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STRUCTURES OF TWO POLYMORPHIC MODIFICATIONS OF TRIS(*p*-CHLOROPHENYL)ARSINOXIDE AND COMPARISON WITH THE STRUCTURE OF TRIS(*p*-CHLOROPHENYL)ARSINSULFIDE

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Summary

A full X-ray structure analysis of two polymorphic modifications of tris(*p*-chlorophenyl)arsinoxide, $C_{18}H_{12}AsOCl_3$, has been performed. Modification I is triclinic, space group $P\bar{1}$, $Z = 4$; modification II is hexagonal, space group $P6_3$, $Z = 2$. The geometrical parameters of the molecules in the two polymorphs are similar; the mean values for the bond distances and angles are: As=O 1.641, As–C 1.928, C–Cl 1.736 Å; C–As–C 107.3, C–As=O 111.6°. The packing modes in I and II are significantly different: in I supersymmetrical relationships between the molecules independent of space-group symmetry are found: in II cylindrical cavities of diameter ca. 5 Å are present along the 6_3 axes. The structures of the molecules in I and II are compared with that of tris(*p*-chlorophenyl)arsinsulfide, $C_{18}H_{12}AsSCl_3$ (III, space group $P2_1/b$, $Z = 4$).

Introduction

During a systematic study of the structural relationships in a series of tertiary arsinoxides and arsinsulfides [1–7], data on the structures of tris(*p*-chlorophenyl) derivatives were needed. When crystallizing I from a mixture of dichloroethane and octane, we obtained simultaneously colourless crystals having two distinct shapes: rod-like and prism-like. Preliminary X-ray analysis revealed that they were crystals of two polymorphic modifications. To determine the differences in the crystal and molecular structures of these polymorphs, we undertook a full X-ray structure analysis. For a comparision with similar $R_3As{=}O$ and $R_3As{=}S$ compounds, the structure of III was also established.

Experimental

Data collection was performed using an automatic Syntex P$\bar{1}$ diffractometer employing λ(Mo-K_α) radiation, a graphite monochromator and $\theta/2\theta$ scanning. The

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experimental intensities were corrected for Lorentz and polarization effects but not for absorption. The main crystallographic parameters are presented in Table 1 *.

All three structures were solved by the heavy-atom technique and were refined by the least-squares method (anisotropic for As, S, O, Cl, C atoms and isotropic for H atoms) to the following R-values: $R_{\mathrm{I}} = 0.036$ (3579 reflections with $I > 3\sigma(I)$), $R_{\mathrm{II}} = 0.034$ (470 reflections), and $R_{\mathrm{III}} = 0.025$ (1657 reflections with $I > 2\sigma(I)$). All calculations were performed on a NOVA-3 computer in a NICOLET R3 system using the SHELXTL (G.M. Sheldrick) set of programs. The non-hydrogen atomic coordinates are given in Table 2.

Molecular conformation

Table 3 gives the essential bond lengths and angles for the As, S, O and Cl atoms. The geometrical features of the molecules are similar to those of other analogous arsinoxide and arsinsulfide structures. The coordination polyhedron of the As atoms is a slightly-distorted tetrahedron, where the C–As–C angles are essentially larger than the C–As=X angles. The As=O distances in I and II (mean 1.639 Å) are slightly less than that found in triphenylarsinoxide hydrate (IV) [5,8]. The latter may be explained by the presence in IV of intermolecular hydrogen bonds, HOH...O=AsR$_3$. Recently published data on anhydrous Ph$_3$AsO [9] coincide with our results, within the limits of experimental error. The bond length As=S (2.074 Å) is in good agreement with that found in Ph$_3$AsS [1,10,11]. As can be seen from Table 3, the replacement of the O atom by S does not lead to a significant change in the As–C bond distances and only slightly increases the height of the AsC$_3$ tetrahedron (deviation of the As atom from the plane of its three neighbours): IA 0.709, IB 0.710, II 0.706, III 0.736 Å. The C–C bonds are in the limits 1.343–1.410 Å.

It is interesting to note that the conformation of the molecules in I resembles that of III more than the second modification (II). This can be seen more clearly from a comparison of the rotation angles of the phenyl ring planes in relation to the plane

(Continued on p. 163)

TABLE 1

MAIN CRYSTALLOGRAPHIC PARAMETERS

	I	II	III
a (Å)	11.969(2)	14.276(2)	9.779(1)
b (Å)	13.174(2)	14.276(2)	18.174(3)
c (Å)	15.366(2)	5.980(1)	10.568(2)
α (°)	91.11(1)	90	90
β (°)	118.24(1)	90	90
γ (°)	119.41(1)	120	90.49(1)
V (Å^3)	1757	1056	1878
Z	4	2	4
Space group	$P\bar{1}$	$P6_3$	$P2_1/b$
d_{calc} (g/cm^3)	1.61	1.34	1.56
μ (cm^{-1})	24.9	20.8	24.3

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* Tables of H-atom coordinates, thermal parameters, bond lengths and angles, and mean planes may be obtained from the authors.

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND THEIR e.s.d.'s IN PARENTHESES

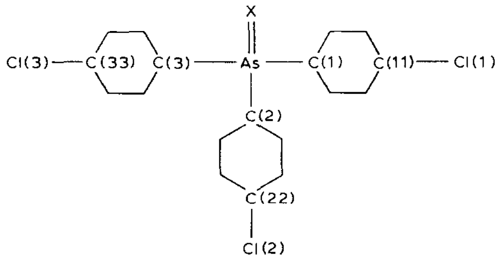
		IA	IB	II	III
As	x	8306(1)	3246(1)	1/3	1312(1)
	y	5774(1)	1059(1)	2/3	3738(1)
	z	3072(1)	3294(1)	0	2750(1)
O (S)	x	7005(4)	1900(4)	1/3	−764(1)
	y	4341(4)	32(4)	2/3	3664(1)
	z	2849(3)	3445(3)	−2741(19)	2365(1)
Cl(1)	x	11891(2)	7017(2)	3520(3)	2182(2)
	y	8540(2)	−1073(2)	2524(3)	3945(1)
	z	7942(1)	3295(2)	3457(9)	8735(1)
Cl(2)	x	12501(2)	7615(2)		4536(1)
	y	6082(2)	6161(2)		1035(1)
	z	1497(2)	6999(1)		266(1)
Cl(3)	x	4941(2)	102(3)		4039(2)
	y	7962(2)	2421(2)		6482(1)
	z	−29(2)	−727(2)		−136(1)
C(1)	x	9508(6)	4493(6)	3404(7)	1669(4)
	y	6750(5)	547(5)	5448(7)	3794(3)
	z	4505(4)	3255(4)	1180(17)	4537(4)
C(2)	x	9168(7)	4197(7)	3814(8)	1756(5)
	y	7473(5)	12(5)	4972(8)	3160(2)
	z	4850(5)	2333(4)	−195(19)	5261(5)
C(3)	x	9900(7)	4972(7)	3860(9)	1903(5)
	y	8031(5)	−487(6)	4062(9)	3202(3)
	z	5900(5)	2333(4)	449(22)	6548(5)
C(4)	x	10985(6)	6062(7)	3456(9)	2004(5)
	y	7866(5)	−410(5)	3632(8)	3888(4)
	z	6616(4)	3291(5)	2552(25)	7099(4)
C(5)	x	11384(7)	6411(6)	3046(9)	1963(5)
	y	7177(5)	147(5)	4089(8)	4531(3)
	z	6299(5)	4227(4)	3936(19)	6404(5)
C(6)	x	10638(7)	5619(6)	3007(8)	1810(5)
	y	6625(5)	646(5)	5015(9)	4480(3)
	z	5253(5)	4215(4)	3258(17)	5118(5)
C(7)	x	9709(7)	4634(6)		2306(4)
	y	5884(5)	2583(5)		2902(2)
	z	2707(4)	4429(4)		2081(4)
C(8)	x	9173(7)	4236(6)		1712(5)
	y	4845(5)	2715(5)		2510(3)
	z	2008(5)	5104(4)		1120(5)
C(9)	x	10044(7)	5150(7)		2392(6)
	y	4905(6)	3819(6)		1936(3)
	z	1635(5)	5902(4)		552(5)
C(10)	x	11438(7)	6465(7)		3671(5)
	y	5994(6)	4771(5)		1766(2)
	z	2001(4)	6005(4)		983(5)
C(11)	x	11981(6)	6890(7)		4278(5)
	y	7022(5)	4646(5)		2147(3)
	z	2717(4)	5347(5)		1959(5)
C(12)	x	11093(6)	5962(6)		3583(5)
	y	6967(5)	3550(5)		2723(2)
	z	3078(4)	4547(4)		2499(4)
C(13)	x	7359(6)	2365(6)		2151(5)
	y	6522(5)	1414(5)		4605(5)

TABLE 2 (continued)

		IA	IB	II	III
	z	2212(4)	2030(4)		1998(4)
C(14)	*x*	5754(7)	826(6)		1329(5)
	y	5784(6)	961(5)		5104(3)
	z	1551(5)	1546(4)		1403(5)
C(15)	*x*	5008(7)	125(7)		1900(6)
	y	6235(7)	1272(6)		5691(3)
	z	850(5)	687(5)		768(5)
C(16)	*x*	5854(7)	966(7)		3291(6)
	y	7369(6)	2010(5)		5763(3)
	z	830(5)	331(4)		747(5)
C(17)	*x*	7444(7)	2491(7)		4124(5)
	y	8121(6)	2457(5)		5284(3)
	z	1480(5)	793(4)		1368(5)
C(18)	*x*	8193(7)	3194(6)		3540(6)
	y	7666(6)	2147(5)		4697(3)
	z	2173(5)	1649(4)		1992(5)

TABLE 3

SOME ESSENTIAL INTERATOMIC DISTANCES (Å) AND VALENCE ANGLES (DEG.)[a]



(I,II, X = O,
III, X = S)

Bond	IA	IB	II	III
As=X	1.639(4)	1.644(5)	1.639(5)	2.074(1)
As–C(1)	1.910(6)	1.940(9)	1.926(6)	1.925(4)
As–C(2)	1.953(9)	1.918(5)	1.926(6)	1.941(4)
As–C(3)	1.932(7)	1.919(6)	1.926(6)	1.936(4)
Cl(1)–C(11)	1.736(6)	1.745(9)	1.717(9)	1.738(5)
Cl(2)–C(22)	1.740(9)	1.735(6)	1.717(9)	1.751(5)
Cl(3)–C(33)	1.749(8)	1.732(7)	1.717(9)	1.754(5)
Angle				
X=As–C(1)	111.8(3)	113.2(3)	111.5(3)	112.8(2)
X=As–C(2)	111.8(3)	110.7(3)	111.5(3)	112.0(2)
X=As–C(3)	111.1(2)	111.0(2)	111.5(3)	112.2(2)
C(1)–As–C(2)	108.1(3)	106.6(3)	107.4(3)	107.4(3)
C(1)–As–C(3)	108.7(3)	107.9(3)	107.4(3)	106.1(3)
C(2)–As–C(3)	105.1(3)	107.2(3)	107.4(3)	105.9(3)

[a] The atomic numeration system used here does not coincide with that used in Table 2.

C(1)–C(2)–C(3). In molecule II all the angles are equal to 66.8° (the molecule is in the special position on axis 3) while in IA the angles are 17.6, 72.9 and 85.0°; in IB 17.1, 81.3 and 81.8°; and in III 17.8, 72.3 and 81.9°. This means that in the crystal state the molecules in I and III lose their C_3 pseudosymmetry while the molecules in II retain it, even in the crystal state. This may be explained by considering the mode of molecular packing.

Molecular packing

In all three structures the intermolecular distances correspond to normal Van der Waals interactions. Most interesting are the differences in the molecular-packing types present in I and II.

Figure 1 represents the projection of structure I. Molecules IA and IB, independent of symmetry operations of the space group, may, nevertheless, be transformed into each other with the aid of the supersymmetrical operation 2_q [12]. This operation comprises rotation by 180° (178°) with subsequent shift. The rotation matrix is as follows:

$$\begin{matrix} -0.9992 & -0.0394 & 0.0088 \\ 0.0151 & -0.1620 & 0.9867 \\ -0.0375 & 0.9860 & 0.1624 \end{matrix}$$

The direction cosines of this "axis" are: $c_1 = -0.01000$, $c_2 = 0.6633$ and $c_3 = 0.6980$. After completing this operation, molecule IA coincides with molecule IB to a mean accuracy limit of 0.12 Å (the maximal deviations are found at the peripheral C atoms of the phenyl rings). The results of this fitting can be seen from Fig. 2. The calculations were performed using a XFIT procedure of the SHELXTL complex.

In the hexagonal modification II, the packing mode is quite different (Fig. 3). Having been arranged spirally around the 6_3 axes, the molecules form specific cylindrical channels along the Z direction. The shape of these channels can be clearly seen from Fig. 4. The diameter of these cavities is ca. 5 Å and is quite sufficient for the inclusion of some solvent, or other, molecules.

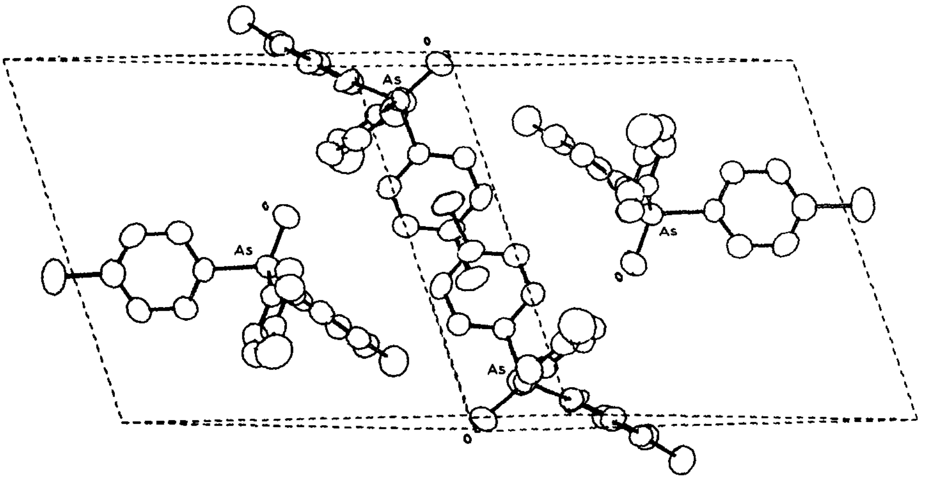


Fig. 1. Projection of structure I.

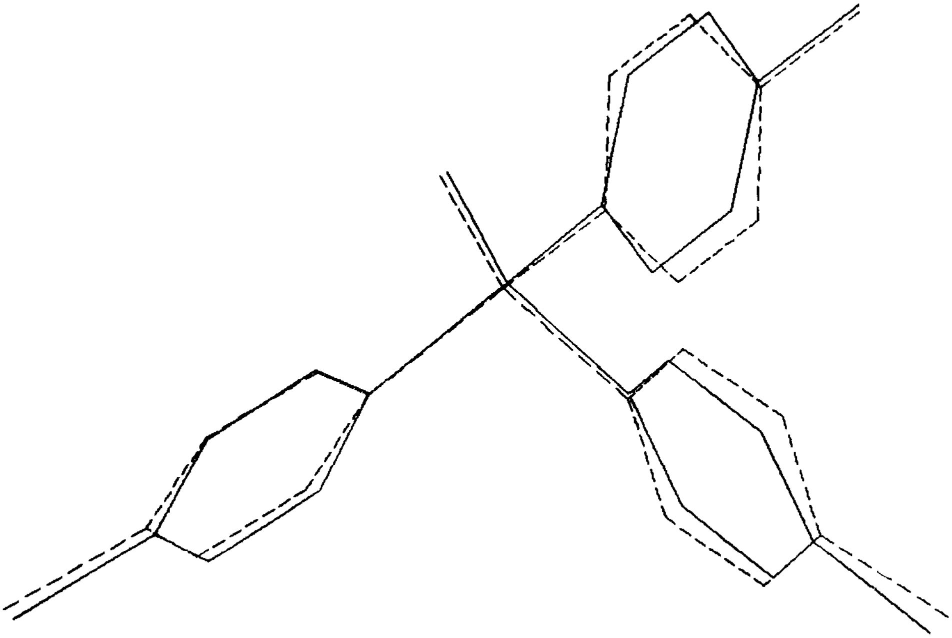


Fig. 2. The result of the "closest" fitting of molecules IA and IB.

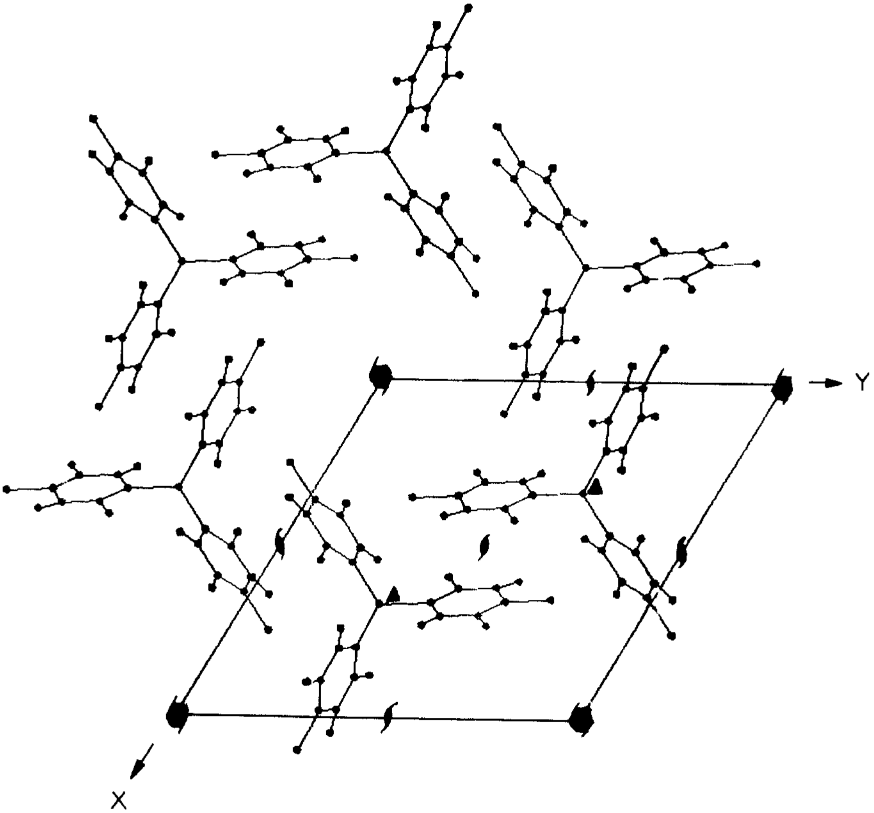


Fig. 3. The [001] projection of structure II.

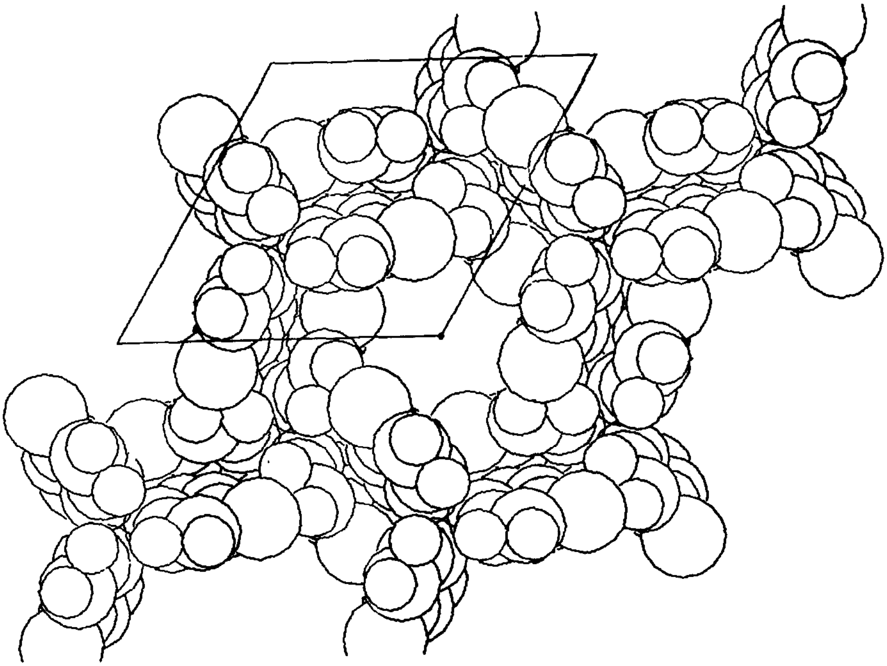


Fig. 4. The channels in structure II.

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