

Solid Adducts of Hexamethylenetetramine and Trihalogenomethanes. Crystal Structure of the 1:1 Iodoform Compound

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Structures of solid addition compounds formed by trihalogenomethanes and hexamethylenetetramine and containing both $N\cdots Hal$ and $N\cdots H-C$ bonds are discussed. Details of the structure determination of the 1:1 iodoform-hexamethylenetetramine adduct are reported.

During recent years a considerable number of crystal structures have been investigated in which donor atoms (D) are directly linked to acceptor atoms, usually halogen atoms, by intermolecular charge-transfer bonds. An interesting example of a solid adduct in which a donor atom (oxygen) is linked to atoms belonging to neighbouring entities both by charge-transfer bonds and by ordinary hydrogen bonds is provided by the 2:1 addition compound formed by methanol and bromine.¹ The first example of a structure in which an "activated" hydrogen atom linked to carbon is forming a bond to a donor atom was found in the adduct of diethylether and bromodichloromethane,² but analogous bonding to amino nitrogen atoms in trihalogenomethane-amine complexes present in solutions have been indicated by spectroscopic observations.³ A direct structural investigation of a solid amine-trihalogenomethane adduct by X-ray crystallographic methods appeared worth while in order to establish the atomic arrangement present in the expected $C-H\cdots N$ bonding. Using a trihalogenomethane partner containing heavy halogen atoms and hexamethylenetetramine as the donor molecule it even appeared possible that solid adducts might be obtained exhibiting both the type of "hydrogen bonding" under consideration and nitrogen-halogen charge-transfer bonds.

The first of the adducts to be examined was the 1:1 addition compound formed by hexamethylenetetramine and iodoform.⁴ Details of the three-dimensional X-ray analysis are given below. The finding that in these crystals certain nitrogen atoms in the donor molecules are linked to iodine atoms, others to $C-H$ -hydrogen atoms belonging to neighbouring iodoform molecules, made it desirable to investigate structures also of adducts of bromoform with varying

proportion of donor and acceptor molecules. With an acceptor to donor ratio greater than 1:1, the relative number of the two kinds of intermolecular bonds might give some indications regarding their relative strengths. Replacing iodoform by bromoform, it must be expected that the halogen-nitrogen bonds are weakened, the $N\cdots H-C$ bonds, however, markedly strengthened. We have succeeded in preparing crystals of a 2:1 adduct formed by bromoform and hexamethylenetetramine showing sufficiently good quality to permit single crystal X-ray work to be carried out. The analysis shows that in these crystals all bromoform hydrogen atoms are linked to nitrogen atoms by $C-H\cdots N$ bonds, but that only one third of the bromine atoms form charge-transfer bonds to nitrogen atoms.

EXPERIMENTAL

If the solvent — methylene chloride — is evaporated at room temperature from a solution containing equimolecular amounts of iodoform and hexamethylenetetramine, orthorhombic crystals of the 1:1 adduct may be obtained which are suitable for X-ray analysis. The unit cell dimensions, determined from Guinier diagrams and choosing potassium chloride as a calibrating substance, are:

$$a = 10.681 \pm 0.001 \text{ \AA}, \quad b = 9.296 \pm 0.001 \text{ \AA}, \quad c = 13.988 \pm 0.002 \text{ \AA}$$

Extinctions criteria led to one of the space groups $Cmc2_1$, or $Ama2$. A Patterson synthesis along [010] showed that the first of these groups is the correct one. The number of both donor and acceptor molecules in the unit cell is *four* and the space group $Cmc2_1$ therefore requires both kinds of molecules to be situated in mirror planes running parallel to (100). This fact made it appear tempting to work out a preliminary trial structure based on iodine coordinates derived from Patterson projections along [100] and [010], supposing that the $I\cdots N$ bond distance is about 3 Å and the $C-I\cdots N$ arrangement nearly linear. The structures of the two molecular components are known with considerable accuracy and the trial structure to which we were led actually indicated the presence of $N\cdots H-C$ bonds in addition to the type of intermolecular iodine-nitrogen bonding which had been anticipated.

The three-dimensional intensity data on which the final structure determination was based were collected from a set of integrated Weissenberg diagrams with rotation about [010] taken with MoK radiation and from integrated Weissenberg diagrams with rotation about [100]. The latter simultaneously registered the zero and first layer, resp. the second and third layer and were taken in order to normalize the intensity values obtained from the diagrams with rotation about [010]. This was found necessary because reflexions with $h+k=2n+1$ are absent. Intensities were measured photometrically except the weakest which had to be estimated visually. Absorption corrections turned out to be essential and were performed according to the procedure described by Busing and Levy.⁵

A three-dimensional Fourier synthesis based on phases, derived from the preliminary iodine coordinates alone, confirmed the essential correctness of the trial structure in a most convincing way. Thus, all C and N atoms were clearly indicated. Least squares refinements were therefore started at this stage.

LEAST SQUARES REFINEMENTS

A series of least squares refinements was carried out in which weight factors (W) of observed reflexions with structure factors $F_o \leq FB$ were put equal to $A1$ and for $F_o > FB$ equal to $A2(F_o)^{B2}$. By choosing $B2 = -0.8$ it was possible to find constants $A1$, $A2$, and FB which led to a nearly constant value of $W^2(|F_o| - |F_c|)^2$ within the different intensity intervals after finishing the refinement procedure. Anisotropic thermal damping was employed in the

case of iodine, but not for the lighter atoms. In the two first cycles unobserved reflexions were left out and hydrogen atoms were not included. New interlayer scale factors were then computed, requiring that for each layer $\sum |F_o| = \sum |F_c|$. Hydrogen coordinates were computed using the coordinates of the I, C, and N atoms, assuming sp^3 hybridization at the carbon atoms and using an isotropic B value of 5.0. In the two following least squares cycles these hydrogen positions were kept unaltered and structure factors of observed reflexions only, 324 in all, included. The final R value thus arrived at was 4.55 %. The corre-

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

	x	y	z	B
I1	.16564 (.00017)	.07009 (.00025)	.16593 (.00032)	
I2	.0	-.14720 (.00042)	.0	
N1	.0	.3103 (.0043)	-.0730 (.0032)	4.3 (.8)
N2	.1121 (.0030)	.4188 (.0034)	-.2045 (.0021)	5.2 (.7)
N3	.0	.5602 (.0040)	-.0965 (.0031)	3.9 (.8)
C1	.0	.0569 (.0049)	.0802 (.0038)	4.2 (1.0)
C2	.1094 (.0033)	.2983 (.0037)	-.1345 (.0025)	4.9 (.8)
C3	.0	.4025 (.0050)	-.2664 (.0040)	4.3 (1.1)
C4	.1066 (.0034)	.5510 (.0041)	-.1512 (.0028)	5.2 (.8)
C5	.0	.4496 (.0052)	-.0255 (.0037)	4.2 (1.1)

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}
I1	.00789 (.00018)	.01737 (.00034)	.00678 (.00014)	-.00294 (.00046)	-.00170 (.00049)	-.00361 (.00052)
I2	.00987 (.00034)	.01493 (.00049)	.00558 (.00022)	.0	.0	-.00350 (.00066)

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

	Uncorrected values	Corrected values
I1—I2	3.549 (.006)	3.556
I1—I3	3.539 (.005)	3.545
I1—C1	2.14 (.03)	2.140
I2—C1	2.20 (.05)	2.140
I1—N4	2.99 (.03)	2.93
I2—N5	3.04 (.04)	2.93
N1—C1	3.18 (.06)	3.22
N1—C2	1.46 (.04)	1.476
N1—C5	1.46 (.04)	1.476
N2—C2	1.49 (.04)	1.476
N2—C3	1.48 (.04)	1.476
N2—C4	1.44 (.04)	1.476
N3—C4	1.37 (.04)	1.476
N3—C5	1.43 (.04)	1.476
\angle I1—C1—I2	109.5 (1.4)	112.4
\angle I1—C1—I3	111.4 (2.4)	111.8
\angle C1—I1—N4	176.5 (1.3)	174.3
\angle C1—I2—N5	175.8 (1.5)	175.0

sponding set of atomic coordinates is listed in Table 2, the interatomic distances and angles in Table 3 (uncorrected values).

Least squares refinements were actually also carried out in which unobserved reflexions having low θ -values were included.* The results of such calculations turned out, however, to depend more than usually on the weight, W , attributed to non-observed reflexions, and led to increased values of standard deviations in the final atomic coordinates. Apparently, the method employed by putting the intensity of non-observed reflexions equal to $\frac{1}{2}I_{\min}$ is not satisfactory in the case of non-centrosymmetrical structures containing atoms differing too much in atomic numbers.

It appeared obvious from the thermal damping parameters for the I atoms that the rigid-body motion of the iodoform molecule strongly influences the interatomic distances obtained for this molecule. Due to the small number of atoms in the molecule corrections could only be performed by approximate methods and by introducing certain simplifications. Length and directions of the chief axes of the damping ellipsoids of the I atoms indicated that the libration movement takes place preferentially about an axis nearly perpendicular to the plane containing the three iodine atoms. A correction of the iodine positions could be carried out under this assumption.⁶

Due to uncertainties in the C and N positions the standard deviation of the uncorrected values listed in Table 3 are relatively large. Centres of the hexamethylenetetramine molecules computed from coordinates determined by the least squares refinements, combined with interatomic distances and

* The F_o -values used for these reflexions (Table 1) are $\frac{1}{2}F_{\min}$ for the $hk0$ -reflexions, $F_{\min}/\sqrt{2}$ for the other reflexions.

angles found by Becka and Cruickshank⁷ for the uncombined molecule actually led to identical values of the two independent $I \cdots N$ bond distances.

The position of the iodoform carbon atom was computed assuming a C—I bond distance of 2.14 Å. The interatomic distances and angles finally arrived at are listed in Table 3 (corrected values). They are believed to be more accurate than the uncorrected values. As a result of correction for rigid-body movement the C(—H) \cdots N and $I \cdots N$ distances reported in the preliminary communication⁴ have been slightly modified.

CONCLUSIONS

The crystal structure derived for the 1:1 hexamethylenetetramine—iodoform adduct (*cf.* Fig. 1) represents a type which appears most reasonable when all molecules of the same kind are crystallographically equivalent and all nitrogen atoms are linked either to iodine atoms or to CH groups. The four intermolecular bonds linking each molecule to its four neighbours are tetrahedrally

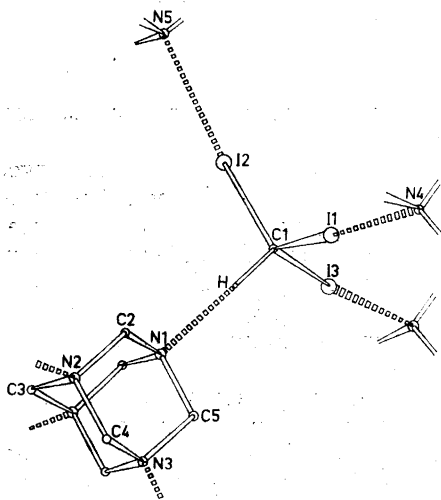


Fig. 1. Schematic presentation of the 1:1 compound of hexamethylenetetramine and iodoform indicating the tetrahedral environment of one of the partners (iodoform).

arranged in space. The $N \cdots I$ bonds, although belonging to two non-equivalent groups, have — within the limits of error — the same length, 2.93 Å. This appears to be the shortest distance so far observed between a nitrogen atom and an iodine atom attached to carbon. The $N \cdots I—C$ arrangement is very nearly linear (Table 3). The distance from the CH carbon atom to the nitrogen atom (3.22 Å) is significantly shorter than expected if regular van der Waals interaction is assumed between nitrogen and hydrogen atoms. Moreover, the direction of the line drawn between the nitrogen and the carbon atom closely coincides with those of the “trigonal axes” of the two interacting molecules.

This finding further supports the suggestion that a "hydrogen bond" is established between the carbon and the nitrogen atom in question.

Structural changes in donor and acceptor molecules caused by intermolecular bonds like those observed in the present structure appear, in general, to be small. This apparently holds even in the present case. Thus, the two intramolecular iodine distances observed in the iodoform molecule are 3.556 and 3.545 Å, the distance observed for iodoform in the gas phase, 3.535 Å.⁸

A set of computer programs written by X-ray crystallographers at the University of Oslo has been used.⁹

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