

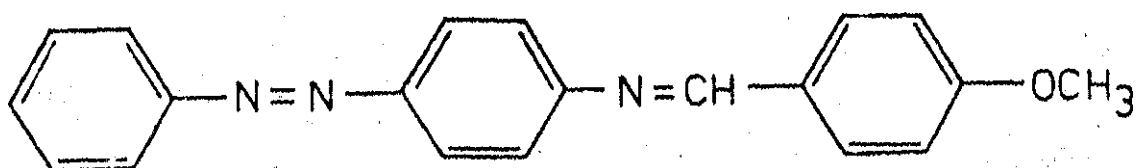
CHAPTER 6

STUDIES ON PARTIAL POSITIONAL DISORDER IN SOME AZO AND AZOXY COMPOUNDS

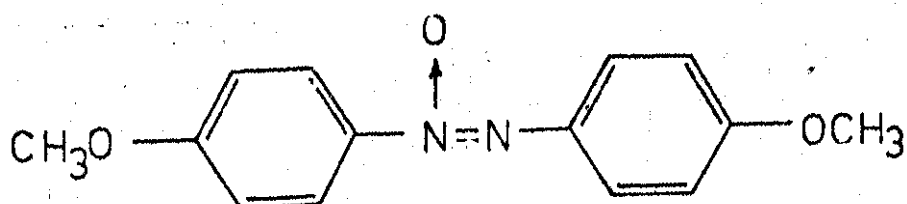
6.1 Introduction

A detailed **analysis** of the positional disorder observed in one of the **independent** molecules in the **crystal** structure of the nematogen **n-p-methoxybenzylidene p-phenyl azoaniline** (MBPAA) has been described in chapter 2. A Literature survey revealed that similar partial positional disorder about azo or azoxy bonds connecting two phenyl **rings also occur** in the **crystal structures** of a few other compounds, both mesogenic and non-mesogenic. We have **investigated in detail** the occurrence of disorder in four crystal structures, **viz.**, MBPAA (chapter 2), **p-azoxyanisole (PAA)**, **trans-azobenzene**, and **p-azotoluene**; **the** first two compounds are **mesogenic**, while the other two **are not** (Fig. 6.1). The **disorder** is about **an azoxy** bond in the crystal structure of PAA and about an **azo** bond in **the** others.

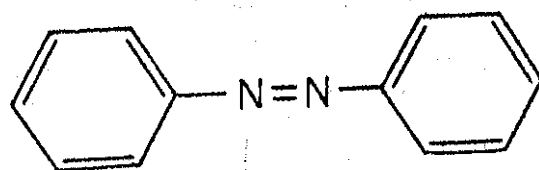
The procedure adopted in this analysis was **(i)** to detect the presence of disorder from electron density maps **(ii)** to determine the relative probability of **occurrence** of the two **rotational conformers**, which give rise to the



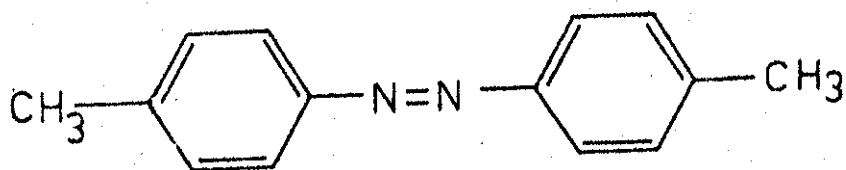
n-p-Methoxybenzylidene p-phenyl azoaniline (MBPAA)



p-Azoxyanisole (PAA)



trans-Azobenzene



p-Azotoluene

FIGURE 6.1.

disordered structure, by **least-squares calculations**, and (iii) to refine the crystal structure by the least **squares** technique after including the **structural** disorder with appropriate weight. It appeared **logical** to expect that if the positional disorder in these crystal structures **was** genuine, **the inclusion of disorder** should reduce the crystallographic R-factor defined as
$$\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$
 The details of the electron density maps and least-squares **calculations** are given in the ensuing sections. In three **crystal** structures out of the four studied by **us**, the disorder was detected from the electron density map and in **p-azotoluene**, the coordinates of the disordered structure were **already** available in literature.

6.2 **Least-squares** refinement

(a) **MBPAA**: Section 2.4 describes the least-squares refinement **including** the disorder **in** the crystal structure of MBPAA. In this **structure**, partial disorder **occurs** about the azo bond of one of the two **crystallographically** independent molecules in the **asymmetric** part of the unit cell. The R-**value** before **including** the disorder in the

refinement was 0.146. From a **difference** electron density map, distinct alternate positions corresponding to two rotational **conformers** were found for the **azo** nitrogen atoms of one of the crystallographically independent molecules. Subsequent **least-squares** refinement of the **occupancy factors** of the two sets of positions yielded the values 0.7 and 0.3 respectively. With this clear evidence for the **simultaneous** occurrence of two rotational **conformers**, two types of refinement were undertaken.

(i) Two sets of positions were **considered** for the two **azo** nitrogen atoms, **assigning** the **occupancy factors** 0.7 and 0.3 respectively. This set **consisted** of 50 independent atomic positions in the **asymmetric part** of the unit cell. Block diagonal least-squares refinement of the positional and thermal **parameters** of this set reduced the R-value to 0.12

(ii) The **aromatic** carbon **atoms** connected by the azo bond were **also assigned** two **sets** of positions based on a diffuse **difference** electron density **distribution**. The two **sets** of **carbon positions** were assumed to have the same occupancy factors, *viz.*, 0.7 and 0.3, **as** the disordered nitrogen atoms. This set had 62 **independent** atomic positions in the asymmetric part of the unit **cell**. When the **least-squares** refinement converged, the R-value had reduced to 0.126 for this set. The R-value for both the sets **were** lower than the initial value of 0.146. The final results of the **refinement** and details of molecular dimensions

have already been presented in Chapter 2.

(b) p-Azoxyanisole (PAA): Krigbaum et al [1] have analysed the crystal structure of the nematogen PAA (Fig. 6.2). They have reported the existence of two extraneous peaks in their final difference Fourier map in the vicinity of the azoxy group. They suggest that the structure is slightly disordered as the result of a small percentage of the molecules entering the crystal with the azo bond reversed, so that the nitrogen atoms occupy an alternate set of positions. This type of disorder would also explain the presence of the two extra peaks in the difference Fourier map. However, no further published results of any refinement including this partial disorder are available. An examination of the atomic parameters of PAA revealed that the azoxy nitrogen atoms had slightly higher thermal parameters compared to the rest of the atoms. The values of the equivalent isotropic temperature factors [2] for N(9) and N(10) were $6.47 \pm 0.15 \text{ \AA}^2$ and $6.73 \pm 0.18 \text{ \AA}^2$ respectively, whereas the average for the rest of the molecule was $8.64 \pm 0.15 \text{ \AA}^2$.

At the beginning of our investigations on PAA, a difference map was computed using the reported coordinates of Krigbaum et al [1]. This map was found to contain two peaks of height $\sim 0.5 \text{ e.\AA}^{-3}$ in the plane of the

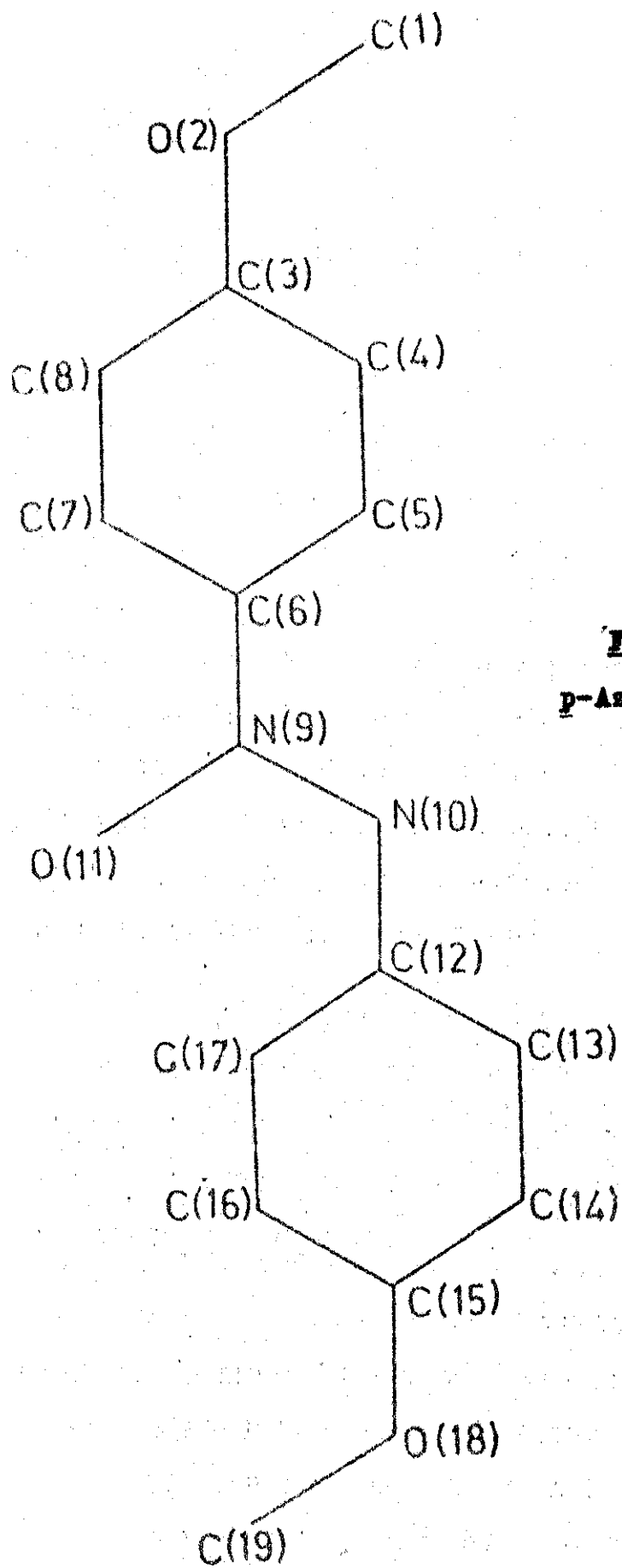


Figure 6.2
p-Azoxyanisole
(PAA)

azoxy group, similar to what has been reported by Krigbaum et al [1]. Another molecular model, which is a rotational conformer of the original model could be fitted so that the nitrogen atoms occupied the peak positions obtained from the difference Fourier map. In Fig. 6.3, the original molecule and the positions of the two new peaks are shown. N(91), N(101) and N(92), N(102) are the original and new positions of the nitrogen atoms respectively. The oxygen atom O(11) is bonded to N(91) in the original model. It is interesting to note that no extra peak corresponding to an alternate position for the oxygen atom was found in the map. The nitrogen atom N(102) was so situated that it could be bonded to O(11). The oxygen atom is thus common to both the conformers.

At this stage, the occupancies of the four positions N(91), N(101), N(92) and N(102) were refined by the least-squares procedure, starting with an initial value, of 0.5 for each of them. In this calculation, the reported anisotropic thermal parameters U_{ij} 's for the non-hydrogen atoms were converted to equivalent isotropic temperature factors, B, using the expression given by Hamilton [2]. The occupancies of the original and the new sets of positions refined to values 0.80 ± 0.02 and 0.20 ± 0.02 respectively. Four more cycles of block-diagonal least-

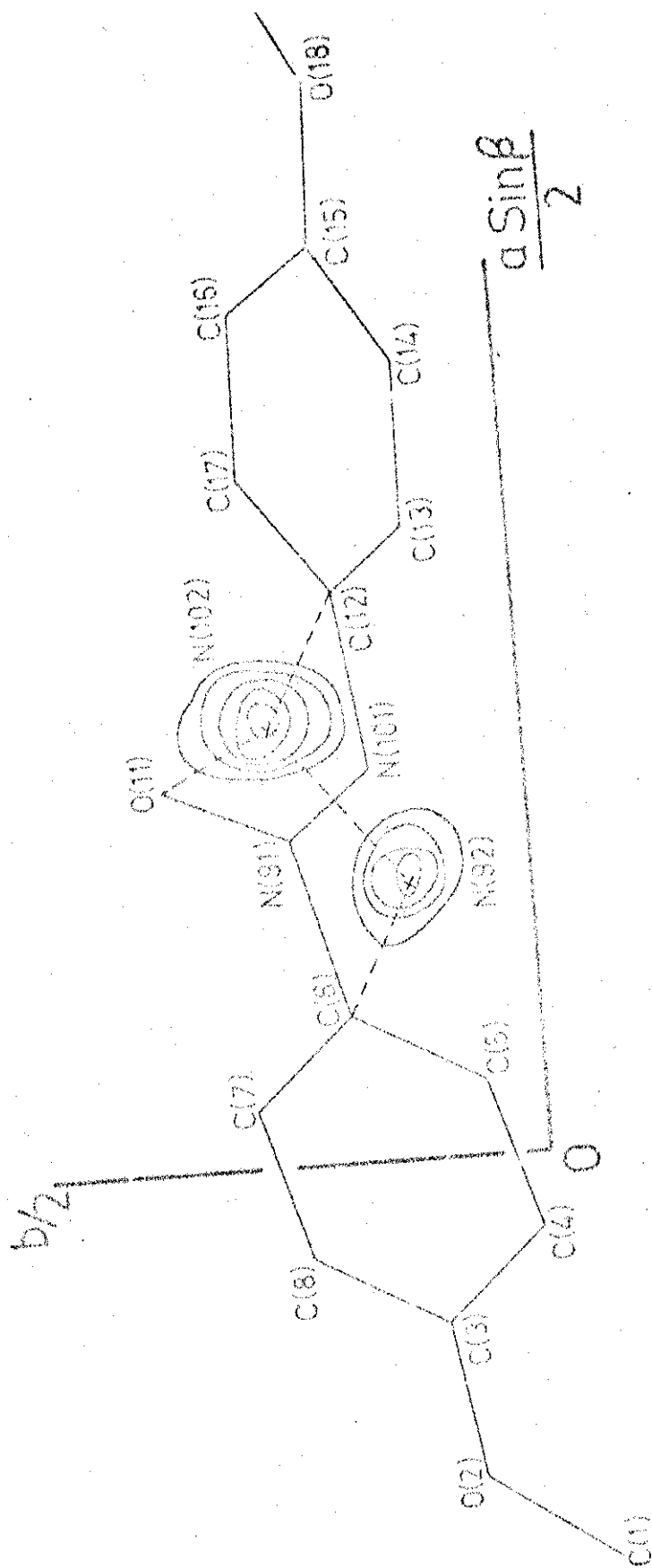


Figure 6.3: The original PAA molecule along with the two peaks from the difference Fourier map. N(91), N(101) and N(92), N(102) are the original and the new positions of the nitrogen atoms respectively.

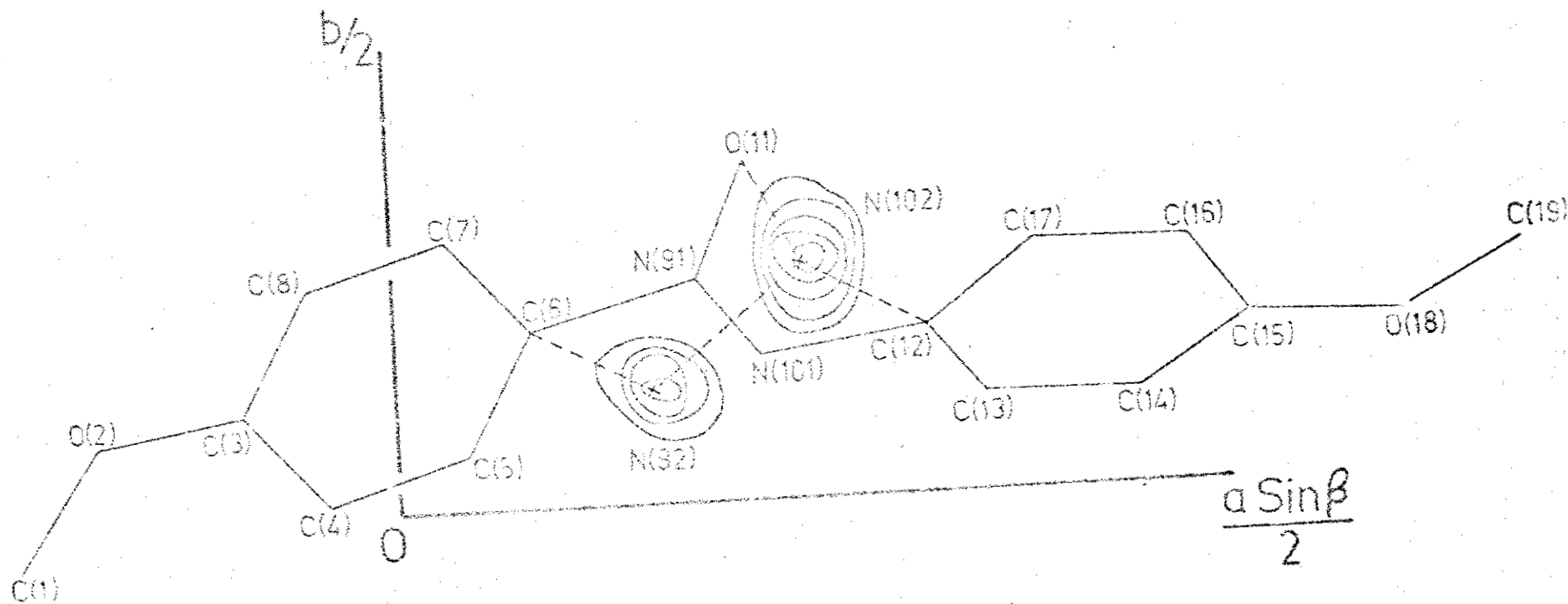


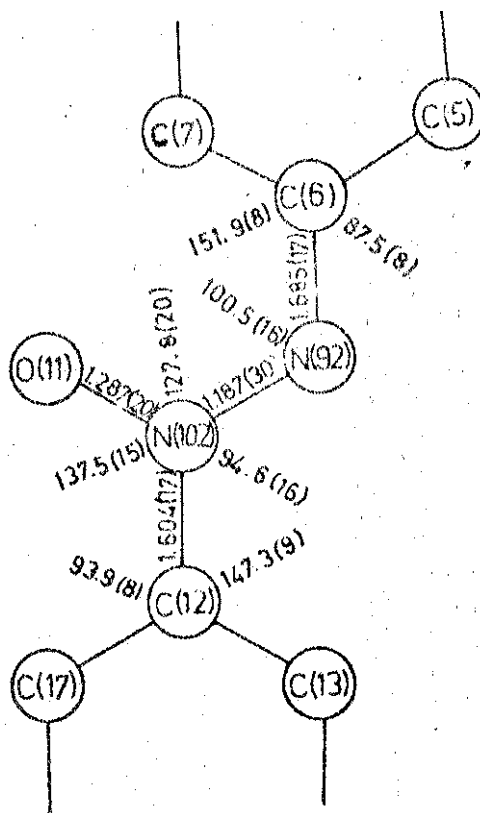
Figure 6.3: 2ke original PAA molecule along with the two peaks from the difference Fourier up. N(91), N(101) and N(92), N(102) are the original and the new positions of the nitrogen atoms respectively.

anisoanis refinement were carried out assigning these occupancy values to the two sets of nitrogen atoms. Isotropic thermal parameters were assigned to the nitrogen atoms and anisotropic thermal parameters for the rest of the non-hydrogen atoms. Hydrogen atoms were included in the structure factor calculations but their coordinates were not refined. The R-value had reduced from the reported value [1] of 0.091 to 0.075 at the end of the refinement

The final positional and thermal parameters of all the non-hydrogen atoms are listed in Table 6.1. Fig. 6.4 shows the bond lengths and angles. Since alternate positions for the carbon atoms of the phenyl rings connected by the azoxy group have not been considered in the above treatment, the external valency angles at C(6) and C(12) are distorted. Also, since the least-squares refinement did not include the correlation between an atom and its disordered counterpart, the atomic parameters as well as the molecular dimensions in the disordered region are less accurate. At the end of the refinement, the isotropic temperature factors for all the four nitrogen atoms were lower than the initial values; the average being $4.19 \text{ \AA}^2$, compared to the initial equivalent B values of $6.47 \text{ \AA}^2$ and $6.73 \text{ \AA}^2$ for N(9) and N(10) respectively.

Table 6.1: The final positional and thermal parameters ($\times 10^4$) of non-hydrogen atoms of PAA.
Estimated standard deviations are given in parentheses.

Atom	x	y	z	B (in $\text{\AA}^2$) or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	-2334(4)	-464(8)	4867(6)	67(3)	232(10)	162(7)	-25(5)	51(4)	-20(7)
C(2)	-943(3)	1142(6)	5461(5)	59(3)	149(7)	127(5)	6(3)	45(3)	-9(5)
C(4)	-435(4)	173(7)	6556(5)	64(3)	185(8)	124(5)	2(4)	43(3)	-1(5)
C(5)	497(4)	566(7)	7332(5)	70(3)	206(9)	113(5)	9(4)	38(3)	-5(6)
C(6)	898(4)	1914(6)	6993(5)	60(3)	184(8)	134(5)	-14(4)	47(3)	-60(5)
C(7)	384(4)	2863(7)	5894(6)	71(3)	175(8)	167(7)	-9(4)	55(4)	-2(6)
C(8)	522(4)	2482(7)	5138(6)	72(3)	176(8)	153(6)	0(4)	47(4)	-14(6)
C(12)	3297(4)	1853(7)	9488(5)	63(3)	189(8)	130(5)	4(4)	40(3)	-34(6)
C(13)	3633(4)	1059(7)	10719(6)	74(3)	197(9)	152(6)	-12(4)	54(4)	-19(6)
C(14)	4563(4)	1072(7)	11533(5)	74(3)	196(9)	131(6)	-7(4)	45(4)	-6(6)
C(15)	5195(4)	1832(6)	11129(5)	63(3)	143(7)	110(5)	-7(3)	37(3)	-15(5)
C(16)	4874(4)	2619(7)	9910(5)	75(4)	200(9)	120(5)	-8(4)	46(3)	-8(6)
C(17)	3924(5)	2635(8)	9107(5)	83(4)	229(10)	105(5)	-18(5)	35(4)	10(6)
C(19)	6795(4)	2435(8)	11635(6)	70(3)	229(11)	160(7)	-16(5)	49(4)	-13(7)
N(91)	1863(3)	2398(6)	7719(4)	3.99(7)					
N(101)	2324(4)	1538(6)	8778(5)	4.47(8)					
N(92)	1900(13)	1427(24)	8301(19)	4.20(32)					
N(102)	2405(13)	2446(23)	8195(18)	4.10(30)					
O(2)	-1847(3)	885(5)	4615(4)	59(2)	216(7)	156(5)	-0(M)	37(2)	23(5)
O(11)	2201(3)	3605(5)	7321(4)	84(3)	177(6)	166(5)	-25(M)	49(3)	37(4)
O(18)	6107(3)	1734(5)	12014(4)	64(2)	231(7)	130(4)	-13(M)	35(2)	4(4)

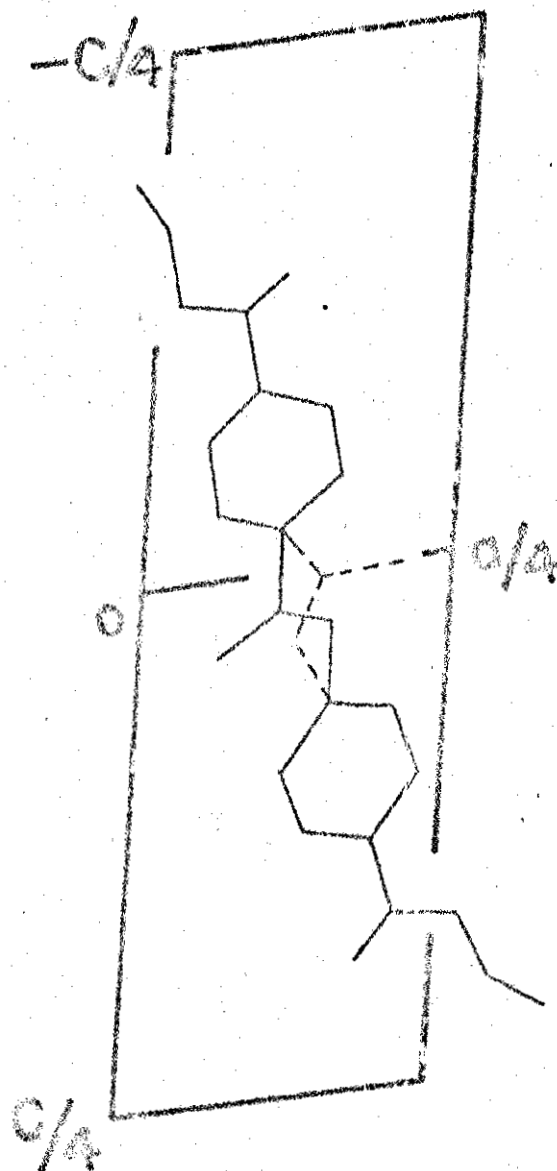
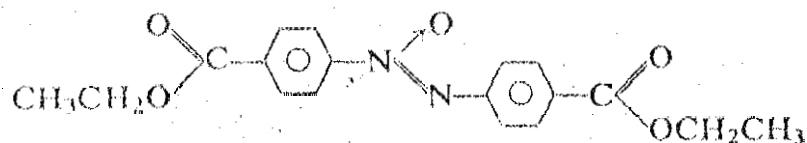


The final interatomic band lengths and angles of PAA.

As mentioned earlier, the difference electron density map did not contain any extra density corresponding to an alternate position for the oxygen atom. In the set corresponding to 0.8 occupancy for the nitrogen atoms, O(11) is bonded to N(91) whereas in the other set corresponding to 0.2 occupancy for the nitrogen atoms, O(11) is bonded to N(102). Thus, the oxygen atom in the azoxy group is bonded to different nitrogen atoms in the two sets. This feature is in contrast to what has been found in the crystal structure of the high temperature polymorph of the smectogen ethyl *p*-azoxybenzoate [3] (Fig. 6.5), where a similar disorder occurs about the azoxy bond of the molecule. Unlike the disorder in the structure of PAA, in ethyl *p*-azoxybenzoate, the oxygen atom of the azoxy group is also disordered in addition to the nitrogen atoms. The two positions of the oxygen atom are on either side of the -N=N- bond and thus the oxygen atom always remains attached to the same nitrogen atom in the group (Fig. 6.5).

(c) trans-Azobenzene: Brown [4] has analysed the crystal structure of trans-azobenzene. This compound crystallizes in the space group $P2_1/a$. There are four molecules in the unit cell with each molecule lying on a centre of symmetry. There are thus, two non-equivalent pairs of molecules in the unit cell and one half of each

Figure 6.5: The two sets of positions for the azoxy group of atoms in the high temperature polymorph of the smectogen ethyl-p-azoxybenzoate.



kind comprises the contents of the asymmetric unit. The two non-equivalent azobenzene moleculea centred at $(0,0,0)$ and $(0,0,\frac{1}{2})$ in the asymmetric part of the unit cell are indicated in Fig. 6.6, along with the atom numbering scheme.

The atoms of the molecule centred at $(0,0,\frac{1}{2})$, viz., C(7) to C(12) and N(2), were found to have appreciably larger thermal parameters compared to the corresponding atoms of the other molecule. The standard deviations of the atomic coordinates were also larger for the atoms of the molecule at $(0,0,\frac{1}{2})$ (molecule 2), compared to those of the molecule at $(0,0,0)$ (molecule 1). Brown [4] suggests that the higher temperature factors of molecule 2 are probably due to the presence of disorder, with the molecule occupying more than one position. But no published results of any further investigations concerning the presence of disorder are available.

At the beginning of our investigations, a difference Fourier map was computed using the reported coordinates of Brown [4]. In the region of the ago-bond of molecule 2, an electron density peak was found in the map. The difference density distribution in the region occupied by the rest of the molecule was very insignificant. The difference map peak and its centrosymmetric equivalent were found to be situated on either side of

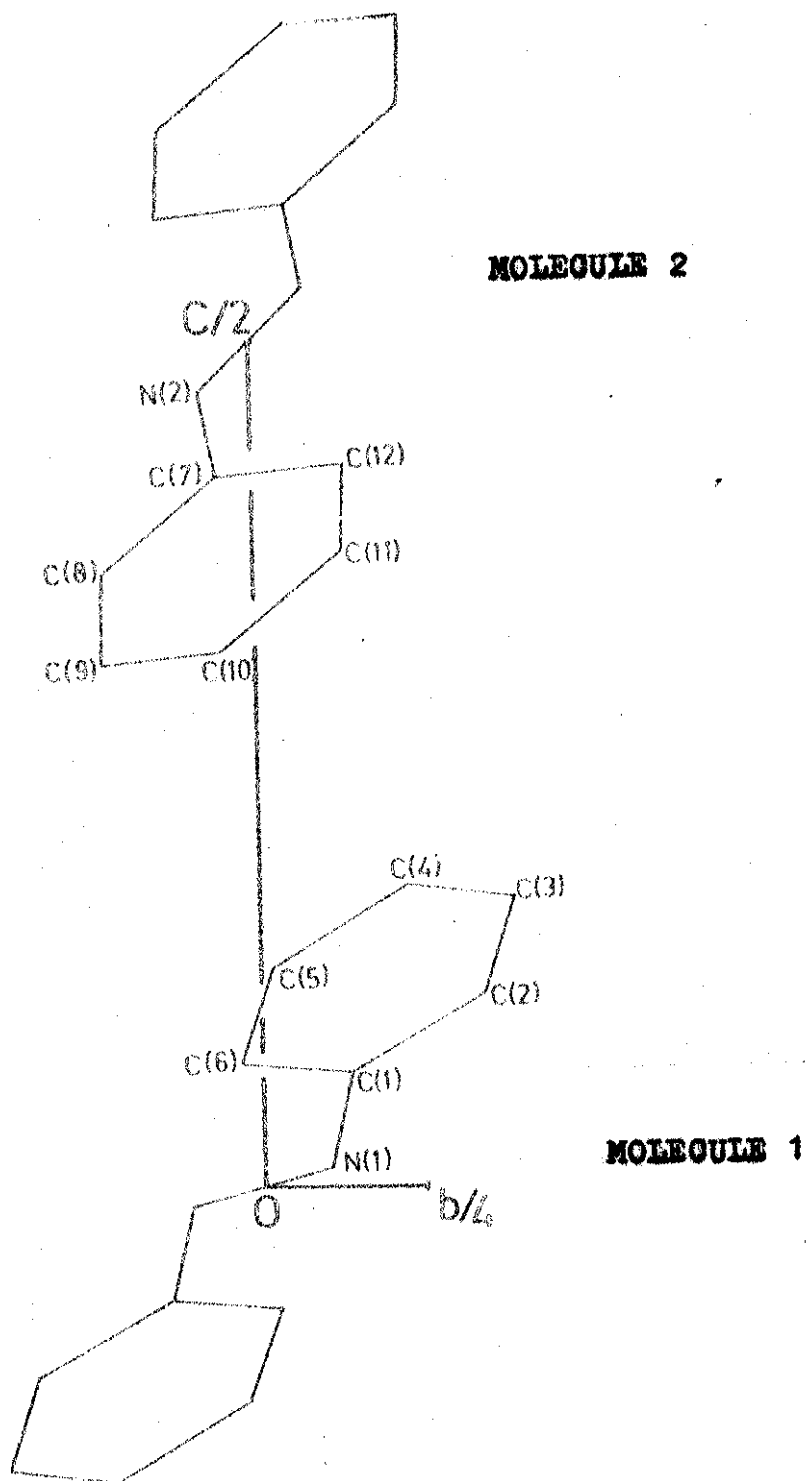


Figure 6.6: Me two non-equivalent trans-azobenzene molecules centred at $(0,0,0)$ and $(0,0,\frac{1}{2})$.

the **-N=N-** bond of molecule 2 (Fig. 6.7) and clearly indicated the alternate positions for N(2) and its centrosymmetric equivalent. This second set of positions for the atoms of the **-N=N-** bond of molecule 2 corresponds to the rotational conformer of the original molecule whose carbon atoms more or less exactly superpose on the original positions. The original and the new positions of N(2) are denoted as N(21) and N(22) respectively (Fig. 6.7). As mentioned earlier, the difference electron density did not indicate the presence of any disorder for the rest of the atoms in the molecule.

Both the positions of the nitrogen atoms in molecule 2 were assigned equal weights of 0.5 each. The reported anisotropic thermal parameters, b_{ij} 's, of the non-hydrogen atoms were converted to their equivalent isotropic temperature factors, B's. Least-squares refinement of the occupancy factors was carried out and the occupancies of N(21) and N(22) refined to 0.85 ± 0.02 and 0.15 ± 0.02 respectively. Five more cycles of block-diagonal structure factor least-squares calculations with b_{ij} 's for all the non-hydrogen atoms except N(21) and N(22), and B's for N(21), N(22) and the hydrogen atoms, reduced the R-value to 0.063. The R-value reported by Brown [4] without including the disorder in the least-squares refinement was 0.069. Though the reduction in

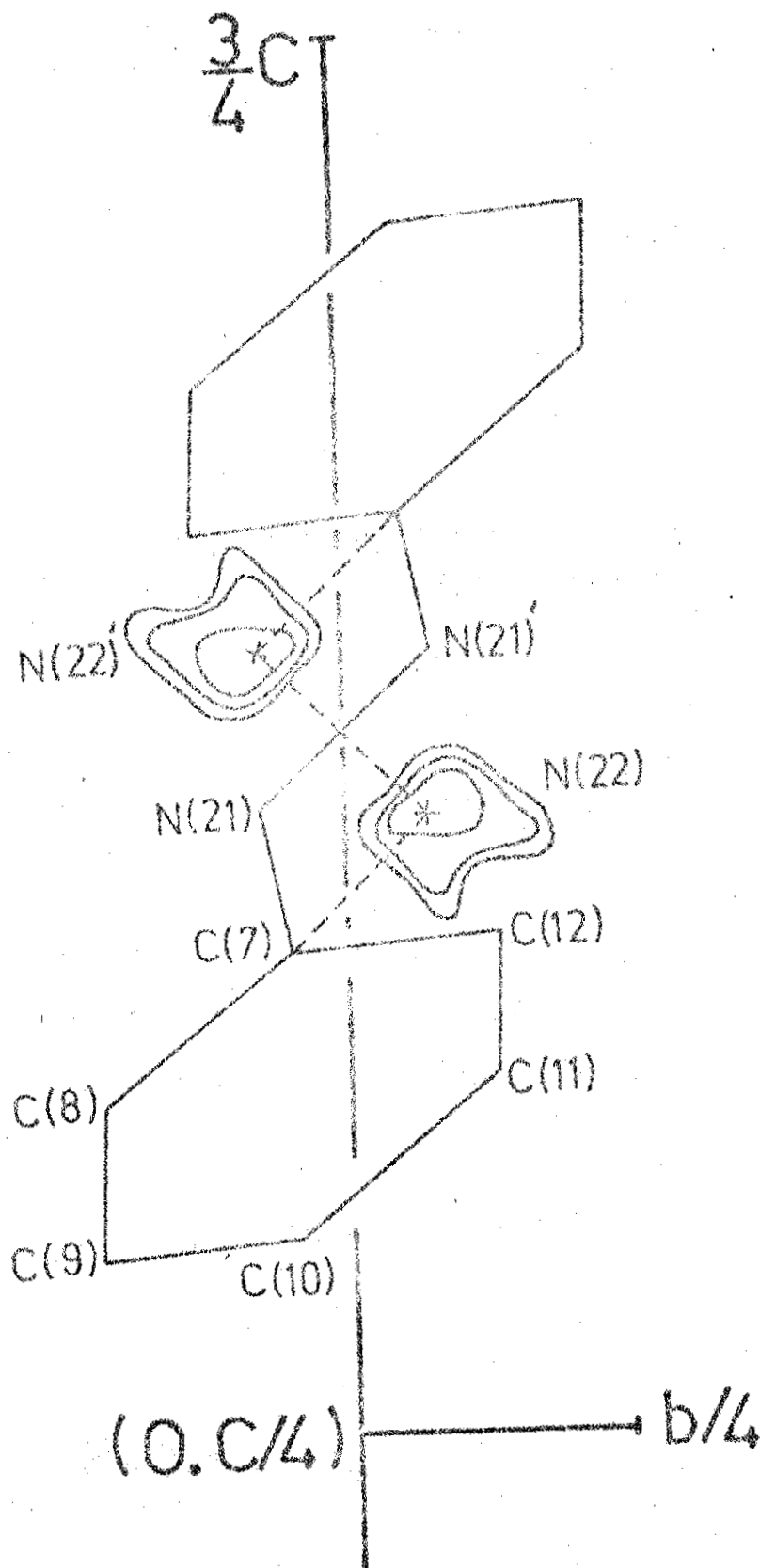


Figure 6.7: The peaks found in the difference Fourier map of *trans*-azobenzene indicating a second set of positions for the azo nitrogen atoms of molecule 2.

the R-factor by **including** the disorder in the refinement is only 0.006, it is found to be significant **according** to **Hamilton's significance** test discussed at the end of this **section**.

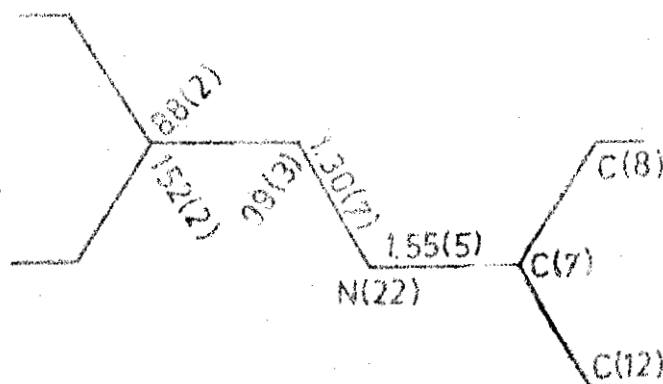
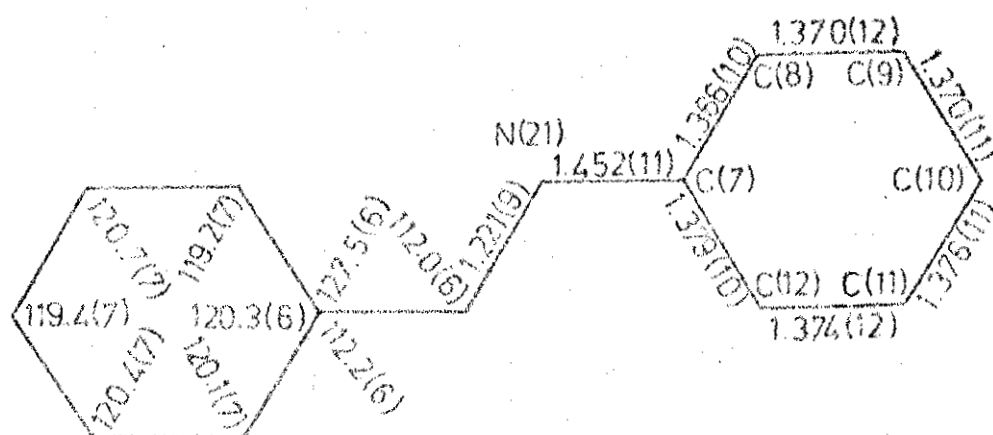
The final **positional** and **thermal** parameters of trans-azobenzene are listed in Table 6.2. The bond **lengths** and angles are shown in **Fig. 6.8**. The two -N=N- bond distances in **molecule 2** are $1.22(1) \text{ \AA}$ and $1.30(7) \text{ \AA}$ for the positions corresponding to the occupancy **factors** 0.85 and 0.15 respectively. For molecule 1, this length is $1.238(6) \text{ \AA}$. In the earlier **refinement** of Brown [4] where two positions were not considered for N(2), the -N=N- bond **lengths** were $1.243 \text{ \AA}$ and $1.172 \text{ \AA}$ in molecule 1 and molecule 2 respectively. As in the case of PAA and for **reasons mentioned** there, the external valency angles at the **phenyl** ring carbon atom O(7) connected by the **azo** bond are distorted.

(d) p-Azotoluene: This compound **crystallizes** in the **monoclinic space group** $P2_1/a$ with 2 molecules per **unit cell**. Thus, the centres of the molecules **coincide** with the centres of **symmetry** in the crystal lattice. This results in only **half** of the symmetric p-azotoluene **molecule being crystallographically independent**.

Brown [5] has **studied** the crystal structure of this compound. We observed high **thermal parameters** for

Table 6.2: The final positional and thermal parameters ($\times 10^4$) of non-hydrogen atoms of trans-azobenzene. Estimated standard deviations are given in parentheses.

Atom	x	y	z	$B(\text{in } \text{\AA}^2)$ or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	1404(4)	1337(9)	678(4)	68(4)	276(17)	44(3)	- 8(7)	24(3)	2(6)
C(2)	1739(5)	3446(10)	1144(4)	88(5)	294(20)	63(3)	- 9(9)	30(4)	-14(7)
C(3)	2944(5)	3884(11)	1711(4)	92(6)	326(21)	63(4)	-32(9)	21(4)	-26(8)
C(4)	3812(5)	2302(12)	1782(4)	80(5)	402(24)	54(3)	-28(10)	17(3)	3(7)
C(5)	3481(5)	219(11)	1291(4)	71(5)	377(22)	55(3)	8(9)	18(3)	3(7)
C(6)	2289(5)	- 273(10)	742(4)	74(5)	291(18)	48(3)	- 3(8)	19(3)	- 3(6)
C(7)	706(5)	- 473(12)	4209(4)	81(5)	487(27)	52(3)	28(10)	22(3)	20(8)
C(8)	623(6)	-2295(13)	3617(5)	106(7)	431(27)	76(4)	-18(11)	35(4)	-22(9)
C(9)	1306(6)	-2320(14)	3096(5)	102(6)	521(31)	64(4)	10(12)	25(4)	-31(9)
C(10)	2073(6)	- 519(14)	3162(4)	105(6)	593(33)	55(4)	22(12)	33(4)	3(9)
C(11)	2152(6)	1318(14)	3756(5)	108(7)	526(32)	62(4)	-23(12)	26(4)	11(9)
C(12)	1471(6)	1358(13)	4282(4)	122(7)	440(27)	54(4)	14(12)	24(4)	-18(8)
N(1)	144(4)	1024(8)	112(3)	69(4)	280(15)	54(3)	- 6(7)	21(3)	- 7(5)
N(21)	- 81(6)	- 756(11)	4702(4)	5.1(1)					
N(22)	311(33)	821(69)	4917(27)	6.1(8)					



the atoms in the **central** **azo** region of the **molecule** and an unusual **length** for the **azo** bond. He attributed these features to the presence of two rotational conformers of the molecule which **randomly coexist** in the **structure**. On refining the structure after **assigning** two **sets** of **positions** for all the **atoms** in the **molecule** (Fig. 6.9), he has **obtained** a lower R-value, better **molecular** dimensions and **lower** atomic **thermal** parameters. However, he has not carried out Least-squares refinement of the occupancy factors, but has **assumed** an equal **probability** of **occurrence** for both the rotational conformers. Our work on p-azotoluene **was** mainly to **determine** the **percentage occurrence** of the two rotational conformers.

Occupancy **factors** of the two sets of atomic positions reported by Brown [5] were refined by least-squares technique. This refinement confirmed that the two conformers **corresponding** to **these** two sets of atomic positions occur with equal probability of 0.5 **each**.

In the crystal **structures** of PAA and **trans-azobenzene**, the difference Fourier maps **clearly** indicated two **sets** of positions, **corresponding** to the two **rotational** conformers, for the **nitrogen atoms** in the **-N=N-** bond; but, a **corresponding** **second** set of **positions** for the rest of the molecule was not **indicated**. This feature **could** be interpreted as follows. When two molecular models **corresponding** to the

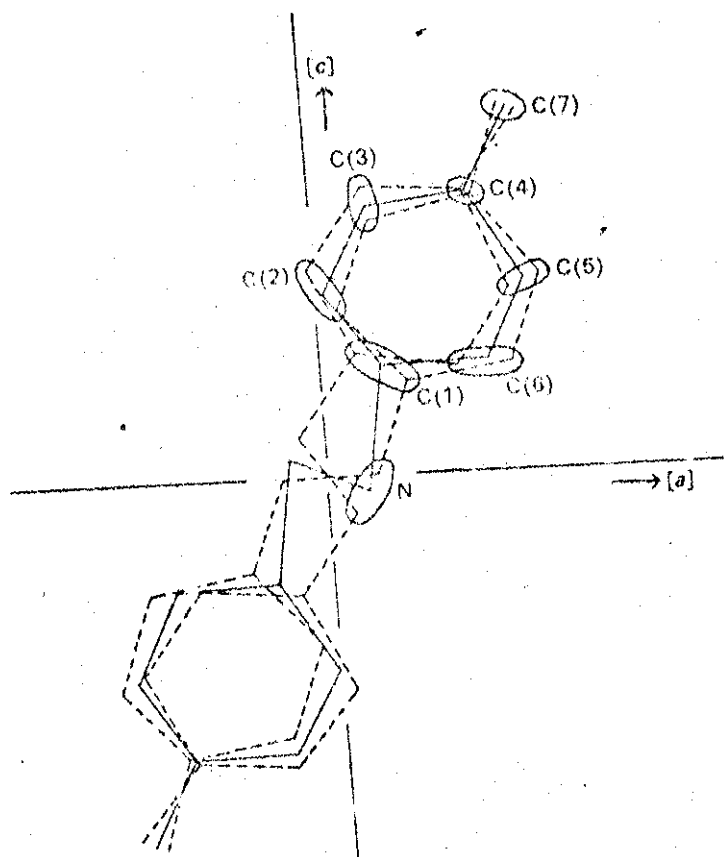


Figure 6.9

The two sets of positions for the p-azotoluene molecule

two **rotational conformers** are overlapped, the **aromatic** carbon atoms can be **made to superpose** more or less exactly, whereas the displacement between the two sets of positions for the nitrogen **atoms** in the **-N=N-** bond is **substantial** ($\sim 1 \text{ \AA}$). When the **displacement** between the two sets of carbon **atoms** is less than the **respective** standard deviations of the **positional coordinates** and also less than the **r.m.s. amplitude** of vibration of that atom, the **difference Fourier map** does **not distinctly resolve** the two sets of positions and the peaks **corresponding to the** two positions merge to give a **diffuse** electron density distribution. **Therefore**, though **considering** two sets of **positions** for **all** the atoms in the molecule amounts to a physically more meaningful model, the **actual displacements** between the alternate **positions** for the carbon **atoms** in such a model **could** be rather exaggerated. **An** indication to this effect was found during **the** refinement of the **crystal** structure of MBPAA. **The 50 atoms** set, **which** includes alternate **positions** for the **azo** nitrogen atoms alone, refined to a lower R-value than the 62 atoms set. As described earlier, the 62 **atoms set** corresponds to two sets of **positions** for the carbon **atoms** in the two phenyl **rings also** (section 2.4). Similarly, the separation between the two sets of positions for the **aromatic carbon** atoms in the **crystal** structure of **p-azotoluene** could also be exaggerated.

Partial positional disorder about the azoxy bond has been found to occur in the crystal structure of the high temperature polymorph of the smectogen ethyl *p*-azoxybenzoate also [3]. Here, the two rotational conformers coexist with probabilities 0.7 and 0.3. Hoekstra et al [6] have reported the existence of positional disorder about the $-O=O-$ bond in the crystal structure of trans-stilbene.

Significance test for the reduction in R-factor

Hamilton's significance test [7,8] was employed to assess the reduction in the R-value obtained after including the disorder in the least-squares refinement of the crystal structures.

The R-factor ratio $\mathcal{R} = R_Q/R_0$, where R_Q is the R-factor corresponding to the set not including the disorder and R_0 is the R-factor for the set including the disorder, was calculated for each of the crystal structures. The calculated $\mathcal{R}$ value was then compared with the significance points for $\mathcal{R}$, via., $\mathcal{R}_{b,n-m,\alpha}$ in the tables found in [8]. As defined by Hamilton [7], b is equal to the number of degrees of freedom of the hypothesis, $(n-m)$ is equal to the degrees of freedom for the refinement and α is the significance level. In other words, b is the

increase in the number of parameters refined on including the disorder in the refinement, $(n-m)$ is the difference between the number of reflections **and** the number of parameters refined and $(1-a)$ is the probability of the hypothesis that R_0 is significantly lower than R_Q being true. Table 6.3 gives the various parameters **involved** in these significance tests for the four crystal structures of interest.

As **can** be seen from a **comparison** of the last two **columns** of Table 6.3, the reduction in the R-factor due to the inclusion of disorder in the least-squares refinement is significant with a probability much greater than 0.995 in the **crystal** structures **of** MBPAA **and** p-azotoluene. In **the case** of PAA **and** trans-azobenzene, the number of parameters for the set without disorder is greater than that for the set with **disorder**. **This** is due to the fact that the nitrogen **atoms** in the disordered region have been treated with **anisotropic** thermal parameters in the former **case** and **isotropically** in the **latter**. Thus, **any** reduction in the **R-factor** due to the inclusion of disorder is very significant **in** these two **crystal** structures and the **significance** test is quite **superfluous**. Thus, the least-squares calculations support the **existence** of partial **positional disorder** in **all** these crystal structures.

Table 6.3: Resulte of the significance test for the reduction in R-factor

Compound	Details of the set refined	No. of reflections	No. of para-meters refined	R-factor	Sets compared	b	n-m	R	$R_{b,n-m,\alpha}$ For $\alpha=0.005$
MBPAA	(i) 48 atom set(disorder not included)	1071	192	0.146	(i) and (ii)	8	871	1.207	1.014
	(ii) 50 atoms set(disorder for the azonitrogen atoms included)	1071	200	0.121	(i) and (iii)	56	823	1.159	1.058
	(iii) 62 atoms set(disorder for the azonitrogen atoms and the carbon atoms in the phenyl rings connected by the aeo-bond included)	1071	248	0.126					
p-azotoluene	(iv) set without disorder	833	60	0.180	(iv) and (v)	60	713	1.765	1.023
	(v) set with disorder	833	120	0.102					
PAA	(vi) set without disorder	2505	213	0.091					
	(vii) set with disorder	2505	169	0.075					
trans-azobenzene	(viii) set without disorder	1646	166	0.069					
	(ix) set with disorder	1646	165	0.063					

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