# On the Order-Disorder Phase Transformation of Anilinium Halides.

## IV. The Crystal Structure of the Low Temperature Phase of Anilinium Bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$. A Neutron Diffraction Study

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The crystal structure of the low temperature phase of anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, was studied by neutron diffraction at $T = 100$ K. The refinement supports an ordered structure. The structures of the low and high temperature phases are compared and the mechanism of the phase transformation is discussed.

### Introduction

The mechanism of the ferroelastic phase transformation $C_6H_5NH_3^{\oplus}Br^{\ominus}(I) \rightleftharpoons C_6H_5NH_3^{\oplus}Br^{\ominus}(II)$ is still not thoroughly understood. Following the X-ray and dilatometric work of Taguchi [1], Nitta et al. [2], and Suga [3], Iwai [4] studied the domain walls and their motion via microscopic observation. Stimulated by the publications of the Osaka group [1–4], Pies and Weiss [5] used $^{79}$Br-NQR spectroscopy to observe the phase transformation of anilinium bromide and its deuterated forms. Terauchi et al. [6] discussed this phase transition on the basis of diffuse X-ray scattering experiments. They suggested a coupling of three mechanisms a) orientational order-disorder of the group $-NH_3^{\oplus}$, b) elastic shear strain associated with a soft acoustical phonon mode, and c) internal displacement of ions connected with a soft optical phonon mode. Temperature dependent Raman scattering studies by Hattori et al. [7], however, do not confirm the presence of a soft optical mode in the range $0 \leqq \tilde{\nu}/\mathrm{cm}^{-1} \leqq 200$. Furthermore, Sawada et al. [8] showed by ultrasonic absorption studies that the phase transformation in $C_6H_5NH_3^{\oplus}Br^{\ominus}$ at 296.2 K ([5]: 296.9 K) is accompanied by a softening of the eleastic constant $c_{55}$ in the high temperature phase. They concluded that the coupling between the "order-disorder system" and the "acoustic phonon system" is weak, however.

To clarify the microscopic mechanism of the ferroelastic transformation of anilinium bromide a reliable knowledge of the geometry of the $-NH_3^{\oplus}$ group in the lattice is needed. In the foregoing paper [9] the crystal structure of the orthorhombic high temperature phase I of anilinium bromide is described, including the positional parameters of the hydrogen atoms and the disorder of the whole cation $C_6H_5NH_3^{\oplus}$. There is a very recent determination of the monoclinic structure of the low temperature phase II by Sakai and Terauchi [10]. These authors performed an X-ray analysis at 163 K, from which no direct information on the $-NH_3^{\oplus}$ hydrogen positions is available. Here we report a neutron diffraction study of the monoclinic $C_6H_5NH_3^{\oplus}Br^{\ominus}(II)$, done at 100 K, which leads to a complete description of the crystal structure of phase II.

### Experiments and Results

The preparation of anilinium bromide and the growth of single crystals were described in [9]. In the monoclinic low temperature phase II the crystals are intrinsically twinned. The ferroelastic domains have the ($\boldsymbol{b}$, $\boldsymbol{c}$)-twinning plane in common [1]. In Fig. 1 the ($\boldsymbol{a}$, $\boldsymbol{c}$)-plane of the crystal is sketched. The angle which is included by the ($\boldsymbol{a}$, $\boldsymbol{b}$)-planes of the two domain orientations is $2\Delta\beta = 2(\beta - 90°)$. Related to the two possible domain

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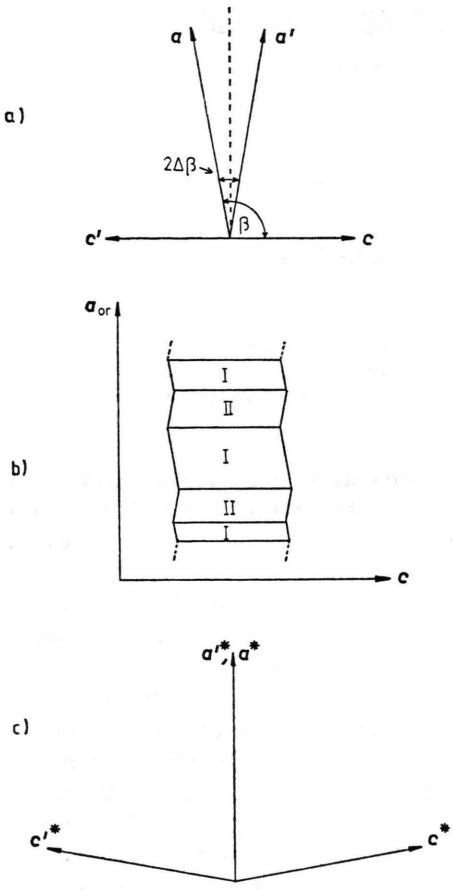


Fig. 1. Orientation of the twin domains perpendicular to $\boldsymbol{b}$ and $\boldsymbol{b}^*$: a) axes $\boldsymbol{a}$ and $\boldsymbol{c}$ of the two domain orientations in real space. b) planes ($\boldsymbol{a}$, $\boldsymbol{c}$) of the domains with respect to the orthorhombic axes $\boldsymbol{a}_{or}$ and $\boldsymbol{c}$. c) axes $\boldsymbol{a}^*$ and $\boldsymbol{c}^*$ of the two domain orientations in reciprocal space.

orientations 1 and 2 in the diffraction pattern, there appears a pair of reflections: $(hkl)_1$ and $(h\bar{k}\bar{l})_2$ and, rotated by 180° around $\boldsymbol{a}^*$ another pair: $(h\bar{k}\bar{l})_1$ and $(hkl)_2$. The corresponding intensities are weighted due to the volume parts of the two domain orientations. They have to be added:

$$I(hkl)_{\text{total}} = I(hkl)_1 + I(hkl)_2\,, \quad \text{and}$$
$$I(h\bar{k}\bar{l})_{\text{total}} = I(h\bar{k}\bar{l})_1 + I(h\bar{k}\bar{l})_2\,.$$

$I(hkl)_{\text{total}}$ means the intensity of the reflection $(hkl)$ related to the whole volume of the sample crystal: $V_{\text{total}} = V_1 + V_2$. The reflections $(hk0)$ are not split, and their intensities give the reflexion power of the whole crystal.

The monoclinic angle $\beta$ increases with decreasing temperature continuously and approaches a "saturation" value asymptotically at $T \cong 160$ K · ($\beta_{T=160\text{K}} = 91.37°$ [1]).

Neutron diffraction experiments were performed at $T = 100$ K, far below the temperature of the phase transition. Therefore it is save to assume that $\beta$ and consequently the splitting of the reflections have reached their maximum values. To separate the intensities of the split reflections, we used the $\varphi$-scan technique and a special orientation of the crystal, where [010] was parallel to the $\varphi$-rotation axis of the goniometer. $I(hkl)_1$ and $I(h\bar{k}\bar{l})_2$ of both domain orientations were registered together in one scan. The intensities of the unsplit reflections $(hk0)$ were measured by the ordinary $\omega$-scan technique. For the measurement a special orientation matrix was selected. It is based on a middled "orthorhombic" lattice and centered on the geometrical mean of the pairs of reflections $(hkl)_1$ and $(h\bar{k}\bar{l})_2$. Reflections of the type $(0kl)$ show maximum splitting and allow a simple and accurate determination of the monoclinic angle: $\beta_{T=100\text{K}} = 91.32(2)°$. The space group $C_{2h}^5$-$P2_1/a$ proposed by Taguchi [1] is confirmed. The experimental details and lattice constants are given in Table 1.

From pairs of clearly split reflections ($(hkl)_1$, $(h\bar{k}\bar{l})_2$) and ($(h\bar{k}\bar{l})_1$, $(hkl)_2$), respectively, the ratio of the volume parts of the two domain orientations $V_1/V_2 = 1.14 \pm 0.05$ was found for the crystal used. The intensity of non-resolved reflection pairs was distributed according to this ratio. After proper correction of Lorentz factor and absorption a set of 527 reflections (including 50 with $F \approx 0$) was used for the Fourier syntheses and the least-squares refinement. For the structure analysis we used scattering lengths from Bacon (times $10^{15}$ m$^{-1}$): $b_C = 6.65$, $b_N = 9.4$, $b_{Br} = 6.8$, $b_H = -3.74$ [11].

The refinement started with the positional parameters of the high temperature phase I. A difference Fourier synthesis showed definitely only one orientation for the $-NH_3^{\oplus}$ group. Based on the standard deviations $\sigma(F)$, a weighting scheme was employed: $W = 1/[\sigma^2(F) + 0.0004F^2]$. Weak extinction effects were taken into account through $F_c^{\text{corr}} = F_c(1 - 0.0001\,x F_c^2/\sin\vartheta)$, with $x$ converging to 0.521 (17). The final reliability factors are $R(F) = 0.040$ and $R_W(F) = 0.031$. For the calculations the program SHELX-76 [12] was used. The relative atomic coordinates and thermal parameters for $C_6H_5NH_3^{\oplus}Br^{\ominus}$(II) are given in Table 2. It is seen

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

**Experimental conditions**

| | |
|---|---|
| crystal habitus and size | prism, $(2.7 \cdot 4.3 \cdot 1.6)$ mm³ |
| characteristic | twin structure |
| diffractometer | 4-circle, P32/FR2, Kernforschungszentrum Karlsruhe |
| wavelength, $\lambda$/pm | 102.01 |
| monochromator | Cu (311) |
| temperature, T/K | 100(2), Displex closed cycle refrigerator |
| linear absorption coefficient, $\mu$/m$^{-1}$ | 176 (exp) |
| method of measurement | pairs of split reflections measured in one scan by means of an "orthorhombic" orientation matrix |
| scan ($\varphi$-axis ∥ [010]) | $\varphi$ for $(hkl)$ reflections, $l \neq 0$<br>$\omega$ for $(hk0)$ reflections |
| Lorentz-factor, $L_\varphi^{-1}$ | $\sin 2\vartheta \cdot \cos \chi$ |
| $L_\omega^{-1}$ | $\sin 2\vartheta$ |
| $(\sin \vartheta/\lambda)_{max}$/pm$^{-1}$ | 0.0045 |
| number of measured refl. | 607 |
| symmetry independent refl. | 527 |
| reflections considered | 527 (incl. 50 with $F = 0$) |
| free parameters | 131 |
| $R(F) = \Sigma \lVert F_0 \rvert - \lvert F_c \rVert / \Sigma \lvert F_0 \rvert$ | 0.040 |
| $R_W(F) = \Sigma \sqrt{W} \lVert F_0 \rvert - \lvert F_c \rVert / \Sigma \sqrt{W} \lvert F_0 \rvert$ | 0.031 |

**Crystal data**

| | | this paper 100 K | Taguchi [1] 163 K | Sakai, Terauchi [10] 163 K |
|---|---|---|---|---|
| lattice constants | $a$/pm | 1676.0(10) | 1672.5(60) | 1673.8(7) |
| | $b$/pm | 600.5(5) | 595.0(30) | 598.1(5) |
| | $c$/pm | 680.9(5) | 681.0(30) | 675.8(3) |
| | $\beta$/deg | 91.32(2) | 91.37 | 91.34(1) |
| space group | | | $C_{2h}^5$-$P2_1/a$ | |
| number of formula units/unit cell | | | 4 | |
| $\varrho_{calc}$/(Mg · m$^{-3}$) | | 1.687 | 1.706 | 1.709 |

**Point positions**

all atoms on general positions 4e: $x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, z.$

**Numbering of atoms in the anilinium cation**

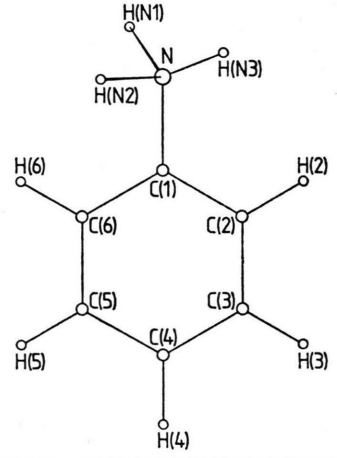


Table 2. Positional and thermal parameters (with standard deviations) of the low temperature phase of anilinium bromide, resulting from neutron diffraction. The isotropic temperature factors are of the form $T = \exp(-8\pi^2 U (\sin \vartheta/\lambda)^2)$, and the anisotropic ones of the form $T = \exp(-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$. $U$ and $U_{ij}$ are given in pm². For numbering see Table 1.

| Atom | $x/a$ | $y/b$ | $z/c$ | $U$ or $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Br | 0.4747(1) | 0.7504(3) | 0.7736(3) | 278(8) | | | | | |
| N | 0.4435(1) | 0.7517(5) | 0.2900(3) | 264(7) | | | | | |
| C(1) | 0.3562(1) | 0.7535(4) | 0.2681(3) | 223(8) | | | | | |
| C(2) | 0.3173(2) | 0.5688(6) | 0.1913(3) | 293(26) | 285(24) | 246(16) | − 38(12) | 11(13) | − 17(18) |
| C(3) | 0.2346(2) | 0.5728(7) | 0.1760(4) | 179(28) | 444(30) | 353(17) | 11(18) | − 35(14) | − 50(22) |
| C(4) | 0.1927(2) | 0.7594(6) | 0.2362(4) | 233(25) | 498(25) | 328(15) | 96(16) | 15(16) | 42(31) |
| C(5) | 0.2335(2) | 0.9450(7) | 0.3123(4) | 339(32) | 403(30) | 342(17) | 5(18) | 89(15) | 139(23) |
| C(6) | 0.3164(2) | 0.9422(6) | 0.3285(4) | 312(28) | 283(24) | 277(16) | − 35(13) | 72(15) | 68(17) |
| H(2) | 0.3518(4) | 0.4258(12) | 0.1438(8) | 569(42) | 300(40) | 625(37) | − 117(30) | − 58(32) | 39(35) |
| H(3) | 0.2020(4) | 0.4294(13) | 0.1180(9) | 457(44) | 517(48) | 751(41) | 66(34) | 108(32) | 120(39) |
| H(4) | 0.1282(5) | 0.7614(14) | 0.2224(9) | 324(46) | 1005(50) | 704(39) | 129(37) | 33(35) | − 44(51) |
| H(5) | 0.2008(4) | 0.0923(14) | 0.3563(10) | 523(47) | 594(50) | 797(43) | − 62(38) | 130(34) | 279(42) |
| H(6) | 0.3480(4) | 0.0819(12) | 0.3878(9) | 482(41) | 430(44) | 657(39) | − 172(33) | 23(31) | − 15(37) |
| H(N1) | 0.4697(3) | 0.8926(11) | 0.2332(8) | 400(35) | 505(39) | 618(34) | 74(29) | − 12(28) | − 108(31) |
| H(N2) | 0.4605(3) | 0.7492(9) | 0.4381(8) | 401(31) | 543(31) | 447(34) | − 56(27) | − 99(26) | 14(32) |
| H(N3) | 0.4679(3) | 0.6077(11) | 0.2307(8) | 336(34) | 452(37) | 700(36) | − 194(29) | 38(28) | 56(29) |

Table 3. Intramolecular bond lengths and angles for the anilinium ion, $C_6H_5NH_3^{\oplus}$, of anilinium bromide, phase II.

| Bond lengths (pm) | | Bond angles (degrees) | |
|---|---|---|---|
| N-H(N1) | 103.2(9) | H(N2)-N-H(N3) | 105.3(4) |
| N-H(N2) | 104.2(7) | H(N3)-N-H(N1) | 111.2(4) |
| N-H(N3) | 104.2(8) | N-C(1)-C(2) | 119.5(3) |
| N-C(1) | 146.8(3) | N-C(1)-C(6) | 117.6(3) |
| C(1)-C(2) | 138.3(4) | C(6)-C(1)-C(2) | 122.8(3) |
| C(2)-C(3) | 138.8(4) | C(1)-C(2)-C(3) | 118.4(4) |
| C(3)-C(4) | 138.9(4) | C(2)-C(3)-C(4) | 120.1(4) |
| C(4)-C(5) | 140.0(5) | C(3)-C(4)-C(5) | 120.4(3) |
| C(5)-C(6) | 139.1(4) | C(4)-C(5)-C(6) | 119.8(3) |
| C(6)-C(1) | 138.3(4) | C(5)-C(6)-C(1) | 118.3(3) |
| C(2)-H(2) | 108.8(12) | H(2)-C(2)-C(1) | 119.7(4) |
| C(3)-H(3) | 108.9(12) | H(2)-C(2)-C(3) | 121.8(4) |
| C(4)-H(4) | 108.3(11) | H(3)-C(3)-C(2) | 120.3(5) |
| C(5)-H(5) | 108.6(12) | H(3)-C(3)-C(4) | 119.5(5) |
| C(6)-H(6) | 106.6(12) | H(4)-C(4)-C(3) | 119.6(6) |
| Bond angles (degrees) | | H(4)-C(4)-C(5) | 120.1(6) |
| C(1)-N-H(N1) | 112.8(4) | H(5)-C(5)-C(4) | 120.4(5) |
| C(1)-N-H(N2) | 110.3(3) | H(5)-C(5)-C(6) | 119.8(5) |
| C(1)-N-H(N3) | 111.4(4) | H(6)-C(6)-C(5) | 120.5(4) |
| H(N1)-N-H(N2) | 105.4(4) | H(6)-C(6)-C(1) | 121.2(5) |

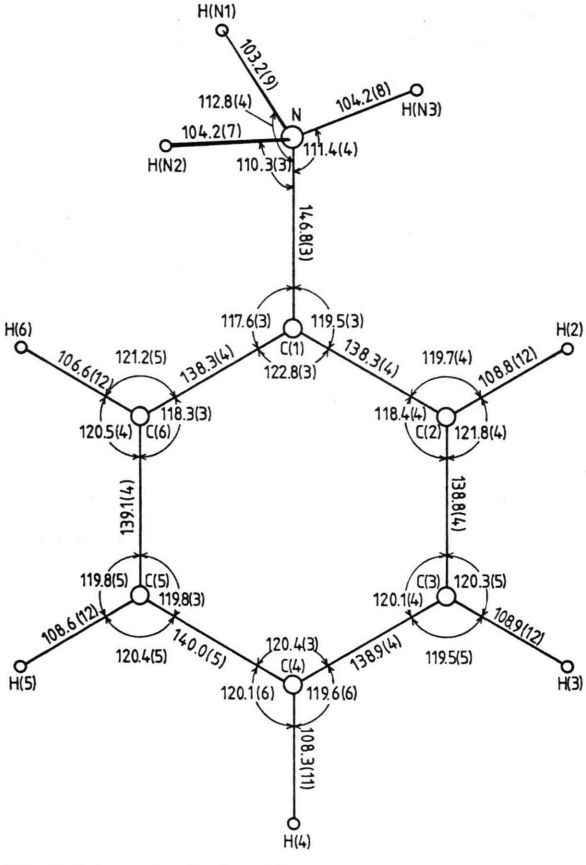


Fig. 2. Intramolecular bond lengths (in pm) and bond angles (in degrees) for the anilinium ion $C_6H_5NH_3^{\oplus}$, in phase II of $C_6H_5NH_3^{\oplus}Br^{\ominus}$.

Table 4. Comparison of intermolecular distances, see Figure 3.

| Molecule II | Molecule I | Distance/pm |
|---|---|---|
| C(5) | C(1) | 374.9 |
| C(5) | C(2) | 358.2 |
| C(5) | C(3) | 359.6 |
| C(5) | C(4) | 379.1 |
| C(6) | C(3) | 358.6 |
| C(6) | C(4) | 352.9 |
| H(5) | C(1) | 291.6 |
| H(5) | C(2) | 310.5 |
| H(5) | C(6) | 302.2 |
| H(6) | C(4) | 287.0 |

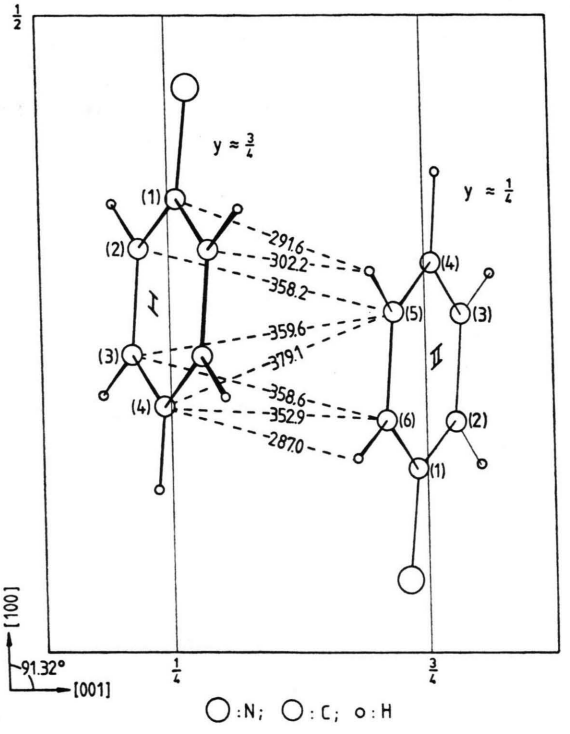


Fig. 3. Intermolecular distances (in pm) between two next neighboured anilinium ions in $C_6H_5NH_3^{\oplus}Br^{\ominus}$(II).

that three atoms, Br, N, and C(1), have been refined assuming isotropic thermal motion only. This was justified by test calculations. Table 3 and Fig. 2 show the intramolecular bond lengths and bond angles. The nearest neighbours distances are given in Table 4 and Figure 3*.

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

## Discussion

The crystal structures of both phases of anilinium bromide are very similar to each other. In Fig. 4 the projection of the unit cell of the low temperature phase (II) along [010] is shown. The prominent distinction to the high temperature phase (I) is the shear of the angle $\beta$ from 90° in phase I to 91.32° ($T = 100$ K) in phase II, which is accompanied by a tilt of the molecular axis N-C(1) ··· C(4)-H(4). This tilt is in antiphase to the shear * of the angle $\beta$. The most important difference between the crystal structures of the two phases lies, however, in the orientation of the $-NH_3^{\oplus}$ group. Whereas in phase I the $-NH_3^{\oplus}$ group is disordered with two orientations of equal weight, in phase II the $-NH_3^{\oplus}$ group is fixed to one position. This ordering effect is also important for the dynamics of the whole ion $C_6H_5NH_3^{\oplus}$.

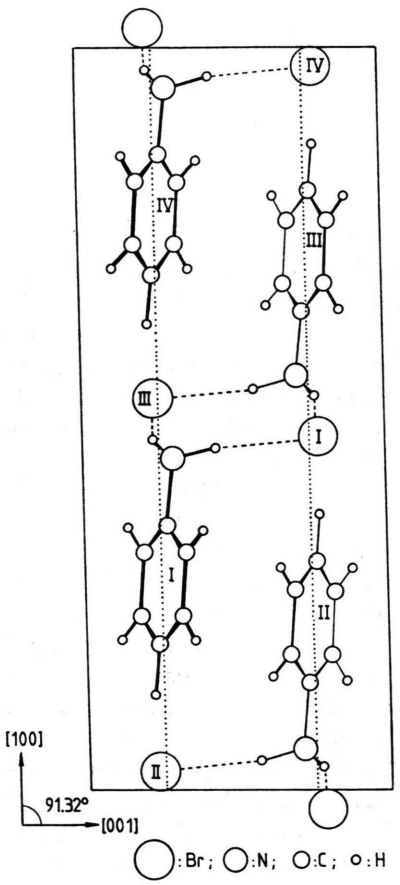


Fig. 4. Projection of the unit cell of anilinium bromide, phase II, along [010]. The numbering of $Br^{\ominus}$ and $C_6H_5NH_3^{\oplus}$ (I...IV) is according to the point positions (4e), see Table 1. --- hydrogen bonds; ··· projections of the vectors $\boldsymbol{r}$, $\boldsymbol{r}'$, $\boldsymbol{r}''$, and $\boldsymbol{r}'''$, respectively (see text).

* Terauchi et al. [6] supposed a tilt of the axis N-C(1)···C(4)-H(4) in phase with the shear of $\beta$. This supposition has been corrected [10].

### *The Anilinium Ion, $C_6H_5NH_3^{\oplus}$, in Phase II*

Intramolecular bond distances and bond angles of the ring system are "normal" and comparable with those of phase I. The ring system is planar and the intramolecular axis C(1) ··· C(4)-H(4) is in good approximation a twofold one. The bond distance C(1)-N = 146.8 pm and the angle $\alpha = \sphericalangle\{C(2)\text{-}C(1)\text{-}C(6)\} = 122.8°$ are in good agreement with literature data. "Mean values" for the C(1)-N distance (146.2 pm) and for the angle $\alpha$(121.7°) of anilinium ions in different compounds have been given by Domenicano et al. [13] and some more data are listed in Table 5.

A deformation of the $C_6$-ring near the $-NH_3^{\oplus}$ group was observed in several compounds; it is caused by the $\sigma$-electron withdrawing character of the substituent $-NH_3^{\oplus}$. Domenicano and Murray-Rust [21] describe the ring deformation of monosubstituted benzene derivatives through angular substituent parameters. Deviations of the angles $\sphericalangle$(C—C—C) from 120° for a $-NH_3^{\oplus}$ group as the deforming substituent are compared with

Table 5. Comparison of C-N distances and angles $\alpha = \sphericalangle\{C(6)\text{-}C(1)\text{-}C(2)\}$ in anilinium ions.

| C-N distance/pm | $\alpha$/deg | Diffr. method | Compound | Ref. |
|---|---|---|---|---|
| 146.2(2) | 121.7(2) | (X) | mean of eight different values | [13] |
| 147.0(9)<br>145.4(5) | 122.3(7)<br>121.8(3) | (X)<br>(N) | anilinium bromide, phase I | [9] |
| 146.8(3) | 122.8(3) | (N) | anilinium bromide, phase II | this paper |
| 146.4(3) | 121.8(2) | (X) | p-fluoroaniline hydrochloride | [14] |
| 146.7(3) | 122.5(2) | (X) | p-cyanoaniline hydrochloride | [14] |
| 146.3(2) | 121.8(2) | (X) | p-aminobenzoic acid hydrochloride | [15] |
| 147.4(9) | 122.7(6) | (X) | o-aminophenol hydrochloride | [16] |
| 147.6(13)<br>146.0(3) | 122.3(8)<br>122.3(2) | (X)<br>(N) | o-phenylenediamine hydrochloride | [17]<br>[18] |
| 144.5(11) | 119.4(5) | (X) | o-phenylenediamine dihydrobromide | [19] |
| 146.2(3) | 121.7(2) | (N) | dianilinium tetracyanoplatinate (II) | [20] |

experimental results for $C_6H_5NH_3^{\oplus}Br^{\ominus}$(I) and (II) in Table 6. The agreement is satisfactory. The smaller value of $\alpha$ found in o-phenylenediamine dihydrobromide (see Table 5) can be nicely explained by the addition of the two increments $\Delta\alpha$ and $\Delta\beta$. The small increase of the C—C-bond lengths with increasing distance from the $-NH_3^{\oplus}$ group, as observed in the two phases of anilinium bromide is probably due to the $\sigma$-electron withdrawing power of this group.

Of interest is also the difference of 1.9° between the angles C(2)-C(1)-N and C(6)-C(1)-N (Figure 2). It is due to the eclipsed position of H(N3) with respect to the ring, see Figure 5. Such an eclipsed arrangement was found for $C_6H_5NH_3^{\oplus}Br^{\ominus}$(I) too, and is probably preferred in the solid state [14]. The widening of the angle C(2)-C(1)-N compared with the angle C(6)-C(1)-N is plausible and corresponds to an in plane bending of the C(1)-N bond in $C_6H_5NH_3^{\oplus}$. Besides that, a slight out of plane bending of the bond C(1)-N by 1.3° is observed, corresponding to a deviation of the nitrogen position of 3.4 pm out of the ring plane. In total the nitrogen atom shifts away from the axis C(1) ··· C(4)-H(4) in direction towards Br(I) (see Figs. 4 and 5). Together with C(1) the $-NH_3^{\oplus}$ group approximates a tetrahedron. The bond lengths N—H are equal within the limits of error and in good agreement with literature data [9].

Table 6. Angular deformations (degrees) in anilinium ions.

| | Angular substit. parameters [21] | Anilinium bromide phase I | Anilinium bromide phase II |
|---|---|---|---|
| $\Delta\alpha = \Delta\sphericalangle\{C(2)\text{-}C(1)\text{-}C(6)\}$ | 1.8(2) | 1.8(3) | 2.8(3) |
| $\Delta\beta = \Delta\sphericalangle\{C(1)\text{-}C(2)\text{-}C(3)\}$ | −1.2(1) | −1.0(3) | −1.6(4) |
| $\Delta\gamma = \Delta\sphericalangle\{C(2)\text{-}C(3)\text{-}C(4)\}$ | 0.4(1) | 0.0(3) | 0.1(4) |
| $\Delta\vartheta = \Delta\sphericalangle\{C(3)\text{-}C(4)\text{-}C(5)\}$ | −0.1(2) | 0.2(4) | 0.4(3) |

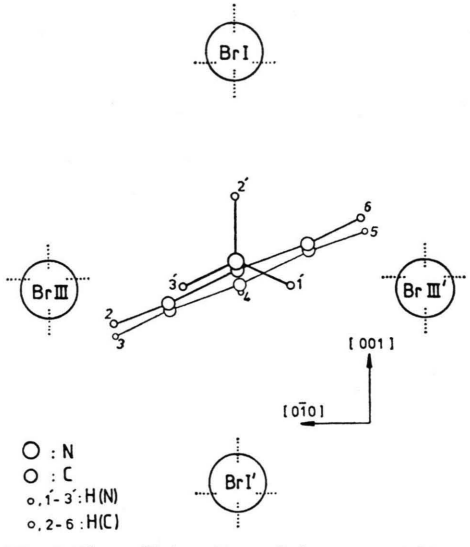


Fig. 5. The anilinium ion and the next neighboured bromide ions. Projection along [100].

Nothing unusual is observed with the thermal parameters. They increase by going from C(2) or C(6) via C(3) or C(5) to C(4) and this is fortified in the amplitudes of the corresponding hydrogen atoms. Similar to $C_6H_5NH_3^{\oplus}Br^{\ominus}$(I) a pendulum motion of the ring is assumed in which the atoms N, C(1), C(2), and C(6) are practically stationary. A detailed discussion of the thermal parameters seems to be not meaningful because of the limited set of data ($\sin\vartheta/\lambda \leqq 0.0045$ pm$^{-1}$).

### *Packing of the Ions $C_6H_5NH_3^{\oplus}$ and $Br^{\ominus}$; Hydrogen Bond System*

Within one layer of anilinium ions the intermolecular distances (Table 4, Fig. 3) agree with the van der Waals values found in molecular crystals. They are practically unchanged by the transformation I→II (for phase I see [9]). The angle of inclination between two neighbouring rings is 45.1° (44.2° in phase I). The inclination of the plane of ring No. I with respect to the crystal planes (100), (010), and (001) is 86.8°, 67.5°, and 23.0°, respectively (90°, 67.9°, and 22.1° for the corresponding molecule of the high temperature phase (I)).

Compared to the averaged structure of phase I, the atoms located in the molecular axis N-C(1) ··· C(4)-H(4) of phase II have changed mainly their z-coordinates. This corresponds to a tilt of this axis around a fixed point, which for the ring I is the intersection of a vector $\boldsymbol{r}$ ($\parallel \boldsymbol{a}$, with $y = \frac{3}{4}$, $z = \frac{1}{4}$) and the plane of ring I; the coordinates of this point are 0.2795, 0.75, 0.25. The geometrical center of ring I is at 0.2752, 0.7570, 0.2521, and therefore almost identical with the intersection point (see also Figure 4). The molecular axis C(1) ··· C(4)-H(4) and $\boldsymbol{r}$ include an angle of 4.6°. Subtracting from this value the shear of the angle $\beta$, an angle of 3.3° remains for the tilt of the molecular axis C(1) ··· C(4)-H(4) against the vector $\boldsymbol{r}$ of the high temperature phase. In [9] a tilt of ±3° against the twofold axis was made plausible for the two

orientations of the ion $C_6H_5NH_3^{\oplus}$ within the split atom model for phase I.

In comparison with the high temperature phase I, in $C_6H_5NH_3^{\oplus}Br^{\ominus}$(II) the nitrogen atoms are shifted by $\pm 27.2$ pm parallel $\boldsymbol{c}$ away from $\boldsymbol{r}$ and $\boldsymbol{r}'$, respectively, where $\boldsymbol{r}'$ is also parallel $\boldsymbol{a}$, but intersecting the plane (100) at $y=\frac{1}{4}$, $z=\frac{3}{4}$. Additionally the $Br^{\ominus}$ are shifted by $\pm 16.1$ pm parallel $\boldsymbol{c}$ away from $\boldsymbol{r}''$ ($\boldsymbol{r}''\parallel\boldsymbol{a}$, with $y=\frac{3}{4}$, $z=\frac{3}{4}$) and $\boldsymbol{r}'''$ ($\boldsymbol{r}'''\parallel\boldsymbol{a}$, with $y=\frac{1}{4}$, $z=\frac{1}{4}$). This can be seen qualitatively in Figs. 4 and 5. Each nitrogen atom is surrounded by four $Br^{\ominus}$ in such a way that three distances N ··· Br are practically equal (332.2, 332.2, and 334.4 pm) whereas the fourth distance N ··· Br is definitely different and larger (356.8 pm). This distance of 356.8 pm seems to be too large for a hydrogen bond N—H ··· Br, in competition to the other three short distances of about 333 pm. Therefore, the coordination of the nitrogen in the low temperature phase of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ suggests a preferential orientation of the $-NH_3^{\oplus}$ group. In the averaged structure of phase I the distances N ··· Br were pairwise 333 pm and 348 pm, respectively, pointing towards a model of at least two energetically equally favoured orientations of the $-NH_3^{\oplus}$ group.

In the Figs. 5 and 6 the coordination of the $-NH_3^{\oplus}$ group with respect to $Br^{\ominus}$ is shown. All relevant bond lengths and bond angles are given in Table 7. The three hydrogen bonds are non-linear and the interatomic distances and angles are practically the same as found for one of the two orientations of $C_6H_5NH_3^{\oplus}$ in phase I on the basis of the dynamical split atom model. Somewhat exaggerated, one can say that the crystal structure of the low temperature phase is a snapshot of phase I.

Table 7. Hydrogen bonding scheme in anilinium bromide, phase II: Interatomic distances (pm) and angles (degrees). For comparison: $d(N\cdots Br(I'))=356.7$ pm.

| Bridge | N-H(N1) ···Br(III′) | N-H(N2) ···Br(I) | N-H(N3) ···Br(III) |
|---|---|---|---|
| N-H | 103.2 | 104.2 | 104.2 |
| H···Br | 233.8 | 229.1 | 235.6 |
| N···Br | 332.2 | 332.2 | 334.4 |
| ∢{C(1)-N-H} | 112.8 | 110.3 | 111.4 |
| ∢{N-H···Br} | 158.7 | 170.0 | 157.9 |

In the high temperature phase (I) the corrugated network of hydrogen bonds forms a two-dimensionally infinite net parallel to the plane (100), and connects consecutive layers of $Br^{\ominus}$ and $C_6H_5NH_3^{\oplus}$ ions. The bonds within this network are of different weight (1 : 2) in two perpendicular directions. In the low temperature phase II all hydrogen bonds have the same weight, but the network is infinite only in the direction [010]. In the direction [001] the hydrogen bonds are limited to one unit cell. This is seen in Fig. 4 (hydrogen bonds marked by dashed lines).

### *The Phase Transition I → II of Anilinium Bromide*

Spontaneous strain, giving rise to the change of the monoclinic angle $\beta$, $\Delta\beta=\beta-90°=f(T_{I,II}-T)$,

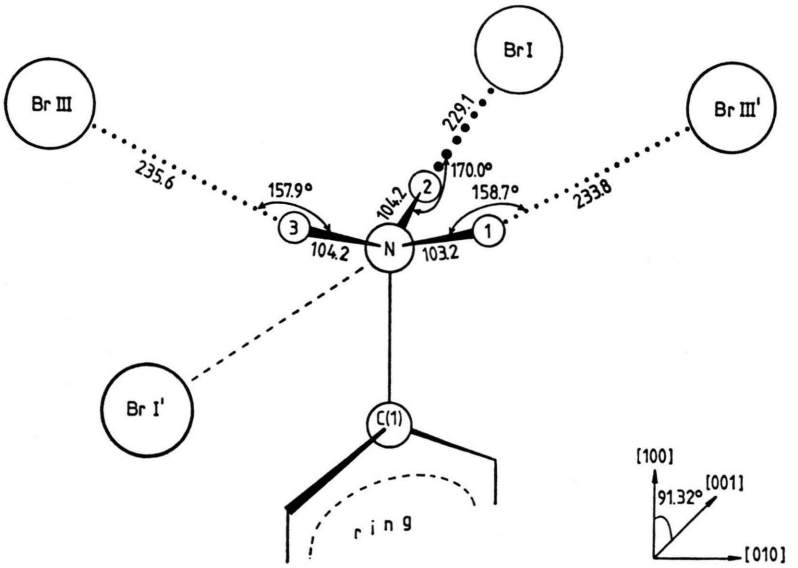


Fig. 6. Coordination of the nitrogen atom in anilinium bromide, phase II. Shown is the $-NH_3^{\oplus}$ group of the ion number I. Distances in pm.

$T_{I,II} = 296.9$ K, is considered as the order parameter of the phase transformation by Terauchi et al. [6]. Pies and Weiss [5] connected $\Delta\beta$ with the $^{79}$Br-NQR frequencies and showed that $\nu(^{79}Br) = f(T)$ leads to a critical exponent $n = \frac{1}{3}$. In this connection internal displacements of the atoms (ions) due to the transformation were discussed. Soft modes were considered as essential for the transformation [6]. The non-existence of soft optical phonons stated by Hattori et al. [7] favours a model for the phase transformation in which atomic displacements are of no importance. There is no support for a displacive character of the transformation. The finding of only very weak coupling between the acoustic phonon system and the order-disorder system [8] is in agreement with the proposal that the ferroelastic transition $C_6H_5NH_3^{\oplus}Br^{\ominus}(I) \rightarrow C_6H_5NH_3^{\oplus}Br^{\ominus}(II)$ is not driven primarily by an elastic instability. Therefore, out of the three possible mechanisms for the phase transformation, put forward by Terauchi et al. [6], only the order-disorder behaviour of the $-NH_3^{\oplus}$ group and the anilinium ion, respectively, remains as the driving force for the phase transformation. This was recognized, however, already 20 years ago by Suga [3] and supported by the $^{79}$Br-NQR studies [5].

Suga connected the order parameter S with the ordering of the $-NH_3^{\oplus}$ groups: $S = 1$ for perfect ordering of all groups $-NH_3^{\oplus}$ in one orientation; $S = 0$ for equal distribution of the groups in two different orientations (complete disorder). It can be assumed that the transition $S = 1 \rightarrow S = 0$ is continuous. By cooling anilinium bromide below $T_{I,II}$ one of the two orientations in the high temperature phase I becomes energetically slightly preferred, i.e. one of the two orientations has a higher occupation number. The inequality of the two orientations grows with increasing $(T_{I,II} - T)$. Finally at $T$ far below $T_{I,II}$ only one orientation is occupied. With these assumptions the order parameter $S$ is defined as the difference in the occupation probability $W$ of orientation $A_1$ and $A_2$ respectively of phase I (see [9]):

$$S = \Delta W = W(A_1) - W(A_2).$$

It is quite probable that $S$ defined in this way is the true (structural) order parameter for the phase transition $C_6H_5NH_3^{\oplus}Br^{\ominus}(I) \rightarrow C_6H_5NH_3^{\oplus}Br^{\ominus}(II)$; hence $S = \Delta W$ should be proportional to $\Delta\beta$. For a proof neutron diffraction experiments at several temperatures below $T_{I,II}$ are necessary. An interesting aspect of our model for the transition is the following: No displacements of atoms occur in connection with the transformation, but the one orientation ($A_1$) of the ion $C_6H_5NH_3^{\oplus}$ remains, while the other ($A_2$) disappears gradually. As a consequence a slight shear of the unit cell appears.

The dynamical properties of the phase transformation of $C_6H_5NH_3Br$ have been studied by inelastic neutron scattering [22]. A phase transformation very similar to that found in $C_6H_5NH_3Br$ occurs in $C_6H_5NH_3I$. It was followed up by $^{127}$I-NQR and neutron diffraction [23], [24].

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