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The Molecular and Crystal Structure of a 1:1-Adduct of AsI_3, prepared from 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)adamantane

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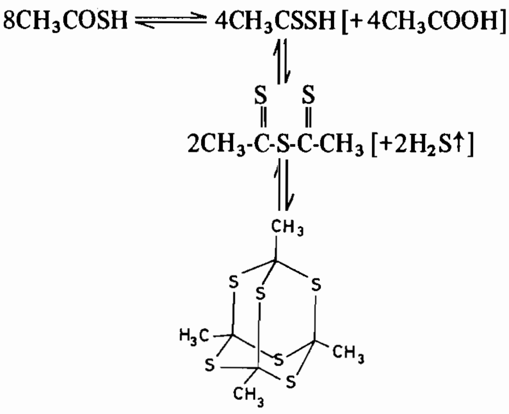
In order to prepare the ternary sulfoiodide AsSI [1] the reaction of AsI_3 with thioacetic acid [2] was tested:

$$AsI_3 + CH_3COSH + H_2O \rightarrow AsSI + CH_3COOH + HI \qquad (I)$$

A mixture of thioacetic acid and powdered AsI_3 was held at room temperature in a closed vessel for four weeks. After a period of 9 days, compact orange-red crystals were grown on top of the AsI_3-solid; in the course of five more days they were partially transformed to yellow monoclinic plates. Finally a third phase was observed, as white platey crystals. The three different phases were isolated (they can be recrystallized in ether and ethanol) and shown by energy-dispersive X-ray analysis to contain significant amounts of sulfur. Arsenic and iodine were only detected in the orange-red and yellow crystals, the latter containing smaller amounts of these elements. In accordance with this observation and AsI_3-ion peak was present only in the mass spectra of the orange-red and yellow phases. As confirmed by a complete crystal structure analysis of the orange–red crystals (see below), the compound is a 1:1-adduct of AsI_3 with 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane. This led to the positive interpretation of a respective mass-peak as belonging to the tetramethyl-hexathia-adamantane molecular ion; this peak is also present in the mass-spectra of the yellow and the white crystals. With the additional consideration of the melting point (224 °C; DTA-investigation), the white crystals were identified as pure tetramethyl-hexathia-adamantane. The yellow crystals (mp 109 °C) are assumed to be an adduct of AsI_3 with tetramethyl-hexathia-adamantane, but in contrast to the orange-red 1:1-compound with a respective molar ratio <1.

Formation of tetramethyl-hexathia-adamantane thus probably takes place as follows, and not as suggested in reaction I:



$$8CH_3COSH \rightleftharpoons 4CH_3CSSH\,[+4CH_3COOH]$$

$$2CH_3\text{-}\overset{S}{\overset{\|}{C}}\text{-}S\text{-}\overset{S}{\overset{\|}{C}}\text{-}CH_3\,[+2H_2S\uparrow]$$

(II)

Reaction II is supposed to be catalysed by HI, which is formed simultaneously by reaction of AsI_3 with water. A similar catalytic effect is observed in the presence of HBr [3].

Single crystals of AsI_3·tetramethyl-hexathia-adamantane were investigated by X-ray methods: $AsI_3 \cdot (CH_3)_4C_4S_6$; monoclinic $P2_1/c$; a = 1119.9(2), b = 1183.9(2), c = 1572.4(2) pm, β = 103.06(1)°; Z = 4; $D_{obs.}$ = 2.53, $D_{calc.}$ = 2.47 g cm^{-3}. 3583 independent reflections up to 2θ = 50° (MoKα) were collected on an automated diffractometer (Syntex $P2_1$); 2713 reflections with $I > 1.96\sigma_I$ were classified as observed. The phase problem was solved by direct methods (E-XTL). Including an empirical correction for absorption, the anisotropic refinement of the heavy-atom parameters was finished with R = 7.9%. Five of the twelve hydrogen atoms were located in a Difference-Fourier-Map; positions of the remaining seven hydrogens were calculated. The final refinement was carried out with fixed parameters of all hydrogen atoms (R = 7.8%). A list of the observed and calculated structure factors, as well as anisotropic thermal parameters of the heavy-atoms and fractional coordinates of the hydrogen positions, can be obtained from the authors. The final non-hydrogen atomic parameters are given in Table I.

Figure 1 shows the molecular structure of the adduct of AsI_3 with 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane. Bond lengths and bond angles (minimum and maximum values) are given in Table II. The arsenic atom bond to three terminal iodine atoms in a slightly distorted trigonal-pyramidal arrangement with a mean bond length of 257.6 pm; this value is in good agreement with the respective distance in the crystal structure of AsI_3 (259.1 pm, [4]). The coordination-sphere of the arsenic atom is modified to a distorted octahedron by additional contacts to three of the six sulfur atoms of the adamantane molecule. Orientation of the remaining lone-pair electrons of the arsenic atom is assumed to be towards the centre of the six-membered ring.

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TABLE I. Positional Parameters of the Non-Hydrogen Atoms in the Crystal Structure of $AsI_3 \cdot 1,3,5,7$-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane. Notation of the Atoms is in Accordance with Fig. 1.

Atom	x	y	z
As	0.5834(1)	0.2550(1)	0.9479(1)
I(1)	0.5491(1)	0.1281(2)	0.8116(1)
I(2)	0.5093(1)	0.4442(1)	0.8733(1)
I(3)	0.3925(2)	0.1970(2)	1.0032(1)
S(1)	0.8695(3)	0.3356(3)	0.9708(2)
S(2)	1.0331(4)	0.3923(3)	1.1461(3)
S(3)	0.9870(4)	0.1590(4)	1.2133(2)
S(4)	0.8229(3)	0.1030(3)	1.0376(2)
S(5)	1.0830(3)	0.1837(3)	1.0492(2)
S(6)	0.7733(3)	0.3130(3)	1.1367(2)
C(1)	0.9223(11)	0.1901(11)	0.9893(9)
C(2)	0.8750(12)	0.3870(9)	1.0813(9)
C(3)	1.0763(12)	0.2437(14)	1.1565(11)
C(4)	0.8331(12)	0.1698(11)	1.1441(8)
C(5)	0.9229(15)	0.1432(13)	0.8980(9)
C(6)	0.8290(16)	0.5117(11)	1.0727(12)
C(7)	1.2112(14)	0.2415(17)	1.2095(12)
C(8)	0.7513(15)	0.0990(15)	1.1888(11)

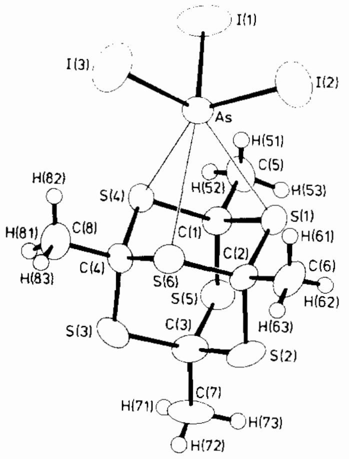

Fig. 1. Molecular structure of the 1:1-adduct of AsI_3 with 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane. Notation of the atoms is in accordance with Table I.

Figure 2 shows the arrangement of the molecular adducts in the crystal structur of $AsI_3 \cdot 1,3,5,7$-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane, as a layer-structure with alternating layers of AsI_3 molecules and adamantane molecules parallel to the (100)-plane.

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TABLE II. Bond Lengths (pm) and Bond Angles (°) in AsI_3. 1,3,5,7-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane (minimum and maximum values). E.s.d. s except for [ ] are 0.2–2.3 pm and 0.1–1.1°.

Bond Lengths	
As–I	257.5–257.7
As–S	327.4–331.0
S–C	179.1–184.7
C–C	152.5–155.9
[C–H	91–109]
Bond Angles	
I–As–I	98.4–100.3
I–As–S	89.5–111.7
	144.3–154.7
S–As–S	55.1–55.2
C–S–C	102.5–102.9
S–C–S	110.7–114.7
S–C–C	104.4–108.6
C–C–H	92–116
H–C–H	100–123

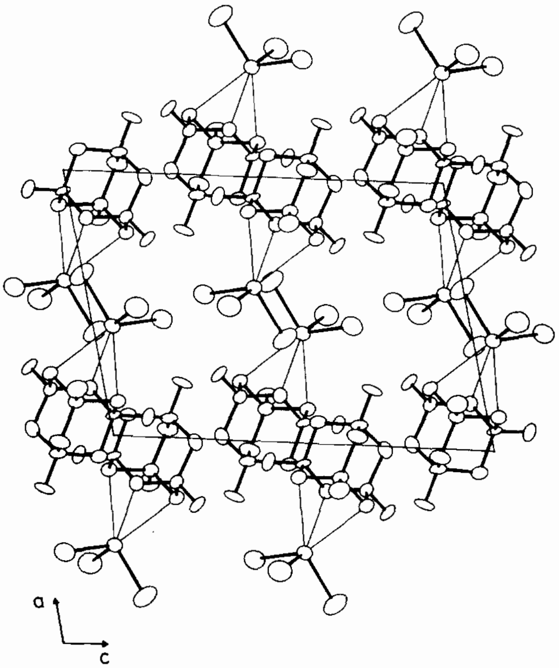

Fig. 2. Arrangement of the molecular adducts in the crystal structure of $AsI_3 \cdot 1,3,5,7$-(tetramethyl)-2,4,6,8,9,10-(hexathia)-adamantane. Projection along the crystallographic b-axis direction.

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