

## The Crystal Structure of Pentachloronitrobenzene

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Crystals of pentachloronitrobenzene are rhombohedral, space group  $R\bar{3}$ , with cell dimensions:  $a_{\text{hex}} = 8.751(2)$ ,  $c_{\text{hex}} = 11.111(5)$  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  $\bar{3}$ . 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  $62^\circ$ .

### Introduction

A number of X-ray investigations on penta- and hexa-substituted 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 & Meinel, 1966; Brot & Darmon, 1970).

Recently the dielectric absorption in the radiowave-frequency region has been observed in the crystal of pentachloronitrobenzene (PCNB) in the temperature range 20 to  $99^\circ\text{C}$ . 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  $K\alpha$ ,  $\bar{\alpha} = 1.5418$ ,  $\alpha_1 = 1.5405$ ,  $\alpha_2 = 1.5433$  and  $\beta = 1.3922$  Å).

Crystal data: pentachloronitrobenzene,  $\text{C}_6\text{Cl}_5\text{NO}_2$ , M.W. 295.3; rhombohedral,  $a_{\text{hex}} = 8.751(2)$ ,  $c_{\text{hex}} = 11.111(5)$  Å ( $a_{\text{rh}} = 9.113$  Å,  $\alpha_{\text{rh}} = 106.8^\circ$ ),  $V_{\text{hex}} = 736.9$  Å<sup>3</sup>;  $Z = 3$  (in a hexagonal cell),  $D_m = 1.96$ ,  $D_x = 2.00$  g cm<sup>-3</sup>; m.p.  $151^\circ\text{C}$ ; linear absorption coefficient  $\mu(\text{Mo } K\alpha) = 14.0$  cm<sup>-1</sup>; Laue symmetry:  $\bar{3}$  in general,  $6/m$  for  $l = 3n$ ; systematic absences:  $h - k + l \neq 3n$  for  $hkl$ ; space group  $R\bar{3}$  or  $R\bar{3}$ . Throughout this paper the hexagonal (reverse setting) indices and coordinates are used.

Intensity data were obtained from integrated equi-inclination 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  $R\bar{3}$  or  $R\bar{3}$  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  $\bar{3}$ . The molecular centre of gravity must lie on special positions (0, 0,  $z$ ) or (0, 0, 0) for the space group  $R\bar{3}$  or  $R\bar{3}$ , respectively.

In addition to the usual Laue symmetry consistent with the space group  $R\bar{3}$  or  $R\bar{3}$ , diffraction patterns of PCNB showed, within experimental errors, other symmetry  $|F(hkl)| = |F(\bar{h}\bar{k}l)|$  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-

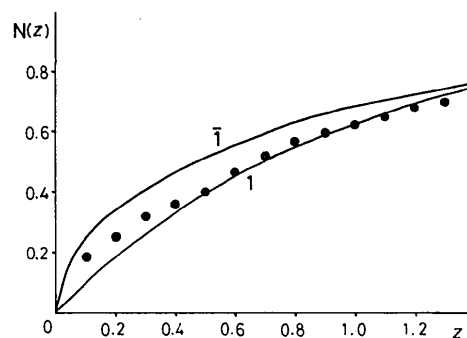


Fig. 1. Statistical distribution of intensities. Black circles: observed in PCNB. Solid lines: theoretical.

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reflexions). The refinements by the full-matrix least-squares method were tried for model (II) (molecular symmetry  $\bar{6}$ ) 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  $\bar{6}$ , 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:  $w = 1/(a|F_o|^2 + b|F_c| + c)$ ; 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,

Yannoni & Krukoni, 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  $\bar{6}$ , 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.*,

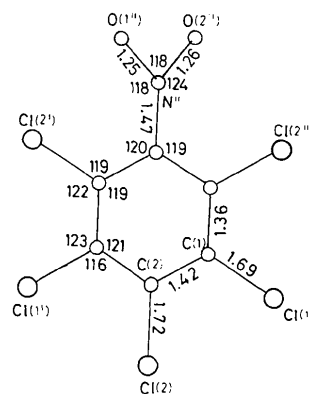


Fig. 2. Bond distances (Å) and angles (°) of PCNB molecule.

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

C(1)-C(2)	1.42 (4)	Cl(1)...Cl(2)	3.25 (1)
C(1)-C(2 <sup>ii</sup> )	1.36 (4)	Cl(1)...Cl(2 <sup>ii</sup> )	2.94 (1)
C(1)-Cl(1)	1.69 (2)	C(2)...O(1 <sup>i</sup> )	2.97 (11)
C(2)-Cl(2)	1.72 (2)	C(2)...O(2)	3.09 (10)
C(1)-N	1.47 (6)	Cl(2)...O(1 <sup>i</sup> )	2.93 (8)
N-O(1)	1.25 (9)	Cl(2)...O(2)	3.20 (10)
N-O(2)	1.26 (7)		
C(2)-C(1)-C(2 <sup>ii</sup> )	121 (2)		
C(1)-C(2)-C(1 <sup>i</sup> )	119 (2)		
C(2)-C(1)-Cl(1)	123 (1)		
C(2 <sup>ii</sup> )-C(1)-Cl(1)	116 (2)		
C(1)-C(2)-Cl(2)	122 (2)		
C(1 <sup>i</sup> )-C(2)-Cl(2)	119 (2)		
C(2)-C(1)-N	119 (3)		
C(2 <sup>ii</sup> )-C(1)-N	120 (3)		
C(1)-N-O(1)	118 (4)		
C(1)-N-O(2)	124 (5)		
O(1)-N-O(2)	118 (7)		

Symmetry code			
Superscript			
None	$x$ ,	$y$ ,	$z$
i	$-y$ ,	$x-y$ ,	$z$
ii	$y-x$ ,	$-x$ ,	$z$

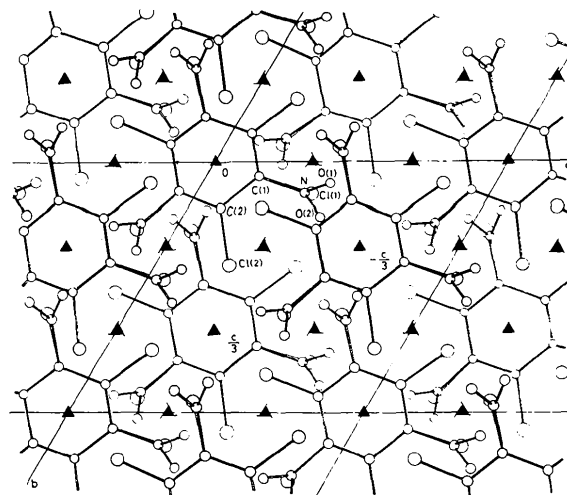


Fig. 3. Projection of the structure along the  $c$  axis.

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)···Cl(2<sup>iv</sup>), 3.49; Cl(1)···O(1<sup>xii</sup>), 3.01 Å]. All other molecular contacts are of the van der Waals type.

Table 4. *Intermolecular distances*

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

Super-script	Symmetry code			Symmetry code			Symmetry code		
None	$x$	$y$	$z$	ix	$x-\frac{1}{2}$	$y+\frac{1}{2}$	$-z-\frac{1}{2}$		
iii	$-y+1$	$x-y$	$z$	x	$y-x+\frac{2}{3}$	$-x+\frac{1}{3}$	$-z-\frac{1}{3}$		
iv	$-y+1$	$x-y+1$	$z$	xi	$x+\frac{1}{3}$	$y-\frac{1}{3}$	$z+\frac{1}{3}$		
v	$y-x+1$	$-x+1$	$z$	xii	$-y+\frac{1}{2}$	$x-y-\frac{1}{2}$	$z+\frac{1}{2}$		
vi	$x-\frac{1}{3}$	$y+\frac{1}{3}$	$z-\frac{1}{3}$	xiii	$y-x+\frac{1}{3}$	$-x+\frac{2}{3}$	$z+\frac{1}{3}$		
vii	$-y+\frac{2}{3}$	$x-y+\frac{1}{3}$	$z-\frac{1}{3}$	xiv	$-y+\frac{1}{2}$	$x-y-\frac{1}{2}$	$-z+\frac{1}{2}$		
viii	$y-x+\frac{2}{3}$	$-x+\frac{1}{3}$	$z-\frac{1}{3}$	xv	$y-x+\frac{1}{3}$	$-x+\frac{2}{3}$	$-z+\frac{1}{3}$		

Cl(1)···Cl(1 <sup>iii</sup> )	3.68 Å	Cl(2)···O(1 <sup>v</sup> )	3.20 Å
Cl(1)···Cl(2 <sup>iii</sup> )	3.64	Cl(2)···O(2 <sup>vi</sup> )	3.39
Cl(1)···Cl(2 <sup>vi</sup> )	3.99	Cl(2)···O(2 <sup>vii</sup> )	3.20
Cl(1)···Cl(1 <sup>viii</sup> )	4.07	Cl(2)···O(1 <sup>ix</sup> )	3.09
Cl(1)···Cl(2 <sup>xi</sup> )	4.18	Cl(2)···O(1 <sup>xiii</sup> )	3.43
Cl(1)···Cl(2 <sup>xiii</sup> )	4.31	Cl(2)···O(2 <sup>xv</sup> )	3.24
Cl(2)···Cl(2 <sup>iv</sup> )	3.49	C(1)···O(1 <sup>xii</sup> )	2.88
Cl(1)···O(2 <sup>iii</sup> )	3.11	C(1)···O(2 <sup>xiv</sup> )	2.96
Cl(1)···O(1 <sup>v</sup> )	3.44	C(1)···O(2 <sup>xv</sup> )	3.26
Cl(1)···O(2 <sup>v</sup> )	3.43	C(2)···O(1 <sup>ix</sup> )	3.51
Cl(1)···O(1 <sup>x</sup> )	3.29	C(2)···O(1 <sup>xiii</sup> )	3.08
Cl(1)···O(1 <sup>xii</sup> )	3.01	C(2)···O(2 <sup>xv</sup> )	2.77

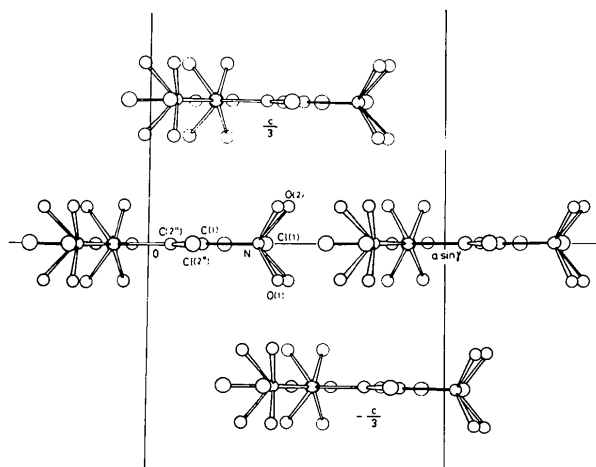


Fig. 4. Projection of the structure along the  $b$  axis.

Recently the molecular packing of this substance has been reported by Rossell & Scott (1972). They assumed that the space group of PCNB is  $R\bar{3}$  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 & Fukushima, 1967), on the HITAC 5020E Computer at the Computer Centre, University of Tokyo.

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