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The Crystal Structure of *p*-Chloronitrobenzene

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Crystals of *p*-chloronitrobenzene are monoclinic with

$$a = 3{\cdot}84,\ b = 6{\cdot}80,\ c = 13{\cdot}35\ \text{Å},\ \beta = 97°\ 31'.$$

The systematically-absent reflexions correspond to space group $P2_1/c$, and there are *two* molecules in the unit cell, so that a molecular centre of symmetry is required. Projections along the *a*- and *b*-axes indicate that this is achieved by a disordered arrangement of molecules involving random interchange of the positions of the chlorine atom and nitro-group. The gross features of the structure have been established, but the disorder has prevented accurate measurement of the molecular dimensions.

1. Introduction

A preliminary investigation of the crystal structure of *p*-chloronitrobenzene (Toussaint, 1952; *Structure Reports*, 1952) indicated that the absent reflexions corresponded to space group $P2_1/c$ (interchanging his *a* and *c* axes), and the measured density to *two* molecules in the unit cell, necessitating a molecular centre of symmetry. Two types of structure were considered possible: (i) a disordered arrangement of molecules in space group $P2_1/c$, giving a statistically centrosymmetric structure, or (ii) an ordered arrangement in space group Pc which gives weak $0k0$ reflexions when k is odd. Arrangement (ii) was considered more likely, and a structure, based on space group Pc, was deduced from consideration of a few structure factors (which were not listed).

We have now re-examined this structure and the analysis, which is described in this paper, suggests that the true space group is $P2_1/c$ and that a disordered arrangement of molecules exists in the crystal.

2. Experimental

Crystals of *p*-chloronitrobenzene, obtained by crystallization from ethanol, are colourless needles elongated along the *a*-axis with the (010) face developed. The density was measured by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, $0kl$ and $1kl$ Weissenberg films, and $hk0$ and $h0l$ precession films.

Crystal data

p-Chloronitrobenzene (1-chloro-4-nitrobenzene), $C_6H_4NO_2Cl$; $M = 157{\cdot}6$; m.p. 83·5 °C.

Monoclinic, $a = 3{\cdot}84 \pm 0{\cdot}01$, $b = 6{\cdot}80 \pm 0{\cdot}01$, $c = 13{\cdot}35 \pm 0{\cdot}02$ Å; $\beta = 97°\ 31' \pm 5'$.

Volume of the unit cell $= 345{\cdot}6$ Å^3.

Density, calculated (with $Z = 2$) $= 1{\cdot}514$, measured $= 1{\cdot}520$ g.cm.$^{-3}$.

Absorption coefficient for X-rays, $\lambda = 1{\cdot}5418$ Å, $\mu = 44{\cdot}1$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}1$ cm.$^{-1}$.

Total number of electrons per unit cell $= F(000) = 160$.

Absent spectra: $h0l$ when l is odd, $0k0$ when k is odd. Space group is $P2_1/c\text{–}C_{2h}^5$.

Crystals of *p*-chloronitrobenzene are highly volatile at room temperature so that a crystal volatilized completely in a few hours. The crystal used for intensity measurement was a needle about 3 mm. in length and $0{\cdot}15 \times 0{\cdot}08$ mm. in cross-section. It was sealed in a thin-walled Lindemann-glass capillary. The intensities of the $0kl$ reflexions were recorded on Weissenberg exposures for a crystal rotating about the *a*-axis, using Cu $K\alpha$ radiation, and multiple-films to correlate strong and weak reflexions. The $h0l$ reflexions were recorded on precession films with Mo $K\alpha$ radiation, using multiple exposures for intensity correlation. The ranges of $0kl$ and $h0l$ intensities were about 3600 to 1 and 1800 to 1 respectively, the estimates being made visually. No absorption corrections were considered necessary. The structure amplitudes were derived by the usual formulae, the absolute scale being established later by correlation with the calculated structure factors. 57 independent $0kl$ reflexions and 35 $h0l$ reflexions were observed, representing 48% and 44% respectively of the possible numbers observable under the experimental conditions.

3. Structure analysis

[100] *projection*

The Patterson map could be interpreted on the basis of both ordered and disordered structures, although the chlorine–chlorine interactions were much weaker than expected, suggesting that the ordered structure was less likely. Nevertheless a few structure factors were calculated using an ordered model, with atomic scattering factors from *Tabellen zur Röntgenstrukturanalyse* (Sagel, 1958). The agreement between measured and calculated structure factors was rather poor, and the calculated values for $0k0$ reflexions with k odd were significantly larger than the maximum possible observed values.

A disordered model was then set up, consisting of two half-molecules, superimposed so that the carbon atoms coincided, but with the positions of the chlorine and nitro groups interchanged. Approximate correlation between measured and calculated structure factors was obtained, the temperature factor being apparently quite high, and an electron-density projection showed good resolution of the six-membered ring and a peak of the expected shape and height at the position of the overlapping chlorine atom and nitro group (Fig. 1). New coordinates were obtained and the $0kl$ structure factors recalculated, a temperature factor $B=8{\cdot}5$ Å^2 being obtained by plotting $\ln\{|F_c|/|F_o|\}$ against $\sin^2\theta$. The strongest reflexions had consistently high F_c values, and these discrepancies were attributed

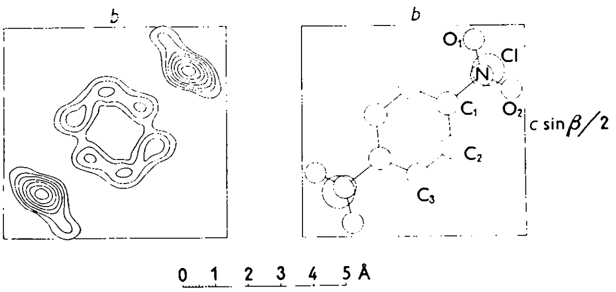

Fig. 1. (*a*) Electron density projection along [100]. Contours are drawn at intervals of approximately 1 e.Å^{-2}, with the lowest contour at 3 e.Å^{-2}. (*b*) The structure viewed along [100].

Table 1. *Comparison of observed and calculated structure factors*

hkl	F_o	F_c
000	—	160
002	12·6 (21·1)	+24·3
004	18·3 (28·9)	−34·3
006	4·8	− 9·2
008	<0·6	+ 3·7
0,0,10	3·6	− 2·4
011	13·6 (16·3)	+12·4
012	19·4 (42·5)	−43·4
013	11·6 (15·0)	+21·2
014	16·2 (16·8)	+12·4
015	4·8	− 0·8
016	7·5	+10·3
017	12·9	− 8·9
018	0·6	+ 2·5
019	1·6	− 2·1
0,1,10	2·1	− 1·3
0,1,11	1·3	+ 1·3
0,1,12	4·7	+ 3·6
020	15·8 (18·6)	−16·9
021	16·1 (22·2)	+25·8
022	7·8	+ 7·5
023	12·5	+12·4
024	10·3	− 8·8
025	15·1	−13·6
026	12·4	− 9·1
027	0·6	− 1·8
028	2·1	+ 0·8
029	5·8	+ 7·3
0,2,10	5·3	+ 4·9
0,2,11	0·8	+ 1·9
031	2·0	− 0·9
032	1·7	− 1·6
033	19·6 (23·2)	−25·6
034	10·3	− 6·9
035	6·1	− 4·9
036	<0·6	+ 2·3
037	9·8	+ 9·9
038	2·8	− 1·1
039	0·7	+ 4·1
040	4·7	− 3·4
041	1·3	− 6·6
042	6·1	− 4·5
043	1·6	+ 2·0
044	1·7	+ 1·4
045	4·0	+ 5·0
046	1·3	− 3·1
047	7·4	− 3·1
048	1·1	+ 0·4
049	4·3	− 4·8
0,4,10	3·5	+ 3·3
051	1·7	+ 1·4
052	2·7	+ 4·9
053	1·3	+ 3·4
054	<0·8	− 0·6
055	<0·8	− 1·6
056	2·4	− 3·7
057	<0·8	− 1·3
058	<0·8	+ 1·4
059	2·4	+ 0·1
060	<0·8	+ 6·0
061	<0·8	+ 2·0
062	<0·8	+ 2·0
063	2·5	+ 1·7
064	0·8	− 2·6
065	1·1	+ 0·9
071	<0·8	+ 1·1
072	<0·8	− 1·0
073	1·8	+ 0·6
074	<0·8	+ 0·4
075	0·7	− 0·3
100	9·3	− 7·3
200	<1·1	+ 5·8
300	3·4	+ 2·1
400	3·0	− 3·1
500	<1·5	+ 0·3
$\bar{3}02$	2·5	+ 3·2
$\bar{2}02$	4·2	−15·7
$\bar{1}02$	37·0	+70·0
002	23·0	+24·3
102	11·7	−10·3
202	9·0	+12·6
302	5·5	− 8·5
402	2·1	− 0·3
$\bar{3}04$	4·9	− 6·2
$\bar{2}04$	3·9	+ 5·5
$\bar{1}04$	2·2	+11·8
004	34·7	−34·3
104	9·1	+11·8
204	6·0	− 7·6
304	3·2	− 1·9
$\bar{4}06$	2·1	− 1·3
$\bar{3}06$	<1·4	− 1·5
$\bar{2}06$	3·1	+ 0·8
$\bar{1}06$	16·7	−17·7
006	4·7	− 9·2
106	2·3	+ 2·8
206	2·3	− 3·9
306	5·1	+ 2·4
$\bar{2}08$	6·4	− 3·8
$\bar{1}08$	5·8	− 9·0
008	<1·2	+ 3·7
108	2·2	− 2·7
208	6·3	+ 4·0
308	3·4	+ 2·4
0,0,10	3·7	− 2·4
1,0,10	3·9	− 2·4
2,0,10	4·2	+ 4·2
$\bar{1}$,0,12	3·5	− 1·9
0,0,12	<1·5	− 2·4
1,0,12	2·1	+ 2·1

to secondary extinction and an empirical correction applied (Pinnock, Taylor & Lipson, 1956); this procedure appeared to have some justification since the corrected values of the $00l$ structure factors agreed with those obtained from the $h0l$ Mo $K\alpha$ data. Measured and calculated structure factors are listed in Table 1 ($R=0{\cdot}23$), both corrected (in parentheses) and uncorrected F_o values being given for the stronger reflexions.

[010] *projection*

The orientation of the molecules was deduced from the Patterson projection and the $h0l$ structure factors calculated. A Fourier series was summed and the resulting map indicated small shifts in atomic positions. Structure factors were recalculated (and are included in Table 1, $R=0{\cdot}26$), a temperature factor of $B=8{\cdot}5$ Å^2 again being indicated; the observed value for the $\bar{1}02$ reflexion was considerably smaller than F_c, probably because of extinction, and this plane was omitted in evaluating R. A final electron-density projection is shown in Fig. 2.

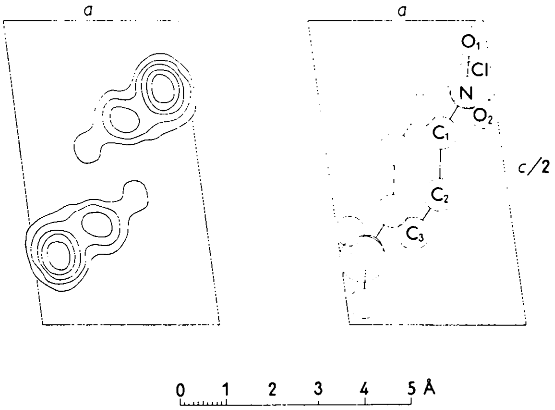

Fig. 2. (*a*) Electron density projection along [010]. Contours are drawn at intervals of approximately 1 e.Å^{-2}, with the lowest contour at 4 e.Å^{-2}. (*b*) The structure viewed along [010].

The final positional parameters of the atoms, expressed as fractions of the unit cell edges, are listed in Table 2.

Table 2. *Final positional parameters*

Atom	x	y	z
$\frac{1}{2}$ Cl	0·376	0·340	0·142
$\frac{1}{2}$ N	0·343	0·312	0·130
$\frac{1}{2}$ O_1	0·404	0·277	0·213
$\frac{1}{2}$ O_2	0·425	0·444	0·097
C_1	0·167	0·153	0·064
C_2	0·110	0·169	−0·038
C_3	−0·065	0·017	−0·102

4. Discussion

The agreement between measured and calculated structure factors is not particularly good, probably because the model used for the structure factors is necessarily rather a crude one, and assumes that the six-membered rings of the two orientations coincide exactly. That this is only approximately so is indicated by the temperature factor, the high value probably resulting from a smearing out of electron-density as a result of the disorder, rather than to large thermal movements. It is also quite difficult to determine the scale factor precisely, since small errors in the steep slopes of the plots of ln $\{|F_c|/|F_o|\}$ against $\sin^2 \theta$ produce significant changes in scale. In view of these difficulties we have not attempted to derive a more elegant model, but consider that the correlation between measured and calculated structure amplitudes is sufficiently satisfactory to indicate that the disordered arrangement is the correct one.

The absence of diffuse scattering on the films indicates that the two orientations must occur randomly throughout the crystal. In *p*-bromochlorobenzene (Hendricks, 1933) and 1-bromo-4-chlorocyclohexane (Hassel & Vihovde, 1953) similar disordered arrangements have been observed. In these structures the interchangeable atoms, chlorine and bromine, are of course very similar in size and chemical behaviour. Although at first glance the chlorine atom and nitro group in *p*-chloronitrobenzene appear to be rather different in nature, closer study suggests that their sizes are not very different and that their electronegativities are similar, so that it is not surprising that the structure is disordered. A direct test of the approximate equivalence of the two orientations is provided by an examination of the packing of the molecules in the crystal. Allowing every molecule to have either arrangement we find that there are several intermolecular distances below 4 Å, the smallest being a C···O contact of 3·35 Å; the approaches thus correspond to normal van der Waals interactions, so that both orientations apparently exist in the crystal with no undue strain.

The disorder prevents accurate determination of the molecular dimensions, but the bond distances and valency angles appear to be normal. The molecule is at least approximately planar, but a twisting of the nitro group, out of the plane of the aromatic ring, of the order of 10°–20° would probably not be detectable.

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