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MOLECULAR AND CRYSTAL STRUCTURES OF TWO ORGANOARSENIC COMPOUNDS WITH As=O BONDS: TRIPHENYLARSINOXIDE HYDRATE AND *p*-CARBOMETHOXYPHENYLARSINOXIDE

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Summary

The full X-ray structure analysis of two organoarsenic compounds with As=O bonds has been performed. I, $(C_6H_5)_3AsO \cdot H_2O$ (a redetermination, see ref. 1), monoclinic, *a* 11.155, *b* 9.461, *c* 16.621 Å, γ 113.24°, $Z = 4$, space group $P2_1/n$; II, $(CH_3OCOC_6H_4)(C_2H_5)_2AsO$, triclinic, *a* 5.973, *b* 9.179, *c* 11.818 Å, α 86.78, β 83.83, γ 97.76°, $Z = 2$, space group $P\bar{1}$. The final *R* values are 0.034 (I) and 0.042 (II). In structure I there are centrosymmetric dimers formed by intermolecular hydrogen bonds between H_2O and I (OH...O 2.795 and 2.820 Å).

Introduction

Triaryl(alkyl)arsinoxides are widely known as effective complexing agents. Therefore it is of interest to investigate the influence of substituents at the As atom on the molecular conformation and the length of the As=O bond. We have started a systematic study of free (uncomplexed) molecules of $(ar)_n(alk)_{3-n}AsO$ type, where $n = 0$—3. At the beginning we did not intend to investigate the structure of $Ph_3AsO \cdot H_2O$, which had been already determined by Ferguson and Macaulay [1], and we were trying to obtain anhydrous Ph_3AsO. However, these attempts failed and because fine single crystals of hydrate were formed, and considering the fact that the previous study [1] was performed with a photomethod of only limited accuracy, we redetermined the structure. Our results and those of Ferguson and Macaulay are in good agreement.

X-ray structure determination

The experiment was performed using a Syntex $P\bar{1}$ automatic four-circled diffractometer employing graphite-monochromatized Mo-*K* radiation, and the $\theta/2\theta$ scan method up to $2\theta_{max} = 50°$. Integral intensities were corrected for

TABLE 1

CRYSTALLOGRAPHIC DATA FOR STRUCTURES I AND II

	I	II
Empirical formula	$C_{18}H_{15}AsO \cdot H_2O$	$C_{12}H_{17}AsO_3$
a (Å)	11.155(3)	5.973(1)
b (Å)	9.461(3)	9.179(2)
c (Å)	16.621(4)	11.818(3)
α (°)	—	86.78(2)
β (°)	—	83.83(2)
γ (°)	113.24(2)	97.76(2)
V (Å^3)	1612	637
μ (cm^{-1})	22.3	28.1
F(000)	696	292
M.W.	343	284
D_c (g/cm^3)	1.40	1.48
Z	4	2
Space group	$P2_1/n$	$P\bar{1}$
No. of reflections	1549	1936
R	0.034	0.042

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND THEIR e.s.d.'s FOR I (X10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
As	2473(1)	4896(1)	3554(1)	C(8)	3871(6)	4000(6)	2347(4)
O(1)	3551(4)	4858(4)	4231(2)	C(9)	3991(6)	3274(7)	1659(4)
O(2)	4685(4)	6589(5)	5598(3)	C(10)	2902(7)	2473(7)	1186(4)
C(1)	2726(6)	6993(7)	3315(4)	C(11)	1682(7)	2415(7)	1404(4)
C(2)	3567(6)	8140(7)	3809(4)	C(12)	1542(6)	2132(7)	2096(4)
C(3)	3747(8)	9639(8)	3672(5)	C(13)	712(6)	3795(7)	3923(4)
C(4)	3051(10)	9948(9)	3054(6)	C(14)	365(7)	2315(8)	4172(5)
C(5)	2212(9)	8798(10)	2548(5)	C(15)	—84(9)	1490(8)	4447(6)
C(6)	2026(7)	7300(8)	2690(4)	C(16)	—1750(7)	2119(10)	4470(5)
C(7)	2645(6)	3931(6)	2566(4)	C(17)	—1413(7)	3603(10)	4238(5)
				C(18)	—178(6)	4466(8)	3960(5)

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND THEIR e.s.d.'s FOR II (X 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
As	4360(1)	6856(1)	3915(1)	H(6)	759(20)	933(13)	279(10)
O(1)	7006(7)	6493(5)	3803(4)	H(7)	742(20)	1140(13)	145(10)
O(2)	5637(7)	12947(5)	64(4)	H(9)	74(22)	985(14)	123(11)
O(3)	1890(7)	12223(4)	166(4)	H(10)	60(22)	784(14)	248(11)
C(1)	3403(11)	7476(7)	5394(5)	H(11)	473(22)	812(14)	566(11)
C(2)	1388(12)	8344(8)	5411(6)	H(12)	295(22)	657(14)	594(11)
C(3)	2153(11)	5235(7)	3625(6)	H(21)	—1(22)	786(14)	510(10)
C(4)	2754(14)	4575(8)	2503(6)	H(22)	245(27)	932(18)	502(14)
C(5)	4097(10)	8476(6)	2823(5)	H(23)	96(21)	861(14)	613(11)
C(6)	6122(10)	9470(7)	2480(6)	H(31)	63(23)	560(15)	361(11)
C(7)	6019(10)	10657(7)	1696(6)	H(32)	204(25)	444(16)	426(11)
C(8)	3989(10)	10813(6)	1256(5)	H(41)	437(23)	419(15)	252(11)
C(9)	2049(10)	9798(7)	1589(6)	H(42)	189(22)	365(14)	223(11)
C(10)	2112(10)	8627(7)	2386(6)	H(43)	253(21)	548(14)	202(11)
C(11)	3962(10)	12113(7)	424(5)	H(121)	257(22)	1328(14)	—129(11)
C(12)	1689(11)	13499(7)	—596(6)	H(122)	236(21)	1455(14)	—51(11)
				H(123)	—4(25)	1360(16)	—46(12)

Lorentz and polarization effects but not for absorption. All calculations were made using the programs of the NICOLET R3 complex employing a NOVA 3 computer. The general crystallographic data are given in Table 1. Both structures were solved by the heavy atom technique. The coordinates of As atoms were found from Patterson maps, subsequent Fourier syntheses revealed all non-hydrogen atoms. The coordinates of H atoms were partly calculated using geometric considerations (phenyl and methylene groups) and partly from difference syntheses (methyl groups and water molecule). The structure refinement was performed by full-matrix least squares using anisotropic (As, C, O) and isotropic (H) thermal parameters. The final *R* factor values are 0.034 (I) and 0.042 (II). The atomic positional parameters and their e.s.d.'s are given in Tables 2 and 3 *. The C—H bonds vary in the range 0.89—1.17 Å.

Discussion

Figures 1 and 2 represent the whole molecular conformation along with the atomic numbering system. Tables 4 and 5 list the interatomic distances, and Tables 6 and 7 the bond angles. As a whole, the geometric features of I and II resemble each other. The As atoms have practically tetrahedral coordination (mean angle CAsC 109.5°). The distance from As to the plane of its C neighbours is 0.691 (I) and 0.730 Å (II). The mean values of the As—C bond distances are 1.927 Å (I) and 1.930 Å (II). The parameters of the organic ligands correspond to normal values.

The molecule I, as has already been shown [1], loses its own symmetry C_{3v}, and the phenyl rings planes with plane C(1)C(7)C(13) make the angles 97.8, 59.2 and 40.6°. In molecule II the angle between the phenyl ring and the carbomethoxy group planes is 6.6°.

The packing of II in the crystal structure is shown in Figure 3. In this case all intermolecular contacts correspond to normal Van der Waals interactions. The structure of I is characterized by the presence of discrete centrosymmetric dimers, each molecule I is hydrogen bonded to two water molecules and vice versa. The schematic view of this dimer is shown in Figure 4. The main geometric parameters of H bonds: O(1)...O(2) 2.795(6) Å, O(2)—H 1.01 Å, O(1)...H 1.78 Å, angle O(1)HO(2) 177°; O(1)...O(2′) 2.820 Å, O(2′)—H 0.70 Å, O(1)...H 2.18 Å, angle O(1)HO(2′) 154°.

Table 8 compares the molecules investigated in this study with previously determined derivatives of triphenylarsinoxide, where intermolecular H bonds are present. As it can be seen from this Table, in all cases the angles CAsC and CAsO are very similar, but the distances As=O vary in the range 1.64—1.69 Å. The comparison of these values with the H bond parameters reveals that increasing H bond force causes lengthening of the As=O bond. It is also clear from Table 8 that replacing the aryl radicals by alkyl ones causes a more significant distortion of the C_3AsO tetrahedron: the angles CAsC decrease, and CAsO increase.

It was found that, within the limits of experimental error, the bond distances As=O are identical in I and II.

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* List of F_0 and F_c, tables of anisotropic thermal parameters for As, C and O atoms, a table of positional and thermal parameters of H atoms in I, and tables of least squares planes may be received upon request from the author.

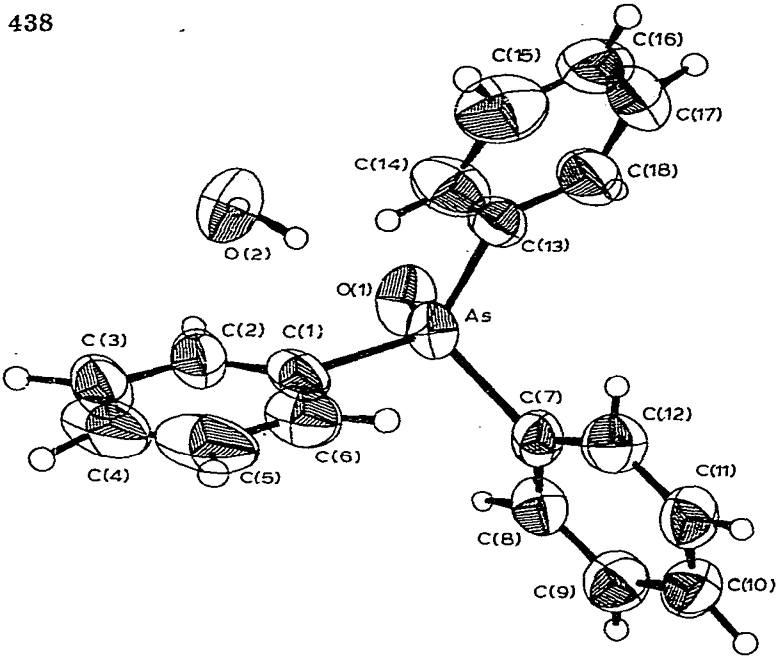

Fig. 1. ORTEP drawing of I (thermal ellipsoids are shown with 50% probability).

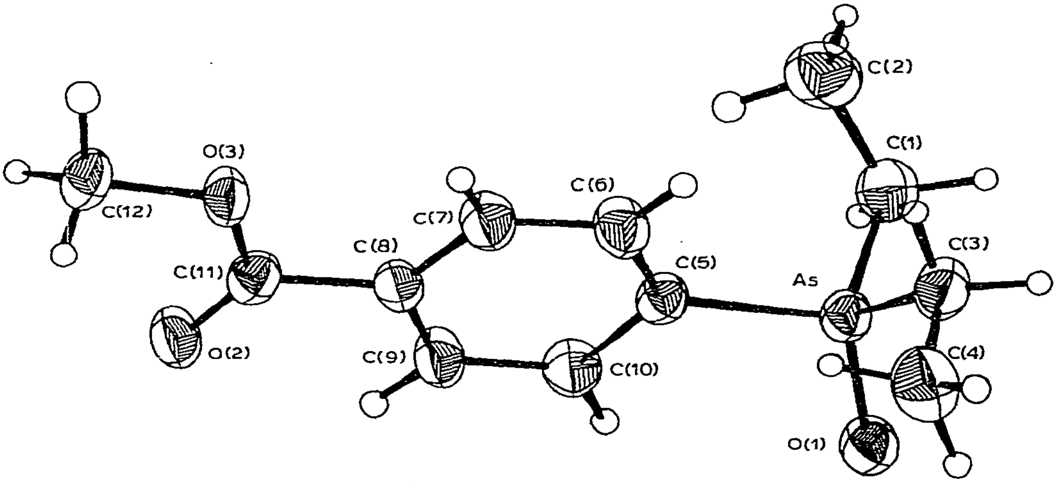

Fig. 2. ORTEP drawing of II (thermal ellipsoids are shown with 50% probability).

TABLE 4

BOND DISTANCES (in Å) AND THEIR e.s.d.'s FOR I

As—O(1)	1.657(4)	C(1)—C(2)	1.389(9)
As—C(1)	1.932(6)	C(2)—C(3)	1.370(9)
As—C(7)	1.925(6)	C(3)—C(4)	1.387(14)
As—C(13)	1.925(7)	C(4)—C(5)	1.401(13)
		C(5)—C(6)	1.369(11)
		C(6)—C(1)	1.398(10)
C(7)—C(8)	1.391(10)	C(13)—C(14)	1.362(9)
C(8)—C(9)	1.368(9)	C(14)—C(15)	1.341(12)
C(9)—C(10)	1.393(10)	C(15)—C(16)	1.364(14)
C(10)—C(11)	1.388(12)	C(16)—C(17)	1.359(13)
C(11)—C(12)	1.375(10)	C(17)—C(18)	1.374(12)
C(12)—C(7)	1.401(9)	C(18)—C(13)	1.375(10)

TABLE 5

BOND DISTANCES (IN Å) AND THEIR e.s.d.'s FOR II

As—O(1)	1.651(4)	C(7)—C(8)	1.391(9)
As—C(1)	1.921(7)	C(8)—C(9)	1.391(8)
As—C(3)	1.922(6)	C(9)—C(10)	1.396(9)
As—C(5)	1.948(6)	C(10)—C(5)	1.364(8)
C(1)—C(2)	1.530(10)	C(8)—C(11)	1.506(8)
C(3)—C(4)	1.516(10)	C(11)—O(2)	1.198(8)
C(5)—C(6)	1.419(8)	C(11)—O(3)	1.322(8)
C(6)—C(7)	1.403(9)	O(3)—C(12)	1.462(8)

TABLE 6

BOND ANGLES (IN °) AND THEIR e.s.d.'s FOR I

O(1)—As—C(1)	110.4(2)	C(6)—C(1)—C(2)	122.5(6)
O(1)—As—C(7)	111.1(2)	C(1)—C(2)—C(3)	119.2(6)
O(1)—As—C(13)	111.5(2)	C(2)—C(3)—C(4)	118.4(8)
C(1)—As—C(7)	108.1(3)	C(3)—C(4)—C(5)	122.6(9)
C(1)—As—C(13)	109.0(3)	C(4)—C(5)—C(6)	118.9(8)
C(7)—As—C(13)	106.6(3)	C(5)—C(6)—C(1)	118.3(7)
		C(12)—C(7)—C(8)	121.1(6)
As—C(1)—C(2)	117.4(5)	C(7)—C(8)—C(9)	119.0(6)
As—C(1)—C(6)	120.0(5)	C(8)—C(9)—C(10)	120.5(6)
As—C(7)—C(8)	118.8(4)	C(9)—C(10)—C(11)	120.4(7)
As—C(7)—C(12)	120.1(5)	C(10)—C(11)—C(12)	119.9(7)
As—C(13)—C(14)	118.0(5)	C(11)—C(12)—C(7)	119.1(6)
As—C(13)—C(18)	122.2(5)	C(18)—C(13)—C(14)	119.8(6)
		C(13)—C(14)—C(15)	121.0(7)
		C(14)—C(15)—C(16)	120.2(8)
		C(15)—C(16)—C(17)	119.5(8)
		C(16)—C(17)—C(18)	120.8(8)
		C(17)—C(18)—C(13)	118.6(7)

TABLE 7

BOND ANGLES (IN °) AND THEIR e.s.d.'s FOR II

O(1)—As—C(1)	112.3(2)	C(6)—C(5)—C(10)	121.8(6)
O(1)—As—C(3)	114.3(2)	C(5)—C(6)—C(7)	118.0(6)
O(1)—As—C(5)	110.0(2)	C(6)—C(7)—C(8)	120.0(6)
C(1)—As—C(3)	107.7(3)	C(7)—C(8)—C(9)	120.5(6)
C(1)—As—C(5)	106.1(3)	C(7)—C(8)—C(11)	118.0(5)
C(3)—As—C(5)	106.5(3)	C(9)—C(8)—C(11)	121.6(5)
		C(8)—C(9)—C(10)	120.2(6)
As—C(1)—C(2)	113.7(5)	C(9)—C(10)—C(5)	119.4(6)
As—C(3)—C(4)	113.1(5)	C(8)—C(11)—C(2)	123.0(6)
As—C(5)—C(6)	115.8(4)	C(8)—C(11)—O(3)	112.0(5)
As—C(5)—C(10)	122.3(4)	O(2)—C(11)—O(3)	125.0(6)
C(11)—O(3)—C(12)	115.7(5)		

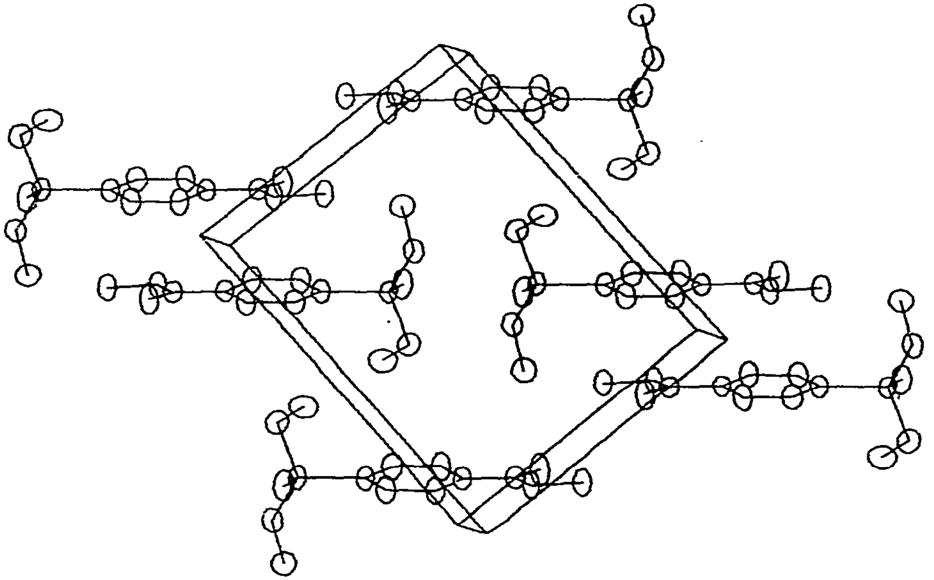

Fig. 3. Molecular packing in II.

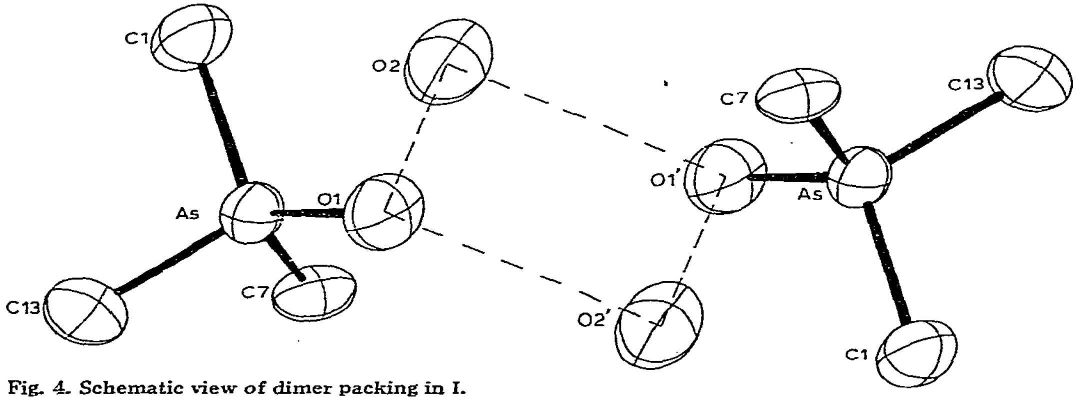

Fig. 4. Schematic view of dimer packing in I.

TABLE 8

COMPARISON OF GEOMETRIC FEATURES IN H-BONDED COMPLEXES OF TRIPHENYLARSINE OXIDE

Compound	C—As—C (°)	C—As—O (°)	As=O (Å)	O ··· O (Å)	Ref.
$Ph_3AsO \cdot H_2O$	107.9	111.0	1.657	2.808	this work
$Ph_3AsO \cdot H_2O$	108.0	110.9	1.644	2.800	1
$Ph_3AsO \cdot C_6H_2O_2Cl_4$	108.4	110.6	1.694	2.616	2
$Ph_3AsO \cdot C_6HOF_5$	107.8	111.1	1.662	2.599	3
$2\ Ph_3AsO \cdot H_2SeO_3$	108.2	110.7	1.68	2.39	4, 5
$MeOCOPh(Et)_2AsO$	106.8	112.2	1.651	—	this work

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