

Structure of the Solid 2:1 Adduct Bromoform – Hexamethylenetetramine

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X-Ray analysis of a crystalline 2:1 adduct, isolated from mixtures of bromoform and hexamethylenetetramine, shows that both $\text{Br}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{N}$ bonds are present in the crystal, and result in the formation of two-dimensional layers extending parallel to the (010) plane of the orthorhombic crystals. All C-H groups in bromoform are linked to nitrogen atoms in neighbouring molecules, but only one third of the bromine atoms are nitrogen-bonded. The four hexamethylenetetramine molecules of the unit cell are crystallographically equivalent, the eight bromoform molecules, however, are in *two* four-fold positions.

Details of the X-ray analysis of the solid 1:1 adduct formed by hexamethylenetetramine and iodoform, have already been reported.¹ Some remarks were included about the possibility of drawing conclusions regarding the relative strengths of halogen \cdots nitrogen and C-H \cdots N bonds in adducts formed by hexamethylenetetramine and trihalogenomethanes from the number of such bonds actually present in solid compounds containing the donor and acceptor partners in varying proportions. Preliminary results of the X-ray structure analysis of a 2:1 compound formed by bromoform and hexamethylenetetramine were also reported.

The compound in question was obtained in the form of thin, orthorhombic plates by slowly evaporating the excess bromoform from a liquid mixture of the two components. The crystals are instable when exposed to the air, and the X-ray investigation was carried out on specimen sealed in capillary tubes, in general at a temperature of about -35°C . Weissenberg diagrams from which accurate lattice parameters were evaluated using potassium chloride as a calibrating substance, were taken at room temperature. The lattice parameters of the orthorhombic unit cell thus obtained were: $a = 10.130(011)$ Å, $b = 26.162(0.015)$ Å, $c = 6.873(003)$ Å. Extinction criteria led to the conclusion that the space group is either $A2,am$ or $Ama2$. The former appeared less probable, however, than the latter from the Patterson projection along [001], which also indicated that the acceptor to donor ratio of the

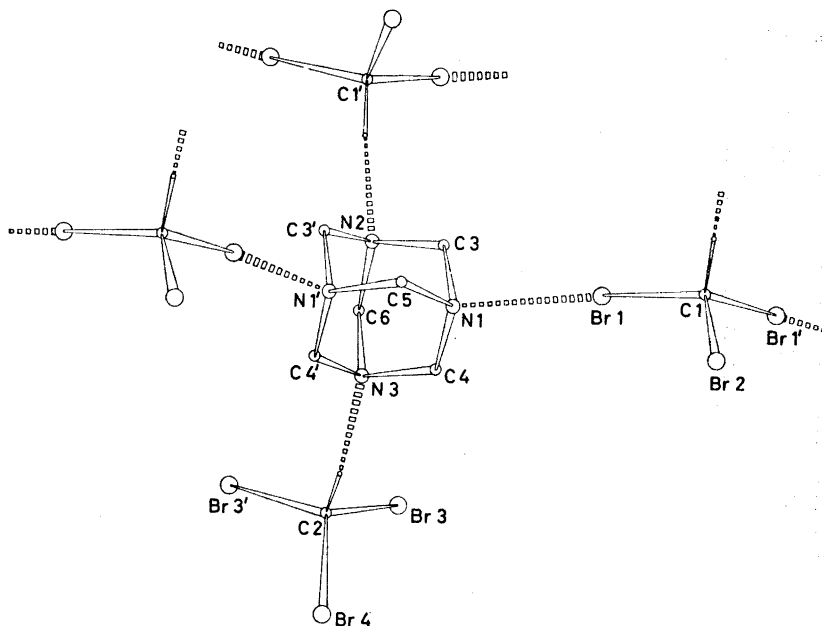


Fig. 1. Schematic presentation of the 2:1 compound of bromoform and hexamethylenetetramine, indicating the tetrahedral environment of hexamethylenetetramine.

compounds is 2:1. The space group $Ama2$ also appeared the most acceptable from considerations regarding the packing of the molecules in the unit cell, particularly if they are all situated in mirror planes. In this case, the bromoform molecules cannot be crystallographically equivalent but occupy two four-fold positions in the unit cell.

Preliminary x - and y -coordinates for the bromine atoms could be derived from the Patterson projection along $[001]$, and under the assumptions mentioned above, it became possible to work out a preliminary trial structure taking advantage of empirical facts previously established, regarding charge-transfer bonding between bromine and nitrogen. From the trial structure indications even of $C-H \cdots N$ bonding between neighbouring molecules were found. Three-dimensional intensity data were collected from Weissenberg diagrams, chiefly with rotations about $[001]$. $CuK\alpha$ -radiation was employed and the intensities were measured photometrically, except for the weakest reflexions which were estimated visually. Some data were also collected from Weissenberg diagrams with rotation about $[100]$ in order to determine inter-layer scale factors. The available crystals were minute and extremely thin plates (parallel to (010)), and the number of available reflexions, therefore, was rather limited. Intensity corrections for absorption were applied.^{2*}

* All programs used are included in Ref. 2.

four cycles, in order to obtain the best possible constancy of the mean value of $W^2(|F_o| - |F_c|)^2$ in the different intensity intervals. In the first four cycles, positions and thermal parameters of the bromine, carbon, and nitrogen atoms were varied. For the bromine atoms, anisotropic thermal parameters were employed, but for carbon and nitrogen we used isotropic parameters. The hydrogen atoms were not included in the structure factor computations, and only the 233 observed reflexions were included in this part of the refinement procedure. On the basis of the atomic positions obtained, hydrogen atomic coordinates were computed assuming a C-H distance of 1.05 Å. These coordinates were kept constant and included in the structure factor computa-

Table 2. Atomic coordinates and isotropic thermal parameters. Estimated standard deviations in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Br1	.40683 (.00058)	.06900 (.00019)	.3816 (.0020)	
Br2	.25	.10435 (.00040)	.0	
Br3	.59123 (.00089)	.22859 (.00037)	.3015 (.0024)	
Br4	.75	.30852 (.00037)	.0439 (.0026)	
N1	.6354 (.0045)	0.881 (.0015)	.664 (.007)	4.7 (1.0)
N2	.75	.0456 (.0028)	.942 (.014)	6.8 (2.0)
N3	.75	.1432 (.0022)	.897 (.013)	5.2 (1.6)
C1	.25	.0607 (.0033)	.230 (.019)	7.0 (2.4)
C2	.75	.2418 (.0028)	.148 (.015)	4.2 (2.0)
C3	.6397 (.0063)	.0489 (.0022)	.818 (.011)	6.4 (1.5)
C4	.6374 (.0054)	.1334 (.0017)	.774 (.009)	4.4 (1.2)
C5	.75	.0766 (.0036)	.555 (.017)	7.3 (2.7)
C6	.75	.0988 (.0029)	.013 (.016)	4.6 (1.9)

Anisotropic thermal parameters according to the expression: $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Estimated standard deviations in parentheses.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br1	.0103 (.0006)	.00209 (.00009)	.0256 (.0015)	.0018 (.0005)	-.0134 (.0037)	.0027 (.0011)
Br2	.0144 (.0014)	.00328 (.00021)	.0262 (.0027)	0	0	.0062 (.0014)
Br3	.0209 (.0013)	.00543 (.00025)	.0595 (.0039)	.0088 (.0011)	.0385 (.0052)	.0195 (.0017)
Br4	.0359 (.0025)	.00204 (.00017)	.0510 (.0049)	0	0	.0062 (.0018)

tion in the four last cycles of the refinement process, using a B value of 6.0 Å². In this last part of the refinement even 37 non-observed reflexions with low θ -values were included. The *R*-factor thus arrived at was 8.1 % if all reflexions were included, 7.2 % if observed reflexions only were considered.

In Table 2 atomic coordinates and thermal parameters resulting from the least squares refinement have been listed, in Table 3 interatomic distances and angles, both "uncorrected" values directly obtained from the least squares refinement and "corrected" values (see below).

Table 3. Uncorrected and corrected interatomic distances (Å) and angles (°) (see Fig. 1). Estimated standard deviations in parentheses.

	"Uncorrected" values	"Corrected" values
C1 - Br1	1.91 (.07)	1.930
C1 - Br2	1.95 (.11)	1.930
C2 - Br3	1.95 (.06)	1.930
C2 - Br4	1.89 (.08)	1.930
Br1 - Br2	3.203 (.012)	
Br1 - Br1'	3.177 (.012)	
Br3 - Br4	3.177 (.014)	
Br3 - Br3'	3.217 (.018)	
Br1 - N1	3.06 (.05)	3.00
C1' - N2	3.41 (.12)	3.43
C2 - N3	3.10 (.10)	3.13
N1 - C3	1.47 (.08)	1.476
N1 - C4	1.41 (.06)	1.476
N1 - C5	1.42 (.07)	1.476
N2 - C3	1.41 (.07)	1.476
N2 - C6	1.48 (.10)	1.476
N3 - C4	1.44 (.07)	1.476
N3 - C6	1.41 (.10)	1.476
∠Br1 - C1 - Br2	112.0 (3.2)	112.1
∠Br1 - C1 - Br1'	112.5 (6.3)	110.7
∠Br3 - C2 - Br4	111.6 (2.5)	110.8
∠Br3 - C2 - Br3'	110.9 (4.8)	113.0
∠C1 - Br1 - N1	172.7 (3.2)	175.3
∠C3 - N1 - C4	101.6 (4.6)	107.2
∠C3 - N1 - C5	102.1 (5.3)	107.2
∠C4 - N1 - C5	116.8 (5.6)	107.2
∠C3 - N2 - C6	98.3 (5.6)	107.2
∠C3 - N2 - C3'	105.2 (7.0)	107.2
∠C4 - N3 - C6	100.6 (4.2)	107.2
∠C4 - N3 - C4'	104.7 (7.2)	107.2
∠N1 - C3 - N2	120.0 (5.8)	113.6
∠N1 - C4 - N3	118.4 (5.1)	113.6
∠N1 - C5 - N1'	110.2 (8.0)	113.6
∠N2 - C6 - N3	125.9 (8.8)	113.6

Positions of the lighter atoms (C,N) are not accurately determined, and more accurate values of interatomic distances and angles were worked out under the assumption that the C-Br bond distance³ is 1.930 Å, and the

structure of the hexamethylenetetramine molecule is that derived by Becka and Cruickshank from X-ray analysis of the solid compound.⁴ The "centre" of this molecule was located using atomic coordinates in the least squares refinement. Interatomic distances and angles thus obtained are the "corrected" values listed in Table 3. In Table 4, the chief axes of the vibration ellipsoids

Table 4. Principal axes of the thermal vibration ellipsoids.

	R.M.S. amplitudes Å	B-values Å ²	Direction cosines relative to the <i>a</i> -, <i>b</i> - and <i>c</i> -axis		
			cos <i>a</i>	cos <i>b</i>	cos <i>c</i>
Br1	0.286	6.46	-0.513	0.340	0.788
	0.280	6.20	0.489	0.872	-0.058
	0.164	2.13	0.707	-0.355	0.613
Br2	0.355	9.96	0	0.915	0.406
	0.274	5.93	1	0	0
	0.224	3.97	0	-0.406	0.915
Br3	0.546	23.56	0.425	0.696	0.580
	0.294	6.81	0.562	-0.704	0.432
	0.233	4.29	0.710	0.143	-0.691
Br4	0.432	14.72	1	0	0
	0.367	10.63	0	0.405	0.915
	0.241	4.59	0	-0.915	0.405

of the bromine atoms, directly obtained from thermal parameters, are given. In the bromoform molecule, which is attached to neighbouring donor molecules only by a single C—H···N bond, some of the axes appear abnormally long, a fact which may be caused even by other factors than vibrational movement. Satisfactory corrections of atomic positions considering libration movement did not appear feasible.

The Br···Br distances found in the bromoform molecules do not deviate significantly from that found in microwave spectroscopic investigations³ (3.177 Å). One of the observed C—H···N distances (3.13 Å) (*cf.* Table 3) is so short that there can be no doubt about the presence of a hydrogen bonding, the other (3.43 Å) is larger than might have been expected, but still somewhat shorter than calculated assuming van der Waals contacts. The direction of the line drawn between the bromoform C-atom (using the corrected coordinates) and the "centre" of the adjacent hexamethylenetetramine molecule forms an angle of 72.5° with the plane of the three bromine atoms of the bromoform molecule in question. The corresponding angle in the case of the bromoform molecule exhibiting a shorter C—H···N distance is 72.6°. This appears to substantiate the suggestion that hydrogen bonding is present in both cases, and that, therefore, a two-dimensional network parallel to the (010) plane is established, depending on N···Br and N···H—C bonds. This is actually the face chiefly developed on the thin crystals used in this investigation.

The N...Br distance (3.00 Å) conforms very well with distances previously found in similar charge-transfer adducts. The fact that only *two* of the six bromine atoms of the formula unit are linked to nitrogen, but both C-H groups, substantiates the expected strengthening of the hydrogen bonding and the weakening of the halogen-nitrogen bond resulting from a replacement of iodoform by bromoform.¹

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