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The Crystal Structure of *p*-Chloroaniline

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p-Chloroaniline ($ClC_6H_4NH_2$) crystallizes in space group *Pnma* with $a=8{\cdot}665$, $b=7{\cdot}397$, $c=9.281$ Å. The unit cell contains four molecules. Cl, C(4), C(1) and N are situated in the space-group mirror planes, in which C(2) and C(3) are mirror images of C(6) and C(5) respectively. The plane of the molecule is thus perpendicular to the space-group mirror planes, and makes an angle of 39° 40′ with the plane of the *a* and *b* axes. Consequently, the angle between the planes of two molecules is 79° 20′, in accordance with the value of 79° (±1°) deduced by Meal from nuclear quadrupole resonance data. However, the orientation of the molecules with respect to the crystallographic axes differs from the one suggested by Meal. No information concerning the position of the hydrogen atoms is presented.

Introduction

During an X-ray crystallographic investigation of some aromatic amines our attention was drawn to a paper by Meal (1956), in which some aspects of the crystal structure of *p*-chloroaniline were deduced from nuclear quadrupole resonance data. It appeared, however, that the author had no knowledge of either the dimensions or the symmetry of the unit cell. We therefore determined the lattice constants and space group of the substance, after which it turned out that the crystal structure could be determined without recourse to three-dimensional work. The ensuing analysis revealed the position of the 'heavy' (non-hydrogen) atoms.

Experimental

Crystals of *p*-chloroaniline suitable for X-ray analysis were readily obtained from alcoholic solutions by slow evaporation. On these crystals only faces of the form {111} were observed.

Approximate lattice constants and systematic absences were determined from the zero and first layers around the *a* and *c* axes, recorded as Weissenberg diagrams. More accurate lattice constants were obtained by applying the method of least-squares to the data of a Guinier–de Wolff powder diagram calibrated with α-Al_2O_3. With the known density the crystallographic data shown in Table 1 were arrived at.

Table 1. *Crystallographic data of p-chloroaniline*

Lattice constants	$a=8{\cdot}666$ Å $b=7{\cdot}397$ $c=9{\cdot}281$ (all $\pm 0{\cdot}002$)
Cell volume	$V=594{\cdot}93$ Å^3
Density (experimental)	$d=1{\cdot}427$ g.cm^{-3}
Density (X-ray)	$d=1{\cdot}425$ g.cm^{-3}
Molecules per unit cell	$Z=4$
Systematic absences	$0kl$ when $k+1=2n+1$ $hk0$ when $h=2n+1$
Space group	*Pnma* (or $Pn2_1a$)

An excellent cylindrical crystal with the *c* axis as cylinder axis was obtained in the following way. A thin-walled Lindemann-glass capillary containing polycrystalline material, a microscope and a thin jet of hot air were installed at right angles to one another and with a common point of intersection. By slowly moving the capillary in the direction of its axis the polycrystalline material could be 'zone-melted' and deposited as a cylindrical single crystal with the *c* axis parallel to the capillary axis while under constant observation. Whenever a nucleus of a differently oriented crystal was formed (as indicated by observation in polarized light) the direction of movement was temporarily reversed in order to redissolve it and a second passage was tried. This method has served us well for several organic substances.

A spherical specimen with which *h*0*l* and *h*1*l* data were collected was prepared as described by Buerger (1956). The reflexions *hk*0, *h*0*l* and *h*1*l* were recorded by means of a Nonius integrating Weissenberg camera, with Cu $K\alpha$ radiation and the multiple film technique. Integrated intensities were measured on a photometer, and routinely corrected for Lorentz and polarization factors and for specimen absorption. All data were brought on a common scale by means of reflexions common to two reciprocal lattice layers.

Structure determination

A molecule of *p*-chloroaniline can be expected to possess molecular symmetry *mm*2, if the hydrogen atoms are not taken into account [Fig. 1(*a*)]. The systematically absent spectra narrow the choice of space group to either $Pn2_1a$ or *Pnma*. These leave three *a priori* possible ways to accommodate four molecules of *p*-chloroaniline in the unit cell:

(1) All atoms in the general position of $Pn2_1a$.

(2) All atoms in positions 4(*c*) of *Pnma*, requiring the entire molecule to be planar, with sp^2 hybridization of the amino nitrogen valencies, and the molecular mirror plane m_1 [Fig. 1(*a*)] coinciding with the space group mirror planes.

(3) Cl, C(4), C(1) and N in positions 4(*c*) of *Pnma* and C(2) and C(3) in positions 8(*d*), thus requiring the molecular mirror plane m_2 to coincide with the space group mirror planes. In this case the plane of the molecule would be perpendicular to the space group mirror planes, with C(5) and C(6) mirror images of (and crystallographically equivalent to) C(3) and C(2), respectively. Both sp^2 and sp^3 hybridization of the nitrogen valencies would obey the symmetry requirements of such a trial structure.

Assumption (1) seemed less probable, since the absence of a piezoelectric effect and crystal morphology (*mmm*) seemed to favour the centrosymmetric space group *Pnma*. The geometry of the unit cell did not allow a choice between assumptions (2) and (3). However, a Patterson projection $P(uv)$ showed maxima outside the mirror planes, in contradiction to assumption (2), and at exactly the distance required for Cl–C(2) and Cl–C(3) vectors by assumption (3). The intramolecular vectors of this Patterson projection furthermore yielded the orientation of the molecule in the unit cell. From the *b*-axis Patterson projection the Cl position and confirmation of the orientation of the molecule was obtained, thus fixing the positions of all 'heavy' atoms. The trial structure was refined by least squares, using the 219 independent observed reflexions. Scattering factors were taken from *International Tables for X-ray Crystallography* (1963) in the approximation of Moore (1963). The least-squares program was based on the principles given by Cruickshank (1961) but with the addition of facilities for automatic treatment of atoms in special positions and for analysis of the weighting scheme as a function of F_o. In the final stages of refinement individual isotropic temperature factors were attributed to the atoms of the benzene ring and individual anisotropic temperature factors to Cl and N. The hydrogen atoms of the benzene ring were added in the final structure factor computation. The weighting scheme used was $w = 1/(0{\cdot}47 + 0{\cdot}05F_o - 0{\cdot}00011F_o^2)$, giving approximately constant averages of $w.(dF)^2$ for groups of reflexions with increasing values of F_o. Final parameters and their e.s.d.'s are entered in Table 2; a table of observed and calculated structure factors is presented as Table 3. The final R index was 6·3%, reflexions with zero observed intensity not being included.

Discussion of the structure

Bond distances and bond angles are presented in Fig. 1(*b*). Bond lengths appear to be normal; our values of C(4)–Cl and C(1)–N (1·75 and 1·40 Å respectively) are in agreement with those found in 2,5-dichloroaniline (1·74 and 1·41 Å respectively) by Sakurai, Sundaralingam & Jeffrey (1963), the standard deviation in both determinations being 0·01 Å.

Table 2. *Final parameters and e.s.d.'s for p-chloroaniline*

(*a*) Coordinates

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·6197	$\frac{1}{4}$	0·8941	0·0010	0	0·0010
C(2)	0·6828	0·4134	0·9438	0·0007	0·0016	0·0007
C(3)	0·8090	0·4122	0·0399	0·0007	0·0016	0·0006
C(4)	0·8674	$\frac{1}{4}$	0·0860	0·0010	0	0·0010
N	0·4984	$\frac{1}{4}$	0·7946	0·0011	0	0·0010
Cl	0·0254	$\frac{1}{4}$	0·2037	0·0003	0	0·0003

(*b*) Temperature factors

Atom	B	$\sigma(B)$
C(1)	3·29	0·19
C(2)	3·65	0·13
C(3)	3·44	0·12
C(4)	2·93	0·18

Atom components of β ($\times 10^4$) and e.s.d. (in parentheses)

	β_{11}	β_{22}	β_{33}	$2.\beta_{13}$
N	141 (±12)	197 (±30)	152 (±14)	−105 (±22)
Cl	109 (±3)	170 (±8)	107 (±3)	−42 (±5)

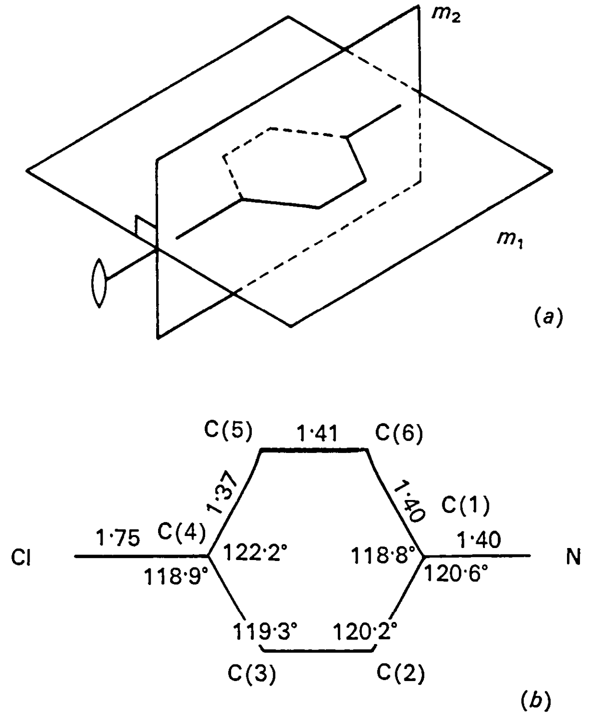

Fig. 1. (*a*) Molecular symmetry of *p*-chloroaniline (neglecting hydrogen atoms). (*b*) Intramolecular bond angles and distances.

The molecule is essentially planar (hydrogen atoms not being taken into account), and the formula of the best-fit plane is $5{\cdot}5306x-7{\cdot}1447z=2{\cdot}9521$. From this equation the angle between the planes of two symmetry-related molecules can be computed. The value of 79° 20′ thus found is in excellent agreement with that derived by Meal (1956) from quadrupole resonance data. However, Meal's correctly deduced relative orientation of the molecules is incorrectly related to the crystallographic axes. The morphological axial ratios are given by Meal as $a:b:c=0{\cdot}939:1:0{\cdot}800$; they should be: $a:b:c=0{\cdot}800:0{\cdot}939:1$, if Meal's conclusions are to retain their validity. (It should be noted that in the latter case our a axis $=b_{\rm Meal}$, and our b axis $=a_{\rm Meal}$.)

Fig. 2 shows the a- and b-axis projections of the structure. The molecular packing arrangement may be understood by first examining the molecules in the layer between $y=\frac{1}{2}$ and $y=1$. These are represented by bolder circles in the b-axis projection. All eight independent distances between these molecules (which straddle the same mirror plane) involve the carbon atoms of the benzene ring of one of them (say I) and either N or Cl of two molecules (say IV and V) lying on either side of the ring in the general direction of the perpendicular through its centre. Molecules in the adjoining half of the unit cell are represented by lighter circles in the b-axis projection. They are related to those in the first-mentioned half by either the n-glide or 2_1 axes parallel to **b**. However, owing to the pseudo-centrosymmetric nature of the 'heavy' atoms in the molecule, and the fortuitously nearly special values of the coordinates of the molecular pseudo-centre of symmetry $(\frac{1}{4}\frac{1}{4}0)$, molecule VI occupies a pseudo-C-centred position with respect to molecules II and IV, except for the interchange of the p-substituents, Cl and N. Most of the shorter distances between the atoms of molecules straddling different space-group mirror planes occur between molecules in the pseudo-C-centred

Table 4. *Intermolecular distances less than* 4 Å *in p-chloroaniline*

C(1)–Cl$^{\rm V}$	3·82 Å	C(3$^{\rm VI}$)–C(3$^{\rm II}$)	3·63
C(2)–Cl$^{\rm V}$	3·75	Cl$^{\rm VI}$ —C(3$^{\rm II}$)	3·66
C(3)–Cl$^{\rm V}$	3·63	C(4$^{\rm VI}$)–C(3$^{\rm II}$)	3·93
C(4)–Cl$^{\rm V}$	3·55		
C(1)–N$^{\rm IV}$	3·72	N——Cl$^{\rm VI}$	3·80
C(2)–N$^{\rm IV}$	3·72	N——C(3$^{\rm VI}$)	3·82
C(3)–N$^{\rm IV}$	3·71	C(2)–C(3$^{\rm VI}$)	3·96
C(4)–N$^{\rm IV}$	3·71	C(2)–Cl$^{\rm VI}$	3·80
C(2$^{\rm VI}$)–C(1$^{\rm IV}$)	3·92		
C(2$^{\rm VI}$)–C(2$^{\rm IV}$)	3·57		
N$^{\rm VI}$——C(2$^{\rm IV}$)	3·82		
N$^{\rm VI}$——C(3$^{\rm IV}$)	3·96		

Table 3. *Observed and calculated structure factors hk*0, *h*0*l and h*1*l of p-chloroaniline*

H	K	L	FO	FC
0	0	2	13.8	15.3
0	0	4	19.7	17.8
0	0	6	13.8	-13.9
0	0	8	20.7	-23.0
0	0	10	6.9	7.1
1	0	2	10.7	-10.4
1	0	3	14.5	-15.6
1	0	4	6.3	7.0
1	0	5	22.6	24.4
1	0	6	1.3	1.8
1	0	7	12.9	-13.1
1	0	8	4.8	5.4
1	0	9	3.8	3.8
1	0	10	1.2	1.8
1	0	11	0.6	0.9
2	0	0	29.4	20.5
2	0	1	25.2	24.0
2	0	2	87.2	-92.5
2	0	3	62.9	65.6
2	0	4	9.0	9.0
2	0	5	25.3	24.9
2	0	6	9.1	8.3
2	0	7	2.4	-2.0
2	0	8	4.8	-4.4
2	0	9	2.3	2.4
2	0	10	13.3	14.9
2	0	11	1.7	-2.1
3	0	1	4.1	4.0
3	0	2	13.6	-13.9
3	0	3	21.5	-21.7
3	0	4	12.3	12.4
3	0	5	9.6	9.4
3	0	6	9.5	-8.2
3	0	7	11.0	-11.9
3	0	8	2.2	2.3
3	0	9	4.3	3.9
3	0	10	2.9	-3.6
4	0	0	19.4	17.0
4	0	1	32.5	-34.2
4	0	2	40.7	-41.1
4	0	3	18.1	-16.8
4	0	4	25.2	23.9
4	0	5	22.1	-21.0
4	0	6	12.4	11.3
4	0	7	18.0	-17.9
4	0	8	7.4	-7.7
4	0	9	2.9	3.3
4	0	10	3.4	4.0
4	0	11	2.2	-2.5
5	0	1	6.9	6.7
5	0	2	9.0	-9.1
5	0	3	5.5	-5.5
5	0	4	4.5	14.1
5	0	5	1.6	10.9
5	0	6	12.2	-11.7
5	0	7	2.7	-2.2
5	0	8	5.8	5.8
5	0	9	5.1	5.5
6	0	0	37.6	38.3
6	0	1	23.1	-20.9
6	0	2	2.5	-3.0
6	0	3	9.4	9.2
6	0	4	11.0	11.3
6	0	5	9.3	9.2
6	0	6	3.3	-3.2
6	0	7	4.4	4.1
6	0	8	8.5	-8.7
6	0	9	9.7	11.2
7	0	1	0.5	-0.5
7	0	2	8.4	-8.3
7	0	3	3.9	-3.3
7	0	4	11.0	10.9
7	0	7	5.0	-4.8
7	0	6	11.6	-11.4
7	0	8	5.7	6.4
7	0	9	1.5	1.9
8	0	0	1.5	2.0
8	0	1	13.0	-13.2
8	0	2	13.6	-14.2
8	0	3	8.8	8.8
8	0	4	4.1	-3.7
8	0	5	0.6	1.1
8	0	6	3.2	-3.2
8	0	7	4.2	-4.9
8	0	8	2.9	3.1
9	0	1	0.5	0.2
9	0	2	4.3	-4.6
9	0	3	2.8	2.7
9	0	4	9.4	9.5
9	0	6	6.7	-8.0
10	0	0	7.1	5.9
10	0	1	7.0	-8.1
10	0	2	2.8	2.0
10	0	3	4.1	4.8
10	0	4	2.6	3.4
10	0	5	3.3	-3.6
11	0	1	2.3	-2.2
0	1	1	26.6	-30.9
0	1	3	18.3	19.1
0	1	5	6.8	-6.8
0	1	7	11.1	-10.6
0	1	9	8.5	8.6
0	1	11	5.0	-5.6
1	1	1	51.2	53.7
1	1	2	65.6	-67.8
1	1	3	19.7	17.7
1	1	4	28.4	27.3
1	1	5	16.1	-14.3
1	1	6	30.4	-29.8
1	1	7	5.3	-5.0
1	1	8	16.5	16.4
1	1	9	2.6	-2.5
1	1	10	2.5	-2.1
2	1	0	16.6	-17.4
2	1	1	25.1	-27.0
2	1	2	15.0	15.7
2	1	3	15.4	16.0
2	1	4	1.6	1.3
2	1	5	1.4	-1.2
2	1	6	1.1	-1.2
2	1	7	4.7	-4.8
2	1	8	1.7	1.3
2	1	9	8.9	9.0
2	1	10	3.2	-3.0
2	1	11	3.9	-4.2
3	1	1	3.7	-2.2
3	1	2	0.9	0.5
3	1	3	7.4	5.8
3	1	4	54.0	53.0
3	1	5	22.4	-20.7
3	1	6	18.1	-17.1
3	1	7	4.8	5.1
3	1	8	9.9	10.7
3	1	9	2.5	2.6
3	1	10	3.0	-3.2
3	1	11	1.3	1.4
4	1	0	23.6	-24.3
4	1	1	16.8	-16.8
4	1	2	12.9	13.5
4	1	3	10.2	9.0
4	1	4	7.1	-6.8
4	1	6	4.0	-3.6
4	1	7	2.9	-2.6
4	1	8	4.1	3.9
4	1	9	2.9	2.9
4	1	10	4.6	-5.1
5	1	1	22.2	-20.7
5	1	2	14.6	-12.1
5	1	3	14.7	13.8
5	1	4	14.0	13.9
5	1	5	7.4	-7.6
5	1	6	23.3	-23.9
5	1	7	11.2	11.4
5	1	8	1.6	2.0
5	1	9	1.6	-1.7
5	1	10	2.7	-3.2
6	1	0	16.9	-17.1
6	1	1	7.8	-7.3
6	1	2	14.6	14.7
6	1	3	4.3	3.3
6	1	4	5.3	-5.5
6	1	5	1.8	-1.6
6	1	8	7.7	7.9
6	1	9	1.4	1.8
7	1	1	1.8	-2.4
7	1	2	9.6	-9.5
7	1	3	18.8	18.0
7	1	4	5.9	6.9
7	1	5	7.8	-8.1
7	1	6	3.9	-4.5
7	1	7	5.9	6.2
7	1	8	7.6	8.4
7	1	9	5.0	-5.3
8	1	0	12.6	-13.0
8	1	1	1.0	-1.1
8	1	2	11.4	10.9
8	1	4	7.0	-6.4
8	1	5	3.1	-3.0
8	1	6	2.0	-2.3
8	1	7	0.9	1.2
8	1	8	4.2	4.5
9	1	1	4.3	-4.7
9	1	2	3.1	-3.1
9	1	3	5.0	5.4
9	1	4	1.0	2.2
9	1	5	10.3	-11.7
10	1	0	6.7	-8.1
10	1	1	2.4	2.5
10	1	2	6.7	7.9
10	1	4	2.7	-3.2
0	2	0	61.7	-68.2
0	4	0	38.5	40.7
0	6	0	47.4	-48.3
0	8	0	11.8	13.6
2	2	0	73.8	-79.9
2	3	0	10.1	9.6
2	4	0	47.8	47.1
2	5	0	7.9	-6.8
2	6	0	9.7	-8.6
2	8	0	12.0	12.2
4	2	0	23.1	-21.6
4	3	0	19.0	17.9
4	4	0	10.7	12.0
4	5	0	12.8	-11.5
4	6	0	8.3	-7.2
4	7	0	6.9	7.4
4	8	0	3.1	3.7
6	2	0	11.5	-11.0
6	3	0	17.8	17.3
6	4	0	7.5	7.6
6	5	0	10.6	-10.3
6	6	0	14.8	-15.0
6	7	0	5.1	5.8
8	2	0	19.8	-18.5
8	3	0	6.9	7.6
8	4	0	16.2	15.5
8	5	0	6.7	-7.6
8	6	0	1.0	-0.8
10	3	0	6.4	8.3

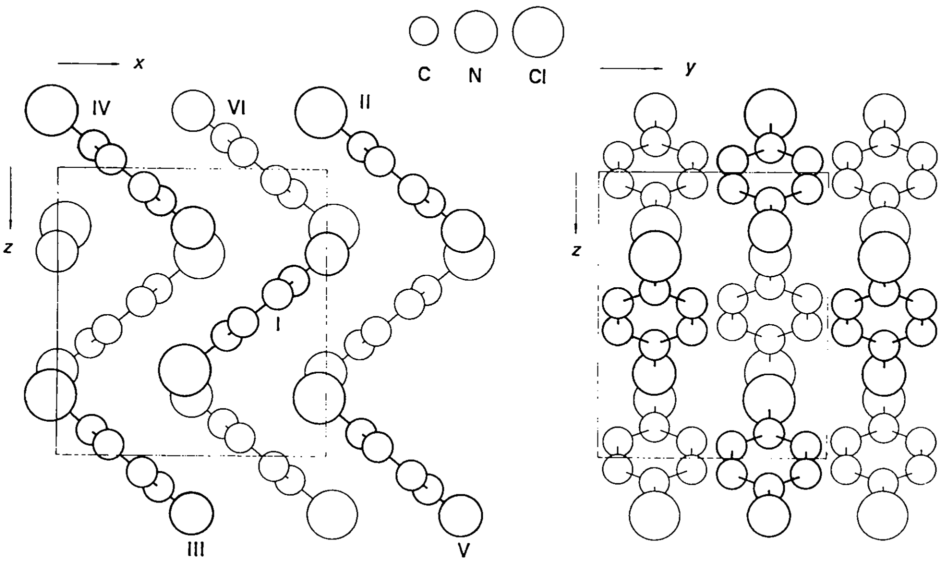

Fig. 2. The crystal structure of *p*-chloroaniline projected along the *a* and *b* axes.

relation to one another. All distances shorter than 4 Å are listed in Table 4, the molecules being labelled as in Fig. 2.

References

Buerger, M. J. (1956). *Elementary Crystallography*, p. 176. New York: John Wiley.

Cruickshank, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 41. Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1963). Vol. III, p. 202. Birmingham: Kynoch Press.

Meal, H. C. (1956). *J. Chem. Phys.* **24**, 1011.

Moore, F. H. (1963). *Acta Cryst.* **16**, 1169.

Sakurai, T., Sundaralingam, M. & Jeffrey, G. A. (1963). *Acta Cryst.* **16**, 354.

Acta Cryst. (1966). **21**, 476

The Crystal Structures of $LuMn_5$ and the RMn_{12} Compounds (where R = Gd, Tb, Dy, Ho, Er and Tm)

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By means of single-crystal and powder X-ray diffraction methods, the crystal structures of six RMn_{12} compounds (where R is a rare earth element) have been shown to be isostructural with that of $ThMn_{12}$. These RMn_{12} compounds were found in the following systems: Gd–Mn, Tb–Mn, Dy–Mn, Ho–Mn, Er–Mn and Tm–Mn.

A hitherto unreported and unexpected compound, $LuMn_5$ ($P6_3mc$) with cell dimensions $a = 5{\cdot}18$, $c = 8{\cdot}56$ Å, has been found in the Lu–Mn system in which the expected compound '$LuMn_{12}$' is absent. The structure of $LuMn_5$ is a variation of the $C14$ ($MgZn_2$ type) structure represented by $LuMn_2$.

Introduction

There has been considerable interest in both the crystal and magnetic structures of the intermediate phases between the rare earth elements and manganese. The crystal structures of the RMn_2 (Laves phase) compounds have been summarized by Elliott (1964) and the magnetic structures were reported by Nesbitt, Williams, Wernick & Sherwood (1963), and Corliss & Hastings (1964). Recently Wang & Holden (1965) iden-