

using Weissenberg photographs around one axis, with scaling by layerwise Wilson plots.

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The Crystal and Molecular Structures of the 1:1 Addition Compounds of Piperidine with *p*-Bromobenzoic Acid and *p*-Chlorobenzoic Acid

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The structures of the two 1:1 addition compounds of piperidine with *p*-bromobenzoic acid, $\text{BrC}_6\text{H}_4\text{CO}_2\text{H} \cdot \text{C}_5\text{H}_{11}\text{N}$, and with *p*-chlorobenzoic acid, $\text{ClC}_6\text{H}_4\text{CO}_2\text{H} \cdot \text{C}_5\text{H}_{11}\text{N}$, have been determined from three-dimensional X-ray diffraction data. Both compounds crystallize in the orthorhombic space group *Pbca* with eight formula units in the unit cell. The cell dimensions are: $a = 10.70$, $b = 27.30$, $c = 9.04$ Å for the *p*-bromo compound, and $a = 10.68$, $b = 26.37$, $c = 9.01$ Å for the *p*-chloro compound. The structures were refined by the block-diagonal least-squares method, with anisotropic temperature factors. The final *R* values for observed reflexions are 0.086 and 0.123 for the *p*-bromo and *p*-chloro compounds respectively. Both structures are isotypic. The structure is composed of an alternate sequence of acid and base moieties held together by $\text{N}^+ - \text{H} \cdots \text{O}^-$ hydrogen bonds. The $\text{N}^+ - \text{H} \cdots \text{O}^-$ distance ranges from 2.67 to 2.76 Å. The hydrogen bonds form an infinite chain around the twofold screw axis parallel to the *c* axis. These molecular chains are packed intimately by van der Waals forces to make up a whole crystal. In either compound, the piperidine ring takes a normal chair form, and the carboxyl group is twisted out of the plane of the benzene ring at an angle of about 8°.

Introduction

The formation of the solid 1:1 and 2:1 addition compounds of benzoic acid and piperidine and those of some *p*-substituted benzoic acids and piperidine have previously been reported (Kashino, 1967; Kashino, Kanei & Hasegawa, 1971). The infrared spectra of the 1:1 compounds were very similar to those of the corresponding sodium benzoates. Thus, it was concluded that the acid moiety in the 1:1 compounds is almost fully ionized. However, the symmetric carboxylate stretching of the adducts showed significantly lower values of $1385\text{--}1375\text{ cm}^{-1}$ compared with the values of $1427\text{--}1406\text{ cm}^{-1}$ for the corresponding sodium benzoates.

It may be desirable to obtain information about the spatial configuration of individual molecules in these crystals and more information about the nature of the bond between the acid and the base components. As a

first step, the crystal structure determinations of the present compounds were undertaken.

Experimental

The 1:1 addition compound of *p*-bromobenzoic acid and piperidine was prepared by dissolving equimolar quantities of *p*-bromobenzoic acid and piperidine in dry benzene. The compound crystallized as transparent tabular plates having well developed {010}. As the compound was hygroscopic and gradually decomposed to its acid and base components, the specimens cut from larger crystals were sealed in glass capillaries. Two different crystals with approximate cross-sections of 0.12×0.18 mm and 0.10×0.15 mm were used for the X-ray analysis, the former for *a* axis photographs and the latter for *c* axis photographs. Using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å), multiple-film equi-inclination Weissenberg photographs were taken for the layers from

$0kl$ to $6kl$ and from $hk0$ to $hk6$. In all, 1300 independent reflexions were observed out of about 3000 possible reflexions within the Cu $K\alpha$ sphere. The intensities were estimated by visual comparison with a calibrated intensity scale. The intensities covered a range of about 11000:1. After Lorentz, polarization, and spot-shape corrections were made, the intensities of various layers were put on the same relative scale by use of all the common reflexions. The relative values thus obtained were put on an absolute scale by Wilson's method. No absorption correction was applied, since the μR values for the crystals were less than 0.5. In the course of refinement, the extinction effect became apparent for the reflexions: 060, 0,12,0, 210, 220, 230, and 400. The extinction effect was eliminated by immersing the crystals in liquid nitrogen.

The unit cell dimensions were determined from zero-layer Weissenberg photographs of $0kl$ and $hk0$ using the reflexions higher than $\theta = 50^\circ$ and ($\text{Cu } K\alpha_1$) = 1.5405 Å; the values of a , b , and c calculated from each reflexion were plotted against $\sin^2 \theta$ and extrapolated to $\theta = 90^\circ$.

The intensity data of the 1:1 addition compound of *p*-chlorobenzoic acid and piperidine were calculated almost in the same way as that of the *p*-bromo compound. Two different crystals with approximate cross-sections 0.21×0.29 mm and 0.14×0.20 mm were used. The total number of reflexions recorded was 1104, corresponding to about 40% of the reflexions within the Cu $K\alpha$ sphere. No correction was made for absorption and extinction.

The crystallographic data of the two compounds are given in Table 1.

Structure analysis

p-Bromo compound

From the three-dimensional Patterson map the position of the bromine atom could easily be deduced.

Two-dimensional electron-density maps projected along the a and c axes were calculated on the basis of the bromine contribution. These maps and the three-

dimensional Patterson map revealed all sixteen non-hydrogen atoms in the asymmetric unit. The nitrogen atom in the piperidine ring was identified by a short interatomic distance of about 2.8 Å from the carboxyl oxygen. The coordinates of the sixteen atoms were subjected to two-dimensional Fourier refinement. After a few cycles of this refinement, the discrepancy factor, R , was 0.309 for all the observed reflexions.

The structure thus deduced was refined by block-diagonal least-squares methods, first assuming isotropic and then anisotropic thermal motion. Unit weight was given to all the observed reflexions. The R index became 0.115. A difference Fourier synthesis at this stage revealed fourteen hydrogen atoms bonded to the carbon atoms. However, two hydrogen atoms which were expected to belong to either the nitrogen atom or the oxygen atoms could not be located. In the subsequent refinements, the positional parameters of the fourteen hydrogen atoms computed by assuming suitable geometries of the C-H bond (C-H = 1.08 Å) and the appropriate isotropic temperature factors, $B = 4.0$ Å², were introduced. However, the parameters of the hydrogen atoms were not refined. From this stage of refinement, the following weighting scheme was adopted:

$$\begin{aligned} \sqrt{w} &= 0.0, & \text{if } F_o \leq F_{\min} (= 4.0), \\ \sqrt{w} &= 1.0, & \text{if } F_{\min} < F_o \leq F_{\max} (= 54.0), \end{aligned}$$

and

$$\sqrt{w} = F_{\max}/F_o, \quad \text{if } F_o > F_{\max}.$$

Six cycles of calculation with anisotropic thermal parameters for all non-hydrogen atoms reduced the R index to 0.098. At this stage, the extinction effect was eliminated as described in the experimental section. After three cycles, the R index reached 0.088, and the shifts in the coordinates and thermal parameters were less than 0.02σ and 0.25σ respectively. The final atomic parameters and their standard deviations for non-hydrogen atoms are given in Table 2 and the final thermal parameters are listed in Table 3(a).

A composite drawing of the final difference synthesis is given in Fig. 1 together with the final electron-density

Table 1. *Crystal data*

| | BrC ₆ H ₄ CO ₂ H · C ₅ H ₁₁ N | ClC ₆ H ₄ CO ₂ H · C ₅ H ₁₁ N |
|------------------------|--|--|
| Formula wt. | 286.2 | 241.7 |
| M.p. | 120°C | 121°C |
| Crystal system | Orthorhombic | Orthorhombic |
| a | 10.70 ± 0.03 Å | 10.68 ± 0.02 Å |
| b | 27.30 ± 0.01 | 26.37 ± 0.03 |
| c | 9.04 ± 0.01 | 9.01 ± 0.02 |
| D_x | 1.44 g.cm ⁻³ | 1.27 g.cm ⁻³ |
| D_m^* | 1.44 (25°C) | 1.27 (25°C) |
| Z | 8 | 8 |
| Absent spectra | $hk0$ when h is odd $0kl$ when k is odd $h0l$ when l is odd | $hk0$ when h is odd $0kl$ when k is odd $h0l$ when l is odd |
| Space group | <i>Pbca</i> | <i>Pbca</i> |
| μ for Cu $K\alpha$ | 45.9 cm ⁻¹ | 25.7 cm ⁻¹ |

* Weld pycnometer and liquid paraffin.

map. All the peaks corresponding to the hydrogen atoms were revealed in the difference map, including the two hydrogen atoms that could not be located during the refinement. The peak heights of two hydrogen atoms belonging to the nitrogen atom were, however, as low as 0.2–0.3 e.Å⁻³. There is no other positive

Table 2. Final positional parameters and e.s.d.'s ($\times 10^4$) for the non-hydrogen atoms

Numbering of atoms as in Fig. 1(a).

| | <i>p</i> -Bromo compound (X=Br) | | | <i>p</i> -Chloro compound (X=Cl) | | |
|-------|---------------------------------|----------|-----------|----------------------------------|----------|-----------|
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>x</i> | <i>y</i> | <i>z</i> |
| C(1) | 4129 (7) | 1237 (2) | 8419 (8) | 4140 (9) | 1277 (3) | 8435 (10) |
| C(2) | 3774 (8) | 1619 (3) | 9345 (8) | 3752 (9) | 1660 (3) | 9370 (10) |
| C(3) | 4290 (9) | 2087 (3) | 9268 (9) | 4316 (10) | 2150 (4) | 9300 (11) |
| C(4) | 5232 (9) | 2166 (3) | 8211 (10) | 5239 (10) | 2228 (3) | 8288 (11) |
| C(5) | 5652 (9) | 1779 (3) | 7276 (10) | 5634 (10) | 1841 (4) | 7314 (11) |
| C(6) | 5081 (8) | 1330 (3) | 7369 (10) | 5087 (9) | 1366 (3) | 7380 (11) |
| C(7) | 3540 (8) | 734 (3) | 8513 (9) | 3534 (9) | 758 (3) | 8528 (10) |
| O(8) | 2791 (6) | 663 (2) | 9599 (7) | 2795 (8) | 686 (2) | 9574 (8) |
| O(9) | 3791 (5) | 411 (2) | 7572 (6) | 3819 (6) | 431 (2) | 7536 (8) |
| X(10) | 6026 (1) | 2790 (0) | 8083 (1) | 5946 (3) | 2819 (1) | 8154 (4) |
| N(11) | 2947 (6) | 277 (2) | 4713 (7) | 2959 (7) | 279 (3) | 4726 (8) |
| C(12) | 1830 (8) | 596 (3) | 4713 (9) | 1782 (8) | 616 (4) | 4705 (11) |
| C(13) | 2169 (8) | 1144 (3) | 4621 (9) | 2161 (9) | 1169 (4) | 4621 (11) |
| C(14) | 2968 (9) | 1241 (3) | 3253 (9) | 2956 (9) | 1269 (3) | 3241 (11) |
| C(15) | 4133 (8) | 916 (3) | 3281 (9) | 4149 (10) | 934 (4) | 3265 (12) |
| C(16) | 3774 (8) | 374 (3) | 3344 (8) | 3734 (9) | 377 (3) | 3333 (11) |

Table 3. Final thermal parameters and e.s.d.'s ($\times 10^4$) for non-hydrogen atoms

The anisotropic temperature factor is defined as

$$\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}.$$

(a) *p*-Bromo compound

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|--------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 91 (8) | 13 (1) | 112 (11) | 7 (5) | -48 (16) | 3 (5) |
| C(2) | 119 (9) | 15 (1) | 113 (10) | 1 (5) | -5 (18) | 8 (6) |
| C(3) | 163 (12) | 18 (1) | 120 (11) | -3 (6) | -1 (20) | -5 (7) |
| C(4) | 171 (12) | 16 (1) | 162 (13) | -13 (6) | -55 (24) | 12 (7) |
| C(5) | 126 (11) | 27 (2) | 141 (14) | -10 (7) | 25 (20) | 10 (8) |
| C(6) | 103 (9) | 20 (1) | 130 (12) | 2 (6) | -15 (18) | -2 (7) |
| C(7) | 139 (11) | 15 (1) | 133 (12) | 13 (5) | -41 (19) | 11 (6) |
| O(8) | 193 (9) | 16 (1) | 186 (10) | -16 (5) | 81 (16) | -6 (5) |
| O(9) | 150 (7) | 15 (1) | 120 (6) | 6 (4) | -16 (13) | -17 (4) |
| Br(10) | 240 (2) | 24 (0) | 257 (2) | -62 (1) | -27 (4) | 23 (1) |
| N(11) | 111 (7) | 15 (1) | 121 (9) | 21 (4) | 2 (14) | -6 (5) |
| C(12) | 93 (8) | 18 (1) | 149 (13) | -2 (5) | 7 (19) | -1 (7) |
| C(13) | 120 (10) | 16 (1) | 136 (12) | 22 (5) | 8 (19) | 3 (6) |
| C(14) | 158 (11) | 14 (1) | 164 (13) | 18 (6) | 65 (22) | 19 (7) |
| C(15) | 127 (11) | 21 (1) | 139 (13) | 17 (6) | 67 (21) | 1 (7) |
| C(16) | 132 (10) | 18 (1) | 112 (11) | 28 (6) | 26 (19) | -8 (6) |

(b) *p*-Chloro compound

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|--------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 73 (9) | 13 (1) | 78 (12) | 10 (6) | -51 (20) | 14 (7) |
| C(2) | 107 (12) | 9 (1) | 83 (12) | 6 (6) | -4 (21) | 1 (7) |
| C(3) | 82 (11) | 18 (2) | 108 (14) | -7 (7) | -28 (22) | 14 (8) |
| C(4) | 94 (11) | 14 (2) | 113 (14) | -16 (7) | 0 (23) | 21 (8) |
| C(5) | 88 (12) | 24 (2) | 90 (14) | -18 (8) | -14 (23) | 17 (9) |
| C(6) | 72 (10) | 17 (2) | 68 (12) | 2 (6) | 21 (20) | 16 (8) |
| C(7) | 90 (11) | 12 (1) | 74 (12) | 14 (6) | -34 (20) | 2 (7) |
| O(8) | 160 (10) | 13 (1) | 121 (10) | -20 (5) | 67 (18) | -18 (6) |
| O(9) | 121 (8) | 13 (1) | 97 (8) | 16 (5) | -52 (16) | 1 (6) |
| Cl(10) | 176 (4) | 19 (0) | 191 (5) | -58 (3) | -10 (9) | 16 (3) |
| N(11) | 73 (8) | 12 (1) | 74 (10) | 15 (5) | 30 (16) | -1 (6) |
| C(12) | 48 (9) | 15 (1) | 116 (15) | 25 (6) | 15 (20) | 3 (8) |
| C(13) | 84 (11) | 14 (2) | 100 (14) | 24 (7) | 50 (21) | 10 (8) |
| C(14) | 86 (10) | 15 (2) | 102 (14) | 29 (7) | 55 (21) | 24 (9) |
| C(15) | 103 (12) | 15 (2) | 161 (18) | 18 (7) | 65 (27) | 5 (9) |
| C(16) | 97 (11) | 13 (1) | 111 (14) | 31 (6) | 63 (23) | 7 (8) |

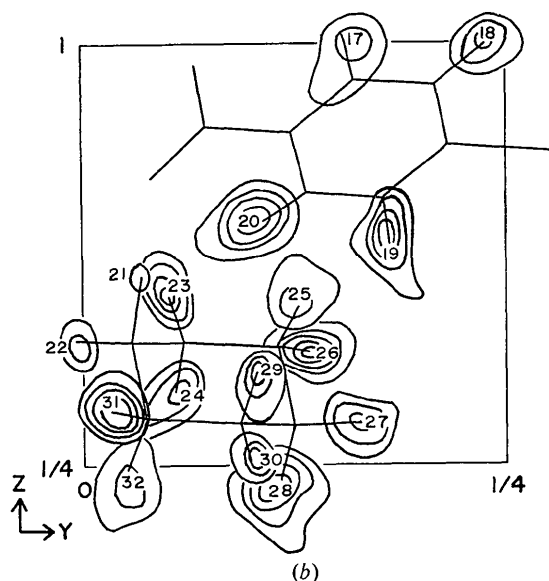
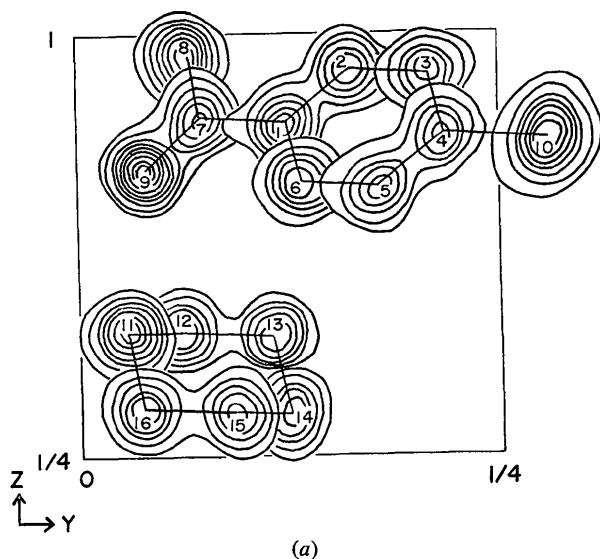


Fig. 1. (a) Composite three-dimensional final electron-density map for the *p*-bromo compound projected along the *c* axis. Contours are at intervals of $1 \text{ e.}\text{\AA}^{-3}$ starting at $1 \text{ e.}\text{\AA}^{-3}$ for C, N and O atoms and at intervals of $5 \text{ e.}\text{\AA}^{-3}$ starting at $1 \text{ e.}\text{\AA}^{-3}$ for the Br atom. (b) Composite of the final difference synthesis for the *p*-bromo compound. Contours are at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$ starting at $0.2 \text{ e.}\text{\AA}^{-3}$.

region exceeding $0.2 \text{ e.}\text{\AA}^{-3}$ except for one peak of $0.7 \text{ e.}\text{\AA}^{-3}$. This positive and some negative regions were associated with the bromine atom. Parameters for the hydrogen atoms obtained from the difference map are shown in Table 4. In the final calculation of the structure factors, these positional parameters were included, and the isotropic temperature factors, $B=4.0 \text{ \AA}^2$, were assumed for all the hydrogen atoms. The final *R* index was 0.086 for all the observed reflexions. The observed and calculated structure factors are listed in Table 5(a).

Table 4. Hydrogen-atom coordinates in the *p*-bromo compound obtained from the final difference map [Fig. 1(b)]

(Numbering of atoms as in Fig. 1(b)).

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|
| H(17) | 0.3131 | 0.1524 | 1.0155 |
| H(18) | 0.4115 | 0.2388 | 1.0041 |
| H(19) | 0.6259 | 0.1818 | 0.6464 |
| H(20) | 0.5358 | 0.1032 | 0.6729 |
| H(21) | 0.3475 | 0.0333 | 0.5892 |
| H(22) | 0.2723 | -0.0063 | 0.4709 |
| H(23) | 0.1259 | 0.0491 | 0.5542 |
| H(24) | 0.1212 | 0.0535 | 0.3805 |
| H(25) | 0.2642 | 0.1246 | 0.5339 |
| H(26) | 0.1396 | 0.1358 | 0.4502 |
| H(27) | 0.3199 | 0.1641 | 0.3263 |
| H(28) | 0.2421 | 0.1148 | 0.2212 |
| H(29) | 0.4760 | 0.1023 | 0.4170 |
| H(30) | 0.4576 | 0.1006 | 0.2441 |
| H(31) | 0.4654 | 0.0174 | 0.3459 |
| H(32) | 0.3115 | 0.0250 | 0.2397 |

p-Chloro compound

An approximate structure of the *p*-bromo compound was of great help in the structure determination of the *p*-chloro compound. The procedure of the structure refinement of the *p*-chloro compound was almost the same as that of the *p*-bromo compound. From the three-dimensional Patterson map of the *p*-chloro compound, approximate positional parameters for all the non-hydrogen atoms could be deduced. After several cycles of least-squares refinement with isotropic thermal parameters, the *R* index was 0.204. The positional corrections for several carbon atoms in the piperidine ring were made on the basis of a three-dimensional difference map. Several subsequent cycles of refinement with anisotropic thermal parameters for the chlorine and the oxygen atoms lowered the *R* index to 0.135. Five cycles of calculation with anisotropic thermal parameters for all non-hydrogen atoms reduced the *R* index to 0.123 for all the observed reflexions. At this stage, the shifts in the coordinates and thermal parameters were less than 0.3σ and 0.6σ respectively, and the refinement was terminated. The weighting scheme was almost the same as that for the *p*-bromo compound, but here F_{max} was 40.0. The final atomic parameters and their standard deviations are given in Table 2 and the final thermal parameters are listed in Table 3(b). The observed and calculated structure factors are listed in Table 5(b).

The atomic scattering factors used in the calculation were those of Hanson, Herman, Lea & Skillman (1964). The numerical calculations were performed mainly on the HITAC 5020E computer of the Computer Center of the University of Tokyo, and partly on the FACOM 230-60 computer of the Computer Center of Kyoto University and the NEAC 2203 computer of this University. Main programs used were:

Patterson synthesis by Yasuoka,
Structure factors and Fourier synthesis (*RSSFR* 5) by Sakurai (1968),

Table 7. Bond angles and *e. s. d.*'s

| | <i>p</i> -Bromo compound (X=Br) | <i>p</i> -Chloro compound (X=Cl) |
|-------------------|------------------------------------|-------------------------------------|
| C(1)—C(2)—C(3) | 123.4 (8)° | 120.5 (9)° |
| C(2)—C(3)—C(4) | 117.2 (9) | 118.4 (9) |
| C(3)—C(4)—C(5) | 121.1 (9) | 121.7 (10) |
| C(4)—C(5)—C(6) | 118.9 (9) | 120.0 (10) |
| C(5)—C(6)—C(1) | 121.5 (8) | 119.0 (9) |
| C(6)—C(1)—C(2) | 117.8 (7) | 120.5 (9) |
| C(3)—C(4)—X(10) | 119.9 (7) | 120.0 (8) |
| C(5)—C(4)—X(10) | 119.0 (7) | 118.4 (8) |
| C(2)—C(1)—C(7) | 122.3 (7) | 119.9 (9) |
| C(6)—C(1)—C(7) | 119.9 (7) | 119.7 (8) |
| C(1)—C(7)—O(8) | 116.1 (7) | 116.7 (9) |
| C(1)—C(7)—O(9) | 120.8 (8) | 117.7 (8) |
| O(8)—C(7)—O(9) | 123.2 (8) | 125.6 (9) |
| N(11)—C(12)—C(13) | 112.4 (7) | 109.8 (8) |
| C(12)—C(13)—C(14) | 110.0 (7) | 110.8 (8) |
| C(13)—C(14)—C(15) | 110.1 (7) | 110.3 (8) |
| C(14)—C(15)—C(16) | 110.9 (7) | 108.0 (9) |
| C(15)—C(16)—N(11) | 109.9 (7) | 110.5 (8) |
| C(16)—N(11)—C(12) | 111.2 (6) | 109.7 (7) |

hydrogen bond. From Fig. 3 it may be seen that these two hydrogen bonds arrange the molecules around the twofold screw axis along the *c* axis.

As shown in Fig. 2, the nitrogen atom is nearly tetrahedrally surrounded by the two carboxyl oxygen and two ring carbon atoms.

The environments of the two oxygen atoms are different; bond angle C(7)—O(9)—N(11) deviates considerably from regular tetrahedral angle (131 or 132°), but the angle C(7)—O(8)—N(11) is approximately tetrahedral (111 or 112°). Corresponding to this difference, the hydrogen bond length between O(8') and N(11) is significantly shorter than that between O(9) and N(11).

Most bond lengths of N⁺—H···O⁻ hydrogen bonds are in the range of 2.8–2.9 Å (Pimentel & McClellan, 1960). The hydrogen bond lengths in ammonium trifluoroacetate have been found to be 2.87, 2.89, 2.91 and 2.92 Å (Cruickshank, Jones & Walker, 1964).

Furthermore, Nahrungbauer (1967) has found in ammonium acetate four N⁺—H···O⁻ hydrogen bonds of approximately the same length (2.804, 2.808, 2.824 and 2.830 Å). The hydrogen bonds in the present compounds (2.687 or 2.674 Å and 2.762 or 2.722 Å) are significantly shorter than these values. N⁺—H···O⁻ hydrogen bonds shorter than 2.8 Å have been found in several cases, for example, β-glycylglycine (2.68 Å) by Hughes & Moore (1949), DL-α-aminocaproic acid (2.73 Å) by Mathieson (1953), and hexamethylenediammonium adipate (2.72 and 2.75 Å) by Hirokawa, Ohashi & Nitta (1954).

Although no N—H bond lengths could be determined precisely, the approximate bond lengths N(11)—H(21) and N(11)—H(22) obtained from the difference map of the *p*-bromo compound were 1.22 and 0.96 Å respectively.

In the infrared spectra of the present compounds, no band characteristic of an un-ionized carboxyl group is observed (Kashino, Kanei & Hasegawa, 1971). Thus it may be concluded that the present compounds are composed of piperidinium cations and *p*-bromo- (or *p*-chloro-)benzoate anions, and the possible hydrogen bonds are of the type N⁺—H···O⁻.

In the *p*-bromo compound the C(7)—O(9) bond is slightly shorter than the C(7)—O(8) bond, while in the *p*-chloro compound the C(7)—O(9) bond is rather longer. Thus, the difference in the two C—O bond lengths does not appear to be significant.

The mean value over the two compounds of the C—C bond lengths in the benzene ring is 1.398 Å, very close to the accepted value of 1.395 Å (*International Tables for X-ray Crystallography*, 1962). The bond length C(1)—C(7) is 1.514 or 1.520 Å and therefore is significantly shorter compared with the standard single-bond value of 1.54 Å, but is longer than that observed in benzoic acid, 1.48 Å (Sim, Robertson & Goodwin, 1955). The observed aromatic C—Br distance of 1.910 Å is slightly longer than the normally accepted value of 1.85 Å (*International Tables for X-ray Crystal-*

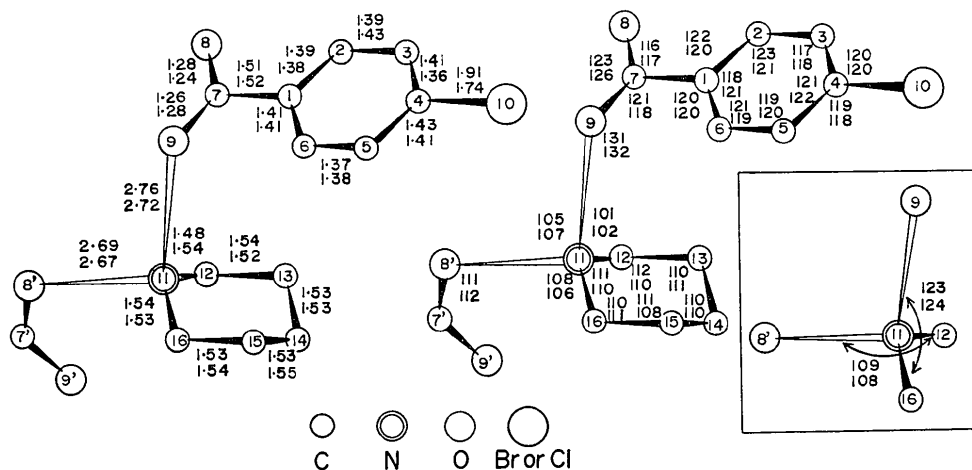


Fig. 2. Bond lengths (Å) and angles (°). The upper values are for the *p*-bromo compound, the lower ones for the *p*-chloro compound. Covalent bonds are filled and open bonds represent hydrogen bonds.

lography, 1962). Such a value has been observed in 3-(*p*-bromophenyl)phthalide, 1.921 Å (Kalyani & Vijayan, 1969). The observed aromatic C-Cl distance of 1.735 Å is also longer than the accepted value of 1.70 Å. In fact, a C-Cl distance as long as 1.741 Å has been

observed in potassium hydrogen di-*p*-chlorobenzoate (Mills & Speakman, 1963).

The average bond lengths in the piperidine ring in both compounds are 1.521 Å for the C-N bonds and 1.533 Å for the C-C bonds, slightly longer than those

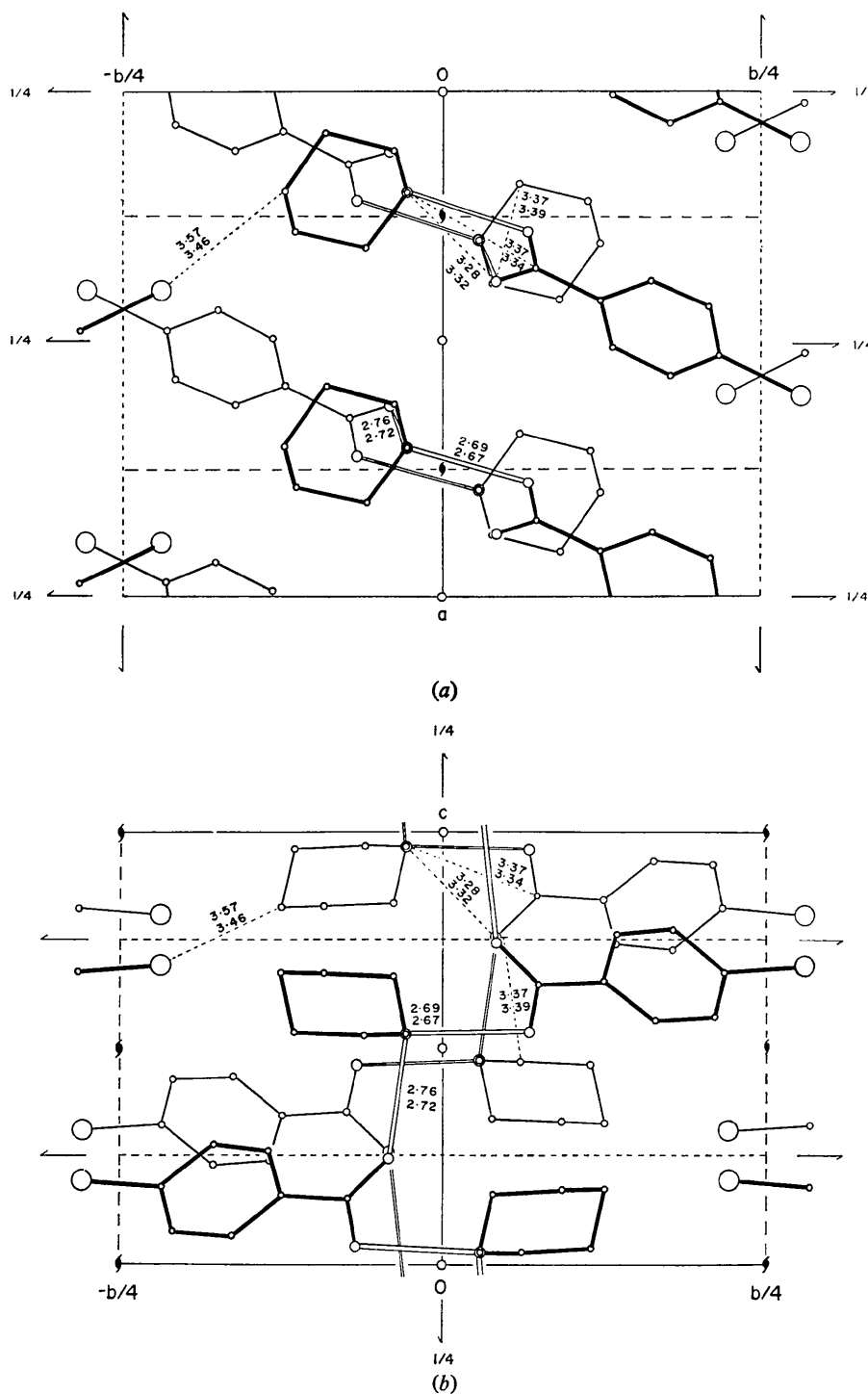


Fig. 3. (a) The projection of the crystal structure along the *c* axis. (b) The projection of the crystal structure along the *a* axis. The notation is the same as in Fig. 2.

observed in piperidine hydrochloride (C-N: 1.497 Å, C-C: 1.505 Å) by Rérat (1960). The deviations from the tetrahedral value of the bond angles in the piperidine ring are not significant.

The least-squares planes are listed in Table 8. The benzene ring is substantially planar. The atom Cl(10) in the *p*-chloro compound is within plane (1) through the benzene ring, while the atom Br(10) in the *p*-bromo compound appears to deviate significantly

from plane (1). In either compound, the atom C(7) is within plane (1), but the atoms O(8) and O(9) are significantly off the plane; plane (2) through C(7), O(8) and O(9) is twisted with respect to plane (1) by an angle of 7.9 or 7.3°. The same kinds of twists have been found in potassium hydrogen di-*p*-nitrobenzoate, 5° (Shrivastava & Speakman, 1961) and in potassium hydrogen di-*p*-chlorobenzoate, 9° (Mills & Speakman, 1963).

Table 8. *Least-squares planes*

(a) Least-squares planes

Each plane is represented by $lX + mY + nZ = p$, where X, Y, Z are Cartesian coordinates in Å, referred to the axes a, b, c .

| (1) The best plane through the benzene ring | | | (2) The best plane through C(7), O(8), O(9) | | | (3) The best plane through C(12), C(13), C(15), C(16) | | |
|---|-----------------------------------|----------------------------------|---|-----------------------------------|---------------------------|---|-----------------------------------|---------------------------|
| | <i>p</i> -Bromo compound (X=Br) | <i>p</i> -Chloro compound (X=Cl) | | <i>p</i> -Bromo compound | <i>p</i> -Chloro compound | | <i>p</i> -Bromo compound | <i>p</i> -Chloro compound |
| <i>l</i> | 0.6881 | 0.6858 | <i>l</i> | 0.7656 | 0.7562 | <i>l</i> | 0.4859 | 0.4800 |
| <i>m</i> | -0.2729 | -0.2860 | <i>m</i> | -0.3102 | -0.3235 | <i>m</i> | -0.0809 | -0.0984 |
| <i>n</i> | 0.6723 | 0.6693 | <i>n</i> | 0.5637 | 0.5688 | <i>n</i> | 0.8703 | 0.8717 |
| <i>p</i> | 7.2402 | 7.1473 | <i>p</i> | 6.6161 | 6.5763 | <i>p</i> | 4.5190 | 4.4404 |
| | Deviation (Å) | | | Deviation (Å) | | | Deviation (Å) | |
| C(1) | -0.005 | 0.006 | C(7) | 0.000 | 0.000 | C(12) | 0.009 | 0.008 |
| C(2) | 0.012 | -0.004 | O(8) | 0.000 | 0.000 | C(13) | -0.009 | -0.008 |
| C(3) | -0.004 | -0.002 | O(9) | 0.000 | 0.000 | C(15) | 0.009 | 0.008 |
| C(4) | -0.011 | 0.004 | | | | C(16) | -0.009 | -0.008 |
| C(5) | 0.018 | -0.002 | | | | | | |
| C(6) | -0.011 | -0.003 | | | | | | |
| | Distance from the above plane (Å) | | | Distance from the above plane (Å) | | | Distance from the above plane (Å) | |
| X(10) | 0.031 | -0.004 | N(11) | 0.660 | 0.715 | | | |
| C(7) | -0.006 | 0.010 | C(14) | -0.691 | -0.710 | | | |
| O(8) | 0.155 | 0.153 | | | | | | |
| O(9) | -0.153 | -0.133 | | | | | | |

(b) Dihedral angle between the planes (1) and (2): *p*-bromo compound: 7.9°; *p*-chloro compound: 7.3°.

Table 9. *Intermolecular distances with their e.s.d.'s in parentheses*

| From molecule I | To atom | Of molecule | Translation | <i>p</i> -Bromo compound (X=Br) | <i>p</i> -Chloro compound (X=Cl) |
|-------------------------------------|---------|-------------|-------------|---------------------------------|----------------------------------|
| (a) Hydrogen bonds | | | | | |
| O(8) | N(11) | IV | 0 0 0 | 2.687 (8) Å | 2.674 (10) Å |
| O(9) | N(11) | I | 0 0 0 | 2.762 (9) | 2.722 (11) |
| (b) Other distances less than 3.6 Å | | | | | |
| X(10) | C(14) | II | 0 0 1 | 3.574 (9) Å | 3.459 (11) Å |
| O(8) | C(12) | IV | 0 0 0 | 3.462 (9) | 3.466 (12) |
| O(8) | C(16) | IV | 0 0 0 | 3.479 (10) | 3.431 (12) |
| O(9) | C(12) | I | 0 0 0 | 3.367 (11) | 3.387 (13) |
| O(9) | C(12) | IV | 0 0 0 | 3.426 (9) | 3.443 (12) |
| O(9) | C(16) | IV | 0 0 0 | 3.551 (12) | 3.533 (12) |
| O(9) | N(11) | IV | 0 0 0 | 3.275 (9) | 3.318 (10) |
| O(9) | C(16) | V | 1 0 1 | 3.473 (11) | 3.461 (12) |
| C(6) | C(13) | VIII | 0 0 1 | 3.556 (13) | 3.532 (15) |
| C(7) | N(11) | IV | 0 0 0 | 3.365 (10) | 3.345 (12) |

Key to molecules

I: x, y, z
V: $-x, -y, -z$

II: $\frac{1}{2} + x, \frac{1}{2} - y, -z$
VIII: $\frac{1}{2} + x, y, \frac{1}{2} - z$

IV: $\frac{1}{2} - x, -y, \frac{1}{2} + z$

$x, y,$ and z are the fractional coordinates of atoms given in Table 2.

The distances from the plane (3) through C(12), C(13), C(15) and C(16) to the atoms N(11) and C(14) are shown in Table 8. In either compound, the atom N(11) deviates upward from the plane (3), while the atom C(14) deviates downward from the plane by almost the same distance. Thus, the piperidine ring takes a normal chair form.

The intermolecular distances less than 3.6 Å are listed in Table 9, and some of these are shown in Fig. 3. All the intermolecular contacts except for the two $N^+ - H \cdots O^-$ hydrogen bonds correspond to normal van der Waals distances.

The cell dimensions of the present two compounds are very similar, but the lattice constant b for the p -bromo compound (27.30 Å) is significantly greater than that for the p -chloro compound (26.37 Å). It can be shown that the contact between X(10) of molecule I(000) and C(14) of molecule II(001) is responsible for this difference.

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Structure des Orthofluoroberyllates de Lithium $M\text{LiBeF}_4$

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The structures of the three orthofluoroberyllates, KLiBeF_4 (hexagonal system, space group $P6_3$, $Z=2$), $\text{NH}_4\text{LiBeF}_4$ (orthorhombic system, space group $Pc2_1n$, $Z=4$) and CsLiBeF_4 (monoclinic system, space group $P2_1/n$, $Z=4$) have been studied by neutron diffraction. For the three compounds, parameters for the different ions and interatomic distances are tabulated. This work shows how the introduction of the ions NH_4^+ and Cs^+ modifies the tridymite structure of KLiBeF_4 .

Introduction

Dans une précédente note (Le Roy & Aléonard, 1970), nous avons signalé l'existence de la série d'orthofluoroberyllates $M\text{LiBeF}_4$ avec $M = \text{K}, \text{Rb}, \text{Tl}, \text{NH}_4$ et Cs . Nous avons donné leurs constantes de mailles et leur groupe spatial:

- Les orthofluoroberyllates de K, Rb et Tl cristallisent dans le système hexagonal (groupe spatial $P6_3$, $Z=2$) avec a variant de 5,07 à 5,22 Å et c de 8,56 à 8,76 Å.
- Le composé de l'ammonium a une maille ortho-

rhombique pseudo-hexagonale (groupe spatial $Pc2_1n$, $Z=4$), dont les constantes sont reliées aux précédentes par:

$$\begin{aligned} a_{\text{orth}} &\neq a_{\text{hex}} \cdot \sqrt{3} \\ b_{\text{orth}} &\neq b_{\text{hex}} \\ c_{\text{orth}} &= c_{\text{hex}} \end{aligned}$$

- Le sel de césium a une maille monoclinique (groupe spatial $P2_1/n$, $Z=4$), analogue à la précédente, mais avec un angle γ légèrement inférieur à 90° .