

## Crystal Structures of the Compounds Dimethylammonium Bromide-Bromine (2:1) and Dimethylammonium Chloride-Iodine (2:1)

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The crystal structures of the compounds (2:1) dimethylammonium bromide-bromine  $[(\text{CH}_3)_2\text{NH}_2\text{Br}]_2 \cdot \text{Br}_2$  and (2:1) dimethylammonium chloride-iodine  $[(\text{CH}_3)_2\text{NH}_2\text{Cl}]_2 \cdot \text{I}_2$  have been determined by X-ray methods. The compounds are isomorphous, the space group is  $C2$  and the lattice parameters are  $a = 20.00 \text{ \AA}$ ;  $b = 6.01 \text{ \AA}$ ;  $c = 5.38 \text{ \AA}$ ;  $\beta = 94.6^\circ$  and  $a = 20.43 \text{ \AA}$ ;  $b = 5.88 \text{ \AA}$ ;  $c = 5.45 \text{ \AA}$ ;  $\beta = 94.3^\circ$ , respectively.

The halogen atoms are arranged in nearly linear chains, *viz.* Br—Br—Br—Br and Cl—I—I—Cl (the halogen-halogen-halogen angle  $\approx 173^\circ$ .) In these chains the distance between the two central atoms is a little longer than those in the free halogen molecules (obs. Br—Br dist. =  $2.42 \text{ \AA}$  and obs. I—I =  $2.74 \text{ \AA}$ ). The bonds from the central atoms to the nearer of the terminal halogen atoms appear to be moderately strong and the distances intermediate between those to be expected for covalent and van der Waals values.

Each terminal halogen atom is connected to three nitrogen atoms. Two of these halogen-nitrogen distances are similar to the halogen-nitrogen distances found in ammonium halides, but the third halogen-nitrogen distance is appreciably shorter (N—Br =  $3.05 \text{ \AA}$ ,  $3.49 \text{ \AA}$ ,  $3.50 \text{ \AA}$ ; N—Cl =  $3.05 \text{ \AA}$ ,  $3.27 \text{ \AA}$ ,  $3.28 \text{ \AA}$ ). This short bond lies along one of the nitrogen's tetrahedral directions, approximately. The angle between this direction and the line joining halogen-halogen is about  $95^\circ$ .

The structures of salts formed by ammonium cations and polyhalide anions are of considerable interest. Among the substances already investigated are several containing the trihalide ion to which a negative charge is attached.

The present report deals with the crystal structures of the 2:1 addition compounds formed by dimethylammonium bromide and chloride with bromine and iodine, respectively. In these compounds a negative charge should be associated with half the number of halogen atoms present in the compound under consideration.

## EXPERIMENTAL

The compounds  $[(\text{CH}_3)_2\text{NH}\cdot\text{HBr}]_2\cdot\text{Br}_2$  or  $[(\text{CH}_3)_2\text{NH}\cdot\text{HCl}]_2\cdot\text{I}_2$  are formed by addition of diluted bromine (or iodine) to a solution containing the dimethylammonium bromide (or chloride) in chloroform.<sup>1</sup> Good crystals may be obtained by careful cooling of a saturated solution or by slow evaporation of the chloroform. The compounds may also be obtained by adding diluted bromine (or iodo monochloride) to the free base in chloroform.<sup>2</sup> The halogen thus reacts with the methyl groups giving halogen substituted amine and hydrobromic (or hydrochloric) acid which in turn neutralizes the free base. The salt then combines with bromine (or iodine, liberated from iodomonochloride) in the given ratio.

The active halogen was determined volumetrically by titration against a standardized solution of thiosulphate.

The bromine compound is orange in colour and the iodine compound reddish brown. Their decomposition points are 73 and 100°C, respectively.

The crystals are instable and were kept in thin-walled boron lithium capillaries when under exposure to X-rays.

Weissenberg and oscillation photographs were taken with Cu-K radiation and rotation about the *b* and *c* axes. Using the multiple film technique two series of Weissenberg photographs were obtained for each compound with exposure times from 1 to 100 h. The intensities were estimated visually and corrected for Lorentz- and polarization effects. No correction for absorption — or secondary extinction effects — was applied.

For the bromine compound 143 *h0l* and 88 *hk0* reflexions are theoretically attainable with Cu-K $\alpha$  radiation. Actually 119 and 81 were observed, respectively. For the compound containing iodine there are 143 theoretical, against 123 exptl. *h0l* reflexions. A correction of the form  $\exp.(-B \sin^2 \Theta/\lambda^2)$  was applied to the calculated structure factors. The *B* factors were found by inspection to be:

	<i>B</i> ( <i>h0l</i> )	<i>B</i> ( <i>hk0</i> )
	(Å <sup>-2</sup> )	(Å <sup>-2</sup> )
Bromine compound	4.90	2.50
Iodine "	4.80	2.50

The atomic scattering factors employed in the calculation of the structure factors are taken from the *Internationale Tabellen*<sup>3</sup>.

## CRYSTAL DATA

The crystals of the two species are isomorphous with monoclinic unit cells. The crystals form flat needles, the needle axes coinciding with the *b* axes. According to the observed X-ray extinctions the three *C*-centered space groups *Cm*, *C2* and *C2/m* are possible. The latter is the only one in which centers of symmetry are present. For reasons mentioned below, however, it turned out that *C2* was the correct space group. It gives rise to only one centrosymmetric projection, that along [010]. The unit cell dimensions are as follows:

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$
$[(\text{CH}_3)_2\text{NH}_2\text{Br}]_2\cdot\text{Br}_2$	20.00 Å;	6.01 Å;	5.38 Å;	94.6
$[(\text{CH}_3)_2\text{NH}_2\text{Cl}]_2\cdot\text{I}_2$	20.43 Å;	5.88 Å;	5.45 Å;	94.3

With densities found by the flotation method (2.15 g/cm<sup>3</sup> and 2.18 g/cm<sup>3</sup>) this leads to 2 molecules of  $[(\text{CH}_3)_2\text{NH}_2\text{Br}]_2\cdot\text{Br}_2$  or  $[(\text{CH}_3)_2\text{NH}_2\text{Cl}]_2\cdot\text{I}_2$  in the unit cell.

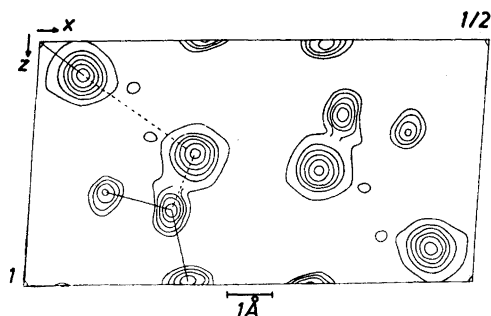


Fig. 1. The electron density projection along the  $b$  axis of dimethylammonium bromide-bromine (2:1).

Contours for bromine : 4, 12, 20, 28..... el.  $\text{\AA}^{-3}$   
 For nitrogen, carbon, etc. : 4, 5, 6, 7, 8, el.  $\text{\AA}^{-3}$ .

#### DETERMINATION OF THE STRUCTURES

Trial and error computations of the parameters of the independent halogen atoms, starting with the bromine compound, led to results which strongly indicated that the plane group for the projection along the  $b$  axes is  $p2$ . This made the space group  $Cm$  improbable. A Patterson projection along  $[010]$  turned out to be in full agreement with these findings and the next step was the computation of the corresponding electron density projection. Starting with the  $x$  and  $z$  coordinates of the bromine atoms already derived and neglecting the lighter atoms, a first Fourier map was obtained which, beside the peaks corresponding to the bromines, also contains lower peaks due to carbon and nitrogen atoms. After four refinements no further phase shifts occurred. The final Fourier map is reproduced in Fig. 1. The reliability factor for this projection is  $R = 0.12$ .

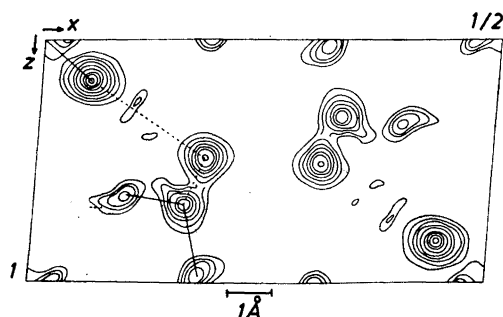


Fig. 2. The electron density projection along the  $b$ -axis of dimethylammonium chloride-iodine (2:1).

Contours for iodine : 4, 13, 23, 33 ..... el.  $\text{\AA}^{-3}$ .  
 For chlorine : 4, 7, 10, 13, 16 ..... el.  $\text{\AA}^{-3}$ .  
 For nitrogen, carbon, etc. : as in Fig. 1.

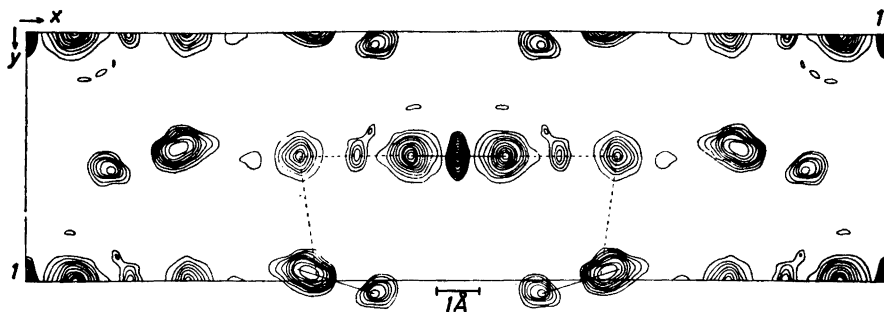


Fig. 3. The electron density projection along the  $c$  axis of dimethylammonium chloride-iodine (2:1).

Contours for chlorine : 4, 8, 12, 16 .....el.  $\text{\AA}^{-2}$ .  
For iodine, nitrogen, carbon etc. as in Fig. 2.

Hoping that a further refinement of the  $x$  and  $z$  parameters should be possible by a difference synthesis, a Fourier chart was worked out subtracting the contributions from the bromine atoms. The map thus obtained did not reveal any electron density gradients in the positions of the removed bromine atoms which could serve as a basis for further refinement. In the case of the light atoms the  $x$  and  $z$  values obtained from this synthesis have been regarded as the more reliable and chosen as the final ones.

The corresponding [010] projection of the isomorphous compound containing iodine was worked out next. Due to the high scattering power of the iodine atom relative to the other atoms approximate values of its  $x$  and  $z$  coordinates could easily be determined by trial and error methods. The Fourier map after three refinements is reproduced in Fig. 2. The  $R$  factor was found to be 0.16. The larger value of the  $R$  factor in this case is probably caused chiefly by more pronounced absorption effects. A difference synthesis led to slight changes in the coordinates of the light atoms but not of the heavy ones.

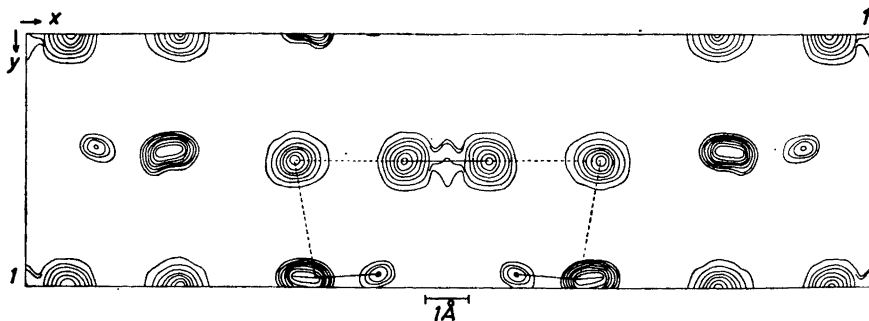


Fig. 4. The electron density projections along the  $c$  axis of dimethylammonium bromide-bromine (2:1).

Contours as in Fig. 1.

It will be noted that the space group  $C2/m$  would have required the four amine groups to be situated in  $m$  with the molecular mirror planes coinciding with those of the space group, thus bringing about one double peak for the two amine carbons in the [010] projection. In Figs. 1 and 2 three peaks for the amine group appear. This finding is not compatible with the above requirement, and  $C2/m$  is thus ruled out in favour of  $C2$ , which has a general 4-fold position and therefore imposes no restriction on the position of the amine group.

The  $y$  parameters of the independent heavy atoms were determined from Patterson projections along the  $c$  axes starting with the iodine compound. It turned out that these parameters in the first step might be set equal to zero, thereby satisfying a condition for a 4-fold position in the centrosymmetric plane group  $cm$ , although the correct plane group is the noncentrosymmetric  $cm$ . According to this finding the phase angles were not expected to deviate much from 0 and  $180^\circ$ , the deviations being dependent on the contributions from the light atoms.

Values of the  $y$  parameters of the amine groups were obtained by a trial and error computation using the correct expressions for the structure factors, the  $x$  parameters obtained from the [010] projection and data for the amine group already known<sup>4</sup>. The contributions from the light and heavy atoms were then included in the calculation of the phase angles and a Fourier synthesis based on the plane group  $cm$  was carried out. After three refinements the electron density map reproduced in Fig. 3 was obtained. The  $R$  factor was found equal to 0.14. The  $x$  parameters found for the halogen atoms in the two projections agree to within 0.001 of the axial lengths.

In the case of the bromine compound the  $y$  parameters of the nitrogen atom was arbitrarily put equal to  $\frac{1}{2}$  (or 0). The corresponding  $y$  parameters of the two independent carbon atoms belonging to the same amine group were then calculated using a model before a Fourier refinement process was started. The electron density map after three refinements is shown in Fig. 4. The value of the  $R$  factor is 0.12. The  $x$  parameters found for the halogen atoms in the two projections agree to within 0.001 of the axial length.

Table 1. Atomic coordinates in fractions of the cell edges. Origin at a 2-fold axis.

A [(CH <sub>3</sub> ) <sub>2</sub> NH·HCl] <sub>2</sub> ·I <sub>2</sub>		B [(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Br] <sub>2</sub> ·Br <sub>2</sub>		
	Atom	$x$	$y$	$z$
A	I	0.055	0.000	0.162
	Cl	0.186	0.001	0.493
	N	0.166	0.480	0.688
	C <sub>1</sub>	0.099	0.551	0.672
	C <sub>2</sub>	0.188	0.456	0.952
B	Br <sub>1</sub>	0.050	0.000	0.143
	Br <sub>2</sub>	0.180	-0.002	0.473
	N	0.157	0.467	0.714
	C <sub>1</sub>	0.083	0.449	0.630
	C <sub>2</sub>	0.183	0.459	0.983

Table 2.  $|F_{\text{obs}}|$ -,  $|F_{\text{calc}}|$ - and  $\alpha_{\text{calc}}$ -values. The  $F$ -values represent one fourth of the absolute values.

$hkl$	Compound containing bromine			Compound containing iodine		
	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$
2 0 0	3.0	2.2	0	14.9	23.5	0
4 0 0	4.1	3.3	180	< 1.6	0.8	0
6 0 0	17.9	17.8	0	5.4	6.7	180
8 0 0	36.9	41.4	180	40.6	47.0	180
10 0 0	13.4	12.7	180	19.2	23.6	180
12 0 0	< 1.8	0.1	180	7.3	11.2	180
14 0 0	15.3	14.4	180	4.2	4.6	180
16 0 0	7.6	7.6	0	15.7	15.5	0
18 0 0	6.1	5.5	0	10.5	11.1	0
20 0 0	< 2.2	0.7	0	7.1	5.7	0
22 0 0	6.6	6.2	0	5.7	6.4	0
24 0 0	< 1.7	0.1	180	5.0	5.3	180
0 0 1	9.3	11.3	0	10.3	9.8	0
2 0 1	23.7	19.7	0	8.8	8.2	0
4 0 1	4.8	4.9	180	19.4	30.2	180
6 0 1	5.9	38.3	180	33.9	46.4	180
8 0 1	3.4	2.0	180	16.1	19.6	180
10 0 1	14.8	14.5	180	14.3	12.8	180
12 0 1	12.3	10.2	180	6.7	9.8	0
14 0 1	16.3	17.6	0	21.8	24.8	0
16 0 1	3.8	4.1	0	10.2	12.8	0
18 0 1	4.5	4.7	0	8.0	9.4	0
20 0 1	7.6	6.4	0	4.7	1.2	0
22 0 1	3.6	2.9	180	7.5	7.9	180
24 0 1	1.4	1.3	180	3.1	5.4	180
2 0 $\bar{1}$	40.5	48.0	0	38.5	43.1	0
4 0 $\bar{1}$	29.3	30.2	0	47.9	46.7	0
6 0 $\bar{1}$	1.9	2.2	180	13.4	17.7	0
8 0 $\bar{1}$	1.6	17.2	0	< 2.4	0.2	0
10 0 $\bar{1}$	11.7	15.2	180	22.3	25.9	180
12 0 $\bar{1}$	19.5	18.4	180	27.5	28.4	180
14 0 $\bar{1}$	4.2	3.0	180	15.2	15.4	180
16 0 $\bar{1}$	12.2	9.8	180	4.7	5.1	180
18 0 $\bar{1}$	3.9	2.7	0	8.7	8.8	0
20 0 $\bar{1}$	7.2	5.9	0	10.4	10.2	0
22 0 $\bar{1}$	< 2.0	0.3	0	5.4	7.4	0
24 0 $\bar{1}$	3.6	3.4	0	3.4	5.6	0
0 0 2	17.7	16.8	0	4.5	5.1	180
2 0 2	31.5	28.1	180	38.2	46.7	180
4 0 2	29.6	29.6	180	30.4	32.1	180
6 0 2	3.2	2.6	0	9.3	10.3	180
8 0 2	20.1	18.4	180	7.7	6.2	180
10 0 2	4.6	5.6	0	22.0	22.8	0
12 0 2	14.3	16.5	0	17.3	20.4	0
14 0 2	4.3	2.1	180	8.2	8.8	0
16 0 2	8.6	8.8	0	11.6	10.6	0
18 0 2	4.9	5.1	0	5.7	6.1	180
20 0 2	4.6	4.6	180	9.2	9.9	180

$h k l$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$	$F_{\text{obs}}$	$ F_{\text{calc}} $	$\alpha,^\circ$
22 0 2	2.4	0.8	0	4.3	5.1	180
24 0 2	< 1.1	2.2	180			
2 0 2	7.1	7.3	180	6.2	3.8	0
4 0 2	27.7	23.2	0	36.2	30.8	0
6 0 2	33.8	30.3	0	40.8	37.3	0
8 0 2	4.6	5.6	180	14.1	13.6	0
10 0 2	11.5	11.4	0	7.6	9.6	0
12 0 2	4.4	2.6	180	13.7	12.1	180
14 0 2	15.3	15.3	180	19.8	20.4	180
16 0 2	2.2	1.4	0	10.1	10.8	180
18 0 2	6.6	7.7	180	1.0	11.5	180
20 0 2	4.2	4.0	180	3.8	2.4	0
22 0 2	4.4	4.4	0	7.3	8.7	0
24 0 2	< 1.4	0.1	0	3.1	4.6	0
0 0 3	22.5	23.5	0	26.8	29.9	180
2 0 3	15.2	12.8	180	23.5	18.5	180
4 0 3	4.4	1.4	180	11.6	8.6	180
6 0 3	13.1	12.2	180	4.7	6.1	0
8 0 3	7.6	8.9	0	24.7	22.5	0
10 0 3	8.9	9.4	0	19.6	16.1	0
12 0 3	3.1	2.7	0	12.3	17.5	0
14 0 3	8.7	9.1	0	< 2.8	1.2	0
16 0 3	2.5	0.6	180	10.1	11.0	180
18 0 3	3.4	3.2	180	6.3	7.5	180
20 0 3	1.7	0.3	180	5.3	6.3	180
2 0 3	6.7	9.1	0	16.9	17.6	180
4 0 3	5.0	5.4	180	< 2.1	5.8	180
6 0 3	5.2	3.0	0	14.8	12.9	0
8 0 3	24.1	23.8	0	30.5	28.1	0
10 0 3	2.8	2.2	0	17.0	16.5	0
12 0 3	4.7	4.1	0	9.7	9.2	0
14 0 3	5.4	4.5	0	< 2.7	1.7	180
16 0 3	9.5	9.8	180	15.1	14.7	180
18 0 3	3.5	2.8	180	8.2	8.6	180
20 0 3	< 2.0	0.7	180	3.5	6.0	180
22 0 3	3.3	3.2	180	4.1	3.0	180
24 0 3	1.4	1.6	0			
0 0 4	< 2.1	0.5	180	10.9	7.7	180
2 0 4	4.8	4.7	180	< 2.6	0.5	180
4 0 4	7.3	6.3	180	11.2	11.2	0
6 0 4	15.0	14.4	0	26.1	22.9	0
8 0 4	3.7	3.9	0	10.9	6.8	0
10 0 4	2.5	2.4	0	7.2	5.3	0
12 0 4	7.2	6.9	0	< 2.7	2.7	180
14 0 4	3.5	4.1	180	11.2	11.0	180
16 0 4	2.4	1.7	180	6.5	6.0	180
18 0 4	2.0	6.2	180	5.8	5.8	180
2 0 4	25.1	21.2	180	28.7	27.5	180
4 0 4	2.6	0.1	180	16.9	14.6	180
6 0 4	5.4	3.9	0	4.6	3.1	180
8 0 4	5.3	5.2	180	5.0	1.9	180
10 0 4	12.5	12.0	0	17.9	17.9	0
12 0 4	6.3	5.3	0	13.6	13.5	0
14 0 4	< 2.2	0.9	180	7.6	6.3	0

$hkl$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$
16 0 $\bar{4}$	4.4	5.0	0	4.2	6.2	0
18 0 $\bar{4}$	3.4	2.8	180	5.4	6.6	180
20 0 $\bar{4}$	2.9	2.9	180	6.1	7.6	180
22 0 $\bar{4}$	< 0.9	0.0	0	< 1.5	2.6	180
0 0 $\bar{5}$	6.8	4.8	180	2.0	1.5	0
2 0 $\bar{5}$	2.7	1.4	0	13.9	12.7	0
4 0 $\bar{5}$	8.1	8.7	0	14.1	10.6	0
6 0 $\bar{5}$	< 2.2	0.1	0	7.4	5.3	0
8 0 $\bar{5}$	5.1	4.4	0	4.4	2.8	0
10 0 $\bar{5}$	3.7	3.2	0	7.2	6.4	180
12 0 $\bar{5}$	3.4	4.1	180	9.4	9.1	180
14 0 $\bar{5}$	2.0	1.1	180	5.9	5.4	180
2 0 $\bar{5}$	2.3	1.9	0	1.6	0.4	180
4 0 $\bar{5}$	7.9	8.6	180	12.5	11.3	180
6 0 $\bar{5}$	6.9	6.6	180	16.6	16.4	180
8 0 $\bar{5}$	2.6	1.6	0	7.4	5.5	180
10 0 $\bar{5}$	2.0	2.2	180	5.6	2.1	180
12 0 $\bar{5}$	3.5	3.8	0	6.1	5.9	0
14 0 $\bar{5}$	4.5	5.0	0	10.4	10.3	0
16 0 $\bar{5}$	< 0.8	0.2	0	5.9	4.8	0
18 0 $\bar{5}$				3.5	2.5	0
0 0 6	3.5	3.0	0	12.2	11.8	0
2 0 6	3.5	3.8	0	11.1	6.4	0
4 0 6	< 1.8	0.4	0	2.0	1.7	0
6 0 6	3.8	4.2	0	4.4	0.0	180
8 0 6	1.8	1.3	180	7.6	8.3	180
10 0 6	1.2	2.0	180	5.3	5.4	180
2 0 $\bar{6}$	2.6	3.3	180	5.4	2.8	0
4 0 $\bar{6}$	< 1.8	0.1	0	< 2.4	0.2	180
6 0 $\bar{6}$	3.2	2.3	180	4.4	3.6	180
8 0 $\bar{6}$	3.8	4.6	180	9.9	9.4	180
10 0 $\bar{6}$	1.6	1.3	0	6.0	4.6	180
12 0 $\bar{6}$	1.4	1.0	180	< 1.8	3.1	180
14 0 $\bar{6}$	< 1.1	0.0	0	< 1.6	0.6	0
0 0 7	0.7	0.1	0	1.8	2.2	0
2 0 0	2.6	2.4	0	20.3	23.1	0
4 0 0	4.6	4.6	180	< 1.5	2.0	0
6 0 0	18.5	19.2	0	5.4	7.6	180
8 0 0	39.4	45.1	180	51.5	49.9	180
10 0 0	16.2	14.8	180	25.6	24.5	180
12 0 0	2.3	5.1	180	10.3	18.4	180
14 0 0	20.0	18.2	180	10.1	4.7	180
16 0 0	9.8	11.0	0	20.7	19.1	0
18 0 0	8.2	7.6	0	16.8	14.5	0
20 0 0	< 2.4	1.1	0	10.8	11.3	0
22 0 0	8.2	9.9	0	9.0	6.2	0
24 0 0	2.0	0.2	180	< 2.2	6.2	180
1 1 0	32.2	35.9	3.7	40.5	42.9	358.5
3 1 0	4.9	3.0	232.2	18.3	21.0	357.7
5 1 0	20.4	20.7	359.4	3.9	3.2	22.2
7 1 0	13.6	15.4	181.9	21.8	32.2	178.8
9 1 0	26.8	31.6	181.2	27.3	35.9	182.1
11 1 0	4.8	2.2	166.9	19.6	20.6	181.0
13 1 0	18.9	16.8	178.2	14.4	10.4	181.2



<i>h k l</i>	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$
15 1 0	4.3	3.4	180.7	16.8	13.2	2.3
17 1 0	16.4	16.5	358.8	22.3	21.5	1.1
19 1 0	1.5	1.3	355.0	10.8	10.2	0.0
21 1 0	5.9	7.3	0.4	9.8	9.7	358.5
23 1 0	4.8	5.8	359.8	< 2.2	1.3	184.0
25 1 0				5.9	6.3	178.5
0 2 0	60.6	61.4	353.9	65.3	62.1	0.8
2 2 0	4.4	2.9	34.4	18.7	20.2	6.7
4 2 0	2.2	2.4	126.5	4.0	3.7	330.4
6 2 0	15.8	1.2	353.0	8.0	7.3	207.3
8 2 0	33.1	36.5	175.7	34.1	41.4	178.2
10 2 0	13.4	12.7	182.7	17.3	21.4	176.2
12 2 0	2.5	2.2	258.6	9.3	10.3	177.9
14 2 0	15.9	15.8	178.1	7.7	3.9	182.9
16 2 0	8.5	9.4	359.2	20.3	17.0	356.3
18 2 0	6.6	6.6	4.1	14.9	12.7	360.0
20 2 0	3.9	1.2	22.0	9.8	10.0	3.3
22 2 0	6.8	8.2	357.7	7.0	5.4	3.2
24 2 0				5.7	5.5	180.0
1 3 0	25.3	25.7	6.8	30.5	30.7	357.9
3 3 0	3.0	4.3	214.8	13.2	20.2	353.4
5 3 0	15.2	13.7	358.0	4.8	2.8	86.9
7 3 0	11.1	11.0	184.1	21.3	23.1	177.8
9 3 0	22.0	23.2	182.5	23.8	26.3	184.7
11 3 0	2.9	0.9	141.5	12.6	14.3	181.3
13 3 0	12.4	12.3	174.9	9.3	8.2	183.7
15 3 0	3.5	2.7	181.4	11.5	10.5	5.5
17 3 0	10.5	12.2	356.5	21.0	14.6	3.8
19 3 0	1.4	0.7	346.6	6.2	8.5	355.8
21 3 0	4.4	5.4	1.2	8.1	7.4	356.7
23 3 0	4.0	4.4	359.2			
0 4 0	35.9	32.7	350.3	35.1	34.5	0.0
2 4 0	2.3	2.4	37.6	15.0	13.1	8.2
4 4 0	2.3	2.0	85.0	6.7	3.1	17.3
6 4 0	10.2	7.5	347.1	4.9	5.0	205.6
8 4 0	21.2	21.8	172.9	26.2	25.9	177.2
10 4 0	8.2	8.0	184.0	13.5	14.2	175.9
12 4 0	2.7	2.2	242.2	7.8	7.3	178.2
14 4 0	9.8	10.5	176.5	< 2.7	2.6	180.0
16 4 0	5.5	6.8	358.5	14.0	12.6	354.7
18 4 0	3.9	4.5	5.7	9.2	9.4	359.6
20 4 0	2.9	0.7	31.9	6.5	6.7	4.8
1 5 0	14.7	14.7	5.0	20.1	17.8	359.3
3 5 0	2.9	3.2	201.4	8.4	6.6	348.3
5 5 0	9.2	7.6	356.2	6.7	2.0	82.1
7 5 0	6.3	6.1	184.0	14.5	14.1	178.2
9 5 0	11.7	13.6	182.6	17.0	16.1	185.4
11 5 0	2.5	0.5	102.6	8.0	7.9	178.7
13 5 0	6.5	6.4	172.2	7.4	5.3	185.6
15 5 0	3.1	1.6	181.2	8.3	5.1	5.3
17 5 0	5.5	6.5	354.5	10.4	8.0	4.9
19 5 0	1.1	0.3	336.7			
0 6 0	16.3	14.7	354.1	20.0	17.4	358.0
2 6 0	< 2.3	1.4	39.5	8.1	6.9	9.2

$hkl$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$\alpha,^\circ$
4 6 0	< 2.3	1.1	63.3	< 2.7	2.1	354.0
6 6 0	5.3	4.2	344.4	4.4	2.7	221.9
8 6 0	9.6	10.0	171.0	15.3	14.2	176.0
10 6 0	3.8	3.9	184.3	8.5	8.5	178.0
12 6 0	2.0	1.9	221.3	< 2.1	4.4	180.9
14 6 0	5.1	4.9	174.9	< 1.7	1.0	167.9
16 6 0				3.9	7.0	352.2
1 7 0	6.0	6.4	4.4	8.8	9.2	1.7
3 7 0	3.2	1.7	192.9	< 1.9	3.2	357.7
5 7 0	2.6	3.0	354.2	< 1.8	1.0	69.7
7 7 0	2.6	2.6	182.5	6.1	6.5	175.8
9 7 0	4.8	5.7	182.0			

It will be observed from Figs. 3 and 4 that a nitrogen and a carbon atom are overlapping in these projections. The  $y$  coordinates of these atoms were found by using standard methods for localization of maxima, the  $x$  parameters for these atoms being taken from the [010] projections. Atomic coordinates are listed in Table 1, observed and calculated structure amplitudes including phase angles in Table 2.

#### DESCRIPTION OF THE STRUCTURE

In Table 3 some calculated bond distances and angles are presented. The listed sums of covalent and ionic radii are based on Pauling's values<sup>5</sup>. Suffixes

Table 3. Bond distances and angles

	Bond	Bond length(Å)	Sum of covalent radii(Å)	Sum of ionic r.(Å) ( $\approx$ sum V.d.W.r.)	Angle	
A	I—I	2.74	2.66		I—I—Cl 173.4°	
	I—Cl	3.11	2.32	3.97	I—Cl—N 94.2°	
	Cl—N <sub>1</sub>	3.05	1.70	3.29		
	Cl—N <sub>1</sub> '	3.28		3.29		
	Cl—N <sub>2</sub>	3.27		3.29		
	N—C <sub>1</sub>	1.47	1.47			
	N—C <sub>2</sub>	1.48	1.47			
	I—N <sub>1</sub>	4.51		3.64		
	B	Br <sub>1</sub> —Br <sub>1</sub>	2.42	2.28		Br—Br—Br 173.0°
		Br <sub>1</sub> —Br <sub>2</sub>	3.03	2.28	3.90	Br—Br—N 95.5°
Br <sub>2</sub> —N <sub>1</sub>		3.15	1.84	3.43		
Br <sub>2</sub> —N <sub>1</sub> '		3.49		3.43		
Br <sub>2</sub> —N <sub>2</sub>		3.50		3.43		
N—C <sub>1</sub>		1.52	1.47			
N—C <sub>2</sub>		1.51	1.47			
Br <sub>1</sub> —N <sub>1</sub>		4.57		3.43		

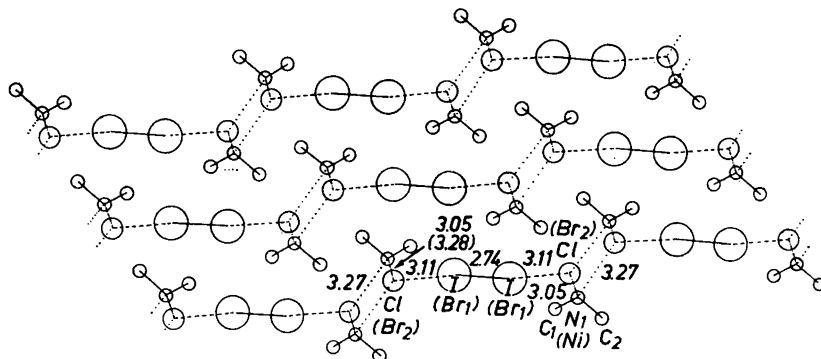


Fig. 5. The structure of dimethylammonium chloride-iodine (2:1) as seen along [010].

attached to the atomic symbols refer to Fig. 5 which shows the structure of dimethylammonium chloride-iodine (2:1) projected along [010].

Standard deviations in bond lengths are as follows:

$$\begin{array}{ll}
 \sigma(\text{I—I}) = 0.003 \text{ \AA} & ; \quad \sigma = (\text{Br}_1\text{—Br}_1) = 0.004 \text{ \AA} \\
 \sigma(\text{I—Cl}) = 0.008 \text{ \AA} & ; \quad \sigma = (\text{Br}_1\text{—Br}_2) = 0.004 \text{ \AA} \\
 \sigma(\text{Cl—N}) = 0.021 \text{ \AA} & ; \quad \sigma = (\text{Br}_2\text{—N}) = 0.020 \text{ \AA}
 \end{array}$$

A striking feature of these structures is the halogen chains, Cl—I—I—Cl or Br—Br—Br—Br, which show only a slight deviation from linearity, the halogen-halogen-halogen angles being approximately  $173^\circ$ . The bond between the two atoms in the middle of the chain is covalent, although a slight bond elongation is observed in both cases. This change in bond length is due to an interaction between the atoms in the middle of the chain and the adjacent terminal ones. The bond distance between a middle and a terminal halogen atom is nearly equal to the mean of the respective covalent and van der Waals radius sums (*cf.* the structure of caesium tetraiodide)<sup>6</sup>. Moreover, each of the terminal halogen atoms is connected to three nitrogen atoms. It will be noticed from Table 3 that one of the corresponding bond distances (Cl—N<sub>1</sub> or Br—N<sub>1</sub>) is considerably shorter than the two others (Cl—N<sub>1</sub>' and Cl—N<sub>2</sub> or Br<sub>2</sub>—N<sub>1</sub>' and Br<sub>2</sub>—N<sub>2</sub>) which are of practically equal length. Furthermore, the Hal—N<sub>1</sub> bond is directed along one of the tetrahedral bond directions from nitrogen thus indicating the presence of a hydrogen bridge.

The lengths of the two other halogen-nitrogen bonds mentioned above agree well with the nitrogen-halogen distances observed in ammonium halides.

The halogen chain may be interpreted as an addition complex formed by two halogen ions (donors) and one halogen molecule (acceptor).<sup>7</sup>

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