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

### References

- ASHIDA, T. (1967). The Universal Crystallographic Computing System (I), p. 65. Japanese Crystallographic Association.
- CHIBA, A., UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). Acta Cryst. 22, 863.
- COREY, R. B. & PAULING, L. (1953). Proc. Roy. Soc. B141, 10.
- Dow, J., JENSEN, L. H., MAZUMDAR, S., SRINIVASAN, R. & RAMACHANDRAN, G. N. (1970). Acta Cryst. B26, 1662. International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- KARLE, I. L. & KARLE, J. (1964). Acta Cryst. 17, 835.
- MARSH, R. E. & DONOHUE, J. (1967). Advanc. Protein Chem. 22, 235.
- NAGANATHAN, P. S. & VENKATESAN, K. (1971). Acta Cryst. B27, 1079.
- SUNDARALINGAM, M. & PUTKEY, E. (1970). Acta Cryst. B26, 790.
- VAUGHAN, P. & DONOHUE, J. (1952). Acta Cryst. 5, 530.
- WRIGHT, D. A. & MARSH, R. E. (1962). Acta Cryst. 15, 54.

Acta Cryst. (1972). B28, 1374

# 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, BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H.C<sub>5</sub>H<sub>11</sub>N, and with *p*-chlorobenzoic acid, ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H.C<sub>5</sub>H<sub>11</sub>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 N<sup>+</sup>-H···O<sup>-</sup> hydrogen bonds. The N<sup>+</sup>-H···O<sup>-</sup> 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 1385–1375 cm<sup>-1</sup> compared with the values of 1427–1406 cm<sup>-1</sup> 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  $0.12 \times 0.18$  mm and  $0.10 \times 0.15$  mm were used for the X-ray analysis, the former for *a* axis photographs and the latter for *c* axis photographs. Using 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  $\mu R$  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 zerolayer Weissenberg photographs of 0kl and hk0 using the reflexions higher than  $\theta = 50^{\circ}$  and (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  $0.21 \times 0.29$  mm and  $0.14 \times 0.20$  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 threedimensional Patterson map revealed all sixteen nonhydrogen 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 blockdiagonal least-squares methods, first assuming isotropic and then anisotropic thermal motion. Unit weight was given to all the observed reflexions. The Rindex 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 Å<sup>2</sup>, were introduced. However, the parameters of the hydrogen atoms were not refined. From this stage of refinement, the following weighting scheme was adopted:

> $Vw = 0.0, \quad \text{if } F_o \le F_{\min} \ (=4.0),$   $Vw = 1.0, \quad \text{if } F_{\min} < F_o \le F_{\max} \ (=54.0),$  $Vw = F_{\max}/F_o, \quad \text{if } F_o > F_{\max}.$

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  $0.02\sigma$  and  $0.25\sigma$  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

	a	bl	le	1.	Crystal	data
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and

	$BrC_6H_4CO_2H_1C_5H_{11}N$	$ClC_6H_4CO_2H_1C_5H_{11}N$
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	$26.37 \pm 0.03$
C	$9.04 \pm 0.01$	$9.01 \pm 0.02$
$D_r$	$1.44 \text{ g.cm}^{-3}$	1.27 g.cm <sup>-3</sup>
$D_m^*$	1.44 (25°C)	1·27 (25°C)
Z	8	8
Absent spectra	hk0 when h is odd	hk0 when $h$ is odd
	0kl when k is odd	0kl when k is odd
	h0l when l is odd	h0l when l is odd
Space group	Pbca	Pbca
$\mu$ for Cu K $\alpha$	45.9 cm <sup>-1</sup>	25.7 cm <sup>-1</sup>

\* 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<sup>-3</sup>. 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> -Bror	no compound	(X = Br)	<i>p</i> -Chloro compound ( $X = Cl$ )				
	x	у	Ζ	x	У	Z		
<b>C</b> (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)		
<b>C</b> (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)		
<b>C</b> (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-Bron	mo compound					
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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)
<b>C</b> (16)	132 (10)	18 (1)	112 (11)	28 (6)	26 (19)	-8 (6)
(b) p-Chlo	oro compound					
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
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)

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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 e.Å<sup>-3</sup> starting at 1 e.Å<sup>-3</sup> for C, N and O atoms and at intervals of 5 e.Å<sup>-3</sup> starting at 1 e.Å<sup>-3</sup> for the Br atom. (b) Composite of the final difference synthesis for the p-bromo compound. Contours are at intervals of 0·1 e.Å<sup>-3</sup> starting at 0·2 e.Å<sup>-3</sup>.

region exceeding  $0.2 \text{ e.}\text{Å}^{-3}$  except for one peak of 0.7e.Å<sup>-3</sup>. 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 Å<sup>2</sup>, 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-bromocompound obtained from the final difference map[Fig. 1(b)]

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

	x	У	Z
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  $0.3\sigma$  and  $0.6\sigma$  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),

# $BrC_6H_4CO_2H.C_5H_{11}N$ AND $ClC_6H_4CO_2H.C_5H_{11}N$

# Table 5. Observed and calculated structure factors ( $\times 10$ )

(a) The *p*-bromo compound.

Unobserved reflexions are marked with an asterisk.

K F0 FC	K PO PC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC
H=0, L=0 2 903 -855 4 605 766 6 1490 -1534 8 342 -256	17 -• -18 18 126 98 19 72 -43 20 108 -92 21 72 65	7 795 827 8	14 334 -334 15 836 -766 16 474 490 17 576 553 18 297 -282	12 149 -157 13 74 48 14 111 81 15 74 -73 16 288 -244	7 45153 8 248 -238 9 370 537 10 377 341 11 745 -752	4 -* -67 5 129 -152 6 -* 43 7 -* 83	7 75 106 8 262 -257 9	13 183 -191 16 106 -132 15 259 270 16 115 138	12 -* 15 13 188 175 14 245 -223 15 348 -308 16 179 177	H=1, L=7 1 -0 - 12 2 -0 129 3 145 153 4 145 153	12 - 41 13 157 -160 14 - 95 15 12) 99 16 120 1+1
10 136 -82 12 1924 -2073 14 858 956 16 957 -1003	22 72 48 23 90 -67 H=12, L=0	12 61 68 1., 271 -257 14 288 284 15 70 -79	19 381 -356 20	17 195 181 18 269 236 19 316 - 320 20 -* -48	12 120 143 13 - 37 14 110 110 15 442 -419	9 - 63 10 92 - 116 11 92 113 12 - 49	12 262 -266 13 262 229 14 178 176 15 403 -396	18 77 -102 19 77 77 20 115 -109 21	17 339 322 18 - 67 19 104 -119 20 113 72	5 -• 35 6 212 258 7 145 111 8 -• 20	H=3, 1=0 0
18 1039 1003 20 1111 -1050 22 145 138 24 136 113 26 -12	1 63 -45 258 3 - 27 4 - 72	17 157 -179 18 70 82 19 201 -207 20 -4 -43	24 130 150 25 93 -80 26 -* 48 27 -* 39	22 74 81 23 130 -154 25 65 62	17 36 18 221 - 231 19	13 66 14 138 166 15 33 16 83 - 111 17 71	17 234 233 1891 19 34 -114 208	22 211 190 23 -* -62 24 125 -116 25 -* 0 26 144 149	H=2, L=6 0 132 -119	y 145 -171 10 145 159 11 116 128 12	227 3 83 86 23 5 56 75
28 199 139 30 90 -54 32 298 227 34 108 -84	5 90 -84 6 -* -28 7 -* 19 8 -* 7	21 -• 11 22 -• 2 23 -• -39 24 70 -42	28 33 29 65 - 71 30 74 79 31 93 86	26 65 -48 27 111 -126 28 65 45	21 110 128 22 .* .45 23 147 174 24 .* .11 25 .* .11	18 101 96 H=9 1=3 165	21 241 269 22 159 -172 23 75 -96 2- 112 109	27 48 -56 28 67 -92 29 48 71 30 48 69	1 292 -300 2 122 -163 3 6-9 561 4 151 173	116 135 15 -• -32 16 -• -67 17 1-5 -17-	6 21-1 7 63 23
H=2, L=0 0 253 325 1 1057 -1090 2 3140 -2248	10 63 56 11 -• 22 12 -• -18 13 117 80	26 -* 10 27 122 -121 28 70 73	H=2, L=2 0 2182 -2206 1 1541 1556 2 251 -228	0 158 162 1 121 139 2 279 -282 3 -4 13	26 20 27 137 100 H=3, L=3	2 2 3	26 47 -65 27 56 56 28 141 146	H=4, 1=5 1 144 132 2 77 -77 3 336 -317	6 132 -1-3 7 160 -159 8 -*6 9 -* 5-	19 96 111 H=2, L=7 1 - 9 93	1 52 2 185 -2- 3 63 -91
3 3305 3369 4 434 446 5 461 -463 6 217 224	14 108 87 15 108 -77 H=0, L=1	H=6, L=1 1 445 426 2 271 258 3 411 - 366	3 22 38 -2297 4 65 48 5 186 162 6 243 213 7 101 115	4 260 264 5 74 -69 6 121 -148 7 - 58	1 322 293 2 515 476 3 478 -478 4 1012 -917 5 166 188	7 83 126 8 -* -22 9 110 -122 10 138 -166	H=6, L=4 0 -* 64 1 -* -21 2 -* 69	77 86 5 144 -157 6 519 -466 7 - 39	10 132 1+3 11 122 -104 12 -265 13 264 265	2 -* 18 3 uu3 343 5 145 -162	5 -• 6' 6 -• 6 7 -• -• 8 63 7:
7 1002 1081 8 -* 29 9 605 668 10 813 789 11 226 -276	2 192 103 4 585 673 6 934 -1115 8 1843 2030 10 1825 -1688	5 376 364 6 428 421 7 349 -338 8 734 -675	6 232 192 9 297 -306 10 56 12 11 130 139	9 74 -74 10 - 54 11 297 273 12 130 -113	6 552 573 7 497 -485 8 1030 -946 9 359 352	11 101 144 HeO, Lei 0 899 896 2 762 295	4 103 -131 5 131 132 6 -5	8 106 -13. 9 -• 37 10 259 -270 11 115 -116 12 125 -135	15 26232 16 151 -165 17 405 373 18 85 83	7 279 275 9 279 275 9 279 -276 10 116 168	10 - 11 11 56 5- 12 - 21 13 56 -102
12 397 -445 13 795 859 14 470 484 15 650 -739	12 550 623 14 1022 -961 16 280 273 18 192 168	9 411 407 10 419 393 11 515 -518 12 323 -327	12 349 403 13 251 -246 14 279 -296 15 919 921 16 65 52	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 616 608 11 369 -603 12 791 -789 13 221 248 16 -4 -15	4 356 266 6 1+1 112 8 103 -67 10 525 -454	8 112 104 9 14 1047 1146	13 87 -89 14 135 -174 15 173 193 16 202 234	H=3, L=6 0 668 -605 1 188 199	11 116 102 12 116 133 13 279 -279 14 -* -16	1
17 668 687 18 99 129 19 822 -855 20 63 86	22 192 169 24 341 -302 26 323 261 28 175 -166	14 183 178 15 271 -301 16 157 165 17 183 193	17 636 - 650 18 139 -171 19 566 605 20 223 226	18 149 155 19 -* -18 20 139 -117 21 -* 39	15 110 -152 16 -* 24 17 322 331 18 129 180 19 11	12 147 -214 14 290 -240 16 -* 15 18 75 106 20 -* -38	13 - 66 14 - 19 15 150 166	18 317 346 19 - 31 20 - 14 21 77 -85	3 141 -143 4 292 -298 5 94 99 6 386 371	16 116 -84 17 145 -175 18 -• -3 19 -• -74	14 - 4 20 56 - 44 H=5, 1 - 4
21 145 205 22 289 342 23 587 -618 24 217 231 25 63 91	H=1, L=1 1 192 -172 2 19 34	19 87 -107 20 192 166 21 66 22 265 -186	22 - 57 23 149 166 24 - 70 25 93 -94	23 65 -55 24 74 -109 25 121 141	20 322 288 21	22 112 101 24 159 -149 H=1, 1=4 0 1171 1120	N=7 1=4 0 176 -220 196 2 412 429 376	H=5, L=5 1 135 -139 2 -* -61	8 57 -103 9 188 292 1) 75 -6- 11 -* 6	H=3, 1=7 1	H=6, L=5 0 165 125
26 199 -209 27 126 129 28 99 101 29 126 -115 30 108 -109	3 358 346 4 917 987 5 314 351 6 480 -525 7 79 -115	23 114 146 24 245 208 25 61 -67 26 166 -150 27 114 115	26 111 117 27 130 -107 28 139 -100 29 -* -15 30 -* 26	0 344 - 324 1 111 - 139 2 93 - 114 3 176 211	25 74 -86 26 138 -140 27 - 49 28 110 126	1 1161 1132 2 731 - 707 3 53 500 - 880 795 5 104- 957	4 103 -147 5 290 317 6 - 28 7 187 212	3 305 326 5 384 - 371 6 77 56 7 240 652	12 311 266 13 85 76 14 262 -256 15 57 63 16 113 109	2 106 121 3 - 2- 4 308 -262 5 - 36 5 308 27-	2 56 -63 3 -8 28 8 -18 5 74 -85
31 163 146 H=4, 1=0 0 1734 -1702	8 699 769 9 541 560 10 655 608 11 87 -101	28 79 69 29 96 -112 H-7, L=1	31 93 -82 32 84 -71 H=3, L=2 0 316 -140	4 260 -252 5 260 -270 6 241 215 7 167 -171	29 74 -111 30 46 -62 31 64 73	6 403 - 378 7 540 - 553 8 169 - 151 9 - 4 - 19	10 - 50 11 112 - 163	106 -1-9 327 -315 10 15- 165 11 259 271	17 57 - AU 16 179 - 201 19 - 26 20 168 215 11 11 15	7 222 -237 5 77 -45 9 58 92 10 125 165 11 - 10	7 . •
2 957 813 3 858 736 4 1219 -1250 5 370 -347	13 -* -11 14 271 -279 15 402 -371 16 175 -170	2 271 250 3 -* -50 4 61 -66 5 140 -179	1 585 538 2 938 864 3 334 267 4 1049 - 978	9 74 68 10 176 193 11 -	1 120 111 2 350 - 367 3 175 156 - 661 701	10 553 539 12 159 -181 13 609 -5%6 14 467 505	13 73 102 14 206 -210 15 -• 33 16 112 1+3 17 -• 58	13 327 -334 14 87 110 15 87 117 16 - 72	H=4, L=6 0 226 -210 1 169 -159	12 56 -78 13 135 139 14 135 151 15 - 49	12 56 -65 13 130 - 65 Hara, 1-9
6 497 486 7 614 -585 8 397 399 9 -* 49 10 475 379	17 157 -168 18 61 -65 19 87 -43 20 192 -201 21 -9 61	6 255 252 7	5 269 260 6 492 441 7 5 8 74 - 86 9 316 273	14 - 4 - 18 15 274 - 236 16 74 84 17 74 84	7 245 -293 8 396 416 9 -81	15 506 473 16 365 - 374 17 468 - 462 18 468 468	18 141 -197 19 -• -33 20 169 162	17 -• -26 18 -• 60 19 211 -205 20 -• -50 21 87 87	2 65 122 3 198 228 17 5 132 -154 6 185 225	16 87 -42 17 - 69 15 106 -112 19 - 10 20 - 21	2 103 104 4 -* -11 6 93 6* 6 121 -1 11 56 73
11 336 -288 12 226 261 13 397 378 16 154 -167	22 - 60 23 1+0 151 24 70 -70 25 131 -133	11 -***1 12 210 -203 13 -***56 14 -***66 14 -***66	10 139 -170 11 223 -203 12 +36 +64 13 -4 6	16 - • - 26 19 130 - 114 20 65 52 21 -• 29 22 111 - 105	10 405 -418 11 221 -212 12 258 255 13 156 150 14 331 - 59	20 169 -192 21 328 -333 2252 23 - 86	1 37 2 50 3 7	22 1 23 125 - 126 24 15 25 115 1-2	7 - 73 8 - 5 83 9 - 9 - 39 10 75 - 92	Rea, 1=7 1 .* 2 2 .* 76	12 149 -136 H=1, 149 1 -4 13
16 903 876 17 190 159 18 506 -468 19 379 -318	27 105 43 H=2, L=1 1 611 -574	16 54 17 185 189 14 - 24 14 16	15 74 106 16 316 312 17 -4 -22 18 464 -439	21 21 2- 93 63 H=9, L=2	15 -• 74 16 -• 22 17 129 122 18 101 -113 19 107 121	24 197 -205 255 2613 2718 28	5 75 -117 6 -• -21 7 75 -116 8 112 1-9	27 67 -65 H=6, L=5 1 -* 62	12 65 61 13 179 201 14 160 -175 15 160 -201	5 193 -227 5 193 -227 63 -61 7 77 -90	3 15166 H=2, 1=9 1 -4 -+5
20 289 285 21 271 238 22 434 -410 23 99 108 24 -* -32	2 969 801 3 751 643 4 391 -338 5 1162 -1255 6 764 -768	20 111 123 21 -• -9 22 70 -65 23 61 -55 24 -• 37	20 279 275 21 251 -256 22 56 -53 23 -* -36	1 176 -163 2 -• -21 3 -• -9 4 74 99	20 74 -85 21 74 -72 22 83 79	29 103 102 3017 31 8100	H=9, L== 0 =	2 96 -108 3 106 146 4 -49 5 221 243 6 529 -433	16 -* 5 17 57 e3 18 -* 8 19 -* -+3 20 10- 131	* 16179 9 1616 10 116 116 11 *7 96 12 16176	2 -* 66 3 112 -1+1 4 -* 16 5 279 2+5 6 -* -19
25 -* 10 26 163 -202 27 244 226 28 -* 0 29 126 -100	7 162+ 1775 8 515 554 9 107+ -1205 10 +2* 395 11 1581 1646	25 - 22 26 54 H=8, L=1 1 71	24 119 158 25 149 -128 26 -* 55 27 56 74 28 111 -106	5 111 -114 6 -6 -6 7 -6 -20 5 156 -125 9 -60	1 - 4 26 $2 7_{-} - 16$ 3 138 - 147 4 212 - 248	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 103 -130 4 103 -163 5 -• 79 6 -• 2	7 221 215 8 173 178 9 202 -229 10 183 190	H=5, L=6 0 132 158 1 320 334	13 F7 69 14 F7 212 15 -* 16 16 -* F7 17 72 55	7
30 -* 10 31 99 89 32 45 -41	12 192 183 13 751 -806 14 376 -352 15 227 234	2 x7 123 3 262 -267 - 166 187 5 2xh 305	29 -0 -50 30 102 93 31 -0 29 32 56 -62	10 -* -1 11 -* 8 12 -* 3a 13 -* 30 1- 7a 80	5 95-4 1085 6 230 -221 7 745 -776 8 30-4 311 9 561 586	4 225 - 205 5 272 212 6 215 196 7 - 31 407 8 -• 75	5 103 123 9 -9 9 10 -* -26 11 103 129	12 67 7'; 13 125 -137 14 77 -5 15 250 -233	3 207 -222 5 85 96 6 85 96	14 106 -144 19 55 68 20 -4 -25 21 58 102	H=3, 1=4 1 =
0 804 - 626 1 235 241 2 668 676 3 668 - 660	17 166 -165 16 271 303 19 227 -238 20 157 -156	7 210 -219 * 140 150 9 31- 35- 10 70 -75	Hem, 1+2 0 1291 1264 1 966 946 2 74 44	15 -14 -5h 16 93 -86 17 111 112 15 -14 1	10 138 135 11 350 - 546 12 540 540 13 366 394	9 215 192 10 -* -54 11 84 108 12 66 76 13 -* 48	H=0, L=5 2 500 475 3 317 -257	16 - 50 17 115 -159 18 115 131 19 58 - 9 20 77 - 52	7 160 -152 8 - 3 9 - 37 10 - 3 11 - 4	22 54 - 59 23 56 - 60 24 58 t3 H=5, 1=7	5 - 46 6 - 49 7 - 15 6 - 45
406 378 6 172 173 7 479 -445 9 54 50	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11 906 - 327 12 - 7 11 - 7 14 - 7 19 14 - 17 15 - 127 14	4 975 954 5 93 -67 6 724 -706 7 -4 -75	20 - 0 11 21 93 66 H=10, 1=2	15 451 -505 16 - 59 17 366 -371 1- 1-7 -167	14 -* 35 15 -* -44 16 75 48 17 122 -133	6 625 576 8 173 166 10 - 19 12 202 -183	21 27 4- H=7, 1=5 1 -# -43	12 .* 75 13 151 -161 14 .* -10 15 104 118 18 .* 88	1 16 2	4 -* +1 10 75 71 11 75 -+1 12 -* -17 13 56 -65
9 136 125 10 596 -536 11 108 93 12 397 373	26 96 10 27 253 -266 28 -8 -28 29 114 139	16 17', 167 17 -* -22 1* 122 -124 19 1*1 131 20 -* -9	+ 130 -132 + 390 -354 10 -4 -54 11 906 315 12 906 -343	1 -	19 129 129 20 -9 56 21 101 -95 22 63 -99 23 256 247	19 234 -233 20 -* -10 21 -* 61 22 141 163	16 27 18 308 - 318 20 57 22 115 - 133	3 -0 52 4 135 -124 5 115 -163 6 250 288	17 188 -210 18 -9 -7 19 75 11- 20 94 -98	6 -4 43 7 -4 -63 8 77 -91 9 173 180	14 56 -64 Han, 149
14 271 -244 15 325 344 16 370 369 17	H=1, 1=1 1 495 480 2 882 -785 3 122 -158	21 210 -159 22 -* -36 21 166 1+3 24 -* -12	13 511 -503 14 65 54 15 158 155 16 371 -365 17 279 -272	5 -4 25 6 -4 47 7 -4 -65 5 -4 -63 7 -4 -63	24	H=3. L=4 O 431 426 I 525 -485 2 1864 -1638	24 144 147 26 87 67 H=1, 1=5 1 327 302	7 - 93 8 221 - 234 9 - 84 10 240 260 11 - 40	H=6, L=6 0 132 -119 1 122 127 2 57 65	10 96 -112 11 -9 -68 12 -9 19 13 -9 46 14 -9 46	3
10 307 - 305 19 307 336 20 126 141 21 181 - 190 22 -* - 31	5 838 -842 6 227 -249 7 175 -158 8 341 392	26 44 59 27 61 70 H=9, 1-1	15 269 286 19 297 285 20 316 - 306 21 - 0	10 -* -30 11 74 -108 12 84 83 13 -* -10	H=6, L=3 1 2+8 -212 2 258 -255 3 74 57	3 75 -62 4 899 845 5 197 -236 6 66 -74	2 58 66 3 615 -575 4 461 443 5 653 590	12 192 -199 13 -• 70 14 -• 77 15 -• -29	3 -• -30 4 57 99 5 57 -62 6 -• 54	15 -4 -21 16 87 102 17 58 76	7 103 -140 8 5a 97 9 -• 23 10 8a -112
23 226 242 24 154 -143 25 117 -145 26 72 68	9 664 -644 10 961 -953 11 271 270 12 -6 10 11 175 157	1 - 26 2 - 6 - 64 1 70 92 4 201 - 175 5 122 131	23 176 191 23 -* 1 24 111 -121 25 121 121 26 139 166	16 93 -112 15 -* e8 16 -* 41 17 -* 35 18 56 -46	5 101 -96 6 138 -135 7 -05 359 8 265 250	7 362 373 8 75 107 9 122 -152 10 309 311 11 75 -76	7 596 -552 8 529 489 9 586 539 10 298 -273	17 106 132 18 -* 15 19 67 -76 20 67 64	8 141 -173 9 122 142 10 94 -88 11 -• 7	1 96 -100 2 -9 10 3 77 -98 4 154 -131	H=5, L=9 34 H=6, L=9 ,
28 72 -59 29 99 -119 30 136 141	14 61 -75 15 376 362 16 79 74 17 288 267	6 -4 11 7 96 -99 8 79 -95 9 70 58	27 74 -76 28 65 52 29 139 123 30 -9 -23 11 76 -85	19 65 71 H=0, L=1 2 64 43	9 184 -160 10 276 -269 11 313 305 12 230 224 11 -9 29	12 468 -452 13 131 166 14 759 719 15 75 85 16 665 -605	11 384 - 371 12 394 413 13 288 298 14 211 - 225 15 163 - 202	21 58 92 22 58 -75 23 58 -64 He8, L=5	H=7, 1=6 0 151 177 1 -* 3	5 194 135 6 193 168 7 -9 -4 8 193 -179 9 183 185	2 <u>2</u> 2 3 % 84 4 - 10 5 - 1
H=8, L=0 0 163 187 1 117 113 2 72 -81 3 425 -417	19 192 211 20 253 -256 21 -* -20 22 297 275	H=10, 1=1 1	12 46 25 M=5, 2=2 0	6 543 576 8 1297 - 1249 10 - 60 12 763 - 746	14 - 33 15 63 13 16 138 -111 17 166 -120	17 -* 58 18 515 480 19 122 -154 20 112 -159	16 96 112 17 - 56 18 - 56 19 77 68	1 -* 63 2 -* 97 3 -* 11 4 106 150	2 85 -102 3 - 40 4 104 115 5 85 91 4 - 9 + 50	10 -* +1 11 -• -33 12 -* 15 13 96 135	6 56 -57 Nan, Lain 0 200 -174 2 200 -189
4 172 164 5 90 75 6 108 -106 7 72 -70 8 165 166	23 166 -162 H=4, 1=1 1 -4 12 2 271 243	2 70 -65 123 6	2 130 -120 3 297 -298 4 .* .26 5 297 293	16 120 125 18 83 68 20 368 371 22 129 -61	19 .• 10 20 101 -105 21 .• .49 22 55 82	22 94 109 23 94 -109 24 - 29 25 56 90	21 135 -121 22 56 23 221 163 24 163 -130	6 - 65 7 - 56 8 163 196	7 - 42 8 - 10 9 19 10 20	15 58 -48 16 -9 -5 17 -9 -18 18 116 -109	4 144 137 6 -0 -23 8 -0 37 10 86 79
9 145 -167 10 271 -260 11 108 84 12 - 10	3 186 365 6 917 -917 5 681 -637 6 847 823	7 .• 29 8 166 156 9 70 68	6 121 -139 7 206 -218 8 306 302 9 86 -85	H=1, l=3 1 653 -630 2 414 407 3 727 716	23	26 94 -85 27 56 -82 28 56 43 29 -4 3 30 84 -96	25 115 -111 26 96 114 H=2, L=5 1 413 -353	H=9, L=5 1 -* 61 2 -* -4 3 -* -26 4 96 -108	12 104 -107 13 85 -98 14 -9 48 15 94 116	20 58 50 21 87 -76 H=0, L=8	14 48 65 16 72 -73 Hel, 1=10
15 253 209 16 181 -172 17 235 -226	8 1205 -1191 9 786 -779 10 943 947 11 803 731	0 1940 - 1934 2 1829 1-21 4 789 - 80L 6 445 472	11 269 263 12 33 13 374 -296 14 84 -109	5 791 -802 5 791 -802 6 791 777 7 911 956	H=7, L=3 1 136 129 2 83 -79	He4, Le4 0 244 263 1 159 -163	2 269 236 3 240 -215 6 58 -75 5 77 69	5 -4 38 6 -4 47 7 -4 -45 8 -4 -46 9 37 6	16 36 17 58 18 75 82 19	0 509 -437 2 509 422 4 139 -146 6 130 150 8 -9 -31	i 200 201
18 108 75 19 145 141 20 136 -129 21 -* -30 22 199 177	12 865 -833 13 -9 57 14 533 561 15 105 -146 16 61 -78	6 385 -341 10 334 -341 12 965 939 14 297 -309 16 808 779	16 76 86 17 399 -403 18 - 62 19 186 168	9 616 -656 10 837 839 11 506 529 12 258 -300	• ••2 •62 • •93 • 136 •114 7 360 •375	3 -* 38 4 440 -419 5 -* 48 6 -* 19	7	10 - 16 11 57 - 117 H=0, L=6	H=8, L=6 0 -* -84 1 -* 13	10 204 -186 12 130 112 14 232 -219 16 259 221	1 120 -1+t
23 -* 34 24 -* -39 25 45 -38 26 235 168 27 53 -57	17 166 177 18 -• 30 19 218 -202 20 -• 32 21 358 3••	18 353 - 368 20 446 450 22 808 -727 24 158 -151 26 -71	20	16 1/1 130 16 1/1 130 17 46	4 32 10 451 -459 11 53 45 12 202 225	7 159 -168 8 94 109 9 75 -76 10 96 108 11 112 -120	11 106 107 12 183 189 13 164 182 16 -* 13 15 202 212	2 198 -144 4 216 184 6 593 -476 8 160 161	3 -0 -109 4 104 130 Re9, 105	20 102 93	N=4, L=10 0 -9 22 1 -9 55
H-10, L-0 0 406 J46 1 - 49	22 131 -120 23 271 -238 24 332 330 25 -4 39 26 251 -254	28 84 -71 30 139 110 32 74 -52 H=1, 1=2	25 74 42 26 .4 33 27 65 18 28 111 -97 29 65 64	18 53 90 19 257 -243 20 156 153 21 83 76 22 156 -151	10 103 15 166 195 16 12 17 12	12 -* 7 13 103 -120 14 103 132 15 -* -74 16 159 163	16 - 26 17 - 27 18 77 - 107 19 106 - 134 20 21	10 282 268 12 235 -249 14 320 288 16 160 -137 18 132 138	1	2 139 203 3 139 -187 4 -25 5 -4 67	H=5, L=10 0 -* 21
3 165 113 4 63 20 5 63 96 6 63 68	27	0 1216 1291 1 1959 -2220 2 1319 1652 3 520 529 6 1105 -1213	H=6, 1=2 0 418 198 1 223 -237 2 212 -220	23 2*5 -22* 24 .* 77 25 258 208 26 234 -206 27 =3 -77	19 184 147 20 101 -110 21 110 -122 22 138 154	17	21 144 -165 H=3, L=5 1 58 -44 2 356 -310	20 273 -277 H=1, L=6 0 207 197 1 489 -437	H=0 L=7 2 510 -472	Haz, Lat Naz, Lat 1 139 146	H=0 L=1
8 108 111 9 +1 10	32 70 61 H=5, L=1 1 140 -145	5 947 -949 6 112 87 7 269 296 8 288 -274 9 167 144	3 545 490 4 297 245 5 204 205 6 91 -133 7 669 617	28 92 97 9-2, 1-3 1 92 -91 2 331 -259	23 -4 58 24 138 -123 25 -4 -38 26 64 65	22 122 -140 H=5, L=4 0 189 119 1 474 -404	3 96 123 4 413 412 5 279 -269 6 529 -466 7 144 354	2 593 577 3 527 485 4 254 -285 5 424 -397 6 113 159	6 453 -403 8 87 63 10 684 -540 12 -9 2 16 -9 -35	1 167 -189 1 167 -189 2 171 5 259 283 - 38	4 - 24 4 - 34 8 - 34 10 74 - 70
13 25 14 63 55 15 5 16 108 91	3 87 67 4 114 -112 5 52 64 6 306 -310	10 316 -28 11 664 -680 12 43 132 13 646 630	8 251 -252 10 111 125 11 84 81	3 662 542 6 147 -145 5 570 506 6 331 314	K=8, [=]   .0 .19 ] .0 .55 ] .0 .[9	2 141 159 3 234 206 6 141 157 5 609 -653 6 -8 -42	8 490 420 9 365 - 354 10 750 - 638 11 231 243 12 269 282	7 - 17 8 160 -167 9 - 18 10 113 -110 11 188 -178	16 135 134 18 173 139 20 -4 73 22 193 149 26 116 -73	8 -• 82 9 -• 41 10 -• -103 11 -• 105	

## Table 5 (cont.)

#### (b) The *p*-chloro compound.

Unobserved reflexions are omitted.

K PO PC	K PO PC	1 10 15	K PO PC	K PO PC	K PO PC	K FO FC	K FO FC	K FO FC	K PO PC	K FO FC	K PO PC
			11111-00.00 MY1211112111.0.0.0.0.00.00 MY12121212121212121212121212121212121212			137 139 <td>איא אים אווייניייי אוויינייי אוויינייי אווייניטער איזיגעוויגעוויייי אווייניטער אוויין אוויייי אוויין אוויין אווי אווייני אווייניטער איזיגערער איזיגערער איזיגערער איזיגערער געער געערערגערער אוויין אווייערער אוויין אווייערערער איזיגערערער איזיגערערערערערערערערערערערערערערערערערערער</td> <td></td> <td>201</td> <td>He- John</td> <td></td>	איא אים אווייניייי אוויינייי אוויינייי אווייניטער איזיגעוויגעוויייי אווייניטער אוויין אוויייי אוויין אוויין אווי אווייני אווייניטער איזיגערער איזיגערער איזיגערער איזיגערער געער געערערגערער אוויין אווייערער אוויין אווייערערער איזיגערערער איזיגערערערערערערערערערערערערערערערערערערער		201	He- John	

Least-squares calculation (HBLS 4) by Okaya & Ashida (1967), and

Bond lengths and angles (RSDA 4) by Sakurai (1967).

### Description and discussion of the structure

Bond lengths and angles of the two compounds are given in Tables 6 and 7, together with standard deviations. The molecular geometry is illustrated in Fig. 2. The projections of the crystal structure along the c and a axes are shown in Fig. 3.

From Table 6 and Fig. 2 it may be seen that the structures of the present two compounds are isotypic.

The two hydrogen bonds of nearly equal length (cf. Figs. 2 and 3) link the nitrogen atom of piperidine with the carboxyl oxygen atoms to form a helical hydrogen bond chain, in which each oxygen atom accepts one

# Table 6. Bond lengths and e.s.d.'s (Å)

	<i>p</i> -Bromo	<i>p</i> -Chloro
	compound	compound
	(X=Br)	(X=Cl)
C(1) - C(2)	1.389 (11)	1.380 (14)
C(2) - C(3)	1.392 (12)	1.428 (14)
C(3) - C(4)	1.405 (14)	1.356 (14)
C(4) - C(5)	1.426 (14)	1.414 (15)
C(5) - C(6)	1.373(13)	1.384 (14)
C(6) - C(1)	1.414 (11)	1.406 (14)
C(1) - C(7)	1.514 (12)	1.520 (14)
C(7) - O(8)	1.281 (11)	1.238 (13)
C(7) - O(9)	1.255 (11)	1.277 (12)
C(4) - X(10)	1.910 (10)	1.735 (11)
N(11) - C(12)	1.478 (10)	1.539 (12)
N(11)-C(16)	1.544 (11)	1.526 (12)
C(12) - C(13)	1.543 (12)	1.515 (14)
C(13) - C(14)	1.526 (13)	1.529 (14)
C(14) - C(15)	1.529 (13)	1.552 (15)
C(15)–C(16)	1.531 (13)	1.536 (15)

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

	<i>p</i> -Bromo compound (X-Br)	<i>p</i> -Chloro compound
C(1) - C(2) - C(3)	123·4 (8) <sup>3</sup>	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  $N^+-H\cdots O^-$  hydrogen bonds are in the range of 2.8–2.9 Å (Pimentel & Mc-Clellan, 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, Nahringbauer (1967) has found in ammonium acetate four N<sup>+</sup>-H···O<sup>-</sup> 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<sup>+</sup>-H···O<sup>-</sup> hydrogen bonds shorter than 2·8 Å have been found in several cases, for example,  $\beta$ -glycylglycine (2·68 Å) by Hughes & Moore (1949), DL- $\alpha$ -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  $N^+-H\cdots O^-$ .

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 1.70Å. 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  $7.3^{\circ}$ . 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, refered to the axes a, b, c.

(b) Dihedral angle between the planes (1) and (2): p-bromo compound:  $7.9^{\circ}$ ; p-chloro compound:  $7.3^{\circ}$ .

	From molecule I	To atom	Of molecule	Trans- lation	<i>p</i> -Bromo compound (X=Br)	p-Chloro compound (X = Cl)
	(a) Hydroge	n bonds				
	O(8)	N(11)	IV	000	2·687 (8) Å	2·674 (10) Å
	O(9)	N(11)	I	000	2.762 (9)	2.722 (11)
	(b) Other dis	stances less	than 3·6 Å			
	X(10)	C(14)	II	001	3∙574 (9) Å	3·459 (11) Å
	O(8)	C(12)	IV	000	3.462 (9)	3.466 (12)
	O(8)	C(16)	IV	000	3.479 (10)	3.431 (12)
	O(9)	C(12)	Ι	000	3.367 (11)	3.387 (13)
	O(9)	C(12)	IV	000	3.426 (9)	3.443 (12)
	O(9)	C(16)	IV	000	3.551 (12)	3.533 (12)
	O(9)	N(11)	IV	000	3.275 (9)	3.318 (10)
	0(9)	C(16)	v	101	3.473 (11)	3.461 (12)
	C(6)	C(13)	VIII	001	3.556 (13)	3.532 (15)
	<b>C</b> (7)	N(11)	IV	000	3.365 (10)	3.345 (12)
Key to molecule	s					
I: $x, y, z$	;		II: $\frac{1}{2} + x$ , $\frac{1}{2} - \frac{1}{2}$	-y, -z	IV: $\frac{1}{2}$ -	$x_{1} - y_{1} + z_{2}$
$\mathbf{V}:\ -x,\ -y,\ -z$	·		VIII: $\frac{1}{2} + x$ ,	$y, \frac{1}{2}-z$	-	

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

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 pbromo 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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#### References

CRUICKSHANK, D. W. J., JONES, D. W. & WALKER, G. (1964). J. Chem. Soc. p. 1303.

- HANSON, H. H., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). Acta Cryst. 17, 1040.
- HIROKAWA, S., OHASHI, T. & NITTA, I. (1954). Acta Cryst. 7,87.
- HUGHES, E. W. & MOORE, W. J. (1949). J. Amer. Chem. Soc. 71, 2618.
- International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- KALYANI, V. & VIJAYAN, M. (1969). Acta Cryst. B25, 1281.
- KASHINO, S. (1967). Bull. Chem. Soc. Japan, 41, 248.
- KASHINO, S., KANEI. K. & HASEGAWA, S. (1972). To be published.
- MATHIESON, A. M. (1953). Acta Cryst. 6, 399.
- MILLS, H. H. & SPEAKMAN, J. C. (1963). J. Chem. Soc. p. 4355.
- NAHRINGBAUER, I. (1967). Acta Cryst. 23, 956.
- OKAYA, Y. & ASHIDA, T. (1967). HBLS 4, The Universal Crystallographic Computing System (I), p. 65. Japanese Crystallographic Association.
- PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). The Hydrogen Bond, p. 286. San Francisco and London: Freeman. Rérat, C. (1960). Acta Cryst. 13, 72.
- SAKURAI, T. (1967). RSDA 4, The Universal Crystallographic Computing System (I), p. 78. Japanese Crystallographic Association.
- SAKURAI, T. (1968). RSSFR 5, The UNICS News (I), p. 27. Japanese Crystallographic Association.
- SHRIVASTAVA, H. N. & SPEAKMAN, J. C. (1961). J. Chem. Soc. p. 1151.
- SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). Acta Cryst. 8, 157.

Acta Cryst. (1972). B28, 1383

# Structure des Orthofluoroberyllates de Lithium MLiBeF<sub>4</sub>

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## (Reçu le 5 novembre 1970)

The structures of the three orthofluoroberyllates, KLiBeF<sub>4</sub> (hexagonal system, space group  $P_{6_3}$ , Z=2), NH<sub>4</sub>LiBeF<sub>4</sub> (orthorhombic system, space group  $Pc2_1n$ , Z=4) and CsLiBeF<sub>4</sub> (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<sub>4</sub><sup>+</sup> and Cs<sup>+</sup> modifies the tridymite structure of KLiBeF<sub>4</sub>.

## Introduction

Dans une précédente note (Le Roy & Aléonard, 1970), nous avons signalé l'existence de la série d'orthofluorobéryllates MLiBeF<sub>4</sub> avec M = K, Rb, Tl, NH<sub>4</sub> et Cs. Nous avons donné leurs constantes de mailles et leur groupe spatial:

- Les orthofluorobéryllates 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 pseudohexagonale (groupe spatial  $Pc2_1n$ , Z=4), dont les constantes sont reliées aux précédentes par:

$$a_{\text{orth}} \neq a_{\text{hex}} \cdot \sqrt{3}$$
  
 $b_{\text{orth}} \neq b_{\text{hex}}$   
 $c_{\text{orth}} = c_{\text{hex}}$ .

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