

2. *The C-I bond.* The parameter of greatest interest is obviously the C-I distance. Unfortunately, different values were obtained in two sets, although statistically the difference cannot be regarded significant. One of the possible reasons is the different atomic scattering factors used which may be important especially for heavy atoms. The Norwegian school computes atomic factors by the partial wave method (details see in Ref. 3), while in Moscow they are taken from the tables of Cox and Bonham.<sup>5</sup> Indeed, when the "hybrid" attempt was made to refine the Norwegian intensity data according to the procedure adopted in Moscow, the result was  $C-I=2.09 \pm 0.01$  Å. Because this corresponds to the arithmetic mean of values cited in Table 1, we regard it as our final result. An associated amplitude of vibration measured in Moscow is lower than might be expected. A similar phenomenon has been observed by Beagley and McAloon<sup>6</sup> in studies of a number of tin compounds. The authors attributed it to overdamping of calculated intensities by the Cox and Bonham scattering factors.

The C-I distance obtained for DIPC is compared to C-I distances measured in different molecules in Table 2. One might anticipate the C-I distance in DIPC to be *larger* than aliphatic types due to a higher coordination number for the exopolyhedral carbon. This is, however, not the case and in fact, the C-I bond distance in question is practically equal to the ethylenic type. The chemical behaviour of carboranes as strong electron acceptors toward substituents on carbon atoms<sup>11</sup> provides a reasonable explanation of this remarkable feature, as pointed out earlier.<sup>12</sup> There is also additional evidence for "short" exopolyhedral bonds formed by six-coordinate carbon:

(1) The C-H stretch frequency in carboranes  $C_2H_4B_{10}H_{10}$  falls into the region which is characteristic for the ethylenic bond.<sup>13</sup>

(2) The frequency of Cl in nuclear quadrupole resonance spectra for Cl-substituted carboranes is quite similar to those compounds where chlorine is bonded to the group with strong acceptor properties as in  $ClCH(NO_2)_2$ .<sup>14</sup>

It should be noted that in contrast exopolyhedral distances in carboranes formed by boron are *longer* than in corresponding reference compounds.<sup>15</sup>

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## The Crystal Structure of Ethylenediammonium Bromide

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Infrared and far infrared spectra of normal and C-deuterated 1,2-ethylenediammonium difluorides, dichlorides, and dibromides have been measured.<sup>1</sup> A number of bands found for the fluorides and the chlorides have no analogues in the spectra of the bromides. Some of these bands may be due to the hydrogen-bonding in the crystals. However, only the crystal structure of the chloride has been reported.<sup>2,3</sup> The present X-ray investigation was carried out in order to find the hydrogen-bonding system of the bromide.

Table 1. Positional and thermal parameters ( $U_{ij} \times 10^4 \text{ \AA}^2$ ) with their estimated standard deviations. The form of the temperature factor expression is  $\exp[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}]$ .

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Br	0.1510(1)	0	0.1722(2)	313(6)	306(6)	269(6)	0	60(4)	0
N	0.3746(7)	0	0.3618(23)	235(35)	362(49)	321(43)	0	41(31)	0
C	0.4698(7)	0	0.3537(21)	229(38)	379(52)	202(36)	0	44(29)	0

*Experimental.* Lattice type and space group were established from Weissenberg and precession photographs using  $\text{CuK}\alpha$ - and  $\text{MoK}\alpha$ -radiation. Three-dimensional data were measured on a semi-automatic equi-inclination diffractometer (Stoe & Cie, Darmstadt, DBR) using graphite monochromated  $\text{MoK}\alpha$ -radiation and  $\omega$ -scan technique. Harmonics were excluded by means of a pulse height discriminator. The crystal was mounted with its [010] axis as rotation axis. Reflections between a cylinder of radius  $Y=5.4^\circ$  and a hemisphere with  $\sin \theta/\lambda < 0.7 \text{ \AA}$  were measured ( $0 \leq k \leq 6$ ) giving 561 independent reflections of which 469 had  $I > 2\sigma(I)$ , where  $\sigma(I) = [(1+k^2)\text{PC} + \text{BC}]$ . The constant  $k$  was 0.04. The diffractometer output was processed by means of a programme which takes into account the polarization of the incident beam.

The dimensions of the crystal used were  $0.32 \times 0.16 \times 0.01 \text{ mm}$ . No correction was made for absorption since the crystal was small. All symmetry related reflections were averaged.

The computations described below were performed on an IBM 370/165 computer using the X-RAY system<sup>4</sup> and the drawing programme ORTEP.<sup>5</sup> The atomic scattering factors used were those given by Cromer and Mann.<sup>6</sup>

*Crystal data.*  $(\text{CH}_2\text{NH}_2)_2\text{Br}_2$ ,  $M = 221.9$  Monoclinic,  $a = 15.24(2) \text{ \AA}$ ,  $b = 4.79(3) \text{ \AA}$ ,  $c = 4.86(3) \text{ \AA}$ ,  $\beta = 101.9(5)^\circ$ ,  $V = 347.2 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 2.12$ ,  $D_o = 2.12$ ,  $F(000) = 212$ ,  $\mu(\text{MoK}\alpha) = 122.3 \text{ cm}^{-1}$ . Systematic absences:  $hkl$  when  $h+k$  odd. The possible space groups are  $C2/m$ ,  $Cm$  and  $C2$ .

*Structure determination.* The coordinates of the bromide ion were found from a 3-dimensional Patterson map, and the positions of the carbon and nitrogen atoms revealed themselves in a subsequent Fourier map. The structure was refined by full matrix least squares minimizing the function  $\sum w(|F_o| - |F_c|)^2$ . With anisotropic temperature factors and  $w = 5.934 - 0.094|F| + 0.006|F|^2 - 7.309 \sin \theta/\lambda$  the refinement resulted in  $R = 0.078$  ( $R_w = 0.096$ ). The contributions of the hydrogen atoms were neglected in all calculations. The initial assumption that the structure has the space group  $C2/m$  was confirmed by the convergence of the refinement.

*Description and discussion of the structure.* The final positional and thermal parameters

Table 2. Distances and angles for possible  $\text{N}\cdots\text{Br}$  hydrogen-bonded contacts. Br1 is at  $(\frac{1}{2}-x, \frac{1}{2}, 1-z)$ , Br2 at  $(\frac{1}{2}-x, -\frac{1}{2}, 1-z)$ .

N-Br	3.34(1)
N-Br1	3.37(2)
C-N-Br	162.8(8)
C-N-Br1	105.7(4)
Br-N-Br1	86.1(3)
Br1-N-Br2	90.4(6)
N-Br-N1	93.8(3)
N1-Br-N2	90.4(5)

are given in Table 1. The donor-acceptor distances and relevant angles where hydrogen bonding is assumed to take place are given in Table 2. A list of the observed and calculated structure factors may be obtained from the author or the department upon request.

The structure is shown in Fig. 1. All the atoms, Br<sup>-</sup>, N and C, lie in the special position  $x, 0, z$  with the centre of the C-C bond at the centre of symmetry. Thus the ethylenediammonium ion has *trans* configuration with planar N-C-C-N chain, and in this respect the structure is similar to that of the chloride analogue.<sup>2,3</sup>

The C-C and C-N bond lengths of the present structure, 1.53(2) and 1.46(1)  $\text{\AA}$ , respectively, agree with those found for ethylenediamine at  $-60^\circ\text{C}$  [1.51(2) and 1.47(1)  $\text{\AA}$ , respectively].<sup>7</sup> The latter molecule too has the *trans* configuration. The C-N bond length is somewhat shorter than those found in the *gauche* isomers [1.49(1)  $\text{\AA}$ ]<sup>8,9</sup> but agree with those found in other *trans* isomers [1.47(1)  $\text{\AA}$ ]<sup>7,8,10</sup> and with the mean value of 1.472(5)  $\text{\AA}$  found in other structures.<sup>11</sup> The C-C-N angle of  $112.7(9)^\circ$  is slightly larger than the tetrahedral angle, a feature which the present structure has in common with ethylenediamine. In the chloride analogue the angle between these atoms is equal to the tetrahedral angle.<sup>2,3</sup>

The N-Br donor-acceptor distances where hydrogen bonding is assumed to take place, are 3.34, 3.37 and 3.37  $\text{\AA}$ , respectively. They are shown as broken lines in Fig. 1. In addition

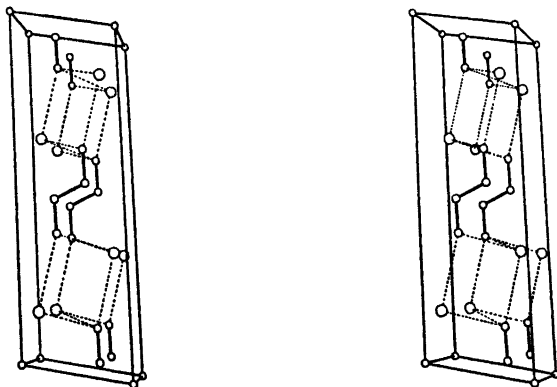


Fig. 1. Stereoscopic view of the structure of ethylenediammonium bromide along the  $b$  axis. The longest axis is the  $a$  axis. The hydrogen bonds are shown as broken lines.

there are two longer N-Br distances of 3.49(2) Å to Br<sup>-</sup>3 and Br<sup>-</sup>4, and the Br<sup>-</sup> ions 1, 2, 3, and 4 form a planar rectangular arrangement with the N atom 0.38 Å from this plane.

The ethylenediammonium ions are stacked above each other in the  $y$  direction, and two of the hydrogen bonds link the ions in this direction. The third hydrogen bond links the ions in the  $x$  direction. This hydrogen bonding system between two ethylenediammonium ions along the  $b$  axis occurs twice in the unit cell (Fig. 1). There is no bonding along the  $a$  axis between these two hydrogen bonding systems. However, along the  $c$  axis the N-Br distances of 3.49 Å make contacts between the hydrogen bonding systems of two neighbouring unit cells.

The hydrogen bonds (3.12, 3.20, and 3.22 Å) in the chloride ( $P2_1/a$ )<sup>2,3</sup> form helices along the  $b$  axis between the ethylenediammonium ions. In the unit cell there are two such helices linked together by hydrogen bonds in the  $c$  direction. In the  $a$  direction there are N-Cl distances of 3.48 Å. In the bromide the N-Br distance of 3.49 Å is slightly longer than the sum of the van der Waals radii,<sup>12</sup> 3.45 Å, whereas in the chloride the difference between the observed value of 3.48 Å and the calculated of 3.30 Å is larger. The main difference between the hydrogen bonding systems in the two structures is the lack of hydrogen bonding coupling between the two hydrogen bonding systems along the  $a$  axis in the bromide. This may be the reason why the infrared spectra of the chloride show a number of strong and medium bands in addition to those found in the bromide.

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