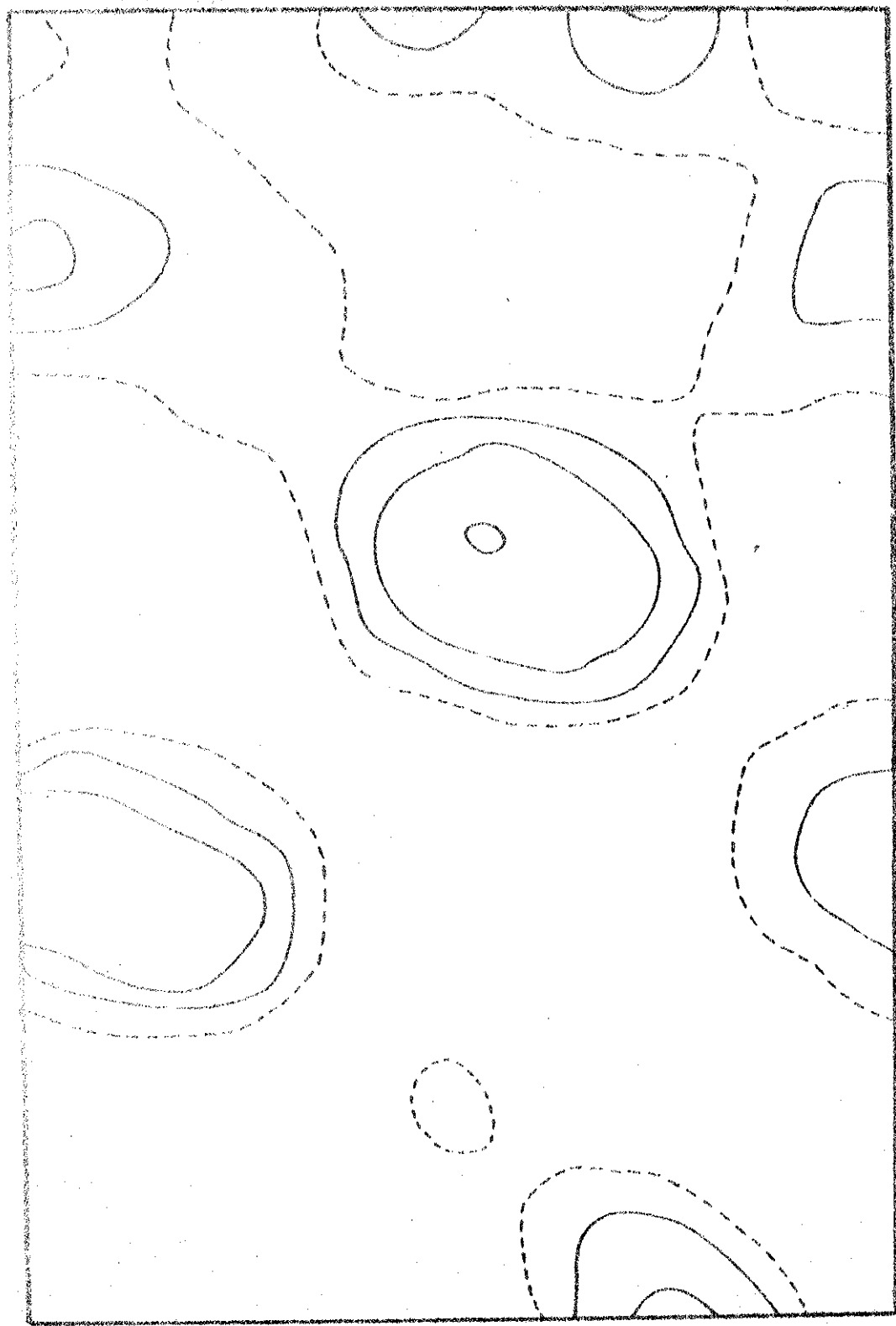
$b/2$

0

Figure 2.2(d)

X = 96/120

C/2



0

b/2

Figure 2.2(e)

cally independent molecules in the asymmetric unit were separated by nearly half the cell translation.

An examination of the diffraction data showed that a group of low angle reflections with $h = 2$ were strikingly intense. The reflections were 200, 210, 220, 232 and 242. This feature, again, suggested that the two molecules in the asymmetric part were separated by approximately $a/2$ and supported the conclusion derived from the three-dimensional Patterson map.

Further examination of the intense, low angle reflections revealed that sign relationships of the type

$$S(F_{hkl}) \approx S(F_{h'k'l'}) \cdot S(F_{h-h',k-k',l-l'}) \quad (2.1)$$

existed among nine out of the fifteen strongest reflections in the structure. Hence, as the next step, a 'mini' symbolic addition procedure was carried out with these nine reflections of which three were used to specify the origin and two were used as symbols. The details of the operation are given in Table 2.3. Four Fourier maps corresponding to the four possible solutions were computed with the F_o 's of the nine reflections as the Fourier coefficients. These maps are hereafter referred to as maps I, II, III and IV respectively and the nomenclature is given in Table 2.3.

All the four maps were very similar in character

TABLE 2.3

Details of the 'mini' symbolic addition
procedure using nine reflections

$$\begin{array}{ccc} \bar{2} & 3 & \bar{2} \\ \bar{1} & 6 & \bar{3} \\ \bar{3} & 4 & \bar{2} \end{array} \quad \begin{array}{c} + \\ + \\ + \end{array} \left. \vphantom{\begin{array}{ccc} \bar{2} & 3 & \bar{2} \\ \bar{1} & 6 & \bar{3} \\ \bar{3} & 4 & \bar{2} \end{array}} \right\} \quad \text{origin}$$

$$\begin{array}{ccc} 0 & 4 & 2 \\ 2 & 4 & 2 \end{array} \quad \begin{array}{c} A \\ B \end{array} \left. \vphantom{\begin{array}{ccc} 0 & 4 & 2 \\ 2 & 4 & 2 \end{array}} \right\} \quad \text{symbols}$$

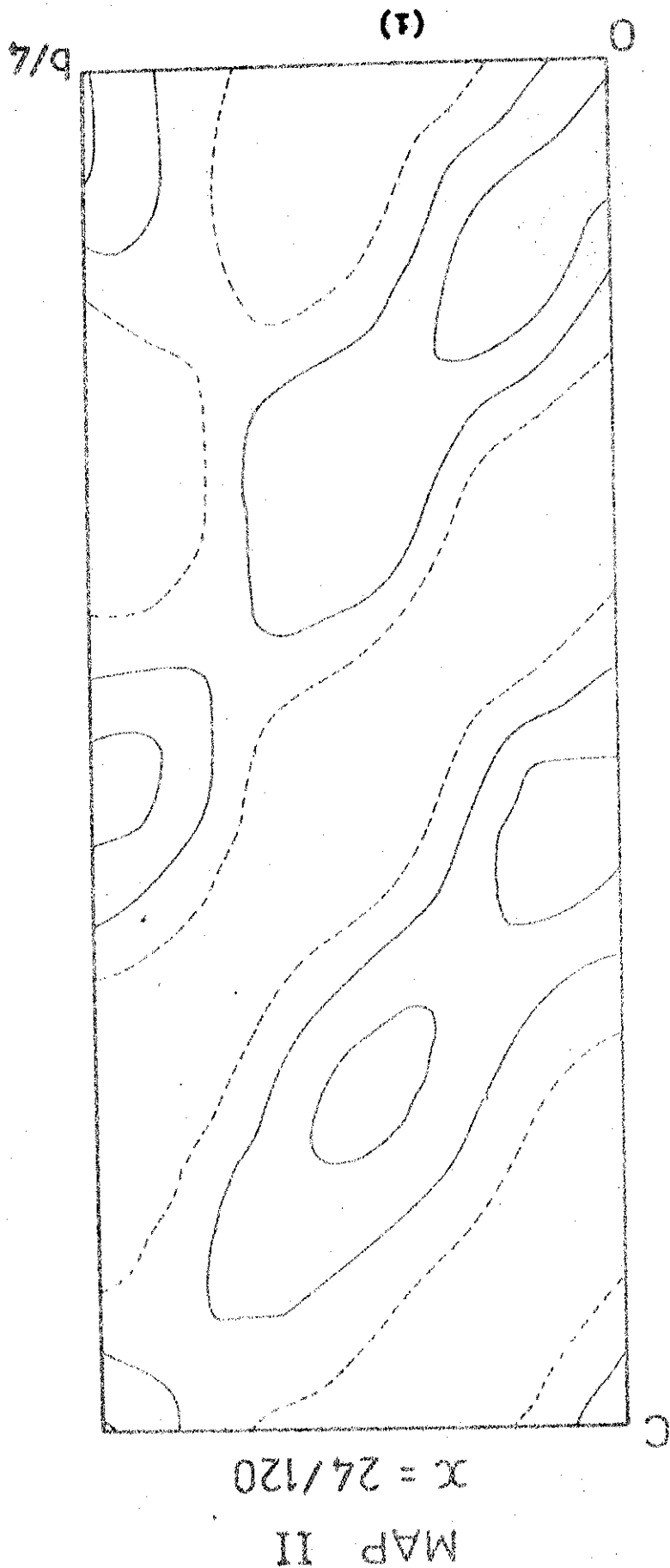
$$\begin{array}{ccc} 2 & 0 & 0 \\ 2 & 1 & 0 \\ 0 & 5 & 2 \\ 2 & 2 & 0 \end{array} \quad \begin{array}{c} AB \\ -A \\ -AB \\ AB \end{array}$$

		Map I	Map II	Map III	Map IV
A	=	+	+	-	-
B	=	+	-	+	-

in that the electron density distribution in all the maps were nearly continuous in the sections perpendicular to the a-axis, Hence, a molecular model could be fitted anywhere along these continuous stretches. The breaks in the electron density corresponding to the ends of the molecule were not clear in any of the maps. In Fig. 2.3, two typical sections of maps II and III are shown. Even though the four maps indicated four different molecular orientations in the bc-plane, all of them had a common feature, viz., that along the a-direction the crystallographically independent molecules appeared to be separated by nearly half the cell translation. In maps II and III, the crystallographically independent molecules appeared to be near the planes $x = \frac{1}{4}$ and $x = \frac{3}{4}$ and in maps I and IV near the planes $x = 0$ and $x = \frac{1}{2}$. All the four maps were, however, individually compatible with the vector distribution in the three-dimensional Patterson map.

In map I, the continuous electron density distribution was passing through the centre of inversion at the origin and hence necessitated a symmetry for the molecule. Since the molecule was not centrosymmetric and any molecular orientation passing through the centre of inversion was not allowed by packing considerations, map I was eliminated from further considerations. Therefore, only the sets of molecular orientations obtained

FIG. 2.3(a): Two typical sections of map II of the wind, symbolic addition procedure. The contours are at arbitrary intervals.



MAP II

$x = 84/120$

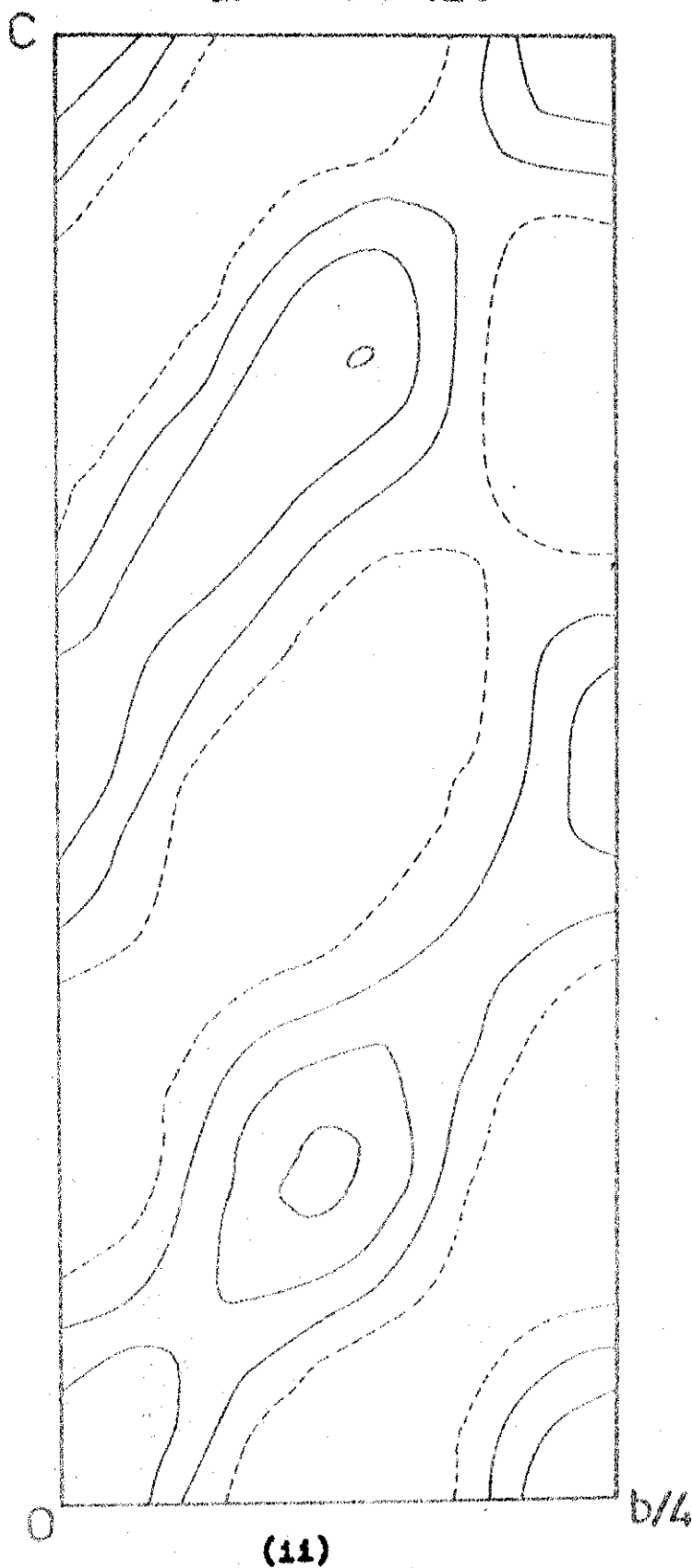


Figure 2.3(a)

MAP III

$x = 24/120$

C

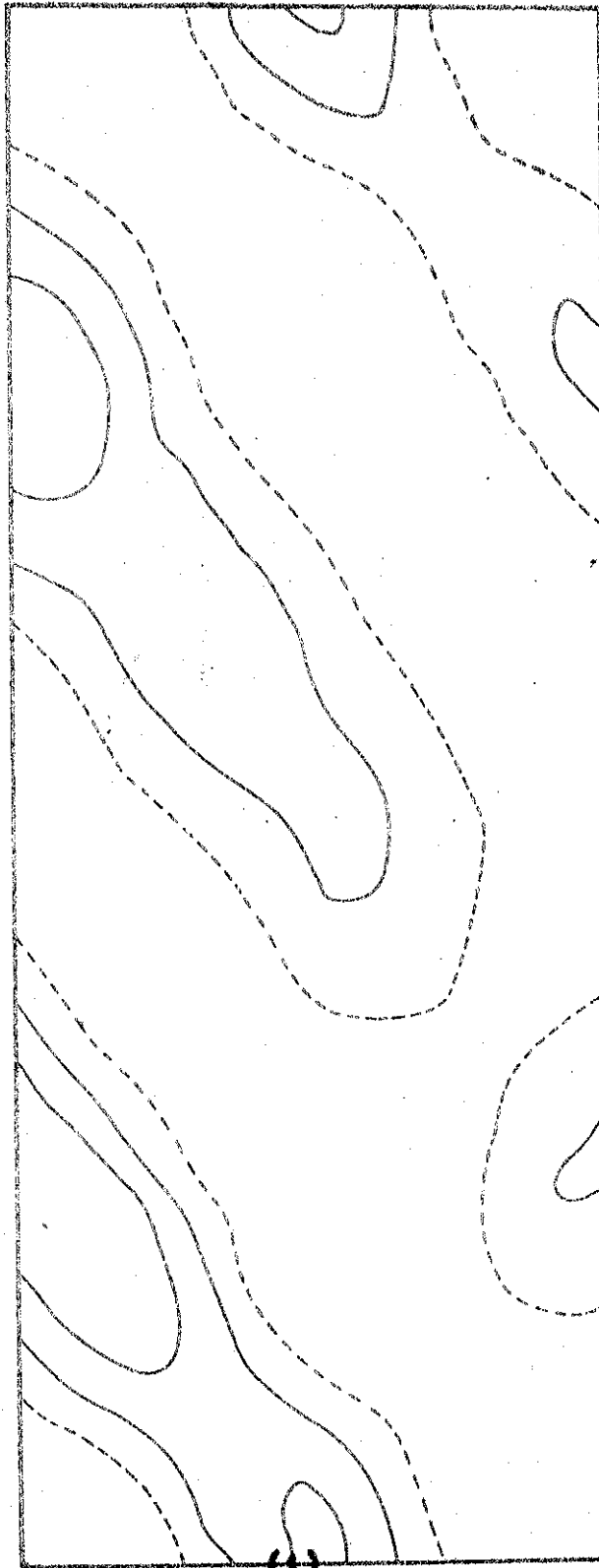
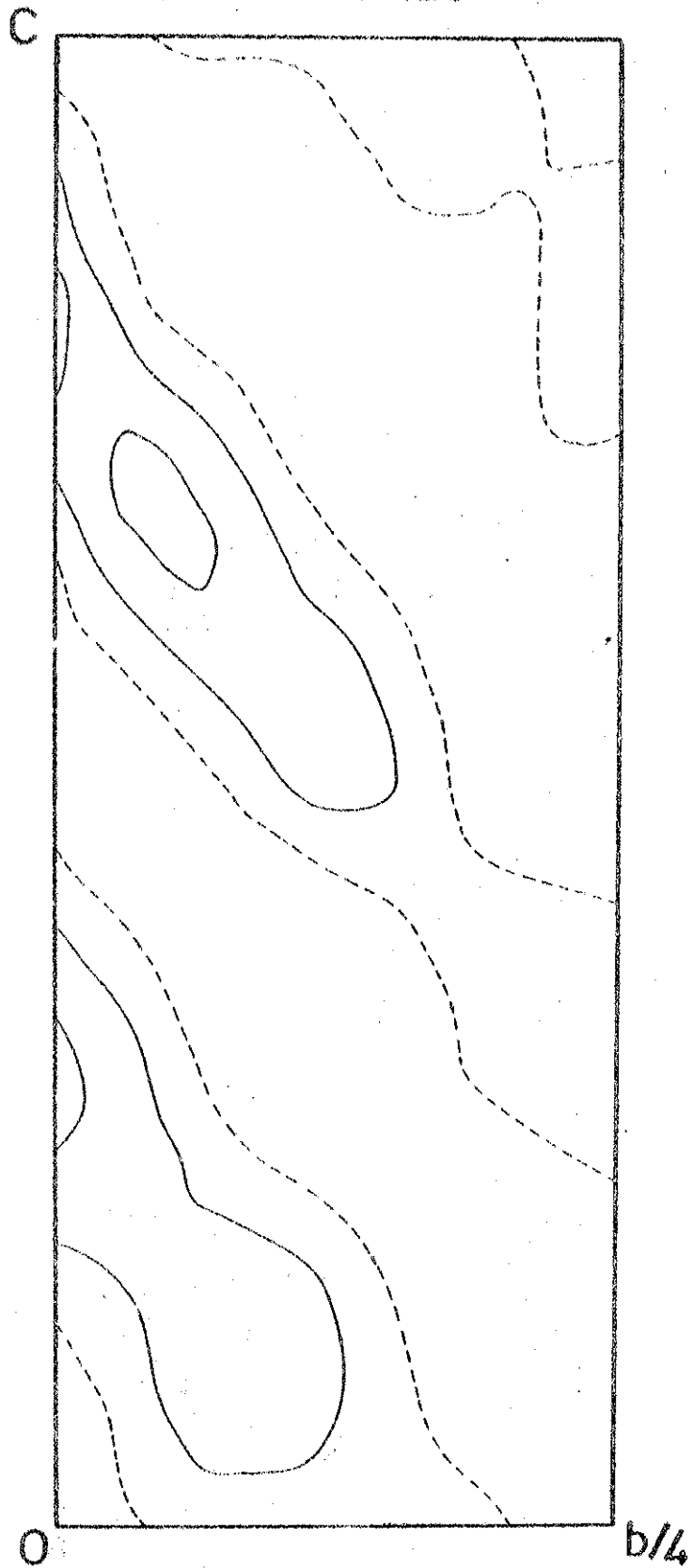


Fig. 2.3(b): Two typical sections of map III of the 'mini' symbolic addition procedure. The contours are at arbitrary intervals. b/l

MAP III

$x = 84/120$



(11)

Figure 2.3(b)

from the maps II, III and IV needed to be considered.

Use of MULTAN

Normalized structure factors E_{hkl} 's conventionally defined as [15]

$$E_{hkl}^2 = \frac{|F_{hkl}|^2}{\epsilon \sum_{j=1}^N f_j^2} \quad (2.2)$$

where f_j is the atomic scattering factor of the j^{th} atom and N is the total number of atoms in the unit cell, were next calculated. The atomic scattering factors used were those given by Cromer and Waber [16]. These were corrected for the thermal motion using the temperature factor $B = 4.0 \text{ \AA}^2$ as obtained from the three-dimensional Wilson's plot (section 2.?). The quantity ϵ in the above expression is equal to 2 for the $h0l$ and $0k0$ type of reflections and 1 for all the others. The largest 290 E 's (≥ 1.40) were used in the subsequent symbolic addition procedure and tangent refinement through the MULTAN programme. The MULTAN programme is now very well-known and commonly used in crystal structure analysis. However, as the author has used the programme for the first time, a brief description of MULTAN is given below.

The MULTAN programme of Germain, Main and Woolfson [17] consists of three parts:

- (i) SIGMA2
- (ii) CONVERGE
- (iii) FASTAN

(i) SIGMA2: In this part of the programme, all the phase relationships of the form

$$\varphi_{\vec{h}} \approx \varphi_{\vec{h}'} + \varphi_{\vec{h}-\vec{h}'} \quad (2.3)$$

are set up with a weight $k_{hh'}$, given by

$$K_{\vec{h} \vec{h}'} = 2\sigma_3\sigma_2^{-3/2} E_{\vec{h}} E_{\vec{h}'} E_{\vec{h}-\vec{h}'} \quad (2.4)$$

where

$$\sigma_n = \sum_{j=1}^N Z_j^n \quad (2.5)$$

Z_j is the atomic number of the j^{th} atom in the unit cell and N is the total number of atoms in the unit cell. The quantities $\varphi_{\vec{h}}$, $\varphi_{\vec{h}'}$, and $\varphi_{\vec{h}-\vec{h}'}$, correspond to the phase values of the reflections with indices h,k,l ; h',k',l' ; and $h-h'$, $k-k'$, $l-l'$ respectively; the $E_{\vec{h}}$, $E_{\vec{h}'}$, and $E_{\vec{h}-\vec{h}'}$, are the corresponding normalized structure factors.

(ii) CONVERGE: In this part, the programme calculates a quantity $\alpha_{\vec{h}}$ estimated as

$$\alpha_{\vec{h}}^2 = \sum_{\vec{h}'} K_{\vec{h}\vec{h}'}^2 + 2 \sum_{\substack{\vec{h}' \\ \vec{h}' \neq \vec{h}''}} \sum_{\vec{h}''} K_{\vec{h}\vec{h}'} K_{\vec{h}\vec{h}''} \frac{I_1(K_{\vec{h}\vec{h}'})}{I_0(K_{\vec{h}\vec{h}'})} \frac{I_1(K_{\vec{h}\vec{h}''})}{I_0(K_{\vec{h}\vec{h}''})} \quad (2.6)$$

where I_0 and I_1 are modified Bessel functions. $\alpha_{\vec{h}}$ gives a measure of the reliability with which the phase $\phi_{\vec{h}}$ is determined. In CONVERGE, the value of $\alpha_{\vec{h}}$ is estimated for each reflection and the reflections are arranged in the order of decreasing $\alpha_{\vec{h}}$. Reflections with weak interactions and hence low $\alpha_{\vec{h}}$ values are then eliminated from this list in a stepwise fashion. At each step, the reflection with the lowest $\alpha_{\vec{h}}$ is eliminated from the list together with all the phase relationships in which the reflection is involved. As these phase relationships are eliminated, the estimated $\alpha_{\vec{h}}$'s for the reflections involved are updated and once again the reflections with the lowest $\alpha_{\vec{h}}$'s and their interactions are eliminated from the list. Thus, the programme converges on a group of reflections with a large number of phase relationships. The programme then uses the space group information to select the best possible starting set of reflections, which include the origin defining reflections also. At the end of the calculations in CONVERGE, a map giving the list of reflections eliminated during the CONVERGE procedure is made. This list starts from the end of the convergence map and working upwards, the phase of each

reflection is computed from the **relationships** listed with it, using the tangent formula described in **FASTAN**. In **CONVERGE**, the $\sum$, **relationships** are also listed, using the formula appropriate to the **space** group.

(iii) **FASTAN**: In this part of the programme, the reflections other than the, origin defining ones in the starting set are assigned phase values $\pm\pi/4$ and $\pm 3\pi/4$ if the space group is non-centric and 0 or π if centric. Thus, a multiple starting set of phases is obtained and for each starting set, phase generation and refinement are carried out using the weighted tangent formula [17],

$$\tan \varphi_{\vec{h}} = \frac{\sum_{\vec{h}', \vec{h}-\vec{h}'} W_{\vec{h}'} W_{\vec{h}-\vec{h}'} \left| \begin{matrix} E_{\vec{h}'} & E_{\vec{h}-\vec{h}'} \end{matrix} \right| \sin(\varphi_{\vec{h}'} + \varphi_{\vec{h}-\vec{h}'})}{\sum_{\vec{h}', \vec{h}-\vec{h}'} W_{\vec{h}'} W_{\vec{h}-\vec{h}'} \left| \begin{matrix} E_{\vec{h}'} & E_{\vec{h}-\vec{h}'} \end{matrix} \right| \cos(\varphi_{\vec{h}'} + \varphi_{\vec{h}-\vec{h}'})} = \frac{T_{\vec{h}}}{B_{\vec{h}}} \quad \dots (2.7)$$

where $w_{\vec{h}}$ is the weight associated with the phase $\varphi_{\vec{h}}$. Each weight is computed from

$$w_{\vec{h}} = \tanh\left(\frac{1}{2}\alpha_{\vec{h}}\right) \quad (2.8)$$

where

$$\alpha_{\vec{h}} = \left| E_{\vec{h}} \right| (T_{\vec{h}}^2 + B_{\vec{h}}^2)^{1/2} \quad (2.9)$$

The **weights** of the reflections whose phases have been determined by the $\sum_1$ **relationships** are initially set at $2|P - \frac{1}{2}|$, where P is the probability of the $\sum_1$ **Set** **termination**. The **weight** of all the other **reflections** in the starting set are set at unity, while the **reflections** whose **phases** are **undetermined** are **given** a weight of **zero**. The **initial** phase values of all the **reflections** are determined in the order indicated by **CONVERGE** and then refined in the **same order**.

At the end of the refinement each **set** of phases is **characterised** by **figures** of merit defined as **ABSFOM** and **RESID**. The absolute figure of merit, or **ABSFOM**, is related to $\sum_{\vec{h}} \alpha_{\vec{h}}$ defined in **equation** (2.9). This quantity **gives** a measure of the **internal consistency** of the **set** of phases and is defined as

$$\text{ABSFOM} = A_F = \frac{\sum_{\vec{h}} \alpha_{\vec{h}} - \sum_r \alpha_r}{\sum_e \alpha_e - \sum_r \alpha_r} \quad (2.10)$$

where $\sum_e \alpha_e$ is the **sum** of the estimated α 's from **equation** (2.6) and

$$\sum_r \alpha_r = \sum_{\vec{h}} \left(\sum_{\vec{h}'} K_{\vec{h}\vec{h}'}^2 \right)^{1/2}, \quad (2.11)$$

is the **value** of

$\sum_{\vec{h}} \alpha_{\vec{h}}$ when random **phases** are assumed.

The second figure of merit, **RESID** is the

crystallographic residual defined as

$$R = \frac{\sum \left| |E_{\vec{h}}| - |E_{\vec{h}_{cal}}| \right|}{\sum |E_{\vec{h}}|} \quad (2.12)$$

where

$$E_{\vec{h}_{cal}} = K \left\langle E_{\vec{h}'} E_{\vec{h}-\vec{h}'} \right\rangle \vec{h}' \quad (2.13)$$

The scale factor is obtained by setting

$$K = \frac{\sum_{\vec{h}} |E_{\vec{h}}|}{\left| \left\langle E_{\vec{h}'} E_{\vec{h}-\vec{h}'} \right\rangle \vec{h}' \right|} \quad (2.14)$$

The correct set of phases tends to have the highest value for ABSFOM and the lowest value for R. Hence, an index combining those two figures of merit ABSFOM and RESID can be calculated to evaluate the different sets of phases obtained from the tangent formula refinement in the MULTAN programme. The combined index, C.I., can be evaluated as

$$C.I. = \frac{R_{max} - R}{R_{max} - R_{min}} + \frac{A_F - A_{Fmin}}{A_{Fmax} - A_{Fmin}} \quad (2.15)$$

Here, R and A_p refer to **RESID** and **ABSFOM** respectively for the particular set of phases considered. The quantities with subscripts 'max' and 'min' refer to the maximum and minimum values of these figures of merit among the different sets of solutions obtained. The set with the highest value for C.I. is likely to be the correct solution, but often, the second or third best sets have also been found to give the correct solution.

In the case of MBPAA, 290 reflections with $|E_{\vec{h}}| \geq 1.40$ were used for sign determination with MULTAN. This MULTAN procedure will hereafter be referred to as MULTAN I. The CONVERGE section of the MULTAN chose the seven reflections given in Table 2.4 as the starting set. With two signs for each of the four symbols, there were sixteen possible sign combinations. However, this number was reduced to eight on account of the relationship

0	9	5	origin
0	5	2	symbol B
0	4	7	symbol C

which existed among the starting set of reflections. The details of all the sets are given in Table 2.5. The set with the best ABSFOM, viz., set 5, did not coincide with the set with the lowest R , viz., set 10. The sets 1, 5, 10, 12 and 16 could be considered to be distinctly superior to the rest, on the basis of the combined index

TABLE 2.4

Origin and symbols used in MULTAN I

0	9	5	} Origin	0	4	2	A	} symbols
$\bar{1}$	0	12		0	5	2	B	
$\bar{1}$	6	$\bar{3}$		0	4	7	C	
				$\bar{2}$	9	$\bar{5}$	D	

TABLE 2.5

RESULTS OF MULTAN I

Set No,	A13SFOM	RESID R	Combined Index C.I.
1	1.0309	39.43	1.4038
2	0.8004	40.59	0.3350
3	0.9586	39.66	1.0981
4	0.8134	38.31	0.8841
5	1.0491	39.02	1.5585
6	0.8077	40.71	0.3342
7	0.9288	41.55	0.5758
8	0.7878	39.31	0.5731
9	0.7980	37.94	0.9115
10	0.9899	37.02	1.7913
11	0.7812	38.47	0.7353
12	1.0054	38.73	1.4684
13	0.7667	38.50	0.6775
14	0.9131	39.06	1.0701
15	0.7655	39.57	0.4371
16	0.9821	37.92	1.5651

The equivalent sets were

12	and	16	11	and	15
10	and	14	9	and	13
1	and	5	4	and	8
3	and	7	2	and	6

given in column 4 of Table 2.5. On comparison, the signs of the reflections in the sets 10 and 16 were found to be related by a shift of origin by the amount $\frac{a+b+c}{2}$. Because of the sign relationship existing between the origin reflection 095 and the symbols B and C, as mentioned earlier, the sets 1 and 5 were found to be equivalent. Sets 12 and 16 were also found to be equivalent for the same reasons. Hence, E-maps were next computed only for the two independent sets of sign combinations, viz., from the sets 10 and 5. The E-map corresponding to set 5 had electron density distribution passing through the origin and for reasons mentioned earlier in this section, could be eliminated from further considerations. The E-map corresponding to set 10 was the only one to be considered.

At this stage, a comparison of the MULTAN I results with those of the 'mini' symbolic addition procedure was made. It may be recalled from Table 2.3 that the reflections 042 and 242 were used as the two symbols in the 'mini' symbolic addition procedure. On comparing the signs of these two reflections in the sets I, II, III and IV of the 'mini' symbolic addition procedure with the various sets of MULTAN I, it was found that the sets 10 and 16 of MULTAN I were related to the sign combination $S_A(042) = -$, $S_B(242) = +$ of the

'mini' symbolic addition procedure and the set 5 to the sign combination $S_A(042) = +$, $S_B(242) = +$. In short,

Set I of the 'mini' symbolic addition set 5
of MULTAN I,

and

Set III of the 'mini' symbolic addition set 10
and hence set 16 of MULTAN I.

Thus, it was not surprising that the electron density distribution corresponding to the sign combinations of set 5 of MULTAN I was similar to that of Map I of the 'mini' symbolic addition procedure.

The distribution of the largest 95 peaks in the E-map corresponding to the set 10 of MULTAN I is shown in Fig. 2.4. Most of the peaks were distributed near $x = 1/4$ and $x = 3/4$. This feature indicated that the two independent molecules in the asymmetric part were separated by nearly $a/2$ and were individually lying close to the planes $x = 1/4$, and $x = 3/4$. Even though the 'gross' molecular orientation was clear from the map, the individual atomic positions could not be identified. Also, since the distribution of peaks was nearly continuous, even the regions corresponding to the terminals of the molecules could not be located. The 'gross' molecular orientations deduced from this E-map, checked well with

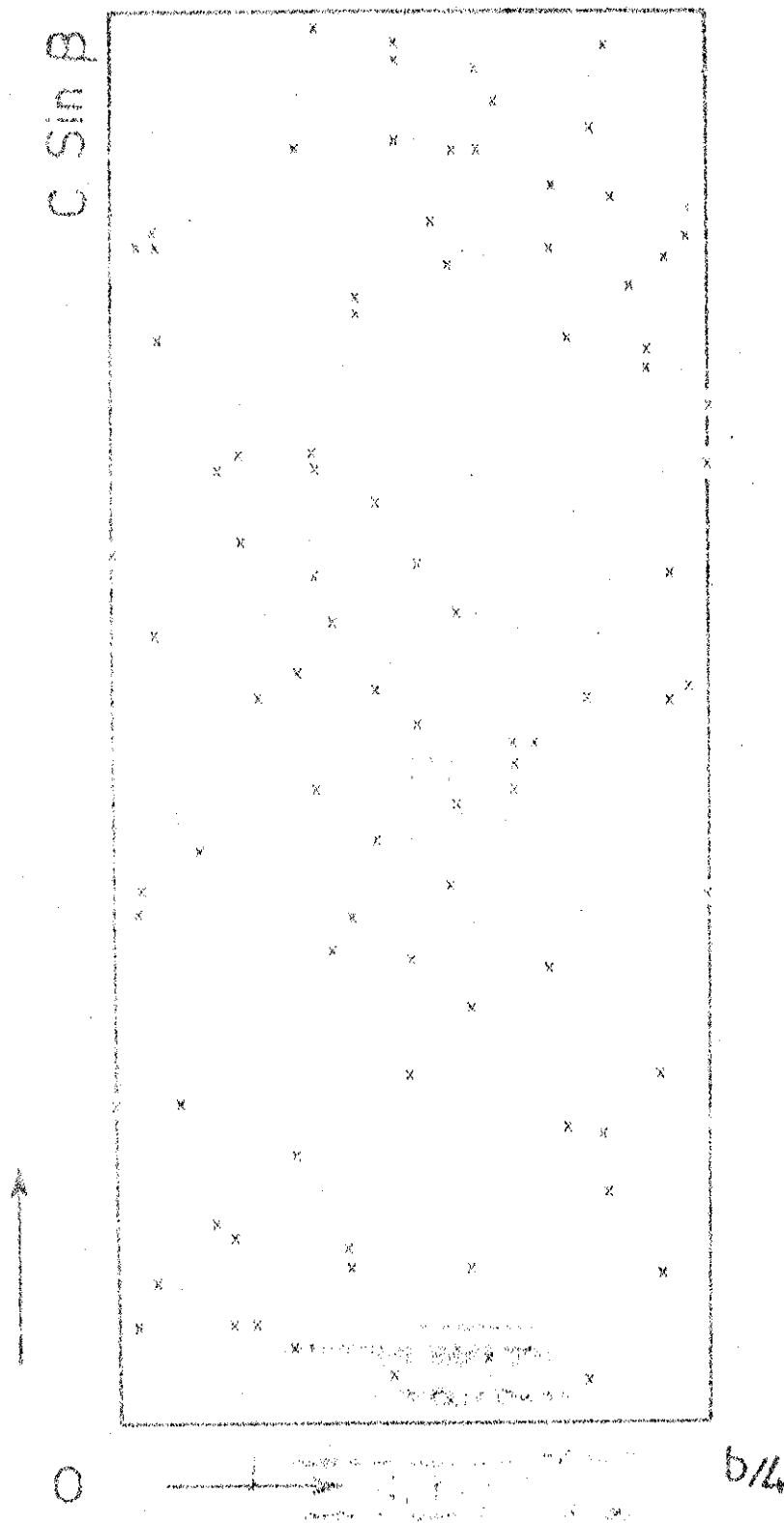


Figure 2.4

Distribution of the largest 95 peak8 in the E-map corresponding to set 10 of MULTAN I.

that obtained from map III of Table 2.3.

A re-examination of the map III of the 'mini' symbolic additor, procedure suggested that in the almost continuous electron density distribution, some regions of slightly low density could be approximated to represent the terminals of the molecules. The low electron density regions were also continuous, Therefore, the identification of the molecular ends was by no means unique and was done only on a trial basis. On interpreting the low electron density regions as representing the molecular ends, the map was found to be compatible with four molecular models. They are described below:

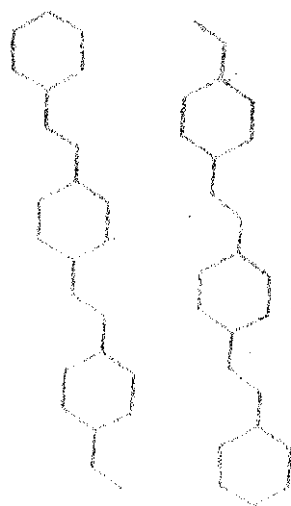
(i) In the bc-plane, the two molecules (referred to as A and B hereafter) were antiparallel and exactly overlapping.

(ii) The two molecules were parallel and exactly overlapping.

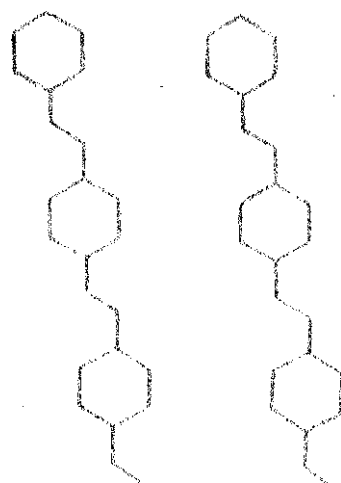
(iii) The two molecules were displaced with respect to each other along their length and were antiparallel.

(iv) The molecules were displaced with respect to each other along their length and were parallel.

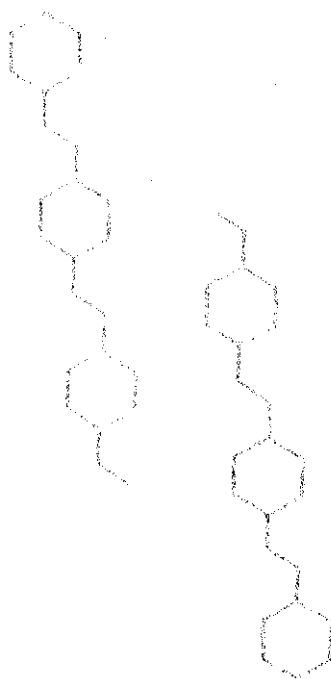
The relative orientation of the two molecules in



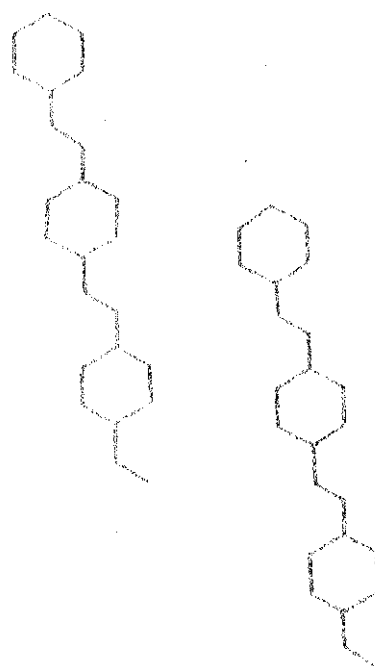
(I)



(II)



(III)



(IV)

Figure 2.5

Schematic representation of the relative orientation of the two independent molecules in the 4 models fitted on map 10 of MULTAN I.

each of the four models is shown schematically in Fig. 2.5.

Based on these molecular models, deduced from the map III of the 'mini' symbolic addition procedure, four similar models were fitted on the E-map corresponding to set 10 of MULTAN I. These trial models accounted for some of the high peaks in the E-map. However, none of the four models could be fitted ideally on the E-map so as to obtain a one to one correspondence between the trial atomic positions and the E-map peaks. Three-dimensional structure factors were computed for the four models and the atomic coordinates were refined by the least-squares technique. But these calculations did not help in discriminating among the four models.

A scrutiny of the intense reflections in the structure showed that out of the 60 strongest reflections, 41 had the same signs in all the four aetn of struoturo faotor learnt-squares calculations. This feature suggested that the four trial models were probably quite close to the oorrect structure. Therefore, the signs of the 41 intense reflections were assumed to be correct. A fourier map waa then synthesized with these 41 reflections as coefficients. As could be expected in a map with only 41 ooeffioicnts, the electron density was indeed diffuse. However, the aim of this operation was

not to identify the atomic positions, but to derive information about the relative orientations of the crystallographically independent molecules in the asymmetric part of the unit cell, Fig. 2.6 gives two sections of the Fourier map with 41 coefficients. In this map, the breaks in the electron density distribution corresponding to the ends of the molecules were very clear. It was found that, as in the trial models (1) and (11), the crystallographically independent molecules were almost exactly overlapping each other along their molecular axes in the *bc*-plane. As indicated by the Patterson map, the Map III of the 'mini' symbolic addition procedure and the E-map corresponding to set 10 of MULTAN I, the molecules appeared to be near the planes $x = 1/4$ and $x = 3/4$.

At this stage, it was suspected that the presence of a large number of aromatic rings in the structure was probably responsible for the failure of MULTAN I to solve the structure. Hence, as the next step, normalized structure factors were recalculated using molecular scattering factors for the benzene rings, i.e., instead of the carbon and hydrogen atomic scattering factors, a spherical average G for the entire ring, placed at its centre, was used. The G values were calculated from the relation [18]

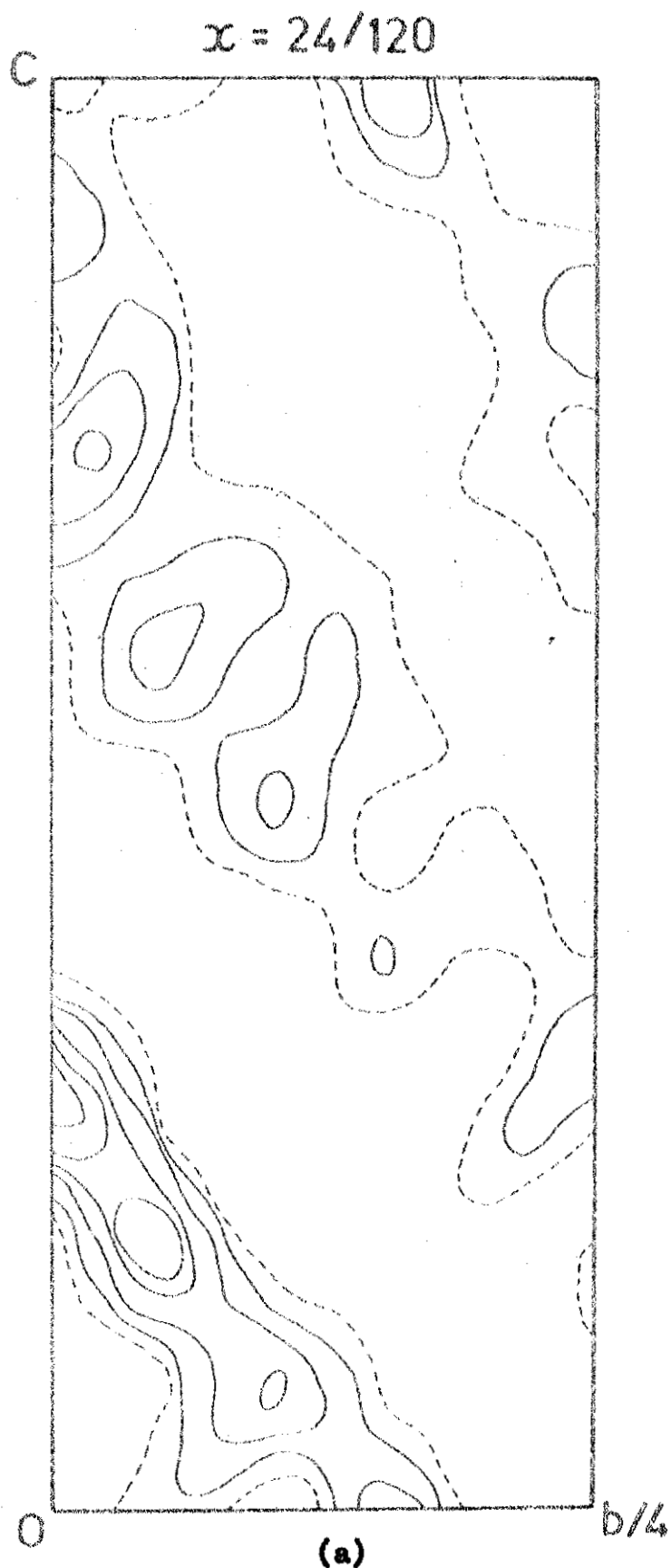


Fig. 2.6: Two typical sections of the Fourier map with 41 coefficients.

$$x = 84/120$$

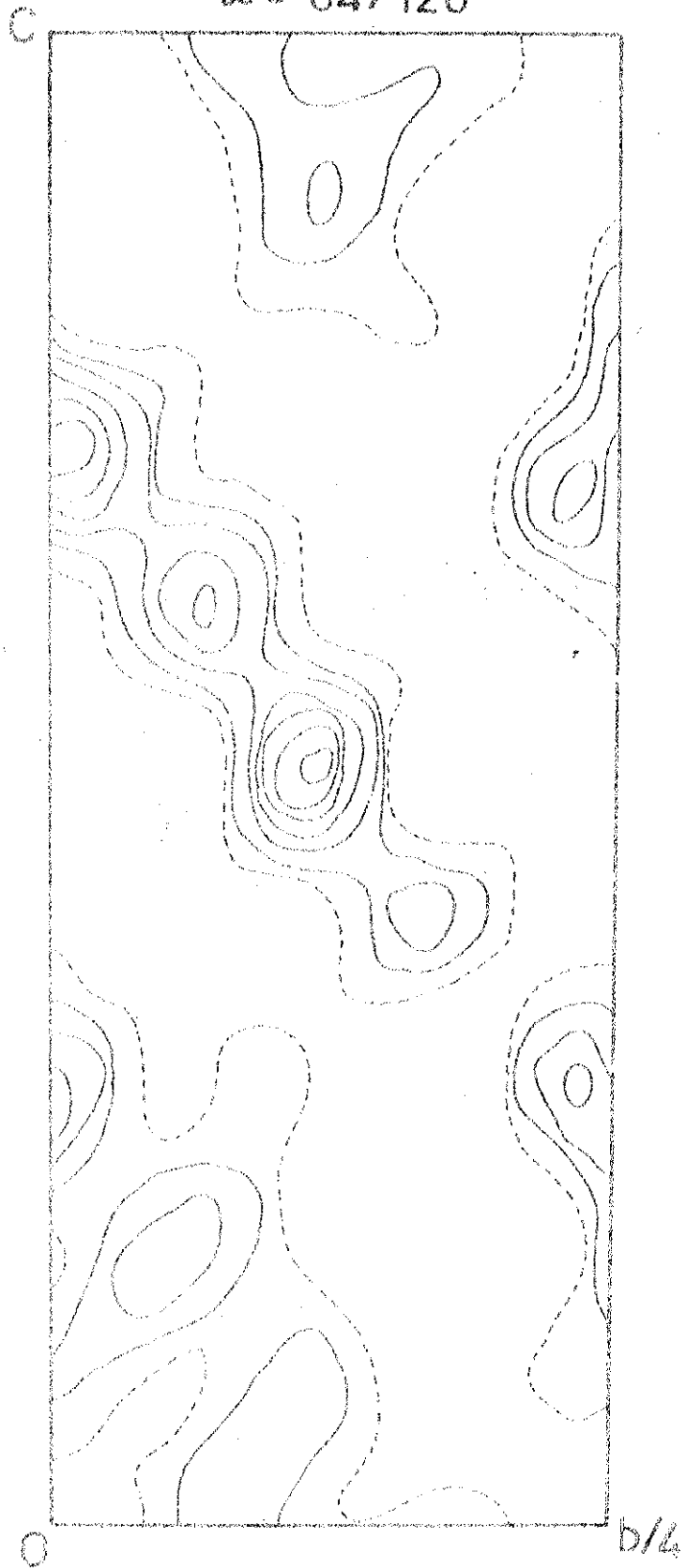


Fig.2.6(b)

$$G^2 = \sum_{i=1}^m \sum_{j=1}^m f_i f_j \frac{\sin(K r_{ij})}{K r_{ij}} \quad (2.16)$$

where

$$K = 4\pi \frac{\sin \theta}{\lambda}$$

r_{ij} = distance between the i^{th} and the j^{th} atoms.

m = number of atoms in the molecule or molecular fragment, and

f_i, f_j = atomic scattering factors for the i^{th} and the j^{th} atoms respectively.

Furthermore, to avoid the effects of 'rational dependence' [19], arising from the rod-like geometry of the molecule, the reflections were divided into seven $(\sin \theta)/\lambda$ ranges and the values of $\langle E^2 \rangle$ were normalieed to unity in each range. A similar normalieation was also done for the eight parity groups of reflections, viz., eee, oee, eoe, eeo, ooe, oeo, eoo and ooo.

The MULTAN calculations were repeated using 290 renormalized E-values with $E \geq 1.53$. This MULTAN is hereafter referred to as MULTAN II. The starting set of reflections chosen by the programme is listed in Table 2.6. It may be noticed that the starting sete of MULTAN I and MULTAN IT have six reflections in common. Also, as

TABLE 2.6

Origin and symbols of MULTAN II

0	9	5	} Origin	1	6	3	A	} symbols
1	0	12		3	6	5	B	
0	4	7		0	5	2	C	
				0	4	2	D	

TABLE 2.7
Results of MULTAN II

Set No.	ABSFOM A_F	RESID R	Combined Index C.I.
1	0.9340	39.90	1.8273
2	0.8145	41.97	1.2204
3	0.7405	40.41	1.2427
4	0.6317	44.33	0.4052
5	0.6104	45.21	1.4860
6	0.7413	40.92	1.1734
7	0.8469	40.29	1.5416
8	0.9553	39.22	1.9790
9	0.6549	46.21	0.2034
10	0.5782	44.04	0.3039
11	0.8164	40.59	1.4188
12	0.9428	39.07	1.9934
13	0.9462	39.25	1.9507
14	0.8450	40.82	1.6025
15	0.6634	45.36	0.3450
16	0.7338	42.53	0.9280

in MULTAN I, the reflections 095, 047 and 052 in the starting set have an internal relationship. Therefore, the sixteen sets of solutions corresponding to four symbols reduced to eight as in the case of MULTAN I. The details of these sets are presented in Table 2.7. Set 12 had the lowest R value and set 8 had the highest value for ABSFOM. Even though the discrimination between sets 12, 8, 13 and 1 was marginal, on the basis of figures of merit, these sets appeared to be distinctly superior to the remainder of the solutions. Comparison of the signs of reflections in these four sets showed that the sets 12 and 13 were related to one another by an origin shift of $\frac{bto}{2}$ and that the sets 1 and 8 were also related by the same shift of the origin. The four solutions thus reduced to two. Also, set 8 was found to correspond to the sign combination $S_A(042) = +$, $S_B(242) = +$, i.e., the set I of the 'mini' symbolic addition procedure and set 12 to the sign combination $S_A(042) = -$, $S_B(242) = +$, i.e., set III of the 'mini' symbolic addition procedure. As could be expected, the E-map corresponding to set 8 had a stretch of positive electron density running through the origin and hence was eliminated for reasons described earlier. Thus, the E-map corresponding to set 12 was the only one to be analysed.

The distribution of the largest 100 peaks in the E-map corresponding to the sign combination of set 12 is shown in Fig. 2.7. The peak distribution compares well with that of set 10 of MULTAN I and map III of Table 2.3. However, the new map was found to be of a better quality than the map of set 10 of MULTAN I. The regions corresponding to the two terminals of the molecule through the plane $x = 3/4$ could be easily confirmed from this map. Also, distinct peaks for nineteen out of twentyfour non-hydrogen atoms in this molecule could be identified. The molecular skeleton obtained from this E-map is marked in Fig. 2.7. However, contrary to expectations, the second molecule near $x = 1/4$ could not be identified from this map. A difference electron density map was next computed removing the contribution of the molecule near $x = 3/4$ (molecule A). The difference electron density near $x = 1/4$ was again diffuse and the atomic positions of the second molecule (molecule B) could not be identified.

At this stage, with an aim to improve the resolution of the map and to identify the atomic positions of molecule B, it was decided to generate the signs of more number of reflections from the hitherto known ones. The largest number of coefficients used so far in any E-map was only 290 - the limited computer storage available restricted the number of coefficients that

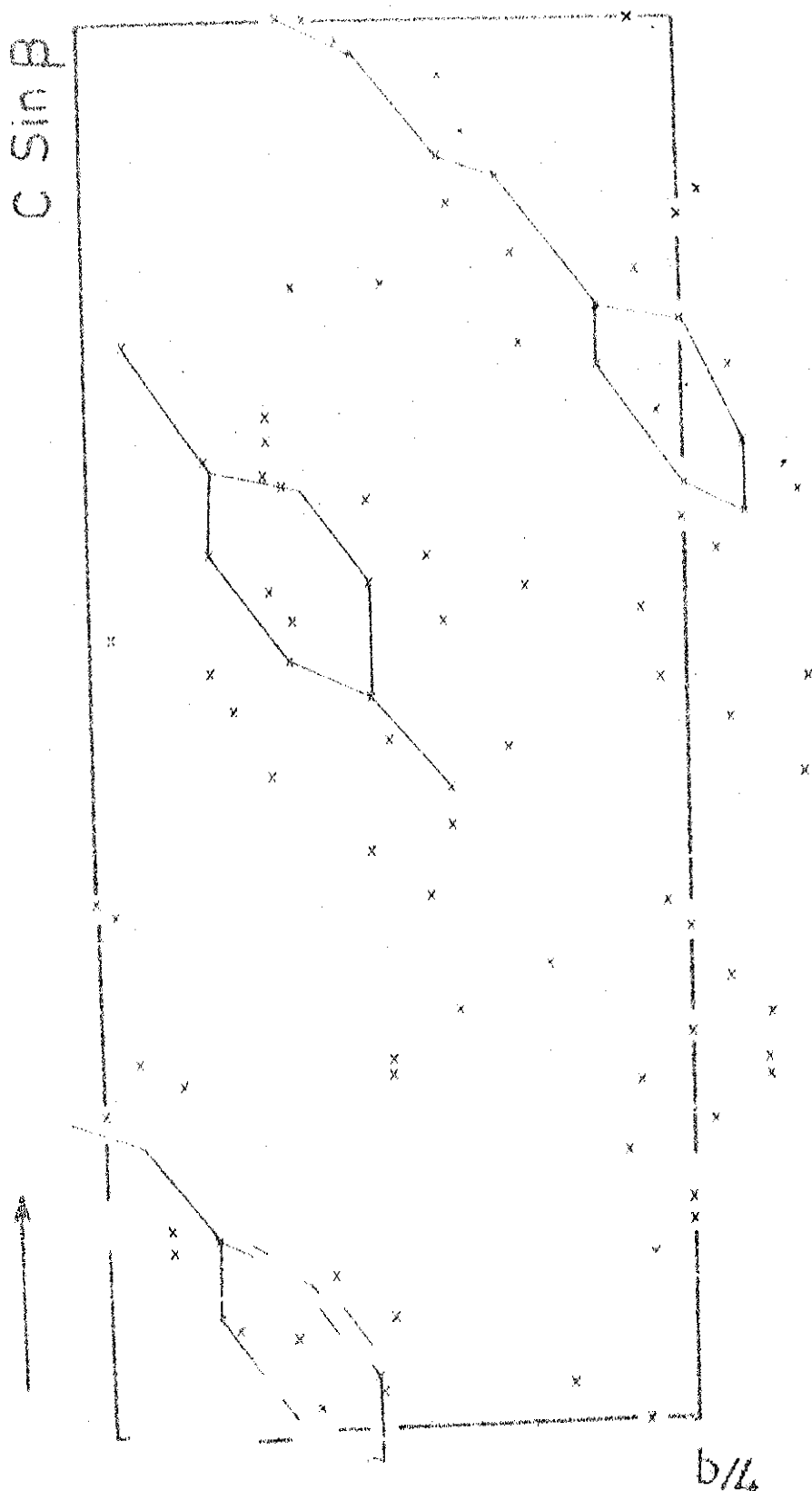


Figure 2.7

Distribution of the 100 largest peaks in the E-map corresponding to set 12 of MULTAN XI. The molecule located near $X = 3/4$ is shown.

could be used in the **MULTAN** programme.

The 290 reflections used for the **MULTAN 11** calculations were used as the starting set for this phase generating operation. These reflections were assigned the signs given by set 12 of **MULTAN 11**, the set from which molecule A was identified. The signs of 202 more **E's** (≥ 1.10 and < 1.53) were then generated using a phase generation programme written by Dr. T.P. Singh. A brief outline of this programme is given below.

The programme has been written specifically for the space group **P2₁/c** where

$$F(hkl) = F(h\bar{k}l) = F(\bar{h}k\bar{l}) = F(\bar{h}\bar{k}\bar{l}) \text{ when } k+l = \text{even} \quad (2.17)$$

and

$$F(hkl) = F(\bar{h}\bar{k}\bar{l}) = -F(\bar{h}k\bar{l}) = -F(h\bar{k}l) \text{ when } k+l = \text{odd} \quad (2.18)$$

The sets of reflections with known and unknown phases are read as two separate sets and stored separately at the beginning of the calculations. For each reflection $(h_1 k_1 l_1)$ with known sign, the programme generates the symmetry related indices $(\bar{h}_1 \bar{k}_1 \bar{l}_1)$, $(\bar{h}_1 k_1 \bar{l}_1)$ and $(h_1 \bar{k}_1 l_1)$. Also, the signs of $E_{h_1 k_1 l_1}$ for these symmetry related sets are determined according to the relations (2.17) and (2.18) and stored. The indices of the reflection whose

sign is to be determined are next compared with all the reflections with known signs and their various symmetry equivalents and a search is made for the relationships of the type:

$$h = h_1 + h_2; \quad k = k_1 + k_2; \quad l = l_1 + l_2 \quad (2.19)$$

where (hkl) corresponds to the indices of the reflection whose sign is to be determined. $(h_1k_1l_1)$ and $(h_2k_2l_2)$ are the indices of the reflections with known signs. If the reflection (hkl) is involved in N interactions of the type (2.19), its sign is calculated as

$$S_{hkl} = \sum_{j=1}^N E_{hkl} \cdot E_{h_1k_1l_1}^j \cdot E_{h_2k_2l_2}^j \quad (2.20)$$

where $E_{h_1k_1l_1}^j$ and $E_{h_2k_2l_2}^j$ are the values of E_s with signs, of the reflections with known signs involved in the j^{th} interaction. The programme thus calculates the quantity S_{hkl} for each reflection with unknown sign. The probability P_{hkl} of the sign of S_{hkl} being correct is calculated using the formula [20]

$$P_{hkl} = \frac{1}{2} + \frac{1}{2} \tanh \left(\frac{\sigma_3}{\sigma_2^{3/2}} \right) |S_{hkl}| \quad (2.21)$$

where $\sigma_n = \sum_{i=1}^M Z_i^n$, with Z_i being the atomic number of the i^{th} atom in the unit cell consisting of M atoms.

The acceptance limit for the probability was set as 0.998 and the signs of 202 reflections with $P_{hkl} > 0.998$ were

determined by the programme.

Thus, the signs of $290 + 202 = 492$ were known at this stage. An E-map was next computed using these 492 reflections with $E \geq 1.10$ as coefficients. The distribution of the 96 largest peaks in this map is shown in Fig. 2.8. The ratio of reflections to the total number of atoms was > 10 . However, in spite of this high value, the E-map was not sufficiently resolved near the $x = \frac{1}{2}$ plane to enable identification of the atoms of molecule B. As in the previous E-map with 290 coefficients, only the atomic positions of molecule A were coming up clearly and this molecule was found to appear less distorted than in the previous E-map.

The model of molecule A obtained from the above E-map fitted the electron density distribution near the plane $x = 3/4$ in the Fourier map with 41 coefficients (Fig. 2.6) and it also checked very well with the orientation indicated by this Fourier map. As the peak distribution near the plane $x = 1/4$ in the E-map with 492 coefficients was not leading to a meaningful model, the only option left; was to fit trial models for molecule B. A diffuse electron density distribution was found to be more suitable for fitting trial models than discrete E-map peaks. Hence it was decided to use the less-resolved electron density distribution of the Fourier

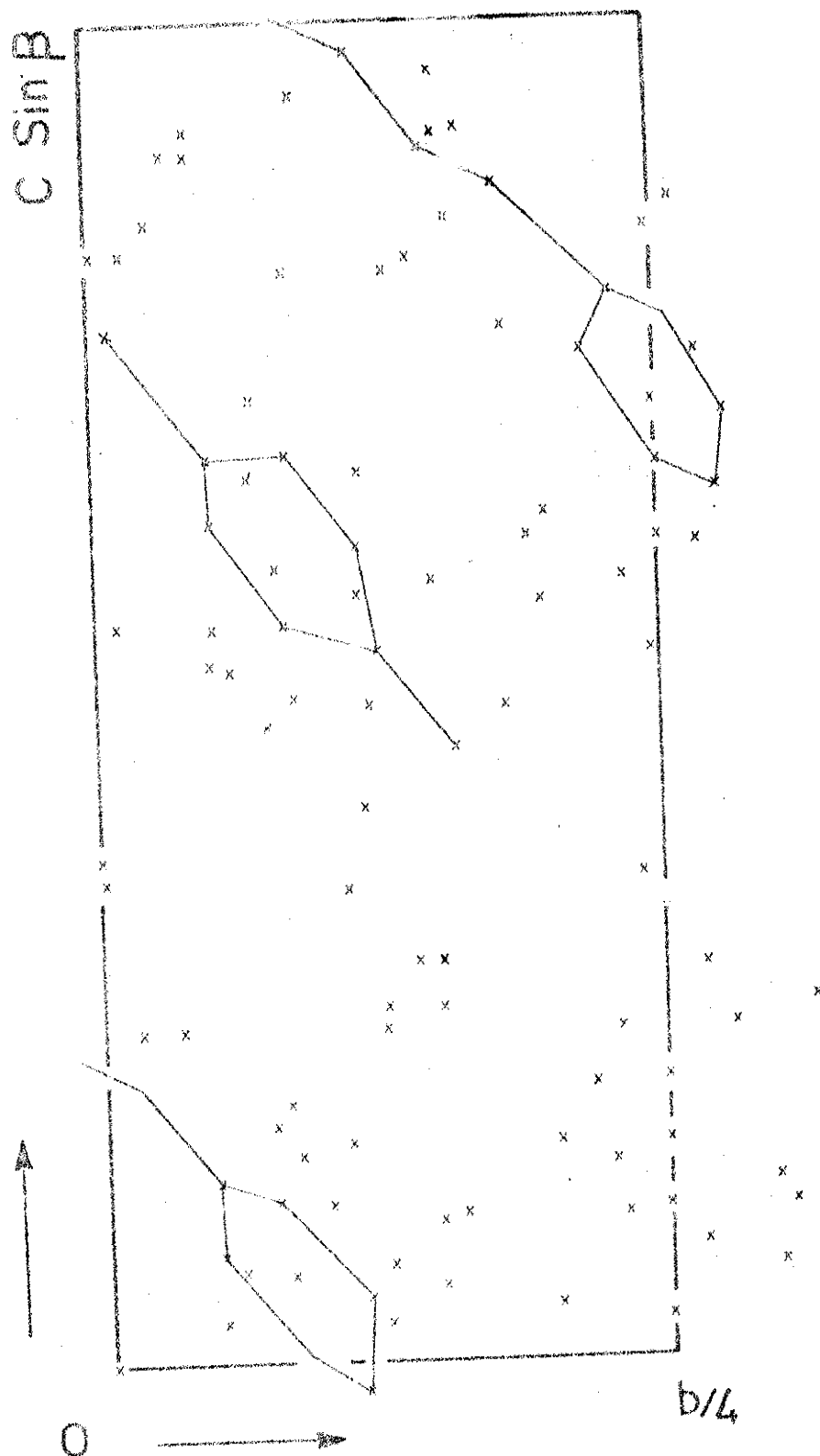


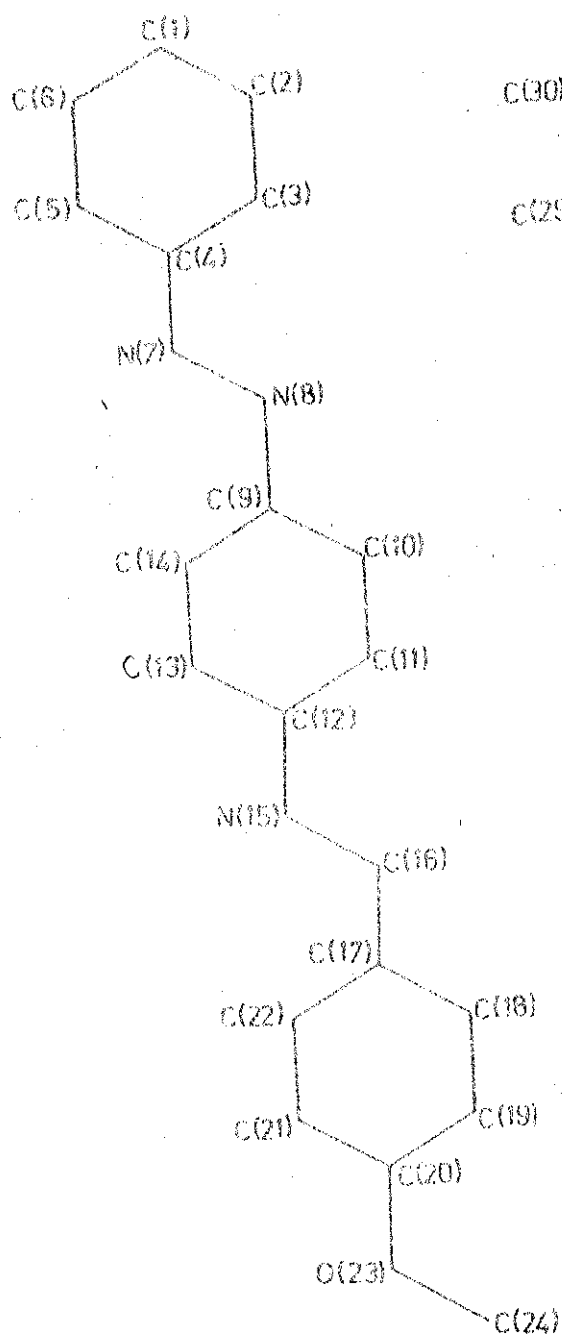
Figure 2.8
 Distribution of the 96 largest peaks in the E-map with 492 coefficients. The molecule near $x = 3/4$ is shown.

map with 41 coefficients for fitting trial models. As the coordinates of molecule A were unambiguously known at this stage, only two trial models had to be considered for molecule B, viz., one in which molecules A and B were parallel and the other in which they were antiparallel. In the subsequent trial structure factor calculations, the methoxy carbon atoms C(24) and C(48) were not included and the oxygen atoms O(23) and O(47) were also treated as carbon atoms. The numbering scheme for the atoms is shown in Fig. 2.9. The initial R-factors defined as $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ for the parallel and the antiparallel models were 0.597 and 0.519 respectively. In six cycles of block-diagonal structure factor least-squares calculations, the antiparallel model refined to $R = 0.356$ whereas the parallel model refined only to $R = 0.464$. A weighting scheme of the form

$$w = \frac{1}{a + bF_o + cF_o^2}$$

with the constants $a = 0.70$, $b = -0.05$ and $c = -0.009$ was used for both the models. Using the R-value as the criterion, all the further calculations were made only on the antiparallel model. From a difference electron density map computed at this stage the positions of the methoxy carbon atoms C(24) and C(48) were fixed. In the subsequent least-squares calculations, the methoxy carbon atoms were included and the oxygen atoms were

MOLECULE A



MOLECULE B

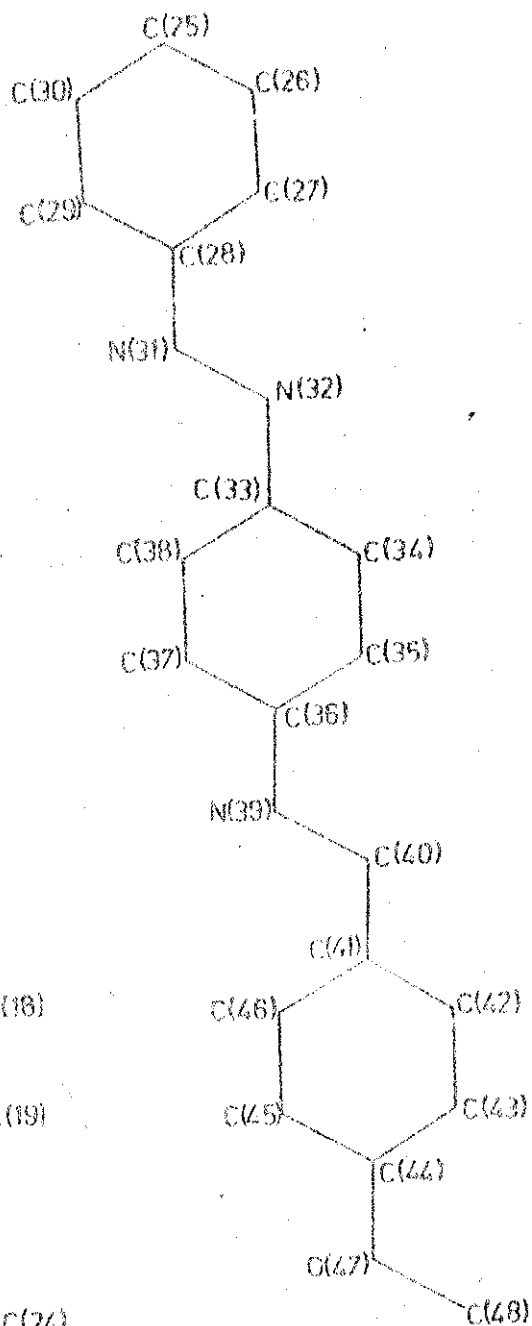


Figure 2.9

The atom numbering scheme for the $O_{h\omega}$ independent MBPAA molecules

assigned oxygen scattering factors. The antiparallel model refined to $R = 0.259$ in six more cycles of least-squares refinement. On refining the layer scale factors, the R -value further reduced to 0.195 and finally converged to 0.146 in 12 more cycles of refinement. In these calculations, all the atoms were treated with isotropic thermal parameters. On account of the low value of the reflection to parameter ratio ($\frac{1071}{440} \approx 2.5$), arising from the extreme paucity of data, refinement of anisotropic thermal parameters was not attempted. In the course of the least-squares refinement, two reflections viz., 200 and 210, were found to have $|F_o| \gg |F_c|$ and hence were corrected for secondary extinction effect using Zachariasen's formula [21]

$$F_{\text{corr}} = K F_{\text{obs}} (1 + \beta(2\theta) g \cdot I_{\text{obs}}) \quad (2.22)$$

where F_{obs} is the observed value of the structure factor,
 I_{obs} is the observed integrated intensity
 K is the scale factor

$$g = \frac{\frac{I_{\text{calc}}}{I_{\text{obs}}} - 1}{2 I_{\text{calc}}} ;$$

I_{calc} is the calculated intensity.

$$\beta(2\theta) = \frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \frac{A^{\frac{1}{2}}(2\theta)}{A^{\frac{1}{2}}(0)} ,$$

θ is the Bragg angle of the reflection, $A^{*1}(2\theta)$ is the absorption factor corresponding to 2θ , $A^{*1}(0)$ is the absorption factor at $2\theta = 0$.

The SFLS programme used in the above analysis was originally written by R. Shiono and modified by B.S. Reddy for the IBM 360/44 computer.

2.4 Disorder

In the course of the least-squares refinement of the structure, some disconcerting features were observed in the thermal parameters as well as the molecular dimensions of one of the molecules. The B-values of the atoms of molecule B, i.e., atoms C(25) through C(48), were found to be generally higher than those of the atoms of molecule A, i.e., C(1) through C(24) (see Table 2.8). In particular, the B-values of the azo nitrogen atoms N(31) and N(32) and the atoms of the phenyl rings on either side of this azo-bond were conspicuously high. The B-values of N(31) and N(32) were the highest, being about 2-2.5 times the average for the rest of the structure. Also, the nitrogen atoms N(31) and N(32) always tended to move towards each other during the least-squares refinement, leading to a very short -N=N- distance. At the end of the above refinement, the N(31) = N(32), distance

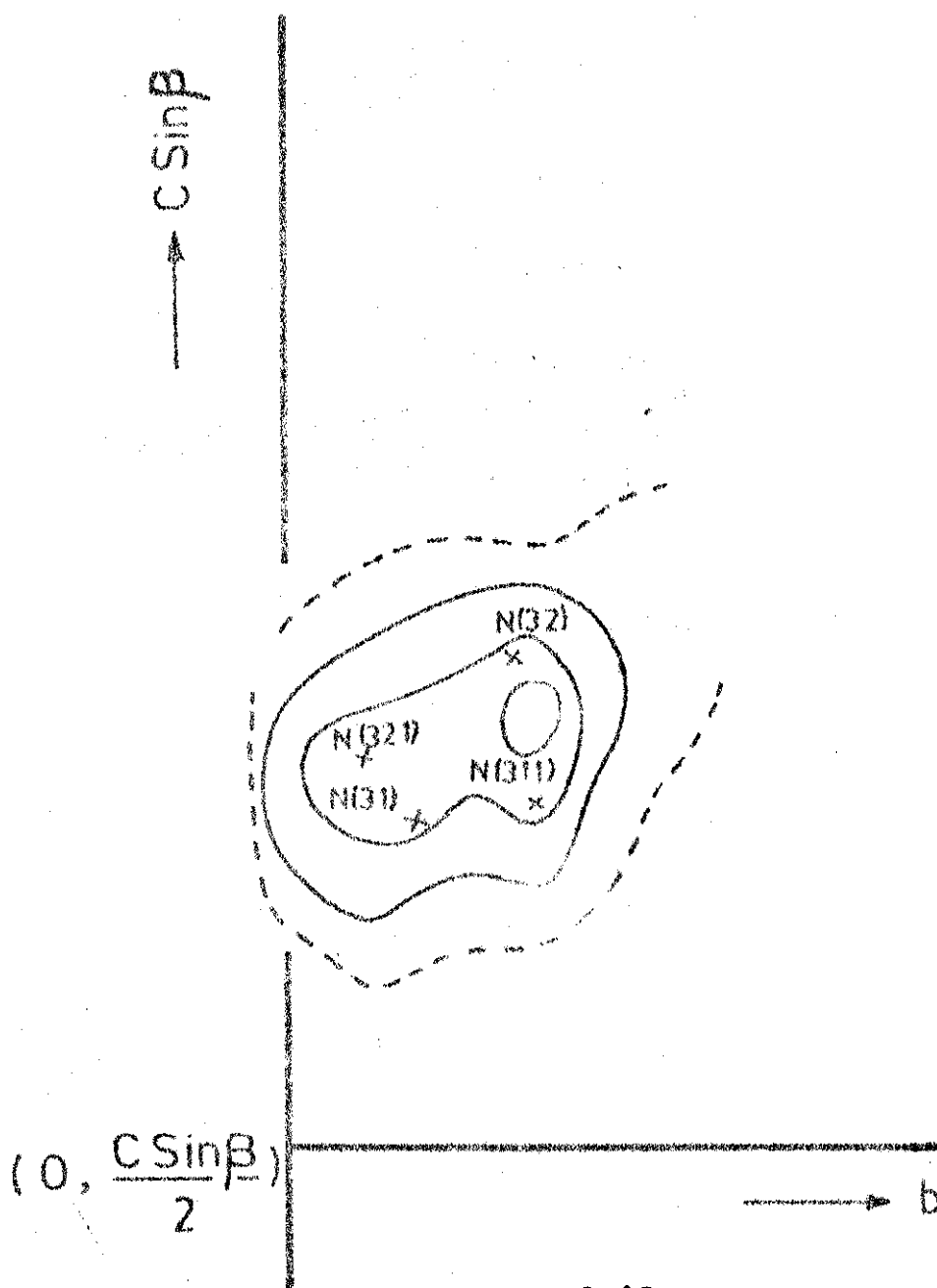
TABLE 2.8

Isotropic thermal parameters at the end of the
refinement, R = 0.146

<u>Atom</u>	<u>B(in Å²)</u>	<u>Atom</u>	<u>B(in Å²)</u>
C1	4.7	C25	5.4
C2	6.5	C26	6.2
C3	3.8	C27	5.7
C4	3.3	C28	6.7
C5	5.7	C29	6.5
C6	5.0	C30	5.9
N7	4.3	N31	10.6
N8	5.2	N32	13.5
C9	5.5	C33	6.1
C10	4.5	C34	7.1
C11	4.5	C35	6.1
C12	5.1	C56	5.2
C13	3.3	C37	5.0
C14	5.2		7.7
N15	4.8	H39	4.9
C16	4.3	C40	3.9
C17	4.5	C41	3.0
C18	3.4	C42	4.9
C19	4.6	C43	4.1
C20	3.3	C44	4.5
C21	3.6	C45	4.7
C22	4.4	C46	4.0
C23	5.0	C47	5.4
C24	6.2	C48	4.6

was 0.94 Å. Manual adjustment of this length in the course of the least-squares refinement was not effective, as the least-squares shifts always made it short again.

A difference Fourier map was now computed which distinctly revealed electron density distribution of about 2 electrons/Å³ in the neighbourhood of the -N(31)=N(32)- bond. This feature clearly suggested the possibility of disorder in that region. In order to analyse this further, another difference Fourier map was computed after removing the contributions of N(31) and N(32). Fig. 2.10 shows the composite electron density of this difference map. On the basis of this map, an alternate pair of positions could be fixed for N(31) and N(32). The two sets of positions for the nitrogen atoms have also been marked in Fig. 2.10. The new model was found to be the rotational conformer of the initial one about the line joining the atoms C(28) and C(33). To estimate the probability of occurrence of the two sets of positions of the nitrogen atoms N(31) and N(32), their positional occupancy factors were refined by least-squares technique. In four cycles of refinement, the occupancy factors refined to 0.7 for the original set of atomic positions and 0.3 for the new set fixed from the difference map. The least-squares calculations thus confirmed the



2.10

Composite difference electron density distribution in the region of the azo-bond of molecule B. The contours are at arbitrary intervals. The two sets of positions for N(31) and N(32) are indicated.

suspected positional disorder in the **neighbourhood** of the **aeo** bond in molecule **B**. The refined **occupancy** factors indicated that, in the unit cell, **70%** of **molecule B** had one type of **conformation** and the remaining **30%** had a different type of conformation, **one** being the rotational conformer of the other. The **N(31)** atoms of the two models were **1.00 Å** apart and the **N(32)** atoms were **1.03 Å** apart.

The crystal **structure** was further refined by including the molecular disorder in the **least-squares calculations**. Two sets of atomic **positions** with appropriate **occupancy** factors were used for the atoms **N(31)** and **N(32)**. With **this**, the total number of independent atoms in the asymmetric part of the unit cell was **50**. Hence, this set which included the disorder about the **aeo**-bond will hereafter be referred to as the **50 atoms set**. When the refinement converged, the **R**-value was **0.121** for **1071** observed reflections.

At this stage, *it was* felt that the aromatic **ring atoms connected** by this **considerably** disordered **ano**-bond could also be **disordered**. The picture of a **disordered** **azo**-bond connecting two perfectly ordered **phenyl** rings appeared to be physically less **meaningful**. Hence, another **difference** map was computed after removing the **contributions** of **N(31)**, **N(32)** and the

oarbon **atoms** of the phenyl **rings** connected by these nitrogen **atoms**. The difference electron density was very diffuse. Even though, **discrete** peaks **correspon-**ding to two sets of positions for the carbon atoms were not found, the diffuse nature of the density **allowed** the possibility of fixing a second set of atomic positions for all the ring atoms. Thus, the alternate **model which was** the rotational **conformer** of the earlier one was extended to the carbon atoms also and two **sets** of positions were assigned to fourteen atoms **C(25) through C(38)** including **N(31)** and **N(32)**. **Fig. 2.11 shows** the two rotational **conformers**. **Least-squares** refinement was done with an occupancy factor of 0.7 for the original set of positions and 0.3 for the new **set of positions**. This set corresponds to 62 independent **atoms** in the asymmetric part of the unit cell and will therefore be referred to as the **62 atoms set**. When the least-squares refinement converged, the **R-value** had reduced to **0.126**. The **R-value** for this **set** is slightly higher than the **value** 0.121 obtained for the **50 atoms set**. This is probably due to the **fact that** in the model fitted for the aromatic carbon atoms, the separations between the, alternate positions of the oarbon atoms were **exaggerated**, and hence were **artificial**. All further **discussion in this**

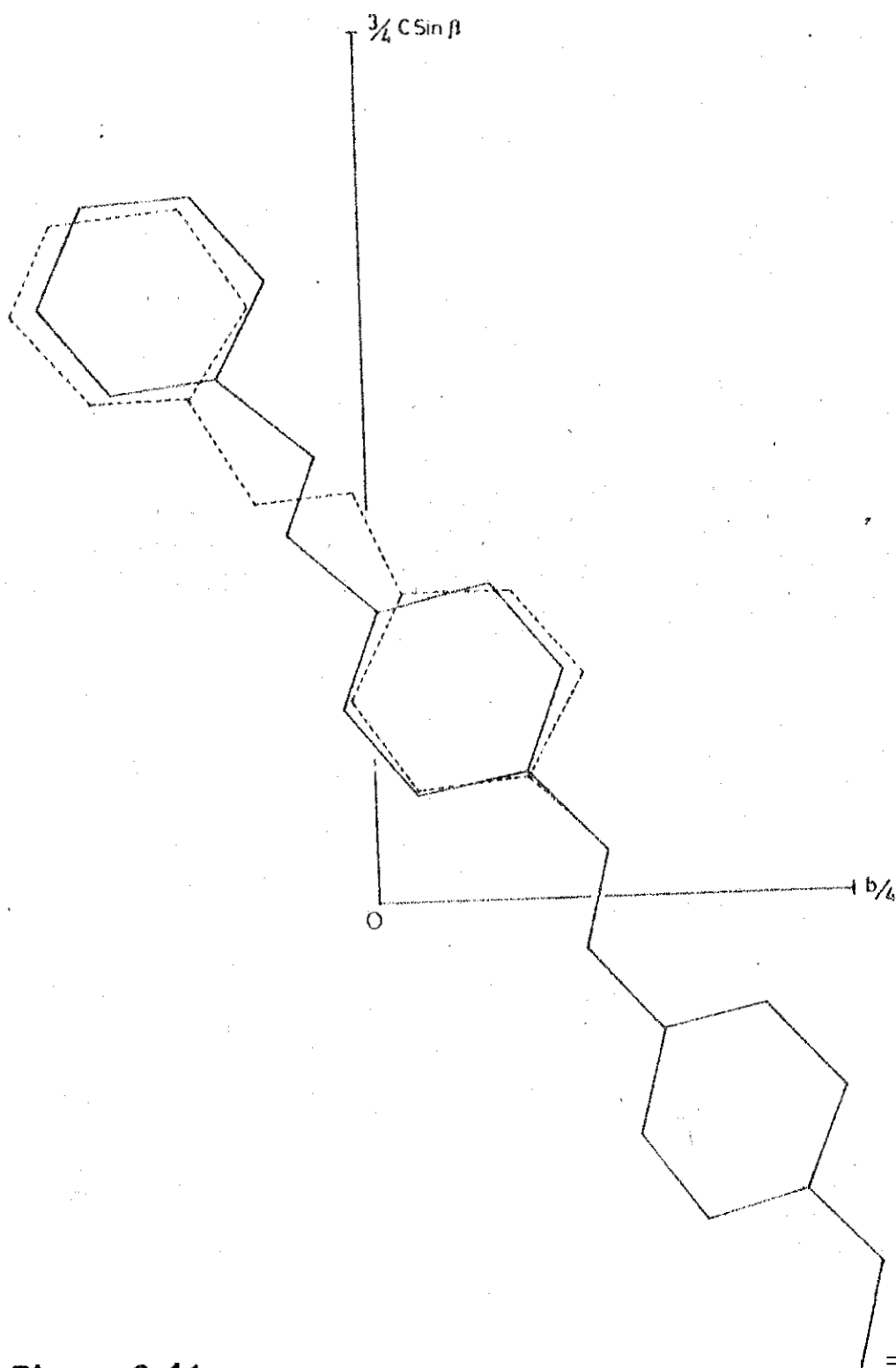


Figure 2.11

Molecule B of the 62 atoms set projected on the bc-plane. In the disordered region, the thick lines connect the positions with 0.7 occupancy and the dotted lines those with 0.3 occupancy.

chapter will mainly be with reference to the 50 atoms set.

Two striking effects of the introduction of disorder were (i) the increase in the length of the -N(31)=N(32) bond which was abnormally short earlier. (This bond length had increased to $1.31 \text{ \AA}$ in the 0.7 conformer and $1.28 \text{ \AA}$ in the 0.3 conformer.) and (ii) the high thermal parameters of some of the atoms of molecule B had decreased, the largest now being $8.0 \text{ \AA}^2$ for N(32), which was only about 1.6 times the average value for the rest of the structure.

It may now be mentioned that the molecule B in which positional disorder was found to occur was the one which could not be identified from the various Fourier and E-maps and for which atomic positions were fixed only from a trial model. The diffuse and ambiguous nature of the electron density observed for this molecule in the various maps was probably a result of the partial positional disorder.

Similar positional disorder about the -N=N- bond connecting two phenyl rings has been observed in the crystal structures of *p*-azotoluene [22], *trans*-azobenzene [23], the high temperature polymorph of ethyl *p*-azoxybenzoate [24] and *p*-azoxyanisole [25], a detailed account of which is given in Chapter 6 of this thesis. Hoekstra, Meertens and Vos [26] have

reported a similar type of disorder about the -C=C- bond connecting two phenyl rings in the crystal structure of stilbene.

2.5 Results and Description

The final positional and thermal parameters of all the atoms in the 50 atoms set are given in Table 2.9. The final positional and thermal parameters of the two sets of positions for the atoms C(25) through C(38) in the 62 atoms set are also included in this table. The observed and calculated values of structure factors for all the measured reflections are listed in Table 2.10. The interatomic distances and valency angles are shown in Fig. 2.12. Fig. 2.13 contains the interatomic bond lengths and angles for molecule B in the 62 atoms set. The estimated standard deviations of the molecular dimensions are generally high. The fractional positional parameters used in the calculation of bond lengths and valency angles were correct up to the sixth decimal place. However, they have been rounded off to the third decimal place in Table 2.9 because of the high standard deviations. The molecular dimensions in the disordered region differ considerably from the standard values. In particular, those involving the atoms C(28), C(33) and C(281), C(331) in

TABLE 2.9

Final fractional positional coordinates and thermal parameters; estimated standard deviations are given in parentheses

(a) 50 atoms set

MOLECULE A

Atom	x($\times 10^3$)	y($\times 10^3$)	z($\times 10^3$)	B ^{eq}
C(1)	917(4)	283(2)	-346(2)	5.2(0.9)
C(2)	1027(5)	259(2)	-323(3)	6.3(1.0)
C(3)	989(4)	221(1)	-245(2)	4.2(0.8)
C(4)	838(4)	212(1)	-196(2)	3.5(0.7)
C(5)	729(4)	236(1)	-218(2)	4.7(0.8)
C(6)	770(4)	273(2)	-296(2)	5.4(0.9)
N(7)	786(3)	174(1)	-117(2)	4.6(0.6)
N(8)	886(3)	153(1)	-99(2)	5.1(0.7)
C(9)	827(4)	117(1)	-18(2)	4.2(0.8)
C(10)	941(4)	93(1)	3(2)	4.4(0.8)
C(11)	908(4)	59(1)	82(2)	4.9(0.8)
C(12)	758(4)	48(1)	138(2)	5.1(0.9)
C(13)	645(4)	72(1)	117(2)	3.9(0.7)
C(14)	680(4)	107(1)	40(2)	5.2(0.9)
N(15)	706(3)	15(1)	220(2)	5.1(0.7)
C(16)	795(4)	-21(1)	235(2)	4.7(0.8)
C(17)	746(4)	-51(1)	322(2)	3.8(0.8)
C(18)	853(4)	-87(1)	334(2)	4.2(0.8)
C(19)	817(4)	-116(1)	418(2)	4.9(0.9)
C(20)	675(4)	-109(1)	487(2)	4.2(0.8)
C(21)	570(4)	-75(1)	474(2)	4.5(0.8)
C(22)	606(4)	-46(1)	389(2)	4.9(0.9)
O(23)	649(3)	-137(1)	567(2)	5.5(0.6)
C(24)	507(5)	-130(2)	643(3)	6.4(1.0)

continued

Table 2.9 continued

MOLECULE B

Atom	x(x10 ³)	y(x10 ³)	z(x10 ³)	B(Å ²)
C(25)	123(5)	-147(2)	600(3)	6.5(1.0)
C(26)	139(5)	- 89(2)	607(3)	6.7(1.1)
C(27)	161(5)	- 52(2)	530(3)	6.1(1.0)
C(28)	178(5)	- 80(2)	450(3)	6.5(1.0)
C(29)	173(5)	-134(2)	438(2)	6.0(1.0)
C(30)	140(5)	-172(2)	515(3)	6.7(1.1)
N(31)	202(5)	- 26(2)	388(3)	6.5(1.2)
N(32)	218(6)	- 44(2)	317(3)	8.0(1.3)
N(311)	216(11)	- 61(4)	348(6)	4.2(2.1)
N(321)	217(11)	- 7(4)	352(6)	5.4(2.4)
C(33)	238(5)	6(2)	252(3)	6.5(1.0)
C(34)	230(5)	64(2)	269(3)	7.2(1.1)
C(35)	244(5)	102 (2)	196(3)	6.2(1.0)
C(36)	269(4)	80(2)	110(2)	5.3(0.9)
C(37)	276(4)	21(2)	92(2)	5.3(0.9)
C(38)	259(5)	-14(2)	169(3)	7.2(1.0)
N(39)	273(3)	121(1)	40(2)	5.0(0.7)
C(40)	354(4)	108(1)	-45(2)	4.6(0.8)
C(41)	359(4)	149(1)	-116(2)	3.5(0.7)
C(42)	290(4)	203(1)	-99(2)	5.3(0.9)
C(43)	298(4)	237(1)	-171(2)	4.1(0.8)
C(44)	385(4)	221(1)	-262(2)	4.5(0.8)
C(45)	457(4)	169(1)	-284(2)	4.8(0.8)
C(46)	437(4)	134(1)	-209(2)	4.8(0.8)
O(47)	391(3)	261(1)	-328(2)	6.1(0.6)
C(48)	473(4)	249(2)	-425(2)	5.4(0.9)

continued

Table 2.9 continued

(b) 62 atoms set

MOLECULE B - Disordered Part

Atom	x($\times 10^3$)	y($\times 10^3$)	z($\times 10^3$)	B($\text{\AA}^2$)
C(25)	124	-145	603	5.0
C(26)	139	- 87	610	6.0
C(27)	160	- 51	536	4.5
C(28)	177	- 77	453	5.7
C(29)	171	-132	441	4.4
C(30)	141	-170	516	5.5
N(31)	201	- 26	385	6.9
N(32)	214	- 43	317	9.6
C(33)	236	4	250	5.6
C(34)	226	62	272	6.6
C(35)	240	100	198	5.3
C(36)	268	80	110	5.3
C(37)	275	22	90	5.2
C(38)	257	-14	167	7.0
C(251)	121	-152	586	6.7
C(261)	137	- 94	598	5.4
C(271)	156	- 59	513	6.3
C(281)	165	- 92	436	8.3
C(291)	156	-142	432	10.2
C(301)	129	-182	509	7.6
N(311)	215	- 59	345	4.8
N(321)	217	- 8	353	9.4
C(331)	238	17	263	8.7
C(341)	227	71	264	10.3
C(351)	244	110	193	8.1
C(361)	277	80	105	6.0
C(371)	286	21	95	5.9
C(381)	263	- 13	177	7.7

TABLE 2.10

The observed and calculated values of structure factors (x10)
for all the measured reflections of MBPAA.

0	K	0	22	111	108	8	-123	-158	1	K	-14	-11	-268	-291
			23	156	87	9	-269	-215				-7	-254	-239
			24	-150	-118	10	-360	-372	-5	-222	-180	-6	-231	-255
2	559	575				16	268	256				-4	280	274
4	-352	-312	0	K	4				1	K	-13	-3	-386	-302
6	-1498	-1309										-2	-443	-301
8	1072	993	0									-1	128	85
10	-520	-425	1	-306	-244	1	-336	-379	-4	-134	-113			
14	243	167	2	250	351	2	342	321	-2	-191	-140			
18	211	167	3	-53	-48	3	138	107						
			4	-309	-294	5	326	305	1	K	-12			
			5	-192	-150	6	223	196	-4	-254	-268	-17	-132	-153
0	K	1	6	-269	-223	7	-372	-372	-2	235	246	-16	-223	-191
4	-953	-870	7	367	334	8	171	158	0	605	548	-15	153	140
5	497	621	8	510	437	10	125	133				-14	-211	-215
6	518	473	10	825	689	11	127	121				-13	-143	-201
7	-345	-265	11	-309	-236	12	164	174	1	K	-11	-12	-160	-112
8	409	333	14	-114	-129	13	-111	-146				-9	-396	-354
9	866	689	17	-319	-248	15	-157	-137	-6	285	-252	-7	-242	-270
10	180	176	18	330	291	16	157	148	-2	-227	-263	-6	-287	-307
11	148	145	19	-175	-139	17						-5	-466	-440
13	83	51	20	-178	-144	18						-4	-321	-303
15	-226	-214	23	134	123				1	K	-10	-3	-330	-365
16	96	-103										-2	-271	-300
17	102	79	0	K	5	1	319	314	-9	-163	-150	-1	116	139
18	-127	-151	2	183	88	7	98	98	-4	-317	-293			
			3	-126	-83	8	-141	-136	-3	305	329			
0	K	2	4	-384	-363	9	-164	-156	-2	-280	-285			
1	-232	-190	5	-126	-126	13	174	144				1	K	-4
2	727	702	6	-69	-51	14	250	208				-17	-132	-111
3	-786	-918	7	442	341	15	209	195	-16	191	187	-11	-103	-150
4	-2680	-2799	8	-889	-727	17	-159	-179	-15	-136	-68	-10	-223	-231
5	-2431	-2397	9	1450	1307	18	111	75	-8	126	149	-8	96	100
6	-312	-294	10	207	242							-4	90	37
7	266	262	11	-420	-356	0	K	10	1	K	-8	-5	210	166
8	-150	-168	12	-180	-185	0	196	246				-4	81	110
9	86	134	13	138	111	1	239	229	-13	-187	-191	-3	471	434
10	178	166	14	-125	-170	4	-101	-126	-11	156	127	-7	657	466
12	-177	-143	15	-159	-122	6	102	86	-8	119	146	-1	358	320
13	-169	-164	17	-156	-130	8	-148	-152	-4	112	74		741	172
14	-108	-319	22			9	130	128	-1	-329	-336			
15	323	293							0	153	130			
16	224	203	0	K	6							-19	-429	-413
19	-134	-149	1	-203	-266				1	K	-7	-18	-131	-137
22	-138	-148	2	-489	-433	4	-213	-216				-17	-179	-192
			3	-147	-149	7	-188	-127	-17	-136	-114	-16	123	33
0	K	3	4	87	123	8	-220	201	-15	188	204	-13	324	280
1	-200	-247	5	692	633	13	195	169	-13	-181	-190	-12	-194	-178
2	-251	-248	6	-713	-631	14	-177	-115	-12	-248	-270	-11	-172	-149
3	401	476	7	305	257				-11	-147	-150	-10	-132	-123
4	-83	-95	8	-114	-68	0	K	12	-10	118	116	-9	156	144
5	-1298	-1140	10	138	114	0	110	33	-7	434	402	-8	388	411
6	-318	-298	12	94	56	3	-192	-175	-9	155	156	-7	627	680
7	448	401	13	-221	-245	4	208	229	-6	130	120	-6	96	117
8	184	189	14	-296	-307	5	-193	-187	-4	-390	-295	-5	-157	-113
9	-221	-241							-3	-250	-239	-4	-383	-410
10	257	208	0	K	7				-1	-143	-122	-3	336	280
11	369	308	1	-132	-137					140	112	-2	361	400
12	403	392	3	-254	-300	3	329	310				-1	152	218
13	-665	-598	4	966	929	5	159	128	1	K	-6			
19	155	159	6	-215	-205	9	-111	-92	-13	173	133	-16	-336	-310
				-83	-50				-12	-144	-168	-13	130	161

9	447	514	-12	215	261	-7	125	152	-11	-173	-202	-2	119	118
10	-366	-399	-11	-119	-172	-1	-543	-450	-10	-154	-165	-1	-517	-498
11	-224	-246	-10	-509	-512				-9	-168	-174	0	62	81
12	193	190	-9	-1069	-1072	2	K	10	-8	364	398			
13	-432	-395	-8	387	377	-2		334	273	-7	-147	-177	3	K
14	184	152	-7	91	87	-1		-217	-217	-5	159	187	-1	
15	-190	-192	-6	-105	-135	0		-217	-190					
16	-151	-154	-5	-171	-160									
			-4	-187	-109	2	K	11	-14	-112	-95	-16	-310	-329
2	K	1	-3	-319	-289	-15			-12	-324	-395	-15	-102	-90
			-2	-642	-580	-13		-156	-127	-11	-274	-295	-12	-222
-12	-154	-116				-4		-239	-241	-4	-227	-242	-11	-86
-10	-95	-68	2	K	6	-2		-304	-304	-3	-260	-276	-10	83
-8	521	431								-2	-158	-152	-9	112
-7	-187	-153	-20	-156	-150								-8	76
-6	440	348	-19	-220	-195	2	K	12	3	K	-5		-7	-203
-5	-610	-577	-18	-315	-323	-6		-260	-226	-12	-198	-219	-6	-137
			-15	-291	-261	-5		-258	-209	-11	-163	-185	-5	-159
2	K	2	-14	-281	-303					-9	-227	-261	-4	-578
			-13	-136	-152	2	K	13		-7	-171	-172	-3	-706
-12	197	240	-12	-487	-514	-5				-6	753	727	-2	-130
-11	-239	-277	-11	-467	-483					-5	305	271	-1	130
-10	-159	-170	-9	-183	-176	2	K	14		-4	137	117		
-9	-96	-140	-7	-162	-378	-5		-154	-171	-3	169	141	3	-448
-8	-435	-374	-6	-134	-158	-4		-217	-234	-2	-206	-164	2	-139
-7	-584	-503	-5	-90	-56	-2		154	80	-1	-231	-205	1	-373
-6	-156	-150	-4	-328	-331								0	-606
-5	3085	2656	-3	-190	-236	2	K	14					0	418
-4	-3239	-3190	0	248	258	0		220	266	3	K	-4	5	-248
-3													4	-340
-2	1245	1153											3	426
			2	K	7								2	-490
2	K	3	-15	-251	-268	3	K	-12	-17	196	210	10	165	-523
			-13	-331	-296	-1		-218	-218	-15	-218	-235	11	155
-13	232	225	-12	-185	-176					-13	-253	-281	12	180
-12	-258	-310	-11	-112	-110	3	K	-11	-10	-262	-242	13	-103	-55
-9	287	327	-8	-151	-169					-8	154	156	14	-132
-8	-360	-343	-7	-579	-531	-5		210	179	-7	-362	-338	15	112
-7	78	24	-6	980	894	-3		138	112	-5	-100	-79		142
-6	142	170	-5	600	505	-1		-196	-176	-4	-373	-344	3	K
-5	560	493	-4							-3	-329	-341	1	
-4	-1290	-1065				3	K	-10		-1	401	369		-88
-3	-492	-309	2	K	8					0	-78	-111	-16	89
-2	1419	1092											-15	109
			-17	220	229	-8		-179	-178	3	K	-3	-14	283
2	K	4	-15	300	180	-6		114	60				-13	333
			-14	356	361	-3		-331	-358	-19	196	193	-12	403
-19	-315	-299	-12	-193	-214	-2		389	391	-18	-253	-259	-11	451
-18	-219	-205	-9	-215	-244					-13	-100	-153	-8	289
-14	159	169	-8	-241	-230	3	K	-9		-12	298	291	-7	-169
-13	-236	-215	-7	-164	-179					-10	-158	-183	-6	-594
-12	-171	-192	-6	-112	-80	-10		179	146	-8	-145	-151	-5	-274
-11	-178	-235	-5	-220	-242	-9		-179	-108	-6	135	191	-4	-164
-10	169	129	-4	-438	-405	-4		-173	-213	-4	-173	-161	-3	
-9	460	447	-3	-210	-231					-3	-335	-365		
-8	-958	-925	-2	-253	-297	3	K	-8		-2	-493	-422	3	K
-7	815	794	-1	-145	-129	-7		265	260	-1	-619	-561	-12	-239
-6	-232	-206	0	236	296	-6		-321	-342				-11	-92
-4	229	281											-10	654
			2	K	9								-9	-389
2	K	5	-14	302	289	3	K	-7	-14	-123	-118	-7	211	229
-15	200	221	-12	249	222	-13		263	245	-9	-116	-111	-6	205
-13	-239	-180	-8	-183	-140	-12		194	170	-4	-83	-66	-4	-1128
										-3	189	162	-3	336

3	K	3	-3	190	271	3	K	11	-13	-284	-280	-7	-278	-192	
-22	-147	-162	-2	43	68	-20	134	109	-12	197	190	-6	-250	-213	
-21	-149	-134	-1	-78	-69	-4	-145	-204	-9	-183	-228	-5	-261	-215	
-13	-151	-174	0	-41	-66	-2	-142	-192	-5	96	64	-4	-143	-183	
-9	-166	191	3	K	7	3	K	12	4	K	-3	4	K	2	
-340	-350	-173	-18	-173	-161	3	K	12	4	K	-3	-15	95	104	
-348	-339	-229	-17	-229	-255	-7	-289	-278	-16	169	182	-11	187	215	
-316	-330	100	-16	100	21	-4	154	219	-15	166	202	-10	267	229	
-232	-219	241	-15	241	260	3	K	13	-9	-187	-189	-9	657	619	
-99	-141	-143	-14	-143	-119	-5	102	140	-11	-175	-204	-8	-198	-196	
300	349	-161	-12	-161	-135	-4	192	226	-9	95	120	-7	-183	-108	
3	K	4	-7	169	151	-3	102	151	-7	106	182	-6	-254	-275	
-17	-164	-171	-5	-137	-103	3	K	14	-2	-194	-184	-5	-489	-508	
-15	182	198	-4	-237	-222	-2	149	189	-19	209	220	-14	-91	-85	
-14	-216	-209	-3	-194	-217	0	-209	-277	-18	-209	-214	-11	-257	-271	
-13	-208	-206	-2	-302	-324	3	K	8	-17	169	145	-10	381	361	
-10	182	218	-1	-99	-157	-2	0	-209	-11	194	231	-9	-238	-299	
-9	-406	-450	3	K	8	0	0	-209	-4	114	164	-8	350	373	
-8	489	511	-17	-182	-222	4	K	-9	-4	-1314	-1297	-6	-207	-191	
-6	-299	-284	-16	-297	-252	-7	-209	-242	0	-1314	-1297	-5	168	154	
-3	86	21	-15	-482	-468	-4	-209	-166	4	K	-1	-4	133	223	
-2	-79	-114	-14	-170	240	4	K	-8	-19	-159	-179	4	K	4	
-1	-64	-62	-13	-164	-204	4	K	-8	-18	-159	-179	-20	156	133	
0	583	557	-12	-225	-232	4	K	-8	-7	157	164	-19	-108	-20	
3	K	5	-11	125	126	4	K	-8	-6	152	245	-15	-97	-123	
-21	154	167	-9	208	220	-6	207	151	-6	-164	-219	-14	128	164	
-18	169	216	-8	83	119	-5	-210	-218	-5	-384	-322	-13	-87	-103	
-17	411	398	-6	-149	-117	4	K	-7	-4	-171	-168	-10	-302	-324	
-16	237	231	-5	73	67	-12	-209	-158	-3	-364	-292	-9	267	322	
-15	-158	-170	-4	-231	-252	-9	-369	-378	-2	207	260	-8	188	144	
-14	-114	-167	-3	85	45	-8	353	387	-1	4	K	0	-7	-642	-685
-13	-158	173	0	-67	-64	-4	114	77	4	K	0	-6	-300	-229	
-12	-149	-182	3	K	9	-3	113	99	0	-203	-40	-5	-382	-429	
-11	-201	-167	-3	147	172	4	K	-6	0	-132	-162	-4	-247	-207	
-10	505	568	-15	179	173	4	K	-6	1	387	316	4	K	5	
-9	-361	-475	-13	243	271	4	K	-6	2	771	937	-18	152	152	
-8	430	461	-10	-127	-127	-11	-118	-135	4	166	196	-11	269	290	
-7	-229	-240	-9	-125	-97	-10	-286	-273	5	-406	111	-9	247	228	
-6	-114	-181	-6	-203	-205	-9	183	192	6	-59	-73	-8	-238	-284	
-5	180	139	-5	272	237	-5	188	141	7	139	153	-7	192	113	
-4	487	435	-3	-93	-117	-4	-254	-261	8	-68	-71	-6	268	142	
-2			-2	-182	-220	-4			9	180	143	-5	-392	-494	
3	K	6				4	K	-5	10	-111	-135	-3	54	67	
-21	169	217	-16	106	106	-13	289	218	11	-115	132	-2	-116	-184	
-20	297	246	-15	-149	-163	-12	-286	-269	13	-207	-223	-1	-104	-101	
-17	128	103	-12	201	204	-11	-114	-143	14	193	192				
-16	125	141	-11	138	160	-5	252	220	15	126	176	4	K	6	
-14	-335	387	-9	172	189	-3	-159	-156	16						
-11	279	284	-7	92	125										
-10	-220	-206	-8	-99	-72	4	K	-4	-12	106	127	-20	156	145	
-9	-217	-231	-7	156	-176	-17	-209	-171	-11	134	119	-19	219	254	
-8	693	639	-6	-102	-147	-16	-299	-189	-10	116	87	-18	168	87	
-7	-314	-286	-3	-130	-156	-15	-293	-265	-9	85	52	-17	-106	-102	
-6	-177	-215	-2	199	-233	-15	255	239	-8	-178	-144	-15	-444	-458	
-5	340	378	-1	-244	-300	-14						-13	-92	-45	
-4	-231	-335	0												

Molecule A

Molecule B

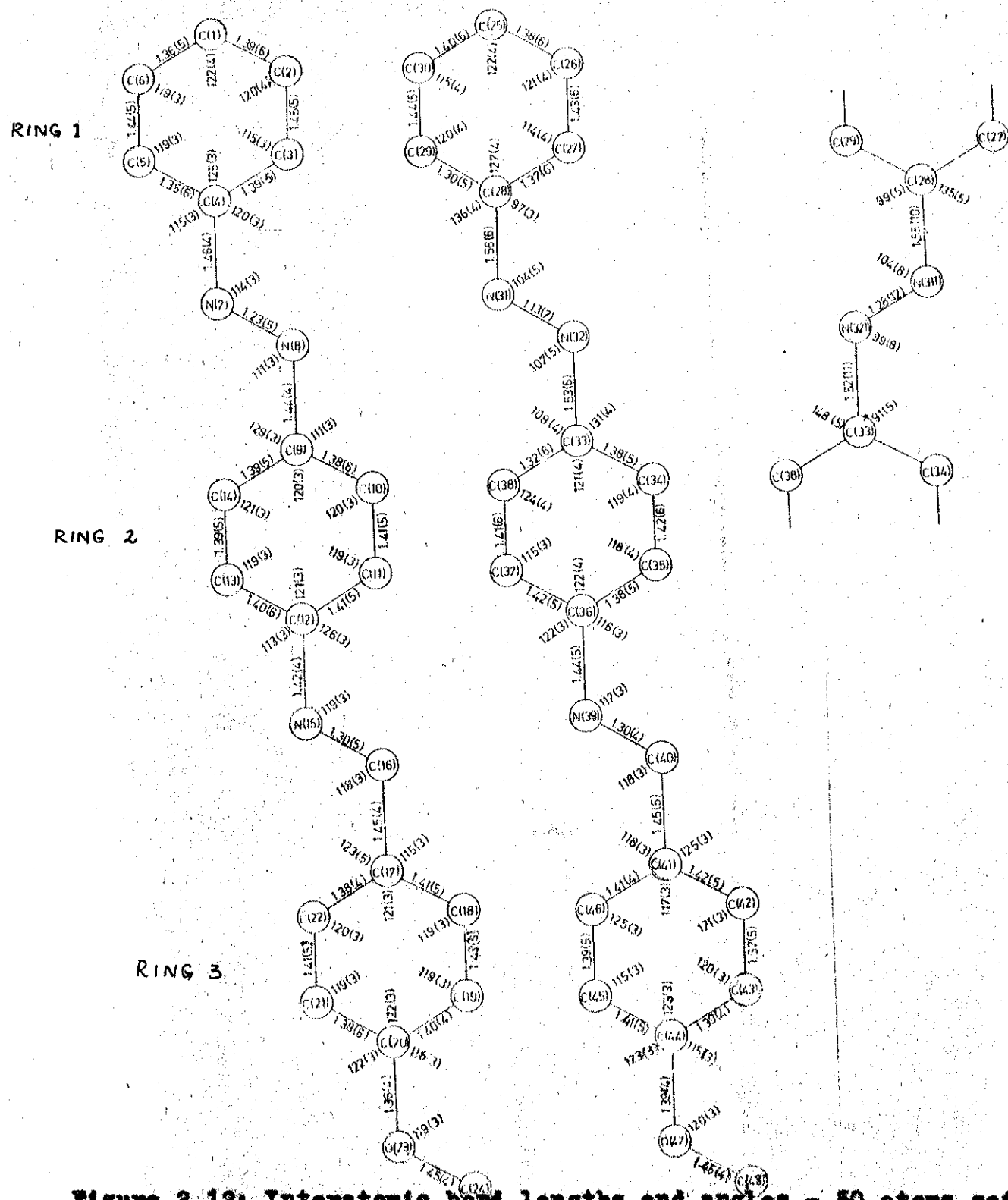
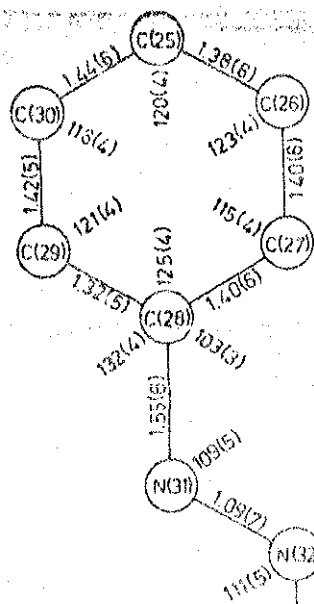
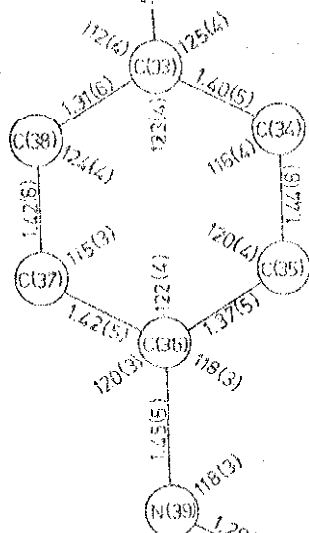


Figure 2.12: Interatomic bond lengths and angles - 50 atoms set.

RING 1



RING 2



RING 3

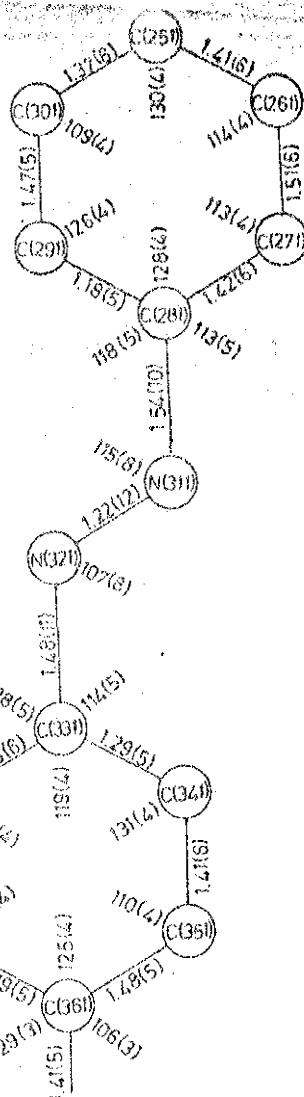
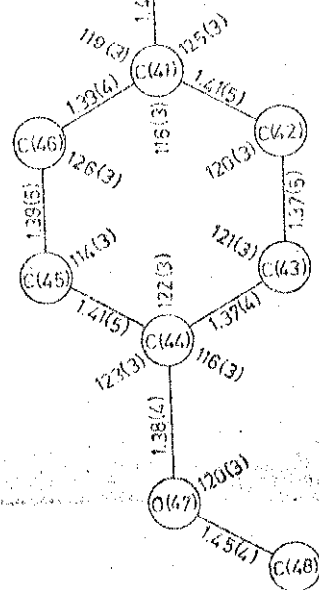


Figure 2.13

Interatomic bond lengths and angles - molecule B of 62 atoms set.

the 62 atoms set are strikingly unusual. The widely different valency angles at C(28), C(281) and C(33), C(331) may be attributed to the fact that even though the separations between N(31) and N(311), and N(32) and N(321) are about $1\frac{1}{4}\text{\AA}$, the pairs of carbon atoms C(28) and C(281), and C(33) and C(331) are quite close. This leads to a strained molecular geometry at C(28), C(281), C(33) and C(331). Similar unusual molecular dimensions have been reported by Krigbaum and Taga (24) in the crystal structure of the high temperature polymorph of ethyl-p-azoxybenzoate where a similar type of disorder has been observed. However, in MBPAA, the molecular dimensions in the disordered region cannot be considered reliable because the cross terms which show the correlation between an atom and its disordered counterpart, have not been included in the least-squares refinement. Therefore, any further discussion on these dimensions is not meaningful. The dimensions of molecule A and the rest of molecule B are normal, within the limits of experimental error.

The least-squares planes through the various groups of atoms in the structure were calculated with respect to an orthogonal set of axes using a programme written by Dr. M. Vijayan for the IBM 360/44 computer, based on the method of Blow [27]. Table 2-11 gives the equations of the various mean planes and the

TABLE 2.11

Equations of the various least-squares mean planes and displacements A in Å of atoms from them.

Mean Plane Number	Atoms defining the mean plane	Equation of the mean plane
(i)	C(1), C(2), C(3), C(4), C(5), C(6)	$0.21135x + 0.77961y + 0.58952z = 3.72199$
(ii)	C(9), C(10), C(11), C(12), C(13), C(14)	$0.22894x + 0.80248y + 0.55102z = 3.90547$
(iii)	C(17), C(18), C(19), C(20), C(21), C(22)	$0.50753x + 0.77503y + 0.37648z = 5.46470$
(iv)	C(4), N(7), N(8), C(9)	$0.21530x + 0.77128y + 0.59898z = 3.67597$
(v)	C(12), N(15), C(16), C(17)	$0.53930x + 0.71791y + 0.44019z = 6.10616$
(vi)	C(25), C(26), C(27), C(28), C(29), C(30)	$0.96972x - 0.08803y - 0.22778z = 2.97884$
(vii)	C(33), C(34), C(35), C(36), C(37), C(38)	$0.97078x + 0.02672y - 0.23846z = 2.84521$
(viii)	C(41), C(42), C(43), C(44), C(45), C(46)	$0.91248x + 0.40483y + 0.05902z = 3.88093$
(ix)	C(28), N(31), N(32), C(33)	$0.97102x - 0.04601y - 0.23453z = 2.86409$
(x)	C(36), N(39), C(40), C(41)	$0.89052x + 0.44530y + 0.09318z = 3.91563$
(xi)	C(28), N(31), N(32), C(33)	$0.97586x - 0.02056y - 0.21744z = 2.97822$

continued

Table 2.11 continued

Mean plane number	Atom	Displacement Δ in Å
(i)	C(1)	0.001
	C(2)	-0.001
	C(3)	0.004
	C(4)	-0.007
	C(5)	0.006
	C(6)	-0.003
	N(7)	0.036
	N(8)	0.045
(ii)	C(9)	0.011
	C(10)	0.002
	C(11)	-0.009
	C(12)	0.003
	C(13)	0.009
	C(14)	-0.017
	N(7)	-0.063
	N(8)	-0.051
(iii)	N(15)	-0.003
	C(16)	0.341
	C(17)	-0.015
	C(18)	0.006
	C(19)	0.003
	C(20)	-0.003
	C(21)	-0.005
	C(22)	0.014
(iv)	N(15)	-0.166
	C(16)	-0.075
	O(23)	-0.035
	C(4)	-0.012
(v)	N(7)	0.012
	N(8)	0.011
	C(9)	-0.012
	C(12)	-0.032
(vi)	N(15)	0.032
	C(16)	0.031
	C(17)	-0.031
	C(25)	-0.018
(vii)	C(26)	0.037
	C(27)	-0.025
	C(28)	-0.007
	C(29)	0.026
	C(30)	-0.013
	N(31)	-0.048
	N(32)	-0.035
	N(311)	0.062
	N(321)	-0.034

Table 2.11 continued

Mean plane number	Atom	Displacement Δ in Å
(vii)	C(33)	0.005
	C(34)	0.005
	C(35)	-0.012
	C(36)	0.011
	C(37)	-0.002
	C(38)	-0.006
	N(31)	-0.041
	N(32)	-0.065
	N(311)	-0.018
	N(321)	0.032
	N(39)	-0.084
	C(40)	0.472
(viii)	C(41)	-0.011
	C(42)	-0.020
	C(43)	0.033
	C(44)	-0.016
	C(45)	-0.014
	C(46)	0.028
	N(39)	0.036
	C(40)	-0.024
	O(47)	-0.034
(ix)	C(28)	-0.009
	N(31)	0.009
	N(32)	0.011
	C(33)	-0.010
	N(311)	0.088
	N(321)	0.046
(x)	C(36)	0.001
	N(39)	-0.001
	C(40)	-0.001
	C(41)	0.001
(xi)	C(28)	-0.039
	N(311)	0.044
	N(321)	0.035
	C(33)	-0.039
	N(31)	-0.005
	N(32)	-0.032

displacements of atoms from these planes. The aromatic rings and the azo groups in the structure are planar. In molecule A, the angle between the plane normals of rings 1 and 2 is 3° , and ring 3 is inclined to rings 2 and 1 by 19° and 21° respectively. The corresponding values for the molecule B are 7° , -28° and -33° respectively in the 50 atoms set. Bigs. 2.14a and 2.14b show the perspective view of the MBPAA molecules in the 50 atoms set. Fig. 2.14c is the perspective view of the disordered molecule B in the 62 atoms set. In each case, the molecule has been projected on We mean plane of ring 1. The ring numbering is shown in Big. 2.12.

Packing: The arrangements of the molecules in planes perpendicular to a- and c-axes are shown in Fig. 2.15 and Fig. 2.16 respectively, The crystallographically independent molecules are differentiated by the thick and the thin lines. For the sake of clarity, the disordered part of molecule B with 0.3 occupancy has been omitted from these packing diagrams. The crystallographically independent molecules A and B form the nearest neighbours in the structure and have a separation of about $5\text{\AA}$ along the a-direction (Fig. 2.15). They are oriented antiparallel to each other. The slightly overlapping phenyl rings in molecules A and B are not oriented parallel but are inclined to one

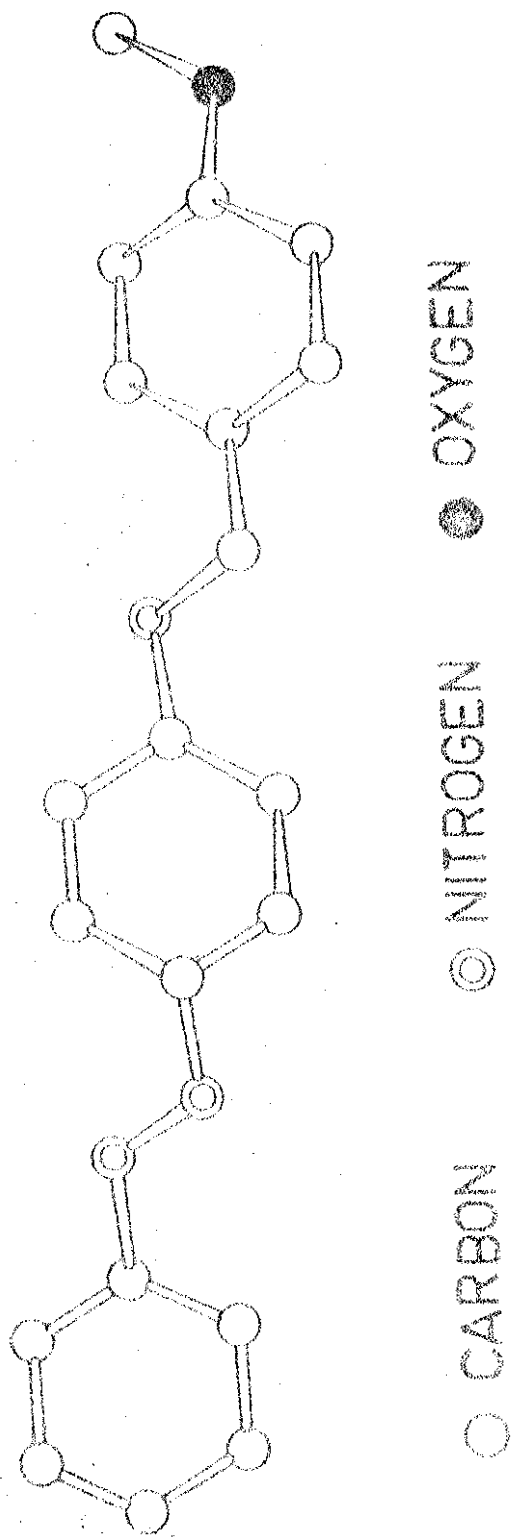
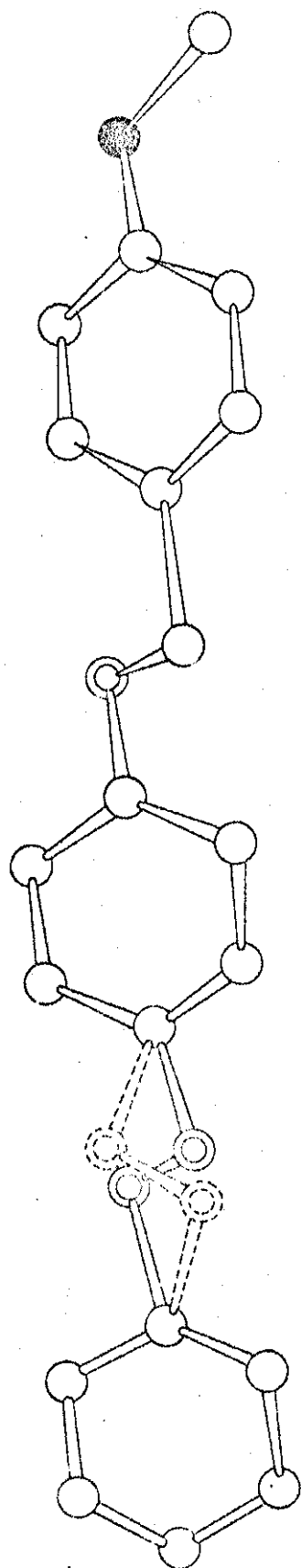


Figure 2.14(a)

Perspective view of molecule A as seen normal to the mean plane of ring 1.



○ CARBON ⊙ NITROGEN ● OXYGEN

Figure 2.14(b)

Perspective view of molecule 3 (50 atoms set) as seen normal to the mean plane of ring 1.

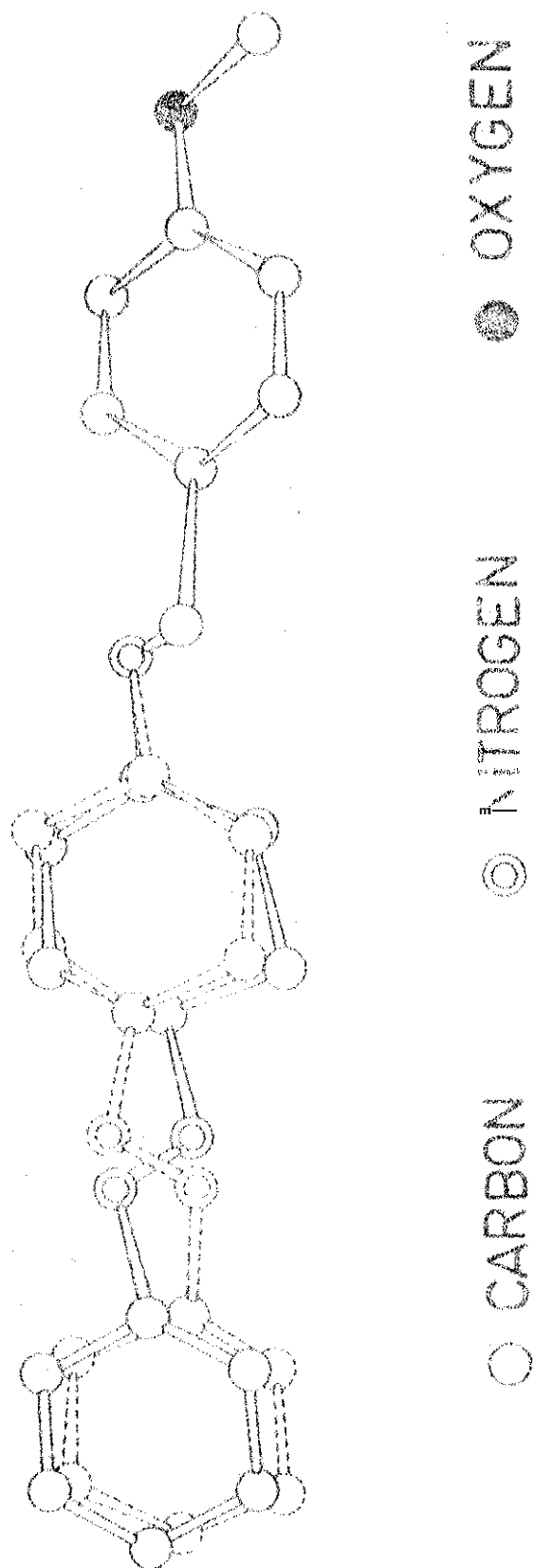


FIGURE 2.14(c)

Perspective view of molecule B (62 atoms set) as seen normal to the mean plane of ring 1 with 0.7 occupancy. In the disordered region, thick lines connect the positions with 0.7 occupancy and the dotted lines those with 0.3 occupancy.

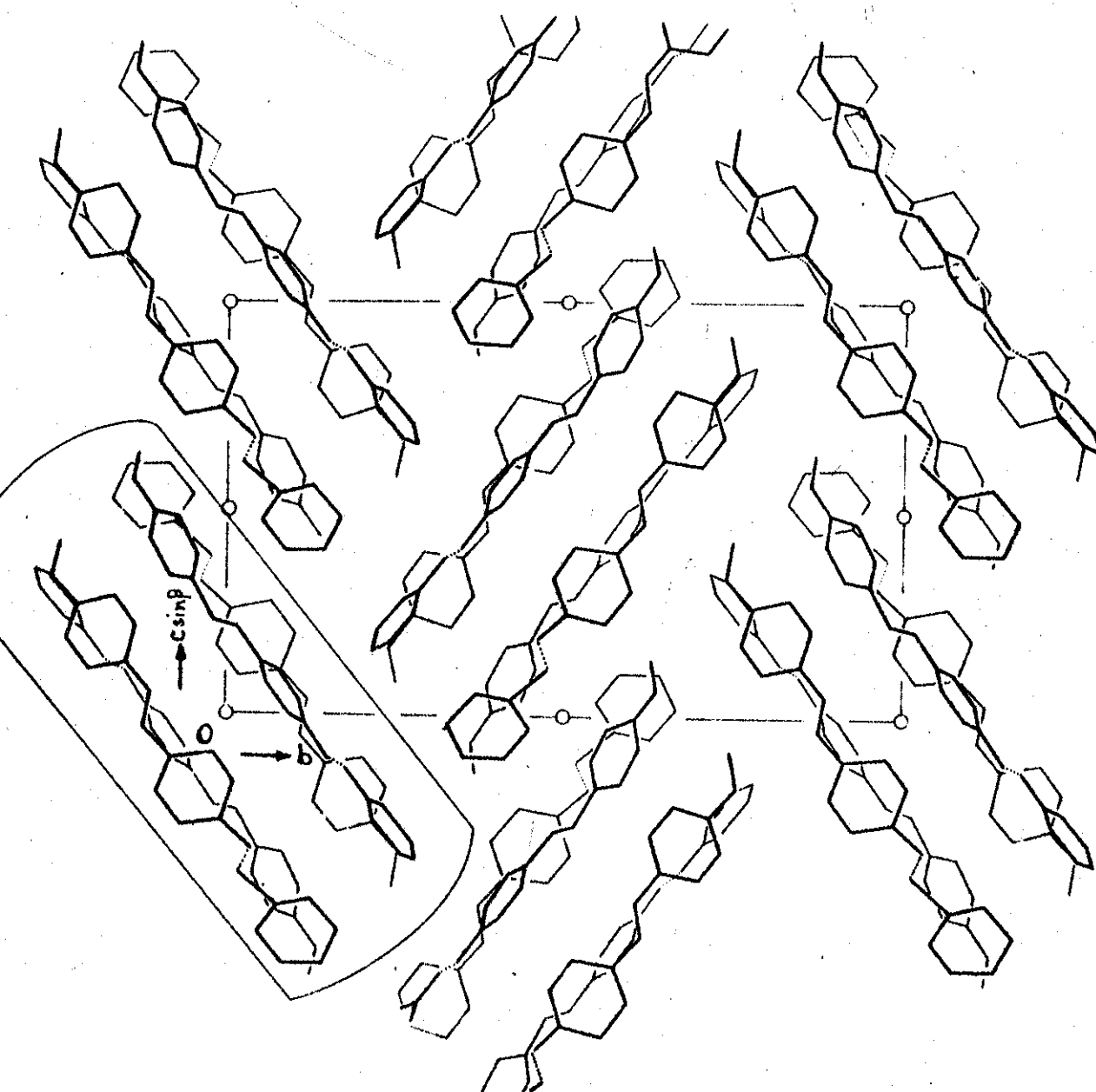


Figure 2.15

Molecular arrangement in the bc -plane. The dotted lines represent the $-N=N-$ bond. The basic quadruple molecular unit used for describing the packing has also been indicated. In the disordered region only the positions with 0.7 occupancy have been marked.

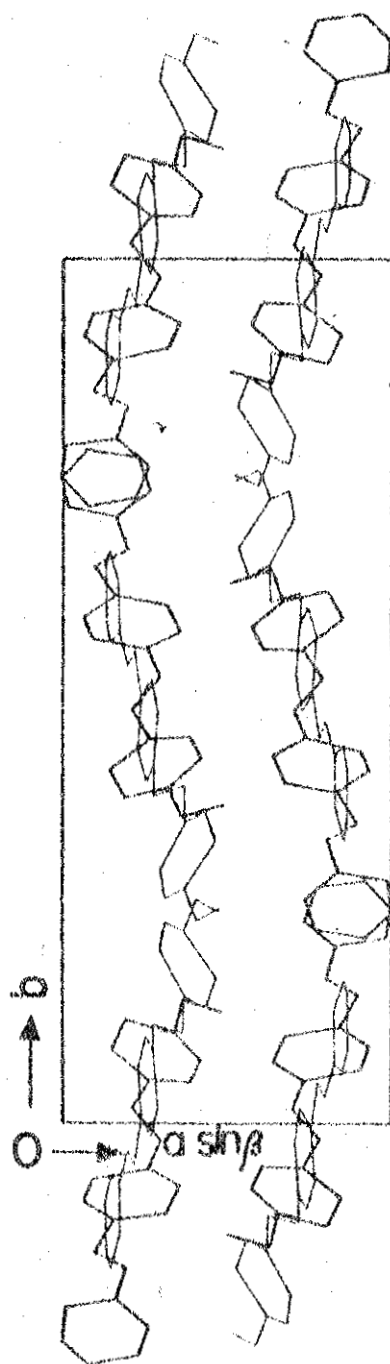


Figure 2.16

Molecular arrangement in the sib-plan0. In the disordered region only the positions with 0.7 occupancy have been marked.

another, the inclination being 58° at one end, changing to 99° near the molecular centre and becoming 108° at the other end. The angles between the various plane normals are tabulated in Table 2.1 2. To describe the packing of the molecules in the crystal, it is convenient to consider the crystallographically independent molecules, and their symmetry equivalents, generated by a centre of inversion at the origin, as one unit. This unit has been indicated in Fig. 2.15. The two pairs of molecules in this quadruple unit are oriented antiparallel to each other. The quadruple unit is inclined to the c-axis by about 55° . Hence, the neighbouring units related by the o-cell translation are so displaced that the end of one unit falls near the centre of the neighbouring unit, forming an infinite column of quadruple molecular unit arranged in an imbricated fashion along the o-axis. According to Gray [28], the Imbricated arrangement of molecules in the crystalline phase is the basic packing arrangement required for the nematic behaviour of the substance, and the crystal structures of most of the nematogenic compounds determined so far exhibit this type of packing arrangement in their respective crystalline states [25, 29, 30, 31, 32]. Along the b-direction, adjacent imbricated columns are related by the 2_1 screw and the c-glide. The molecular units in adjacent columns are

TABLE 2.12

Angles between the normals of the various mean planes
defined in Table 2.11

Serial numbers of the, mean planea	Angle between the plane normals in degrees
1 , 2	3
1 , 3	21
1 , 4	1
2 , 3	19
2 , 4	3
2 , 5	20
3 , 5	5
6 , 7	7
6 , 8	-33
6 , 9	2
6 , 11	4
7 , 9	4
7 , 11	3
7 , 8	-28
7 , 10	-31
8 , 10	3
1 , 8	57
1 , 10	54
1 , 7	-85
2 , 10	53
2 , 7	-84
2 , 9	-87
2 , 11	-85
2 , 6	-89
2 , 8	56
3 , 6	-70
3 , 7	-65
3 , 9	-68
3 , 11	-67
4 , 8	57
4 , 10	54
4 , 7	-85
5 , 9	-67
5 , 11	-65
5 , 7	-64
5 , 6	-69

inclined to each other by about 70° and form a herringbone-like pattern. Similar herringbone type of molecular packing has been found in the crystal structure of the nematogens benzylidene aniline-p-carboxylic acid [31], and 2,2'-dibromo-4,4'-bis-(p-methoxybenzylidene amino) biphenyl [32], and the smectogens CBOOA (Chapter 3 of this thesis) and the high temperature polymorph of ethyl p-azoxybenzoate [24]. Along the a-direction, the molecular arrangement consists of an alternate antiparallel stacking of the A and the B type of molecules extending infinitely.

In the structure, the methoxy end group of each molecule is oriented in the direction of the $-N=CH-$ group of a neighbouring molecule. This feature, viz., the methoxy or the ethoxy group of one molecule pointing towards a nitrogen atom in the central region of its neighbouring molecule, has also been observed in the crystal structures of 4,4'-azodiphenetole [30], anisaldehyde-azine [29] and p-azoxyanisole [25], which are also nematogenic.

The three-dimensional crystal structure is stabilised by non-bonded van der Waals forces between molecules. Table 2.13 lists all the intermolecular contact distances less than the sum of the van der Waals radii, in the 50 atoms set. All the contacts

TABLE 2.13

Intermolecular contact distances less than
the sum of the van der Waals radii

C(3)a - C(18)b	3.56 Å
C(5)a - C(45)a	3.57 Å
C(17)a - C(46)c	3.53 Å
C(17)a - C(45)c	3.58 Å
C(21)a - C(22)d	3.59 Å
C(22)a - C(45)c	3.49 Å
C(26)a - C(34)e	3.43 Å
C(29)a - C(45)c	3.59 Å

a : x, y, z ; b : $\bar{x} + 2$, $\bar{y}$, $\bar{z}$
c : $\bar{x} + 1$, $\bar{y}$, $\bar{z}$; d : $\bar{x} + 1$, y, $\bar{z} + 1$
e : $\bar{x}$, $\bar{y}$, $\bar{z} + 1$

are between carbon atoms, the average value being 3.54 Å. The structure has 106 contact distances less than 4 Å and none of them is abnormally short.

Molecule A is surrounded by 14 neighbouring molecules with contact distances less than 4 Å, whereas, molecule B has only 12 neighbours. However, in the 50 atoms set, the number of contacts less than 4 Å is the same for both the molecules, the number being 106. On the other hand, in the 62 atoms set, molecule A has 154 contacts less than 4 Å, as compared to 188 for molecule B. This feature could be attributed to the exaggerated separations between the two sets of positions for the carbon atoms of molecule B in the 62 atoms set, resulting in an artificially increased volume. This, in turn, would cause molecule B to have a larger number of contacts with the neighbouring molecules, compared to molecule A. This artificial increase in the volume of molecule B is found to result mainly in an increase in the number of contacts between this molecule and its own symmetry equivalent neighbours. Thus, the number of contacts for molecule A in the 62 atoms set is only about 25% more than that in the 50 atoms set, whereas, for molecule B, the number of contacts in the former set is about 75% more than that in the latter set.

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