On the Order-Disorder Phase Transformation of Anilinium Halides.

III. High Temperature Phase Crystal Structure of Anilinium Bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$. An X-ray and Neutron Diffraction Study

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The crystal structure of the high temperature phase of anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, was studied by X-ray and neutron diffraction at $T = 343$ K. The refinement supports disordered positions of the $-NH_3^{\oplus}$ group. A split-atom model is proposed which includes disorder of the benzene ring. The thermal parameters, hydrogen bond distances, and other experimental data (NMR, NQR, inelastic neutron scattering) are in accordance with this model.

Introduction

Anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, shows at $T = 296.9$ K a reversible solid$\rightleftharpoons$solid phase transformation by which the orthorhombic high temperature phase $C_6H_5NH_3Br(I)$ (space group D_{2h}^{10}-Pnaa, $Z = 4$) changes into the monoclinic low temperature phase $C_6H_5NH_3Br(II)$ (space group C_{2h}^{5}-P2_1/a), Taguchi [1], Suga [2]. The transition is of higher order, as shown by dilatometric studies [1], by ^{79}Br Nuclear Quadrupole Resonance (NQR) studies (Pies and Weiss [3]; part I of this series), and by investigations of the ^{1}H-NMR spin-lattice relaxation times (Ratcliffe and Dunell [4]). An orientational order-disorder transition $C_6H_5NH_3Br(I) \rightleftharpoons C_6H_5NH_3Br(II)$ was proposed [2]. The ^{79}Br-NQR of $C_6H_5NH_3Br$ and $C_6H_5ND_3Br$ as a function of temperature and the ^{1}H-NMR studies confirm the close connection between the mechanism of the phase transition and the dynamics of the hydrogen bonds N-H $\cdots$ Br in the solid.

Nitta et al. [5] determined the crystal structure of the orthorhombic phase $C_6H_5NH_3Br(I)$. No hydrogen atoms, however, were located. It was therefore decided to refine the crystal structure of $C_6H_5NH_3Br(I)$ by X-ray and neutron diffraction in order to gain a more detailed knowledge of the hydrogen and nitrogen positions and of the thermal parameters of the ring atoms. The knowledge of precise hydrogen positions is essential for the interpretation of the ^{79}Br-NQR results and the discussion of the phase transition mechanism. Here we report the structure of orthorhombic $C_6H_5NH_3Br(I)$ based on X-ray (X) and neutron diffraction data (N). In the following paper the results for the low temperature phase (II) are given.

Experimental

Anilinium bromide is prepared from aniline and aqueous hydrobromic acid. Colourless orthorhombic bipyramidal crystals of $C_6H_5NH_3Br(I)$ are obtained by slow cooling of the solution from 318 K to 298 K. The habitus of the crystals is described by Lang [6] and Hiortdahl [7]. Suitable crystals were kept in Lindemann glass capillaries (X-ray diffraction) or in thin walled Al-tubes (N) to prevent them from decomposition.

Lattice constants were refined from single crystal diffractometer data. They are in agreement with the lattice constants given by Nitta et al. [5] (Table 1). The space group of $C_6H_5NH_3Br(I)$ given by Nitta et al. was confirmed to be Pnaa. Experimental details of the data collection and the structure refinement for X-ray and neutron diffraction are given in Table 1. The measured intensities were corrected for background radiation, LP-factor (X), L-factor (N) and absorption.

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Table 1. Experimental conditions and crystal structure data of anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, phase I.

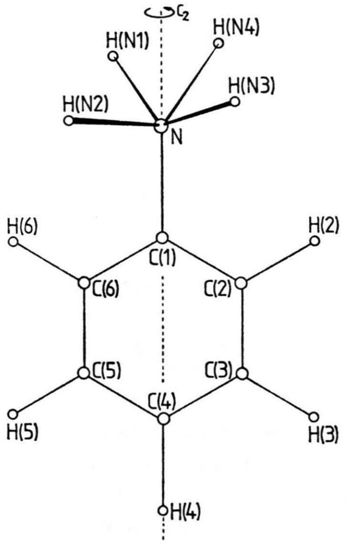
Experimental conditions

	X	N
crystal habitus and size	needle; length ‖[010]: 2 mm	prism (3.3 · 3.3 · 1.8) mm^3
diffractometer	2-circle Stoe-Stadi 2	4-circle P110/FR2 Kernforschungszentrum Karlsruhe
wavelength, λ/pm	154.18 (CuKα)	91.88
monochromator	Graphite (002)	Cu(220)
temperature, T/K	343(1) (heated air)	343(1) (electric furnace)
linear absorption coefficient, μ/m^{-1}	6721 (CuKα, calc)	176 (exp)
scan	$\omega/2\vartheta$ (rotation ‖[010])	ω
$(\sin\vartheta/\lambda)_{\max}$/pm^{-1}	0.0061	0.0067
number of measured reflections	2250 $(h0l)\ldots(h5l)$	1400
symmetry independent reflections	569	892
reflections considered	569	411 $(I \geqq 2\sigma(I)$
free parameters	54	81
$R(F)$	0.047	0.052
$R_W(F)$	0.044	0.060

Crystal data

		X		N
		this paper	Nitta [5]	
lattice constants	a/pm	1680.4(10)	1677.0(60)	1681.3(10)
	b/pm	607.5(5)	605.0(30)	607.5(5)
	c/pm	686.1(5)	686.0(30)	686.4(5)
space group			D_{2h}^{10}-Pnaa	
number of formula units/unit cell			4	
ϱ_{calc}/(Mg · m^{-3})		1.650	1.661	1.649

Numbering of atoms in the anilinium cation



Point positions

Br	in 4c: $x, \frac{3}{4}, \frac{3}{4}; \bar{x}, \frac{1}{4}, \frac{1}{4}; \frac{1}{2}+x, \frac{3}{4}, \frac{3}{4}; \frac{1}{2}-x, \frac{1}{4}, \frac{1}{4}$
N, C(1), C(4), H(4)	in 4d: $x, \frac{3}{4}, \frac{1}{4}; \bar{x}, \frac{1}{4}, \frac{3}{4}; \frac{1}{2}+x, \frac{3}{4}, \frac{1}{4}; \frac{1}{2}-x, \frac{1}{4}, \frac{3}{4}$
{[C(2) + C(6)], [C(3) + C(5)], [H(2) + H(6)], [H(3) + H(5)], [H(N1) + H(N3)], [H(N2) + H(N4)]}	in 8e: $x, y, z; x, \frac{1}{2}-y, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}+y, \bar{z}; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$ $\bar{x}, \bar{y}, \bar{z}; \bar{x}, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, z; \frac{1}{2}+x, y, \frac{1}{2}-z$

The X-ray single crystal intensities were strongly influenced by extinction. Therefore, a powder pattern of 23 reflections was registered (CuKα, $4° \leqq 2\vartheta \leqq 42°$, $T = (313 \pm 2)$ K) to obtain data free of extinction. It is assumed that the extinction correction is not affected by different temperatures of measurement (343 K: single crystal, 313 K: powder).

The scattering factors (including corrections for anomalous dispersion for $Br^{\ominus}$) were taken from International Tables [8] (X-ray diffraction) and from the compilation of Bacon [9] (N diffraction). The calculations were carried out by the SHELX-76 [10] and X-Ray System [11].

The positional and thermal parameters were refined by least squares methods starting with the parameters of Nitta et al. [5]. Individual weights were attributed to each reflection as $W = 1/\sigma^2(F)$ for X-ray and $W = 1/[\sigma^2(F) + 0.0002 \cdot F^2]$ for neutron diffraction.

Results

X-ray Diffraction

Careful inspection of difference Fourier syntheses gave the positions of the hydrogen atoms at the benzene ring. They were included in the parameter set with an isotropic temperature factor. The reliability factors obtained were

$$R(F) = \Sigma \| F_0| - |F_c \| / \Sigma |F_0| = 0.094;$$

$$R_W(F) = \Sigma \sqrt{W} \| F_0| - |F_c \| / \Sigma \sqrt{W} |F_0| = 0.088.$$

Table 2. Positional and thermal parameters (with standard deviations) of the high temperature phase of anilinium bromide, X-ray (X) and neutron diffraction (N). The temperature factor is of the form $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$, the U_{ij} are given in pm². The occupation factor of H(N1) is 1, that of H(N2) is 0.5. For the numbering see Table 1.

Atom		x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	(X)	0.4768(1)	0.7500(—)	0.7500(—)	504(5)	681(6)	565(5)	0(—)	0(—)	15(7)
	(N)	0.4767(2)	0.7500(—)	0.7500(—)	529(21)	371(19)	623(21)	0(—)	0(—)	− 3(23)
N	(X)	0.4425(4)	0.7500(—)	0.2500(—)	442(34)	673(45)	825(59)	0(—)	0(—)	− 48(53)
	(N)	0.4424(2)	0.7500(—)	0.2500(—)	453(18)	406(21)	948(33)	0(—)	0(—)	− 2(27)
C(1)	(X)	0.3551(4)	0.7500(—)	0.2500(—)	395(35)	670(41)	392(34)	0(—)	0(—)	74(56)
	(N)	0.3559(2)	0.7500(—)	0.2500(—)	406(18)	353(16)	439(17)	0(—)	0(—)	− 9(19)
C(2)	(X)	0.3157(4)	0.5667(12)	0.1840(8)	547(35)	847(40)	452(33)	− 12(38)	− 32(27)	− 58(28)
	(N)	0.3159(2)	0.5661(5)	0.1832(4)	560(17)	427(17)	545(16)	− 61(15)	− 49(12)	− 70(12)
C(3)	(X)	0.2337(4)	0.5643(14)	0.1843(10)	579(39)	972(49)	556(38)	− 125(40)	− 112(30)	21(35)
	(N)	0.2336(2)	0.5660(6)	0.1839(5)	555(19)	671(22)	626(17)	− 176(18)	− 107(13)	14(15)
C(4)	(X)	0.1932(6)	0.7500(—)	0.2500(—)	504(48)	1180(76)	622(54)	0(—)	0(—)	235(76)
	(N)	0.1923(2)	0.7500(—)	0.2500(—)	413(23)	848(34)	640(24)	0(—)	0(—)	128(27)
H(2)	(X)	0.3458(31)	0.4393(81)	0.1265(71)	573(159)					
	(N)	0.3489(5)	0.4269(12)	0.1330(12)	928(52)	519(39)	1201(64)	18(43)	− 29(44)	− 267(39)
H(3)	(X)	0.2050(34)	0.4191(90)	0.1360(80)	682(180)					
	(N)	0.2015(5)	0.4246(16)	0.1336(15)	956(60)	951(68)	1303(75)	− 433(52)	− 248(48)	− 129(50)
H(4)	(X)	0.1369(38)	0.7500(—)	0.2500(—)	275(138)					
	(N)	0.1275(7)	0.7500(—)	0.2500(—)	583(61)	1577(123)	1204(90)	0(—)	0(—)	307(101)
H(N1)	(X)	—								
	(N)	0.4663(4)	0.8977(15)	0.2513(19)	737(57)	660(60)	1346(83)	− 137(39)	− 37(48)	− 51(80)
H(N2)	(X)	—								
	(N)	0.4599(6)	0.7496(29)	0.4113(23)	527(62)	1039(108)	990(107)	119(96)	− 197(54)	− 24(115)

Applying an extinction correction (23 reflections corrected experimentally, further 61 reflections corrected numerically according to Zachariasen [12]) lowered $R(F)$ to 0.056.

Finally the hydrogen atoms of the $-NH_3^{\oplus}$ group were located according to the neutron diffraction results but fixing the N-H distances to 85 pm. $R(F) = 0.047$ and $R_W(F) = 0.044$ were obtained. The concluding difference Fourier synthesis did not show any electron densities above 0.3 el/10⁶ pm³.

In Table 2 atomic coordinates, thermal parameters and standard deviations are given. The numbering scheme is shown in Table 1. The nitrogen atom N, the atoms C(1) and C(4) and the hydrogen atom H(4) are located on a twofold axis in special positions.

Neutron Diffraction

Refinement of the neutron data started with the positional and thermal parameters of the X-ray

Table 3a. Intramolecular bond distances and bond angles for the anilinium ion, $C_6H_5NH_3^{\oplus}$, phase I.

Bond lengths (pm)			Bond angles (degrees)		
	X	N		X	N
N-H(N1)		98.3(9)	C(1)-N-H(N1)		114.2(5)
N-H(N2)		114.6(15)	C(1)-N-H(N2)		104.9(5)
N-C(1)	147.0(9)	145.4(5)	H(N1)-N-H(N2)		83.6(11)
C(1)-C(2)	137.2(7)	138.2(4)	N-C(1)-C(2)	118.8(4)	119.1(2)
C(2)-C(3)	137.7(9)	138.4(5)	C(6)-C(1)-C(2)	122.3(7)	121.8(3)
C(3)-C(4)	139.3(9)	139.2(4)	C(1)-C(2)-C(3)	119.4(7)	119.0(3)
C(2)-H(2)	100.6(48)	106.9(8)	C(2)-C(3)-C(4)	118.7(7)	120.0(3)
C(3)-H(3)	105.9(55)	107.2(10)	C(3)-C(4)-C(5)	121.4(9)	120.2(4)
C(4)-H(4)	94.6(63)	108.9(13)	C(1)-C(2)-H(2)	120.8(30)	119.6(5)
			C(3)-C(2)-H(2)	119.7(30)	121.4(5)
			C(2)-C(3)-H(3)	117.7(31)	120.2(6)
			C(4)-C(3)-H(3)	123.6(31)	119.9(6)
			C(3)-C(4)-H(4)	119.3(4)	119.9(2)

Table 3b. Nearest neighbours' distances (N diffraction only) for the ring atoms. Ring I and ring II are compared, see Figure 2.

Molecule II	Molecule I	Distance/pm
C(5)	C(2)	362.6
C(5)	C(3)	356.7
C(5)	C(4)	375.6
C(5)	plane of the ring	348.1
C(6)	C(3)	361.7
C(6)	C(4)	354.2
H(5)	C(1)	299.8
H(5)	C(2)	310.6
H(5)	C(6)	309.1
H(5)	plane of the ring	288.1
H(6)	C(4)	292.3

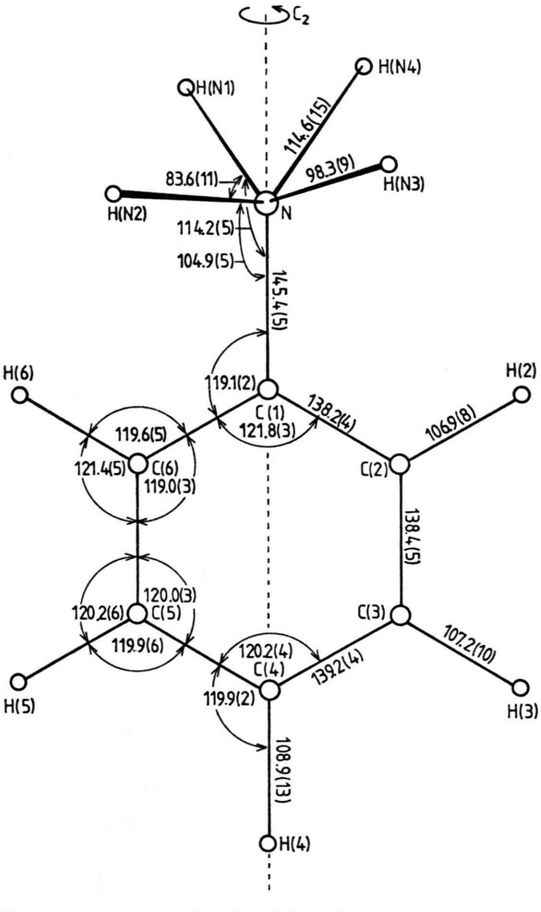


Fig. 1. Intramolecular bond lengths (pm) and angles (degrees) in the ion $C_6H_5NH_3^{\oplus}$ of anilinium bromide (I). Least squares data from neutron diffraction. The ion contains a twofold axis C_2. Standard deviations are given in parentheses. Fully occupied: H(N1), H(N3); half occupied: H(N2), H(N4).

data set including anisotropic temperature factors for the H atoms of the ring. A difference Fourier synthesis showed that the three hydrogens of the $-NH_3^{\oplus}$ group are split in four positions located between the atom N and its four next bromine neighbours. Within the limits of error the occupation number of H(N1) is 1 (found: 0.998(41)), for H(N2) it is 0.5 (found: 0.488(37)). Including an isotropic extinction correction with $c = 3.7 \cdot 10^{-6}$ [13], the refinement resulted in $R(F) = 0.052$ and $R_W(F) = 0.060$. The positional and thermal parameters are given in Table 2. Figure 1 shows the intramolecular distances and angles based on N-diffraction. The relevant intra- and intermolecular distances and angles are listed in Table 3*.

Discussion

The Packing of the Ions $C_6H_5NH_3^{\oplus}$ and $Br^{\ominus}$

The coarse crystal structure of $C_6H_5NH_3Br$(I) is simple. Bromide and anilinium ions are located on twofold axes ∥ [100] (each of the anilinium ions has a twofold axis through the atoms N-C(1) ··· C(4)-H(4)). The packing is described by layers parallel to (100) occupied alternately by $Br^{\ominus}$ and $C_6H_5NH_3^{\oplus}$ ions (Figure 2a). The planes of the bromide ions are at $x = 0$ and $x = 0.5$ with deviations of ± 39 pm. The centers of the C_6 rings of the cations lie in planes at $x = 0.25$ and $x = 0.75$ with $\Delta x = \pm$ 41.1 pm. Regarding only the centers of the anilinium ions, $C_6H_5NH_3^{\oplus}Br^{\ominus}$ crystallizes with a slightly distorted CsCl-type lattice. Within the anilinium ion layers the two next nearest neighbours with nearly equal x-coordinates of the ring center are orientated antiparallel to each other with respect to the direction N-C(1) ··· C(4)-H(4). The planes of the benzene rings include an angle of 44.2° and they are inclined by 22.1° against the plane (001) (Figs. 2b and 2c).

Neighbouring anilinium ions are bonded by van der Waals forces whereby twodimensional molecular planes ∥ (100) are formed, approximately 800 pm thick and positively charged on both surfaces. In Fig. 3 the shortest intermolecular distances within one anilinium layer are shown. Additional distances are listed in Table 3b. C(5) and H(5) approach the

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* The observed and calculated structure factors are listed in the thesis of Gerhard Fecher, Technische Hochschule Darmstadt, Fachbereich 7, Darmstadt (presumably 1982).

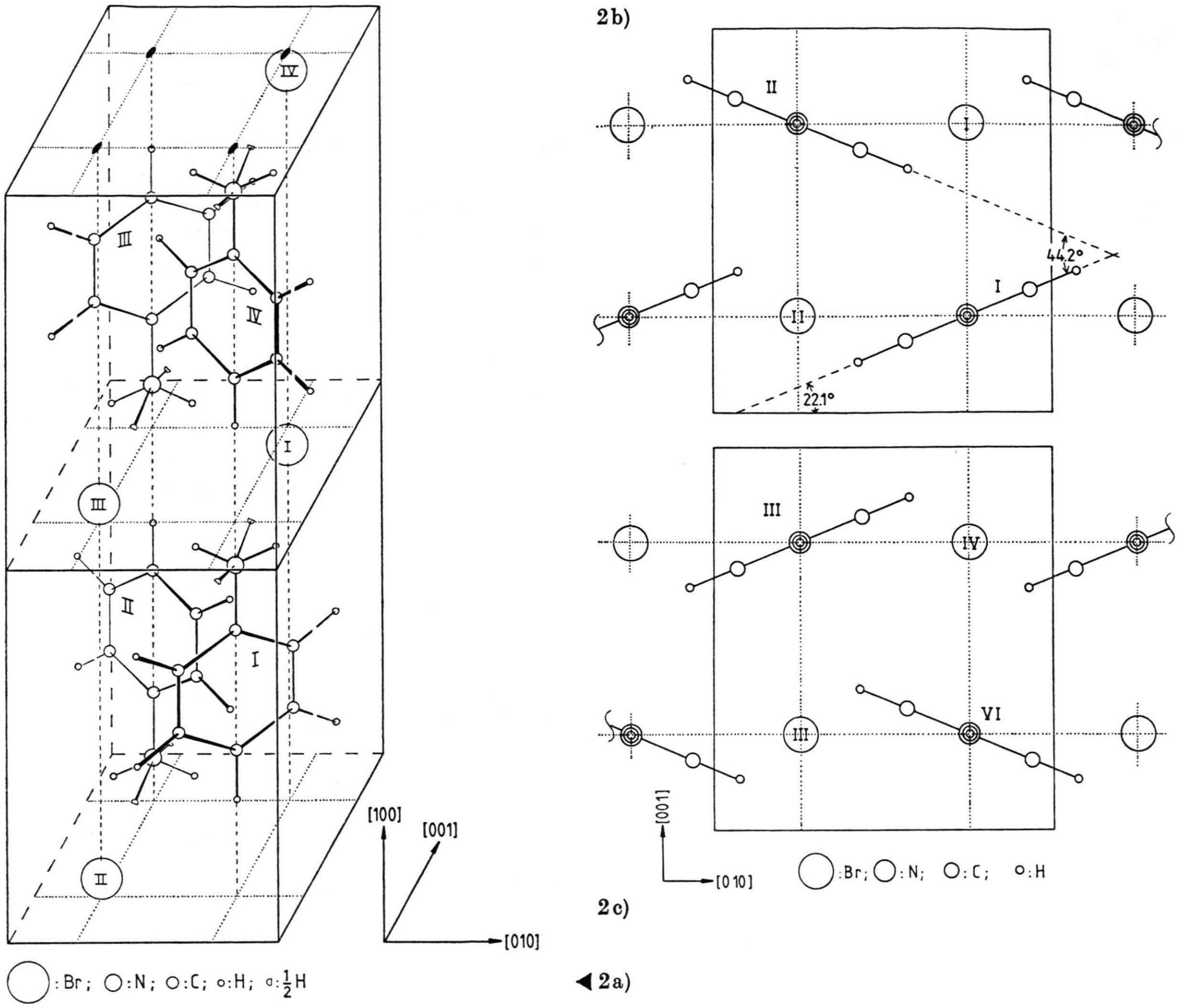

Fig. 2. a) Overall view of the unit cell. The positional parameters of the anilinium and bromide ion I are given in Table 2. The coordinates of the ions II, III, and IV are available by appropriate symmetry operations, see Table 1. — b) Projection of one half of the unit cell, $0 \leqq x \leqq 0.5$, onto the plane (100). — c) Projection of one half of the unit cell, $0.5 \leqq x \leqq 1$, onto the plane (100).

π-system of the next neighbouring ring closest. The distances found are in good agreement with literature values for molecular crystals. They are comparable with van der Waals distances assuming $r_{\mathrm{C,vdW}} = 180$ pm and $r_{\mathrm{H,vdW}} = 117$ pm for hydrocarbons [14].

The bonding between the alternating layers $(C_6H_5NH_3^{\oplus})_{\infty,\infty}$ and $(Br^{\ominus})_{\infty,\infty}$ is of electrostatic nature and enforced by hydrogen bonds. Disregarding the hydrogens, the mutual coordination number of nitrogen and bromine is four. The two shortest distances N ··· Br are located in the plane (001): $d(\mathrm{N} \cdots \mathrm{Br})$ (X) = 332.6 pm ($d(\mathrm{N} \cdots \mathrm{Br})$ (N) = 332.8 pm). These distances are noticeably shorter than the two other ones lying in the plane (010): $d(\mathrm{N} \cdots \mathrm{Br})$ (X) = 347.9 pm ($d(\mathrm{N} \cdots \mathrm{Br})$ (N) = 348.0 pm). Both pairs of N ··· Br distances are comparable with or smaller than the sum of the van der Waals radii: $(r_{\mathrm{N,vdW}} + r_{\mathrm{Br,vdW}}) = (155) + 185)$ pm = 340 pm (Bondi [15]); $(r_{\mathrm{N,vdW}} + r_{\mathrm{Br,vdW}}) = (165 + 195)$ pm = 360 pm (Pimentel [16]). The observed bond shortening indicates hydrogen bonding which causes in turn a compression of the unit cell in the direction [010] compared to [001].

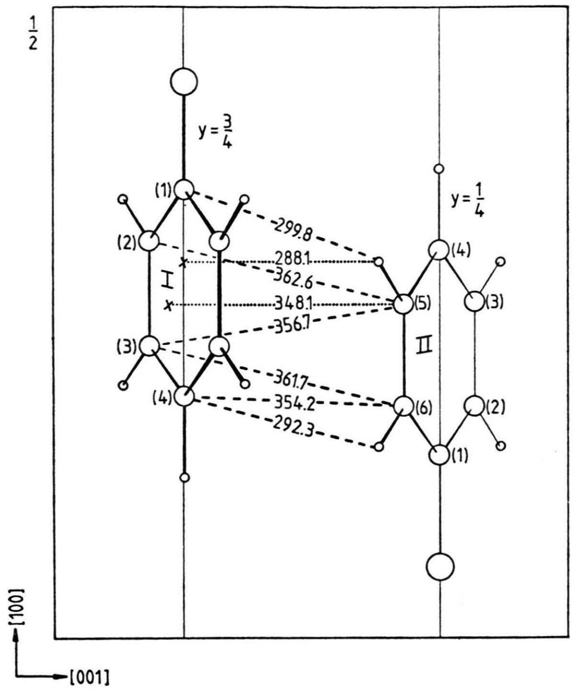

Fig. 3. Intermolecular distances (pm) of two next neighbouring anilinium ions.

The Ring System

Atomic positions, intramolecular bond distances, and bond angles of the anilinium ion from X-ray and neutron diffraction are in good agreement with the exception of C-H distances. As generally known (e.g. [17]), the neutron diffraction gives larger (and more reliable) values. The C_6-ring is a very slightly distorted regular hexagon; the intramolecular distances C-C are practically constant (138.2 to 139.2 pm) and within the range found for benzene derivatives. Domenicano et al. [18] compared the crystal structure data of eight substituted and unsubstituted anilinium ions and found for the average distance $\langle d(\mathrm{C(1)\text{-}N})\rangle = 146.2(2)$ pm as the "standard length of the bond connecting an $-NH_3^{\oplus}$ group to an aromatic C". For the corresponding angle $\langle \mathrm{C(6)\text{-}C(1)\text{-}C(2)}\rangle$ they give 121.7(2)°. The results for $C_6H_5NH_3^{\oplus}Br^{\ominus}$(I) are in good agreement with these mean values: $d(\mathrm{C(1)\text{-}N}) = 145.4(5)$ pm, $\sphericalangle\{\mathrm{C(6)\text{-}C(1)\text{-}C(2)}\} = 121.8(3)°$.

The thermal parameters derived from the X-ray respectively the neutron diffraction experiments are distinctly different (Table 2). The differences are especially pronounced for U_{22} because the X-ray data are restricted to $k = 5$ in the b direction. The tendencies are the same, however, in both sets. The discussion in the following refers to the neutron diffraction data. Nitta et al. [5] have discussed thermal oscillations of the ring around its twofold axis N-C(1) ··· C(4)-H(4). In Fig. 4 the ring system of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ is shown with its 50%-probability thermal motion ellipsoids of the individual atoms (ORTEP [19]). Besides the thermal vibrations around the twofold axis C_2 the vibrations around one or two axes perpendicular to C_2 are significant. A transformation of the thermal ellipsoids into the main axes system corroborates the visual impression one has by looking on Figure 4. The direction of greatest mean thermal amplitude of the atoms C(4) and H(4) is parallel to the plane of the C_6-ring. This is due to a fairly strong vibration of the ring around an axis perpendicular to it, an axis which intersects the plane of the ring near the atom C(1). C(1) shows an almost spherical thermal ellipsoid with relatively small amplitudes (Fig. 4) and Table 2)). The thermal ellipsoid of the nitrogen atom is quite anisotropic, however, with the maximum elongation parallel to [001] — in contrast to the C_6-ring.

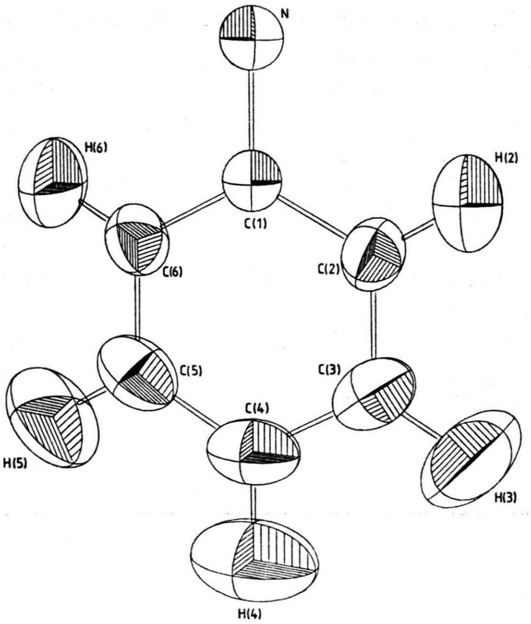

Fig. 4. 50% probability ellipsoids of the ring system C_6H_5N in anilinium bromide (I), $T = 343$ K, neutron diffraction results.

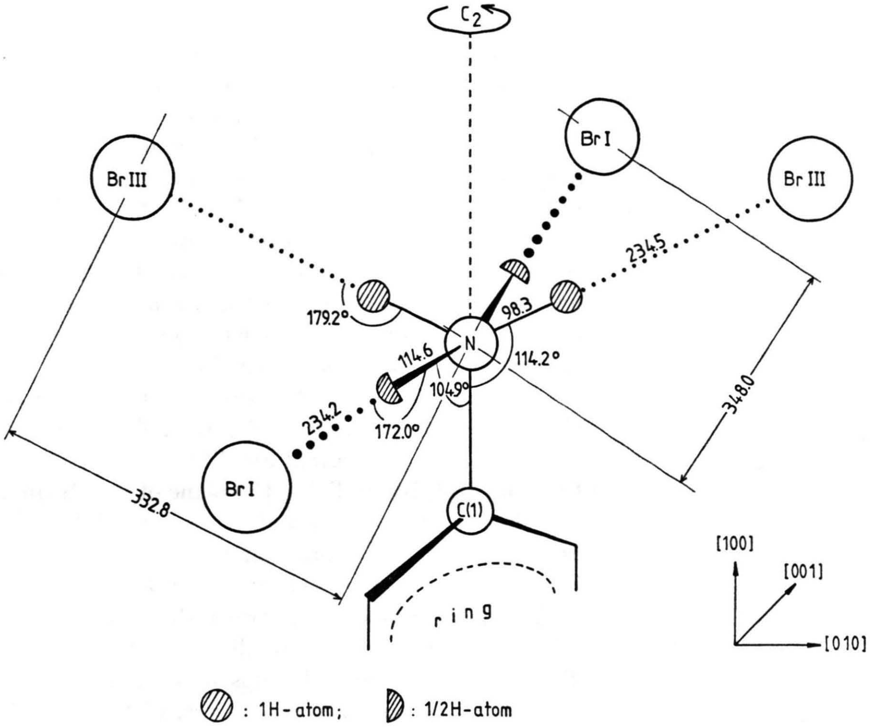

Fig. 5. Coordination of the nitrogen atom in anilinium bromide (I). The amino group of the anilinium ion I is given together with the bromide ions I and III (see Figure 2.). Neutron diffraction data. Atomic distances in pm.

The $-NH_3^{\oplus}$ group: Orientational Disorder and the Hydrogen Bond System

In Fig. 5 the coordination of the nitrogen atom to its hydrogens and the four neighbouring $Br^{\ominus}$ ions is given. The corresponding interatomic distances and angles are listed in Table 4. The three hydrogen atoms of the $-NH_3^{\oplus}$ group are distributed over four point positions, an arrangement which is in accordance with the symmetry of the crystal. For the distribution of the hydrogens on these four positions the pairwise occupation numbers 0.5 and 1.0 have been found. Assuming an approximate symmetry C_{3v} for the $-NH_3^{\oplus}$ group in the ion $C_6H_5NH_3^{\oplus}$ the twofold rotation axis N-C(1) ··· C(4)-H(4) of the anilinium ion is in contradiction to it. To realize the symmetry of the ion $C_6H_5NH_3^{\oplus}$ found from the X-ray diffraction experiment, Taguchi [1] assumed an orientational disorder for the $-NH_3^{\oplus}$ group in such a way that by statistical occupation of several point positions by the hydrogen atoms the twofold rotation axis is realized.

Table 4. Hydrogen bonding scheme (N diffraction): Interatomic distances (pm) and angles (degrees).

bridge	N-H	N···Br	H···Br
N-H(N1)···Br(III)	98.3(9)	332.8	234.5
N-H(N2)···Br(I)	114.6(15)	348.0	234.2
bridge	C(1)-N-H	C(1)-N···Br	N-H···Br
N-H(N1)···Br(III)	114.2(5)	114.1	179.2
N-H(N2)···Br(I)	104.9(5)	99.5	172.0

Taking the hydrogen bonds N—H ··· Br into account, four orientations of the $-NH_3^{\oplus}$ group with respect to the neighbouring ions $Br^{\ominus}$ are energetically favoured as shown in Figure 6. The orientations A_1 and A_2 have equal probability and they lead to two "strong" (dashed lines) and to one "weak" hydrogen bond (pointed line) in each case. "Weak" and "strong" hydrogen bonds correspond to N ··· Br distances of 348.0 and 332.8 pm respectively.

The orientations B_1 and B_2 are energetically less probable than A_1 and A_2 since only one hydrogen bond is short ("strong") and two hydrogen bonds are long ("weak") in these two positions. In each of the four orientations $A_1, \ldots, B_2$ a distortion of the group $-NH_3^{\oplus}$ has to be assumed in such a way

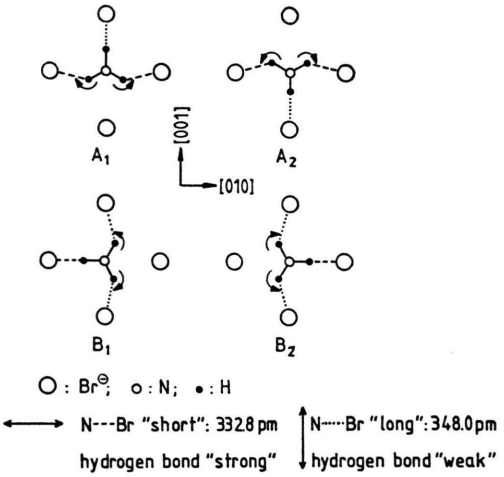

Fig. 6. Energetically favoured orientations of the -$NH_3^{\oplus}$ group.

that two of the hydrogen atoms are displaced towards the connecting line N ··· Br. This is marked in Fig. 6 by arrows. From combination of these distorted four orientations $A_1, \ldots, B_2$ an overall structure results, in which the three hydrogen atoms of the group $-NH_3^{\oplus}$ are distributed over four averaged positions. This "smearing out" of hydrogen atoms within the plane (100) should be indicated by high temperature factors of the $-NH_3^{\oplus}$ hydrogen atoms. The occupation factors for the four resulting positions reveal the contribution of each of the four orientations $A_1, \ldots, B_2$ to the averaged structure. An equipartition leads to the occupation factor 0.75 for each of the four positions. Since the interaction via hydrogen bonds is stronger in the positions A_1 and A_2 these orientations should have more weight. Indeed, the occupation factor 1.0 results for the H-positions on the short distances N ··· Br and the two other positions are only half occupied. The symmetry requirements are still fulfilled. This in turn means that A_1 and A_2 are realized, each with the probability 0.5 (see Figure 6). B_1 and B_2 are not observed in the phase $C_6H_5NH_3Br(I)$. It is interesting to note that during the phase transition $C_6H_5NH_3Br(I) \rightarrow C_6H_5NH_3Br(II)$ at $T = 296.9$ K the equipartition between A_1 and A_2 orientation is lost and one of these two possibilities is preferred. The resulting ordering is observed at temperatures far below $T_{I,II}$ (see the following paper). Overlap of the positions A_1 and A_2 in phase I creates a high thermal parameter of the hydrogen atom H(N1) in the direction [001].

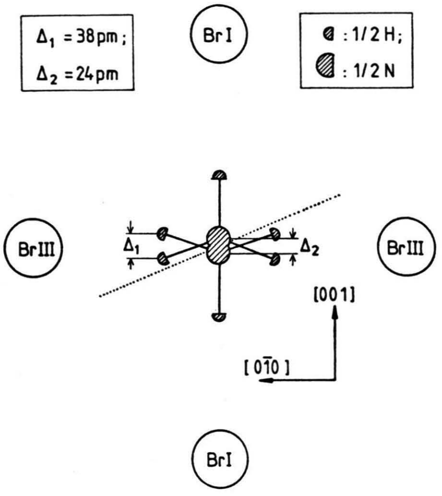

Fig. 7. Split-atom model for the -$NH_3^{\oplus}$ group in $C_6H_5NH_3^{\oplus}Br^{\ominus}(I)$. The pointed line represents the averaged projection of the ring C_6H_5 on the plane (100).

The averaged configuration of the nitrogen atoms shows two peculiarities:

a) The mean thermal amplitude of N is highest in the direction [001] (31 pm compared to 21 pm and 20 pm parallel to [100] and [010] respectively).

b) The bond lengths 114.6 pm (N—H(N1)) and 98.3 pm (N—H(N2)) differ remarkably from each other and they are considerably different from the mean, 102.6 pm, which is evaluated from 90 different values taken out of 25 papers published in Acta Cryst. 1977—1980 (see also [17], p. 226, [20], [21]).

The bond angles C(1)-N-H(N1) = 114.2° and C(1)-N-H(N2) = 104.9° deviate by +5° and −5° respectively from the ideal tetrahedral angle (109.5°). The hydrogen bond N-H(N1) ··· Br is practically linear whereas the bond N-H(N2) ··· Br deviates by 8° from linearity. This has no influence on the bond distances H(N1) ··· Br (234.2 pm) and H(N2) ··· Br (234.5 pm) which are appreciably shorter than the sum of the van der Waals radii $(r_{H,vdW} + r_{Br,vdW}) = (100 + 185)$ pm $= 285$ pm ([22], [15]). The geometrical criterion for the existance of a hydrogen bond ([23], [20]) is fulfilled. By the hydrogen bonds directed approximately in the directions [001] and [010] a corrugated net of hydrogen bonds parallel to the plane (100) is formed.

The van der Waals bonds between the ions $C_6H_5NH_3^{\oplus}$ connect the hydrogen bond network in the direction [100]. A perfect cleavage parallel to (001) is observed [1]. This is in accordance with the fact that weak hydrogen bonds are found in the direction [001].

The Split-Atom Model

The unusually large distance N-H(N2) suggests the assumption of distinct point positions of nitrogen for the two orientations A_1 and A_2 for each amino group, respectively. These positions are slightly shifted away from the twofold axis in the direction of H(N2) and H(N4) respectively and the attributed occupation numbers are 0.5. In the average structure a mean point position results, which is occupied by one nitrogen vibrating strongly in the direction [001], however. It is obvious to extend this split-atom model to the point position of H(N1), too. The position of H(N2) and H(N4) can be assumed to be fixed since it is the only point position of all atoms involved in the model which is not influenced by the overlap.

Firstly, we assume three equal distances N—H (d(N-H) = 103 pm) for one orientation. Secondly we tolerate displacements only in the direction [001] for the atoms N, H(N1), and H(N3) — these atoms contribute to the overlap density. The displacements of ± 12 pm for nitrogen and ± 19 pm for hydrogen are found with respect to the mean atomic positions. They coincide with the mean thermal vibrations found for the direction [001]: 30.8 pm for N, 36.8 pm for H(N1). In Fig. 7 the split-atom model for the $—NH_3^{\oplus}$ group is sketched in projection along [100].

A consequence of different nitrogen positions in A_1 and A_2 is the loss of a static twofold axis of the molecular fragment C_6H_5N; this twofold axis is now a dynamical one. Therefore, it is appropriate to assume for the whole anilinium ion two slightly different orientations. Consider the anilinium ion I (Fig. 2) with the center of gravity at $x = 0.3041$, $y = 0.75$, $z = 0.25$. In a first approximation it is fixed and the intramolecular twofold axis of the system C_6H_5N is rigid. Then this axis determined by N-C(1) ··· C(4)-H(4) has two orientations within the disorder model which are inclined by $\pm 3°$ with respect to the crystallographic twofold axis.

The displacements of the individual atoms of the group C_6H_5N with respect to their mean positions given in Table 2 are markedly smaller than half of the mean thermal amplitudes found for the direction [001]. This and the observed increase of the thermal amplitudes U_{ii} from C(1) over C(4) to H(4) supports the proposed split-atom model. Furthermore, the individual orientations of the model lower the deviations of the $—NH_3^{\oplus}$ group symmetry from that of an ideal tetrahedron. Additionally the distances N ··· Br are almost equal in this model and the system tends towards equally strong, nonlinear hydrogen bonds.

The split-atom model offers an explanation for the dominant mean vibrational amplitudes of C(4) and H(4) which are directed parallel to the plane of the ring. In Fig. 7 one can see that in both orientations the ring is practically in an eclipsed position to one H atom of the $—NH_3^{\oplus}$ group. Such an eclipsed configuration is known from several crystal structure studies of anilinium compounds [18], [24]. The resulting eclipse-angle C—C—N is up to 2° larger than the staggered one. This corresponds to a small in plane bending of the C—N-bond. During the reorientations of the $—NH_3^{\oplus}$ group in anilinium bromide (I) a small motion of the ring parallel to its plane is expected which goes in the opposite direction, and this can be seen from the thermal parameters. The crystal structure determination of the low temperature phase $C_6H_5NH_3^{\oplus}Br^{\ominus}$(II) supports this model (see the following paper).

The Reorientation

The orientational disorder of the high temperature phase $C_6H_5NH_3^{\oplus}Br^{\ominus}$(I) is by its nature dynamical. The ^{79}Br-NQR experiments [3] and the ^{1}H-NMR spin lattice relaxation time measurements [4] support the model of a fast reorientational motion of the $—NH_3^{\oplus}$ group with a correlation time $\tau \approx 10^{-12}$ s. Recent inelastic neutron scattering experiments [25] reveal a hindered rotation of the $—NH_3^{\oplus}$ group with residence times of about 10^{-12} s.

The split-atom model proposed here extends the picture assumed about the reorientation in $C_6H_5NH_3Br$(I) until now. Not only the $—NH_3^{\oplus}$ group but the whole ion $C_6H_5NH_3^{\oplus}$ is reorientating. During the switch over of the anilinium ion from the position A_1 to the position A_2 and vice versa the $—NH_3^{\oplus}$ group rotates around the twofold axis of the molecule by 60° and simultaneously jumps into a new position, shifted slightly along the z-axis. Thereby, the axis N-C(1) ··· C(4)-H(4) is tilted over in its new position. A tunneling process for the hydrogen position at the half occupied point position is not excluded in this model.

Reorientational disorder not restricted to the $-NH_3^{\oplus}$ group in solid systems $R\text{-}NH_3^{\oplus}X^{\ominus}$ is known and was studied several times. An extensively investigated family of compounds with an order-disorder phase transition involving the whole ion $R\text{-}NH_3^{\oplus}$ are the layered solids

$$(C_nH_{2n+1}NH_3)_2[XCl_4]\,,\ X = Cu, Cd, Mn, Fe.$$

For bis(ethylammonium)tetrachloromanganate(II) the transition high (β)→low (γ) occurs at 225 K [26]. In the β-phase the ion $CH_3CH_2NH_3^{\oplus}$ occupies two positions, each with the probability 0.5 [27], [28]. In the γ-phase only one of these positions is (fully) occupied. As for the anilinium bromide the disorder in the β-phase is mainly given by two definitely different positions of the $-NH_3^{\oplus}$ group whereas the point positions of the rest R ($R = CH_3CH_2-$) differ only slightly for the two situations. For bis(n-butylammonium)tetrachloromanganate(II) the disorder of $R\text{-}NH_3^{\oplus}$ is quite noticeable in two different positions of R (besides $-NH_3^{\oplus}$) [29].

Considering size and crystal structure, there is a close relation of anilinium bromide with the n-propylammonium halides, which have been studied by King and Lipscomb [30] by X-ray diffraction. The high temperature phases of $n\text{-}C_3H_7NH_3^{\oplus}Y^{\ominus}$, $Y = Cl, Br, I$ are isomorphous and show most probably dynamical disorder of the cations $n\text{-}C_3H_7NH_3^{\oplus}$. As in $C_6H_5NH_3Br$(I), planes of cations are present in which the direction of the dipole is perpendicular to the planes and alternating within the planes. In the low temperature phases the cations are probably fixed to one position.

Close at hand is a comparison of the anilinium halides $C_6H_5NH_3^{\oplus}Y^{\ominus}$, $Y = Cl, Br, I$. No phase transition is observed for $C_6H_5NH_3Cl$ [31] and the packing of the cations is different from that in the bromide and iodide in principle: The dipoles $C_6H_5NH_3^{\oplus}$ are colinear within one plane [32]. A phase transition at 241 K is observed for $C_6H_5NH_3^{\oplus}I^{\ominus}$, which is very similar to the transition in the bromide as shown by ^{127}I-NQR studies ([33], part II of this series). Isomorphism of the high temperature phases and low temperature phases of the bromide and iodide, respectively, is observed. The crystal structures of $C_6H_5NH_3^{\oplus}I^{\ominus}$(I, II) have been studied by neutron diffraction and the ^{127}I-NQR was investigated in detail [34].

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