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Structure of Anilinium Bromide in the Low-Temperature Phase

BY TOORU SAKAI

Faculty of Science, Kobe University, Kobe 657, *Japan*

AND HIKARU TERAUCHI

Faculty of Science, Kwansei Gakuin University, Nishinomiya 662, *Japan*

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Abstract. $C_6H_8N^+.Br^-$, monoclinic, $P2_1/c$, $a = 6{\cdot}758\,(3)$, $b = 5{\cdot}981\,(5)$, $c = 16{\cdot}738\,(7)$ Å, $\beta = 91{\cdot}34\,(1)^\circ$, $Z = 4$, $D_x = 1{\cdot}71$ Mg m^{-3}, $U = 676{\cdot}4$ Å^3, $T = 163$ K. The structure was refined by the least-squares method to a final R value of 0·086 using 475 even-l reflections. The result shows that the anilinium and bromide ions shift in opposite directions along **a** from their positions in the high-temperature phase.

Introduction. Some ferroelastic compounds are known to undergo a phase transition associated with the freezing of the acoustic phonon mode (Axe & Shirane, 1973; Sawada, Udagawa & Nakamura, 1977). The orientational ordering of the molecular group triggers the freezing of a particular phonon mode near the phase-transition temperature. Anilinium bromide is considered to be a ferroelastic compound. The crystal undergoes a phase transition at $T_c = 301$ K. The space groups of the high- and low-temperature phases are the orthorhombic $Pccn$ and the monoclinic $P2_1/c$ respectively. The purpose of the present study is to determine the crystal structure below T_c and to elucidate the mechanism of the ferroelasticity. The orientation of the NH_3 group, which takes two equilibrium orientations randomly above T_c, is also discussed.

A twin structure is present in the low-temperature phase (Taguchi, 1961). The twinning face is parallel to the ab plane. The monoclinic angle β increases gradually with decreasing temperature and levels off near 163 K. The present study was carried out at this temperature.

The crystals were obtained by addition of aniline to an excess of an aqueous solution of hydrobromic acid. The precipitated salt was washed with cold distilled water and recrystallized at 281 K. These crystals are transparent colourless rods elongated along the b axis. An ordinary cold-gas-flow technique (Richard, 1955) was applied. The cell parameters of the crystal were determined from the reflections of high Bragg angles by using a two-circle diffractometer (SG-5 type, Rigaku Denki Co.). Twinning, which occurs below T_c, causes splitting of reflection spots. The monoclinic angle β was obtained by measuring the split spots of $h0l$ and $h0\bar{l}$ reflections.

Intensity data were collected with unfiltered Cu $K\alpha$ radiation from zero- to fourth-layer Weissenberg photographs about the b axis and an equatorial photograph along the a axis. The sample was 0·38 mm in length and 0·08 mm in diameter. Individual intensities from a twin crystal were estimated visually and were calibrated as follows. (i) For the $0kl$ ($k = 0$, 1, 2, 3, and 4) reflections, where the equal-intensity spots overlapped, one half of each observed intensity was used. (ii) For the hkl and $hk\bar{l}$ reflections, where the two spots were distinctly separate, the observed intensities of the split spot themselves were used. (iii) The partially overlapped reflections were divided into two classes. (a) For the class in which the splitting in the upper half of the film was imperfect but that in the lower half was perfect because of the elongation and shrinkage of the split spots, the individual intensity is calculated from

$$I(h,k,\pm l) = \frac{I_o^l(h,k,\pm l)}{I_o^l(hkl) + I_0^l(hk\bar{l})}\, I_o^g(hkl). \qquad (1)$$

(b) For the class in which the splitting in both halves was incomplete,

$$I(h,k,\pm l) = \frac{F_c^2(h,k,\pm l)}{F_c^2(hkl) + F_c^2(hk\bar{l})}\, I_o^g(hkl), \qquad (2)$$

where $I_o^g(hkl)$ indicates the observed intensity of the overlapping hkl and $hk\bar{l}$ reflections, $I_o^l(hkl)$ and $I_o^l(hk\bar{l})$ indicate the observed intensities of hkl and $hk\bar{l}$ reflections on the lower side of the film. The F_o's calibrated by the relation (iii$b$) were not used for the least-squares refinements or in the difference map. The intensities were corrected for polarization and Lorentz factors and brought to a common scale in the usual way (Takwale & Pant, 1971). An absorption ($\mu_l = 8{\cdot}24$ mm^{-1}) correction was employed, the sample being considered a cylindrical rod.

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The systematic absence of the reflections is compatible only with space group $P2_1/c$. Almost all 530 *hkl* reflections with $l = 2n + 1$ were too weak to be detected and only 15 intensities were observed. These odd-l reflections were used only to determine the unit-cell volume and the space group. These reflections could not be used for the least-squares refinements because the split spots overlapped each other.

The intensity pattern of the 0*kl* reflections of the monoclinic phase is similar to that of the orthorhombic phase. No intensities were observed in this set of reflections with $l = 2n + 1$. In some cases additional extinctions limit the positions of the atoms or molecules (Sakai, 1978). In the present study, the lack of the intensities observed for the 0*kl* reflections restricts the *y* coordinates of Br, N, C(1) and C(4) atoms to some special positions. The structure factors calculated tentatively by shifting the *x* coordinate of the Br^- ion in the high-temperature phase (Nitta, Watanabe & Taguchi, 1961) are useful for the determination of the signs of the observed reflections in the low-temperature phase. The crystal structure was refined for all even-l reflections with anisotropic temperature factors only. For the calculation of the structure analysis with this condition, the usual method is to treat a crystal belonging to space group $P12_11$ with the cell parameter *c* half as large as that of the present case. However, to perform the least-squares refinements, as the space group of the crystal is $P2_1/c$, the following constraining conditions were introduced. (i) The *y* coordinates of Br, N, C(1) and C(4) were fixed at $\frac{1}{4}$ or $\frac{3}{4}$. (ii) Thermal parameters b_{12} and b_{23} of Br, N, C(1) and C(4) were fixed at zero.

The positions of the H atoms in the NH_3 group were not obtained even after the end of the refinements. The final *R* value was 0·086.* The scattering factors were taken from *International Tables for X-ray Crystallography* (1968). In all of the cycles, unit weight was given to all F_o's. The fractional atomic parameters and their e.s.d.'s are given in Table 1. The intramolecular bond lengths and angles are listed in Table 2. The arrangement of the molecules in the cell and intermolecular distances (<4·0 Å) are shown in Fig. 1.

Table 1. *Final atomic parameters of anilinium bromide at* 163 K

The e.s.d.'s of the atomic parameters are given in parentheses and refer to the last significant figures. Numbers marked by an asterisk are assumed values deduced from the extra extinction of 0*kl* reflections. For non-hydrogen atoms the equivalent isotropic temperature factor B_{eq} is that defined by Hamilton (1959). For H atoms $B_{iso} = 2{\cdot}3$ Å^2.

	x	*y*	*z*	B_{eq} (Å^2)
Br	0·2307 (2)	0·2500*	0·5242 (1)	1·56 (4)
N	0·2884 (17)	0·7500*	0·4467 (7)	1·93 (23)
C(1)	0·2755 (18)	0·7500*	0·3620 (8)	1·92 (28)
C(2)	0·1987 (30)	0·5605 (38)	0·3218 (14)	2·12 (46)
C(3)	0·1863 (40)	0·5615 (40)	0·2384 (12)	1·78 (43)
C(4)	0·2430 (24)	0·7500*	0·1930 (10)	2·49 (32)
C(5)	0·3189 (33)	0·9401 (37)	0·2344 (12)	2·07 (50)
C(6)	0·3331 (29)	0·9392 (36)	0·3185 (12)	2·06 (48)
H(2)	0·164 (44)	0·440 (49)	0·355 (18)	
H(3)	0·141 (47)	0·420 (57)	0·201 (21)	
H(4)	0·211 (39)	0·7500*	0·128 (16)	
H(5)	0·353 (41)	0·097 (45)	0·197 (18)	
H(6)	0·390 (43)	0·078 (52)	0·359 (18)	

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for anilinium bromide at* 163 K

N–C(1)	1·418 (18)	N–C(1)–C(2)	119·3 (12)
C(1)–C(2)	1·41 (2)	N–C(1)–C(6)	120·4 (11)
C(2)–C(3)	1·40 (3)	C(6)–C(1)–C(2)	120·1 (16)
C(3)–C(4)	1·42 (3)	C(1)–C(2)–C(3)	119·1 (18)
C(4)–C(5)	1·42 (2)	C(2)–C(3)–C(4)	121·9 (20)
C(5)–C(6)	1·41 (3)	C(3)–C(4)–C(5)	118·3 (17)
C(6)–C(1)	1·41 (2)	C(4)–C(5)–C(6)	120·0 (18)
		C(5)–C(6)–C(1)	120·5 (17)

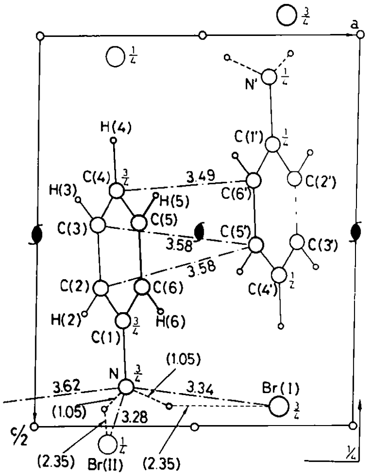

Fig. 1. Projection of the molecules of anilinium bromide in the cell along the *b* axis at 163 K. The numbering scheme of the atoms and the interionic and intermolecular distances (<4·0 Å) are also shown. Distances in parentheses are assumed values. The fractions $\frac{1}{4}$ and $\frac{3}{4}$ indicate the *y* coordinates of corresponding atoms. The relative positions of other atoms are represented by the thickness of the lines drawn between neighbouring atoms. For the exact positions of the atoms, see Table 1.

Discussion. The average bond length of the benzene ring is 1·413 Å; N–C(1) is 1·418 Å. The longest axis of the anilinium ion is parallel to the *ac* plane and its *y* coordinate is $\frac{3}{4}$. This axis is inclined from the *ab* and *bc* planes by 87·67 and 3·66° respectively. The angle

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36018 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

between the *ac* plane and the aromatic plane is 68·7°, which is 1·2° larger than the corresponding angle of the orthorhombic phase. The increase is caused by the cancellation of the stresses arising from the enlargement of the monoclinic angle β from 90°. The *x* coordinate of the centre of an anilinium-ion and a bromide-ion pair is conserved at about $\frac{1}{4}$. The shortest intermolecular atomic distance is C(4)—C(6'). Next-shortest distances are C(2)—C(5') and C(3)—C(5'). These are a little shorter than those of many other aromatic compounds.

Between consecutive layers, the strongest interactions can be expected between the Br^- ions and the NH_3^+ group. Every Br^- ion is surrounded by four NH_3^+ ions or each NH_3^+ by four Br^-. However, the distances between an N atom and the surrounding four Br^- ions are not equal to those of the high-temperature phase. One of the Br—N distances is a little longer than the other three.

When an N atom and its surrounding four Br^- ions only are taken into account, there is a local symmetry of a mirror plane perpendicular to the *b* axis containing the N atom and a $Br(I)^-$ ion. If the local symmetry determines the orientation of the assumed regular triangular pyramid of NH_3^+ with N—H 1·05 Å and H—N—H 109° 28', then the distances between three H atoms and their nearest bromines are all estimated to be 2·35 Å. This distance is nearly equal to that of the sum of the H and Br ionic radii. Any other positions for the H atoms obtained by rotating the NH_3^+ group about the longest axis are unreasonable because of the interionic distances between the H atoms and Br^- ions and also because of the Coulomb potential between these ions.

The calculations were carried out on a FACOM M-190 computer at the Data Processing Center, Kyoto University. Programs for least-squares refinements and Fourier syntheses were *RSFLS*-4 and *RSSFR*-3 in *UNICS* (1967).

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Structure of 19-Acetylteuspinin, a New Clerodane Diterpenoid from the Species *Teucrium*

By L. Eguren, J. Fayos and A. Perales

Departamento de Rayos-X, Instituto de Química-Física, 'Rocasolano', Serrano 119, *Madrid*-6, *Spain*

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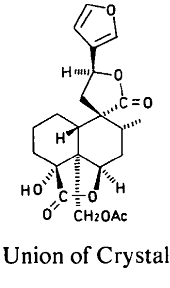
Abstract. $C_{22}H_{26}O_8$, orthorhombic, $P2_12_12_1$, a = 25·569 (2), b = 13·560 (1), c = 11·993 (1) Å, U = 4158·2 (6) Å^3, M_r = 420·458, Z = 8, D_c = 1·32 Mg m^{-3}, $F(000)$ = 1776. The structure has been solved by direct methods and refined to a final R value of 6·5% for 5800 observed reflexions. Both crystallographically independent molecules are indistinguishable, showing the *ent*-clerodane-type structure. They are joined together by two H bonds, forming dimers in the crystal. The cyclohexane rings show a chair conformation and the γ-spirolactone and lactone rings have an envelope conformation. The absolute configuration is the same as that found for other molecules of the species *Teucrium*.

Introduction. From the species *Teucrium* a number of clerodane and *ent*-clerodane diterpenoids have been isolated (Piozzi, 1981). In the present work we report the crystal structure of a new clerodane, teuspinin (I) (Savona, Paternostro, Piozzi & Rodríguez, 1980).



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