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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  $a = 15\cdot84 \pm 0\cdot03$ ,  $b = 5\cdot33 \pm 0\cdot03$ ,  $c = 8\cdot58 \pm 0\cdot03$  A.,  $\beta = 101^{\circ} \pm 30'$ .  $\rho_{exp.} = 1\cdot210$ , while that required for four molecules per unit cell is  $1\cdot211$ . 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<sub>2</sub> 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]:

$$a = 15 \cdot 84 \pm 0.03, \quad b = 5 \cdot 33 \pm 0.03,$$
  
 $c = 8 \cdot 58 \pm 0.03 \text{ A}, \quad \beta = 101^{\circ} \pm 30',$ 

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 C2/c. As only four molecules are present in the cell, the space group C2/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.<sup>-1</sup>, 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  $\alpha = 1.56$ ,  $\beta = 1.57$  and  $\gamma = 1.60$ , 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 coordinates 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  $B=4 \times 10^{-16} \text{ A.}^{-2}$ . This is an unusually large value for a crystal whose meltingpoint is as high as 198° C., although a value of



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.<sup>-2</sup> up to 10, then at intervals of 2 e.A.<sup>-2</sup>. The 3-electron contour is dotted.



Fig. 3. Two-dimensional Fourier projection along [a]. The contours are at intervals of 2 e.A.<sup>-2</sup>, the 2-electron contour being dotted.

Table 1. Final co-ordinates

	x	$\boldsymbol{y}$	z
C <sub>1</sub>	0.343	0.232	0.292
C <sub>2</sub>	0.302	0.030	0.210
C,	0.212	0.030	0.178
C₄	0.111	0.232	0.236
C <sub>5</sub>	0.212	0.434	0.320
C <sub>e</sub>	0.302	0.434	0.352
Ň	0.430	0.232	0.324
Cl	0	0.768	0

 $B=2.6\times10^{-16}$  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

# THE CRYSTAL STRUCTURE OF ANILINE HYDROCHLORIDE

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

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	hkl	$F_{\rm exp.}$	$F_{\rm calc.}$	• a		hkl	$F_{\rm exp.}$	${F}_{\mathrm{calc.}}$	α
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	000		272			16.0.5	6	5	333°
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	002	32	40	228°		$16.0.\bar{4}$	9	8	<b>344°</b>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	004	`27	38	21°		$16.0.\bar{2}$	17	15	$20^{\circ}$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	006	39	37 •	6°		16.0.0	10	10	$323^{\circ}$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	008	7	8	310°		16.0.2	11	10	18° 240°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0.10	6	8 7	23		10/0/4	5	6	342°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.0.10	11	15	0°		18.0.4	7	8	21°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	206	27	20	0°		18.0.2	7	7	$352^{\circ}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\overline{2}\widetilde{0}\overline{4}$	29	15	349°	•	18.0.0	9	8	343°
200         10*         28         255         55         7°         20.0.3         6         6         0°           204         55         46         13°         20.0.3         6         6         0°           206         10         18         34°         110         6         8         60°           2.00         11         12         34°         100         5         5         34°           4.017         0         4         14°         310         5         5         34°           406         14         13         20°         17.1.0         0         1         0°           402         32         26         349°         18.1.0         0         1         0°           400         35*         61         342°         02.0         43         42         18°           402         42         43         20°         17.1.0         0         1         0°           406         7         8         14°         20.0         3         2         18°           406         1         352*         60.0         35         3420°         10.0         1	$20\overline{2}$	111	122	<b>7</b> °		18.0.2	6	5	11°
202       55       58       7°       20.0.3       6       0       0         206       10       18       34°       10       6       8       60°         20.0       4       4       30°       310       5       5       11°         20.0       4       4       30°       310       5       5       11°         406       39       34       341°       010       0       3       342°         402       54       49       10°       13.1.0       0       1       0°         400       35°       61       345°       15.1.0       4       1       315°         402       42       43       20°       17.1.0       0       1       0°         404       29       26       349°       10.1       0       1       0°         404       29       26       349°       12.0.0       3       2       18°         4.010       6       6       10°       420       23       18       124°         606       16       13°       12.2.0       3       2       18°         606       16	<b>200</b>	10* .	28	$252^{\circ}$		20.0.4	1	2	00
214         55         460         10°         200.01         6         6         10°           208         11         12         14°         110         6         8         60°           208         11         12         14°         310         5         5         11°           40.01         0         4         12°         510         5         5         36°           400         36°         11         20         18°         11.10         6         2         332°           402         54         49         10°         13.10         0         1         0°           400         35°         61         345°         10.10         0         1         0°           404         29         26         349°         10.10         0         1         0°           406         7         8         14°         200         34         42         180°           40.10         6         6         10°         420         23         18         124°           605         16         21         352°         10.20         3         218°           606	202	55	58 ·	. 1 <sup>70</sup>		20.0.2	6	6	100
200       10       13 $3^{+4}$ 10       6       8 $60^{\circ}$ 2.0.0       4       6 $35^{\circ}$ $310$ 5       5 $11^{\circ}$ 4.06       14       3 $39^{\circ}$ $710$ 7       5 $349^{\circ}$ 4.06       30 $34$ $341^{\circ}$ $710$ 7       5 $349^{\circ}$ 4.02 $54$ $49$ $10^{\circ}$ $11.0$ 6       2 $333^{\circ}$ 400 $35^{\circ}$ $61$ $343^{\circ}$ $15.10$ 4 $1$ $315^{\circ}$ 402 $42$ $43$ $20^{\circ}$ $17.10$ 0 $1$ $0^{\circ}$ $400$ $21$ $18$ $357^{\circ}$ $020$ $43$ $42$ $18^{\circ}$ $4.010$ 6 $6$ $10^{\circ}$ $420$ $23$ $18$ $12^{\circ}$ $60.5$ $16$ $21$ $352^{\circ}$ $620$ $34$ $32$ $176^{\circ}$ $666^{\circ}$ $132^{\circ}$ $122.0$ $35$ $34$ $201^{\circ}$ $60^{\circ}$ $162.0$ $9$	204	55	40	15- 2540		20.0.0	o	0	10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	200	10	18	30 <del>1</del> 14°		110	e	0	600
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.0.10	4	6	350°		110	0 5	8 5	110
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.0.10	ō	4	14°		510	5	5	349°
$40\overline{6}$ $39$ $34$ $341^\circ$ $910$ $0$ $3$ $342^\circ$ $402$ $54$ $49$ $10^\circ$ $13.1.0$ $0$ $10^\circ$ $400$ $35^\circ$ $61$ $343^\circ$ $15.1.0$ $4$ $1$ $116^\circ$ $404$ $29$ $26$ $340^\circ$ $19.10$ $0$ $1$ $0^\circ$ $406$ $21$ $18$ $357^\circ$ $020$ $43$ $42$ $18.124^\circ$ $6.0.10$ $6$ $6$ $10^\circ$ $420$ $23$ $18$ $124^\circ$ $605$ $16$ $21$ $352^\circ$ $820$ $32$ $18^\circ$ $182^\circ$ $606$ $16$ $21$ $352^\circ$ $820$ $32$ $136^\circ$ $142.0$ $9$ $10$ $166^\circ$ $600^\circ$ $33$ $355^\circ$ $182.0$ $7$ $9$ $86^\circ$ $600^\circ$ $730$ $4$ $9$ $806^\circ$ $730$ $4$ $9$ $806^\circ$ $730^\circ$ $13.30$ $10$ $10$ $12.26^\circ$ $830^\circ$ $90^\circ$	408	14	13	29°		710	7	5	27°
$403$ 11       20 $18^{\circ}$ 11.1.0       6       2 $333^{\circ}$ $400$ $35^{\circ}$ 61 $343^{\circ}$ 15.1.0       4       1 $315^{\circ}$ $402$ $422$ $423$ $349^{\circ}$ 19.1.0       0       1 $0^{\circ}$ $404$ $29$ $26$ $349^{\circ}$ 19.1.0       0       1 $0^{\circ}$ $405$ 7       8 $14^{\circ}$ $220$ $57$ $68$ $172^{\circ}$ $40.10$ 6       6 $10^{\circ}$ $420$ $23$ $18$ $124^{\circ}$ $6.05$ 16       21 $352^{\circ}$ $820$ $25$ $24$ $195^{\circ}$ $606$ 5 $3$ $342^{\circ}$ $102.0$ $3$ $2$ $135^{\circ}$ $606$ 16 $21$ $14$ $8^{\circ}$ $162.0$ $9$ $9$ $162^{\circ}$ $600$ $13$ $35^{\circ}$ $130$ $7$ $7$ $722^{\circ}$ $805$ $7$ $734^{\circ}$ $9$ $9$ $162^{\circ}$ $1330$ $11$ $170$	$40\bar{6}$	39	<b>34</b>	341°		910	0	3	342°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$40\bar{4}$	11	20	18°		11.1.0	6	2	333°
400 $35^{\circ}$ 61 $343^{\circ}$ $15.1.0$ 4       1 $315^{\circ}$ 404       29       26 $349^{\circ}$ $19.1.0$ 0       1       0^{\circ}         408       7       8 $14^{\circ}$ $220$ $57$ $68$ $172^{\circ}$ $40.10$ 6       6 $10^{\circ}$ $4230$ $23$ $18$ $124^{\circ}$ $6.0.10^{\circ}$ 6       7 $23^{\circ}$ $620$ $34$ $32$ $176^{\circ}$ $606$ 5 $3$ $342^{\circ}$ $10.2.0$ $3$ $2$ $135^{\circ}$ $606^{\circ}$ 5 $3$ $342^{\circ}$ $10.2.0$ $3$ $2$ $136^{\circ}$ $600^{\circ}$ $13$ $35^{\circ}$ $14.2.0$ $9$ $10$ $156^{\circ}$ $600^{\circ}$ $15.3$ $355^{\circ}$ $14.2.0$ $9$ $162^{\circ}$ $600^{\circ}$ $15.3$ $355^{\circ}$ $14.2.0$ $9$ $162^{\circ}$ $600^{\circ}$ $15.3$ $15.3$ $15.3$ $16.2^{\circ}$ $930^{\circ}$ $10.2^{\circ}$ $800^{\circ}$ 1	402	54	49	10°		13,1,0	. 0	1	0°
402       42       43       20'       17.1.0       0       1       0°         406       21       18       357°       020       43       42       180'         4.0.10       6       6       10°       420       23       18       122'         608       16       21       352°       830       25       24       195'         604       41       40       13°       12.2.0       35       34       20'       135'         604       41       40       13°       12.2.0       35       34       20'       15''       130''       10''       15''         600       53       54       0°       16.2.0       9       10       15''       10''       10''       10''       15'''       10'''       10'''''       11'''''''       10''''''''''''''''''''''''''''''''''''	400	35*	61	343°		15,1,0	4	1	$315^{\circ}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	402	42	43	20°		17.1.0	0	1	0°
400       21       15 $51^{\circ}$ $020$ $43$ $42$ $180^{\circ}$ 401       6       6 $10^{\circ}$ $420$ $23$ $18$ $122^{\circ}$ 6008       16       21 $352^{\circ}$ $820$ $25$ $24$ $195^{\circ}$ 6004       41       40 $13^{\circ}$ $12.2.0$ $35$ $34$ $201^{\circ}$ 6004       41       40 $13^{\circ}$ $12.2.0$ $9$ $9$ $162^{\circ}$ 6004       37 $33$ $355^{\circ}$ $130$ $7$ $7$ $198^{\circ}$ 6004       37 $33$ $355^{\circ}$ $130$ $7$ $7$ $122^{\circ}$ $604$ $37$ $33$ $355^{\circ}$ $130$ $7$ $7$ $122^{\circ}$ $630$ $10$ $11$ $170^{\circ}$ $90$ $162^{\circ}$ $80^{\circ}$ $7$	404	29	26	349		19.10	0	1	· 0°
$1000$ $1$ $0$ $10^{\circ}$ $220$ $0^{\prime}$ $08$ $112^{\circ}$ $6.0.10$ $6$ $7$ $23^{\circ}$ $620$ $23$ $18$ $124^{\circ}$ $606$ $16$ $21$ $352^{\circ}$ $620$ $34$ $32$ $176^{\circ}$ $606$ $5$ $3$ $342^{\circ}$ $10.2.0$ $3$ $2$ $135^{\circ}$ $602$ $30$ $35$ $345^{\circ}$ $14.2.0$ $9$ $10$ $156^{\circ}$ $602$ $12$ $14$ $8^{\circ}$ $18.2.0$ $7$ $9$ $186^{\circ}$ $606$ $16$ $15$ $11^{\circ}$ $330$ $10$ $10$ $225^{\circ}$ $606$ $16$ $15$ $11^{\circ}$ $330$ $10$ $10$ $225^{\circ}$ $606$ $16$ $15$ $11^{\circ}$ $330$ $10$ $10$ $225^{\circ}$ $8.0.10$ $5$ $8$ $0^{\circ}$ $730$ $4$ $9$ $186^{\circ}$ $8.05$ $7$ $7$ $0^{\circ}$ $930$ $9$ $7$ $70^{\circ}$ $806$ $17$ $18$ $357^{\circ}$ $11.3.0$ $3$ $2$ $186^{\circ}$ $806$ $17$ $18$ $352^{\circ}$ $11.3.0$ $3$ $2$ $186^{\circ}$ $806$ $14$ $7$ $231^{\circ}$ $17.3.0$ $2$ $2$ $186^{\circ}$ $806$ $14$ $7$ $231^{\circ}$ $17.3.0$ $2$ $2$ $186^{\circ}$ $806$ $13$ $17$ $36^{\circ}$ $640$ $13$ $18$ $0^{\circ}$ $806$ $7$ $7$ $34$	400	21	. 18	307 14°		020	43	42	180°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.0.10	6	6	· 10°		220	57	08	172*
$00\bar{5}$ 16         21 $35^2$ $05^2$ $05^2$ $05^2$ $01^2$ $05^2$ $01^2$ $05^2$ $01^2$ $05^2$ $01^2$ $05^2$ $01^2$ $05^2$ $01^2$ $05^2$ $24$ $105^2$ $00^2$ $30$ $35$ $34$ $205^2$ $10^2$ $35^2$ $142.0$ $9$ $1062$ $00^2$ $10^2$ $35^2$ $142.0$ $9$ $1062$ $00^2$ $12^2$ $142.0$ $9$ $106^2$ $00^2$ $162.0$ $9$ $90^2$ $106^2$ $00^2$ $11^2$ $330$ $10$ $11$ $10^7$ $7$ $11^2$ $330$ $10$ $11$ $10^7$ $7$ $10^7$	6.0.10	ő	7	23°		420	20 34	10	124
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	608	16	21	352°		820	25	24 ·	195°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	60Ē	5	3	342°		10.2.0	3	$\frac{1}{2}$	135°
$602$ $30$ $35$ $345^\circ$ $14.2.0$ $9$ $10$ $156^\circ$ $602$ $12$ $14$ $8^\circ$ $18.2.0$ $7$ $9$ $186^\circ$ $604$ $37$ $33$ $355^\circ$ $130$ $7$ $7$ $172^\circ$ $606$ $16$ $15$ $11^\circ$ $330$ $10$ $10$ $225^\circ$ $606$ $16$ $15$ $11^\circ$ $330$ $10$ $11$ $170^\circ$ $806$ $7$ $7$ $0^\circ$ $930$ $9$ $7$ $207^\circ$ $806$ $17$ $18$ $357^\circ$ $11.3.0$ $3$ $8$ $144^\circ$ $804$ $20$ $21$ $16^\circ$ $133.3.0$ $4$ $2$ $243^\circ$ $800$ $14$ $7$ $231^\circ$ $17.3.0$ $3$ $2$ $180^\circ$ $800$ $14$ $45$ $332^\circ$ $440$ $10$ $13$ $337^\circ$ $806$ $13$ $17$ $36^\circ$ $640$ $13$ $18^\circ$ $100.$	$60\overline{4}$	41	40	13°		12.2.0	35	34	$201^{\circ}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$60\overline{2}$	30	35	345°		14.2.0	9	10	156°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	600	53	54	0.		16.2.0	9	9	162°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	602 604	12	14	355°		18.2.0	7	9	186°
$300$ $10$ $10$ $10$ $10$ $10$ $10$ $11$ $170^{\circ}$ $80.010$ $5$ $8$ $0^{\circ}$ $730$ $4$ $9$ $180^{\circ}$ $806$ $17$ $18$ $357^{\circ}$ $113.0$ $3$ $8$ $144^{\circ}$ $804$ $20$ $21$ $16^{\circ}$ $133.0$ $4$ $2$ $243^{\circ}$ $802$ $36$ $54$ $352^{\circ}$ $153.0$ $3$ $2$ $180^{\circ}$ $800$ $14$ $7$ $221^{\circ}$ $17.3.0$ $2$ $2$ $180^{\circ}$ $800$ $14$ $7$ $235^{\circ}$ $240$ $17$ $13$ $337^{\circ}$ $804$ $20$ $22$ $355^{\circ}$ $240$ $17$ $13$ $337^{\circ}$ $806$ $13$ $17$ $36^{\circ}$ $6440$ $13$ $18$ $0^{\circ}$ $10.0.5$ $9$ $9$ $339^{\circ}$ $104.0$ $6$ $9$ $18^{\circ}$ $10.0.6$ $12$ $12$ $10^{\circ}$ $12.4.0$ $12$ $11.$ $17^{\circ}$ $10.0.4$ $18$ $24$ $0^{\circ}$ $144.0$ $8$ $8$ $0^{\circ}$ $10.0.4$ $7$ $10$ $22^{\circ}$ $350$ $9$ $7$ $344^{\circ}$ $10.0.4$ $7$ $10$ $294^{\circ}$ $550$ $6$ $7$ $326^{\circ}$ $10.0.4$ $7$ $10$ $294^{\circ}$ $550$ $6$ $7$ $326^{\circ}$ $10.0.4$ $7$ $10$ $294^{\circ}$ $550$ $6$ $7$ $326^{\circ}$ $10.0.4$ $7$ <	606	16	, 15	110		130	10	10	172-
8.010       5       8       0°       730       4       9       110° $806$ 7       7       0°       930       9       7       207° $806$ 17       18 $357°$ 11.3.0       3       8       144° $804$ 20       21       16°       13.3.0       4       2       243° $802$ 36       54 $352°$ 15.3.0       3       2       180° $802$ 41       45       14°       040       36       34       0° $804$ 20       22 $355°$ 240       17       13 $337°$ $806$ 7       7 $341°$ 440       10       13 $337°$ $806$ 7       7 $349°$ 104.0       6       9       18° $10.0.5$ 9       9 $339°$ 104.0       11       11° $10.0.5$ 20       14 $321°$ 164.0       4       5       338° $10.0.2$ 22       24 $350°$ 9       7       344°       18	608	5	10	354°		33U 520	10	10	220 170°
808       7       7       0°       10°       10°       11°       10°	8.0.10	$\tilde{5}$	8	0°		730	10	9	180°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	808	7	7	0°		930	$\overline{9}$	7	207°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	806	17	18	357°	-	11.3.0	3	8	144°
$802$ $30$ $04$ $302^{\circ}$ $15.3.0$ $3$ $2$ $180^{\circ}$ $800$ $41$ $45$ $14^{\circ}$ $17.3.0$ $2$ $2$ $180^{\circ}$ $804$ $20$ $22$ $355^{\circ}$ $240$ $17$ $13$ $337^{\circ}$ $806$ $7$ $7$ $341^{\circ}$ $440$ $10$ $13$ $337^{\circ}$ $808$ $13$ $17$ $36^{\circ}$ $640$ $13$ $18$ $0^{\circ}$ $10.0.5$ $9$ $9$ $339^{\circ}$ $10.4.0$ $6$ $9$ $18^{\circ}$ $10.0.6$ $12$ $12$ $10^{\circ}$ $12.4.0$ $12$ $11$ $17^{\circ}$ $10.0.6$ $12$ $20$ $14$ $321^{\circ}$ $164.0$ $4$ $5$ $338^{\circ}$ $10.0.7$ $22$ $20$ $14$ $321^{\circ}$ $164.0$ $4$ $5$ $338^{\circ}$ $10.0.6$ $12$ $22$ $24$ $350^{\circ}$ $350$ $9$ $7$ $344^{\circ}$ $10.0.2$ $22$ $24$ $350^{\circ}$ $350$ $9$ $7$ $344^{\circ}$ $10.0.4$ $7$ $10$ $294^{\circ}$ $550$ $6$ $7$ $326^{\circ}$ $10.0.4$ $7$ $10$ $294^{\circ}$ $550$ $6$ $7$ $326^{\circ}$ $12.0.5$ $6$ $13$ $347^{\circ}$ $13.5.0$ $3$ $3$ $326^{\circ}$ $12.0.6$ $4$ $4$ $104^{\circ}$ $260$ $5$ $4$ $166^{\circ}$ $12.0.6$ $4$ $4$ $104^{\circ}$ $660$ $6$ $13^{\circ}$ <	804	20	21	16°		13.3.0	4	2	$243^{\circ}$
$000$ $14$ $4$ $231$ $17,3.0$ $2$ $2$ $180$ $804$ $20$ $22$ $355^{\circ}$ $240$ $17$ $13$ $337^{\circ}$ $806$ $7$ $7$ $341^{\circ}$ $440$ $10$ $13$ $337^{\circ}$ $808$ $13$ $17$ $36^{\circ}$ $640$ $13$ $18$ $0^{\circ}$ $100.10$ $2$ $6$ $18^{\circ}$ $640$ $9$ $6$ $350^{\circ}$ $100.6$ $12$ $12$ $10^{\circ}$ $12.4.0$ $12$ $11$ $17^{\circ}$ $10.0.4$ $18$ $24$ $0^{\circ}$ $14.4.0$ $8$ $8$ $0^{\circ}$ $10.0.5$ $20$ $14$ $321^{\circ}$ $160.4.0$ $4$ $5$ $338^{\circ}$ $10.0.4$ $18$ $24$ $0^{\circ}$ $14.4.0$ $8$ $8$ $0^{\circ}$ $10.0.2$ $22$ $24$ $350^{\circ}$ $350$ $9$ $7$ $344^{\circ}$ $10.0.2$ $22$ $24$ $350^{\circ}$ $350$ $9$ $7$ $344^{\circ}$ $10.0.4$ $17$ $22$ $39^{\circ}$ $750$ $6$ $7$ $326^{\circ}$ $10.0.4$ $17$ $22$ $39^{\circ}$ $750$ $6$ $7$ $326^{\circ}$ $10.0.4$ $17$ $22$ $39^{\circ}$ $750$ $6$ $7$ $326^{\circ}$ $10.0.4$ $17$ $22$ $39^{\circ}$ $36$ $326^{\circ}$ $3326^{\circ}$ $12.0.4$ $4$ $4104^{\circ}$ $660$ $13$ $13$ $180^{\circ}$ $12.0.4$ $4$ $42$ $28$ <td>802</td> <td>30</td> <td>54</td> <td>302-</td> <td></td> <td>15.3.0</td> <td>. 3</td> <td>2</td> <td>180°</td>	802	30	54	302-		15.3.0	. 3	2	180°
$804$ $20$ $22$ $356^{\circ}$ $040$ $30$ $34^{\circ}$ $07^{\circ}$ $806$ 77 $341^{\circ}$ $440$ 1713 $337^{\circ}$ $808$ 1317 $36^{\circ}$ $640$ 1318 $0^{\circ}$ $100.6$ 26 $18^{\circ}$ $840$ 96 $350^{\circ}$ $100.6$ 1212 $10^{\circ}$ $124.0$ 12 $11.1$ $17^{\circ}$ $100.6$ 1212 $10^{\circ}$ $124.0$ 12 $11.1$ $17^{\circ}$ $100.6$ 1223 $822^{\circ}$ $150$ 8 $11.63^{\circ}$ $100.0^{\circ}$ 20 $14$ $321^{\circ}$ $164.0$ 45 $100.0^{\circ}$ 22 $24$ $350^{\circ}$ $350$ 97 $100.2$ 22 $24$ $350^{\circ}$ $350$ 97 $100.2$ 22 $24$ $350^{\circ}$ $350$ 97 $100.4$ 7 $10$ $294^{\circ}$ $350^{\circ}$ 97 $120.6$ 613 $347^{\circ}$ $13.50^{\circ}$ 3	800	41	45	14°		17,3,0	2	2	180°
80677341°2401713031' $808$ 131736°64013180° $10 0.10$ 2618°84096350° $10.0.5$ 99339°10.4.06918° $10.0.6$ 121210°12.4.0121117° $10.0.4$ 18240°14.4.0880° $10.0.5$ 2014321°16.4.045338° $10.0.2$ 2224350°35097344° $10.0.4$ 710294°550670° $10.0.4$ 710294°55067326° $10.0.4$ 710294°35033326° $10.0.6$ 172239°7506734° $10.0.6$ 172239°15.0430° $12.0.6$ 613347°13.5.033326° $12.0.7$ 16154°46066158° $12.0.7$ 16154°46066158° $12.0.6$ 67337°2336°180° $12.0.6$ 15264°021301996° $12.0.6$ 67337°1019164°0222532180° <t< td=""><td>804</td><td>20</td><td>22</td><td><math>3\overline{5}\overline{5}^{\circ}</math></td><td></td><td>040</td><td>30 17</td><td>04 19</td><td>0 227°</td></t<>	804	20	22	$3\overline{5}\overline{5}^{\circ}$		040	30 17	04 19	0 227°
$808$ 1317 $36^{\circ}$ $140$ $13$ $18$ $0^{\circ}$ $100.10$ 26 $18^{\circ}$ $840$ 96 $350^{\circ}$ $10.05$ 121210^{\circ} $12.4.0$ 1211 $17^{\circ}$ $10.05$ 121210^{\circ} $12.4.0$ 1211 $17^{\circ}$ $10.05$ 122014 $321^{\circ}$ $164.0$ 45 $338^{\circ}$ $10.0.2$ 2014 $321^{\circ}$ $164.0$ 45 $338^{\circ}$ $10.0.2$ 2224 $350^{\circ}$ $350$ 97 $344^{\circ}$ $10.0.4$ 710 $294^{\circ}$ $550$ 67 $34^{\circ}$ $10.0.4$ 710 $294^{\circ}$ $550$ 67 $34^{\circ}$ $10.0.4$ 710 $294^{\circ}$ $550$ 67 $34^{\circ}$ $10.0.4$ 710 $294^{\circ}$ $350$ 97 $344^{\circ}$ $10.0.4$ 710 $294^{\circ}$ $350$ 97 $342^{\circ}$ $10.0.4$ 712 $347^{\circ}$ $11.5.0$ 430^{\circ} $12.0.5$ 613 $347^{\circ}$ $13.5.0$ 33 $326^{\circ}$ $12.0.5$ 4406^{\circ}66066158^{\circ} $12.0.4$ 2428 $354^{\circ}$ 26054166^{\circ} $12.0.5$ 4101313180^{\circ}12.0.23180^{\circ} $12.0.6$ 6 <td< td=""><td>806</td><td>7</td><td>7</td><td>341°</td><td></td><td>240 440</td><td>10</td><td>13</td><td>337°</td></td<>	806	7	7	341°		240 440	10	13	337°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	808	13	17	36°		640	13	18	0°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$10 \ 0.10$	2	6	18°		840	. 9	6	350°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.8	9	9	339°		10.4.0	6	9	18°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.6	12	12	10		12.4.0	12	11.	17°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.2	20	14	321°		14.4.0	8	8	0° 990°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.0	32	38	$22^{\circ}$		10,4,0	4	11	63°
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.2	22	24	350°		350	9	7	344°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.4	7	10	294°		550	6	7	0°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.6	17	22	39°		750	6	7	<b>34°</b>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.0.8	3	9	297°		950	6	7	$326^{\circ}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12,0,10	5 6	19	300 347°		11.5.0	4	3	0°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.0.6	4	4	104°		13,5,0	3	3	326°
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$12.0.\bar{4}$	24	$2\hat{8}$	$354^{\circ}$		000	13	13	160
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	12.0.2	$\overline{16}$	15	<b>4</b> °		460	5	÷ 6	158°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.0.0	19	16	<b>4</b> °		660	ĕ	ő	180°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.0.2	<b>24</b>	20	348°		860	2	3	180°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.0.4	16	13	23°					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	12.0.6	6	7	337~		021	· 30	19	96°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.0.8	, U 15 ·	ن 96	140- 140-		022	25	<b>32</b>	$156^{\circ}$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	14.0.2	5	20 7	304°		023	23	9	315°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.0.2	17	• 10	11°		024	39	36	205°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.0.0	25	24	10°		025	18	10	1180
$14.0.4$ 11       10 $18^{\circ}$ $02^{\circ}$ $02^{\circ}$ $02^{\circ}$ $10^{\circ}$ $14.0.6$ 4       7 $352^{\circ}$ $352^{\circ}$ $16.0.8$ 5       9 $6^{\circ}$ * Probably low owing to absorption.	14.0.2	12	9	319°		020	19	4	135 76°
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	14.0.4	11	10	18°		041	3	Ŧ	15
	14,0,6	4 K	·/	302- 6°		* Pro	bably low ow	ving to absor	ption.

. .

## Table 2 (cont.)

				· · ·				
hkl	$F_{exp}$	$F_{ m calc.}$	α		hkl	$F_{exp.}$	$F_{\rm calc.}$	α
028	13	13	189°		046	18	11	0°
029	-0	1	0°		047	0	3	$288^{\circ}$
0.2.10	10	6	198°		048	<b>5</b>	3	$342^{\circ}$
041	0	7	352°.		061	10	8	130°
042	7	<b>2</b>	333°		062	6	6	166°
043	20	20	$270^{\circ}$		063	0	3	$34^{\circ}$
044	<b>24</b>	17	0°		064	9	7	$225^{\circ}$
<b>045</b>	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 Fwere used as coefficients for planes 200 and 400 instead of the experimental values.

The errors, as represented by the function

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

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  $1.395 \pm 0.005$  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 coordination, 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

Substance	C–N distance (A.)	Reference				
(a) Aromatic (i.e. with the $C-N$ bond external to the ring)						
<i>m</i> -Tolidine hydrochloride Dichlorobenzidine <i>trans</i> -Azobenzene	1·39 1·40 1·41	Hargreaves & Taylor (1941) Smare (1948) de Lange, Robertson & Woodward (1939)				
$p$ -Nitroaniline (to $NO_2$ ) (to $NH_2$ )	1·39) 1·36	Abrahams & Robertson (1948)	•			
Aminopyrimidines Adenine hydrochloride <i>p</i> -Toluidine	1.285 1.34 1.18*	Clews & Cochran (1948) Broomhead (1948) Wyart (1935)				
(b) Aliphatic						
Glycine DL-Alanine Nickel glycine Acetamide Dicyandiamide	1·39 1·42 1·42 1·38 1·34 1·36 1·37	Albrecht & Corey (1939) Levy & Corey (1941) Stosick (1945) Senti & Harker (1940) Hughes (1940)				
(c) Heterocyclic (i.e. with C–N bonds in the ring)						
Melamine Cyanuric triazide Diketopiperazine Aminopyrimidines Adenine hydrochloride	1·346 (average) 1·345 (average) 1·41 1·32 1·33 (average)	Hughes (1941) Knaggs (1935) Corey (1938) Clews & Cochran (1948) Broomhead (1948)				

Table 3. Short C–N bond lengths

\* 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)
Gəranylaminə hydrochloridə	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 crystalstructure 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 coordination 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  $106^{\circ}$ ,  $106^{\circ}$ ,  $110^{\circ}$ ,  $115^{\circ}$ ,  $117^{\circ}$  and  $117^{\circ}$ , the mean of these six being  $112^{\circ}$ . 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<sub>4</sub> 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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