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The Crystal Structure of Aniline Hydrochloride

By C. J. Brown

Research Laboratories, Imperial Chemical Industries Limited (Dyestuffs Division), Hexagon House, Blackley, Manchester 9, Great Britain

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The crystal structure of aniline hydrochloride has been determined by the X-ray method. The space group is *Cc*, with cell dimensions $a = 15{\cdot}84 \pm 0{\cdot}03$, $b = 5{\cdot}33 \pm 0{\cdot}03$, $c = 8{\cdot}58 \pm 0{\cdot}03$ A., $\beta = 101° \pm 30'$. $\rho_{\text{exp.}} = 1{\cdot}210$, while that required for four molecules per unit cell is 1·211. X-ray intensities were obtained from Weissenberg photographs taken of the zero levels about [*a*], [*b*] and [*c*]. The trial structure was found by means of a Patterson projection along [*b*], and this was refined by means of successive two-dimensional Fourier syntheses. The structure is ionic, each nitrogen atom being equidistant at 3·17 A. from three chlorine ions. The dimensions of the benzene ring are normal, but the C–N bond is considerably shorter (1·35 A.) than that given by the sum of the atomic radii (1·47 A.).

Introduction

In all the crystal structures of aromatic amines which have been determined, the C–NH_2 bond has been found to be considerably shorter than that to be expected from the sum of the atomic radii of carbon and nitrogen. This shortening has been observed in a wide variety of aliphatic compounds as well as aromatic, and some of the published values of the C–N bond length are listed in Table 3. The crystal structure of acetanilide (Brown & Corbridge, 1948) also revealed a low value for the C–N bonds, and it was during the course of this work that interest was first aroused in the structure of aniline hydrochloride. It was considered possible that in some of the compounds listed in Table 3, the short C–N bond might be due to the influence of other substituents in the benzene ring; further, the only simple amine which has been attempted is *p*-toluidine (Wyart, 1935), and the C–N bond value obtained for that substance (1·18 A.) was so low that its reliability may be doubtful. For these reasons, it was decided to work out the structure of aniline hydrochloride in order to obtain more data regarding the bond lengths in amines.

Experimental

Crystals of aniline hydrochloride grown from ethanol exhibited a pronounced platy development, and were not very suitable for obtaining accurate X-ray intensities. In addition, very perfect cleavage parallel to (100) and (011) rendered the production of suitable crystal shapes by grinding or cutting impossible, so it was necessary to choose fairly small crystal fragments to minimize absorption errors.

The dimensions of the unit cell were obtained by measurement of the layer lines of rotation photographs. The monoclinic angle was obtained by calculation from the unit lengths of [*a*], [*c*] and [101]:

$$a = 15{\cdot}84 \pm 0{\cdot}03, \qquad b = 5{\cdot}33 \pm 0{\cdot}03,$$
$$c = 8{\cdot}58 \pm 0{\cdot}03 \text{ A.}, \quad \beta = 101° \pm 30'.$$

For four molecules per unit cell the specific gravity required is 1·211, while that observed experimentally by flotation is 1·210. Observed extinctions were $\{hkl\}$ for $(h+k)$ odd and $\{h0l\}$ for l odd, whence the space group may be either *Cc* or *C*2/*c*. As only four molecules are present in the cell, the space group *C*2/*c* would require the twofold axis of the aniline molecule to be parallel to [*b*]. As [*b*] is 5·33 A., this is clearly impossible, assuming standard bond lengths and angles, so the space group is determined without ambiguity as *Cc*.

Weissenberg moving-film photographs were taken of the zero levels of the *a*, *b* and *c* axes, using a modified multiple-film technique with batches of six films. The intensities of the spots were estimated visually by comparison between the batches of films. The absorption coefficient is 39 cm.$^{-1}$, and as very small crystals were used, no allowance for absorption has been made.

Determination of the structure

The optical data recorded (Bolland, 1910) show the refractive indices as $\alpha=1\cdot56$, $\beta=1\cdot57$ and $\gamma=1\cdot60$, which give no clues as to the disposition of the molecules in the unit cell. Consideration of the cell dimensions and space group, however, shows that there is only one reasonable location for the molecule, i.e. with the long direction roughly parallel to [101]. As the b axis was fairly short, it was considered that a projection parallel to this axis would be free from overlap of atoms. A two-dimensional Patterson synthesis, computed using $\{h0l\}$ terms, confirmed the suggested orientation of the molecule by giving a ridge in the vector map parallel to [101].

Preliminary structure-amplitude calculations were made with the length of the aniline molecule taken as parallel to [101]. As there is no centre of symmetry in any of the projections in this space group, the choice of the origin of the x and z co-ordinates was arbitrary. For convenience in calculation, though, the chlorine ion was taken as the origin, to which the x and z co-ordinates of the other atoms are referred. Thus the value of $A(h0l)$ was made positive in nearly every case owing to the relatively high scattering power of the chlorine.

About forty $\{h0l\}$ terms were used in the first Fourier projections. Refinement of the co-ordinates proceeded in the usual way, and, after four successive syntheses, was judged to be practically complete. The alteration in phase angles between the third and fourth syntheses was very small. It was found that the true position of the molecule was with its length parallel to a^*, i.e. inclined by about 20° to its initial position.

Using the x co-ordinates from this set of syntheses, a set of y co-ordinates was calculated, assuming standard bond lengths and angles. From these co-ordinates, the phases of $F(hk0)$ were calculated and used in a Fourier projection parallel to [c]. In this case, only one synthesis was necessary to complete the refinement; four of the carbon atoms overlapped with others from adjacent molecules, and resolution of the individual atoms would not be possible with the small number of terms available.

Finally, a Fourier projection parallel to [a] was computed, using the phases of $F(0kl)$ calculated from the y and z co-ordinates given by the [c] and [b] Fourier projections. In this case also, considerable overlapping of atoms occurred, and it was not possible to effect any refinement. No three-dimensional work was undertaken. The electron-density contour maps are shown in Figs. 1–3. The final set of atomic co-ordinates are given in Table 1.

Structure-amplitude calculations

In order to secure agreement between the experimental and calculated structure amplitudes it was found necessary to use a temperature factor for the atomic scattering factors in which $B=4\times10^{-16}$ A.$^{-2}$. This is an unusually large value for a crystal whose melting-point is as high as 198° C., although a value of $B=2\cdot6\times10^{-16}$ was required in the structure determination of m-tolidine hydrochloride (Hargreaves & Taylor, 1941).

The values of the experimental and calculated structure amplitudes, together with the calculated phase angles, are listed in Table 2. The experimental

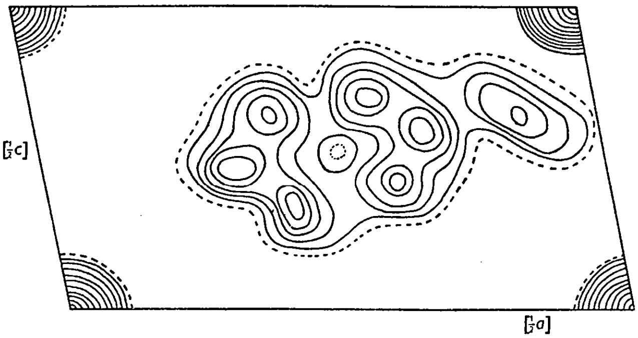

Fig. 1. Two-dimensional Fourier projection along [b]. The contours are at intervals of 1 e.A.$^{-2}$ up to 6, then at intervals of 2 e.A.$^{-2}$. The 1-electron contour is dotted.

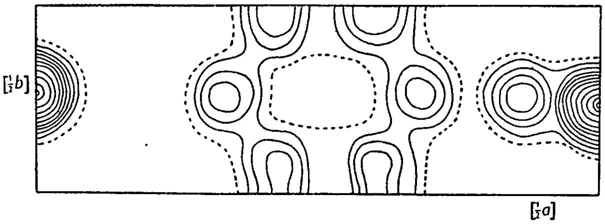

Fig. 2. Two-dimensional Fourier projection along [c]. The contours are at intervals of 1 e.A.$^{-2}$ up to 10, then at intervals of 2 e.A.$^{-2}$. The 3-electron contour is dotted.

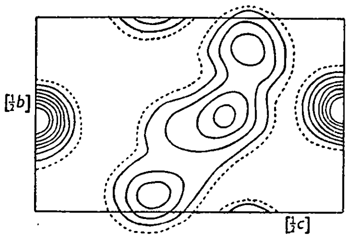

Fig. 3. Two-dimensional Fourier projection along [a]. The contours are at intervals of 2 e.A.$^{-2}$, the 2-electron contour being dotted.

Table 1. *Final co-ordinates*

	x	y	z
C_1	0·343	0·232	0·292
C_2	0·302	0·030	0·210
C_3	0·212	0·030	0·178
C_4	0·171	0·232	0·236
C_5	0·212	0·434	0·320
C_6	0·302	0·434	0·352
N	0·430	0·232	0·324
Cl	0	0·768	0

Table 2. *Experimental and calculated structure amplitudes and calculated phase angles*

hkl	$F_{\text{exp.}}$	$F_{\text{calc.}}$	α
000	—	272	—
002	32	40	228°
004	27	38	21°
006	39	37	6°
008	7	8	310°
0,0,10	6	8	23°
$2,0,\overline{10}$	8	7	333°
$20\bar{8}$	11	15	0°
$20\bar{6}$	27	20	0°
$20\bar{4}$	29	15	349°
$20\bar{2}$	111	122	7°
200	10*	28	252°
202	55	58	7°
204	55	46	15°
206	10	18	354°
208	11	12	14°
2,0,10	4	6	350°
$4,0,\overline{10}$	0	4	14°
$40\bar{8}$	14	13	29°
$40\bar{6}$	39	34	341°
$40\bar{4}$	11	20	18°
$40\bar{2}$	54	49	10°
400	35*	61	343°
402	42	43	20°
404	29	26	349°
406	21	18	357°
408	7	8	14°
4,0,10	6	6	10°
$6,0,\overline{10}$	6	7	23°
$60\bar{8}$	16	21	352°
$60\bar{6}$	5	3	342°
$60\bar{4}$	41	40	13°
$60\bar{2}$	30	35	345°
600	53	54	0°
602	12	14	8°
604	37	33	355°
606	16	15	11°
608	5	7	354°
$8,0,\overline{10}$	5	8	0°
$80\bar{8}$	7	7	0°
$80\bar{6}$	17	18	357°
$80\bar{4}$	20	21	16°
$80\bar{2}$	36	54	352°
800	14	7	231°
802	41	45	14°
804	20	22	355°
806	7	7	341°
808	13	17	36°
$10\ 0,\overline{10}$	2	6	18°
$10,0,\bar{8}$	9	9	339°
$10,0,\bar{6}$	12	12	10°
$10,0,\bar{4}$	18	24	0°
$10,0,\bar{2}$	20	14	321°
10,0,0	32	38	22°
10,0,2	22	24	350°
10,0,4	7	10	294°
10,0,6	17	22	39°
10,0,8	3	9	297°
$12,0,\overline{10}$	5	6	350°
$12,0,\bar{8}$	6	13	347°
$12,0,\bar{6}$	4	4	104°
$12,0,\bar{4}$	24	28	354°
$12,0,\bar{2}$	16	15	4°
12,0,0	19	16	4°
12,0,2	24	20	348°
12,0,4	16	13	23°
12,0,6	6	7	337°
$14,0,\bar{8}$	0	3	146°
$14,0,\bar{6}$	15	26	4°
$14,0,\bar{4}$	5	7	304°
$14,0,\bar{2}$	17	10	11°
14,0,0	25	24	10°
14,0,2	12	9	319°
14,0,4	11	10	18°
14,0,6	4	7	352°
$16,0,\bar{8}$	5	9	6°
$16,0,\bar{6}$	6	5	333°
$16,0,\bar{4}$	9	8	344°
$16,0,\bar{2}$	17	15	20°
16,0,0	10	10	323°
16,0,2	11	10	18°
16,0,4	6	5	349°
$18,0,\bar{6}$	5	6	342°
$18,0,\bar{4}$	7	8	21°
$18,0,\bar{2}$	7	7	352°
18,0,0	9	8	343°
18,0,2	6	5	11°
$20,0,\bar{4}$	1	2	0°
$20,0,\bar{2}$	6	6	0°
20,0,0	6	6	10°
110	6	8	60°
310	5	5	11°
510	5	5	349°
710	7	5	27°
910	0	3	342°
11,1,0	6	2	333°
13,1,0	0	1	0°
15,1,0	4	1	315°
17,1,0	0	1	0°
19,1 0	0	1	0°
020	43	42	180°
220	57	68	172°
420	23	18	124°
620	34	32	176°
820	25	24	195°
10,2,0	3	2	135°
12,2,0	35	34	201°
14,2,0	9	10	156°
16,2,0	9	9	162°
18,2,0	7	9	186°
130	7	7	172°
330	10	10	225°
530	10	11	170°
730	4	9	180°
930	9	7	207°
11,3,0	3	8	144°
13,3,0	4	2	243°
15,3,0	3	2	180°
17,3,0	2	2	180°
040	36	34	0°
240	17	13	337°
440	10	13	337°
640	13	18	0°
840	9	6	350°
10,4,0	6	9	18°
12,4,0	12	11	17°
14,4,0	8	8	0°
16,4,0	4	5	338°
150	8	11	63°
350	9	7	344°
550	6	7	0°
750	6	7	34°
950	6	7	326°
11,5,0	4	3	0°
13,5,0	3	3	326°
060	13	13	180°
260	5	4	166°
460	6	6	158°
660	6	6	180°
860	2	3	180°
021	30	19	96°
022	25	32	156°
023	23	9	315°
024	39	36	205°
025	18	10	119°
026	19	14	135°
027	8	4	76°

* Probably low owing to absorption.

Table 2 (*cont.*)

hkl	F_{exp}	$F_{\text{calc.}}$	α	*hkl*	$F_{\text{exp.}}$	$F_{\text{calc.}}$	α
028	13	13	189°	046	18	11	0°
029	0	1	0°	047	0	3	288°
0,2,10	10	6	198°	048	5	3	342°
041	0	7	352°	061	10	8	130°
042	7	2	333°	062	6	6	166°
043	20	20	270°	063	0	3	34°
044	24	17	0°	064	9	7	225°
045	0	3	162°	065	9	6	90°

values of $F(200)$ and $F(400)$ are very considerably lower than the calculated values; this is probably owing to absorption since the crystals used were tabular on (100), which is also a cleavage face. No correction was made for this absorption effect, but in the final Fourier syntheses the calculated values of F were used as coefficients for planes 200 and 400 instead of the experimental values.

The errors, as represented by the function

$$\frac{\Sigma \mid F_{\text{exp.}} \mid - \Sigma \mid F_{\text{calc.}} \mid}{\Sigma \mid F_{\text{exp.}} \mid},$$

amount to 0·15 for the $\{h0l\}$ terms, 0·10 for the $\{hk0\}$ and 0·17 for the $\{0kl\}$ terms. (In these calculations the absorption discrepancies for $F(200)$ and $F(400)$ were neglected.)

Discussion of the structure

Aniline hydrochloride is an ionic structure. The cation is an organic radicle in which the bonds are of the usual covalent type. The crystals are polar, an expression of the fact that all the molecules point in the same direction in the lattice.

The benzene ring is regular, with C–C bonds 1·38, 1·40, 1·40, 1·39, 1·40 and 1·40 A. The mean value of these is 1·395 ± 0·005 A., in good agreement with those obtained in a wide variety of other aromatic compounds. Neighbouring benzene rings make an angle of 64° with each other.

The C–N bond distance of 1·35 A. calls for some comment. Whereas the sum of the carbon and nitrogen atomic radii given by Pauling is 1·47 A., in the majority of crystal structures which have been determined, aromatic, aliphatic and heterocyclic, the C–N bond length is shorter than this value. A selection of these short bond lengths is given in Table 3.

It may be seen from Table 3 that, in many instances, when carbon is attached directly to nitrogen, the bond distance is less than that expected from the sum of the atomic radii. There is good reason, therefore, to accept the short C–N bond found in aniline hydrochloride as genuine.

With regard to the chlorine and nitrogen co-ordination, there are three ions of opposite charge situated at distances of 3·16, 3·16 and 3·18 A., with angles of 106°, 106° and 115° between the bond directions. The low chlorine co-ordination number of three has been found also in adenine hydrochloride (Broomhead, 1948), but it is more usually four in this class of compound. Various values of Cl–N distances

Table 3. *Short* C–N *bond lengths*

Substance	C–N distance (A.)	Reference
	(*a*) Aromatic (i.e. with the C–N bond external to the ring)	
m-Tolidine hydrochloride	1·39	Hargreaves & Taylor (1941)
Dichlorobenzidine	1·40	Smare (1948)
trans-Azobenzene	1·41	de Lange, Robertson & Woodward (1939)
p-Nitroaniline (to NO_2) (to NH_2)	1·39 1·36	Abrahams & Robertson (1948)
Aminopyrimidines	1·285	Clews & Cochran (1948)
Adenine hydrochloride	1·34	Broomhead (1948)
p-Toluidine	1·18*	Wyart (1935)
	(*b*) Aliphatic	
Glycine	1·39	Albrecht & Corey (1939)
DL-Alanine	1·42	Levy & Corey (1941)
Nickel glycine	1·42	Stosick (1945)
Acetamide	1·38	Senti & Harker (1940)
Dicyandiamide	1·34 1·36 1·37	Hughes (1940)
	(*c*) Heterocyclic (i.e. with C–N bonds in the ring)	
Melamine	1·346 (average)	Hughes (1941)
Cyanuric triazide	1·345 (average)	Knaggs (1935)
Diketopiperazine	1·41	Corey (1938)
Aminopyrimidines	1·32	Clews & Cochran (1948)
Adenine hydrochloride	1·33 (average)	Broomhead (1948)

* It is not improbable that this value is underestimated because the space group may possibly be incorrect.

Table 4. Cl–N *bond lengths*

Substance	Cl–N distance (A.)	Reference
Adenine hydrochloride	3·11, 3·18	Broomhead (1948)
Geranylamine hydrochloride	3·17, 3·24 3·24, 3·24	Jeffrey (1945)
m-Tolidine hydrochloride	3·13, 3·25 3·25, 3·32	Hargreaves & Taylor (1941)
Hydrazonium hydrochloride	Four at 3·10	Donohue & Lipscomb (1947)
Hydroxylamine hydrochloride	3·16, 3·21 3·23, 3·26	Jerslev (1948)
Methylammonium chloride	Four at 3·18	Hughes & Lipscomb (1946)

found in other structures are listed in Table 4. From this table it is apparent that the mean value of 3·17 A. found in aniline hydrochloride is in good agreement with similar distances found in previous crystal-structure determinations.

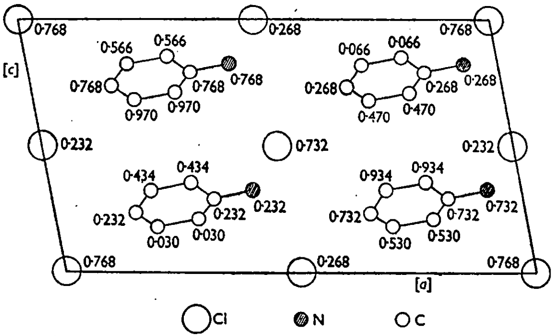

Fig. 4. Contents of the unit cell projected along [*b*].

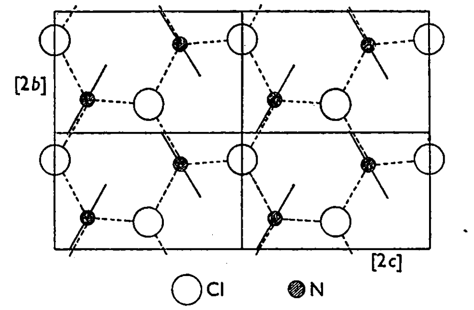

Fig. 5. Contents of half the unit cell projected normally on to (100). The inclined full lines represent the end view of the benzene rings and the broken lines show the threefold co-ordination of nitrogen and chlorine.

The disposition of bonds around the nitrogen atom is roughly tetrahedral, i.e. the angles subtended at the nitrogen atom by the carbon atom and three chlorine ions are 106°, 106°, 110°, 115°, 117° and 117°, the mean of these six being 112°. The three nitrogen atoms are arranged around the chlorine ions pyramidally.

The nearest intermolecular approach distances are 3·85 A. between carbon atoms of neighbouring benzene rings, and distances of 3·85, 3·93 and 4·18 A. are found between C_4 of a benzene ring and chlorine ions.

It is interesting to observe that the structure may be described as being built up of layers containing aniline and chlorine parallel to (100); this feature is readily seen in Fig. 4, which depicts the contents of the unit cell, projected along [*b*], in diagrammatic fashion. The end-on view of the composition of one of these layers is shown in Fig. 5, which depicts half the contents of four unit cells projected perpendicularly to (100).

The determining factor in the build-up of the crystal structure of aniline hydrochloride is the size of the cation. The benzene rings pack together as tightly as possible, leaving the chlorine ions to arrange themselves equidistantly from as many nitrogen atoms as possible, which in this case is only three. There is no contact between neighbouring chlorine ions, the nearest distance of approach being 5·05 A.

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