

Intermolecular N-I and N-H-C Bonds in the Solid (1:1) Adduct of Iodoform and Hexamethylenetetramine

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Solid adducts formed by n donor molecules with acceptor molecules containing either halogen or "active" hydrogen atoms may exhibit a striking structural relationship.^{1,2} Most conspicuously, perhaps, is the analogous behaviour of the two kinds of acceptor groups illustrated by adducts in which a particular oxygen atom is bonded to other oxygen atoms partly by hydrogen bonds, partly by halogen molecule bridges.³

A new addition compound containing iodoform and hexamethylenetetramine in the proportion 1:1 has been obtained in the form of single crystals and its crystal structure determined using three-dimensional X-ray methods. The purpose was to establish if, in this adduct, bonds between nitrogen and CH groups is present beside the obvious N-I bonds. The unit cell of this compound belonging to the space group $Cmc2_1$ contains $Z=4$ molecules of either kind and has the parameters:

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

These facts require that all the molecules are situated in mirror planes parallel to (100). When iodine coordinates had been determined from Patterson charts simple considerations made it possible to derive a preliminary crystal structure based on the assumption that the N-I bonds are about 3 \AA long and the C-I-N arrangements nearly linear. Starting with a particular iodine atom situated in a symmetry plane, the position of the nitrogen atom to which it is bonded (and lying in the same mirror plane) is approximately fixed. This also holds for a second nitrogen atom of the donor molecule in question, situated in the same mirror plane. This second nitrogen atom cannot, obviously, be bonded to a iodine atom of a neighbouring acceptor molecule. A rather short distance to a CH group belonging to such an acceptor molecule would, however, result.

Using the structure factor phases derived from the iodine coordinates a three-dimensional Fourier synthesis was computed in which even electron density maxima for the light atoms and situated in the expected regions of space turned up. Least squares refinements eventually led to atomic coordinates corresponding to an R value of 0.045.

The C(-H)-N distance thus obtained was $3.18 \pm 0.06 \text{ \AA}$ and the two non-equivalent N-I bond distances, respectively, 3.04 ± 0.05 and $2.99 \pm 0.03 \text{ \AA}$. Relatively large uncertainties in the light atom coordinates made it natural to take advantage of an available accurate determination of the hexamethylenetetramine structure⁴ and of previous determinations of aliphatic C-I distances according to which the distance in iodoform cannot deviate appreciably from 2.14 \AA. The structure thus deduced is probably more accurate than that directly obtained and leads to a C(-H)-N distance of 3.21 \AA and two equal N-I distances of $2.94 \pm 0.01 \text{ \AA}$. It may therefore safely be concluded that each hexamethylenetetramine molecule besides forming three nitrogen-iodine bonds is also linked to a fourth iodoform molecule by a bond of the N-(H-)C type. The tetrahedral environment of the iodoform molecules is outlined in Fig. 1.

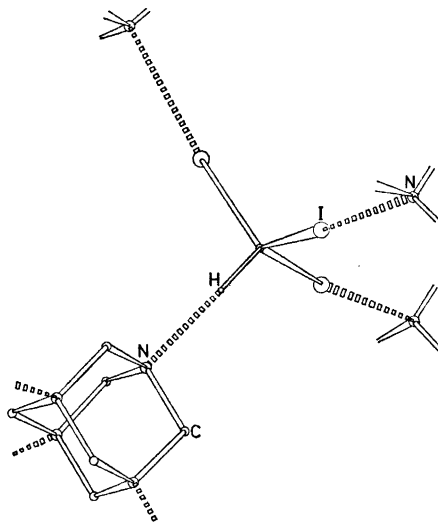


Fig. 1. The tetrahedral environment of the iodoform molecules.

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Received June 22, 1968.

On the Isolation of Trimethylphosphine as a Silver Iodide Complex

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According to Mann and Wells,¹ trimethylphosphine is most conveniently isolated as its silver iodide complex. No analysis or yield was given in their paper,

but the white complex obtained was assumed to be $[(AgIME_3P)_4]$ by analogy with the known complexes with higher aliphatic tertiary phosphines.² In a recent paper, however, Evans, Goggin, Goodfellow and Smith³ reported that they were not able to obtain any compound with a 1:1 silver iodide to trimethylphosphine ratio using the method of Mann and Wells. The compound which they obtained showed variable composition approximating a silver iodide to trimethylphosphine ratio of 1:0.3. Their results prompt us to report here of our findings using the method of Mann and Wells for the isolation of trimethylphosphine.

The details of the synthesis of trimethylphosphine and of the silver iodide complex used in our laboratory are given in a previous paper.⁴ When the crude silver iodide complex is washed with saturated aqueous potassium iodide and then water and finally dried *in vacuo* over $CaCl_2$, the pure 1:1 complex is obtained. Analyses, melting points and yields of three independent preparations are listed in Table 1. Thus the claim of Evans *et al.*³ that "it does not seem possible to produce the stoichiometric $[AgIPMe_3]$ in this way" cannot be substantiated.

The problem concerning the value of n in $[(AgIME_3P)_n]$ rests to be solved. As

Table 1. Analyses, melting points, and yields of trimethylphosphine silver iodide.

	C	Analyses H	I	m.p., °C ^a	Yield, % ^b
Calc. for C_3H_9AgIP	11.59	2.92	40.83		
prep. I	11.52	3.00	41.00	137–140	44
prep. II	11.51	2.80	40.94	140–142	40
prep. III	11.42	2.73	41.14	133–142	30

^a In closed capillary tubes. ^b Based on PCl_3 .

Table 2. Molecular weight of trimethylphosphine silver iodide.

Weight of compound, g	Weight of benzene, g	ΔT	Molecular weight, found	Calc. for $[(AgIME_3P)_4]$
0.2424	18.62	0.051	1310	1243.6
0.2247	17.11	0.053	1260	