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The Crystal Structure of 1-*endo*-Carboxypyrrolizidine Hydrobromide

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The crystal structure of 1-*endo*-carboxypyrrolizidine hydrobromide, $C_8H_{14}NO_2Br$, has been determined and refined from three-dimensional X-ray data. The unit cell is orthorhombic with the constants $a = 11.3036 \pm 14$, $b = 11.4033 \pm 13$, and $c = 7.8763 \pm 7$ Å. The space group is $P2_12_12_1$ and there are four formula units in the unit cell. The structure was determined with the heavy atom method and all atoms were refined by a full matrix least squares program, the non-hydrogen atoms anisotropically and the hydrogen atoms with isotropic temperature factors. The final R value is 0.048. The ring skeleton of the cation is bent, and the angle between the two five membered rings is 116.2°. The cations are linked together in the b axis direction by hydrogen bonds to the bromine atom.

The primary object of this investigation was to gain information necessary for the explanation of some rather unexpected features in the UV spectrum of the alkaloid (+)-1-methoxypyrrolizidine. The alkaloid was extracted from the orchid *Chysis bractescens* Lindl. This structure determination, however, also gives a good example of structure investigations with X-ray methods as a method of analysis.

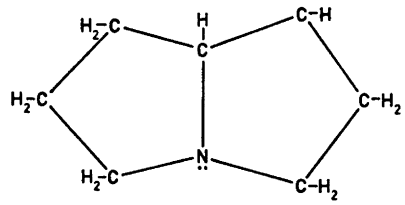

Fig. 1. The pyrrolizidine ring system.

The pyrrolizidine ring system (*cf.* Fig. 1) is rather common in natural product compounds but has not yet been the object of extensive research. It has, however, been shown that the ring system possesses some interesting characteristics.[1] The UV spectrum cannot be easily interpreted. Also the ring

system breaks quite easily. Thus, information on the detailed molecular structures of different pyrrolizidine derivatives is of considerable interest. What was said to be the hydrobromide salt of the alkaloid was kindly supplied by Drs. Björn Lüning and Hans Tränkner. The X-ray diffraction investigation revealed, however, that the crystals consisted of the hydrobromide salt of the acid corresponding to the ester (+)-1-methoxycarbonylpyrrolizidine.

EXPERIMENTAL

The crystals were easily hydrolyzed so that the single crystal selected for study had to be sprayed with a thin protective layer of lacquer (Zapon). No systematic decrease in diffracted X-ray intensity was observed during a three months period after the spraying. Oscillation and Weissenberg photographs showed that the crystals are orthorhombic and the systematic extinctions of reflexions indicated the space group $P2_12_12_1$. A summary of the crystal data is given in Table 1. A crystal which measured 0.33 × 0.14 × 0.16

Table 1. Crystallographic data of 1-*endo*-carboxypyrrolizidine hydrobromide.

Lattice constants	a 11.3036 (14)
	b 11.4033 (13)
	c 7.8763 (7)
Cell volume	1015.24
Density	1.54
Formula units per unit cell	4
Absent reflexions	$h00$ with $h = 2n + 1$
	$0k0$ $k = 2n + 1$
	$00l$ $l = 2n + 1$
Space group	$P2_12_12_1$

mm³ was used for the collection of X-ray diffraction data. The measurements were made on a Siemens AED (Automatischer Einkristall Diffractometer) equipped with a scintillation counter with pulse height discrimination and with Ni-filtered CuK-radiation. The $\theta - 2\theta$ scan technique was used (scan range 1.5°) and the background intensities were calculated as the average of the background intensities at each end of the scan interval. Intensitites for 1179 reflexions were measured, of which 1096 were observable. 990 reflexions had an intensity for which $\sigma I/I \leq 0.20$ and these were included in the refinement. Lp and absorption corrections (μ = 58 cm^{-1}) were applied to the net intensities.

STRUCTURE DETERMINATION

The bromine atom position was obtained from Patterson projections. From these coordinates it was possible, by means of successive electron density maps and least squares refinements, to determine the positions of the non-hydrogen atoms in the unit cell except for the carbon atom in the methyl group in what at this stage still was believed to be an ester. A full matrix least squares refinement was carried out (program LALS) allowing the positional parameters and the anisotropic temperature factors to vary. This resulted in an R index of 0.057. ($R = \sum|kF_o| - \sum|F_c|/\sum|kF_o|$.) A difference Fourier synthesis was then carried out. No peaks indicating the existence of the missing carbon atom were found, but instead the positions

Table 2. Positional parameters with e.s.d.

Br	0.49131 (7)	0.01214) 6)	0.16642 (9)
O1	0.19112 (45)	0.53678 (42)	0.41186 (65)
O2	0.17604 (52)	0.37899 (48)	0.57660 (64)
N	0.33868 (44)	0.24452 (48)	0.10844 (61)
C1	0.30962 (50)	0.36710 (54)	0.35372 (76)
C2	0.37750 (68)	0.43295 (63)	0.21858 (98)
C3	0.43128 (58)	0.33774 (70)	0.11249 (113)
C4	0.26592 (78)	0.24001 (85)	0.94984 (89)
C5	0.14399 (85)	0.21452 (114)	0.01054 (155)
C6	0.13722 (62)	0.28213 (88)	0.17764 (131)
C7	0.25678 (51)	0.26359 (53)	0.26006 (73)
C8	0.22000 (58)	0.43934 (55)	0.44770 (79)
HO2	0.8748 (50)	0.5770 (54)	0.1301 (82)
HN	0.3590 (65)	0.1788 (65)	0.1123 (102)
HC1	0.3616 (47)	0.3423 (46)	0.4382 (71)
HC2A	0.4567 (98)	0.5054 (101)	0.2592 (185)
HC2B	0.3305 (60)	0.4675 (58)	0.1599 (81)
HC3A	0.4560 (54)	0.3584 (54)	0.0194 (92)
HC3B	0.4911 (66)	0.2941 (58)	0.1818 (95)
HC4A	0.2753 (57)	0.3159 (63)	0.9184 (85)
HC4B	0.2998 (67)	0.1833 (72)	0.8734 (108)
HC5A	0.1009 (101)	0.2424 (98)	0.9432 (153)
HC5B	0.1454 (60)	0.1332 (64)	0.0531 (94)
HC6A	0.1353 (52)	0.3649 (61)	0.1503 (80)
HC6B	0.0943 (76)	0.2586 (75)	0.2489 (114)
HC7	0.2543 (51)	0.1903 (60)	0.3204 (80)

Table 3. Thermal parameters with e.s.d.

Br	0.01505 (8)	0.01245 (7)	0.02646 (15)	0.00470 (15)	0.01793 (18)	0.00823 (18)
O1	0.01603 (45)	0.01248 (42)	0.02557 (65)	0.00669 (52)	0.00477 (127)	0.00477 (113)
O2	0.01694 (59)	0.01344 (50)	0.02377 (107)	0.00580 (96)	−0.01483 (130)	0.00097 (120)
N	0.00952 (43)	0.01005 (45)	0.01530 (82)	−0.00014 (78)	0.00404 (99)	−0.00132 (109)
C1	0.00915 (47)	0.01129 (53)	0.01527 (104)	−0.00182 (87)	0.00478 (127)	−0.00238 (129)
C2	0.01105 (62)	0.01106 (60)	0.02395 (143)	−0.00432 (111)	0.00151 (165)	−0.00285 (159)
C3	0.00885 (53)	0.01323 (69)	0.02291 (145)	−0.00230 (102)	0.00307 (152)	−0.00250 (171)
C4	0.01445 (85)	0.01408 (96)	0.01840 (145)	0.00404 (142)	−0.00133 (176)	0.00523 (191)
C5	0.01234 (86)	0.01783 (119)	0.03448 (245)	0.00438 (167)	0.00553 (244)	−0.02015 (307)
C6	0.00871 (54)	0.01478 (88)	0.03198 (198)	0.00424 (115)	−0.00327 (180)	−0.01473 (241)
C7	0.01012 (53)	0.00829 (47)	0.01834 (104)	−0.00093 (82)	−0.00688 (127)	0.00156 (121)
C8	0.01105 (56)	0.01020 (53)	0.01596 (112)	−0.00142 (96)	0.00273 (130)	−0.00331 (123)
HO2	5.5 (1.5)					
HN	7.0 (2.0)					
HC1	4.2 (1.2)					
HC2A	14.7 (3.0)					
HC2B	6.0 (1.9)					
HC3A	5.4 (1.6)					
HC3B	7.4 (1.8)					
HC4A	5.8 (2.2)					
HC4B	8.0 (2.2)					
HC5A	11.4 (3.9)					
HC5B	6.3 (1.9)					
HC6A	5.2 (1.5)					
HC6B	7.8 (2.4)					
HC7	5.5 (1.4)					

Table 4. Bond lengths (Å) with e.s.d.

C1 – C2	1.512	(10)	C2 – HC2A	1.260	(116)
C1 – C7	1.515	(8)	C2 – HC2B	0.806	(66)
C1 – C8	1.501	(9)	C3 – HC3A	0.819	(71)
C2 – C3	1.499	(11)	C3 – HC3B	1.002	(73)
N – C3	1.492	(9)	N – HN	0.784	(75)
N – C4	1.497	(9)	C4 – HC4A	0.896	(72)
N – C7	1.527	(8)	C4 – HC4B	0.963	(83)
C4 – C5	1.487	(13)	C5 – HC5A	0.787	(117)
C5 – C6	1.527	(16)	C5 – HC5B	0.986	(74)
C6 – C7	1.514	(10)	C6 – HC6A	0.969	(70)
C8 – O1	1.192	(8)	C6 – HC6B	0.789	(88)
C8 – O2	1.323	(8)	C7 – HC7	0.961	(67)
C1 – HC1	0.931	(55)	O2 – HO2	0.872	(60)

Table 5. Bond angles in the molecule with e.s.d.

C7 – C1 – C2	104.14	(0.51)	N – C3 – HC3A	115.12	(4.52)
C7 – C1 – C8	113.70	(0.49)	N – C3 – HC3B	97.56	(4.01)
C2 – C1 – C8	114.66	(0.54)	C2 – C3 – HC3A	115.42	(4.37)
C1 – C2 – C3	103.80	(0.58)	C2 – C3 – HC3B	109.29	(4.16)
C2 – C3 – N	104.09	(0.55)	HC3A – C3 – HC3B	113.59	(6.11)
C3 – N – C7	107.88	(0.51)	N – C4 – HC4A	97.67	(4.30)
C3 – N – C4	115.33	(0.58)	N – C4 – HC4B	109.07	(4.82)
C7 – N – C4	108.94	(0.49)	C5 – C4 – HC4A	112.61	(4.26)
N – C4 – C5	104.34	(0.66)	C5 – C4 – HC4B	115.99	(4.69)
C4 – C5 – C6	102.99	(0.79)	HC4A – C4 – HC4B	114.86	(6.55)
C5 – C6 – C7	104.73	(0.66)	C4 – C5 – HC5A	106.12	(8.51)
C6 – C7 – N	103.05	(0.54)	C4 – C5 – HC5B	106.17	(4.08)
C6 – C7 – C1	116.87	(0.59)	C6 – C5 – HC5A	110.20	(8.52)
N – C7 – C1	104.66	(0.46)	C6 – C5 – HC5B	100.53	(4.42)
C1 – C8 – O1	125.43	(0.59)	HC5A – C5 – HC5B	128.23	(9.25)
C1 – C8 – O2	110.27	(0.54)	C5 – C6 – HC6A	107.53	(3.84)
O1 – C8 – O2	124.30	(0.62)	C5 – C6 – HC6B	118.21	(6.39)
C8 – O2 – OH	108.61	(4.17)	C7 – C6 – HC6A	104.55	(3.60)
C3 – N – HN	118.34	(5.37)	C7 – C6 – HC6B	101.31	(6.38)
C4 – N – HN	99.24	(5.74)	HC6A – C6 – HC6B	118.44	(7.26)
C7 – N – HN	106.44	(5.72)	N – C7 – HC7	106.29	(3.72)
C2 – C1 – HC1	109.47	(3.35)	C1 – C7 – HC7	116.59	(3.81)
C7 – C1 – HC1	111.11	(3.90)	C6 – C7 – HC7	107.90	(3.51)
C8 – C1 – HC1	103.89	(3.38)			
C1 – C2 – HC2A	120.49	(6.56)			
C1 – C2 – HC2B	108.17	(4.76)			
C3 – C2 – HC2A	109.18	(5.57)			
C3 – C2 – HC2B	107.54	(4.68)			
HC2A – C2 – HC2B	107.05	(7.37)			

of fourteen hydrogen atoms were detected at reasonable positions with respect to the carbon, nitrogen, and oxygen atoms. Evidently, the compound was not an ester but a carboxylic acid with the composition $C_8H_{14}NO_2Br$ instead of $C_9H_{16}NO_2Br$. A subsequent, full matrix least squares refinement using anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms gave an R index of 0.048. The scattering factor curves used were derived from tables given by Freeman [2] for the bromine, carbon, nitrogen, and oxygen atoms. The hydrogen curve was given by Ste-

Table 6. Observed and calculated structure factors of 1-*endo*-carboxypyrrolizidine hydrobromide. Reflexions marked with an asterisk were not included in the refinement.

	H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC
	0	0	2	25.4	-25.4		1	1	4	16.6	-16.5		0	2	8	10.3	-10.4		0	3	5	48.7	49.0
	0	0	4	51.5	-50.6		1	1	5	26.6	-26.4		1	2	0	62.2	62.4		0	3	6	12.4	-12.4
	0	0	6	15.5	15.6		1	1	6	4.7	4.2		1	2	1	78.5	-78.6		0	3	7	15.5	-14.8
	0	0	8	6.7	-6.0		1	1	7	14.1	-14.8		1	2	2	88.3	-83.7		1	3	0	39.0	36.8
	1	0	1	6.4	-6.3		1	1	8	4.2	-4.6		1	2	3	23.9	-23.2		1	3	1	61.1	-60.1
	1	0	2	105.4	105.8		1	1	9	9.6	8.3		1	2	4	54.5	-54.9		1	3	2	36.1	-35.7
	1	0	3	5.6	5.4		2	1	0	17.6	16.6		1	2	5	13.0	-13.3		1	3	3	60.2	59.9
	1	0	4	51.5	-50.9		2	1	1	107.1	106.5		1	2	6	7.2	-6.6		1	3	4	18.1	-18.3
	1	0	5	8.4	8.4		2	1	2	33.6	-32.8		1	2	7	7.6	7.5		1	3	5	16.2	-16.0
	1	0	6	4.6	-4.5		2	1	3	13.2	-11.6		1	2	8	7.4	-11.0		1	3	6	10.9	10.0
	1	0	7	7.1	-6.4		2	1	4	20.0	19.9		2	2	0	124.3	125.6		1	3	7	14.4	-14.4
	1	0	8	6.7	6.5		2	1	5	36.5	-36.7		2	2	1	32.4	31.2		1	3	9	6.5	5.7
	2	0	0	6.9	6.4		2	1	6	7.2	-6.5		2	2	2	61.8	-60.7		2	3	0	25.1	23.8
	2	0	1	43.2	42.7		2	1	7	21.0	-19.8		2	2	3	24.5	-23.9		2	3	1	88.4	86.4
	2	0	2	71.2	-73.0		2	1	8	4.0	-3.5		2	2	4	19.7	-17.6		2	3	2	18.5	-18.5
	2	0	3	20.8	21.0		3	1	0	13.2	13.3		2	2	5	11.6	-11.7		2	3	3	23.4	22.1
	2	0	4	25.5	-25.3		3	1	1	80.8	-80.8		2	2	6	27.6	27.0		2	3	4	22.5	22.2
	2	0	5	10.8	-11.3		3	1	2	10.6	11.0		2	2	7	5.4	6.1		2	3	5	31.5	31.3
	2	0	6	43.5	40.8		3	1	3	65.4	62.8		2	2	8	3.1	-3.5		2	3	7	13.5	-13.3
	2	0	7	8.8	-7.9		3	1	4	14.2	14.1		3	2	0	12.2	12.6		3	3	0	20.0	20.2
	2	0	8	5.5	-4.2		3	1	5	16.0	-14.9		3	2	1	44.4	41.8		3	3	1	54.2	-54.9
*	3	0	1	10.4	2.6		3	1	6	12.1	12.1		3	2	2	50.7	-50.5		3	3	2	21.3	-20.8
	3	0	2	56.5	-55.8		3	1	8	4.8	-5.7		3	2	3	12.8	12.7		3	3	3	79.4	78.6
	3	0	3	84.1	82.5		3	1	9	7.1	7.0		3	2	4	42.1	-42.5		3	3	4	11.9	12.2
	3	0	4	31.4	30.2		4	1	0	17.9	19.3		3	2	5	8.8	8.7		3	3	5	14.6	-14.8
	3	0	5	55.8	-54.1		4	1	1	78.1	-76.9		3	2	6	5.8	-7.1		3	3	6	12.8	13.1
	3	0	6	9.0	8.1		4	1	2	34.7	33.7		3	2	8	8.4	8.4		3	3	7	12.1	-11.5
	3	0	8	5.4	3.9		4	1	3	18.5	-18.1		4	2	0	83.5	84.2		3	3	9	6.7	6.2
	3	0	7	5.2	-5.9		4	1	4	14.0	13.1		4	2	1	25.2	23.0		4	3	0	15.6	14.9
	4	0	0	14.9	14.6		4	1	5	35.2	35.1		4	2	2	37.5	-37.9		4	3	1	58.4	58.7
	4	0	1	61.8	60.8		4	1	6	14.7	15.6		4	2	3	29.3	29.7		4	3	2	19.4	-18.9
	4	0	2	12.7	11.4		4	1	7	15.1	13.8		4	2	4	31.7	-30.7		4	3	3	10.0	-9.4
	4	0	3	35.7	-35.0		4	1	8	6.3	-6.0		4	2	5	10.9	-11.3		4	3	4	19.0	19.1
	4	0	5	17.7	17.7		5	1	0	22.7	21.9		4	2	6	29.2	28.2		4	3	5	22.7	-22.6
	4	0	4	13.7	-13.9		5	1	1	14.7	-15.1		4	2	7	5.0	-4.4		4	3	7	13.0	12.9
	4	0	5	4.7	-5.3		5	1	2	23.1	-21.4		4	2	8	7.5	-6.6		5	3	0	6.7	6.9
	4	0	6	21.0	20.3		5	1	3	55.3	56.6		5	2	0	2.4	-2.3		5	3	1	14.3	-15.1
	4	0	8	5.0	-7.6		5	1	4	4.3	3.9		5	2	1	22.8	22.0		5	3	2	24.0	-23.6
	5	0	1	12.3	-11.8		5	1	5	26.3	-25.2		5	2	2	57.4	56.4		5	3	3	45.7	45.9
	5	0	2	45.6	45.9		5	1	6	7.0	6.8		5	2	3	23.5	-23.2		5	3	4	6.6	7.4
	5	0	3	5.5	5.9		5	1	7	5.4	-10.1		5	2	4	25.1	-24.6		5	3	5	19.1	-18.8
	5	0	4	30.1	-29.4		5	1	8	4.1	-5.0		5	2	5	8.5	7.9		5	3	6	13.3	13.0
	5	0	5	14.5	14.6		6	1	0	34.6	32.6		5	2	6	4.3	-4.3		5	3	7	4.6	-5.1
	5	0	6	5.8	4.7		6	1	1	46.5	45.6		5	2	7	11.2	11.7		6	3	0	33.4	32.6
	5	0	7	5.0	-5.6		6	1	2	19.4	-18.6		5	2	8	8.0	8.1		6	3	1	32.8	-32.7
	5	0	8	7.5	8.2		6	1	3	5.7	5.6		6	2	0	52.6	51.7		6	3	2	2.7	-1.9
	6	0	0	70.2	70.2		6	1	4	13.6	-14.3		6	2	1	18.4	-18.3		6	3	3	12.5	12.2
	6	0	1	14.6	14.7		6	1	5	13.9	14.4		6	2	2	29.9	-29.0		6	3	4	20.2	20.7
	6	0	2	16.8	-16.3		6	1	6	4.5	-4.0		6	2	3	14.3	14.2		6	3	5	21.7	-21.5
	6	0	3	7.6	7.7		6	1	7	13.2	-12.5		6	2	4	7.6	-7.4		6	3	6	6.4	-6.7
	6	0	4	25.4	-25.1		7	1	0	12.5	13.0		6	2	5	13.6	-15.3		6	3	7	14.4	13.9
	6	0	5	23.8	-24.7		7	1	1	24.7	-24.8		6	2	6	14.7	14.5		7	3	0	17.5	16.9
	6	0	6	22.3	21.2		7	1	2	21.6	-21.7		6	2	8	6.1	-5.9		7	3	1	16.5	-17.4
	6	0	8	7.2	-6.3		7	1	3	31.8	30.3		7	2	0	3.7	3.7		7	3	2	17.7	-18.0
	7	0	2	25.1	25.2		7	1	4	6.5	7.2		7	2	1	13.2	12.3		7	3	3	23.2	23.2
	7	0	3	9.2	10.4		7	1	5	11.5	-11.0		7	2	2	22.9	23.0		7	3	4	7.1	-7.2
	7	0	4	31.3	-30.8		7	1	6	10.7	11.2		7	2	3	7.6	8.2		7	3	5	14.8	-14.2
	7	0	5	5.6	5.2		7	1	8	4.8	-5.7		7	2	4	32.4	-31.3		7	3	6	8.8	8.6
	7	0	7	9.5	-10.1		8	1	0	11.4	11.3		7	2	5	9.0	-8.7		8	3	0	7.6	7.2
	7	0	8	4.0	3.9		8	1	1	25.7	-26.2		7	2	6	3.8	3.1		8	3	1	21.5	-20.9
	8	0	0	29.0	28.6		8	1	2	4.4	-4.1		7	2	7	9.0	-10.0		8	3	2	4.6	-4.4
	8	0	1	11.4	11.7		8	1	4	17.0	15.5		7	2	8	3.8	5.6		8	3	3	4.1	4.4
	8	0	2	25.5	-25.3		8	1	5	15.5	-15.3		8	2	0	17.2	16.9		8	3	4	11.7	11.7
	8	0	3	20.3	20.9		8	1	6	4.6	-5.6		8	2	1	9.6	9.4		8	3	5	7.5	8.1
	8	0	4	8.6	8.1		8	1	7	9.6	-9.2		8	2	2	17.1	-16.2		8	3	6	6.2	-7.1
	8	0	5	5.5	-6.7		9	1	1	11.1	-11.1		8	2	3	5.1	5.4		8	3	7	8.3	8.1
	8	0	6	14.5	13.7		9	1	2	7.7	-8.5		8	2	4	9.1	-9.2		9	3	0	6.6	6.5
	9	0	1	20.3	-19.8		9	1	3	18.1	17.6		8	2	5	8.9	-9.5		9	3	1	4.7	-4.8
	9	0	2	11.2	10.6		9	1	4	5.6	5.9		8	2	6	13.0	12.5		9	3	2	9.7	-9.9
	9	0	3	12.2	12.9		9	1	5	9.0	-8.0		9	2	0	3.6	-3.5		9	3	3	16.6	16.0
	9	0	4	15.5	-15.4		9	1	6	7.7	7.7		9	2	1	7.5	7.7		9	3	4	6.5	7.4
	9	0	5	3.5	3.0		9	1	7	2.3	-1.9		9	2	2	21.6	-21.6		9	3	5	9.5	-9.1
	9	0	6	8.5	8.1		10	1	0	9.0	9.1		9	2	3	9.6	10.6		9	3	6	6.7	6.9
	9	0	7	7.8	-8.1		10	1	1	12.7	-11.9		9	2	4	12.5	11.9		10	3	0	3.5	4.1
	10	0	1	1.7	1.7		10	1	2	5.0	4.7		9	2	5	5.5	-5.7		10	3	1	11.1	10.7
	10	0	2	4.5	-4.2		10	1	3	7.3	6.2		9	2	6	5.3	-4.9		10	3	2	6.1	-5.7
	10	0	4	4.2	-4.9		10	1	5	7.4	6.8		9	2	7	4.6	5.2		10	3	3	5.1	-4.6
	10	0	5	7.0	-7.9		10	1	6	5.5	-6.0		10	2	0	25.5	25.0		10	3	4	5.3	6.0
	10	0	6	8.3	7.9		11	1	0	4.4	4.1		10	2	1	10.0	10.7		10	3	5	5.6	5.9
	11	0	2	7.6	7.2		11	1	1	5.5	-5.3		10	2	2	8.9	-8.2		10	3	6	2.5	2.9
	11	0	3	3.6	4.5		11	1	2	8.7	-9.3		10	2	3	10.4	10.2		11	3	0	3.1	3.1
	11	0	4	8.8	-8.4		11	1	3	8.8	8.4		10	2	5	7.6	-8.5		11	3	1	5.6	-5.7
	12	0	0	7.2	6.6		11	1	5	8.0	-7.3		10	2	6	5.9	5.8		11	3	2	3.4	-4.1
	12	0	1	3.8	4.5		12	1	0	3.6	4.4		11	2	1	7.3	-7.5		11	3	3	7.7	7.3
	12	0	2	4.7	-4.0		12	1	1	8.2	-7.3		11	2	2	3.8	-3.3		11	3	5	6.3	-5.5
	12	0	3	3.4	3.4		12	1	2	2.6	-2.1		11	2	3	6.8	-7.3		12	3	0	3.5	4.0
	13	0	2	5.2	5.0		12	1	3	2.9	2.3		11	2	4	8.4	7.5		12	3	1	5.3	-5.0
	0	1	1	50.5	-50.6		12	1	4	5.5	-5.7		11	2	5	3.4	3.0		12	3	3	2.9	2.6
	0	1	2	47.5	-48.2		13	1	2	3.2	-3.8		12	2	0	2.7	1.7		12	3	4	4.6	4.9
	0	1	3	7.4	-8.8		13	1	3	3.9	3.6		12	2	1	2.8	3.3		13	3	1	3.0	-2.7
	0	1	4	3.1	2.5		0	2	0	56.2	52.2		12	2	2	5.6	-5.0		0	4	0	109.6	114.8
	0	1	5	39.5	40.6		0	2	1	36.3	-38.8		12	2	3	3.4	3.3		0	4	1	5.3	-5.5
	0	1	6	7.6	7.1		0	2	2	45.5	-47.3		13	2	1	3.6	3.6		0	4	2	39.3	-41.0
	0	1	7	18.6	-17.4		0	2	3	3.3	3.3		13	2	3	2.4	3.1		0	4	3	22.4	21.7
	1	1	0	22.5	22.2		0	2	4	34.1	-32.3		0	3	1	86.5	-90.1		0	4	4	15.0	-14.7
	1	1	1	69.4	-68.5		0	2	5	3.0	-2.4		0	3	2	20.0	-20.4		0	4	5	8.6	-8.2
	1	1	2	24.4	-24.0		0	2	6	28.8	28.0		0	3	3	13.4	-14.1		0	4	6	19.3	19.2
	1	1	3	85.4	85.5	*	0	2	7	0.3	0.0		0	3	4	3.7	3.0		0	4	8	3.7	-3.2

Table 6. Continued.

H	K	L	FO	FC
1	4	C	7.5	7.9
1	4	1	44.5	43.9
1	4	2	77.7	77.8
1	4	3	7.7	6.9
1	4	4	31.5	32.7
1	4	5	9.4	-8.6
1	4	6	4.C	4.0
1	4	7	7.5	7.3
1	4	8	8.6	-8.6
2	4	C	54.6	55.5
2	4	1	21.8	-21.7
2	4	2	33.5	-34.0
2	4	3	23.8	-23.0
2	4	4	31.5	-30.8
2	4	5	16.5	-16.9
2	4	6	28.5	28.8
3	4	C	4.7	-3.4
3	4	1	36.2	37.6
3	4	2	18.6	-19.4
3	4	3	8.7	-9.4
3	4	4	46.6	47.8
3	4	5	9.2	-8.7
3	4	6	6.5	-6.9
3	4	7	5.3	5.5
3	4	8	6.1	5.5
4	4	C	62.7	64.9
4	4	1	25.0	24.3
4	4	2	26.C	-27.6
4	4	3	15.8	20.7
4	4	4	9.5	-9.8
4	4	5	12.3	-12.9
4	4	6	14.C	14.2
5	4	C	8.C	-7.5
5	4	1	18.7	18.9
5	4	2	54.1	55.0
5	4	3	10.9	-11.4
5	4	4	22.8	-23.5
5	4	5	5.1	-4.9
5	4	7	9.3	9.8
6	4	C	35.3	35.9
6	4	1	6.6	6.8
6	4	2	18.C	-18.6
6	4	3	10.1	-9.7
6	4	4	15.5	-17.7
6	4	5	11.7	-12.5
6	4	6	15.5	15.5
7	4	C	5.5	-5.4
7	4	1	14.3	14.7
7	4	2	25.1	25.7
7	4	3	15.1	-16.1
7	4	4	15.1	14.4
7	4	5	7.6	-7.5
7	4	6	2.5	-3.1
7	4	7	6.4	7.5
8	4	C	33.3	33.6
8	4	1	9.3	10.5
8	4	2	13.E	-14.0
8	4	3	14.C	14.6
8	4	4	4.8	-4.7
8	4	5	9.C	-10.3
8	4	6	10.2	10.0
9	4	C	2.4	-2.0
9	4	1	3.C	3.7
9	4	2	10.1	10.7
9	4	3	5.3	5.7
9	4	4	4.9	5.9
9	4	5	14.4	13.7
10	4	C	2.7	2.4
10	4	1	3.C	2.5
10	4	2	6.2	6.9
10	4	3	6.5	-6.0
10	4	4	4.5	5.1
10	4	5	6.E	-7.5
10	4	6	6.2	6.1
11	4	C	4.6	4.4
11	4	1	5.2	-9.1
11	4	2	5.2	-6.2
11	4	3	6.6	6.6
11	4	4	3.6	-3.3
12	4	C	6.4	6.1
12	4	2	4.7	-4.3
12	4	3	3.C	2.9
13	4	1	3.3	3.6
C	5	1	44.C	-45.9
C	5	2	27.5	-28.5
C	5	3	5.C	-5.7
C	5	4	32.5	30.9
C	5	5	28.1	29.0
C	5	7	12.E	-12.7
C	5	E	1.1	0.6
1	5	C	26.1	29.5
1	5	1	37.4	-37.4
1	5	2	20.1	-20.3
1	5	3	53.C	53.8
1	5	4	8.5	-8.5
1	5	5	15.1	-14.7
1	5	6	5.2	4.4
1	5	7	6.C	-6.3
1	5	8	5.E	5.3
2	5	C	11.2	10.4
2	5	1	53.5	-55.9
2	5	2	15.E	-15.6
2	5	3	8.6	-8.2
2	5	4	16.C	15.5
2	5	5	19.5	19.9
2	5	6	15.1	-14.5
2	5	7	9.5	9.4
3	5	C	2.5	2.8
3	5	1	22.5	-22.8
3	5	2	21.2	-20.3
3	5	3	38.1	37.9
3	5	4	4.7	5.1
3	5	5	14.2	-13.6
3	5	6	17.4	16.1
3	5	7	10.3	-10.5
4	5	C	12.1	11.5
4	5	1	40.9	-40.4
4	5	2	7.7	-7.3
4	5	3	6.4	5.7
4	5	4	13.4	12.7
4	5	5	22.8	22.7
4	5	7	12.9	-11.6
5	5	C	27.5	26.7
5	5	1	21.9	-22.1
5	5	2	9.1	-9.1
5	5	3	26.7	26.6
5	5	4	11.1	11.C
5	5	5	9.2	-8.7
5	5	7	8.2	8.5
5	5	7	3.6	-3.5
6	5	C	8.C	7.9
6	5	1	25.8	-26.4
6	5	2	25.0	-24.7
6	5	3	7.1	6.4
6	5	4	12.7	12.8
6	5	5	14.9	15.1
6	5	6	4.9	-5.7
6	5	7	8.8	8.1
7	5	C	15.2	19.0
7	5	1	11.4	-12.0
7	5	2	15.0	-15.3
7	5	3	25.2	26.1
7	5	4	6.6	-6.7
7	5	5	8.0	-7.8
8	5	6	6.9	7.0
8	5	7	3.3	-3.0
8	5	C	9.4	10.1
8	5	1	15.9	-15.8
8	5	2	5.7	-5.1
8	5	3	4.7	-4.6
8	5	4	13.3	14.C
8	5	5	6.5	-6.2
8	5	6	4.1	-4.2
8	5	7	5.4	5.6
9	5	C	6.5	5.7
9	5	1	11.1	-11.2
9	5	2	10.5	-11.0
9	5	3	11.9	12.1
9	5	5	8.0	-7.7
9	5	6	5.4	6.1
10	5	C	7.2	7.8
10	5	1	10.8	10.8
10	5	2	5.3	-5.1
10	5	3	3.3	3.5
10	5	4	6.C	6.5
10	5	5	4.5	-4.5
11	5	C	4.3	4.1
11	5	2	4.3	-5.1
11	5	3	3.5	3.3
12	5	C	4.1	5.C
12	5	1	3.5	-3.2
12	5	3	2.4	-2.5
13	5	C	2.1	1.7
0	6	C	29.3	30.1
0	6	2	17.9	-18.6
0	6	3	3.4	3.9
0	6	4	28.4	-29.0
0	6	5	15.6	-16.C
0	6	6	20.1	21.6
1	6	C	19.9	-19.6
1	6	1	24.6	26.3
1	6	2	43.5	+44.0
1	6	4	25.1	27.2
1	6	5	8.5	-8.7
1	6	7	6.9	7.2
1	6	8	6.1	-6.8
2	6	C	73.3	73.0
2	6	1	17.6	-18.2
2	6	2	16.C	-17.3
2	6	3	24.5	25.3
2	6	4	13.6	-14.7
2	6	5	7.2	-7.4
2	6	6	10.4	11.3
2	6	8	2.8	-2.7
3	6	C	4.6	4.7
3	6	1	16.2	17.5
3	6	2	42.3	-44.1
3	6	3	11.3	-12.C
3	6	4	18.9	-2C.7
3	6	5	7.6	-8.5
3	6	6	34.9	3.6
3	6	7	7.7	7.6
3	6	8	4.9	5.7
4	6	1	17.1	17.8
4	6	2	22.C	-22.0
4	6	3	21.7	22.C
4	6	4	14.5	-15.5
4	6	5	13.5	-13.7
4	6	6	15.7	16.6
4	6	7	5.4	-5.4
4	6	8	2.9	-3.6
5	6	C	8.2	8.7
5	6	1	23.8	24.6
5	6	2	22.5	23.C
5	6	3	13.8	-14.1
5	6	4	2C.5	20.2
5	6	5	9.0	-8.2
5	6	6	4.9	-5.1
5	6	7	7.2	7.C
5	6	8	3.5	4.1
6	6	1	12.3	12.4
6	6	2	14.8	-14.8
6	6	3	13.1	12.9
6	6	5	10.5	-10.5
6	6	6	9.7	9.4
7	6	0	12.8	-13.4
7	6	1	12.7	12.2
7	6	2	9.6	10.1
7	6	3	5.7	-6.0
7	6	4	14.4	14.6
7	6	5	3.5	-3.6
7	6	6	2.8	2.8
7	6	7	5.2	5.8
8	6	0	5.7	5.9
8	6	1	10.1	10.2
8	6	2	5.0	-5.0
8	6	3	6.7	-6.4
8	6	4	4.4	-5.3
8	6	5	6.6	-7.6
8	6	6	7.8	7.9
9	6	0	7.0	7.3
9	6	1	4.8	4.4
9	6	2	8.3	-8.4
9	6	3	5.7	-5.9
9	6	4	7.2	-7.5
9	6	5	3.1	-3.3
9	6	6	2.3	-2.3
10	6	0	9.9	9.8
10	6	2	6.2	-6.0
10	6	3	7.4	7.0
10	6	5	4.2	-4.5
11	6	1	5.5	5.5
11	6	2	3.2	3.3
11	6	3	2.3	-3.1
11	6	4	4.0	3.6
12	6	0	2.5	2.5
12	6	2	1.9	-2.0
0	7	1	40.7	-43.4
0	7	2	17.9	-19.3
0	7	4	16.4	17.0
0	7	5	7.7	8.4
0	7	6	5.9	-5.7
0	7	7	8.8	-9.0
0	7	8	3.6	-3.2
1	7	0	30.2	32.1
1	7	1	20.0	-20.8
1	7	2	12.9	-13.3
1	7	3	28.6	29.7
1	7	4	9.8	9.6
1	7	5	10.1	-10.6
1	7	6	8.0	7.7
1	7	7	7.9	-8.6
1	7	8	4.6	-4.8
2	7	C	3.7	3.3
2	7	1	29.4	-29.8
2	7	2	16.1	+17.5
2	7	4	13.6	13.7
2	7	5	24.0	24.9
2	7	7	6.4	6.5
3	7	C	16.5	17.5
3	7	1	15.9	-16.7
3	7	2	16.6	-17.0
3	7	3	27.2	28.4
3	7	4	5.3	5.5
3	7	5	4.4	-4.6
3	7	6	8.1	8.2
3	7	7	3.9	-3.9
4	7	0	11.7	11.7
4	7	1	25.3	26.3
4	7	2	16.1	-15.9
4	7	3	5.0	-5.6
4	7	4	12.8	13.7
4	7	5	11.9	-12.8
4	7	6	5.3	-5.8
4	7	7	5.6	-6.0
5	7	0	16.5	16.6
5	7	1	15.3	-15.5
5	7	2	8.8	-9.1
5	7	3	21.3	22.6
5	7	4	3.9	-3.8
5	7	5	6.8	-6.9
5	7	6	6.8	7.2
5	7	7	5.2	-5.3
6	7	1	14.8	-15.2
6	7	2	5.8	-6.4
6	7	4	14.8	14.6
6	7	5	9.6	-10.1
6	7	6	4.1	-4.4
6	7	7	6.0	5.9
7	7	0	10.5	9.7
7	7	1	5.5	-5.7
7	7	2	10.7	-11.0
7	7	3	11.8	12.0
7	7	4	3.7	3.9
7	7	5	7.0	-6.6
7	7	6	7.1	7.0
8	7	0	11.2	11.3
8	7	1	16.4	-16.8
8	7	2	7.1	-7.0
8	7	3	4.1	-3.2
8	7	4	7.1	7.5
8	7	5	6.2	6.2
8	7	6	3.4	-3.7
9	7	C	5.1	4.5
9	7	1	6.2	-6.4
9	7	2	7.6	-8.2
9	7	3	7.6	7.8
9	7	5	2.7	-2.9
10	7	C	4.8	5.4
10	7	1	3.8	3.9
10	7	2	5.C	-5.2
10	7	4	4.E	5.3
11	7	C	4.6	4.3
11	7	2	4.9	-5.4
11	7	3	5.C	5.2
12	7	0	2.4	3.3
0	8	0	40.3	41.5
0	8	1	3.C	-2.8
0	8	2	10.5	-11.2
0	8	3	19.8	20.3
0	8	4	15.0	-16.2
0	8	5	12.2	-12.3
0	8	6	7.6	8.2
1	8	0	4.9	-4.0
1	8	1	14.4	15.9
1	8	2	22.7	23.3
1	8	3	9.1	-9.3
1	8	4	13.4	-13.5
1	8	5	5.5	-5.7
1	8	6	5.3	5.1
2	8	0	20.2	20.5
2	8	1	14.0	13.9
2	8	2	7.7	-7.1
2	8	3	19.5	20.1
2	8	4	9.9	-9.8
2	8	5	9.4	-9.6
2	8	6	11.6	11.6
3	8	C	5.4	5.0
3	8	1	20.6	21.4
3	8	2	24.1	24.6
3	8	3	6.E	-7.2
3	8	4	12.7	13.0
3	8	5	8.4	-8.1
3	8	6	4.4	-3.9
3	8	7	6.9	6.7
4	8	0	23.2	23.0
4	8	1	8.C	-8.3
4	8	2	16.4	-16.5
4	8	3	11.7	-11.4
4	8	4	5.4	-5.5
4	8	5	7.9	-7.2
4	8	6	8.C	8.1
5	8	1	16.2	15.4
5	8	2	9.9	9.6
5	8	3	5.1	-4.7
5	8	4	14.C	-13.6
5	8	5	4.7	-4.0
5	8	7	5.2	4.8
6	8	0	20.8	20.4
6	8	1	11.7	11.4
6	8	2	4.5	-4.9
6	8	3	12.2	11.8
6	8	4	10.6	-10.7
6	8	5	6.4	-6.5
6	8	6	6.3	6.1
7	8	1	8.9	7.9
7	8	3	6.0	6.5
7	8	5	3.7	-3.8
8	8	0	6.1	6.1
8	8	1	7.7	7.7
8	8	2	3.8	-3.9
8	8	3	9.4	8.8
8	8	5	4.6	-5.0
9	8	1	8.E	8.9
9	8	2	3.9	3.9
9	8	3	4.4	5.1
9	8	4	6.1	6.2
10	8	1	2.4	2.7
10	8	2	2.6	-2.7
10	8	3	3.5	3.8
11	8	1	3.5	3.1
11	8	2	2.2	-2.2
0	9	1	20.7	-20.8
0	9	2	15.3	-16.8
0	9	3	12.4	-12.6
0	9	4	7.5	7.C
0	9	5	8.7	8.5
0	9	7	2.2	-2.5
1	9	0	21.C	22.2
1	9	1	14.9	-14.4
1	9	2	8.C	8.1
1	9	3	21.C	21.9
1	9	4	7.E	8.9
1	9	5	4.3	-4.8
1	9	6	7.7	7.4
1	9	7	4.1	-4.5
2	9	0	9.5	9.6
2	9	1	18.3	18.3
2	9	2	10.C	-1C.7
2	9	3	3.1	2.7
2	9	4	13.5	13.8
2	9	5	10.E	-11.5
2	9	6	3.E	-3.5
2	9	7	2.5	3.0
3	9	C	7.4	7.8
3	9	1	9.C	-9.1
3	9	2	14.9	-15.0
3	9	3	11.2	11.7
3	9	4	4.4	-4.7
3	9	5	5.3	5.7
3	9	7	4.1	-4.6
4	9	0	7.7	8.5
4	9	1	11.2	11.2
4	9	2	7.E	-7.9
4	9	3	4.E	-5.1
4	9	4	11.6	12.0
4	9	5	9.1	9.7
4	9	6	3.5	-3.8
5	9	0	18.5	19.1

Table 6. Continued.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	5	1	6.7	-9.0	2	10	1	6.0	-5.5	0	11	5	4.8	4.3	0	12	5	5.4	-4.4
5	5	2	9.1	-9.7	2	10	2	9.4	-8.8	0	11	6	4.5	-4.3	1	12	0	4.0	-4.4
5	5	3	9.1	8.9	2	10	3	10.4	9.8	1	11	0	7.9	7.2	1	12	1	10.7	9.5
5	5	5	2.5	-3.0	2	10	4	7.1	-6.5	1	11	1	8.2	-7.6	1	12	2	10.2	8.8
5	5	6	4.5	5.2	2	10	5	5.7	-5.1	1	11	2	7.2	6.3	1	12	3	3.7	-2.9
6	5	1	5.6	-10.1	2	10	6	3.1	3.1	1	11	3	7.7	6.6	1	12	4	3.6	-2.8
6	5	2	10.7	-11.0	3	10	0	3.3	-3.5	1	11	5	3.2	-2.7	2	12	0	9.5	7.5
6	5	4	7.2	7.1	3	10	1	13.3	12.7	2	11	1	6.2	-5.6	2	12	1	7.1	6.8
6	5	5	4.2	3.6	3	10	2	17.2	16.1	2	11	2	6.2	-5.1	2	12	3	7.7	6.7
6	5	6	2.6	-2.7	3	10	3	3.0	3.3	2	11	4	10.6	9.7	2	12	4	6.4	-5.4
7	5	0	7.1	6.3	3	10	4	4.5	4.0	2	11	5	7.3	6.9	3	12	1	7.6	6.7
7	5	2	7.6	-7.2	3	10	5	3.8	-3.5	3	11	0	14.6	13.5	3	12	2	3.6	2.8
7	5	3	9.8	9.9	4	10	0	5.3	8.9	3	11	1	4.9	-4.2	3	12	4	3.1	2.7
7	5	4	3.2	2.9	4	10	1	5.1	5.1	3	11	2	8.3	-7.8	4	12	0	6.7	5.5
7	5	5	5.1	-4.6	4	10	2	7.0	-6.8	3	11	3	9.8	9.1	4	12	1	4.0	3.1
8	5	0	8.3	7.9	4	10	3	10.6	10.6	4	11	0	5.3	4.8	4	12	3	5.9	4.9
8	5	1	4.6	4.1	4	10	4	7.5	-7.3	4	11	1	8.8	8.1	4	12	4	2.6	-2.4
8	5	2	2.5	-2.9	4	10	5	6.9	-6.6	4	11	2	9.1	-8.5	5	12	1	5.6	5.0
8	5	3	2.6	-2.2	4	10	6	5.0	5.0	4	11	4	7.0	6.1	5	12	2	3.8	3.2
8	5	4	7.6	7.2	5	10	1	6.0	5.2	4	11	5	2.4	-2.3	5	12	3	3.0	-2.3
9	5	0	4.2	3.9	5	10	2	7.4	-7.5	5	11	0	11.1	10.2	5	12	2	4.0	3.2
9	5	1	3.0	-3.2	5	10	3	5.7	-5.7	5	11	1	3.8	-3.5	5	12	3	2.7	-2.3
9	5	2	4.8	-4.4	5	10	4	8.3	8.2	5	11	2	6.1	-5.5	6	12	1	2.6	2.4
9	5	3	2.2	2.5	5	10	5	4.3	-4.4	5	11	3	5.1	4.8	7	12	1	4.7	4.4
10	5	1	3.6	-3.6	6	10	0	8.8	8.9	6	11	0	3.5	3.3	0	13	2	7.0	-6.2
10	5	2	3.1	-2.8	6	10	1	7.1	6.5	6	11	1	4.0	-3.6	0	13	3	3.6	-3.0
0	10	1	10.4	-9.8	6	10	2	3.8	-3.8	6	11	2	5.8	-5.4	1	13	0	8.3	7.6
0	10	2	8.0	-5.7	6	10	3	8.5	7.6	6	11	3	2.7	-2.3	1	13	1	3.5	-2.8
0	10	3	14.2	13.2	6	10	5	3.5	-3.1	6	11	4	5.4	4.9	1	13	2	3.4	-2.5
0	10	4	7.0	-6.1	7	10	1	9.2	8.9	7	11	0	4.4	3.7	1	13	3	3.9	3.3
0	10	5	6.7	-6.3	7	10	2	4.4	4.4	7	11	2	4.6	-4.0	2	13	1	4.6	4.0
0	10	6	5.4	9.3	7	10	3	3.1	-3.3	7	11	3	4.4	4.0	2	13	2	4.1	-3.4
1	10	0	0.7	-0.4	8	10	0	4.6	4.3	8	11	0	2.6	2.8	3	13	0	5.2	4.0
1	10	1	15.5	14.9	8	10	2	2.5	-2.6	8	11	1	3.1	3.1	3	13	2	5.5	-4.6
1	10	2	10.8	-10.0	9	10	1	4.4	4.1	8	11	2	4.2	-3.8	4	13	1	2.6	-1.7
1	10	3	5.0	-5.0	9	10	2	2.5	-3.0	0	12	0	8.2	6.5	4	13	2	4.2	-4.0
1	10	4	8.8	-8.3	0	11	1	14.6	-13.7	0	12	2	4.0	-3.3	5	13	0	5.3	4.8
1	10	5	5.6	-5.4	0	11	2	9.0	-9.0	0	12	3	8.8	7.9	5	13	1	3.5	-3.1
1	10	6	2.7	-2.1	0	11	3	2.9	-2.4	0	12	4	3.7	-3.1	0	14	0	7.6	2.1
2	10	0	23.5	21.7	0	11	4	5.2	4.2										

wart, Davidson and Simpson.[3] The anomalous dispersion correction, applied to the bromine data, was given by Cromer.[4] In the refinement, a weighting scheme recommended by Hughes,[5] was used with $F_{o\,min} = 6.0$. The final positional and thermal parameters with their standard deviations are listed in Tables 2 and 3. The interatomic distances and angles are given in Tables 4 and 5 with standard deviations as calculated with the program DISTAN. A list of observed and calculated structure factors after the last cycle of refinement is given in Table 6.

DISCUSSION

Since the crystals are non-centrosymmetric an attempt has been made to establish the absolute configuration. The method used was that of Hamilton [6] which does not entail additional experimental work but only calculations of F_c's for both possible configurations. The correct configuration should give the lower R and the significance can be tested with Hamiltons "R-factor ratio".[7] The configuration presented in this paper gave $R = 0.048$. Its antipode gave $R = 0.055$. Thus the R-factor ratio is 1.15. This value is significant at the 0.005-level. The absolute configuration presented also agrees with that determined by classical chemical methods.[1] This method of absolute configuration determination and all other statistical methods are based mainly on the assumption of random errors in the data. Systematic errors might favour one configuration and thus lead to the wrong conclusion.

The cation (except for hydrogen atoms) is shown in Fig. 2 and the unit cell content of non-hydrogen atoms is shown in Fig. 3. The cation is bent, the two five-membered rings making an angle of 116.2° with each other. The cations

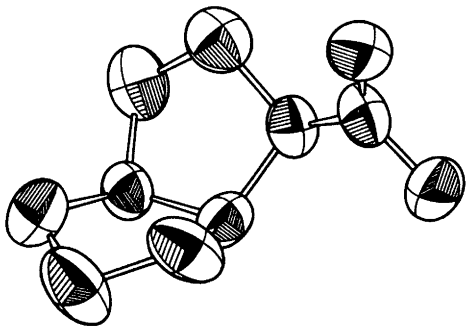

Fig. 2. The cation (except the hydrogen atoms).

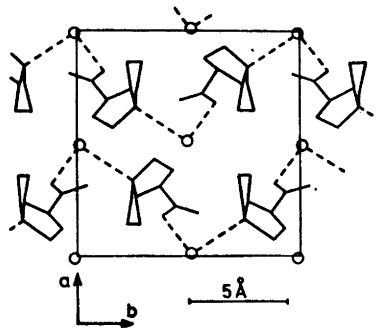

Fig. 3. Projection of the unit cell on the *ab*-plane.

are linked together in the *b*-axis direction by hydrogen bonds to the bromine atom. The strings form layers in the *bc* plane, interfoiled by approximate planes formed by the bromine atoms. All intermolecular distances shorter than four Å are tabulated in Table 7. The only unusual values are those for the

Table 7. Intermolecular distances shorter than 4 Å with e.s.d.

Br – O2	3.159	(6)	Br in	0.4913	0.0121	0.1664	O2 in	0.3240	−0.1210	0.4234
N	3.195	(6)					N	0.3387	0.2445	0.1084
C1	3.609	(6)					C1	0.6904	0.1329	−0.1463
C8	3.731	(7)					C8	0.7800	0.0607	−0.0523
C3	3.798	(8)					C3	0.4313	0.3377	0.1125
C2	3.877	(8)					C2	0.6225	0.0670	−0.2814
O1	3.920	(5)					O1	0.3089	0.0368	0.5881
C6	3.936	(10)					C6	0.6372	−0.2821	0.3224
C8	3.954	(6)					C8	0.2800	−0.0607	0.5523
C7	3.974	(6)					C7	0.2568	0.2636	0.2601
C5	3.975	(13)					C5	0.3560	−0.2855	−0.0105
O1 – C3	3.273	(9)	O1 in	0.1911	0.5368	0.4119	C3 in	−0.0687	0.6623	0.3875
C7	3.703	(8)					C7	0.2432	0.7636	0.7399
C4	3.704	(10)					C4	0.2341	0.7400	0.0502
C2	3.707	(9)					C2	−0.1225	0.5670	0.2814
O2 – C5	3.807	(12)	O2 in	0.8240	0.1210	0.0766	C5 in	1.1440	0.2145	0.0105
C2 – C5	3.691	(15)	C2 in	0.3775	0.4330	0.2186	C5 in	0.3560	0.7145	−0.0105

assumed hydrogen bonds $N-H-Br^-$ and $O2-H-Br^-$, which are 3.195 (6) and 3.159 (5) Å, respectively, and thus shorter than those normally found. There should, however, be little doubt of the correctness of the assumption of hydrogen bonds since the positions of the hydrogen atoms were found, the linearity of the bonds being reasonable (the angles are 157.7° and 164.5°, respectively) and the $H-Br^-$ distances in both cases are shorter than the sums of their van der Waals radii. The short $N-H-Br^-$ distance might be explained by the fact that the protonation which occurred at the nitrogen atom gives it a positive electrostatic charge which contributes a large amount of electrostatic interaction energy to the bond.

Very few hydrogen bond distances O – H – Br^-, involving the acidic hydrogen atom in a saturated carboxylic acid, seem to have been reported. Clark [8] has presented an average value of 3.34 Å for O – H – Br^- distances in organic hydrates. In carboxylic acids, however, the distance should be shorter due to the more acidic character of the hydrogen atom. It must also be pointed out that the standard deviations in the bond lengths do not exclude the possibility of somewhat longer hydrogen bond lengths.

The carboxyl group is approximately planar (*cf.* Table 8). Bond lengths and angles are in good agreement with values reported previously. The torsion

Table 8. Planarity of the carboxyl group.

Eqn. for LS plane: $0.6923X + 0.3554Y + 0.6281Z = 5.72498$

Departure from LS plane (Å).

O1	−0.017	C1	−0.008
O2	−0.041	C8	0.049

The torsion angle in the C1 – C8 bond is 7.5°.

angle in the C1 – C8 bond is 7.5° (*cf.* Fig. 4), in good agreement with the rule pointed out by Leiserowitz and Schmidt [9] and by Dunitz and Strickler,[10] that

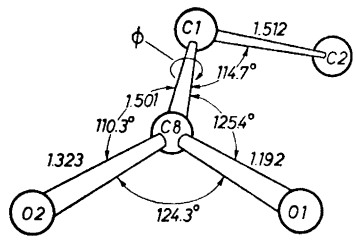

Fig. 4. The carboxyl group $\theta = 7.5°$.

the syn-planar arrangement seems to be a general feature of the molecular shapes of carboxyl acids, especially saturated ones, as well as of esters and amides.

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