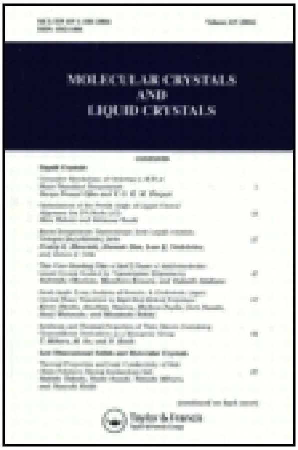

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Molecular Packing in Pentachloronitrobenzene: A Partial Structure Determination

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Abstract—Pentachloronitrobenzene crystallized from ethanol at room temperature is trigonal, space group R $\bar{3}$. Referred to hexagonal axes the unit cell has parameters $a = 8.769$ Å, $c = 11.209$ Å and contains three molecules which lie flat in close packed planes parallel to (0001). The structure is disordered in the sense that the nitro-group is not distinguishable in the crystal from the chlorine atoms: there is not, however, free rotation of the molecules.

1. Crystal Data

Crystals of pentachloronitrobenzene ($C_6Cl_5NO_2$) grown from a solution in ethanol by slow evaporation at room temperature were trigonal, chunky in habit and bounded by faces of the forms {0001}, {10$\bar{1}$1} and {1$\bar{1}$02}. The axial ratio, $c:a$, determined by optical goniometry was 1.271. The crystals were optically unaxial with negative birefringence, an observation typical of structures in which planar molecules lie with their planes normal to the unique axis.$^{(1)}$

Weissenberg photographs taken with Cu Kα radiation showed the systematic absences characteristic of a rhombohedral cell and, together with Laue photographs and the external morphology, established the space group as R $\bar{3}$. Lattice parameters were determined from powder photographs taken with a Guinier focussing camera using thoria ($a = 5.5966$ Å) as an internal standard. The parameters were $a = 8.769$ Å, $c = 11.209$ Å, the corresponding axial ratio being 1.278 (cf. 1.271 from external morphology). The density measured with a pyknometer was 1.970 g cm^{-3}, which is in excellent agreement with the density of 1.971 g cm^{-3} calculated from the experimental lattice parameters assuming that there are three molecules in the unit cell.

2. Molecular Packing

Since there are only three molecules in the unit cell these must be "centred" on the special positions 0, 0, 0; $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{3}$; and $\frac{2}{3}$, $\frac{1}{3}$, $\frac{2}{3}$. For an essentially planar molecule, as we believe pentachloronitrobenzene to be, the point symmetry of these positions, $\bar{3}$, requires that (i) the molecular plane is parallel to (0001) and (ii) the molecular orientation is disordered in the sense that the six substituent positions round the benzene ring are indistinguishable, i.e. on the average the nitro group occupies with equal probability, each of the six sites. Free rotation of the molecules is excluded as this would result in the space group being R $\bar{3}$m.

With these restrictions on the molecular packing the only variable remaining is the angular orientation, ϕ (see Fig. 1), of the molecule. An estimate of ϕ was obtained by assuming closest packing of molecules having the same orientation. This implies that a substituent on one benzene ring is equidistant from two others on an adjacent ring, and leads to the expression $\phi = 30° \pm \arcsin\ (r/2a)$ where r is the radius of the substituent ring. Ignoring the distinction between the chlorine atoms and the nitro group the bond lengths in Fig. 1⁽²⁾ give $r \simeq 3.10$ Å, which with the measured lattice parameter $a = 8.769$ Å predicts a value for ϕ of 19.8°.

3. X-Ray Intensity Data

To test the plausibility of the molecular packing deduced above, observed X-ray intensities were compared with those calculated for this structure. Atomic scattering factors from the International Tables for X-ray Crystallography,(2) weighted to allow for the proposed disorder were used, together with an overall temperature factor $B = 3.25$ Å^{-2} appropriate to structures of this type at room temperature.(3) Lorentz and polarization factors were taken into account but no corrections were made for extinction or absorption. Intensities were calculated for orientations in the range $\phi = 17°$ to $\phi = 23°$ for a molecule having the dimensions indicated in Fig. 1.

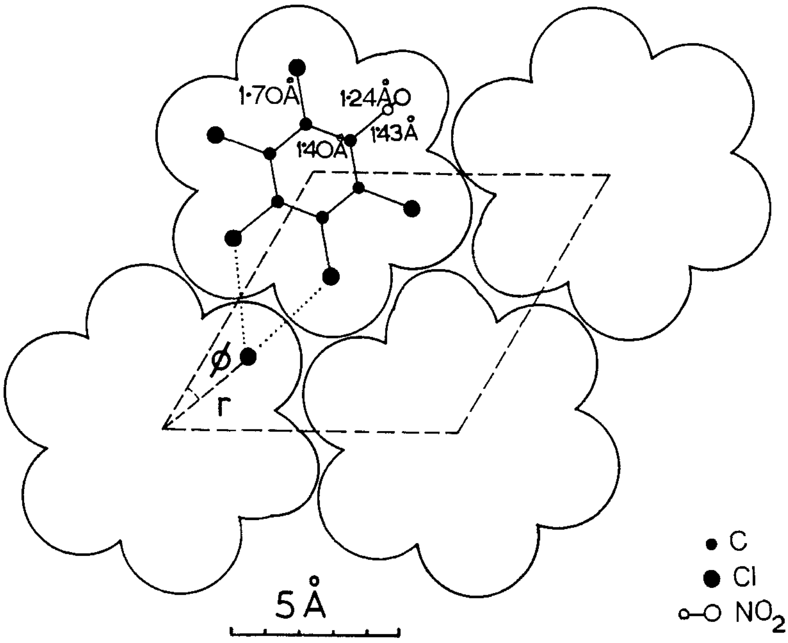

Figure 1. Packing of pentachloronitrobenzene molecules in layers parallel to (0001).

Observed intensities were estimated from Weissenberg photographs and classified into six groups from "very strong" to "not measurable". Since only a single film was exposed for each layer, distinctions concerning the stronger reflexions are poor, all reflexions above a certain value appearing almost equally intense. In estimating the best fit, particular emphasis was placed on pairs of reflexions of the type $hkil$ and $khi\bar{l}$. Since these were recorded on the same film at the same value of $\sin\theta$, the errors inherent in the comparison of intensities were reduced; further it was found that the relative intensities calculated for such pairs were often very sensitive to small changes in ϕ.

Qualitatively the most satisfactory value of ϕ was $20° \pm 1°$: Table 1 lists observed and calculated intensities of reflexions with $\sin\theta$ less than 0.6 in order of increasing $\sin\theta$. The agreement for low angle reflexions which are relatively insensitive to the exact atomic positions, is *prima facie* evidence for the substantial correctness of the structure at the level of accuracy sought here; for

Table 1 Calculated and Observed X-ray Intensities (listed in order of increasing Bragg angle)

$h\,k\,l$	$\sin\theta$	I (calc)	I (obs)	$h\,k\,l$	$\sin\theta$	I (calc)	I (obs)
$0\,1\,\bar{1}$	0.123	123	s	$1\,1\,6$	0.449	8	vw
$0\,1\,2$	0.171	84	s	$1\,1\,\bar{6}$	0.449	8	vw
$1\,1\,0$	0.176	111	s	$1\,3\,4$	0.458	2	nil
$0\,0\,3$	0.206	3711	vs	$3\,1\,\bar{4}$	0.458	60	s
$0\,2\,1$	0.214	172	vs	$1\,4\,0$	0.465	34	s
$0\,2\,\bar{2}$	0.245	117	s	$4\,1\,0$	0.465	141	vs
$1\,1\,3$	0.271	38	s	$0\,4\,\bar{4}$	0.490	22	m
$1\,1\,\bar{3}$	0.271	38	s	$0\,1\,\bar{7}$	0.492	3	w
$1\,2\,\bar{1}$	0.277	1057	vs	$1\,3\,\bar{5}$	0.502	2	vw
$2\,1\,1$	0.277	48	m	$3\,1\,5$	0.502	41	s
$0\,1\,\bar{4}$	0.293	32	s	$1\,4\,\bar{3}$	0.509	21	m
$1\,2\,2$	0.302	707	vs	$4\,1\,3$	0.509	59	s
$2\,1\,\bar{2}$	0.302	33	m	$1\,4\,3$	0.509	21	m
$0\,3\,0$	0.305	74	s	$4\,1\,\bar{3}$	0.509	59	s
$0\,2\,4$	0.342	38	s	$0\,5\,1$	0.512	<1	w
$2\,2\,0$	0.352	<1	vw	$0\,3\,6$	0.513	5	w
$0\,1\,5$	0.358	17	m	$0\,2\,7$	0.522	9	w
$0\,3\,3$	0.368	26	s	$0\,5\,\bar{2}$	0.526	<1	w
$1\,3\,1$	0.372	<1	vw	$3\,3\,0$	0.527	<1	vw
$3\,1\,\bar{1}$	0.372	139	vs	$0\,4\,5$	0.532	16	m
$1\,2\,\bar{4}$	0.384	211	vs	$2\,4\,1$	0.541	123	s
$2\,1\,4$	0.384	11	m	$4\,2\,\bar{1}$	0.541	<1	nil
$1\,3\,\bar{2}$	0.391	1	nil	$2\,2\,6$	0.542	1	vw
$3\,1\,2$	0.391	115	s	$2\,2\,\bar{6}$	0.542	1	nil
$0\,2\,\bar{5}$	0.399	21	m	$1\,2\,\bar{7}$	0.551	64	s
$2\,2\,3$	0.408	1	w	$2\,1\,7$	0.551	3	w
$2\,2\,\bar{3}$	0.408	1	w	$0\,1\,8$	0.559	1	w
$0\,4\,\bar{1}$	0.412	47	s	$3\,3\,3$	0.566	<1	w
$0\,0\,6$	0.413	433	vs	$3\,3\,\bar{3}$	0.566	<1	w
$0\,4\,2$	0.429	40	s	$1\,5\,\bar{1}$	0.569	<1	vw
$1\,2\,5$	0.436	124	s	$5\,1\,1$	0.569	7	m
$2\,1\,\bar{5}$	0.436	6	w	$0\,5\,4$	0.577	<1	w
$3\,2\,1$	0.448	40	m	$1\,5\,2$	0.582	<1	vw
$2\,3\,\bar{1}$	0.448	23	m	$5\,1\,\bar{2}$	0.582	7	m

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, nil = not measurable.

The third hexagonal index, which is equal to $\bar{h}+\bar{k}$, had been supressed in the table above.

reflexions with $\sin\theta$ greater than 0.6 the agreement deteriorates markedly.

4. Polymorphism

Thermodynamic arguments suggest that a disordered structure may be stabilized above some critical temperature by the increased entropy and hence decreased free energy arising from the disorder, but that at a sufficiently low temperature an ordered structure should be stable. Calorimetric measurements on pentachloronitrobenzene from 180 K to room temperature have failed to reveal any phase change in this temperature range.

We have however observed a phase change on heating pentachloronitrobenzene; this transition takes place at 408 K (9 K below the melting point) with an enthalpy change of 628 J mol^{-1}. It is also indicated by a change in the powder diffraction pattern at the same temperature. The high temperature form, which may correspond to a structure with freely rotating molecules, is probably triclinic but even the unit cell is not yet established.

5. Discussion

This partial structure determination has two points of interest, the high symmetry and the disordered nature of the structure, at room temperature. For comparison, it is noted that pentachloroaniline and pentachlorophenol with similar molecular shapes, as well as the more symmetrical hexachlorobenzene, all crystallize in the monoclinic system.

The disordered structure, in which the chlorine atoms and nitro group are effectively isomorphous is similar to that found for *p*-chloronitrobenzene by Mak and Trotter.(4) While X-ray studies do not distinguish between a purely spatial disorder and hindered rotation of the molecules, recent measurements of the dielectric constant suggest that in pentachloronitrobenzene hindered rotation occurs.(5)

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