The Crystal Structure of Pentachloronitrobenzene

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Crystals of pentachloronitrobenzene are rhombohedral, space group R3, with cell dimensions: $a_{hex} = 8.751$ (2), $c_{hex} = 11.111$ (5) Å and three molecules in a hexagonal cell. The structure was determined by a three-dimensional X-ray analysis. The final R value was 0.107 for 225 observed reflexions. Diffraction patterns showed a partial enhancement of symmetry. The crystal has a disordered structure with an apparent molecular symmetry $\vec{6}$. The positions of the nitro groups overlap those of one of two crystallographically non-equivalent chlorine atoms. The nitro group has two orientations about the C-N axis. The angle between the plane of nitro group and that of the benzene ring is 62° .

Introduction

A number of X-ray investigations on penta- and hexasubstituted benzenes which exhibit disordered crystal structures at room temperature have been reported (Tulinsky & White, 1958; Charbonneau & Trotter, 1967, 1968; Khotsyanova, 1966; Khotsyanova, Babushkina, Kuznetsov & Semin, 1969; Krigbaum & Wildman, 1971). Dielectric as well as nuclear magnetic resonance measurements have also been performed in relation to the molecular-rotational disorder in these crystals (White, Biggs & Morgan, 1940; Eveno & Meinnel, 1966; Brot & Darmon, 1970).

Recently the dielectric absorption in the radiowavefrequency region has been observed in the crystal of pentachloronitrobenzene (PCNB) in the temperature range 20 to 99 °C. The molecule of PCNB is supposed to perform rotational reorientations between several equilibrium positions in the crystal (Aihara, Kitazawa & Nohara, 1970). In order to investigate the relationship between the crystal structure of PCNB and the dielectric absorption, a crystal structure analysis was undertaken.

Experimental

Crystals suitable for X-ray work were obtained from a benzene solution of commercially available PCNB as colourless plates with well developed form {001}. Cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs (Cu K, $\bar{\alpha} = 1.5418$, $\alpha_1 = 1.5405$, $\alpha_2 = 1.5433$ and $\beta = 1.3922$ Å).

Crystal data: pentachloronitrobenzene, C₆Cl₅NO₂, M.W. 295·3; rhombohedral, $a_{hex} = 8.751$ (2), $c_{hex} =$ 11·111 (5) Å ($a_{rh} = 9.113$ Å, $\alpha_{rh} = 106.8^{\circ}$), $V_{hex} = 736.9$ Å³; Z=3 (in a hexagonal cell), $D_m = 1.96$, $D_x = 2.00$ g cm⁻³; m.p. 151°C; linear absorption coefficient μ (Mo K α) = 14·0 cm⁻¹; Laue symmetry: $\overline{3}$ in general, 6/m for l=3n; systematic absences: $h-k+l \neq 3n$ for hkl; space group R3 or R $\overline{3}$. Throughout this paper the hexagonal (reverse setting) indices and coordinates are used. Intensity data were obtained from integrated equiinclination Weissenberg photographs with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) from h0l to h7l and from hk0 to hk8. The intensities were measured with a microphotodensitometer. Lorentz, polarization and spot-shape corrections were applied, but because of the size of the specimens (max. $\mu R \sim 0.35$) no absorption corrections were made. In all, 225 non-zero independent reflexions were observed.

Structure determination

With three molecules in a unit cell of the space group R3 or $R\overline{3}$ the molecule must have either a threefold rotation axis or a threefold rotatory-inversion axis. Therefore the crystal should exhibit an orientational disorder with molecules having an apparent symmetry of 3 or $\overline{3}$. The molecular centre of gravity must lie on special positions (0, 0, z) or (0, 0, 0) for the space group R3 or $R\overline{3}$, respectively.

In addition to the usual Laue symmetry consistent with the space group R3 or $R\overline{3}$, diffraction patterns of PCNB showed, within experimental errors, other symmetry $|F(hkl)| = |F(h\overline{k}l)|$ for l = 3n. As far as these reflexions are concerned, therefore, the patterns strictly exhibit the hexagonal symmetry 6/m. Such a higher symmetry is explained by a composite structure con-



Fig. 1. Statistical distribution of intensities. Black circles: observed in PCNB. Solid lines: theoretical.

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The anisotropic temperature factors are of the form $\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$.

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(a) Heavy atoms. All values are $\times 10^4$

	x	у	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	3980 (9)	1291 (14)	0 (0)	58 (9)	132 (14)	174 (11)	38 (10)	0 (0)	0 (0)
Cl(2)	2540 (9)	4072 (8)	0 (0)	152 (10)	121 (13)	248 (12)	71 (11)	0 (0)	0 (0)

Table 1 (cont.)

(b) Light atoms. Positional parameters are $\times 10^3$

	x	У	Z	$B(A^2)$
C(1)	180 (2)	62 (3)	0 (0)	2.3 (3)
C(2)	114 (3)	182 (3)	0 (0)	3.5 (4)
Ν	372 (7)	133 (8)	0 (0)	1.4 (8)
O(1)	437 (9)	91 (8)	-85 (6)	4.1 (13)
O(2)	472 (9)	219 (9)	86 (6)	3.6 (14)

sisting of three identical substructures whose space group is isogonal with the point group 6, $\overline{6}$ or 6/m and the origins of which are located at (0,0,0), $(\frac{1}{3},\frac{2}{3},\frac{1}{3})$ and $(\frac{2}{3},\frac{1}{3},\frac{2}{3})$, respectively. This is a typical example of the partial enhancement of diffraction symmetry (Sadanaga & Takeda, 1968; Iwasaki, 1972). Possible local space group for the substructure is P6, $P\overline{6}$ or P6/m. Since a unit cell of each substructure contains only one molecule, the apparent molecular symmetry must be 6, $\overline{6}$ or 6/m, respectively.

The molecular orientation was deduced from a threedimensional Patterson synthesis. The molecular plane was found to be perpendicular to the c axis. Three models were assumed for the disordered structures: two for the space group R3 and one for $R\overline{3}$. In the first model, (I), the nitro groups are distributed through the crystal at only one of two crystallographically nonequivalent chlorine positions, Cl(1); in the second

Table 2. Observed and calculated structure factors $(\times 3)$

* indicates the strong reflexions which were excluded from the refinements.

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model, (II), the nitro groups are distributed at the other chlorine position Cl(2). The third model, (III), has the nitro groups distributed through all the chlorine positions with equal probability. If the oxygen atoms are neglected, models (I) and (II) correspond to the local space group $P\overline{6}$, and model (III) to P6 or P6/m.

For all three models block-diagonal least-squares refinements were carried out with anisotropic temperature factors for chlorine atoms and isotropic temperature factors for carbon atoms. At this stage the nitro groups were omitted from the structure-factor calculations. The R values dropped to 0.12 for (I) and (II), and to 0.13 for (III). However, peaks corresponding to the nitro groups could not be found on difference Fourier maps for all the models. Therefore the positions of the nitro groups were assumed for each model so as to conform to the intra- and intermolecular packing. In addition to the above three models, those with the nitro groups superposed on both of two non-equivalent chlorine positions, Cl(1) and Cl(2)⁴ at various ratios were also taken into consideration. The multiplicities of Cl(1), Cl(2), $NO_2(1)$ and $NO_2(2)$ were changed from 2 to 3, 3 to 2, 1 to 0 and 0 to 1, respectively, each by 0.1, and in total, 11 models were checked. Each model was refined by the least-squares procedure with fixed multiplicities. The positions of the nitro groups were included only in the structurefactor calculations. The case with the nitro group localized at the position of Cl(1) [model (I)] gave the lowest value for the R index.

At this stage an N(z) test (Howells, Phillips & Rogers, 1950) was carried out and the result indicated the non-centrosymmetrical space group, R3, (Fig. 1). Accordingly, the molecule should have an apparent symmetry of 3, but not $\overline{3}$; and the local space group corresponding to the substructure should be $P\overline{6}$. If the local space group were either P6 or P6/m, the entire structure would be approximately centrosymmetric for P6 and strictly centrosymmetric for P6/m. This is inconsistent with the result of the N(z) test. With the local space group $P\overline{6}$, the molecule must have a mirror symmetry as well as the threefold axis and, therefore, the molecule should exhibit another form of disorder with respect to the orientations of the nitro groups.

The full-matrix least-squares refinement with anisotropic temperature factors for chlorine atoms and isotropic temperature factors for carbon, nitrogen and oxygen atoms was continued for model (I), whose molecular symmetry is $\overline{6}$, until the *R* value reduced to 0.095 (weighted *R* 0.116) for all the observed reflexions except three strong ones (0.107 including these three reflexions). The refinements by the full-matrix leastsquares method were tried for model (II) (molecular symmetry $\overline{6}$) and also for the models with molecular symmetry 6 and 6/m. For model (II) the R value for all the observed reflexions except three strong ones was reduced to 0.112 (weighted R 0.142) but the temperature factor of nitrogen atom became negative and dimensions of the nitro group became abnormal. For the models with molecular symmetry 6 and 6/m, the R values were 0.126 and 0.112 (weighted R 0.154 and 0.147), respectively, and the nitro groups were also distorted. Significance tests on the *R* values (Hamilton, 1965) were applied. The hypothesis that the correct model is (II) or the models with the molecular symmetry 6 and 6/m can be strongly rejected at the 0.005 significance level.

In view of these results it is most likely that the space group of PCNB crystal is R3, the apparent molecular symmetry being $\overline{6}$, and that the positions of the nitro groups overlap those of Cl(1) with two possible orientations about the C-N axis.

At the final stage of the refinement, $\sum w(|F_o| - k|F_c|)^2$ was minimized, where w was calculated according to the equation: $w = 1/(a|F_o|^2 + b|F_o| + c)$; final values for a = -0.002, b = 0.470 and c = 2.079. Atomic scattering factors for all the atoms were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters with their estimated standard deviations are shown in Table 1. A comparison of the observed and calculated structure factors is listed in Table 2.

Results and discussion

The bond distances, bond angles and some non-bonding distances of the PCNB molecule are given in Table 3 and Fig. 2. The mean C-C distance of the benzene ring is 1.39 Å. The C-Cl distances, 1.69 and 1.72 Å, are in agreement with the carbon-chlorine distances found in other benzene derivatives (Sakurai, 1962; Holden & Dickinson, 1967; Silverman, Soltzberg,

Table 3. Interatomic distances (Å) and bond angles(°) of PCNB molecule

$\begin{array}{cccc} C(1)-C(2) & 1.42\\ C(1)-C(2^{11}) & 1.36\\ C(1)-Cl(1) & 1.69\\ C(2)-Cl(2) & 1.72\\ C(1)-N & 1.47\\ N-O(1) & 1.25\\ N-O(2) & 1.26\\ \end{array}$	2 (4) (4) (2) 4 (2) (6) (9) (7)	$Cl(1) \cdots Cl(1) \cdots Cl(2) \cdots Cl(2$	Cl(2) Cl(211) O(11) O(2) O(11) O(2) O(2)	3·25 (1 2·94 (1 2·97 (1 3·09 (1 2·93 (8 3·20 (1)) 1) 0) 0)
$\begin{array}{c} C(2) &C(1) - C(2^{1i}) \\ C(1) &C(2) - C(1^{1}) \\ C(2) &C(1) - C(1) \\ C(2^{1i}) - C(1) - C(1) \\ C(1^{1}) - C(2) - C(1) \\ C(1^{1}) - C(2) - C(1) \\ C(2) &C(1) - N \\ C(2^{1i}) - C(1) - N \\ C(1) &N \\ C(2) \\ O(1) \\N \\ C(2) \\ O(2) \\ C(2) \\ C(2$	121 (2) 119 (2) 123 (1) 116 (2) 122 (2) 119 (2) 119 (3) 120 (3) 118 (4) 124 (5) 118 (7)	Syr Superscr None i ii	nmetry c ipt x, -y, y-x, y-x, x	ode y, x-y, -x,	z z z

Yannoni & Krukonis, 1971). The two independent intramolecular Cl···Cl distances, 3·25 and 2·94 Å, are considerably different. The coordinates of the nitro group cannot be determined with sufficient accuracy because of a disordered structure. However, the distances C-N (1·47 Å), N-O (1·25 and 1·26 Å) and angle ONO (118°) have normal values. The plane of the nitro group is:

$$0.301X - 0.831Y + 0.467Z = 0.0$$

where X, Y and Z are the coordinates in Å referred to the axes a, b^* and c. The angle between this plane and the plane of the benzene ring is 62° .

The molecular arrangement is shown in Figs. 3 and 4. The PCNB crystal has a disordered structure with an apparent molecular symmetry of $\overline{6}$, the positions of the nitro groups overlapping those of Cl(1). Thus, the molecule may perform rotational reorientations in the crystal between three equivalent equilibrium positions. This result is quite consistent with the conclusion derived from the dielectric measurement (Aihara *et al.*,



Fig. 2. Bond distances (Å) and angles (°) of PCNB molecule.



Fig. 3. Projection of the structure along the c axis,

1970). Moreover, the nitro group has two orientations about the C-N axis.

The intermolecular distances are listed in Table 4. There are some short intermolecular distances $[Cl(2)\cdots Cl(2^{iv}), 3\cdot49; Cl(1)\cdots O(1^{xii}), 3\cdot01 \text{ Å}]$. All other molecular contacts are of the van der Waals type.

Table 4. Intermolecular distances

The e.s.d.'s are for $Cl \cdots Cl 0.01$, $Cl \cdots O 0.08$, $C \cdots O 0.10$ Å.

Super-

Symmetry code

script	
None x y z iii $-y+1 x-y z$ iv $-y+1 x-y+1 z$ v $y-x+1 -x+1 z$ vi $x-\frac{1}{3} y+\frac{1}{3} z-\frac{1}{3}$ vii $-y+\frac{2}{3} x-y+\frac{1}{3} z-\frac{1}{3}$ viii $y-x+\frac{2}{3} -x+\frac{1}{3} z-\frac{1}{3}$	ix $x - \frac{1}{3}$ $y + \frac{1}{3}$ $-z - \frac{1}{3}$ x $y - x + \frac{2}{3}$ $-x + \frac{1}{3}$ $-z - \frac{1}{3}$ xi $x + \frac{1}{3}$ $y - \frac{1}{3}$ $z + \frac{1}{3}$ xii $-y + \frac{1}{3}$ $x - y - \frac{1}{3}$ $z + \frac{1}{3}$ xiii $y - x + \frac{1}{3}$ $-x + \frac{2}{3}$ $z + \frac{1}{3}$ xiv $-y + \frac{1}{3}$ $x - y - \frac{1}{3}$ $-z + \frac{1}{3}$ xv $y - x + \frac{1}{3}$ $-x + \frac{2}{3}$ $-z + \frac{1}{3}$
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Fig. 4. Projection of the structure along the b axis.

Recently the molecular packing of this substance has been reported by Rossell & Scott (1972). They assumed that the space group of PCNB is $R\overline{3}$ and their structure was based on a small number of reflexions which were not measured quantitatively.

The computations were carried out by the program system UNICS, Universal Crystallographic Computation Program System (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967), on the HITAC 5020E Computer at the Computer Centre, University of Tokyo.

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