The Crystal Structure of Orthorhombic Aniline Hydrobromide, $C_6H_5NH_3Br$

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It has been reported in the previous paper[1], that aniline hydrobromide, $C_6H_5NH_3Br$, shows a phase transition of λ-type in the neighborhood of room temperature. It is monoclinic below 27.5°C, and is orthorhombic above this temperature. In the present paper, the crystal structure of the high temperature modification will be given.

Experimental

Crystals of aniline hydrobromide were obtained by slow evaporation from methanol solutions. They were made into small cylindrical rods parallel to the b- and c-axis, less then 0.1 mm. in diameter, by partial dissolution with filter paper moistened with methanol. The hot air stream method[2] was applied to take oscillation and Weissenberg photographs. The temperature of the crystals was maintained at 70 ± 1°C during exposure.

The unit cell containing four formula units was found to have the following dimensions:

$$a=16.77\pm0.06\,\text{Å}$$

$$b=6.05\pm0.03\,\text{Å}$$

and

$$c=6.86\pm0.03\,\text{Å}$$

The space group was uniquely determined, from missing reflections, to be D_{2h}^{10}-Pnaa.

In order to collect intensity data, unfiltered Cu-K radiations were used for taking Weissenberg photographs. This allowed us to make use of K_β in addition to K_α[3]. The multiple-film technique was applied, and the relative intensities of reflections were visually estimated by comparison with standard intensity scales for each series due to K_α and K_β. Corrections for Lorentz and polarization factors were made in the usual way. Corrections for absorption were made using Bradley's method for cylindrical specimens[4]. The linear absorption coefficients for Cu-K_β were calculated using Walter's rule[5] from the values for Cu-K_α. The extinction effect was more or less minimized by putting larger weights on the relative intensity values obtained from smaller specimens.

Structure Determination

Since there are four formula units in the unit cell, four bromine atoms must lie on one of the four-fold equivalent positions, a, b, c and d, given by D_{2h}^{10}-Pnaa[6]. Two of these, a and b, have the eigen symmetry C_i-$\bar{1}$, and the other two, c and d, have C_2-2. Inspection of the observed intensities of reflections $(h\,0\,0)$ ruled out the possibility of placing these four bromine atoms either on a or b, hence they must lie either on c or d. There are four aniline molecules in the unit cell and their longest molecular axis on which lie the atoms, N, C_1 and C_4 must occupy either c or d. Now neither the bromine atoms nor aniline molecules can occupy simultaneously the same equivalent positions, neither c nor d, since the axial length a is too short to be accommodated with these. This case is definitely eliminated also by a qualitative disagreement between observed and calculated structure factors $(0\,k\,l)$ even for lower order reflections. Therefore, if the bromine atoms are placed on c, the atoms N, C_1 and C_4 must be placed on d, or vice versa. The choice of these two alternatives is immaterial, since it depends only on the choice of origin. Thus, the atomic coordinates for each atom are those given in Table I.

TABLE I. ATOMIC COORDINATES ASSIGNED TO EACH ATOM

4Br	$x\,\frac{1}{4}\,\frac{1}{4},\ \bar{x}\,\frac{3}{4}\,\frac{3}{4},\ \frac{1}{2}+x\,\frac{1}{4}\,\frac{1}{4},\ \frac{1}{2}-x\,\frac{3}{4}\,\frac{3}{4};$
4N, $4C_1$ and $4C_4$:	$x\,\frac{3}{4}\,\frac{1}{4},\ \bar{x}\,\frac{1}{4}\,\frac{3}{4},\ \frac{1}{2}+x\,\frac{3}{4}\,\frac{1}{4},\ \frac{1}{2}-x\,\frac{1}{4}\,\frac{3}{4};$
$8C_2$ and $8C_3$:	$x\,y\,z,\ x\,\frac{1}{2}-y\,\frac{1}{2}-z,\ \frac{1}{2}-x\,\frac{1}{2}+y\,\bar{z},\ \frac{1}{2}-x\,\bar{y}\,\frac{1}{2}+z,$ $\bar{x}\,\bar{y}\,\bar{z},\ \bar{x}\,\frac{1}{2}+y\,\frac{1}{2}+z,\ \frac{1}{2}+x\,\frac{1}{2}-y\,z,\ \frac{1}{2}+x\,y\,\frac{1}{2}-z$

The number of positional parameters to be determined is ten in all. However, if we assume the usual bond distances and bond angles for the aniline molecule, they can be reduced to only three. They are x_{Br}, x_{N} and α, the last one representing the angle between the benzene ring and the plane (010). An approximate value 0.025 for x_{Br} was easily obtained from the Patterson synthese, $P(xz)$ and $P(xy)$. Using this value, trial and error methods gave

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† Deceased, 26 May, 1959.

[1] I. Taguchi, This Bulleten, **34**, 392 (1961).

[2] I. Taguchi, *Annual Report Inst. Fibre Research, Osaka Univ.*, **8**, 45 (1945).

[3] T. Watanabé and I. Taguchi, *Acta Cryst.*, **14**, 67 (1961).

[4] A. J. Bradley, *Proc. Roy. Soc.*, **A47**, 879 (1935).

[5] "Internationale Tabellen zur Bestimmung von Kristallstrukturen", II., Gebrüder Bornträger, Berlin (1935), p. 576.

[6] "International Tables for X-Ray Crystallography", I. The Kynoch Press, Birmingham (1952), p. 144.

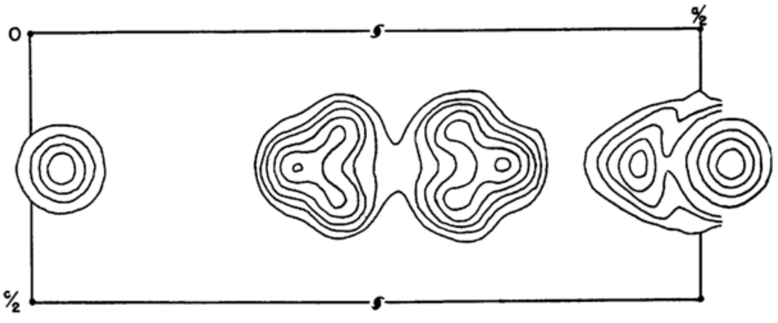

Fig. 1. Electron density projection along the b-axis. Contours for the carbon and nitrogen atoms are drawn at intervals of 1 Å^{-2}, starting at the 3 eÅ^{-2} level. Contours for the bromine atom are drawn at intervals of 10 eÅ^{-2}, starting at the 10 eÅ^{-2} level.

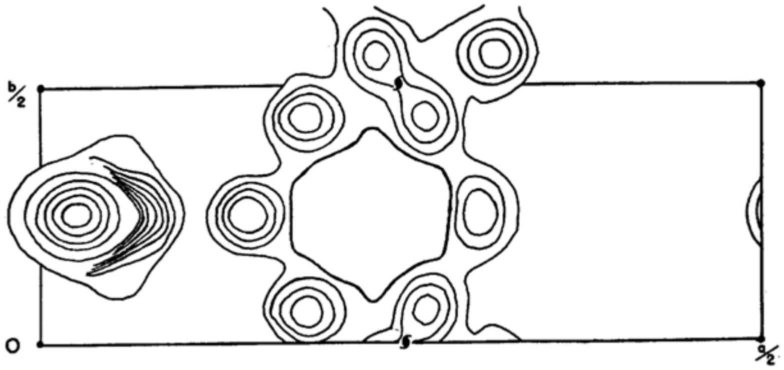

Fig. 2. Electron density projection along the c-axis. Contours intervals are the same as in Fig. 1.

approximate values, $x_N=0.43$ and $\alpha=25°$, from $(0kl)$ reflections.

The electron density projections along the b- and c-axis were then calculated, based on this trial structure, a few terms of doubtful sign being ommitted. They showed all the atoms except nitrogen. Afer three cycles of refinement, there were no terms whose signs were to be changed. The final electron density projections, $\rho(xz)$ and $\rho(xy)$, are shown in Figs. 1 and 2. From the $\rho(xz)$ projection, a more accurate value for x_{Br} was obtained assuming the Gaussian curvature near the peak. Those of the carbon atoms were also obtained graphically from these two projections. As the nitrogen atom in these projections is partially masked by the bromine atom, the location of the nitrogen atom was evaluated by subtracting the observed electron density distribution of the bromine atom from $\rho(xz)_{z=(1/4)}$, assuming that the former has the same distribution along $+X$ and $-X$ from x_{Br}. Using the atomic coordinates thus obtained, the discrepancy factors were found to be 11.5% for $(h0l)$ and 11.2% for $(hk0)$ reflections, the overall temperature factor being assumed to be isotropic, with a value 4.0 Å^2.

Refinement of the Structure

Two difference syntheses, $D(xz)$ and $D(xy)$, prepared at this stage indicated an appreciable anisotropy of thermal vibration of the bromine atom, in addition to a slight shift of the atomic coordinates for each atom. The bromine parameter was refined, using mainly $(h0l)$ reflections, and those of the other atoms were made, using both $(h0l)$ and $(hk0)$ reflections. Since the direction of the maximum vibration of the bromine atom is along the c-axis, its atomic scattering factor can be given by[7]

$$f_{Br}=f_{Br}\ (\text{free atom})\ \exp(-\gamma)$$

$$\gamma=(A+B\sin^2\varphi)\sin^2\theta/\lambda^2$$

where φ is the angle between $\boldsymbol{a}$ and $\boldsymbol{h}$, and A and B are unknown quantities to be determined. In order to allow for the anisotropic vibration of the bromine atom, the variation of the temperature parameter with φ was first determined

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[7] E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1717 (1941).

in the following way. The contributions of the carbon and nitrogen atoms were subtracted from the observed structure factors to give a set of F'_O values. These F'_O values were divided into groups with $\varphi=0\sim15°$, $15\sim30°, \cdots\cdots$, $75\sim90°$, and for each group γ was obtained from a plot, $\log F_{Br}/F'_O$ against $(\sin\theta/\lambda)$, where F_{Br} stands for the calculated bromine contribution without temperature factor. Further refinement followed, assuming that the temperature factors for the carbon and nitrogen atoms were the same and isotropic.

At this stage, the secondary extinction effect was corrected using the equation[8],
$I_o=I_c \exp(-gI_c)$.

Finally the contributions of the hydrogen atoms were allowed for. It was assumed that the hydrogen atoms attached to the carbon atoms were located in the outward directions bisecting the angle between consecutive C–C bonds, at a distance 1.05 Å, and that the hydrogen atoms attached to the nitrogen atom were distributed tetrahedrally with respect to the C–N bond, at a distance 1.01 Å. It was further assumed that these hydrogen atoms were rotating freely around the C–N bond as in the case of methylammonium chloride[9]. Now the contribution from the rotating hydrogen atoms to the structure factor can be written by

$$\pm 12 f_H \exp-(\sin\theta/\lambda)^2 B_H \times J_0(K\sin\theta/\lambda)\genfrac{}{}{0pt}{}{\cos 2\pi h x_H}{\sin 2\pi h x_H}$$

where J_o is the zeroth order Bessel function and the argument K is $4\pi r_o \sin\theta_o$. In this expression, r_o and θ_o are the radius of the orbit and the angle between $\boldsymbol{a}$ and $\boldsymbol{h}$ respectively, and x_H is the common x parameter for hydrogen atoms. The temperature factor for hydrogen, B_H, was assumed to be isotropic with a value 6.5 Å². The agreement between observed and calculated strucrure factors was found definitely improved especially for lower order reflections. The discrepancy factors were decreased to 7.9% and 6.5% for $(h0l)$ and $(hk0)$ reflections, including all the non-observed terms up to $\sin\theta/\lambda=0.67$. The final positional parameters and temperature factors for each atom are listed in Table II. The interatomic distances and bond angles calculated from these positional parameters are given in Tables III and IV. In Tables V and VI, the observed and calculated structure factors for $(h0l)$ and $(hk0)$ reflections are given.

TABLE II. POSITIONAL PARAMETERS AND TEMPERATURE FACTORS

	Positional parameter			Temperature factor, Å²		
	x	y	z	Bx	By	Bz
Br	0.0230	0.25	0.25	4.3	3.7	5.3
N	0.4441	0.75	0.25		6.0	
C_1	0.3564	0.75	0.25			
C_2	0.3152	0.5650	0.1833			
C_3	0.2323	0.5650	0.1833			
C_4	0.1914	0.75	0.25			

TABLE III. BOND DISTANCES AND BOND ANGLES

Bond distance, Å		Bond angle	
C_1–C_2	1.42	$\angle$N–C_1–C_2	121°34′
C_2–C_3	1.39	$\angle C_2$–C_1–C_2'	116°52′
C_3–C_4	1.42	$\angle C_1$–C_2–C_3	121°34′
N–C_1	1.47		

TABLE IV. INTERMOLECULAR ATOMIC DISTANCES, Å

C_4(I)……C_5(II)	3.76
C_2(I)……C_5(II)	3.61
C_3(I)……C_5(II)	3.57
C_4(I)……C_6(II)	3.54
Br(A)……N(II)	3.30
Br(A)……N(III)	
Br(C)……N(II)	3.48
Br(E)……N(II)	

Discussion

The crystal structure of aniline hydrobromide can be said to belong to a distorted CsCl-type, consisting of bromine and anilinium ions. The C_2–C_3 distance in the benzene ring is slightly shorter than the other C–C distances. The C_1–N distance is 1.47 Å, suggesting a single bond nature.

The structue can also be described as built up with alternating layers, parallel to the (100) plane, one layer containing anilinium ions and the other bromine ions. The structure may further be taken as a superstructure along the a-axis, since every other layer contains anilinium ions in different orientations, as can be seen in Fig. 4. The inclination of the benzene ring to the plane (010) is ±22.5°, so that the angle between the neighboring benzene rings is 45°. The bromine ions lie nearly on the same plane, the deviation from the plane being 0.386 Å.

The shortest intermolecular atomic distances are found between carbon atoms. These distances (see Table IV) are somewhat shorter than the usually accepted van der Waals' contact, 3.70 Å.

Between the consecutive layers, the strongest interactions will be those between the bromine ion and the nitrogen atom of the anilinium ion. Each bromine ion is surrounded by four nitrogen atoms, and each nitrogen atom by four bromine ions, which from a rhomb parallel to

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[8] J. Houstry and J. Clastre, *Acta Cryst.*, **10**, 696 (1957).

[9] E. W. Hughes and W. N. Lipscomb, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

the (100) plane. Of the interatomic distances between the nitrogen and bromine atoms, two are shorter, 3.3 Å, and the other two are longer, 3.48 Å. The angles subtended at the nitrogen atom by the four bromine atoms are 99° and 114°. The direction of the maximum thermal vibration of the bromine atom within the layer is nearly parallel to the longer distance of Br

TABLE V. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (h 0 l) REFLECTIONS

h 0 l	$F_{\rm O}$	$F_{\rm C}$	h 0 l	$F_{\rm O}$	$F_{\rm C}$
0 0 0		344.0	0 0 4	66.0	71.2
2 0 0	58.8*	61.2	2 0 4	50.8	56.4
4 0 0	115.6*	114.4	4 0 4	36.0	40.0
6 0 0	75.2*	73.2	6 0 4	30.4	31.6
8 0 0	8.8	12.0	8 0 4	12.4	11.6
10 0 0	—	0.8	10 0 4	—	0.8
12 0 0	10.4	−9.6	12 0 4	10.4	−6.4
14 0 0	17.2	−17.6	14 0 4	8.0	−7.2
16 0 0	11.6	−12.0	16 0 4	10.0	−8.8
18 0 0	17.2	−16.8	18 0 4	11.6	−9.6
20 0 0	11.6	−12.4			
			2 0 5	11.6	−9.6
2 0 1	11.6	3.6	4 0 5	13.5	−15.6
4 0 1	42.0	−41.6	6 0 5	28.4	−25.6
6 0 1	70.8*	−70.8	8 0 5	24.8	−25.2
8 0 1	33.2	−41.6	10 0 5	19.6	−19.2
10 0 1	67.2*	−70.4	12 0 5	27.2	−26.0
12 0 1	39.2	−42.4	14 0 5	11.6	−11.6
14 0 1	32.8	−37.6	16 0 5	8.8	−8.4
16 0 1	16.8	−17.2			
18 0 1	10.4	−10.4	0 0 6	24.0	−25.6
20 0 1	—	2.4	2 0 6	26.4	−30.8
			4 0 6	15.6	−16.4
0 0 2	189.6*	−190.4	6 0 6	15.6	−15.2
2 0 2	58.8*	−72.8	8 0 6	7.2	−6.4
4 0 2	78.8*	−82.0	10 0 6	—	−0.4
6 0 2	57.2*	−55.6	12 0 6	7.2	3.6
8 0 2	12.4	−14.0	14 0 6	—	2.8
10 0 2	—	−1.2	16 0 6	4.4	5.2
12 0 2	10.8	8.8			
14 0 2	13.6	14.0	2 0 7	5.6	4.8
16 0 2	12.0	11.2	4 0 7	5.6	4.8
18 0 2	16.0	14.4	6 0 7	14.0	11.6
20 0 2	10.0	10.8	8 0 7	13.2	11.6
			10 0 7	7.2	7.6
2 0 3	10.8	11.6	12 0 7	15.6	12.0
4 0 3	25.6	28.8			
6 0 3	46.4	48.0	0 0 8	9.2	8.8
8 0 3	35.2	39.6	2 0 8	12.0	12.0
10 0 3	42.4	44.0	4 0 8	5.6	6.0
12 0 3	35.2	36.8	6 0 8	6.8	5.6
14 0 3	23.6	24.8	8 0 8	3.6	2.4
16 0 3	12.8	13.6			
18 0 3	8.4	8.0			
20 0 3	—	2.0			

* Corrected for extinction

TABLE VI. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (h k 0) REFLECTIONS

h k 0	$F_{\rm O}$	$F_{\rm C}$	h k 0	$F_{\rm O}$	$F_{\rm C}$
2 1 0	62.8*	−60.0	0 4 0	68.8	68.8
4 1 0	80.4*	−81.6	2 4 0	54.8	53.6
6 1 0	68.4*	−73.3	4 4 0	38.0	39.2
8 1 0	82.4*	−84.0	6 4 0	32.4	30.4
10 1 0	47.6	−53.2	8 4 0	14.0	12.0
12 1 0	35.2	−39.6	10 4 0	5.6	1.6
14 0 1	26.8	−26.8	12 4 0	6.4	−6.0
16 1 0	18.4	−19.6	14 4 0	8.4	−7.6
18 1 0	8.4	−8.0	16 4 0	8.0	−9.2
20 1 0	4.0	−3.6	18 4 0	8.8	−12.4
22 1 0	—	0.0			
			2 5 0	21.6	−16.4
0 2 0	104.4*	−110.0	4 5 0	21.6	−21.2
2 2 0	116.8*	−123.2	6 5 0	26.0	−25.2
4 2 0	57.2*	−60.4	8 5 0	32.0	−31.2
6 2 0	54.0	−53.2	10 5 0	20.4	−20.0
8 2 0	18.8	−20.8	12 5 0	19.2	−19.6
10 2 0	—	−0.4	14 5 0	10.4	−11.2
12 2 0	15.2	11.6	16 5 0	7.6	−10.4
14 2 0	6.4	9.2			
16 2 0	15.2	14.8	0 6 0	40.0	36.8
18 2 0	14.8	14.8	2 6 0	22.8	−21.6
20 2 0	6.4	8.8	4 6 0	22.0	−22.4
22 2 0	6.8	8.0	6 6 0	16.4	−15.6
			8 6 0	5.6	−6.0
2 3 0	28.8	25.2	10 6 0	—	−1.2
4 3 0	58.4	56.4	12 6 0	—	2.8
6 3 0	41.2	42.8	14 6 0	6.4	5.2
8 3 0	45.6	46.8			
10 3 0	15.2	11.6	2 7 0	7.6	5.2
12 3 0	13.6	16.8	4 7 0	11.2	10.8
14 3 0	28.8	27.6	6 7 0	11.2	10.8
16 3 0	12.4	11.6	8 7 0	11.6	12.4
18 3 0	6.0	6.4	10 7 0	10.0	11.6
20 3 0	—	2.8			
			0 8 0	8.0	10.4
			2 8 0	11.2	11.6
			4 8 0	6.4	8.0

* Corrected for extinction

TABLE VII. MELTING POINTS AND TEMPERATUER FACTORS OF SEVERAL AMINE HYDROHALIDES

Substance	M. p. °C	Mean temp. factor, Å^2
Aniline hydrochloride[a)]	198	4.0
Aniline hydrobromide[b)]	283	5.8
Aniline hydroiodide[c)]	365	6.0
Cyclohexylamine hydrochloride[d)]	206	5.0

a) C. J. Brown, *Acta Cryst.*, **2**, 228 (1949).

b) Present investigation

c) I. Nitta, I. Taguchi and H. Hiyama, to be published.

d) A. Shimada, Y. Okaya and M. Nakamura, *Acta Cryst.*, **8**, 819 (1955).

···Br. The cleavage plane, (001), is also perpendicular to this longer distance.

Since the anilinium ion in this structure should have the two-fold rotational symmetry demanded by the space group, the three hydrogen atoms bound to the nitrogen atom must occupy statistical positions by some means. Two plausible models of arrangement of these three hydrogen atoms are shown in Fig. 5. Case A, in Fig. 5, includes two strong and one weak hydrogen bonds. On the other hand, in case B there are one strong and two weak hydrogen bonds. These are the two extremes. A model of free rotation around the C–N axis is another extreme. This model of free rotation was incorporated into the structure factor calculations as described in the section of refinement.

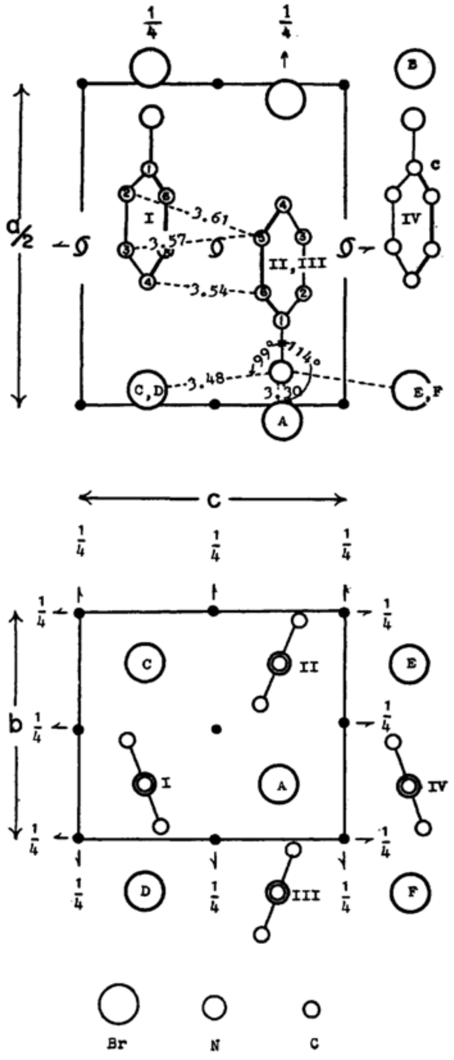

Fig. 3. The structure of the orthorhombic aniline hydrobromide projected on to the (010) and (100) planes.

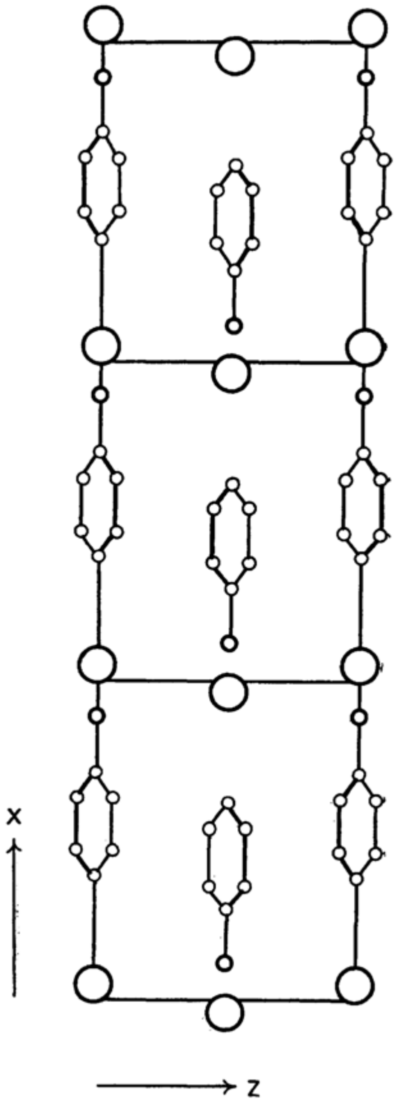

Fig. 4. A schematic representation of the superstructure along the b-axis.

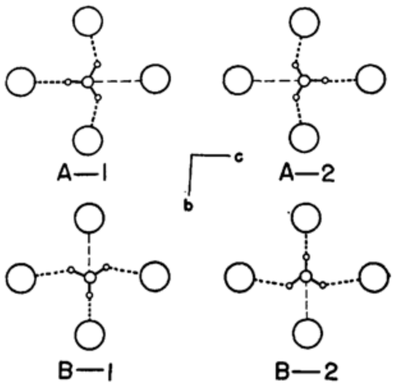

Fig. 5. Statistical arrangements of the three hydrogen atoms bound to the nitrogen atom.

Now, the actual structuer may be represented by an average of all the possible states arising from these extremes stated above, with an appropriate weight on each. Such a statistical arrangement of the hydrogen atoms will vanish when the phase transition takes place.

The mean temperature factor is 5.8Å². This value is considerably large for a crystal whose melting poing is as high as 283°C. The temperature factors and melting points of several related compounds are listed in Table VI. That these amine hydrohalides have large thermal vibration and relatively high melting points will probably be due to the partially ionic and partially molecular character of these compounds. The large thermal motion will arise from their molecular character, whereas the ionic character will be responsible for their high melting points. It is interesting to note that these amine hydrohalides have these common characteristics notwithstanding their different crystal structures.

Let us now compare the crystal structure of aniline hydrobromide with those of alkylamine hydrohalides. Both methyl- and propyl-ammonium chlorides crystallize in the tetragonal system, and the alkylammonium ions are characterized by the four-fold axial symmetry. In methylammonium chloride, the three hydrogen atoms attached to nitrogen occupy statistical positions, or they are in rotation. In propylammonium chloride, not only these hydrogen atoms but also the nitrogen and carbon atoms, too, are rotating. The difference between the four-fold axial symmetry of the alkylammonium ions and the two-fold axial symmetry of the anilinium ions may be due to the difference in their molecular shape. All these crystals are apolar, so that their structures can be described as an alternating disposition or antiparallel arrangement of dipoles along their principal axes. The nitrogen atoms in these alkylammonium chlorides have four halogen atoms as their immediate neighbors, so also the nitrogen atoms in aniline hydrobromide, though these four distances in the latter are not exactly the same.

There are some indications of a possible hindered oscillation of the anilinium ion around its longest axis. The final difference projection, $D(xz)$, shows that the temperature factors of C_2 and C_3 are larger than those of C_1 and C_4. Some reflections such as (112) whose structure factors have contributions from C_2 and C_3 alone are associated with diffuse spots, presumably due to the thermal motion stated above.

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