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The Crystal Structure of *p*-Azotoluene

BY C. J. BROWN

Research Laboratories, Imperial Chemical Industries Limited (Dyestuffs Division), Hexagon House, Manchester 9, *England and The Sir William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London W.C.*1, *England*

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The crystal structure of *p*-azotoluene has been determined in an attempt to explain the geometrical differences between the two non-equivalent molecules found in *trans*-azobenzene. A full three-dimensional analysis has been carried out, resulting in the discovery of a type of disorder in which the sense of the step of the azo group is randomly in either of two directions at equivalent lattice points. This accounts for the abnormalities observed in bond lengths and thermal parameters.

Introduction

In the crystal structure of *trans*-azobenzene (de Lange, Robertson & Woodward, 1939; Brown, 1966), there are associated with each lattice point two molecules which have differences in their dimensions greater than the experimental error. In order to explore the reasons for these differences, and to determine which set of molecular dimensions should be regarded as standard in azo compounds, the crystal structure determination of the next homologue, *p*-azotoluene, $CH_3-C_6H_4-N=N-C_6H_4-CH_3$, in which there is only one molecule per lattice point, was undertaken. While it was not found possible to derive a very accurate set of molecular dimensions from this work, owing to the incidence of an unexpected type of disorder, an explanation was found for the peculiar differences between the two non-equivalent molecules of *trans*-azobenzene.

Molecules of *p*-azotoluene are found to pack together in the crystal in either of the two configurations shown in Fig. 1, both of which occupy approximately the same volume in the unit cell. The randomness of the two molecular orientations is evinced in abnormal values of the anisotropic temperature factors B_{ij} in certain directions, and because the atomic coordinates determined are the resultant of two sets of atomic parameters, some of the bond lengths calculated for the mean structure assume ridiculous values.

A preliminary account of this work was presented at the Fifth Congress of the International Union of Crystallography at Cambridge (Brown, 1960), but at that time the resolution of the disordered pair of molecules had not been accomplished. Unit-cell dimensions and the space group of *p*-azotoluene were published by Kapadia (1938), and an approximate structure determined from three projections has been given by Padmanabhan, Shankar & Khubchandani (1958). Their structure bears some resemblances to the present one, but there are variations of up to 5% in the unit-cell dimensions, and a large number of different signs for the calculated structure amplitudes. While the orientation of their molecule is roughly the same as ours, there are differences of up to 1·0 Å in the z parameters and this results in some non-bonded interatomic contacts of 2·41 Å, so that their structure must be regarded as wrong.

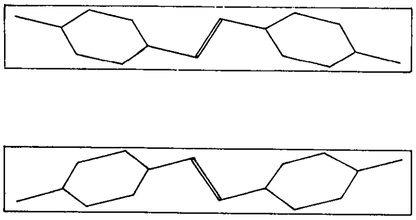

Fig. 1. Two permissible configurations for the molecule of *p*-azotoluene.

Experimental

The sample of *p*-azotoluene was obtained from the I.C.I. chemical specimen collection and was recrystallized by slow evaporation from ethanol solution. Orange coloured laths separated, which were elongated along **b** and tabular on (100). Unit-cell dimensions were obtained first from rotation photographs, and then more accurately from high-order reflexions on Weissenberg photographs taken with Cu $K\alpha$ radiation at 18 °C:

$$a=11\cdot914,\ b=4\cdot850,\ c=9\cdot713\ \text{Å};\ \beta=91\cdot0°.$$

The specific gravity of the crystals, measured by flotation in sodium iodide solution, was 1·243, while that required for two molecules of $C_{14}H_{14}N_2$ per unit cell was 1·244. The absent reflexions indicated the space group to be unambiguously $P2_1/a$, so that the centres of molecules must coincide with the centres of symmetry in the crystal lattice.

Intensity data were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation about **b** (zero and four layers) and **c** (zero and eight layers). Multiple packs of films were used and the intensities of the reflexions were estimated by comparison with a calibrated film strip. The usual correction factors were applied, and the structure amplitudes reduced to an approximately absolute scale by Wilson's statistical method.

Some of the Weissenberg X-ray photographs were repeated with Co *Kα* radiation, and zero level Weissenberg photographs were taken from about a dozen different crystal specimens to see if there were any appreciable variations in intensities. Intensity data were also obtained at low temperature, but difficulties with the apparatus working over long periods prevented a complete set of data being obtained. It was evident, though, from the *h*0*l* reflexions that there was no phase change between room temperature and −70°C, and that there was no great change in the relative intensities.

Determination of the structure

The approximate structure was found by trial and error, working first with the **b** projection and taking into account the most probable spatial arrangement of the molecule. Refinement of this projection was carried out manually with the use of Beevers–Lipson strips and a desk adding machine. The best **b** projection is shown in Fig. 2, and although this appears reasonable and there is general overall agreement between the calculated and observed structure amplitudes, it was not possible to reduce the *R* value for the *h*0*l* terms below 28%. A limited amount of three-dimensional refinement was also computed manually: although there was a semblance of agreement, the *R* value was poor, and a number of structure amplitudes showed very considerable disagreement.

When the I.C.I. Pegasus electronic computer became available in 1958, attempts were made to refine this structure further. Programs compiled by Cruickshank & Pilling (1961) were used, and anisotropic temperature factors as well as the atomic coordinates were refined by least squares. Hydrogen atoms were included at their calculated positions, and after several cycles of least squares and structure factor calculations, the residual *R*, using 813 *hkl* terms, was reduced to 8·8%. The bond lengths and angles obtained for the central part of the molecule were, however, quite unreasonable, and at this stage a complete survey of the experimental data was undertaken to see whether systematic errors had arisen during the work and had affected the intensities. This survey led to the conclusion that the data were reasonably reliable, and the structure approximately correct, but that some unusual effects within the molecule were causing the discrepancies. Attempts were also made to carry out the refinement assuming the lower space group symmetries $P2_1$ and *Pa*, but in neither case was there any improvement in the agreement.

Eventually, as a result of discussion with colleagues, and by consideration of the published structures of azulene (Robertson, Shearer, Sim & Watson, 1962) and cyclododecane (Dunitz & Shearer, 1959), it was suggested that the abnormalities in *p*-azotoluene could be accounted for by the superposition of two molecules

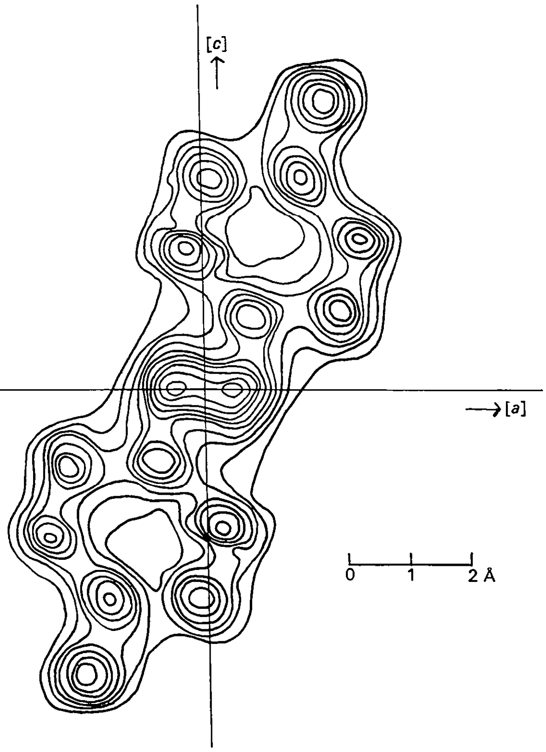

Fig. 2. Electron density projection along **b**. Contours are at intervals of 1 e.Å^{-2}.

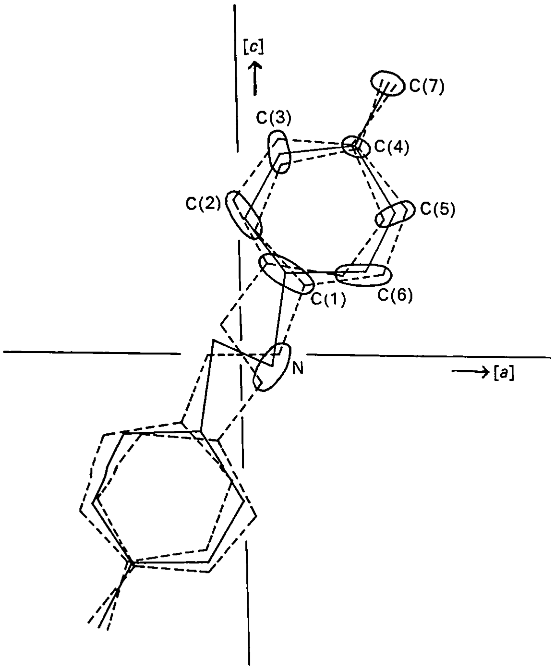

Fig. 3. Superposition of two molecules of *p*-azotoluene. The ellipses represent projections of the values of U_{ij} for each atom. The full line shows the molecule as determined by the least-squares refinement, and the broken lines indicate the two separated molecules.

as shown in Fig. 3. The approximate projections of the values of U_{ij} for each atom are shown, and on this basis an attempt was made to separate the two constituent molecules from the combined projection.

Resolution of the disordered pair

Three lines of approach were followed. First, the positional parameters x,y,z of each atom separately, as determined by the three-dimensional least-squares refinement, were divided into pairs $x \pm \delta x$, $y \pm \delta y$, $z \pm \delta z$, where δx, δy, δz were the vibration amplitudes derived from the U_{ij} for each atom. These new parameters were then submitted to further least-squares refinement using isotropic thermal parameters and small ($\simeq$0·10) fractional shifts. This is effectively equivalent to replacing each thermal ellipsoid by two nearest-equivalent spheres, and bears some resemblance to the method described by Kartha & Ahmed (1960). The results were not very satisfactory, probably because the spherical approximation was not nearly good enough; bond lengths and angles throughout the molecule were very irregular and the R value showed no significant decrease. In addition, experimental errors probably distorted the result, and it was considered that this analysis showed no improvement.

Secondly, an empirical manipulative procedure based on the $x \pm \delta x$, $y \pm \delta y$, $z \pm \delta z$ atomic coordinates was tried, which aimed at experimenting with various configurations for the azo linkage in the centre of the molecule, while preserving the plane hexagonal ring. Structure factors calculated for a number of trials of this kind all showed much poorer agreement, and the method was abandoned.

Thirdly, the direction of the axis of inertia along the length of one-half of the superposed molecule was calculated with a computer program written by Milledge (1964). It was found by trial that a rotation of this axis by ± 5·0° about a point one-third of the way along the C(4)–C(7) bond gave a very reasonable fit for the $x \pm \delta x$, $y \pm \delta y$, $z \pm \delta z$ sets of coordinates for all the carbon atoms. Satisfactory sets of coordinates for the nitrogen atoms were obtained by geometry. As this process resulted in two molecules of similar dimensions which

Table 1(*a*). *Atomic parameters: superposed molecule*

The values of B are defined by the expression

$$\exp\,[-\tfrac{1}{4}(h^2a^{*2}B_{11}+2hka^*b^*B_{12}+\ldots)]$$

used in the structure amplitude calculations.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(1)	0·0463	0·2558	0·1160	9·73	2·33	4·30	−0·27	0·03	−2·87
C(2)	−0·0280	0·3647	0·2108	5·06	4·28	5·52	−1·20	0·51	−1·82
C(3)	0·0059	0·5573	0·3040	3·52	4·16	4·86	−0·37	0·56	−0·23
C(4)	0·1163	0·6554	0·3062	3·26	2·20	3·40	0·12	0·16	−0·29
C(5)	0·1891	0·5489	0·2094	4·20	3·54	3·88	0·41	0·01	0·20
C(6)	0·1554	0·3546	0·1157	6·43	3·64	4·00	0·53	−0·32	−0·17
C(7)	0·1539	0·8655	0·4082	5·09	3·09	4·17	−0·19	−0·52	−0·64
N	0·0415	0·0064	−0·0184	4·10	10·59	8·99	2·78	6·87	2·47
H(2)	−0·1141	0·2947	0·2102	Mean isotropic B=6·59					
H(3)	−0·0531	0·6359	0·3774						
H(5)	0·2747	0·6219	0·2083						
H(6)	0·2140	0·2778	0·0412						
H(7*a*)	0·0832	0·9910	0·4368	Mean isotropic B=10·06					
H(7*b*)	0·2157	0·9938	0·3593						
H(7*c*)	0·1934	0·7621	0·4948						

Mean e.s.d.'s given by the computer program $\sigma(x)=\sigma(y)=\sigma(z)=0·004$ Å
$\sigma(B_{ij})=0·18$ Å^2

Table 1(*b*). *Atomic parameters: two separated molecules*

	Molecule rotated through +5·0°				Molecule rotated through −5·0°			
	x/a	y/b	z/c	B	x/a	y/b	z/c	B
C(1)	0·0628	0·2546	0·1082	3·43	0·0305	0·2571	0·1256	3·49
C(2)	−0·0181	0·3636	0·1946	3·73	−0·0367	0·3657	0·2281	3·87
C(3)	0·0092	0·5568	0·2908	3·62	0·0037	0·5578	0·3174	3·58
C(4)	0·1191	0·6550	0·3048	2·95	0·1136	0·6558	0·3078	2·95
C(5)	0·1986	0·5484	0·2164	3·37	0·1791	0·5494	0·2035	3·37
C(6)	0·1717	0·3536	0·1195	3·68	0·1390	0·3556	0·1136	3·79
C(7)	0·1494	0·8649	0·4104	4·01	0·1583	0·8661	0·4056	4·00
N	0·0469	0·0562	0·0003	2·86	−0·0294	0·0580	0·0437	3·77
H(2)	−0·1040	0·2936	0·1849	4·83	−0·1224	0·2958	0·2366	5·78
H(3)	−0·0548	0·6355	0·3575	4·83	−0·0498	0·6362	0·3971	5·78
H(5)	0·2841	0·6215	0·2243	4·83	0·2642	0·6223	0·1933	5·78
H(6)	0·2354	0·2767	0·0518	4·83	0·1919	0·2789	0·0329	5·78
H(7*a*)	0·0786	0·9904	0·4390	10·92	0·0875	0·9916	0·4342	11·17
H(7*b*)	0·2112	0·9932	0·3615	10·92	0·2200	0·9944	0·3567	11·17
H(7*c*)	0·1888	0·7615	0·4970	10·92	0·1977	0·7627	0·4922	11·17

Table 2. *Observed and calculated structure amplitudes*

H	K	L	F(OBS)	F(CAL)
0	0	1	27.2	+29.5
0	0	2	23.9	−26.9
0	0	3	6.1	+5.0
0	0	4	2.3	−3.2
0	0	7	6.2	+6.1
0	0	8	2.4	−2.7
0	0	9	9.3	+9.0
0	0	10	11.5	+11.8
0	0	11	5.6	−5.2
0	0	12	4.6	−4.4
2	0	−11	5.6	+4.3
2	0	−10	6.5	+5.8
2	0	−9	4.8	−5.0
2	0	−6	4.3	−4.3
2	0	−5	15.7	−13.9
2	0	−4	13.5	+11.5
2	0	−3	37.6	+41.5
2	0	−2	7.0	−5.8
2	0	−1	73.7	+75.4
2	0	0	42.3	+44.8
2	0	1	29.1	−28.5
2	0	4	4.8	+5.7
2	0	5	2.7	−4.7
2	0	6	18.3	+20.7
2	0	7	11.5	+10.0
2	0	9	8.4	+8.3
2	0	10	3.2	−3.3
2	0	11	5.4	−5.5
4	0	−10	4.7	−4.2
4	0	−9	1.5	+1.6
4	0	−7	3.9	−3.4
4	0	−6	9.8	−8.5
4	0	−5	1.6	−2.0
4	0	−4	29.9	+28.0
4	0	−3	2.1	+1.5
4	0	−2	12.1	−10.6
4	0	−1	8.3	−7.4
4	0	0	6.8	+5.6
4	0	1	37.0	+40.9
4	0	2	2.9	−2.8
4	0	4	3.1	−2.9
4	0	5	16.8	+13.7
4	0	6	21.3	+19.8
4	0	7	4.4	−4.8
4	0	8	2.2	−1.3
4	0	11	2.2	+2.4
4	0	12	1.9	−1.5
6	0	−11	2.1	−2.5
6	0	−10	2.2	+2.0
6	0	−9	2.6	+2.6
6	0	−8	4.7	−5.2
6	0	−7	2.4	−2.4
6	0	−6	3.8	−2.5
6	0	−4	10.2	−9.8
6	0	−3	6.6	−5.7
6	0	−2	2.2	−1.5
6	0	−1	11.1	−9.6
6	0	0	26.6	+27.9
6	0	1	10.3	+8.0
6	0	2	19.7	−18.3
6	0	3	3.3	−4.1
6	0	5	6.9	+6.9
6	0	7	4.9	+4.5
6	0	8	1.9	+1.5
6	0	9	1.7	−1.5
6	0	10	3.8	+4.1
6	0	11	2.9	−1.9
8	0	−9	3.4	−2.8
8	0	−8	3.9	−3.5
8	0	−6	4.1	−4.2
8	0	−5	16.9	−15.5
8	0	−4	5.2	−5.1
8	0	−3	16.3	+16.3
8	0	−2	9.5	−10.1
8	0	−1	12.1	−10.3
8	0	0	2.8	+2.1
8	0	1	13.8	−10.3
8	0	2	9.4	−6.4
8	0	5	5.1	−5.0
8	0	6	10.6	+10.1
8	0	7	11.9	+11.5
8	0	8	7.8	−7.5
8	0	9	3.3	−3.2
10	0	−9	1.5	−1.6
10	0	−8	2.9	−3.1
10	0	−6	3.8	−4.2
10	0	−5	8.1	−7.6
10	0	−4	8.2	+8.5
10	0	−3	1.5	−0.9
10	0	−2	17.1	−17.7
10	0	−1	8.1	−6.7
10	0	0	2.4	−2.0
10	0	1	2.5	−2.8
10	0	2	4.9	−4.3
10	0	3	2.2	+2.5
10	0	4	3.5	−3.1
10	0	6	10.7	+11.2
10	0	7	3.5	−3.0
10	0	8	7.5	−7.8
12	0	−7	1.1	+1.9
12	0	−6	2.6	−2.4
12	0	−5	3.7	−2.8
12	0	−4	2.4	−2.1
12	0	−3	6.6	−6.4
12	0	−2	2.5	−3.0
12	0	0	2.2	−2.5
12	0	1	5.0	−5.2
12	0	3	3.3	+3.4
12	0	4	5.4	−5.4
12	0	7	1.7	−1.8
14	0	−1	3.6	−3.8
14	0	0	1.8	−2.0
14	0	2	1.7	+1.7
14	0	3	2.0	−2.0
14	0	4	1.8	−2.2
0	1	1	3.1	−2.2
0	1	2	63.4	−64.7
0	1	3	13.6	−14.1
0	1	4	1.7	+1.1
0	1	5	3.0	+3.2
0	1	6	1.5	+1.4
0	1	7	6.9	+8.4
0	1	8	5.8	+6.9
0	1	9	5.9	−6.7
0	1	10	1.9	−1.7
0	1	11	1.5	−1.6
0	1	12	3.2	−3.3
1	1	−12	2.2	+2.0
1	1	−11	1.5	−1.5
1	1	−10	4.8	−5.4
1	1	−8	9.1	+9.7
1	1	−7	2.4	−0.6
1	1	−5	14.8	+14.8
1	1	−4	1.1	−1.3
1	1	−3	18.7	+20.7
1	1	−2	26.3	+28.2
1	1	−1	8.1	−9.6
1	1	0	22.4	−24.4
1	1	1	31.8	+33.2
1	1	2	69.8	+71.2
1	1	3	3.7	−4.1
1	1	4	6.1	+6.5
1	1	5	14.4	+13.0
1	1	6	2.1	−2.0
1	1	7	4.8	+5.4
1	1	9	4.1	−3.8
1	1	10	1.5	−1.5
1	1	11	4.1	+4.1
1	1	12	3.2	+2.7
2	1	−12	1.1	+1.0
2	1	−11	1.1	−1.2
2	1	−10	3.4	+3.4
2	1	−9	3.2	−3.3
2	1	−8	9.5	−10.2
2	1	−7	2.9	−2.3
2	1	−6	6.1	+6.0
2	1	−5	10.6	+12.1
2	1	−3	13.3	+15.5
2	1	−2	2.4	+0.9
2	1	−1	12.5	−13.5
2	1	0	14.4	+13.2
2	1	1	49.4	−50.8
2	1	2	30.9	−32.6
2	1	3	7.8	+8.7
2	1	4	22.7	+23.1
2	1	5	6.9	+6.8
2	1	6	4.3	−4.5
2	1	7	3.3	+3.7
2	1	8	6.1	−6.4
2	1	9	4.1	−3.3
2	1	11	4.4	−4.0
3	1	−12	1.5	−1.3
3	1	−11	1.1	+0.2
3	1	−9	3.7	+3.4
3	1	−7	5.3	−5.6
3	1	−6	9.2	+8.5
3	1	−5	3.2	+3.9
3	1	−4	8.7	−9.1
3	1	−3	10.8	−10.5
3	1	−2	13.7	+14.4
3	1	−1	36.3	+32.7
3	1	0	4.3	+6.5
3	1	1	28.4	+25.9
3	1	2	6.5	+6.7
3	1	4	20.4	+19.4
3	1	6	4.0	−3.1
3	1	8	5.1	+5.8
3	1	9	3.7	+3.8
3	1	12	1.9	−1.6
4	1	−9	3.7	−3.2
4	1	−6	4.3	+3.8
4	1	−5	1.1	−1.4
4	1	−4	4.8	+3.0
4	1	−2	15.3	−15.2
4	1	−1	14.5	+15.6
4	1	0	6.9	−6.1
4	1	1	9.1	−9.5
4	1	3	2.0	+0.8
4	1	4	8.7	+8.2
4	1	5	4.3	−4.6
4	1	7	5.3	−4.7
4	1	8	5.6	−4.4
4	1	9	2.4	+2.5
4	1	10	3.4	−2.8
4	1	11	1.1	−1.1
5	1	−11	1.1	+1.3
5	1	−10	2.2	−1.6
5	1	−9	2.9	−3.1
5	1	−8	3.4	−3.3
5	1	−6	3.3	−3.0
5	1	−5	6.7	−5.7
5	1	−4	5.7	−6.7
5	1	−3	1.1	−0.9
5	1	−2	22.4	+22.2
5	1	−1	8.5	+8.7
5	1	0	16.6	−14.7
5	1	1	7.9	−7.9
5	1	2	5.8	+5.6
5	1	3	14.5	+15.1
5	1	6	2.1	+1.8
5	1	7	3.9	+3.9
5	1	8	6.7	+7.2
5	1	9	2.4	−1.6
5	1	10	3.4	−2.8
5	1	11	1.5	−1.1
6	1	−7	5.1	−5.2
6	1	−6	4.0	−3.5
6	1	−5	3.6	+2.6
6	1	−4	5.8	+4.7
6	1	−3	9.9	−9.5
6	1	−2	8.0	+6.6
6	1	−1	3.9	+3.9
6	1	0	8.7	−7.7
6	1	1	2.3	+1.7
6	1	2	12.9	−12.0
6	1	3	6.4	−4.9
6	1	4	4.4	+3.6
6	1	5	10.1	+9.4
6	1	7	7.9	−7.3
6	1	9	2.9	−1.7
6	1	10	2.9	−2.2
7	1	−11	1.5	−1.3
7	1	−10	2.7	−2.2
7	1	−9	2.2	−2.1
7	1	−7	5.6	−4.9
7	1	−6	6.5	−7.4
7	1	−5	5.2	+5.1
7	1	−4	2.4	−2.0
7	1	−3	8.2	−8.4
7	1	−2	4.8	−4.1
7	1	−1	5.5	−4.7
7	1	0	7.8	−8.0
7	1	1	3.1	−2.4
7	1	2	9.9	+10.0
7	1	3	3.9	−3.1
7	1	4	1.8	−1.4
7	1	5	10.0	+9.7
7	1	6	3.3	−2.3
7	1	7	3.3	−2.4
7	1	10	1.1	−0.7
8	1	−8	2.9	−3.3
8	1	−7	3.5	−3.5
8	1	−6	1.9	+2.1
8	1	−5	6.3	+7.0
8	1	−4	4.2	−4.4
8	1	−2	4.3	+3.9
8	1	−1	8.7	−8.9
8	1	2	4.9	−4.0
8	1	4	11.1	+11.0
8	1	5	8.4	+7.3
8	1	6	8.5	−7.9
8	1	7	2.7	−2.1
8	1	8	2.5	−1.8
8	1	9	4.4	−3.4
9	1	−10	1.2	−1.5
9	1	−7	5.8	−5.7
9	1	−5	2.1	+1.6
9	1	−4	11.6	−11.4
9	1	−3	13.4	−13.5
9	1	−1	5.5	+4.7
9	1	0	8.5	−8.7
9	1	1	2.3	−2.1
9	1	3	7.0	−5.8
9	1	4	6.3	+6.1
9	1	6	7.5	−7.6
9	1	7	2.9	−2.7
9	1	8	4.2	+4.9
9	1	9	2.2	+2.7
10	1	−6	2.8	+3.0
10	1	−5	2.4	−1.2
10	1	−4	2.9	−2.5
10	1	−3	3.6	+3.7
10	1	−2	5.7	−5.9
10	1	−1	3.0	−3.6
10	1	0	5.8	+5.4
10	1	1	4.8	+5.1
10	1	4	6.4	+5.8
10	1	5	2.9	−2.9
10	1	6	2.4	−2.2
10	1	8	3.9	−4.1
11	1	−7	2.6	−2.7
11	1	−6	2.2	−2.2
11	1	−5	3.1	−3.2
11	1	−4	5.3	−5.4
11	1	−3	2.8	−3.3
11	1	−2	3.7	+3.3
11	1	−1	5.4	−5.5
11	1	0	9.3	−7.5
11	1	2	4.4	−3.5
11	1	3	2.9	−3.0
11	1	6	2.2	−2.1
11	1	8	2.3	+2.9
12	1	−5	2.4	−1.8
12	1	−4	2.4	+2.0
12	1	−2	2.5	−2.3
12	1	−1	2.4	+2.3
12	1	0	3.8	+4.2
12	1	1	1.9	+2.3
12	1	2	3.1	−2.4
12	1	6	2.2	+2.3
12	1	7	2.1	−2.1
13	1	−4	1.8	−1.6
13	1	−3	2.9	−3.0
13	1	−2	3.0	−2.8
13	1	−1	2.8	−3.2
13	1	2	3.7	−3.4
13	1	3	2.5	−2.6
13	1	5	2.2	+2.3
13	1	6	1.5	−1.8
14	1	−2	2.0	+1.3
14	1	4	1.1	−1.1
15	1	−1	1.1	+0.9
15	1	0	2.1	−2.1
15	1	1	1.5	−1.5
0	2	0	5.9	+5.6
0	2	2	2.2	−1.6
0	2	3	13.2	+12.5
0	2	4	19.0	+19.3
0	2	5	13.8	+12.6
0	2	6	4.8	+5.1
0	2	7	2.1	−2.4
0	2	8	3.9	−3.5
0	2	9	1.5	−1.5
1	2	−9	2.7	−2.2
1	2	−8	7.3	+7.5
1	2	−7	10.8	+12.6
1	2	−6	10.4	−11.5
1	2	−4	4.7	+4.1
1	2	−3	12.2	−10.4
1	2	−2	5.1	+4.5
1	2	−1	1.9	−1.4
1	2	0	2.9	+1.5
1	2	1	2.6	−1.3
1	2	2	31.0	+29.7
1	2	3	3.8	+3.1
1	2	4	37.3	−34.8
1	2	6	2.9	−2.5
1	2	7	5.7	−5.6
2	2	−10	2.7	−2.1
2	2	−9	3.4	−3.1
2	2	−8	2.9	−3.4
2	2	−7	5.5	+6.2
2	2	−6	9.7	+10.5
2	2	−3	9.4	+8.8
2	2	−2	6.3	+5.5
2	2	−1	3.3	−4.4
2	2	0	2.0	+1.1
2	2	1	1.1	+1.6
2	2	2	13.1	+12.3
2	2	3	28.8	+30.0
2	2	4	18.0	+18.4
2	2	5	2.8	−2.4
2	2	6	3.3	−2.7
2	2	7	2.2	+3.0
2	2	9	2.2	−2.1
3	2	−8	6.6	+6.4
3	2	−7	6.7	−7.5
3	2	−6	9.2	−9.9
3	2	−5	1.5	+1.1
3	2	−3	13.9	+13.9
3	2	−2	2.4	+2.5
3	2	−1	1.2	+0.8
3	2	0	7.1	−6.9
3	2	2	13.4	+11.5
3	2	3	29.0	−29.5
3	2	4	12.2	−12.3
3	2	5	3.6	+4.2
3	2	7	3.0	+4.1
3	2	8	3.7	−2.5
3	2	9	1.5	−1.6
3	2	10	3.0	−2.6
4	2	−11	2.2	−2.9
4	2	−7	3.2	+2.9
4	2	−5	4.8	−4.9
4	2	−4	4.5	+4.3
4	2	−3	9.7	+9.9
4	2	−2	13.0	−12.9
4	2	−1	9.8	−10.9
4	2	0	13.9	+13.0
4	2	1	9.8	+8.8
4	2	2	9.4	+8.3
4	2	3	14.0	+12.1
4	2	4	3.8	+3.9
4	2	5	3.9	−2.8
4	2	6	4.2	+4.2
4	2	7	1.9	+2.2
4	2	8	5.4	−5.3
4	2	10	3.0	+4.0
5	2	−10	2.7	−2.2
5	2	−9	1.5	−1.6
5	2	−8	4.2	−4.5
5	2	−7	1.9	−1.6
5	2	−6	5.8	+5.8
5	2	−5	3.1	−4.1
5	2	−4	3.8	+3.4
5	2	−3	4.9	+4.7
5	2	−1	4.3	−5.1
5	2	0	15.5	−13.8
5	2	2	3.9	−3.2
5	2	3	5.7	+4.6
5	2	4	3.7	+4.4
5	2	5	8.0	−8.0
5	2	7	2.0	−1.0
5	2	8	3.3	−2.9
5	2	9	4.0	−3.5
5	2	10	2.9	−1.7
6	2	−10	1.5	+1.3
6	2	−9	3.0	−3.0
6	2	−8	3.8	−4.2
6	2	−5	3.4	−3.2
6	2	−3	4.7	−4.4
6	2	−2	12.1	−11.4
6	2	−1	3.9	+4.3
6	2	0	8.0	+6.3
6	2	1	3.1	−3.5
6	2	3	12.2	+11.0
6	2	4	4.4	+4.7
6	2	5	2.9	−2.5
6	2	7	3.5	−3.1
6	2	9	2.9	+3.7
6	2	10	1.5	+2.6
7	2	−9	1.9	−2.3
7	2	−7	7.4	+7.7
7	2	−6	4.1	−4.0
7	2	−5	7.5	−8.0
7	2	−4	1.9	+1.7
7	2	−1	3.9	−4.6
7	2	0	2.4	+2.0
7	2	1	1.1	−1.0
7	2	2	6.5	+7.5
7	2	3	13.5	+12.8
7	2	4	15.9	−14.3
7	2	5	7.9	−7.6
7	2	6	2.2	+2.9
7	2	8	1.5	−1.0
7	2	9	2.7	−1.7
8	2	−10	1.5	−1.9
8	2	−9	2.7	−3.1
8	2	−7	2.4	+2.0
8	2	−6	2.7	−2.1
8	2	−5	7.2	−6.6
8	2	−4	3.0	−3.2
8	2	−3	1.9	−2.1
8	2	−2	2.9	−2.5
8	2	−1	2.8	−3.2
8	2	0	4.4	−3.4
8	2	1	1.5	−1.9
8	2	2	4.8	+4.7
8	2	3	6.1	+6.0
8	2	4	3.7	−4.2
8	2	5	6.0	−5.4
8	2	6	1.5	−1.7
8	2	7	1.5	+0.8
9	2	−9	2.2	−2.6
9	2	−6	7.7	−6.8
9	2	−1	6.5	+8.0
9	2	1	7.0	−7.2
9	2	2	7.5	+8.6
9	2	4	7.0	−7.5
9	2	5	1.9	+2.0
9	2	6	1.5	+2.1
9	2	9	1.5	+2.2
10	2	−7	2.0	−1.7
10	2	−6	2.4	−2.7
10	2	−5	2.9	−3.0
10	2	−3	1.9	−2.3
10	2	−2	5.3	−5.7
10	2	−1	3.9	−3.5
10	2	0	2.5	+2.2
10	2	2	2.4	−2.8
10	2	3	2.2	−2.5
10	2	4	2.2	−2.0
10	2	5	2.4	−2.4
11	2	−3	1.5	−1.3
11	2	−2	4.0	+4.0
11	2	−1	5.3	+5.6
11	2	0	8.5	−7.9
11	2	2	5.1	+5.4
11	2	3	1.5	+1.4
11	2	4	2.2	+2.0
12	2	−5	3.1	−2.9
12	2	−4	2.6	−2.6
12	2	−2	2.2	−2.3
12	2	1	4.4	−4.9
12	2	2	3.7	−4.2
12	2	3	1.5	+1.5
12	2	5	2.6	−3.6
13	2	−2	2.6	+2.1
13	2	1	2.6	+2.7
13	2	3	2.1	+2.8
13	2	4	1.1	+0.5
14	2	−2	2.3	−2.3
14	2	1	2.2	−2.5
14	2	3	1.1	+1.0
0	3	1	14.7	+15.3
0	3	2	3.3	−4.1
0	3	5	3.6	−3.7
0	3	6	5.7	−4.7
0	3	7	2.1	−1.9
0	3	9	4.1	−3.5
0	3	10	1.5	+1.6
0	3	11	2.2	+2.3
1	3	−10	1.9	+1.5
1	3	−9	3.4	+3.5
1	3	−6	5.0	−4.6
1	3	−5	6.1	−6.1
1	3	−4	11.1	+11.5
1	3	−3	2.2	+1.5
1	3	−2	2.2	+1.9
1	3	−1	10.9	+10.5
1	3	0	12.5	+12.7
1	3	1	8.9	+8.0
1	3	2	5.7	−4.9
1	3	4	8.3	−7.3
1	3	5	2.5	+2.6
1	3	6	11.1	+12.6
1	3	8	1.5	+1.6
1	3	9	1.9	+2.3
2	3	−10	1.1	+1.3
2	3	−8	2.7	−1.9
2	3	−6	9.0	+8.0
2	3	−5	7.9	+8.1
2	3	−4	8.7	−9.6
2	3	−3	5.5	−5.6
2	3	−2	4.7	−4.0
2	3	−1	3.0	−3.4
2	3	0	12.7	+12.2
2	3	2	5.4	−4.3
2	3	4	6.3	+6.0
2	3	5	5.9	−4.7
2	3	6	15.9	−14.3
2	3	7	3.0	−3.1
2	3	10	2.2	+2.6
3	3	−9	2.7	−2.1
3	3	−7	3.1	−3.0
3	3	−6	6.5	−6.9
3	3	−5	12.2	+12.9
3	3	−4	8.3	+8.3
3	3	−3	6.1	−6.5
3	3	−2	1.1	+1.2
3	3	−1	2.8	+2.8
3	3	0	5.0	+3.7
3	3	1	4.4	−4.4
3	3	2	4.9	+4.1
3	3	3	3.5	−2.0
3	3	5	19.2	+19.5
3	3	6	3.2	+3.3
3	3	7	4.6	−4.5
4	3	−10	1.5	−1.5
4	3	−8	2.4	+1.7
4	3	−6	3.1	+3.1
4	3	−5	5.5	−5.5
4	3	−4	8.5	−8.4
4	3	−3	1.5	−1.0
4	3	−2	1.5	−1.5
4	3	−1	1.5	+2.5
4	3	0	2.6	+2.0
4	3	1	6.9	+6.7
4	3	3	4.7	−4.1
4	3	4	2.6	−1.8
4	3	5	12.7	−12.5
4	3	6	7.1	−7.1
5	3	−10	2.7	−3.6
5	3	−8	4.2	+3.5
5	3	−7	3.1	−3.7
5	3	−6	1.5	+1.3
5	3	−5	5.3	+4.8
5	3	−4	7.0	−7.4
5	3	−3	2.6	−2.6
5	3	−1	1.1	−0.8
5	3	0	7.4	−6.4
5	3	1	8.8	+9.5
5	3	2	11.4	+12.1
5	3	3	7.8	−7.2
5	3	4	3.9	+5.4
5	3	5	3.1	+4.0
5	3	6	3.7	−3.3
6	3	−9	2.4	+2.6
6	3	−8	2.2	−1.8
6	3	−7	5.1	−4.7
6	3	−6	3.0	−2.5
6	3	−3	2.9	−2.7
6	3	0	7.4	+6.6
6	3	1	7.0	+9.0
6	3	2	10.2	−9.6
6	3	3	9.2	−8.6
6	3	4	3.0	−2.0
6	3	5	1.5	−1.1
6	3	6	1.8	−0.7
6	3	7	2.9	−1.7
6	3	8	1.1	+2.1
7	3	−9	3.4	+3.5
7	3	−7	4.8	−5.1
7	3	−6	1.1	−1.1
7	3	−5	3.9	−4.3
7	3	−1	4.9	−4.8
7	3	1	12.1	+13.0
7	3	2	7.3	−6.4
7	3	3	8.4	−7.3
7	3	6	3.3	+4.1
7	3	9	2.4	−1.2
8	3	−8	3.1	−2.7
8	3	−7	2.2	−2.0
8	3	−6	1.5	+1.3
8	3	−5	1.5	+1.5
8	3	−4	4.4	−4.9
8	3	−2	3.1	+3.5
8	3	−1	1.5	−1.7
8	3	0	4.8	+4.0
8	3	2	5.5	−5.3
8	3	3	2.2	−1.8

Table 2 (*cont.*)

H	K	L	F(OBS)	F(CAL)
8	3	4	2·2	+2·3
8	3	6	4·4	-3·5
8	3	7	1·1	+1·6
8	3	8	1·5	+2·2
9	3	-8	3·5	-3·8
9	3	-6	1·5	-1·7
9	3	-2	1·5	-1·2
9	3	-1	3·6	-3·8
9	3	0	2·2	+1·9
9	3	1	3·2	-3·8
9	3	2	4·7	-4·4
9	3	3	1·5	+1·3
9	3	4	1·9	-1·8
9	3	5	1·9	+2·4
9	3	6	1·5	+2·4
9	3	8	1·9	-1·8
10	3	-5	2·4	-2·2
10	3	-3	4·3	+4·5
10	3	-1	2·8	-2·8
10	3	0	3·2	+2·3
10	3	1	4·6	+4·6
10	3	3	3·3	-3·0
10	3	7	2·8	+3·1
11	3	-6	1·9	-2·2
11	3	-2	2·9	-2·7
11	3	-1	1·1	-1·8
11	3	0	3·9	-4·0
11	3	1	1·1	-1·9
11	3	2	5·3	+5·2
11	3	3	2·2	-2·1
11	3	4	3·7	-3·8
11	3	6	1·1	+1·0
12	3	0	3·3	+2·8
12	3	1	2·4	+2·9
12	3	2	3·1	-2·7
12	3	4	2·8	+2·3
13	3	-3	1·9	-2·1
13	3	0	3·1	-3·3
13	3	1	1·8	+2·6
0	4	0	8·7	-7·2
0	4	1	5·7	+7·5
0	4	2	5·1	+4·0
0	4	3	2·2	-2·0
0	4	5	1·9	-1·6
0	4	6	2·8	+2·2
0	4	8	2·8	+2·9
1	4	-9	2·2	-2·1
1	4	-8	1·1	-1·1
1	4	-7	2·2	+1·6
1	4	-6	3·1	+2·0
1	4	-5	2·8	-2·8
1	4	-3	7·3	+5·6
1	4	-2	4·1	+3·7
1	4	-1	3·4	+2·6
1	4	0	4·0	-4·2
1	4	1	7·3	-8·1
1	4	2	3·4	-2·6
1	4	3	3·2	+4·0
1	4	5	5·0	-4·5
1	4	8	1·9	-1·1
1	4	9	1·9	-1·7
2	4	-9	2·2	+2·0
2	4	-7	3·7	+4·1
2	4	-6	1·5	+1·2
2	4	-5	3·7	-3·4
2	4	-4	7·8	-7·3
2	4	-3	3·2	-3·3
2	4	-2	11·8	+11·4
2	4	-1	0·9	-1·0
2	4	0	3·7	+4·1
2	4	1	5·7	+6·7
2	4	2	1·1	-0·9
2	4	3	3·6	+4·7
2	4	4	3·2	-2·8
2	4	5	4·5	-3·9
2	4	6	4·7	-3·3
2	4	7	3·1	+4·6
2	4	8	5·2	+7·1
2	4	9	1·9	-0·9
3	4	-9	1·9	-1·3
3	4	-7	2·2	+1·9
3	4	-6	2·5	-2·2
3	4	-5	1·5	-1·3
3	4	-4	8·5	+8·2
3	4	-3	1·5	-0·9
3	4	-2	7·9	-8·0
3	4	0	2·2	+2·3
3	4	1	3·0	-3·2
3	4	3	2·2	+2·6
3	4	4	6·1	-5·8
3	4	6	2·4	+2·9
3	4	7	5·5	-4·6
3	4	8	5·1	-4·6
4	4	-6	3·0	-3·3
4	4	-5	4·9	-5·0
4	4	-4	5·1	-5·2
4	4	-3	7·9	+8·6
4	4	-2	5·2	+3·9
4	4	-1	4·0	+3·9
4	4	0	8·0	+8·3
4	4	1	6·2	-6·2
4	4	2	2·7	-1·9
4	4	3	2·9	-2·1
4	4	4	2·6	-2·0
4	4	5	3·2	-2·0
4	4	7	10·0	+10·8
5	4	-7	1·9	+1·6
5	4	-6	2·2	-2·3
5	4	-5	1·5	+1·5
5	4	-3	7·8	-7·7
5	4	-1	8·8	+9·7
5	4	1	8·8	-8·4
5	4	2	1·1	+1·9
5	4	4	4·4	-3·4
5	4	6	2·9	-2·0
5	4	7	4·9	-4·3
6	4	-4	3·5	+3·5
6	4	-3	1·5	+1·4
6	4	-2	2·2	-1·7
6	4	-1	7·2	+8·2
6	4	0	4·9	-4·0
6	4	1	8·7	-8·4
6	4	2	3·7	-3·4
6	4	3	1·5	+1·9
6	4	4	3·9	+4·5
6	4	6	4·2	+5·8
7	4	-7	1·9	-1·0
7	4	-6	2·9	-3·0
7	4	-2	2·9	+2·9
7	4	-1	2·6	+2·3
7	4	0	5·7	-5·6
7	4	1	2·4	-1·4
7	4	2	3·5	+3·4
7	4	3	2·4	-1·8
7	4	4	2·9	-1·5
7	4	7	1·9	-1·1
8	4	-7	1·1	+1·0
8	4	-3	4·9	-5·3
8	4	-2	2·2	+2·5
8	4	0	4·3	-4·4
8	4	1	2·4	-2·2
8	4	3	3·3	+4·0
8	4	5	1·5	+1·8
8	4	7	2·5	-1·8
9	4	-5	2·2	+1·6
9	4	-3	1·8	-1·7
9	4	-2	1·8	-2·0
9	4	0	2·5	+1·8
9	4	2	1·9	-1·8
9	4	4	1·9	+1·8
9	4	5	1·9	+1·8
10	4	1	1·5	-1·6
10	4	3	1·6	-1·9
10	4	4	1·5	+1·2
11	4	-1	2·8	+2·9
11	4	0	1·9	+1·7
11	4	1	1·9	-2·5
11	4	2	1·9	+1·1
11	4	3	2·9	+3·3
0	5	2	5·1	+4·3
0	5	3	6·1	-5·9
0	5	4	4·0	-3·5
0	5	6	3·0	+3·5
1	5	-4	2·0	+2·4
1	5	2	2·3	-1·8
1	5	7	1·3	-0·7
2	5	-7	4·1	-4·4
2	5	-2	6·1	+5·7
2	5	-1	3·6	+4·3
2	5	0	5·7	-4·5
2	5	2	6·1	-5·4
2	5	3	7·7	-7·2
2	5	7	2·5	-1·4
3	5	-1	3·5	-3·3
4	5	-3	6·4	+7·0
4	5	-2	9·6	+9·4
4	5	-1	8·7	-10·3
4	5	0	7·9	-6·1
4	5	2	4·7	-3·5
4	5	6	2·0	-0·9
5	5	-2	2·5	-2·5
6	5	-3	4·7	+5·8
6	5	-2	5·1	-5·2
6	5	-1	7·0	-8·1
8	5	-1	2·3	+2·2
8	5	3	3·6	+3·5
9	5	-1	1·9	-1·9
0	6	1	2·4	-2·2
0	6	2	1·7	-1·0
0	6	3	1·9	+1·9
1	6	-1	2·2	+2·5
1	6	0	3·3	-2·9
1	6	1	2·2	-2·1
1	6	3	1·6	+1·4
2	6	-2	3·2	-3·0
2	6	0	3·0	-2·1
2	6	1	3·4	-3·0
2	6	2	1·9	+1·8
3	6	-2	2·7	-2·6
3	6	0	1·3	+1·7
3	6	2	1·6	-1·0
4	6	0	3·8	-4·1

appeared to fit the experimental evidence, it was judged that this was the best way to resolve the disorder. This hypothesis was tested by calculating sets of structure factors for the superposed molecules and for the two separated molecules and comparing the resultant *R* values. Three cycles were computed for each case; the atomic positional parameters were kept constant, but the isotropic thermal parameters and the overall scale factor were refined, with the following results:

R for the superposed molecule with anisotropic *B*'s: 8·8%.

R for the superposed molecule with isotropic *B*'s over three cycles: 25·0, 21·1, 18·6%.

R for two separated molecules with isotropic *B*'s over three cycles: 12·4, 10·6, 10·2%.

It is thus evident that the agreement for the two separated molecules is considerably better than that for the superposed molecule, and that there is not a great deal of difference between the results for the two molecules with spherical thermal coefficients and for the superposed molecule with ellipsoidal thermal coefficients. Unfortunately the separation is too small for it to be feasible to replace the original ellipsoid by two equivalent ellipsoids instead of by two nearest-equivalent spheres; otherwise it would be expected that the isotropic *R* value of 10·2% might be reduced still further. The values of the atomic parameters for the two separated molecules are given in Table 1(*b*).

Long-exposure X-ray photographs with a stationary crystal show no indication of any molecular short-range order, so it may be concluded at this stage that the disorder in the specimens examined was truly random, although we can not be certain that exactly equal numbers of molecules fall into each of the two orientations in any given sample.

Description of the structure

There are two molecules of *p*-azotoluene in the unit cell with space group $P2_1/a$ so that each molecule lies with its mid point on a centre of symmetry. Each molecule is discrete, with only van der Waals forces between neighbours, so that it may be regarded as occupying a given parallelepiped of space. Within this parallelepiped there are two permissible dispositions of the molecule and it has been shown that the molecules may adopt either of these two dispositions randomly. This results in abnormal apparent anisotropic thermal parameters being obtained during the least-squares refinement process.

The atomic positional and thermal parameters obtained from the final cycle of refinement are shown in Table 1(*a*). For the hydrogen atoms, only the isotropic thermal parameters were refined, assuming the C–H distance to be 1·08 Å. The hydrogen atoms in the methyl group were determined from a difference projection along **b**. The agreement between the calculated and observed structure amplitudes is given in Table 2; no corrections were applied, and indeed did not appear to be necessary, for either absorption or extinction.

The intermolecular contacts are of the usual order, the shortest being 3·44 Å between C(1) and C(1′), 3·53 Å between N and C(3′), and 3·54 Å between C(1) and C(4), in each case between adjacent molecules along **b**.

The dimensions of the molecule of *p*-azotoluene are shown in Fig. 4. As these have been derived from the separation of two superposed molecules, the values can not be regarded as of high accuracy, but it would seem that there may be evidence of a small amount of quinonoid character in the benzene ring, two of the bonds, C(2)–C(3) and C(5)–C(6) being 0·03 Å shorter

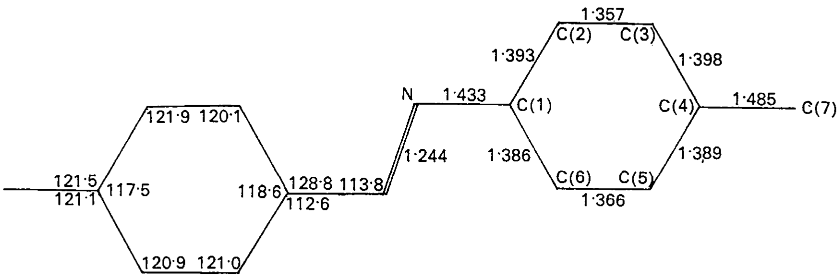

Fig. 4. Mean molecular dimensions.

than the other four. The overall mean C–C length is 1·382 Å, which agrees well with that found in many other compounds. The C(1)–N bond deviates by 8° from linearity, presumably in order to relieve the close approach between N′ and C(6) while maintaining the whole molecule as nearly planar as possible.

The equation of the plane of the mean half-molecule, referred to standard orthogonal axes, is

$$0{\cdot}2540X-0{\cdot}7236Y+0{\cdot}6418Z=0{\cdot}0549$$

while those of the two constituent pairs, rotated from the mean through ±5·0° are

$$0{\cdot}1973X-0{\cdot}7223Y+0{\cdot}6628Z=0{\cdot}0656$$
$$0{\cdot}3089X-0{\cdot}7241Y+0{\cdot}6166Z=0{\cdot}0602$$

The mean deviation of the atoms from these two planes respectively is 0·007 Å, and the perpendicular separation of the two centrosymmetric halves is 0·125 Å.

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References

Brown, C. J. (1960). *Acta Cryst.* **13**, 1049.
Brown, C. J. (1966). *Acta Cryst.* **21**, 146.
Cruickshank, D. W. J. & Pilling, D. E. (1961). In *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
Dunitz, J. D. & Shearer, H. M. M. (1959). *Proc. Chem. Soc.* p. 268.
Kapadia, M. R. (1938). *J. Bombay Univ.* **7**, 2.
Kartha, G. & Ahmed, F. R. (1960). *Acta Cryst.* **13**, 532.
Lange, J. J. de, Robertson, J. M. & Woodward, I. (1939). *Proc. Roy. Soc.* A **171**, 398.
Milledge, H. J. (1964). *Proc. Roy. Soc.* A **267**, 566, and private communication.
Padmanabhan, V. M., Shankar, J. & Khubchandani, P. G. (1958). *Proc. Indian Acad. Sci.* A **47**, 323.
Robertson, J. M., Shearer, H. M. M., Sim, G. A. & Watson, D. G. (1962). *Acta Cryst.* **15**, 1.

Acta Cryst. (1966). **21**, 158

Neutron Diffraction Investigation of WO_3[*]

By B. O. Loopstra and P. Boldrini
Reactor Centrum Nederland, Petten (NH), The Netherlands

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The structure of the room-temperature modification of stoichiometric WO_3 was determined by a neutron-diffraction powder investigation. The space group is $P2_1/n$ and the cell constants are $a=7{\cdot}297$, $b=7{\cdot}539$, $c=7{\cdot}688$ Å, $\beta=90{\cdot}91°$. W–O bonds form zigzag chains in three directions with W–O–W angles of 158° and O–W–O angles of 166°. In the x direction the bonds are of equal length, while in the y and z directions they are alternately long and short.

Introduction

The room-temperature modification of polycrystalline WO_3 has been extensively investigated by X-ray methods. Recent unit-cell data show that it is monoclinic, pseudocubic, with space group $P2_1/a$ and cell dimensions: $a=7{\cdot}306(1)$, $b=7{\cdot}541(1)$, $c=3{\cdot}845(1)$ Å and $\beta=90{\cdot}85(5)°$ (Westman & Magnéli, 1958). Tungsten coordinates have been determined from the X-ray powder intensities (Andersson, 1953), but the oxygen atoms were placed on the basis of packing considerations, resulting in a deformed ReO_3-type structure.

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