The Crystal Structures of Racemic 3-Benzylamino-4-hydroxypent-2-enoic Acid Lactone Hydrochloride and of Spontaneously Resolved 3-Benzylamino-4-hydroxypent-2-enoic Acid Lactone Hydrobromide

BY PEI-TAK CHENG, CHUNG HOE KOO, IAN P. MELLOR, S. C. NYBURG AND JOHN M. YOUNG

Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario, Canada

(Received 8 August 1969)

The crystal structure of the hydrochloride of the reaction product of 4-hydroxypent-2-enoic acid lactone with benzylamine, $C_{12}H_{16}CINO_2$, has been determined. System: monoclinic, $P2_1/c$, a=9.183 (7), b=11.278 (20), c=12.218 (10) Å; $\beta=101.3$ (1)° Z=4. The *trans* configuration of the C(12) methyl group and the N atom about C(8)-C(9) has been confirmed. Structure analysis of the spontaneously resolved (and hence non-isomorphous) hydrobromide is also reported. System: monoclinic, $P2_1$. a=6.612 (1), b=10.824 (3), c=9.054 (2) Å, $\beta=98.4^{\circ}$, Z=2. A possible reason is given for the signicant difference in the conformation of the lactone ring in the two structures.

Introduction

Certain lactones are known to be moderately carcinogenic (Dickens & Jones, 1961) and their mode of action has been attributed to chemical reaction with the bases of deoxyribonucleic acid and of ribonucleic acid. Thus the reaction of such carcinogenic lactones with nitrogenous bases is of considerable biological interest and we have examined the crystal structures of both the hydrochloride and of the hydrobromide of the reaction product of 4-hydroxypent-2-enoic acid lactone (I) with benzylamine, namely 3-benzylamino-4-hydroxypent-2-enoic acid lactone (II).



Although Lukeš & Linhartová (1960) presented evidence that the product (II) had the N atom and the methyl group at C(12) disposed *trans* with respect to C(8)–C(9) [see Fig. 1(*a*) for numbering], this particular stereochemical feature is of biological interest and an X-ray analysis was undertaken to check it. The *trans* conformation has been confirmed and already reported in a preliminary communication from these laboratories (Jones, Koo, Mellor, Nyburg & Young, 1968)

Our original intention was to examine only the hydrobromide of (II) but preliminary X-ray examination indicated a space group at variance with that thought to be likely on chemical grounds. Accordingly the hydrochloride was first analyzed and later the hydrobromide with which it is not isomorphous.

CRYSTAL STRUCTURE OF THE HYDROCHLORIDE

Experimental

The salt was obtained as colorless columnar crystals by recrystallization from ethanol-methanol. The calculated linear absorption coefficient for Cu $K\alpha$ radiation is 26.6 cm⁻¹ and all crystals were kept smaller than $2/\mu = 0.75$ mm; no absorption corrections were made.

All data were collected photographically on Weissenberg cameras and intensities eye-estimated. Cell dimensions were obtained from zero-level photographs calibrated with aluminum wire at high Bragg angles and refined by least squares.

Crystal data are:

C₁₂H₁₆ClNO₂, M.W. 241·7 Monoclinic, $P_{2_1/c}$ a=9.183 (7), b=11.278 (20), c=12.218 (10) Å $\beta=101.3$ (1)°. V=1240.7 Å³. $\varrho=1.29_0$ g.cm⁻³. (chloroform-benzene); Calculated for Z=4 molecules per cell, 1.304 g.cm⁻³.

Since the molecule is asymmetric the crystal is clearly that of the racemate.

Equi-inclination, eye-estimated intensity data were collected on multiple-film packs: one set h0l through h.11l, the other 0kl through 6kl. Of the 2772 independent reflections lying in the Cu $K\alpha$ sphere, 2120 (76.5%) were observed and measured. After interfilm scaling and data reduction, the overall temperature factor B=3.85 Å² and scale factor were obtained from a Wilson plot.

The unsharpened Patterson function could be interpreted in terms of either of two sets of Cl⁻ positions but sharpening did not resolve the ambiguity. Accord-

Table 1. Fractional coordinates and anisotropic thermal parameters of non-hydrogen atoms of the hydrochloride

Temperature factor in the form: $10^{-4} \exp \left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$.

	<i>x</i>	У	Z	β_{11}	β22	β33	β_{12}	β_{13}	β_{23}
Cl-	-0·0433 (2)	0·4022 (1)	0.1801 (1)	153 (2)	75 (29)	57 (1)	-6(1)	28 (1)	-5(1)
N	-0.0584(4)	0.3202 (4)	0.1828 (3)	79 (4)	77 (29)	57 (1)	-1(3)	22 (3)	-0(2)
O(1)	0.2433 (4)	0.2160 (4)	0.0556 (4)	96 (5)	111 (30)	45 (3)	10 (3)	29 (3)	-21(3)
O(2)	0.1456 (6)	0.0914 (4)	-0.0818(5)	188 (8)	120 (30)	84 (3)	-3(4)	59 (5)	-46(3)
C(1)	-0.3075 (5)	0.3206 (5)	0.2364 (4)	68 (5)	100 (30)	104 (5)	7 (3)	10 (3)	4 (3)
C(2)	-0.3812 (6)	0.2169 (6)	0.2586 (6)	109 (7)	114 (30)	57 (3)	1 (4)	18 (5)	10 (4)
C(3)	-0.4636 (7)	0.2163 (7)	0.3421 (7)	121 (8)	133 (31)	89 (5)	-8(5)	38 (6)	25 (5)
C(4)	-0·4739 (7)	0.3180 (7)	0.4039 (6)	98 (7)	181 (31)	107 (6)	11 (6)	32 (5)	20 (5)
C(5)	-0·3999 (7)	0.4209 (7)	0.3831 (6)	100 (7)	161 (31)	88 (5)	18 (5)	38 (5)	-23(4)
C(6)	-0.3165 (6)	0.4214 (5)	0.2998 (5)	85 (5)	114 (30)	83 (5)	6 (4)	24 (4)	0 (4)
C(7)	-0·2225 (6)	0.3205 (6)	0.1414 (5)	81 (6)	142 (30)	77 (4)	2 (4)	12 (3)	1 (4)
C(8)	0.0225 (5)	0.3073 (4)	0.0879 (4)	76 (5)	82 (30)	60 (4)	-3(3)	18 (3)	1 (2)
C(9)	0.1921 (5)	0.2992 (4)	0.1326 (4)	72 (5)	89 (30)	42 (3)	3 (3)	10 (3)	0 (3)
C(10)	0.1256 (6)	0.1584 (5)	-0·0108 (5)	118 (6)	96 (30)	56 (3)	-7(4)	30 (4)	-3(3)
C(11)	-0·0146 (5)	0.1949 (4)	0.0223 (4)	98 (6)	96 (30)	64 (4)	-13 (4)	22 (3)	-12(3)
C(12)	0·2752 (6)	0.4124 (5)	0.1301 (6)	93 (6)	109 (30)	52 (3)	-16 (4)	7 (5)	2 (4)

ingly electron densities, phased on both sets, were computed. For every peak X on these maps the corresponding vectors of Cl^--X were verified on the sharpened Patterson function. Every such verified X position gave an intelligible molecular skeleton for the 15 nonhydrogen 'light' atoms for one Cl^- set but not for the other. The former proved to be the true set.

Full-matrix anisotropic least-squares refinement was carried out on the sixteen non-hydrogen atomic parameters with scattering factors taken from International Tables for X-ray Crystallography (1962) and using Hughess' (1941) weighting scheme with $|F_{\min}| = 0.75$ and unobserved reflections weighted as $\sqrt{\frac{1}{3}}|F_{\min}|$. Final positional and anisotropic thermal parameters for non-hydrogen atoms are given in Table 1. A difference Fourier synthesis showed all sixteen hydrogen atoms lying close to the positions expected theoretically. The theoretical positions, listed in Table 2, were incorporated into the final F_c calculations with scattering factors from International Tables for X-ray Crystallography (1962) and anisotropic thermal parameters the same as those of the atoms to which the hydrogen atoms are attached.

Table 2. Fractional coordinates of hydrogen atoms of the hydrochloride obtained theoretically, using C-H, 1.07 Å

Hydrogen	Attached			
atom	to	x	У	z
1	Ν	-0.026	0.401	0.225
2	N	-0.029	0.248	0.239
3	C(2)	-0.373	0.138	0.210
4	C(3)	-0.519	0.137	0.359
5	C(4)	-0.538	0.317	0.467
6	C(5)	-0.407	0.498	0.431
7	C(6)	-0.2258	0.499	0.284
8	C(7)	-0.252	0.243	0.091
9	C(7)	-0.251	0.397	0.091
10	C(8)	-0.004	0.381	0.034
11	C(9)	0.212	0.267	0.216
12	C(11)	0.021	0.128	0.072
13	C(11)	-0.098	0.210	-0.049
14	C(12)	0.257	0.449	0.043
15	C(12)	0.237	0.475	0.184
16	C(12)	0.390	0.396	0.158

The final F_o , F_c listing is given in Table 3, the conventional R index for observed reflections being 0.099, and that for all reflections, 0.121.

Description of the structure

Bond lengths and interbond angles derived from Table 1, together with estimated standard deviations, are illustrated in Fig. 1(a) and (b). As stated earlier, the methyl group at C(9) is *trans* with respect to C(8)-N as postulated by Lukeš & Linhartová (1960). This can





Fig. 1. Molecular geometry of the hydrochloride (schematic): (a) bond lengths, (b) interbond angles (e.s.d. ca. 1° in each case).

Table 3. F_o and F_c values for the hydrochloride

Asterisks refer to unobserved reflections with intensity assigned $\frac{1}{3}$ of the locally observed minimum (Hamilton, 1955).

T,	۱ ۵۰٬ _۵ ۱۵٬ _۵	1 0 1 10 1 11 • 1 12 • 1 12	43 48 51 -31 151 [43 164 [53 93 -14 [43 -14 [43 -14 14 21 64 64 [4 -42	1 102 11 - 0 120 - 150 - 0 220 32 - 0 2 20 15 - 0 3 35 - 0 - 0 5 - 2 - 5 - 2 - 5 - 5 - 5 -	 7 184 -184 8 10 -32 8 10 -34 9 10 -34 9 14 -34 9 14 -34 9 14 -37 11 -41 -57 13 15 75 13 15 -36 13 15 -31 14 10 -31 15 10 -31 15 10 -31 16 -31 17 40 -31 		235 206 225 206 657 212 436 -223 238 -215 88 -75 131 116 63 -62 65 55	u - 1 42	9	5 0 108 v8 5 1 113 115 5 1 2132 116 5 1 200 200 5 4 107 100 5 228 230 5 0 111 - 108 5 7 10 - 1 5 8 15 - 13 5 9 75 - 70	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• U 1 18 - U 1 19 1 - 19 1 U 1 19 1 U 1 45 U 8 198 1 • 0 10 17 - • 0 11 11 • 0 12 16	12 + 54 23 83 29 + 170 - 46 - 28 + -3 13	7 -11 8 -11 8 -10 8 -9 8 -8 8 -7 8 -7 8 -5 5 -3	+ 10 23 -14 34 -20 +1 31 10 -3 55 55 110 121 11 -1 +1 -49 20 5+
	2 404 -398 4 458 -419 6 167 180 8 126 -155 10 41 62 12 322 103 14 110 -84 -14 V4 -154 -12 64 76 -10 251 225	- L 15 2 - 14 2	20 - 35 20 - 57 20 - 27 234 - 233 34 - 233 34 - 203 224 - 203 443 416 134	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		• • • • • • • • • • • • • • • • • • • •	22 - 154 22 - 154 1 22 - 154 1 22 - 154 1 20 1 3 - 12 1 50 - 16 1 157 - 174 1 157 - 174	9 -11 10 9 -10 19 -10 9 -9 16 9 -9 16 9 -0 16 9 -0 18 9 -0 18 9 -0 18 9 -0 18 9 -0 18 9 -0 18 9 -2 90	• • •	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 -7 55 52 3 -8 55 101 3 -5 107 100 3 -4 70 73 3 -2 31 -706 3 -2 31 -70 3 -1 17 -136 3 0 107 133 3 1 394 477 3 2 134 177	• 0 13 17 • 0 34 17 1 -14 26 1 -13 33 - 1 -12 13 - 1 -10 100 -1 1 -10 100 -1 1 -10 110 -1 1 -1 10 100 -1 1 -1 10 -1 1 -1 -1 10 -1 1 -1 10 -1 1 -1 10 -1 1 -1 10 -1 1 -1 -1 10 -1 1 -1 -1 10 -1 1 -1 -1 10 -1 1 -1 -1 -1 10 -1 1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1	17 +2 +3 -6 -7 -7 -7	8 -2 8 -1 8 0 8 2 8 3 8 3 8 3 8 3 8 3 8 3 8 3 8 3 8 3 8 3	54 61 123 130 11 17 54 -34 11 -3 51 46 52 52 52 -33 24 12 23 -20
	-8 390 -37- -6 408 347 -4 291 206 -2 840 542 0 935 875 2 73 -57 6 -38 -87 6 -38 -83 8 333 -300	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	638 -027 94 120 94 120 94 -020 94 -020 100 -70 100 -70 758 612 756 177	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 -2 110 -120 5 -1 341 143 5 -1 341 143 5 -1 341 143 5 -1 378 81 5 -1 98 37 5 -1 99 -17 5 -1 90 -11		0 130 -107 130 -244 5 130 -244 5 140 -244 5 140 -244 5 140 -244 5 140 -244 5 140 -114 1 145 -151	• v -1 18 • 0 122 -1, v 1 •3 -' v 2 29 • 3 28 • 4 65 -' v 5 101 -11 • 9 7 8 10 -10 +2 -	2 . 2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 3 107 -113 4 3 4 13 -14 5 5 58 67 3 6 00 61 3 7 195 197 3 8 51 49 3 9 62 -69 3 10 34 -27 4 3 11 17 -17 8 3 12 117 75	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27 62 14 71 56 52 14 71 56 52 14 71 71 71 71 71	v -10 v -9 v -3 v -3 v -3 v -3 v -3 v -1	52 -55 52 40 36 -30 60 51 42 43 44 43 44 43 44 43 77 -78 74 67 74 67 74 67 70 20
•	12 145 127 14 15 -10 -14 19 -10 -14 19 -10 -12 53 37 -10 361 346 -8 123 -305 -6 259 207 -4 247 249 -2 1078-1013		210 -210 163 -162 15 -16 17 -17 16 16 16 16 20 -10 119 -115 16 11	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• • • • • • • • • • • • • • • • • • •	• • • •	5 351 -401 1 154 171 2 40 41 3 261 -251 4 182 -167 5 18 -45 6 124 -46 7 16 -8 6 227 264 4 104 -174	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 . 10 . 11 . 10 . 11 . 11 .	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+ 3 13 / 2 + 4 -14 H + + -13 185 -124 + -12 45 -13 + -11 54 5 + -10 14 6 + -9 152 151 + -8 74 -60 + -7 237 -252	1 5 194 - 1 1 5 194 - 1 1 7 125 1 1 8 159 1 1 10 79 1 10 79 1 11 40 - 1 12 63	41 .97 .14 .15 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17		83 85 10 -22 41 -41 31 24 5 5 7 30 3- 70 -7 8 1
*******	0 270 374 2 675 724 6 410 300 8 226 -216 10 87 82 12 287 244 14 121 -118 -14 74 -71 -12 74 -71	(12 - 24 38 - 49 90 100 23 - 11 20 - 28 120 - 11 63 - 54 14 - 2 100 - 210 230 - 210	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 -10 4 -67 0 -4 50 42 0 -7 40 51 0 -5 18 -51 0 -6 81 -64 0 -3 82 -66 0 -3 82 -66 0 -2 17 -7 0 -1 11* 103	· · · · · · · · · · · · · · · · · · ·	0 203 -180 1 85 77 2 87 44 3 14 -14 4 10 18 5 10 18 5 10 18 5 10 -4 2 208 -194 4 40	10 1 30 10 2 20 - 10 3 22 - 10 4 11 11 -5 10 11 -5 10 11 -5 10 11 -5 20 - 13 - 86 - 11 -3 70	54 55 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	* * -5 12 12 * -8 56 53 * -2 16 -73 * -2 16 127 * -2 16 127 * -2 177 163 * 0 52 -56 * 1 253 281 * - 2 11 17 * - 3 10 -17	2 -19 8 2 -13 9 2 -13 16 2 -11 17 2 -10 17 2 -10 17 2 -8 25 2 -1 65 2 -1 65 2 -1 7 4 27 -1 7 -1	10 -0 -30 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3	10 -3 10 -2 10 -1 10 0 10 1 10 2	36 -18 8 4 8 6 44 34 38 14 16 -18
)))))))))))))))))))	-10 263 273 -8 371 -156 -6 327 -225 -4 637 621 -2 851 -472 0 431 455 2 216 -206 4 132 133 6 372 372 8 21 -22	3 -0 1 -5 1 -3 1 -4 1 -3 1 -4 1 -3 1 -4 1		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	* 6 0 17 -13 b 1 200 (27 * 2 18 8 5 3 -2 -33 b 4 10 17 6 5 182 173 6 7 1 48 6 7 1 48 6 30 7 38 -30 6 5 107 -58	· · ·	0 1/6 103 8 230 207 7 264 -274 6 318 -308 5 231 213 6 234 223 5 115 87 2 10 3	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• 5 33 10 • 6 35 -21 • 9 35 22 • 9 130 -100 • 10 13 11 • • 10 14 11 • • 11 11 17 • • 12 4 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	110 -34 -34 -17 140 147 50	00000000000000000000000000000000000000	3/3 -381 2/00 -148 2/00 -148 2/00 -148 2/00 -148 2/01 -06 88 -47 10 -14 11 - 105
	10 v3 -03 12 155 142 14 114 -122 -14 v -12 -12 111 -116 -10 37 55 -6 331 -327 -6 24 46 -2 165 165	+ + + + + + + + + + + + + + + + + + +	300 -294 247 221 157 -155 18 -27 71 62 122 115 63 -59 113 -155 2 76 -67	x # 2 0 0 1186-1481 0 1 440 486 0 2 152 -156 0 3 624 546 0 4 150 -150 0 5 55 45 0 6 49 9-	* 0 10 15 -7 0 11 36 31 * 7 -16 8 -0 7 -13 33 -68 7 -12 50 -59 7 -11 12 12 * 7 -9 20 -10 * 7 -8 20 -18	• 3	0 +00 -487 1 104 43 2 290 284 3 143 -134 4 30 -413 5 153 -150 5 10 10 7 80 -76 8 79 -76 8 79 -76	0 8 123 1 0 10 124 -1 0 11 17 0 12 60 - 0 13 79 - 0 14 63 1 -15 57 1 -13 36 1 -12 62 - 1 -11 27 -	32 72 83 80 72 50 18 18	8 -12 50 47 8 -11 50 57 8 -10 56 -89 4 -8 14 -16 5 -7 15 -8 8 -6 57 11 8 -5 15 5 8 -5 15 5 8 -5 15 5 8 -5 15 5 8 -5 5 8 -5 5 8 -5 5 8 -5 5 8 -10 5 8 -	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 5 17 2 8 132 - 2 7 06 2 8 76 2 11 04 2 12 17 2 12 17 2 12 17 3 -14 27 4 -13 18	- 31 1 3 3 7 1 7 1 6 1 - 6 5 7 1 7 1 6 1 - 6 5 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1 7 1	0 11 0 12 0 13 1 -13 1 -12 1 -11 1 -10 1 -9 1 -8	53 40 74 -68 17 10 23 -38 144 137 22 33 174 -167 13 8 109 -104
•	0 6+0 553 2 4+3 341 + 518 -530 6 202 190 8 21 -28 10 96 -75 12 82 03 -14 54 52 -17 141 -161	3 1 3 1 4 -1 4 -1 4 -1 4 -1 4 -1 4 -1	3 31 -37 4 56 -74 5 56 -74 5 56 -74 5 56 -74 5 36 -75 3 74 80 2 107 -93 1 100 -98 0 82 87 9 168 -161 8 74 60	0 7 457 427 0 6 157 -1-2 0 9 17 40 0 10 112 102 0 11 69 61 0 12 10 -30 0 13 60 -72 0 14 15 -17 0 15 62 60 1 -5 30 -61	7 -6 187 166 7 -5 187 166 7 -6 48 -50 7 -3 95 -40 7 -2 106 183 7 -1 66 75 7 0 66 95 7 1 189 206 7 2 69 67	3 1 3 1 3 1 4 -1 4 -1 4 -1	0 85 -80 1 125 110 2 37 41 3 51 35 5 45 74 - 65 86 3 15 7 2 43 -45 1 86 86	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	60 37 37 74 00 79 61 51 71	8 -7 56 -44 8 -1 14 -150 8 0 74 74 1 108 112 8 2 67 -65 8 3 17 -72 8 5 14 27 4 6 31 -38 4 7 11 10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 -12 120 140 -98 -98 -154 -10 255		100 87 15 -23 180 -200 100 -108 204 241 55 57 160 207 17 36 190 -431 105 -114
	-6 100 -134 -6 100 -134 -6 100 -134 -6 485 487 -2 127 111 0 176 156 2 125 101 - 540 -564 - 6 82 47 - 8 151 121	• • •	7 255 242 6 34 72 5 48 -51 4 706 651 3 13 -0 2 275 273 1 46 48 0 68 23 1 691 -667	+ 1 -14 15 -7 + 1 -13 10 -13 1 -12 34 63 + 1 -12 34 63 + 1 -10 24 3 1 -8 74 -84 1 -7 264 257 1 -6 125 -117 1 -5 135 -117	7 3 50 7 4 98 -103 7 5 47 104 7 6 98 -107 7 5 47 104 7 8 17 11 7 8 17 11 7 8 167 7 10 2832 8 -13 41 -72 8 -13 -10	•	9 31 27 9 31 27 9 42 -41 7 16 -6 9 452 -438 9 176 156 9 452 -438 9 176 156 9 40 158 1 61 66 1 94 168 1 225 -620	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	88 05 67 91 67 91 67 91 91 91 91	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5 7 14 18 5 8 34 26 5 9 109 -104 5 10 11 -2 5 11 8 11 6 -13 156 -114 6 -12 21 26 6 -11 17 11 6 -10 34 -26 6 -1 34 -26 7 7 8 00	3 -2 200 3 -1 27 3 0 137 - 5 1 105 3 2 03 3 3 100 5 119 - 5 0 150 - 5 0 150 - 4 7 12	211 -33 134 152 -55 171 167 -132 -171	1 5 1 6 1 7 1 8 1 10 1 11 1 11 1 11 1 11 1 11	100 114 71 7. 86 78 86 78 80 -61 20 -38 112 114 75 75 80 -78
	10 103 -87 12 47 51 1-12 43 -147 1-12 43 -147 -12 43 -147 -41 131 -145 -41 131 -145 -5 100 -105 -4 131 -145 -5 207 -745 0 20 14		2 300 -308 3 483 434 5 64 86 6 148 -115 7 214 -208 8 20 10 9 108 101 0 95 -47 1 18 -25	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• 8 -11 10 33 A -10 43 48 • 8 -0 10 43 48 • 8 -8 84 74 8 -8 71 0 0 8 -6 71 -0 8 -4 81 -58 8 -206 -206	••••	2 270 -200 1 205 200 9 94 90 3 307 -294 - 15 5 5 40 -39 5 17 11 7 131 11 7 131 11 8 92 19 9 18 17	$\begin{array}{cccccccccccccccccccccccccccccccccccc$)2 5 61 52 50 92 50 1 5 50 1 50 1 5 1 50 1 50 1 50 1 50 5	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 B 30 3 Y 73 4 3 10 11 3 11 85 3 12 19 4 -14 13 4 -13 20 4 -12 43 4 -11 27	26 -64 - 7 - 76 - 18 - 16 - 14 - 34 - 24		25 -41 153 140 80 7w 73 -71 131 -127 63 -60 172 -174 1w1 200 48 55
•	> > 145 204 > > 205 -222 0 > 3 147 117 > 10 42 -73 T -10 42 -73 T -10 147 -117 T -10 147 -137	• • • • • • • • • • • • • • • • • • • •	2 15 -18 1 36 -31 5 56 -76 4 52 62 1 71 76 2 19 22 1 90 -95 0 83 66 9 127 -116 5 211 216		B - 2 - 20 - 52 B - 1 - 143 - 142 B - 1 - 143 - 142 B - 50 - 52 B - 155 B - 2 - 71 - 78 B - 4 - 2-7 B - 4 - 2-7 B - 5 - 19 - 2-8 B - 17 - 2-8 B - 17 - 2-1 B - 7 - 3% - 51	· · · · · · · · · · · · · · · · · · ·	2 43 -41 1 15 10 2 13 5 3 43 37 4 15 -8 7 41 -48 1 18 21 0 74 -40 0 74 -40	2 -0 400 - 2 -0 202 2 -7 224 2 -5 209 2 -5 209 2 -4 23 2 -2 385 2 -1 154 - 154	21 • 1 15 25 107 161 • 1 161 • 1 1761 •	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• 6 7 14 1 • 7 14 1 • 8 1 01 56 • 8 4 21 • 9 36 33 • 8 4 -56 • 7 15 27 • 6 8 12 27 • 6 8 12 27 • 6 8 12 27 • 6 9 10 6 -10	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	112 112 112 112 112 112 112 112		35 33 72 68 130 141 80 97 233 -237 68 65 146 -256 75 77
:	1 - 11 - 11 - 11 1 - 2 - 14 - 44 1 - 4 - 14 - 44 1 - 10 - 15 - 24 12 - 54 - 64 1 - 10 - 15 - 64 1 - 10 - 10 - 10 - 64 1 - 10 - 10 - 10 - 64 1 - 10 - 11 - 10 - 10 - 64 1 - 10 - 10 - 10 - 10 - 64 1 - 10 - 10 - 64 1 - 10 - 10 - 10 - 64 1 - 10 - 10 - 10 - 10 - 10 - 10 - 10 -	5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 -	7 226 217 6 71 64 5 174 -156 6 12 26 3 85 92 2 275 368 1 260 224 0 9 -10 1 283 -250 2 159 -138	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		••••••	8 H 2 2 9 2 - 28 5 203 - 25 5 03 - 46 5 13 - 99 5 13 - 99 5 13 - 99 5 120 - 88 1 120 - 188 1 317 296	2 1 396 - 2 2 203 - 2 3 141 2 4 13 2 5 107 2 6 130 - 2 7 59 2 8 155 2 9 102 2 9 102 2 10 30	105 147 147 174 174 174 174 174	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 -11 36 -41 1 -10 31 -21 1 -10 31 -21 1 -10 31 -21 1 -10 16 16 1 -8 16 -10 1 -7 67 -66 1 -6 16 -81 1 -5 169 157 1 -6 72 -17 1 -3 95 -81 1 -3 95 -81	• 1 58 • 2 10 • • 3 91 • • 1 10 • • 5 82 • • 82 • 8 • 8 • 8 • 8 • 8 • 9 • 1 • 1 • 1 • 1 • 1 • 1 • 1 • 1 • 1 • 1	53 12 96 -89 -108 -79 -75 -71	2 10 2 10 2 11 2 12 3 13 3 12 3 11	12 -10 107 -179 11 -02 130 170 11 37 76 -76 7 -7 180 133 10 -17
•		• •	3 22 35 a 203 -146 5 13 -10 6 117 117 7 84 -88 8 40 3- 9 81 84 9 81 84 18 -5 1 16 -13	2 10 - 10 - 10 - 10 - 10 - 10 - 10 -	• $v -3$ 20 29 • -2 1 $v5$ -154 • $0 -1$ 20 $-3v$ • $0 -1$ 20 $-3v$ • $0 -1$ 20 $-3v$ • $v -1$ 10 $-v$ • $v -1$ 10 $-v$ • $v -2$ 10 18 • $0 -3$ 10 -62 • $v -2 -5v$ • $v -$	•••••	2 425 437 3 16 -27 4 145 139 5 164 -165 6 337 -334 7 127 112 8 107 99 4 17 6 10 16 -18	2 11 17 2 12 17 2 13 74 2 14 18 3 -14 18 3 -12 84 1 -11 15 3 -10 97	-76 -76 -53 -66 -11 -67	11 0 37 37 11 1 7 -0 0 1 81 01 2 152 167 0 3 169 157 0 3 169 157 0 5 267 269	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 10 53 - 11 36 - 12 5 - 12 5 - 11 26 - 11 26 - 11 26 - 10 80 9 125 8 57 3 12	-27 -27 -52 -52 -53 -28 -18 123 -33	· j -10 j -9 j -8 j -7 j -7 j -7 j -5 j -5 j -5 j -2 j -1	11 -13 01 -57 182 -105 110 -117 200 240 45 47 105 -174 8 -17 19 -18
	2 -10 82 -56 - 8 20 -6 - 8 20 -6 - 6 21 -16 - 10/ 1/2 - 10/ 1/2 - 2 10/ 10/ - 2 10/ 10/ - 4 10 -34	8 -1 8 - 8 0 - 6		2 3 360 254 2 6 16 11 - 12 2 7 12 2 8 13 10 - 12 2 9 10 2 9 10 2 10 2 10 2 11 2 15 2	i 0 7 11 -7 10 -10 37 61 10 -9 32 -52 10 -9 32 -53 10 -7 55 -63 10 -6 16 -0 10 -6 16 -0 10 -6 16 -0 10 -6 16 -0 10 -5 16 -10 10 -1 17 -10	• • • • • • • • • • • • • • • • • • • •	2 10 + 4 25 58 13 13 18 2 39 -51 11 18 -39 0 45 -88 9 18 31 8 201 215 7 277 -279 14 201	3 -8 154 5 -7 242 3 -8 154 5 -7 242 3 -8 154 3 -8 154 3 -8 164 3 -8 164 3 -1 244 5 -2 350 5 -1 222 5 0 175 - 1 22	100 101 101 101 101 101 101 101	J n 27 31 J 2 5 40 U n 13 -30 0 4 154 -151 1 10 14 -23 1 1 47 44 1 13 74 -74 1 14 8 -74 1 14 8 -74 1 14 8 -74	7 8 45 -54 7 8 45 -54 8 -12 6 15 8 -11 114 -74 8 -10 11 7 8 -9 61 63 8 -6 40 47 8 -7 34 -51 8 -5 14 44	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-220 55 55 -220 55 -22 -178 -21 -103 22 191	3 0	116 121 14 10 164 -206 40 -37 67 68 163 -160 14 -20 82 -180 150 -130 33 -34
10 • 10 • 10 • 10 • 10 • 10 • 10 • 10	1 -10 113 -14 8 115 104 8 115 104 8 11 -21 8 10 -82 - 0 14 -15 - 2 68 -82 - 0 14 -15 - 4 14 -7 - 8 10 9	6 - 6 - 6 - 6 - 6 - 6 - 6 - 6 - 6 - 6 -	111 - 121 110 - 23 2 8 - 43 1 19- 23 0 885 1 104 - 122 2 177 162 3 112 - 101 4 74 85	3 -15 - 1318 3 -14 - 2318 3 -13 - 03 - 42 3 -12 - 49 - 64 3 -11 - 61 - 50 3 -10 - 35 - 38 4 - 9 - 135 - 108 3 -8 - 48 - 15 3 - 7 - 87 - 75	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• • • • •	-5 90 95 -6 140 -122 -3 566 -122 -3 766 -122 -1 28 -20 0 18 -33 1 16 147 3 17 5	5 2 70 5 3 132 - 5 4 206 5 185 5 185 6 3 7 15 7 8 73 9 4 112 5 10 77 10 77	84 - 138 - 146 - 177 - 167 - 177	1 -13 A5 -40 1 -12 13 -21 1 -12 14 -4 1 -10 150 147 1 -4 51 67 1 -4 55 47 1 -5 50 58 1 -5 50 58	8 -6 30 -23 8 -3 35 -23 8 -2 57 -55 8 -1 16 -5 8 -1 10 8 -	5 4 41 7 5 150 7 6 42 7 4 11 7 9 74 5 10 36 7 11 6 6 -12 16	30 =161 =27 12 55 31 -20 58 31	3 10 3 11 3 17 13 11 10 10 10	11 8 8 1 8 1 8 1 8 1 8 1 8 1 8 1 8 1 8
• 11 • 11		• • • • • • • • • • • • • • • • • • •	7 174 17 7 176 -170 8 80 85 9 18 19 0 53 -50 1 12 13 58 63 3 48 49 7 10 6	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5 175 -170 6 131 -113 7 101 -61 8 81 -11 9 81 -11 10 15 -17 10 13 -w 11 10 -18 13 11 -28 13 14 -39	3 11 100 3 13 43 3 13 41 4 -14 13 4 -13 13 4 -13 13 4 -13 13 4 -11 38 4 -11 38 4 -11 38 4 -11 38 5 -11 38 5 -11 58 5 -11 58		3 40 37 2 70 -50 2 80 11 - 0 137 -138 - 1 80 -1 - 1 80 -1 - 1 97 -138 - 1 97 -138 - 1 97 -1 - 1 97 -1	8 6 36 8 7 25 33 8 8 8 6 7 9 -11 5 7 9 -10 20 -12 9 -10 20 -12 9 -12 57 9 -12 57 9 -12 9 -12 57 9 -12 9	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-35 -30 -30 -30 -30 -30 -30 -30 -30 -35 -35 -35 -35 -35 -35 -35 -35 -35 -35	• • • • • • • • • •	209 220 10 -v 90 -78 111 -110 115 -115 138 -135 192 223 107 115 184 -212 100 -188
• • • • • • • •			1 04 55 0 14 -16 4 134 -125 4 71 -54 7 145 151 5 20 17 5 20 17 5 20 17 5 217 - 4 7 17 77	1 4 300 - 625 5 4 4 90 - 62 5 10 - 91 100 5 1 10 - 155 5 8 101 - 155 5 9 71 - 56 • 1 10 13 - 15 • 1 10 13 - 15 • 3 12 59 - 55 • 11 5 97 - 68	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• • • •	11 14 -76 10 17 -10 -9 31 40 -8 205 197 -8 205 197 -0 130 -127 -5 128 -116 -5 2 -61 -5 17 196	5 33 5 107 5 107 5 107 3 107 3 107 1 320 - 0 75 - 1 117 - 1 117 - 1 117	273 34 115 153 35 274 360 77 77 151	1 2 103 1.7 2 8 17 24 1 4 127 24 1 11 14 45 1 12 15 30 1 12 15 30 1 13 13 724 1 14 15 30 1 15 13 724 1 14 20 24	v 31 30 v 3 161 174 v 2 13 1v v 1 35 1v v 2 15 1v v 1v v 1v v 1v v 1v v 1v v 1v v 1v v 1v v	6 -1 40 6 0 40 6 1 20 6 2 20 6 4 80 6 4 80 7 1 22 7 8 7 12 7 8 7 12 8 7 12 7 8 7 12 7	- 63 28 - 18 29 - 27 - 27 - 17	• • • • • • • • • • • • • • • • • • •	72 00 103 -104 76 78 46 48 116 -104 25 -36 8 15 14 15 5 0
• • • •	11 14 11 14 15 8 15 12 70 -15 12 -14 -15 12 -14 -15 12 -14 -15 12 -14 -11 16 16 -11 16 17 -11 16 17 -11 16 17 -11 162 111 -11 162 111	•	1 200 200 201 200 201 200 201 201 201 201 201 201 201 201 20	1 14 1 13 1 14 14 13 1 14 14 14 1 14 14 14 1 14 14 1 14 14 1 14	0 10 10 100 -175 0 11 15 -5 0 12 157 125 0 13 16 - 9 0 14 15 -75 0 14 15 -75 1 -15 10 17 1 -15 10 -77 1 -17 10 -77	• • • • • • • • • • • • • • • • • • • •	-1 140 -130 0 151 -143 1 18 -27 2 45 -46 3 86 -75 4 87 84 5 45 -41 6 43 -46 7 84 -45 7 84 -77 8 26 27	- 3 271 - 136 - 5 277 - 6 110 - 7 39 - 8 16 - 9 67 - 40 103 - 11 82 - 11 82 - 12 31	100 · · · · · · · · · · · · · · · · · ·	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	• • • • • • • • • • • • • • • • • • •	6 10 56 6 10 6 7 -12 8 7 -13 8 7 -10 47 7 -10 47 7 -10 47 7 -10 47 7 -0 40 8 - 3 40 8 - 3 40 9 - 3 40 9 - 10 6 10 9 - 10 57 1 - 6 40 9 - 10 57 1 - 6 40 1 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 -	100 - 100 -	5 -14 5 -10 5 -9 5 -8 5 -5 5 -5	72 46 36 33 39 36 73 -80 104 -103 150 174 56 -57 46 32 96 -90
	-6 84 7, -7 181 170 -6 185 117 -5 280 -255 -6 636 350 -1 637 635 -2 16 15 -2 16 15 -0 110 -43	• / 1 • / 1 • -1 • -1 • -1 • -1 • -1 • -1 • -1 •	4 15 21 1 12 21 3 10 21 4 60 751 1 52 54 1 52 54 1 52 54 1 52 54 1 52 54 1 52 54 1 52 54		$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4 1.5 0 10 4 6 13 7 17 14 11 7 15 11 7 10 15 -53 10 15 10 -9 17 10 -9 17 80 -1 27 76	• 5 -116 V • 5 -11 107 • 5 -11 10 • 5 -10 107 • 5 -10 118 • -10 28 • -10 28 • -10 28 • -10 28 • -10 107 • -10 1		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 1 10 10 10 1 10 10 10 3 60 76 11 -5 6 -77 11 -8 30 -77 11 -7 36 -77 11 -7 30 -82 4 4 6		117 117 135 147 - 53 7 - 43 30 07		67 -65 201 208 0 20 10 -148 60 -64 26 -56 26 26 26 26 180 188
	2			 3 211 -725 4 180 1-7 5 82 85 6 18 72 	1 -1 116 -NU		-4 /4 -61 -6 /65 -2/3 -3 160 151		20		5 0 234 -215 0 1 167 189 9 2 155 175	• / 5 11 • / 6 10 • / 7 7	-10	• • •	108 -41

Table 3 (cont.)

	······································		 	
1956-2559-22996-19195-2212-121-121-121-121-121-121-12-121-12-12				
		······································		

be clearly seen on the ORTEP plot (Johnson, 1965) of the molecule (Fig.2).

The lactone ring has an envelope conformation, atoms C(9), O(1), C(10) and C(11) being fairly coplanar (see Table 4) whereas C(8) at the 'flap' is 0.38 Å out of plane in a direction away from the nitrogen atom side of the ring. Atom O(2) is also slightly out-of-plane 0.06 Å, in the same direction. The benzene ring is accurately coplanar, the out-of-plane e.s.d. being 0.005 Å.

Table 4. Displacements, δ , of lactone atoms of the hydrochloride from best least-squares plane through atoms O(1), C(9), C(10), and C(11)

	δ
O(1)	— 0·017 Å
C(9)	0.097
C(10)	0.017
C(11)	−0.010
C(8)	0.384

The equation of the plane is 0.0402X + 0.7286Y - 0.6837Z = 1.421 where X, Y, Z are real orthogonal coordinates with axes X along x and Z along z^* .

There appear to be few known structure analyses containing the C_6H_5 - \ddot{C} - \ddot{N} moiety for comparison. The two independent benzylammonium ligands in the chlorocuprate examined by Bonamico & Dessy (1967) showed large bond-length differences but with averages (present numbering) C(1)-C(7), 1.50; C(7)-N, 1.53₅ Å, angle C(1)-C(7)-N 113.5°. Hence that structure has C-N longer than C-C as is also found in 1-benzyl-1,2,2-trimethylazetidinium bromide (Moret & Trefonas, 1968): C-C, 1.51₃; C-N, 1.54₃ Å; C-C-N, 110.0°. In the corresponding lactone hydrobromide (see below) the values are 1.484, 1.506 Å and 112.3° . This tends to throw some doubt on the values in the present structure where C-C is longer than C-N [Fig. 1(*a*)]. No other bond lengths or angles seem to warrant special comment.

Fig. 2. Thermal ellipsoid ORTEP plot (Johnson, 1965) of the hydrochloride molecule viewed along y from a distance of about 20 Å.

Atoms C(1), C(7), N and C(8) have closely similar y coordinates (Table 1) and hence are closely coplanar with the plane of Fig. 2. Thus the twist of the benzene ring with respect to this plane can be clearly seen. It is in fact 73.4°, reminiscent of the 70.5° in dibenzyl (Jeffrey, 1947). In the hydrobromide it is much nearer to the perpendicular value, 84.2°, as it is in the two other compounds discussed above,* namely in the benzylammonium ligands (86.7 and 87.4°) and in benzylazetidinium bromide, 89.7°. These results illustrate the flexibility of the benzyl system.

The molecular packing is shown in Fig. 3. The extended direction of the molecules lies normal to the y axis and close to the (102) plane. The molecules are so stacked that a Cl⁻ ion is closely associated with an NH_2^+ group (they overlap in y projection) either due to weak hydrogen bonding or ionic attraction, or both. The screw axes operate so as to make this into a spiral (Fig. 4). Centrosymmetrically related (as opposed to screw related) pairs of molecules have their lactone rings fairly close together and these are thus required

*Angles not given by the authors cited but calculated from their published data.

to be close to $y = \frac{1}{4}$ and $\frac{3}{4}$ (the actual mean of the lactone atom fractional y coordinates is 0.235).

Apart from possible hydrogen bonding between the nitrogen atom and Cl⁻ there are no non-bonded interactions of note. The Cl⁻···O distances are all in excess of 3.74 Å and N···O(2) at 3.265 Å is too long for a hydrogen bond.

The packing resembles that of the hydrobromide which crystallizes in the $P2_1$ space group.

CRYSTAL STRUCTURE OF THE HYDROBROMIDE

Introduction

The collection of X-ray data for the hydrobromide actually preceded that for the corresponding hydrochloride but because the assigned space group seemed unlikely on chemical grounds, X-ray analysis was delayed until we could be certain that this assignment was correct. Analysis was then followed through to see how the molecule differed, if at all, from that of the corresponding hydrochloride.



Fig. 3. Molecular packing of the hydrochloride in y projection.

Experimental

Colorless crystals were obtained from ethanol solution. Smaller specimens tended to be platy, larger crystals were prismatic. Two sets of intensity data were collected with Cu K α radiation, one by the multi-film photographic technique and the other by automated four-circle diffractometer in the ω -2 θ scan mode.

The calculated linear absorption coefficient for Cu K α radiation is 49.08 cm⁻¹. For both sets of data the crystal was a prismatic needle about 0.1×0.1 mm in cross section and about 0.75 mm long. No absorption corrections were applied to either set of intensities.

Cell dimensions were obtained by Al-wire calibration of the photographs as for the hydrochloride. The dimensions were later checked from diffractometer settings and found to match exactly. Accordingly no refinement of cell parameters from diffractometer settings was carried out.

Crystal data are:

C₁₂H₁₆Br NO₂, M.W. 287·1 Monoclinic (space group, see text) a=6.612 (1), b=10.824 (3), c=9.054 (2) Å. $\beta=98.4$ (3)° V=641.04 Å³ $\varrho=1.50$ g.cm⁻³ (chloroform-carbon tetrachloride), calculated for Z=2 molecules per cell, 1.499 g.cm⁻³.

Systematic absences were only 0k0 for k odd, implying either space group $P2_1$ or $P2_1/m$. However the latter would require the molecule to have either msymmetry, which would be highly improbable on stereochemical grounds, or $\overline{1}$ symmetry which is impossible. However $P2_1$ requires the crystal to be composed of molecules of one hand only, whereas the chemical preparation would generate both enantiomers in equal amounts. The case for $P2_1$ was however strengthened by N(z) tests (Howells, Phillips & Rogers, 1950; Hargreaves & Gogoi, 1966) indicating a centric h0lzone and acentric 0kl zone. Spontaneous resolution on crystallization from the racemic solution seemed to be the only likely explanation. We were able to confirm this as follows. Methanol solutions of the compound were allowed to evaporate slowly over several weeks and from the crystalline deposit eight of the largest crystals, several mm in overall dimensions, were picked out. Although we could not be sure that each was a



Fig. 4. The $NH_2^+ \cdots Cl^- \cdots NH_2^+$ spiral along y.



Fig. 5. Molecule of hydrobromide in y projection viewed from about 20 Å with 40% probability thermal ellipsoids (Johnson, 1965).

Table 5. Fractional coordinates and anisotropic thermal parameters of non-hydrogen atoms of the hydrobromide Temperature factor in form: $10^{-4} \exp \left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$.

	x	у	Z	B 11	B22	B33	B12	B 13	B23
Br	0.1962 (1)	0.2500(1)	0.0962(1)	273 (2)	69 (1)	228 (1)	-19(2)	58 (1)	-18(1)
Ν	-0·1420 (1)	0.0549 (6)	-0.0646(8)	244 (17)	65 (6)	161 (10)	-21(8)	36 (10)	-7 (6)
O(1)	-0·4169 (16)	-0.0369 (7)	0.2200 (9)	662 (34)	96 (7)	233 (13)	-13(13)	162 (18)	48 (8)
O(2)	-0·7174 (20)	-0·1076 (11)	0.1128 (14)	691 (40)	177 (14)	564 (34)	-229(23)	294 (29)	-96 (17)
C(1)	<i>−</i> 0·0149 (14)	0.0830 (8)	0·3073 (9)	336 (25)	92 (8)	126 (10)	-7(11)	44 (13)	5 (8)
C(2)	0.0227 (19)	-0.0254 (10)	-0.3732 (12)	461 (35)	107 (10)	191 (15)	-12(15)	99 (18)	- 5 (10)
C(3)	0.1809 (20)	-0.0345 (12)	-0.4602(15)	509 (43)	138 (14)	252 (19)	19 (19)	143 (24)	-24 (14)
C(4)	0.2973 (19)	0.0670 (15)	-0.4815 (12)	420 (35)	207 (18)	172 (15)	-27(21)	79 (19)	13 (14)
C(5)	0.2630 (20)	0.1747 (14)	-0·4124 (12)	397 (32)	168 (16)	199 (17)	- 64 (19)	51 (19)	42 (13)
C(6)	0.1075 (18)	0.1859 (10)	-0.3245(11)	469 (34)	117 (10)	145 (13)	-27 (16)	27 (17)	12 (9)
C(7)	<i>−</i> 0·1907 (16)	0.0973 (11)	-0.2244(10)	358 (28)	150 (13)	131 (12)	50 (15)	56 (14)	24 (10)
C(8)	-0·3116 (13)	0.0833 (8)	0.0240 (10)	279 (22)	69 (7)	159 (11)	5 (10)	55 (13)	-5 (8)
C(9)	-0·2530 (15)	0.0466 (10)	0.1880 (11)	303 (25)	121 (10)	182 (14)	48 (14)	67 (15)	40 (10)
C(10)	-0.5646 (22)	<i>−</i> 0·0488 (10)	0.0981 (17)	540 (46)	87 (10)	302 (25)	61 (17)	163 (29)	-49 (13)
C(11)	-0.5090 (18)	0.0101 (12)	-0.0325(10)	256 (21)	105 (9)	173 (18)	18 (11)	49 (18)	-2(12)
C(12)	-0.2478(17)	0.1566(13)	0.2919(12)	417 (33)	184 (16)	150 (1 <i>1</i>)	- 89 (20)	A2 (17)	- 34 (12)

single crystal, they were separately dissolved in the minimum of ethanol and the solution checked by plane polarized light. Four solutions gave + ve rotation, two - ve and the other two a rotation too small to be determined with certainly. Clearly spontaneous resolution had occurred, a phenomenon not as rare as sometimes suspected (Secor, 1963).

Structure analysis was carried out on the photographic intensity data, the diffractometer data were used for refinement and are those listed (Table 5).

A total of 1404 photographic intensities were collected and measured out of a possible 1493. A threedimensional sharpened Patterson function was computed using $F^2 = F_o^2/(\sum f_r) \exp(-2.5 \sin^2 \theta/\lambda^2)$, $\sum f_r$ being the sum of the scattering factors per unit cell. The Harker section $v = \frac{1}{2}$ yielded Br⁻ ion (x, z) coordinates of (0.197, 0.0965) and y was set arbitrarily to $\frac{1}{4}$. Electron density phased on Br⁻ positions had, of course, false symmetry $P2_1/m$ but it was easy to pick out at least 15 independent non-hydrogen atoms of one molecule by carefully checking against the Patterson map.

Refinement, although uneventful, was not completely satisfactory. A final conventional R of 0.097 was reached but there were a number if inexplicable photographic intensity discrepancies and the difference map calculated to determine hydrogen atom positions was poorly defined. Accordingly a complete new set of data was collected by diffractometer. A total of 1170 reflections were measured, only 7 of which were too weak to be considered observable. Refinement com-



Fig. 6. (a) Bond lengths and (b) interbond angles of the hydrobromide (schematic).

menced with the atomic parameters found from the photographic data (hydrogen atoms excluded). We used the XFLS variant of ORFLS (Ellison, 1967) with scattering factors including anomalous dispersion taken from International Tables for X-ray Crystallography (1962).

When refinement had converged to a conventional R index of 0.058 a difference Fourier synthesis was carried out but there were no clearly resolved hydrogen peaks. Accordingly we calculated hypothetical positions for all hydrogen atoms except those of the methyl group. When these were included with the same anisotropic thermal parameters as the atoms to which these are attached, R fell to 0.052 (all reflections) and the non-hydrogen parameters changed slightly; their final values are given in Table 5. The 40% probability ellipsoids are plotted via ORTEP in Fig. 5. (Johnson, 1965). The hydrogen atom positions were again slightly adjusted but the new values were not included in the F_c calculation. These hydrogen atom positions are given in Table 6 and final F_c and F_o values in Table 7. The three hydrogen atoms attached to C(12) were excluded owing to uncertainty in their location.

Table 6. Fractional coordinates of hydrogen atoms of the hydrobromide obtained theoretically, using C-H, 1.07 Å

Hydrogen	Attached			
atom	to	x	У	z
1	N	-0.138	-0.044	-0.073
2	N	0.039	0.088	0.035
3	C(2)	<i>-</i> −0·068	-0.101	-0.328
4	C(3)	0.212	-0·117	-0.209
5	C(4)	0.397	0.063	-0.542
6	C(5)	0.356	0.220	-0.426
7	C(6)	0.083	0.269	-0.273
8	C(7)	-0.362	0.056	-0.324
9	C(7)	0·215	0.195	-0.221
10	C(8)	-0.350	0.180	0.005
11	C(9)	<i>-</i> −0·076	0.004	0.260
12	C(11)	- 0.494	-0.065	-0.102
13	C(11)	-0.666	0.065	-0.125

Description of the structure

Bond lengths and interbond angles obtained from the coordinates of Table 5 are given in Fig. 6(a) and (b). The methyl group at C(9) is *trans* with respect to C(8)-N as in the hydrochloride, but the lactone ring itself shows significant differences. Whereas in the latter C(8) is at the envelope 'flap', in the hydrobromide C(11) is at the flap, being 0.12 Å out of plane on the 'nitrogen side' of the ring (see Table 8). The differences in the lactone ring of the hydrochloride and the hydrobromide can be most easily recognized (Fig. 7) by use of a molecular least-squares fit on atoms C(4), C(1), C(7), N and C(8) of the two molecules (Nyburg, 1969). The conclusion that the lactone ring is flexible enough to respond to packing forces seems inescapable. There is some clue to this. If, in the hydrochloride, one lists all the non-bonded halide distances less than 4 Å then

3-BENZYLAMINO-4-HYDROXYPENT-2-ENOIC ACID LACTONE

Table 7. F_o and F_c values for the hydrobromide

Second column $10F_o$, third column $10F_c$.

10 177474780 W 177474780 W 177474780 W 177474780 W 0177474787 W 017747478 W 017747478 W 17747478 W 177474 W 17747 W 0177474 W 177474 W 177
1974 267 A 412 2014 2 412 214 214 2 412 214 214 2 412 214 2 414 214 2
tit i seereeren ikitetitetitetitetitetitetitetitetitetit
bilikisaanee i isilikisaanee i kiikisaanee i tilikisaanee i tilikisaane i tiliksaanee i siisilikisteree i siikistekikistekistekistekistekistekiste
3 311111111111111111111111111111111111
. 1922-1922 - 1922-1923 - 1923-1923 - 1923-1923 - 1923-1923 - 1923-1923-1923-1923-1923-1923-1923-1923-
5 debeled i debeled in and a debeled in a debele
titionne oo. 3 116111410nneee, 3 16111410nneee 5 61141410nnee 5 111410nne 5 11410nn 5 66196144400nneeee 5 661999444400nneeee 5 6619944440400
unere, i dérédételennere, i krétételennere, i krétételennere i tétételenner i tétételenne i tétététenne i tététététennere.
192222 (19222)2022222222222222222222222222222222
2 222222222222222222222222222222222222
tilionne & 1984 illonne & 1984 illonne & tilionne & 1981 illonne & 1981 illonne & 1980 illonne i tilionne i tilionne i tilione
1922 (1923) (1929) (1929) (1920) (1937) (1923) (1923) (1924) (1924) (1924) (1925) (192

C(8) appears three times in the list with C(8)–Cldistances 3·49, 3·56 and 3·67 Å, whereas other lactone ring atoms appear only once in the list. Conversely, in the hydrobromide, only C(11) appears twice, with C(11)–Br⁻ 3·55 and 3·59 Å; C(10) appears only once and the rest not at all. There seems to be a *prima facie* case therefore for concluding that the relatively large interatomic forces between halide ions and carbon atoms are responsible for the observed lactone ring variations.



Fig. 7. Projection of the molecule of hydrochloride and hydrobromide (broken lines) compared by best least-squares fit of atoms C(4), C(1), C(7), N and C(8). Separation of corresponding atoms normal to the plane of the diagram is given in Å.

Table 8. Displacements, δ , of lactone atoms of the hydrobromide from the best least-squares plane through O(1), C(8), C(9) and C(10)

	δ
O(1)	0∙010 Å
C(8)	0.005
C(9)	-0.009
C(10)	- 0.006
C(11)	0.123

The equation of the plane is 0.5319X - 0.7955Y - 0.2903Z = -1.876 where X, Y,Z are real orthogonal coordinates with axes X along x and Z along z^* .

The remaining features of the hydrobromide molecule compare well with those of the hydrochloride except, as we noted in the previous paper (Jones *et al.*, 1968), the lengths of C(1)-C(7) and C(7)-N are reversed in order; in addition the plane C(1)-C(7)-N is more nearly perpendicular, 84.2° , to the plane of the benzene ring than in the hydrochloride, 73.4° .

Molecular packing

Fig. 8 shows the crystal structure in y projection. Although the space groups are different there is a very close relation between the packing in the hydrobromide



Fig. 8. Structure of the hydrobromide in y projection.

and that in the hydrochloride. This can be seen by a suitable comparison of the two projections (Fig. 9). In the hydrochloride the two enantiomorphously related molecules have been designated L and R, in the hydrobromide R has been arbitrarily assigned to all the molecules. The essential difference between the two modes of packing is that centers of symmetry retlating L and R molecules in the hydrochloride are replaced by screw axes relating molecules of the same hand in the hydrobromide.

The Br⁻ ions are located adjacent to the NH₂⁺ ion in a way similar to that for Cl⁻ in the hydrochloride. The actual dimensions are given in Fig. 10.

As in the hydrochloride, no non-bonded interactions call for special comment.

Computer programs used were local variants of *ORFLS* (Busing, Martin & Levy, 1962) and *ORFFE* (Busing, Martin & Levy, 1964).

Thanks are due to Mr J. C. Rylaarsdam for assistance with drawings and to the National Research Council of Canada for financial asupport. The subject matter formed part of a thesis by J.M.Y. for the degree of Ph.D. (Toronto).

References

- BONAMICO, M. & DESSY, G. (1967). Theor. Chim. Acta, 7, 367.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R., MARTIN, K.O. & LEVY, H. A. (1964). Report ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.
- DICKENS, F. & JONES, H. E. H. (1961). Brit. J. Cancer, 15, 85.
- ELLISON, R. D. (1967). Private Communication.
- HAMILTON, W. C. (1955). Acta Cryst. 8, 185.
- HARGREAVES, A. & GOGOI, B. N. (1966). Acta Cryst. 21, 27.
- Howells, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). Acta Cryst. 3, 210.



Fig.9. Scale drawings comparing (a) the hydrochloride and (b) the hydrobromide. The region between broken lines in (a) should be compared with (b). The R, L designation is arbitrary and the symbols are located on the bonds C(7)-N, in both cases.



Fig. 10. The $NH_2^+ \cdots Br^- \cdots NH_2$ spiral along y.

HUGHES, E. W. (1941). J. Amer. Chem. Soc. 63, 1737.

- International Tables for X-ray Crystallography (1962). Vol. III p. 202. Birmingham. Kynoch Press.
- JEFFREY, G. A. (1947). Proc. Roy. Soc. A188, 222.
- JOHNSON, C. K. (1965). Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- JONES, J. B., KOO, C. H., MELLOR, I. P. NYBURG, S. C. & YOUNG. J. M. (1968). *Canad J. Chem.* 46, 813.
- LUKEŠ, R. & LINHARTOVÀ, Z. (1960). Coll. Czech. Chem. Comm. 25, 502.
- MORET, C. L. & TREFONAS, L. M. (1968). J. Hetero. Chem. 5, 149.
- NYBURG, S. C. (1969). *Best Molecular Fit* (local program). SECOR, R. M. (1963). *Chem. Rev.* **63**, 297.