

An X-Ray Analysis of the 1:1 Compound Trimethylamine-Iodine

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The crystal structure of the 1:1 molecular compound trimethylamine-iodine has been determined by X-ray methods. The nitrogen-halogen arrangement is linear. A short N—I distance (2.27 Å) suggests a strong interaction between nitrogen and halogen. The observed I—I distance (2.83 Å) is 0.17 Å longer than the covalent I—I bond length observed in the "free" I₂ molecule.

Structure determinations of addition compounds between weak organic amines (with dissociation constants in water solution of the order 10⁻⁹) and halogens^{1,2} show the nitrogen-halogen-halogen arrangement to be linear. The interaction between the donor (nitrogen) atom responsible for the Lewis base properties of the amine, and the acceptor (halogen) atom is strong, and the nitrogen-halogen distance slightly larger than that to be expected for a normal covalent bond. It might be questioned whether or not appreciably stronger organic bases behave in a similar way towards halogens. According to Hantzsch³ the addition reaction between trimethylamine (diss. const. 7.4 × 10⁻⁵) and bromine leads to the formation of bromotrimethylammonium bromide.



Attempts to obtain single crystals of this compound were not successful. Using iodine instead of bromine, however, single crystals of the corresponding addition compound suitable for X-ray analysis could be grown without too great difficulty.

EXPERIMENTAL

The compound trimethylamine-iodine was obtained as an orange coloured precipitate by adding a solution of potassium triiodide to a solution of the amine in water⁴. After filtration the precipitate was dried over phosphorus pentoxide in a desiccator. The composition was determined by titration of iodine against a standardized solution of sodium thiosulphate. Decomposition point 68°C. Recrystallisation was effected by cooling a

solution of the compound in methylene chloride to -50°C . The crystals show a marked tendency to twin.

The rather unstable crystals were mounted in boronlithium capillaries before exposure to X-rays. Their cross-sectional dimensions perpendicular to the rotation axis were about $0.15 \times 0.20 \text{ mm}^2$.

Weissenberg and oscillation photographs were taken with $\text{Cu-K}\alpha$ radiation at about -20°C , the cooling being achieved by an adjustable stream of cold air. Using the double film technique two series of Weissenberg photographs were given exposure times from 1 to 100 h. The intensities estimated visually by comparison with a standard scale, were corrected for Lorentz- and polarization effects. No correction for absorption and secondary extinction effects was applied. 66 $hk0$ and 125 $h0l$ reflections are attainable with $\text{Cu-K}\alpha$ radiation. Actually, 50 and 92 were observed, respectively. The atomic scattering factors employed in the calculations of the structure factors are given by the Hartree and Thomas-Fermi f -curves⁵. A correction of the form $\exp. (-B \sin^2 \theta/\lambda^2)$ was applied to the calculated structure factors. The temperature factor, B , was found by inspection to be 1.70 \AA^2 and 1.20 \AA^2 for the $(hk0)$ and $(h0l)$ zones, respectively. Absorption effects are probably mainly responsible for the smallness of these figures.

CRYSTAL DATA

The crystals are orthorhombic with axial dimensions: $a = 11.37 \text{ \AA}$, $b = 8.30 \text{ \AA}$, $c = 8.34 \text{ \AA}$. With four $(\text{CH}_3)_3\text{N}\cdot\text{I}_2$ molecules per unit cell the calculated density is 2.64 g/cm^3 , as compared to the experimental value of 2.57 g/cm^3 .

When twinning occurs the individual crystals retain a common orientation of the a axis, whereas the orientations of the b and c axes interchange. Since these axes differ only slightly in length, superposition of X-ray reflections may occur.

Absence of reflections excludes all space groups but $Pnma$ and $Pna2_1$. The former is centrosymmetric and was assumed to be the correct one. It demands that the four amine groups be situated in mirror planes.

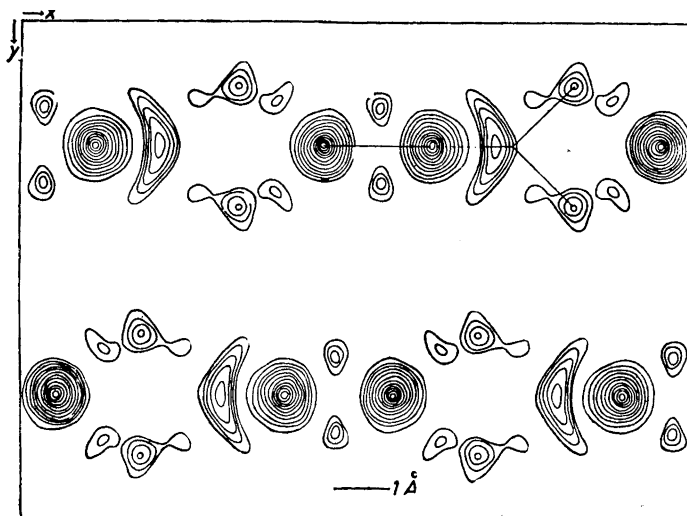


Fig. 1. Electron density projection along the c axis. Contour intervals: $10 \text{ e} \cdot \text{\AA}^{-3}$ for iodine atoms and $2 \text{ e} \cdot \text{\AA}^{-3}$ for nitrogen and carbon atoms. The first contour is the 6-electron line.

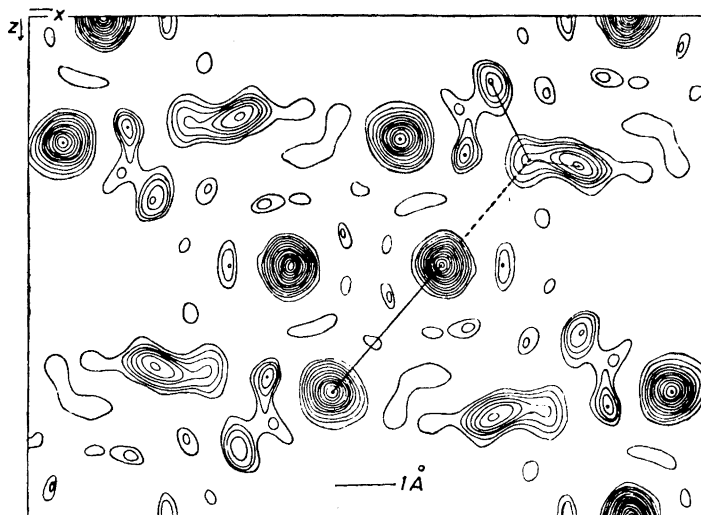


Fig. 2. Electron density projection along the b axis. Contours as in Fig. 1.

DETERMINATION OF THE STRUCTURE

The positions of the iodine atoms were found from two dimensional Patterson syntheses based on the $(hk0)$ and $(h0l)$ reflections, combined with trial and error computations. Using the heavy atom method for the sign determination, the electron density map, Fig. 1 was worked out. In this figure the full lines represent bonds within the amine and the halogen groups, whereas the broken line indicates the bond between the groups. The iodine atoms are seen to be situated in mirror planes, *i.e.* in fourfold positions.

For the (010) projection which is shown in Fig. 2, successive refinements had to be carried out. The small contributions of the heavy atoms to the structure factors with indices $h = 2n + 1$ and $l = 2n$ made the successive introduction of the light atoms necessary. Except for two crystallographically equivalent N—C distances the projection along the b axis on the mirror plane gives the intramolecular bond distances in their true lengths.

Table 1 contains a list of atomic parameters. The suffixes attached to the atomic symbols refer to the structure formula shown below. The y para-

Table 1. Atomic coordinates in fractions of the cell-edges. Origin at a center of symmetry.

Atom	x	y	z
I ₁	0.613	0.250	0.498
I ₂	0.448	0.250	0.752
N	0.741	0.250	0.289
C ₁	0.812	0.101	0.302
C ₂	0.812	0.399	0.302
C ₃	0.686	0.250	0.133

Table 2. Standard deviations of peak positions ⁶.

I ₁ :	$\sigma(x) = 0.005 \text{ \AA};$	$\sigma(z) = 0.006 \text{ \AA}$
I ₂ :	$\sigma(x) = 0.007 \text{ \AA};$	$\sigma(z) = 0.007 \text{ \AA}$
N:	$\sigma(x) = 0.069 \text{ \AA};$	$\sigma(z) = 0.073 \text{ \AA}$

meters of two carbon atoms situated outside the mirror plane are derived from a ($F_{\text{obs}} - F_{\text{hal}}$) synthesis using the ($hk0$) reflections. Almost identical values of the x parameters of the heavy atoms are obtained from the two projections.

The agreement factor, defined as $R = \Sigma ||F_{\text{obs}}| - |F_{\text{calc}}|| / \Sigma |F_{\text{obs}}|$, including not observed reflections when $|F_{\text{calc}}| > |F_{\text{obs, min.}}|$ is 0.13₇ for the ($hk0$) zone and 0.16₇ for the ($h0l$) zone. Observed and calculated F -values are listed in Table 3.

Table 3. Observed and calculated structure factors. The figures represent one fourth of the absolute values.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
0	2	0	99.4	-102.6	1			31.7	-29.6
	4		67.0	72.4	2			<5.4	0.0
	6		51.8	-56.0	3			30.1	25.5
	8		35.2	42.6	4			<5.8	1.6
	10		16.1	-29.1	5			26.6	-20.7
2	0	0	26.8	32.1	6			<5.7	0.4
	1		19.2	18.7	7			18.9	19.0
	2		34.2	-39.5	8			<4.2	-2.1
	3		26.0	-21.5	10	0	0	<5.9	-5.8
	4		31.0	34.3	1			20.3	20.6
	5		19.2	15.9	2			<5.6	6.6
	6		22.3	-24.2	3			17.6	-15.0
	7		11.8	-6.5	4			<5.7	-6.7
	8		13.7	15.9	5			17.0	13.0
	9		<5.2	5.8	6			<4.8	5.0
4	0	0	26.6	-28.8	7			13.3	-13.6
	1		24.9	-31.2	12	0	0	20.4	-19.4
	2		28.8	27.5	1			26.6	26.0
	3		30.4	29.5	2			20.7	19.6
	4		21.8	-21.2	3			23.3	-23.1
	5		21.4	-23.4	4			17.4	-18.7
	6		21.9	16.7	5			16.6	20.2
	7		13.8	13.8	6			6.0	14.7
	8		11.7	-12.7	14	0	0	17.7	-13.2
	9		<4.0	-9.5	0	1		<3.5	7.6
6	0	0	26.4	-24.7	2			14.6	11.6
	1		53.8	-59.8	0	0	2	25.4	-11.9
	2		31.1	27.3	4			72.5	78.1
	3		56.9	50.4	6			10.1	1.8
	4		33.2	-26.1	8			37.2	40.4
	5		46.9	-40.4	10			6.9	2.0
	6		20.1	18.3	1	0	1	32.6	-34.6
	7		36.9	32.4	2			<2.4	3.5
	8		11.5	-11.9	3			42.9	-35.8
	9		18.1	-24.2	4			3.7	-4.8
8	0	0	<5.2	1.0	5			19.8	-21.5

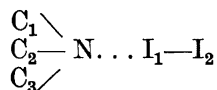
<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
		6	10.4	6.8			9	8.1	— 15.0
		7	24.1	— 21.3	7	0	1	9.8	— 9.7
		8	6.6	— 1.0			2	5.9	— 2.0
		9	10.1	— 9.0			3	7.3	— 6.0
		10	<3.6	— 0.1			4	<4.8	— 0.7
2	0	0	24.7	29.9			5	5.1	— 8.2
		1	20.7	— 25.5			6	<5.2	— 1.0
		2	20.6	— 20.5			7	5.7	— 4.2
		3	15.3	19.7			8	4.2	0.0
		4	29.5	30.2			9	7.9	— 5.5
		5	19.4	— 20.5	8	0	0	<4.5	— 3.5
		6	15.9	— 19.9			1	17.4	— 13.9
		7	11.0	14.2			2	48.1	47.1
		8	16.9	20.7			3	16.1	— 17.1
		9	14.3	— 14.8			4	<5.1	— 1.0
		10	6.6	— 11.7			5	10.2	— 10.6
3	0	1	16.4	20.5			6	29.0	32.2
		2	<2.8	— 2.8			7	10.9	10.3
		3	22.8	25.0			8	<3.7	0.4
		4	10.3	4.2	9	0	1	34.9	— 26.8
		5	19.7	15.7			2	<5.0	0.3
		6	4.8	— 4.4			3	25.0	— 20.1
		7	9.2	11.4			4	<5.2	1.6
		8	8.4	5.6			5	24.7	— 24.0
		9	11.3	10.6			6	<4.5	— 0.9
		10	<3.3	— 0.2			7	16.1	— 15.7
4	0	0	27.6	— 24.5			8	<3.9	1.0
		1	35.4	— 43.8	10	0	0	7.8	— 6.6
		2	43.6	— 52.0			1	<5.2	— 0.2
		3	33.0	37.5			2	40.6	36.5
		4	19.1	— 20.5			3	<5.2	— 0.4
		5	26.8	— 29.3			4	<5.0	— 6.4
		6	31.0	— 31.3			5	<4.7	0.2
		7	15.1	18.5			6	27.1	29.2
		8	15.9	— 13.9			7	<5.1	— 1.8
		9	10.3	— 13.8	11	0	1	<5.1	1.2
		10	14.5	— 17.4			2	<5.0	0.4
5	0	1	39.0	36.7			3	4.9	— 4.1
		2	<3.6	0.0			4	<4.6	0.4
		3	22.7	27.8			5	<4.2	0.3
		4	<4.3	1.3			6	<3.6	1.8
		5	28.8	26.5	12	0	0	24.3	— 28.4
		6	5.0	— 3.0			1	13.6	14.5
		7	15.6	19.3			2	4.9	0.8
		8	<4.8	1.3			3	13.9	— 14.6
		9	16.6	15.3			4	21.6	— 25.6
		10	<2.5	— 1.9			5	10.4	10.8
6	0	0	31.1	— 25.3	13	0	1	19.2	15.1
		1	30.5	— 31.0			2	<3.9	0.8
		2	6.6	— 2.0			3	21.4	18.8
		3	24.1	28.1			4	<3.0	— 2.0
		4	24.4	— 22.0			5	6.0	11.5
		5	17.7	— 21.9	14	0	0	14.4	— 18.3
		6	<5.2	— 0.1			1	10.5	12.7
		7	17.8	21.6			2	12.9	— 7.9
		8	13.6	— 14.3					

Table 4. Interatomic distances and angles in $(\text{CH}_3)_3\text{N} \cdot \text{I}_2$.

Bond type	Bond length (Å)	Sum of covalent radii (Å)	Angle type	Angle- dimension (degrees)
I_1-I_2	2.83	2.66	$\text{N}-\text{I}_1-\text{I}_2$	179
I_1-N	2.27	2.03	$\text{I}_1-\text{N}-\text{C}_1(a)$	107
$\text{I}_1-\text{C}_1(a)$	3.05		$\text{I}_1-\text{N}-\text{C}_3$	114
I_1-C_3	3.15		$\text{C}_1-\text{N}-\text{C}_2$	114
$\text{N}-\text{C}_1(a)$	1.48	1.47	$\text{C}_1(a)-\text{N}-\text{C}_3$	108
$\text{N}-\text{C}_3$	1.44	1.47		
C_1-C_2	2.36			
$\text{C}_1(a)-\text{C}_3$	2.47			

CONCLUSION

Table 4 contains calculated intramolecular distances and angles and some covalent bond lengths⁷. The suffixes attached to the atomic symbols refer to the structure formula



Intermolecular distances are found to be in satisfactory agreement with the sums of accepted van der Waals' radii⁷. Standard deviations in bond lengths⁸ are as follows:

$$\begin{aligned} \sigma (\text{I}_1-\text{I}_2) &= 0.009 \text{ \AA} \\ \sigma (\text{I}-\text{N}) &= 0.070 \text{ \AA} \end{aligned}$$

The structure of this compound is closely related to the structures of the 1:1 complexes between weak organic bases and halogen^{1,2}. The nitrogen-halogen-halogen group is linear. The short N—I distance indicates a strong interaction between donor and acceptor atoms. At the same time the I—I bond is weakened, the bond being about 0.2 Å longer than in the "free" I₂ molecule. The values of the N—I bond lengths observed in the 1:1 compounds pyridine-iodomonochloride and trimethylamine-iodomonochloride are 2.26 Å² and 2.30 Å¹⁰, respectively. A reinvestigation of the compound pyridine-iodomonochloride gave 2.30 Å for the N—I bond length¹⁰.

The value of the dissociation constant of the amine or the nature of the second halogen atom appears to be of minor importance in determining the nitrogen-iodine bond length. The iodine atom directly linked to nitrogen is believed to possess in its valence shell five electron pairs in $sp^3d_{z^2}$ hybrid orbitals, whereas the second iodine atom retains its octet of electrons in its valence shell. The atomic arrangement to be expected is then a linear grouping of nitrogen-halogen-halogen. A more comprehensive discussion of these problems is given by Hassel^{9,10}.

Finally it should be stressed that the results of this investigation appear to contradict the assumption first expressed by Hantzsch that the addition compounds between trimethylamine or other tertiary amines and halogens^{3,4} should be interpreted as salts of a halogen substituted ammonium cation.

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