## 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 fourfold positions.

Details of the X-ray analysis of the solid 1:1 adduct formed by hexamethylenetetramine and iodoform, have already been reported. Some remarks were included about the possibility of drawing conclusions regarding the relative strengths of halogen...nitrogen and C-H...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  $-35^{\circ}$ 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  $A2_1am$  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

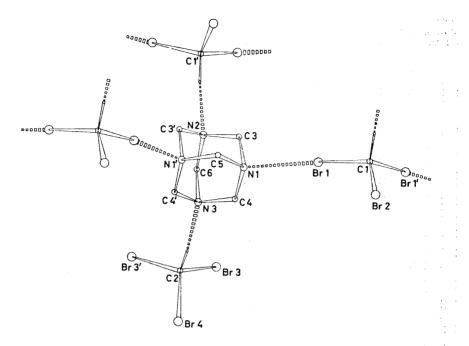


Fig. 1. Schematical presentation of the 2:1 compound of bromoform and hexamethylenetetramine, indicating the tetrahedral environment of hexamethylentetramine.

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 interlayer 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.<sup>2\*</sup>

<sup>\*</sup> All programs used are included in Ref. 2.

Table 1. Observed and calculated structure factors, ten times the absolute values. The columns listed are  $h,\,k,\,l,\,F_{\rm o}$ , and  $F_{\rm c}$ . Unobserved reflexions are marked with asterisks, and their  $F_{\rm o}$ -values are  $\frac{1}{2}F_{\rm min}$  for the hk0-reflexions;  $F_{\rm min}/\sqrt{2}$  for the other reflexions.

0	0	2	2816	2817	0	23	5	346	320	2	8	2	624	743	5		2	724	868
0	0	4	871	846	0	24	0	682 348	588 246	2	9	3	1145	1054	5		0	378 369	431
0	0	6	625	587	0	29	3	338	293	5	10	0	1100	1197	5		2	720	396 779
0	ì	1	969 1665	1024	0	31	ĭ	252	1/2	2	13	ĩ	785	713	5		6	519	623
0	1	5	1049	1163	i	J.	ī	740	829	ž	14	ō	1353	1409	5		ō	571	667
ŭ	i	7.	424	398	i	i	ŝ	220	2/4	ž	iė	ō	418	332	ě		ŏ	3233	3187
ŏ	ż	ż	1361	1376	ī	ī	5	691	654	ž	20	0	8.15	772	6	0	2	1476	1374
ŏ	2	Ã	1431	1428	ī	ž	ō	1298	1187	3	1	1	608	757	6	i	1	1012	1039
ŏ	Ž	6	415	459	1	2	2	1816	18/3	3	1	3	1468	1442	6		3	1189	946
ŏ	3	1	258	2+3	1	2	6	344	418	3	2	0	533	497	6	2	0	392	87
ò	3	3	.988	1033	1	3	1	3561	32u7	3	2	2	1729	1598	6		2	944	829
e	4	-2	1953	1905	1		3	1801	1952	3	2	4	1614 4839	1646 4152	6		2	996	1016
9	•	4	654	735	1	3	5	657	714	3	3	1	978	991	6		3	920	922
0	4	6	306	257	1	*	2	558 20/1	652 2007	3	4	0	3141	3155	6		2	1713 1091	1733
0	5	1	1372	1458 2358	1	7	4	564	5/0	3	7	2	1842	1634	6	7	í	1551	1108 1632
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8	6	Ü	4540	4429	i	5	3	801	8 4 3	3	5	i	898	756	6		ĭ	1023	991
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ŏ	ě	4	723	787	ī	6	6	447	439	3	6	2	1238	11.5	7	2	Ó	929	897
	7	7	3591	3798	ī	7	i		2336	3		4	8/0	705	7	3	1	1200	1156
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ŏ	7	5	520	500	1		.5		571	3		3	1443	1579	7	4	0	1043	997
ŏ	7	7	500	419	1		U		544	3		0	1232	1301	7	4	2	794	964
ō	8	0	1557	1926	ì		2		1434	3		4	973	950	7	10	0	724	904
	8	2	900	976	1		4		413	3		1	1516	1416	8	0	0	785	756
0	6	4	901	955	1	9	1		935	3		3	1296	1439	9	-2	,	446	324
	8	6	681	726	1	9	5		679	3		2	2149	1845	9	. 4	0	636	731
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0	9	5	720	6/8	1		ì		804	3		ž	1577	14/2	ŭ	4	0	39	230 W
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9	10	0	2112	2225	i		ā		1542	3		ž	845	900	ŏ	11	3	223	158 *
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ă	11	ĭ	1108	1145	î		4		1939	3	18	0	562	660	ŏ	ië	ō	1/2	108 *
8	ii	- 5	544	533	ī		1		1107	3		ō	574	605	ŏ	18	4	3,8	207 .
ŏ	iż	ő	392	415	ī		3	653	:517	3	24	0		323	Ó	19	3	264	105 *
ŏ	iż	ž	475	517	1				1109	4		0		842	0	50	0	177	193 •
ō	12	- 4	949	1022	1	. 14			432	4		2		2841	0	22	0	184	233 *
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0	13	3	1157	1107	1				419 532			3		1133	1	6	Ü	218	4:5
0	14	0	744	815	ļ				1003			õ		211	1	6	ž	162	511 +
0	14	2	1551	1563	1				427	7		ŭ		1159	i	Š	3	190	101 *
0	14	6	7u2	720 478					582	7		ž		817	i	ni	5	258	210 4
0	14	ı	1475	1471					430	- 2		ī		1747	i	i.	ž	249	515 *
0	15	3	632	806					473		5	3		869	î	15	1	213	250 *
0	15	5	507	462	i			441	306	4				1454	i	17	3	241	203 *
ě	15	7	350	404	1	26		364	3/0					1251	1	18	2	251	190 *
ŏ	16	Ö	922	931	2			2414	1934					1055	1	19	1	234	190 *
ŏ	16	2	719	667	7			3002	3015	4				1355	1	21	ļ	238	122 *
0	16	4	7/1	799	3			1007	1003	4	7			1094 320	5	2 8	0	73	119 +
0	16	6	592	498	9			1 1874	1691					731	2		0	116	104 *
0	17	1	903	848		2 1		2 944	815		. 9			845	5	12 16	0	156 172	311 *
0-	17	3	512	570		2 3		707	745					1551	3	16	0	107	1/0 *
. 0	18	2	509	486				1348	1533		10			914	3	18	0	148	155 *
0	19	1	948	965		2 4		414	403		12			601	5	14	ŏ	187	185 *
0	20	2	670 688	619				696	800		13			946	5	16	ō	205	76 *
0	51	3	616	545		5		2218	2144		i 14		10/3	1190	6		ō	150	56 ●
ŏ	22	ž	546	518		2 5	. :	1216	Stof		16	0		358	6	10	o	175	92 *
ŏ	22	4	521	3/0	- 1	26		559	511			0		636	6	12	0	191	351 *
	23	i	569	625				967	904					1222	7	6	9	169	113 *
ŏ	23	3	420	314		2 6		808	798					7/6	7	. 8	0	174	214 *
•		_						1 1039	1155		3			743	7	12	0	202	88 *
						2 7		3 880	755		5 4	0	743	752	8	2	0	179	154.*

The essential correctness of the proposed trial structure was confirmed by evaluation of structure factors for the (0kl) reflexions. More accurate z coordinates for the bromine atoms were obtained from a two-dimensional Fourier synthesis along [100] and combined with the previously determined x- and y-coordinates of the bromine atoms. In a three-dimensional Fourier synthesis, worked out on the basis of the bromine parameters, maxima corresponding to the N and C atoms, situated approximately in positions anticipated by the trial structure, were actually present. Atomic coordinates derived from the three-dimensional Fourier synthesis were used, when starting the least squares refinements. In these calculations, the weight factor (W) was kept constant for structure factors  $F_o \leq FB$ ; for  $F_o > FB$ , W was put equal to  $A(F_o)^B$ , with B = -0.8 in the first four cycles, and -1.0 in the last

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.

	$oldsymbol{x}$	$oldsymbol{y}$	z	$\boldsymbol{B}$
Br1	.40683	.06900	.3816	
	(.00058)	(.00019)	(.0020)	
${ m Br}2$	.25	$.10435^{^{\prime}}$	.0	
		(.00040)		
$\mathbf{Br3}$	.59123	`.22859 <sup>'</sup>	.3015	
	(.00089)	(.00037)	(.0024)	
$\mathbf{Br4}$	`.75	`.30852 <sup>´</sup>	`.0 <b>439</b> ´	
		(.00037)	(.0026)	
N1	.6354	0.881	.664	4.7
	(.0045)	(.0015)	(.007)	(1.0)
N2	.75	.0456	.942	6.8
		(.0028)	(.014)	(2.0)
N3	.75	.1432	.897	5.2
		(.0022)	(.013)	(1.6)
C1	.25	.0607	.230	7.0
		(.0033)	(.019)	(2.4)
C2	.75	.2418	.148	4.2
		(.0028)	(.015)	(2.0)
C3	.6397	.0489	.818	6.4
	(.0063)	(.0022)	(.011)	(1.5)
C4	.6374	.1334	.774	4.4
	(.0054)	(.0017)	(.009)	(1.2)
C5	.75	.0766	.555	7.3
		(.0036)	(.017)	(2.7)
C6	.75	.0988	.013	4.6
		(.0029)	(.016)	(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.

	$B_{11}$	$B_{22}$	$B_{33}$	$\boldsymbol{B_{12}}$	$B_{13}$	$B_{23}$
$\mathbf{Brl}$	.0103	.00209	.0256	.0018	0134	.0027
	(.0006)	(.00009)	(.0015)	(.0005)	(.0037)	(.0011)
$\mathbf{Br2}$	`.0144	`.00328	`.0262 <sup>'</sup>	`0 ′	` 0 ´	.0062
	(.0014)	(.00021)	(.0027)			(.0014)
$\mathbf{Br3}$	.0209	.00543	.0595	.0088	.0385	`.0195
	(.0013)	(.00025)	(.0039)	(.0011)	(.0052)	(.0017)
$\mathbf{Br4}$	$\hat{\ }.0359^{'}$	.00204	`.0510	`0 ′ ′	`0 '	`.0062
	(.0025)	(.00017)	(.0049)			(.0018)

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tion in the four last cycles of the refinement process, using a B value of 6.0 Å<sup>2</sup>. In this last part of the refinement even 37 non-observed reflexions with low  $\theta$ -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.

<u></u>	"Uncorrected" values	"Corrected" values
Cl-Brl	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)	
Brl-Brl'	3.177 (.012)	
Br3-Br4	3.177 (.014)	
$\mathbf{Br3} - \mathbf{Br3}'$	3.217 (.018)	
Brl-Nl	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
$\angle \mathbf{Br1} - \mathbf{C1} - \mathbf{Br2}$	112.0  (3.2)	112.1
$\overline{\angle}$ Brl – Cl – Brl'	112.5  (6.3)	110.7
$\angle \operatorname{Br3} - \operatorname{C2} - \operatorname{Br4}$	111.6  (2.5)	110.8
$\angle \operatorname{Br3} - \operatorname{C2} - \operatorname{Br3}'$	110.9  (4.8)	113.0
$\angle Cl - Brl - Nl$	172.7  (3.2)	175.3
$\angle C3 - N1 - C4$	101.6  (4.6)	107.2
$\angle C3 - N1 - C5$	102.1  (5.3)	107.2
$\angle C4-N1-C5$	116.8  (5.6)	107.2
$\angle C3-N2-C6$	98.3 (5.6)	107.2
$\angle C3 - N2 - C3'$	105.2  (7.0)	107.2
$\angle C4-N3-C6$	100.6 (4.2)	107.2
$\overline{\angle}$ C4 - N3 - C4'	104.7  (7.2)	107.2
$\overline{\angle}$ N1 – C3 – N2	120.0  (5.8)	113.6
$\overline{\angle}$ N1 – C4 – N3	118.4  (5.1)	113.6
$\angle N1 - C5 - N1'$	110.2  (8.0)	113.6
$\sqrt{N2-C6-N3}$	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 distance 3 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.<sup>4</sup> 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

	R.M.S. amplitudes Å	$egin{aligned} B ext{-values} \ \mathring{\mathbf{A}}^2 \end{aligned}$	Direction cosines relative to the $a$ -, $b$ - and $c$ -axis				
			cos a	$\cos b$	cos c		
Brl	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		

Table 4. Principal axes of the thermal vibration ellipsoids.

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  $C-H\cdots N$  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  $\text{Br}\cdots\text{Br}$  distances found in the bromoform molecules do not deviate significantly from that found in microwave spectroscopic investigations <sup>3</sup> (3.177 Å). One of the observed  $C-H\cdots N$  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  $C-H\cdots N$  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  $N\cdots Br$  and  $N\cdots H-C$  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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