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The Crystal Structure of Octahydrodipyrido-[1,2-a:1′,2′-c]imidazol-10-ium Bromide, $C_{11}H_{17}BrN_2$

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The arrangement of the non-hydrogen atoms of the bromide salt of an Orchidaceae alkaloid, octahydrodipyrido[1,2-a:1′,2′-c]imidazol-10-ium bromide ($C_{11}H_{17}BrN_2$), has been derived on the basis of three-dimensional X-ray film data and refined using least-squares methods. The monoclinic unit cell (space group $P2_1/n$), which contains four formula units, has the dimensions

$a = 9.909 \pm 4$ Å
$b = 9.271 \pm 6$ Å
$c = 12.788 \pm 6$ Å
$\beta = 93.39° \pm 3$

The crystal structure analysis has established that the compound is tricyclic and an imidazolium salt in concordance with the findings by Leander and Lüning.[1] The crystals are built up of cations, $[C_{11}H_{17}N_2]^+$, which are held together by the bromide ions. No distances indicating hydrogen bonds within the structure have been observed.

The isolation of an optically inactive quaternary compound from the orchids *Dendrobium anosmum* Lindl. and *Dendrobium parishii* Rchb. f. was recently reported by Leander and Lüning.[1] From chemical and spectroscopical (UV, IR, and NMR) investigations it was concluded that the compound contains an imidazolium ion with the schematic formula as given in Fig. 1.

The compound thus found is not related to any substance previously found in Nature. Therefore it was thought of considerable interest to find the details

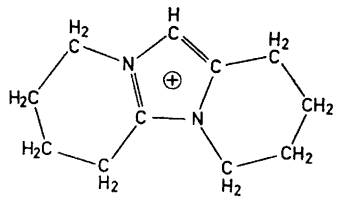

Fig. 1. Schematic formula of the imidazolium ion.

of the three-dimensional atomic arrangement. This article describes the result obtained from an X-ray investigation of the bromide of the alkaloid cation.

EXPERIMENTAL

Crystals. A crystalline sample of the bromide was kindly supplied by Drs. Leander and Lüning. The crystals, white needles, were rapidly hydrolyzed in ambient atmosphere and thus had to be kept in closed and moisture-free vessels.

X-Ray diffraction data and computing methods. The powder pattern could be interpreted by assuming a monoclinic unit cell. Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å) in a focusing camera of Guinier-Hägg type. Silicon ($a = 5.4301$ Å) [2] was used as an internal standard. (Potassium chloride, which is normally used as a standard substance at this Institute, was found to react with the sample. The powder photograph thus obtained showed many additional lines). The unit-cell dimensions (at 25°C) are:

$$\begin{aligned} a &= 9.909 \pm 4 \text{ Å} \\ b &= 9.271 \pm 6 \text{ Å} \\ c &= 12.788 \pm 6 \text{ Å} \\ \beta &= 93.39° \pm 3 \end{aligned}$$

The value of 1.48 g/cm³ for the density, found from the apparent loss of weight in benzene, gives four formula units in the unit cell. (Calculated density = 1.46 g/cm³.)

Single-crystals — investigated under the microscope in a nitrogen atmosphere — were put into thin-walled Lindemann glass capillaries, with diameters of about 0.2 mm and wall thicknesses of approximately 0.02 mm.

Rotation and Weissenberg photographs ($0kl - 5kl$) of a single crystal were taken with Cu$K\alpha$ radiation. The reflections systematically absent in the photographs are $h0l$ with $h+l$ odd and $0k0$ with k odd, which is characteristic of the space group $P2_1/n$.

The reflections were recorded photographically with the multiple film technique (three films). The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. A total of 710 independent reflections of non-zero intensity were measured.

In the computational work the refinement of lattice constants,[3] the correction for Lorentz-polarization effects,[4] and least-squares refinement (block diagonal matrix approximation, No. 6023) [5] were performed on the electronic computer IBM 1800. Further computational work including least-squares refinement (full matrix program, No. 384),[5] calculation of interatomic distances and angles [6] and calculation of a plane to a set of points by a least-squares method [7] was performed on the electronic computers IBM 360/75 and CD 3600.

STRUCTURE DETERMINATION

From the three-dimensional Patterson function $P(uvw)$ approximate parameter values were derived for the four bromine atoms, situated in the point position 4(e): $\pm(xyz)$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and with $x \approx 0.32$, $y \approx 0.23$, and $z \approx 0.05$.

Three-dimensional electron density sections were then calculated, using signs for the observed structure factors derived from the bromine contribution only. (In the calculations scattering curves [7] for un-ionized atoms were used. The real part of the anomalous dispersion correction [9] was applied to the scattering curve for the bromine atoms.) From these and subsequent calculations the positions of the eight nitrogen atoms and the forty-four carbon atoms could be obtained. All the atoms were found to be situated in point positions 4(e).

A refinement of the coordinates so obtained was then performed using the least-squares technique. At first a refinement with isotropic temperature factors was performed by means of a block diagonal matrix approximation program but later on a full matrix least-squares refinement with anisotropic temperature factors for the bromine atoms was undertaken. Initially all 710 of the independent reflections measured were included in the calculations, but after some cycles fifteen strong low-angle reflections were omitted as suffering from extinction. The refinement was considered as complete when the parameter shifts were less than 1 % of the standard deviations, at which stage the discrepancy index, R, was down to 0.113.

Cruickshank's weighting function [9]

$$w = (A + |F_{obs}| + C|F_{obs}|^2)$$

Table 1. Weight analysis.

Interval $\sin\theta$	Number of reflections	$\overline{w\,\Delta^2}$	Interval F_o	Number of reflections	$\overline{w\,\Delta^2}$
0.0 −0.46	196	1.62	0− 14	71	1.48
0.46−0.58	150	1.05	14− 17	71	1.20
0.58−0.67	120	0.64	17− 20	71	0.87
0.67−0.74	71	0.54	20− 23	71	0.87
0.74−0.79	58	0.81	23− 26	71	0.89
0.79−0.84	36	0.55	26− 31	71	0.69
0.84−0.89	31	0.35	31− 36	71	0.90
0.89−0.93	17	0.83	36− 43	71	1.20
0.93−0.97	9	0.66	43− 56	71	0.78
0.97−1.00	7	1.16	56−119	56	1.15

Table 2. Atomic parameters and temperature factors with their standard deviations.

Atom	x	σx	y	σy	z	σz	B	σB
C1	0.4394	(25)	0.0435	(19)	0.7952	(15)	2.88	0.41
C2	0.3207	(29)	0.9400	(20)	0.8257	(17)	3.58	0.45
C3	0.1883	(28)	−0.0031	(21)	0.7946	(17)	3.56	0.45
C4	0.1599	(27)	0.0147	(20)	0.6746	(17)	3.36	0.43
N5	0.2818	(19)	0.0800	(13)	0.6313	(11)	1.79	0.26
C5a	0.2851	(25)	0.1341	(16)	0.5322	(13)	1.88	0.32
C6	0.1643	(30)	0.1405	(22)	0.4500	(18)	4.17	0.49
C7	0.2202	(33)	0.1718	(25)	0.3437	(21)	4.99	0.55
C8	0.3269	(39)	0.2950	(30)	0.3540	(26)	6.79	0.73
C9	0.4593	(35)	0.2531	(21)	0.4298	(19)	4.00	0.50
N10	0.4125	(22)	0.1822	(16)	0.5245	(12)	2.69	0.32
C11	0.4951	(24)	0.1567	(17)	0.6176	(14)	2.53	0.37
C11a	0.4120	(25)	0.0916	(17)	0.6821	(14)	2.00	0.33
Br	0.3257	(3)	0.2262	(2)	0.0515	(2)		

B_{11}	σB_{11}	B_{22}	σB_{22}	B_{33}	σB_{33}
0.00815	0.00171	0.01151	0.00029	0.00444	0.00016

B_{12}	σB_{12}	B_{13}	σB_{13}	B_{23}	σB_{23}
0.00491	0.00054	0.00287	0.00047	0.00125	0.00032

Table 3.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	-2	63.2	89.8	0	8	0	11.1	10.9	1	4	0	44.3	44.2	2	6	-7	39.8	-40.8
0	0	-4	28.5	17.8	1	0	-1	12.3	-23.1	1	4	1	48.9	-48.8	2	6	-9	22.7	-23.4
0	0	-8	70.1	-74.7	1	0	-3	78.3	85.2	1	4	2	27.7	21.3	2	6	-10	13.6	-16.9
0	0	-10	56.4	+54.7	1	0	-5	72.6	78.0	1	4	3	65.9	-61.3	2	6	-12	18.1	-18.2
0	0	-12	39.4	-40.1	1	0	-7	61.0	63.1	1	4	5	58.2	-56.5	2	7	-1	21.4	18.6
0	0	-14	9.9	-11.4	1	0	-9	54.2	45.9	1	4	6	29.3	-26.1	2	7	-3	45.8	51.4
0	0	-16	7.6	10.6	1	0	-11	20.8	-16.1	1	4	7	25.9	-20.9	2	7	-4	25.6	25.3
0	1	-1	35.9	-42.3	1	0	-13	31.1	-27.1	1	5	0	15.0	-9.9	2	7	-5	40.3	47.4
0	1	-2	68.0	70.3	1	0	-15	17.1	-19.6	1	5	1	39.7	-36.8	2	7	-8	24.4	25.0
0	1	-4	89.5*	97.9	1	1	-1	26.3	-28.4	1	5	2	48.5	-50.4	2	7	-9	15.8	-14.7
0	1	-5	25.9	17.5	1	1	-2	28.7	23.3	1	5	4	53.6	-57.8	2	7	-10	13.6	16.0
0	1	-6	72.1	79.0	1	1	-3	86.0*	-113.1	1	5	5	20.9	21.9	2	8	-2	16.8	-14.6
0	1	-7	43.5	-34.4	1	1	-4	35.9	25.4	1	5	6	19.5	-19.2	2	8	-4	20.1	-19.8
0	1	-8	42.9	42.7	1	1	-5	32.4	-27.1	1	5	7	39.0	37.8	2	8	-5	31.5	29.1
0	1	-10	15.1	12.1	1	1	-6	22.0	-13.9	1	5	8	20.6	-15.8	2	8	-7	26.2	27.3
0	1	-14	25.6	-25.9	1	1	-7	45.5	39.8	1	6	0	28.0	-28.6	2	9	-1	23.3	-25.1
0	1	-16	17.2	-17.4	1	1	-8	27.7	22.1	1	6	1	23.9	19.4	2	9	-3	18.4	-19.6
0	2	-1	31.0	-27.7	1	1	-9	46.5	43.5	1	6	2	20.0	-18.7	2	9	-5	20.2	-20.7
0	2	-2	119.4*	-158.8	1	1	-11	46.9	51.4	1	6	3	34.9	32.9	2	9	-6	19.4	-20.4
0	2	-4	24.4	-21.9	1	1	-13	28.5	27.1	1	6	5	38.4	39.3	2	10	-1	19.9	17.9
0	2	-5	38.1	32.5	1	2	-1	83.1*	-99.7	1	6	6	22.0	21.4	2	1	0	100.5*	137.0
0	2	-6	51.3	45.9	1	2	-2	85.9*	-103.7	1	6	8	29.3	29.1	2	1	1	16.7	-17.2
0	2	-7	17.4	15.4	1	2	-3	41.6	-39.0	1	7	0	26.9	25.7	2	1	2	88.3*	106.9
0	2	-8	36.3	36.9	1	2	-4	40.0	-29.4	1	7	1	15.8	12.9	2	1	3	13.0	-8.5
0	2	-9	12.0	-8.0	1	2	-5	45.0	-49.9	1	7	2	34.3	34.1	2	1	4	78.2	88.7
0	2	-10	56.4	58.7	1	2	-6	27.0	-14.1	1	7	4	37.1	37.2	2	2	0	18.7	28.6
0	2	-11	25.3	-23.5	1	2	-7	66.1	-76.9	1	7	5	20.2	-17.1	2	2	1	42.6	39.4
0	2	-12	19.7	22.2	1	2	-9	30.5	-26.7	1	7	6	20.4	21.7	2	2	2	20.3	-14.0
0	2	-13	8.4	-8.6	1	2	-10	19.7	15.8	1	8	0	23.7	26.2	2	2	3	29.5	23.5
0	3	-1	17.9	16.6	1	2	-13	21.0	20.0	1	8	1	12.4	-11.5	2	2	4	45.4	-40.4
0	3	-2	8.6	4.8	1	2	-14	13.0	9.4	1	8	3	23.4	-20.8	2	2	6	60.1	-73.6
0	3	-3	18.3	-16.0	1	2	-15	16.1	21.3	1	8	6	26.9	-25.6	2	3	0	66.9	-74.8
0	3	-4	73.8	-89.6	1	3	-1	95.4*	142.4	1	9	2	29.6	-29.1	2	3	2	52.2	-77.1
0	3	-5	28.2	22.5	1	3	-3	41.6	65.6	1	9	4	18.8	-19.9	2	3	4	63.0	-69.7
0	3	-6	69.7	-72.0	1	3	-4	39.3	-26.5	1	10	0	13.6	-16.5	2	3	5	34.7	-28.6
0	3	-7	13.4	11.4	1	3	-5	40.2	37.7	1	10	2	14.1	-15.7	2	3	6	19.3	-16.2
0	3	-8	16.8	-13.8	1	3	-6	42.4	-40.5	2	0	-2	82.0*	-99.0	2	4	0	28.6	-27.2
0	3	-9	28.6	26.9	1	3	-9	48.2	-48.1	2	0	-4	91.8*	-110.1	2	4	1	44.0	-48.2
0	3	-11	7.9	8.8	1	3	-10	19.4	-15.6	2	0	-6	78.3	-91.7	2	4	3	34.1	-35.6
0	3	-12	19.0	21.8	1	3	-11	33.8	-36.8	2	0	-8	16.5	-8.7	2	4	4	45.0	41.5
0	3	-14	17.5	18.9	1	3	-13	33.3	-31.0	2	0	-10	39.7	34.1	2	4	5	12.4	-8.3
0	4	-1	30.9	-30.3	1	4	-1	24.5	-23.1	2	0	-12	30.4	35.5	2	4	6	34.5	33.5
0	4	-2	29.1	26.4	1	4	-2	74.7	72.7	2	0	-14	27.6	27.7	2	5	0	46.1	47.4
0	4	-3	24.3	-24.9	1	4	-3	63.0	61.6	2	0	-16	13.4	11.1	2	5	1	17.3	-13.1
0	4	-4	23.2	19.2	1	4	-4	52.6	53.5	2	1	-1	25.8	27.7	2	5	2	69.4	74.4
0	4	-5	28.1	-26.3	1	4	-5	43.4	44.9	2	1	-2	50.4	59.0	2	5	4	33.6	21.3
0	4	-6	28.2	-24.2	1	4	-6	17.8	14.3	2	1	-4	50.8	-43.9	2	5	5	30.9	25.4
0	4	-7	26.2	-24.6	1	4	-7	37.7	33.6	2	1	-6	71.0	-71.6	2	5	7	31.5	32.9
0	4	-8	44.7	-48.9	1	4	-8	21.2	-20.4	2	1	-7	20.9	17.1	2	6	0	22.3	14.8
0	4	-10	24.7	-25.0	1	4	-9	28.1	31.0	2	1	-8	55.6	-55.7	2	6	1	41.8	42.5
0	4	-11	12.4	10.0	1	4	-14	14.6	-12.0	2	1	-10	35.0	-33.9	2	6	3	26.5	24.2
0	4	-13	18.5	19.6	1	5	-1	61.2	-66.8	2	1	-14	13.4	11.4	2	6	4	21.0	-20.1
0	4	-15	11.0	11.7	1	5	-2	18.4	-17.7	2	1	-16	11.2	13.5	2	6	5	33.4	32.1
0	5	-1	53.4	52.5	1	5	-3	83.5*	-88.1	2	2	-1	17.9	-18.0	2	6	6	19.5	-17.3
0	5	-2	36.3	34.2	1	5	-4	31.3	27.9	2	2	-2	73.1	88.8	2	7	0	23.9	-22.5
0	5	-3	12.7	9.7	1	5	-5	29.1	-28.0	2	2	-4	81.6*	83.4	2	7	1	31.2	30.0
0	5	-4	27.2	24.8	1	5	-6	67.7	44.8	2	2	-5	31.2	-23.1	2	7	2	23.5	-23.2
0	5	-6	27.2	27.2	1	5	-7	13.5	10.5	2	2	-6	62.1	56.7	2	7	4	16.5	-15.9
0	5	-7	27.3	-25.3	1	5	-8	23.8	22.6	2	2	-7	38.1	-34.6	2	7	5	27.5	-28.2
0	5	-8	24.7	24.1	1	5	-9	16.1	17.2	2	2	-10	35.4	-33.2	2	7	7	26.1	-23.3
0	5	-9	22.7	-22.7	1	5	-11	13.7	29.2	2	2	-12	25.9	-27.8	2	8	0	8.9	-7.4
0	5	-10	11.8	-15.0	1	5	-13	13.3	13.0	2	2	-14	18.4	-19.4	2	8	1	17.9	-18.2
0	5	-11	27.8	-24.3	1	6	-1	21.0	15.3	2	3	-2	53.0	-58.7	2	8	3	27.7	-33.1
0	5	-12	17.7	-18.6	1	6	-2	33.1	-31.0	2	3	-3	15.0	15.3	2	10	1	20.6	23.3
0	5	-13	13.6	-12.4	1	6	-4	34.3	-31.5	2	3	-4	46.0	42.7	3	0	-3	63.2	60.7
0	5	-14	12.6	-13.7	1	6	-5	44.0	-43.2	2	3	-5	9.0	9.6	3	0	-5	23.1	-20.6
0	6	-1	13.7	8.5	1	6	-7	21.3	-22.9	2	3	-6	65.8	61.1	3	0	-7	75.7	-74.6
0	6	-2	36.4	-21.3	1	6	-10	20.3	16.9	2	3	-8	45.3	44.7	3	0	-9	67.6	-67.1
0	6	-3	37.9	35.2	1	7	-1	25.6	27.3	2	3	-10	25.9	25.3	3	0	-11	34.6	-32.2
0	6	-5	35.1	35.5	1	7	-2	22.0	-21.9	2	3	-11	18.0	-15.1	3	0	-13	18.8	-18.1
0	6	-6	16.1	15.9	1	7	-3	23.4	23.2	2	3	-13	22.2	-18.2	3	1	-1	52.6	61.7
0	6	-7	25.9	25.0	1	7	-4	21.0	-20.6	2	4	-1	31.1	-23.2	3	1	-2	27.6	26.3
0	6	-8	25.4	23.4	1	7	-5	20.8	19.6	2	4	-2	20.3	-11.9	3	1	-3	79.6	94.6
0	6	-10	18.7	19.1	1	7	-6	15.7	-15.3	2	4	-3	47.3	49.8	3	1	-4	16.1	-11.8
0	7	-1	44.8	-50.1	1	7	-8	31.4	-27.8	2	4	-4	49.3	-48.8	3	1	-5	60.0	61.4
0	7	-2	15.8	-15.3	1	8	-2	27.4	30.6	2	4	-5	27.7	24.5	3	1	-7	25.4	27.2
0	7	-3	25.3	-25.5	1	8	-10	19.7	-20.0	2	4	-6	30.0	-24.8	3	1	-10	26.7	-24.1
0	7	-4	10.9	-6.8	1	9	-6	22.4	22.8	2	4	-7	20.4	15.6	3	1	-13	27.9	-28.4
0	7	-6	16.3	-15.2	1	10	-2	11.8	-16.4	2	4	-8	13.3	12.0	3	1	-15	22.0	-23.8
0	7	-7	15.3	17.3	1	10	-4	20.2	-21.8	2	4	-9	46.6	46.0	3	2	-1	76.9	-91.0
0	7	-9	30.6	29.3	1	11	-4	12.7	-12.8	2	4	-12	26.7	24.7	3	2	-2	59.0	54.4
0	7	-11	16.4	16.9	1	1	0	44.2	-48.7	2	4	-14	18.9	17.4	3	2	-3	38.8	-39.9
0	8	-1	7.9	-6.9	1	1	2	13.1	-17.8	2	5	-1	58.0	-67.3	3	2	-4	8.1	7.8
0	8	-2	14.2	14.7	1	1	3	39.2	-36.0	2	5	-2	19.5	-17.8	3	2	-5	17.3	13.5
0	8	-3	24.1	-24.7	1	1	4	30.3	-26.2	2	5	-3	39.0	-41.6	3	2	-6	31.9	27.7
0	8	-4	11.2	8.2	1	2	0	78.7	-102.8	2	5	-4	14.8	-11.3	3	2	-7	61.9	61.2
0	8	-5	35.1	-34.8	1	2	1	81.6*	115.5	2	5	-5	21.9	-19.4	3	2	-8	36.9	34.8
0	8	-6	14.6	-12.9	1	2	3	82.6*	98.3	2	5	-6	35.9	-35.6	3	2	-9	55.1	54.8
0	8	-7	18.2	-17.1	1	2	4	9.9	8.0	2	5	-7	24.8	-19.5	3	2	-10	20.7	-13.4
0	8	-8	17.0	-15.5	1	2	5	40.9	35.7	2	5	-8	30.5	-33.0	3	2	-11	39.5	43.1
0	9	-1	23.8	29.5	1	3	0	43.7	40.1	2	5	-9	12.7	11.3	3	2	-12	13.1	-14.6
0	9	-3	18.5	17.5	1	3	1	37.3	57.4	2	5	-10	20.9	-19.3	3	2	-13	15.0	13.0
0	10	-3	17.7	19.6	1	3	2	58.4	51.3	2	5	-11	24.3	27.3	3	3	-1	48.0	-51.3
0	10	-5	15.3	14.3	1	3	3	20.1	-18.1	2	5	-13	14.7	18.1	3	3	-2	22.3	-22.4
0	11	-1	15.3	-16.9	1	3	4	24.1	34.1	2	5	-14	15.7	15.6	3	3	-4	30.6	-20.7
0	2	0	73.3	-99.7	1	3	5	36.1	-32.9	2	6	-1	23.7	20.0	3	3	-5	61.0	-58.8
0	4	0	55.7	63.2	1	3	6	43.1	42.0	2	6	-2	37.7	35.6	3	3	-7	37.8	-34.6
0	6	0	28.9	-25.6	1	3	7	51.7	-47.7	2	6	-5	29.2	-27.2	3	3	-8	33.3	28.7

Table 3. Continued.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	3	-9	27.2	-21.6	3	7	0	46.1	-54.1	4	8	-11	11.9	-13.8	5	3	-8	14.7	-8.6
3	3	-11	25.7	24.2	3	7	3	26.2	25.9	4	9	-7	20.7	20.3	5	3	-12	27.0	-23.8
3	3	-13	31.7	28.4	3	7	5	18.8	16.0	4	0	2	59.5	-76.3	5	4	-1	36.3	-34.3
3	4	-1	54.2	61.3	3	8	2	20.0	18.8	4	1	0	40.4	-56.4	5	4	-2	6.7	8.8
3	4	-3	35.6	31.3	3	8	4	17.5	21.0	4	1	1	23.1	-28.0	5	4	-3	52.0	-43.7
3	4	-4	42.4	-43.4	3	8	5	13.0	-17.2	4	1	2	37.7	-45.2	5	4	-4	19.8	14.9
3	4	-5	14.2	-10.4	3	8	6	15.6	17.6	4	1	3	25.3	21.0	5	4	-5	17.8	-16.5
3	4	-6	37.5	-38.2	3	9	0	15.8	22.4	4	1	6	46.6	51.1	5	4	-6	25.2	25.5
3	4	-7	30.3	-28.0	3	9	2	22.0	26.5	4	2	0	17.1	17.1	5	4	-8	28.4	24.9
3	4	-9	51.9	-52.9	4	0	-2	44.5	43.9	4	2	1	22.3	-25.0	5	4	-9	15.2	11.5
3	4	-11	21.7	-25.3	4	0	-4	67.2	66.7	4	2	2	67.2	72.8	5	4	-11	27.1	26.6
3	5	-1	29.8	26.0	4	0	-6	73.3	72.4	4	2	4	69.1	78.5	5	4	-13	18.2	22.2
3	5	-2	49.8	50.4	4	0	-8	53.5	49.7	4	2	6	38.7	38.3	5	5	-1	14.4	9.2
3	5	-3	41.4	37.8	4	0	-10	19.2	21.5	4	3	0	67.1	72.9	5	5	-2	43.3	-45.0
3	5	-4	28.3	22.5	4	0	-12	35.4	-32.8	4	3	3	16.8	12.7	5	5	-4	22.8	-18.3
3	5	-5	42.1	39.2	4	0	-14	25.9	-27.7	4	3	4	21.8	-19.6	5	5	-5	35.9	-34.0
3	5	-6	29.6	-31.1	4	1	-1	12.9	9.4	4	3	5	21.3	22.6	5	5	-7	38.7	-38.0
3	5	-7	40.0	41.8	4	1	-3	17.9	-14.2	4	3	6	20.4	-16.7	5	5	-9	22.3	-22.2
3	5	-8	17.5	-18.7	4	1	-4	33.4	-31.1	4	3	8	48.6	-52.3	5	5	-10	17.8	16.4
3	5	-10	17.4	-11.6	4	1	-5	34.6	31.5	4	4	1	50.4	56.9	5	5	-11	10.8	-11.6
3	5	-11	14.0	-12.4	4	1	-7	8.7	5.7	4	4	2	44.7	-41.0	5	6	-1	24.4	24.8
3	6	-1	27.5	-28.8	4	1	-8	22.5	21.1	4	4	4	34.9	-30.5	5	6	-3	14.7	12.5
3	6	-2	29.6	30.3	4	1	-9	25.4	-21.6	4	4	5	9.0	-5.7	5	6	-5	17.4	12.5
3	6	-3	40.1	-37.7	4	1	-10	56.3	57.0	4	4	6	34.7	-39.5	5	6	-6	26.3	-22.9
3	6	-4	16.4	17.8	4	1	-11	18.6	14.7	4	5	0	35.1	-29.5	5	6	-8	17.8	-18.1
3	6	-6	16.0	16.7	4	1	-12	34.7	36.4	4	5	1	22.6	-22.5	5	7	-1	20.2	-15.6
3	6	-7	31.2	31.0	4	2	-1	34.7	-37.3	4	5	2	22.0	-19.0	5	7	-2	24.8	20.9
3	6	-11	11.5	11.1	4	2	-2	23.4	-17.4	4	5	3	30.2	-30.8	5	7	-4	29.1	27.8
3	7	-2	14.4	-14.6	4	2	-3	43.3	-39.5	4	5	4	18.4	16.5	5	7	-6	17.2	15.3
3	7	-5	22.1	-23.1	4	2	-4	54.3	-60.6	4	5	5	36.9	-35.8	5	7	-7	14.4	14.7
3	7	-8	24.9	21.4	4	2	-5	9.7	-11.3	4	5	6	28.2	29.0	5	8	-4	8.4	11.0
3	7	-10	16.9	21.5	4	2	-6	59.6	-64.2	4	5	7	20.3	-17.6	5	8	-6	20.8	19.1
3	8	-2	29.8	-29.5	4	2	-7	20.8	17.5	4	5	8	15.2	12.7	5	8	-8	19.3	18.3
3	8	-4	22.0	-23.1	4	2	-8	42.3	-40.7	4	6	0	17.8	12.0	5	8	-10	10.6	9.3
3	9	-2	19.2	22.2	4	2	-14	19.5	19.8	4	6	1	35.8	-37.4	5	9	-2	24.6	-26.8
3	10	-4	25.3	29.2	4	3	-1	34.5	30.0	4	6	2	24.3	21.3	5	9	-4	20.9	-22.8
3	0	3	39.3	36.3	4	3	-2	48.0	50.2	4	6	3	25.5	-27.2	5	10	-4	10.7	-14.2
3	1	1	16.5	-16.3	4	3	-3	45.1	-46.1	4	6	4	31.0	33.3	5	10	-6	12.4	-17.8
3	1	2	30.9	28.8	4	3	-5	37.0	-35.3	4	7	0	25.7	27.0	5	1	1	59.8	77.2
3	1	3	31.7	-33.6	4	3	-6	8.8	8.2	4	7	1	10.5	8.7	5	1	2	23.0	-20.4
3	1	4	19.3	15.1	4	3	-8	40.3	-40.5	4	7	3	26.9	28.0	5	1	3	47.9	61.5
3	1	5	44.6	-47.0	4	3	-10	23.2	-22.1	4	7	5	32.8	36.8	5	2	0	15.4	-10.3
3	2	2	34.8	-29.9	4	3	-12	30.7	-25.6	4	7	7	22.4	19.1	5	2	1	28.0	30.0
3	2	3	59.3	-68.3	4	4	0	33.4	-31.1	4	8	1	20.5	22.7	5	2	2	42.3	51.2
3	2	4	32.6	-34.7	4	4	-1	53.4	56.8	4	8	4	18.2	-9.3	5	2	4	33.8	26.1
3	2	5	13.1	9.3	4	4	-2	13.5	14.0	4	8	7	17.9	-18.7	5	2	5	31.6	-28.3
3	2	6	40.0	-37.4	4	4	-4	42.3	41.1	4	9	3	25.7	-25.2	5	2	6	16.1	-13.7
3	2	7	47.6	43.7	4	4	-5	20.1	15.9	5	0	-3	81.8*	-90.1	5	3	0	39.5	24.3
3	3	0	34.9	-29.9	4	4	-6	42.6	46.1	5	0	-5	76.9	-76.8	5	3	1	47.1	-56.0
3	3	1	15.7	-11.2	4	4	-9	29.0	-26.7	5	0	-9	33.8	31.7	5	3	3	58.5	-71.3
3	3	2	15.0	-10.1	4	4	-11	26.0	-23.4	5	0	-13	27.6	25.8	5	3	5	36.0	-38.8
3	3	3	47.8	55.1	4	4	-13	11.9	-9.0	5	0	-15	18.1	19.6	5	3	6	17.6	-12.5
3	3	4	41.7	-41.3	4	4	-14	14.0	-14.6	5	1	-1	40.1	50.1	5	3	7	19.2	17.9
3	3	5	61.6	63.0	4	5	-1	21.4	15.0	5	1	-2	18.2	-19.9	5	4	0	47.9	-27.0
3	3	7	40.8	35.6	4	5	-2	56.5	-57.5	5	1	-4	23.8	18.9	5	4	1	38.1	-31.6
3	3	8	29.8	26.8	4	5	-3	37.6	33.6	5	1	-5	54.4	-57.5	5	4	2	29.7	-25.3
3	4	0	15.4	-12.6	4	5	-5	44.2	42.3	5	1	-7	67.1	-67.4	5	4	4	24.6	-22.4
3	4	1	51.5	54.4	4	5	-7	37.9	36.0	5	1	-9	41.0	-35.0	5	4	5	35.1	34.3
3	4	2	33.6	31.2	4	5	-9	15.1	18.1	5	1	-10	19.6	16.0	5	4	6	8.3	-9.1
3	4	3	38.4	42.4	4	5	-10	29.4	28.3	5	1	-11	15.1	-12.2	5	4	7	18.6	14.3
3	4	4	35.0	36.4	4	5	-12	16.0	16.1	5	1	-15	12.2	14.3	5	5	0	12.2	-7.8
3	4	6	31.4	32.0	4	6	-1	35.2	-36.9	5	2	-2	19.4	-16.1	5	5	1	45.2	47.3
3	4	7	22.2	-20.3	4	6	-2	16.1	-12.4	5	2	-3	59.6	70.2	5	5	2	8.9	7.9
3	4	8	38.2	38.5	4	6	-3	27.8	-29.8	5	2	-5	25.8	43.6	5	5	3	39.7	45.2
3	4	9	25.7	-28.2	4	6	-4	38.3	-35.5	5	2	-6	21.0	-17.0	5	5	6	25.5	24.6
3	5	0	14.6	12.0	4	6	-6	18.4	-15.5	5	2	-7	17.2	13.2	5	5	8	38.4	30.2
3	5	2	42.6	42.4	4	6	-8	22.2	-18.9	5	2	-8	27.3	-22.9	5	6	0	19.7	13.8
3	5	3	24.0	-20.9	4	6	-9	23.1	25.8	5	2	-9	15.7	-11.8	5	6	2	34.0	34.6
3	5	4	18.1	18.3	4	6	-11	24.5	23.7	5	2	-10	19.6	-18.5	5	6	4	14.1	14.9
3	5	5	39.7	-43.6	4	7	-2	20.2	18.6	5	2	-11	38.0	-38.8	5	6	7	27.4	-24.0
3	5	6	15.3	-13.6	4	7	-3	29.5	-28.1	5	2	-13	21.6	-20.3	5	7	0	21.4	23.4
3	5	7	39.9	-43.7	4	7	-4	13.8	16.4	5	2	-14	10.0	8.8	5	7	1	24.2	-23.7
3	5	8	24.8	-23.0	4	7	-5	36.1	-42.6	5	2	-15	10.7	-10.5	5	7	4	20.8	-19.6
3	6	1	24.2	-21.0	4	7	-7	30.3	-27.5	5	3	-2	13.8	15.6	5	7	6	25.4	-23.7
3	6	2	27.3	-24.4	4	7	-9	18.2	-14.0	5	3	-3	27.5	23.4	5	8	2	18.5	-19.7
3	6	3	14.9	-11.8	4	7	-10	12.2	-13.1	5	3	-4	20.1	15.6	5	8	3	14.7	10.9
3	6	4	30.0	-30.0	4	8	-1	24.0	24.9	5	3	-5	43.8	38.4	5	8	4	25.3	-25.2
3	6	6	22.8	-25.3	4	8	-3	16.3	18.1	5	3	-6	16.4	-13.1	5	8	5	20.2	18.2
3	6	7	18.8	20.7	4	8	-6	24.0	19.2	5	3	-7	32.3	31.0	5	10	0	17.6	16.2
3	6	8	13.3	-13.5	4	8	-9	11.4	-14.7										

was used in the refinement with the following final values for the parameters:

$$A = 8.0 \quad C = 0.10$$

A weight analysis obtained in the last cycle is given in Table 1. The positional parameters and the temperature factors of all the atoms and their standard deviations are given in Table 2.

A list of the observed and calculated structure factors is presented in Table 3.

A three-dimensional difference synthesis calculated over the asymmetric part of the unit cell at points 0.25 Å apart showed no maxima higher than about 25 % of the heights of the carbon peaks in the electron density functions. From these calculations as well as from a computation of the interatomic distances and angles—listed with their standard deviations in Table 4—which were found to have reasonable values (see below), further evidence was obtained that the atomic coordinates arrived at in the last cycle represent an adequate description of the structure of $C_{11}H_{17}BrN_2$. By a series of least-squares calculations it was finally confirmed that the distribution of nitrogen atoms within the five-membered ring given in Table 2 is the one which gives the lowest standard deviations and reasonable temperature factors. The results thus obtained are obviously in concordance with straight forward chemical evidence.

In the unit cell there are also sixty-eight hydrogen atoms. It was not attempted to determine their parameters from the present set of experimental data.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure may be described as consisting of cations of the composition $[C_{11}H_{17}N_2]^+$, held together by bromine ions. The cation is tricyclic so that two six-membered rings, each of which is formed by five carbon atoms and one nitrogen atom, and one five-membered ring formed by two nitrogen and three carbon atoms are coupled together in a way as suggested by Leander and Lüning.[1] The *xz* projection of the structure is schematically shown in Fig. 2 and the cation is represented in Fig. 3.

The standard deviations of the interatomic distances (*cf.* Table 4) within the cation are relatively large. This is likely to be associated with the moderate accuracy of the intensity data associated with the film technique and probably even more with the contributions of the hydrogen atoms not being taken into account. A solid basis for a discussion of the details of bonding within the

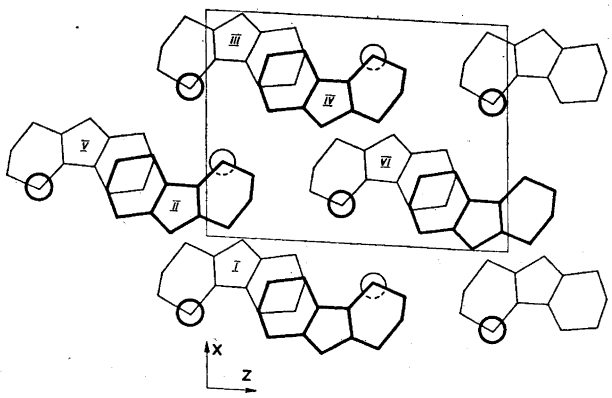

Fig. 2. Schematic drawing showing the structure of $C_{11}H_{17}BrN_2$ projected on the *xz* plane. The Roman numerals denote different cations.

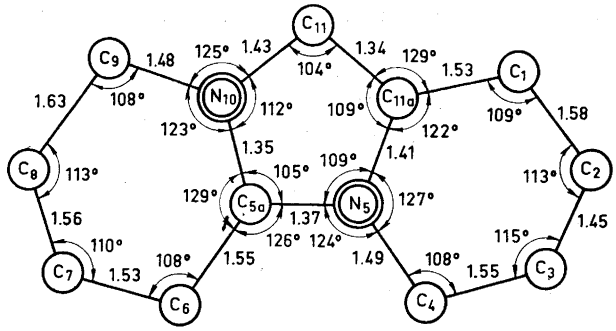

Fig. 3. Bond distances (in Å) and bond angles within the imidazolium ion, $[C_{11}H_{17}N_2]^+$.

Table 4. Interatomic distances (Å) and angles and standard deviations ($\pm\sigma$) within the cation.

N5 —C4	1.487	(30)	C2 —C3	1.448	(38)
N5 —C5a	1.366	(21)	C3 —C4	1.554	(30)
N5 —C11a	1.413	(30)	C5a—C6	1.548	(34)
N10—C5a	1.346	(31)	C6 —C7	1.527	(37)
N10—C9	1.477	(30)	C7 —C8	1.556	(43)
N10—C11	1.427	(27)	C8 —C9	1.632	(48)
C1 —C2	1.583	(33)	C11—C11a	1.342	(29)
C1 —C11a	1.525	(26)			
C2 —C1 —C11a	108.5	1.8	C6 —C7 —C8	110.1	2.2
C1 —C2 —C3	112.6	1.7	C7 —C8 —C9	113.2	2.2
C2 —C3 —C4	114.8	2.0	N10—C9 —C8	108.3	2.5
C3 —C4 —N5	107.9	1.9	C5a—N10 —C9	123.2	2.0
N5 —C5a—C6	125.9	2.0	C5a—N10 —C11	112.2	1.6
N5 —C5a—N10	105.2	1.7	C9 —N10 —C11	124.6	2.2
N10—C5a—C6	128.9	1.6	N10—C11 —C11a	104.2	2.0
C4 —N5 —C5a	124.0	1.8	N5 —C11a—C1	121.5	1.8
C4 —N5 —C11a	126.7	1.5	N5 —C11a—C11	109.1	1.6
C5a—N5 —C11a	109.2	1.7	C1 —C11a—C11	129.3	2.1
C5a—C6 —C7	107.9	2.3			

Table 5. Distances (and standard deviations $\pm\sigma$) to closest neighbours of the bromide ion. Roman numerals denote atoms from different molecules (*Cf.* Fig. 2).

Br—C^{I} (11) = 3.596±23 Å	Br—C^{III}(6) = 3.867±28 Å
C^{I} (9) = 3.869±34 Å	
N^{I} (10) = 4.174±22 Å	C^{IV}(6) = 3.870±21 Å
	C^{IV}(2) = 4.057±27 Å
C^{II} (6) = 3.840±20 Å	
C^{II} (4) = 3.949±20 Å	C^{V}(1) = 3.914±20 Å
C^{II}(5a) = 4.062±16 Å	C^{V}(2) = 3.920±20 Å
N^{II} (5) = 4.132±13 Å	
	C^{VI}(8) = 3.924±33 Å
	C^{VI}(7) = 3.973±27 Å

cation should require a further structural refinement preferably founded on diffractometer data. Considering the precision obtained in the present study the interatomic distances may, however, be characterized as normal in length.

The atoms of the five-membered ring and also two neighbour atoms of each of the six-membered ring (*viz.* C_1, C_4, C_6, and C_9) are all close to a plane (*cf.* Table 6). The remaining carbon atoms (C_2, C_3, C_7, and C_8) deviate significantly from this plane and in such a way that the conformation of the ion may be described as a twisted chair.

Table 6. Analysis of planarity of the cation.

Atom	Deviation (Å)	Atom	Deviation (Å)
C1	−0.022	C6	0.001
C2	0.364	C7	0.385
C3	−0.329	C8	−0.384
C4	−0.004	C9	−0.019
N5	−0.007	N10	0.001
C5a	0.010	C11	0.014
		C11a	0.025

The Br atoms have closest contacts with the C_{11} and C_9 atoms of one cation and with the C_6 and C_1 of another four different cations (*cf.* Table 5). In this way a three-dimensional structure is likely to be formed by probably weak interionic bondings. No further interionic contacts likely to correspond to hydrogen bonds are present in the structure.

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REFERENCES

1. Leander, K. and Lüning, B. *Tetrahedron Letters* **8** (1968) 905.
2. Swanson and Fuyat, ASTM *X-Ray Powder Data File*, Card 15−503.
3. Werner, P.-E. *To be published.*
4. Institute of Chemistry, University of Uppsala, Uppsala, Sweden, List of crystallographic programs for CD 3600 computer, Sept. 1968.
5. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., July 1966.
6. Brändén, C. I. *Private communication.*
7. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. I.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
9. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon, Oxford 1961, p. 32.

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