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Conformational trends in arsocane dithiophosphinates $X(CH_2CH_2S)_2AsS_2PR_2$ (X = O or S; R = Me, Et or Ph)†

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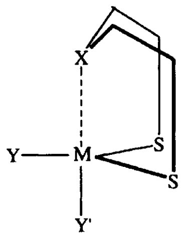
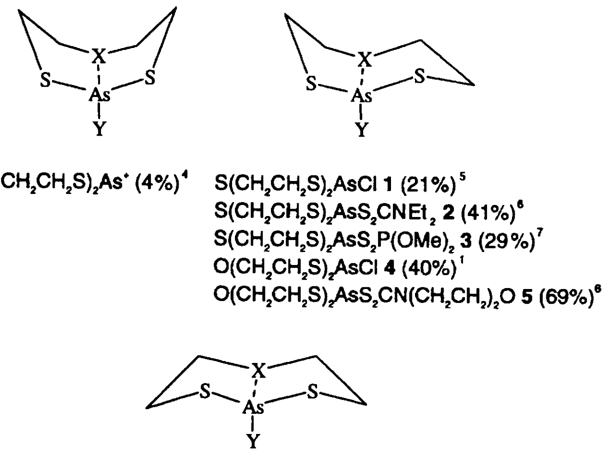
Six arsocane diorganodithiophosphinates $X(CH_2CH_2S)_2AsS_2PR_2$ (X = O or S; R = Me, Et or Ph) have been prepared in CH_2Cl_2 or benzene from $X(CH_2CH_2S)_2AsCl$ (X = O or S) and the corresponding sodium or ammonium dithiophosphinates. The compounds were characterised by IR, mass and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The single-crystal structures of $O(CH_2CH_2S)_2AsS_2PPh_2$ and $S(CH_2CH_2S)_2AsS_2PPh_2$ were determined. Both show an endocyclic, transannular As $\cdots$ X interaction and an exocyclic As $\cdots$ S secondary interaction. The co-ordination geometry can be described as trigonal bipyramidal with a face-capping intramolecular As $\cdots$ S secondary bonding. The oxa derivative is the first example of an arsocane of the type $X(CH_2CH_2S)_2AsY$ with a chair–chair conformation, while the thia derivative, as with other thiaarsocanes, shows a boat–chair conformation.

A variety of metallocanes of the type $X(CH_2CH_2S)_2MY(Y')$ have been prepared and characterised.[1] These rings consist of an acceptor atom (heavy Group 14 or 15 element M) and a donor chalcogen transannular atom X. Halide, alkyl, aryl and dithiolate ligands are attached to the heavy element. The 1,5 intramolecular secondary bonding in these compounds has been studied mainly by vibrational spectroscopy and single-crystal X-ray diffraction.‡ It is a stabilising factor, whereas the cyclooctane ring exhibits additional Pitzer tension in the 1,5 positions.[2] Additionally, the conformation adopted by the eight-membered ring has been extensively investigated both in solution, using ^1H NMR spectroscopy, and in the solid state, employing single-crystal X-ray diffraction. The latter studies have conclusively revealed that the metallo-ring XC_4S_2M is able to exhibit various conformations.[3] Nevertheless, it is possible to propose three extreme conformations: the boat–boat, boat–chair and chair–chair. These conformations, together with the known examples from X-ray diffraction data and the secondary bonding strength, are shown in Fig. 1. The secondary bonding strength is evaluated by taking the difference between the transannular distance M $\cdots$ X and the sum of the covalent radii, Σ_{cov}, multiplied by 100 (Σ_{cov} = 1.75 for As–O, 2.25 Å for As–S[4]).

The trends in Fig. 1 lead us to propose that in the arsocanes there is a relationship between the strength of the transannular interaction and the conformation of the eight-membered ring. When the transannular interaction is strong the boat–boat conformation tends to be the most favourable; thereafter the boat–chair and then the chair–chair. The latter conformation has not been observed for an $X(CH_2CH_2S)_2MY(Y')$ arcosane.[5,6]



X = O, S, NR
M = Ge, Sn, Pb, P, As, Sb, Bi
Y, Y' = lone pair, halide, alkyl, aryl



$S(CH_2CH_2S)_2As^+$ (4%)[4]

$S(CH_2CH_2S)_2AsCl$ **1** (21%)[5]
$S(CH_2CH_2S)_2AsS_2CNEt_2$ **2** (41%)[6]
$S(CH_2CH_2S)_2AsS_2P(OMe)_2$ **3** (29%)[7]
$O(CH_2CH_2S)_2AsCl$ **4** (40%)[1]
$O(CH_2CH_2S)_2AsS_2CN(CH_2CH_2)_2O$ **5** (69%)[8]

Fig. 1 Extreme conformations in arsocanes $X(CH_2CH_2S)_2AsY$ with the known examples from X-ray diffraction

Bearing in mind the previous ideas, we decided to explore the structural changes that take place when the chloro atom is replaced in the arsocanes **1** and **4** with potentially sulfur-binding bidentate ligands such as dithiocarbamates ($^-S_2CNR_2$), dithiophosphates [$^-S_2P(OR)_2$] and dithiophosphinates ($^-S_2PR_2$). These ligands may compete for the residual affinity of the arsenic atom which has implications for the co-ordination number around the metal, the strength of the endocyclic transannular interaction, and the conformation adopted by the eight-membered heterocycle.

In previous papers we reported the crystal structures of the arsocane dithiocarbamates $O(CH_2CH_2S)_2AsS_2CN(CH_2CH_2)_2O$ **5** and $S(CH_2CH_2S)_2AsS_2CNEt_2$ **2**, and an arsocane dithiophosphate $S(CH_2CH_2S)_2AsS_2P(OMe)_2$ **3**.[7,8] We describe here the synthesis and spectroscopic characterisation of a series

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

‡ The phosphacane $S(CH_2CH_2S)_2P(S)Bu^t$ does not show transannular interaction. The P $\cdots$ S distance (3.8 Å) is similar to the sum of the van der Waals radii (3.75 Å).[1]

Table 1 Preparative, analytical * and physical data for the dithioarsocane derivatives

Starting material						
$X(CH_2CH_2S)_2AsCl$ (g, mmol)	$MS_2PR_2{\cdot}nH_2O$ R, M, n (g, mmol)	Product	M.p./°C	Yield (%)	Analysis (%) C	H
X = O						
0.5, 2.0	Me, Na, 2 0.37, 2.0	$O(CH_2CH_2S)_2AsS_2PMe_2$	71–72	56	21.9 (21.4)	4.1 (4.2)
0.5, 2.0	Et, Na, 2 0.43, 2.0	$O(CH_2CH_2S)_2AsS_2PEt_2$	81–83	82	26.4 (26.5)	5.0 (5.0)
0.5, 2.0	Ph, NH_4, 0 0.54, 2.0	**6** $O(CH_2CH_2S)_2AsS_2PPh_2$	116–118	65	41.4 (41.75)	3.9 (3.9)
X = S						
1.0, 3.4	Me, Na, 2 0.63, 3.4	$S(CH_2CH_2S)_2AsS_2PMe_2$	118–119	61	18.9 (19.4)	3.7 (3.6)
0.3, 1.1	Et, Na, 2 0.24, 1.1	$S(CH_2CH_2S)_2AsS_2PEt_2$	58–60	86	25.2 (25.3)	4.5 (4.8)
1.0, 3.4	Ph, NH_4, 0 0.91, 3.4	**7** $S(CH_2CH_2S)_2AsS_2PPh_2$	140–142	75	37.6 (37.9)	3.8 (3.6)

* Required values are given in parentheses.

Table 2 Infrared (cm^{-1}) data for the dithioarsocane derivatives

Compound	$\nu_{asym}(PS_2)$	$\nu_{sym}(PS_2)$	Δ*	$\nu_{asym}(CXC)$	$\nu_{sym}(CXC)$	$\nu(AsS)$
X = O						
$O(CH_2CH_2S)_2AsS_2PMe_2$	590s	460s	130	1100vs (br)	1000s, 975w	390w, 365s, 350s
$O(CH_2CH_2S)_2AsS_2PEt_2$	578s	442m	136	1110vs, 1085m	1000s, 940w	390w, 370s, 350s
6 $O(CH_2CH_2S)_2AsS_2PPh_2$	642s	520vs	122	1100w, 1680s	990w, 972w, 15w	375w, 350s, 330w
X = S						
$S(CH_2CH_2S)_2AsS_2PMe_2$	585vs	477vs	108	946s, 930m, 905s, 850m	732s, 662w	355w, 335m, 310s
$S(CH_2CH_2S)_2AsS_2PEt_2$	582vs	483s	98	927m, 898m, 837w, 824w	762vs, 715s, 689s	360w, 338m, 308m
7 $S(CH_2CH_2S)_2AsS_2PPh_2$	646s	538vs	108	920w, 906w	747m, 711s, 689s	350w, 340s, 310s

* $\Delta = \nu_{asym}(PS_2) - \nu_{sym}(PS_2)$.

of oxa- and thia-arsocanes substituted with dithiophosphinate ligands (R = Me, Et or Ph), as well as the crystal and molecular structures of 1-oxa-4,6-dithia-5-arsocane diphenyldithiophosphinate **6** and 1,3,6-trithia-2-arsocane diphenyldithiophosphinate **7**. We also discuss the conformational trends of **6** and **7** together with those of other arsocanes in the solid state.

Results and Discussion

The six oxa- and thia-arsocane diorganodithiophosphinates were prepared from the chloro oxa- and thia-arsocanes, **4** and **1**, and sodium or ammonium salts of the appropriate dithiophosphinic acid in CH_2Cl_2 or benzene according to equation (1) (X = O or S, R = Me or Et, M = Na, $n = 2$;

$$O/S(CH_2CH_2S)_2AsCl + MS_2PR_2{\cdot}nH_2O \longrightarrow O/S(CH_2CH_2S)_2AsS_2PR_2 + MCl + nH_2O \quad (1)$$

X = O or S, R = Ph, M = NH_4, $n = 0$). All the compounds are air-stable, colourless, crystalline solids, soluble in organic solvents (*e.g.* CH_2CH_2, MeCl, benzene, but not hexane). Experimental details, yields and melting points are given in Table 1. The compounds were characterised by IR, electron-impact (EI) mass and multinuclear NMR (^1H, ^{13}C, ^{31}P) spectroscopy. The crystal and molecular structures of $O(CH_2CH_2S)_2AsS_2PPh_2$ **6** and $S(CH_2CH_2S)_2AsS_2PPh_2$ **7** were determined.

Infrared spectra

Infrared bands of the new compounds were assigned by comparison with the spectra of the starting materials and literature data,[9] and are listed in Table 2. Two medium-to-strong absorption bands were assigned to symmetrical and asymmetrical phosphorus–sulfur stretching vibrations.[9] For the oxaarsocane derivatives the larger difference, Δ, than for the thiaarsocanes suggests a lesser π-electron-density delocalisation in the fragment PS_2.[9] Characteristic absorption bands for the CXC group in the arsocanes are present for all the compounds.[10] The presence of bands in the region 390–308 cm^{-1} is indicative of As–S covalent bonding,[9] but it is difficult to distinguish between the bands due to the arsocane moiety or the dithiophosphinate ligand.

Mass spectra

The most important fragment ions observed in the 70 eV EI mass spectra are listed in Table 3. The molecular ion was observed for all compounds except for the thiaarsocane **7**. For the thiaarsocanes the ion fragment corresponding to the eight-membered ring $X(CH_2CH_2S)_2As^+$ is intense, contrary to the oxaarsocanes. The arsenic dithiophosphinate fragment $R_2PS_2As^+$ is only intense for the oxaarsocanes. In all the spectra the ion assigned to the dithiophosphinate fragment $R_2PS_2{}^+$ is weak. The intense ion fragment assigned to the five-membered heterocycle $\overline{X{-}As^+{-}S}$ seems to be the result of the elimination of a thiirane or oxirane molecule from the original eight-membered $X(CH_2CH_2S)_2M$ heterocycle. This is consistent with the mass spectra of other halogeno- and aryl-metallocanes.[1] Other fragments arise from the elimination of the alkyl and aryl groups and the sulfur atoms from the $R_2PS_2{}^+$ group.

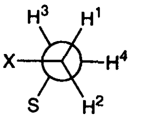
NMR spectra

Tables 4 and 5 summarise the ^1H, ^{31}P and ^{13}C NMR data of the compounds. The Newman projection of the SCH_2CH_2X fragment (see Table 4) in the normal chair–chair conformation is used for assignment of the proton and carbon chemical shifts

Table 3 The 70 eV EI mass spectra of the dithioarsocane derivatives [m/z (% intensity)]

	X = O			X = S		
Ion fragment	Me	Et	Ph	Me	Et	Ph
$X(CH_2CH_2S)_2AsS_2PR_2^+$	336 (7)	364 (18)	460 (3)	352 (2)	380 (2)	
$X(CH_2CH_2S)_2As^+$	211 (17)	211 (15)	211 (8)	227 (100)	227 (100)	227 (64)
$\overline{X\text{–}As^+\text{–}S}$	151 (50)	151 (80)	151 (44)	167 (48)	167 (36)	167 (44)
$R_2PS_2As^+$	200 (100)	228 (75)	324 (54)	200 (5)	228 (10)	324 (6)
$R_2PS_2^+$	125 (14)	153 (45)	249 (10)	125 (20)	153 (7)	249 (13)
R_2PS^+	93 (45)	121 (100)	217 (88)	93 (46)	121 (30)	217 (100)
R_2P^+	61 (6)	89 (5)	185 (18)	61 (11)	89 (2)	185 (30)
AsS^+	107 (53)	107 (88)	107 (100)	107 (33)	107 (10)	107 (75)

Table 4 Proton and ^{31}P NMR data* in $CDCl_3$ for the $X(CH_2CH_2S)_2AsS_2PR_2$ derivatives



X	R	Nuclei	
O	Me	^1H	2.09 [d, 6 H, PCH_3, $^2J(PH)$ = 13.2]
			2.98 [ddd, 2H^4, $^2J(H^5H^4) = -14.25$, $^3J(H^1H^4) = 3.30$, $^3J(H^2H^4) = 2.90$]
			3.23 [ddd, 2H^3, $^2J(H^3H^4) = -14.25$, $^3J(H^1H^3) = 3.45$, $^3J(H^2H^3) = 10.20$]
			3.53 [ddd, 2H^2, $^2J(H^1H^2) = -10.20$, $^3J(H^2H^3) = 10.20$, $^3J(H^2H^4) = 2.90$]
			4.10 [ddd, 2H^1, $^2J(H^1H^2) = -10.20$, $^3J(H^1H^3) = 3.45$, $^3J(H^1H^4) = 3.30$]
		^{31}P	57.4
	Et	^1H	1.20 [dt, 6 H, PCH_2CH_3, $^3J(HH) = 7.5$, $^3J(PH) = 21.9$]
			2.09 [dq, 6 H, PCH_2CH_3, $^3J(HH) = 7.5$, $^2J(PH) = 10.8$]
			2.95 [ddd, 2 H^4, $^2J(H^3H^4) = -14.37$, $^3J(H^1H^4) = 3.41$, $^3J(H^2H^4) = 2.87$]
			3.15 [ddd, 2 H^3, $^2J(H^3H^4) = -14.37$, $^3J(H^1H^3) = 3.60$, $^3J(H^2H^3) = 10.05$]
			3.50 [ddd, 2 H^2, $^2J(H^1H^2) = -10.20$, $^3J(H^2H^3) = 10.05$, $^3J(H^2H^4) = 2.87$]
			4.17 [ddd, 2 H^1, $^2J(H^1H^2) = -10.20$, $^3J(H^1H^3) = 3.60$, $^3J(H^1H^4) = 3.41$]
		^{31}P	79.4
	6 Ph	^1H	2.77 [ddd, 2 H^4, $^2J(H^3H^4) = -14.40$, $^3J(H^1H^4) = 3.98$, $^3J(H^2H^4) = 2.70$]
			2.95 [ddd, 2 H^3, $^2J(H^3H^4) = -14.40$, $^3J(H^1H^3) = 3.15$, $^3J(H^2H^3) = 9.80$]
			3.34 [ddd, 2 H^2, $^2J(H^1H^2) = -10.06$, $^3J(H^2H^3) = 9.80$, $^3J(H^2H^4) = 2.70$]
			3.99 [ddd, 2 H^1, $^2J(H^1H^2) = -10.06$, $^3J(H^1H^3) = 3.15$, $^3J(H^1H^4) = 3.98$]
			7.25 [m, 6 H, PC_6H_5 (*m*- and *p*-H)]
			7.71 [ddd, 4 H, PC_6H_5 (*o*-H), $^3J(HH) = 7.90$, $^4J(HH) = 1.6$, $^3J(PH) = 14.5$]
		^{31}P	58.2
S	Me	^1H	2.12 [d, 6 H, PCH_3, $^2J(PH) = 12.94$]
			2.83 [ddd, 2 H^1, $^2J(H^1H^2) = -14.82$, $^3J(H^1H^3) = 2.93$, $^3J(H^1H^4) = 8.18$]
			3.20 [ddd, 2 H^2, $^2J(H^1H^2) = -14.82$, $^3J(H^2H^3) = 7.70$, $^3J(H^2H^4) = 2.70$]
			3.21 [ddd, 2 H^4, $^2J(H^3H^4) = -14.29$, $^3J(H^1H^4) = 8.18$, $^3J(H^2H^4) = 2.70$]
			3.41 [ddd, 2 H^3, $^2J(H^3H^4) = -14.29$, $^3J(H^1H^3) = 2.93$, $^3J(H^2H^3) = 7.70$]
		^{31}P	58.6
	Et	^1H	1.29 [d, 6 H, PCH_2CH_3, $^3J(HH) = 7.5$ $^3J(PH) = 21.6$]
			2.15 [dq, 6 H, PCH_2CH_3, $^3J(HH) = 7.5$, $^2J(PH) = 9.15$]
			2.81 [ddd, 2 H^1, $^2J(H^1H^2) = -14.61$, $^3J(H^1H^3) = 3.15$, $^3J(H^1H^4) = 8.18$]
			3.18 [ddd, 2 H^2, $^2J(H^1H^2) = -14.61$, $^3J(H^2H^3) = 7.61$, $^3J(H^2H^4) = 2.82$]
			3.21 [ddd, 2 H^4, $^2J(H^3H^4) = -14.18$, $^3J(H^1H^4) = 8.18$, $^3J(H^2H^4) = 2.82$]
			3.39 [ddd, 2 H^3, $^2J(H^3H^4) = -14.18$, $^3J(H^1H^3) = 3.15$, $^3J(H^2H^3) = 7.61$]
		^{31}P	76.8
	7 Ph	^1H	2.73 [ddd, 2 H^1, $^2J(H^1H^2) = -14.30$, $^3J(H^1H^3) = 2.93$, $^3J(H^1H^4) = 8.10$]
			3.08 [ddd, 2 H^2, $^2J(H^1H^2) = -14.30$, $^3J(H^2H^3) = 7.88$, $^3J(H^2H^4) = 2.81$]
			3.09 [ddd, 2 H^4, $^2J(H^3H^4) = -14.41$, $^3J(H^1H^4) = 8.10$, $^3J(H^2H^4) = 2.81$]
			3.41 [ddd, 2 H^3, $^2J(H^3H^4) = -14.41$, $^3J(H^1H^3) = 2.93$, $^3J(H^2H^3) = 7.88$]
			7.41 [m, 6 H, PC_6H_5 (*m*- and *p*-H)]
			7.92 [ddd, 4 H, PC_6H_5 (*o*-H), $^3J(HH) = 7.35$, $^4J(HH) = 2.1$, $^3J(PH) = 14.55$]
		^{31}P	58.6

* Chemicals shifts in δ, J in Hz. s = Singlet, d = doublet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, dq = doublet of quartets.

in the methylene groups belonging to the eight-membered ring. These assignments were made using literature data for the related chloroarsocane derivatives.[11] The ^1H and ^{13}C NMR spectra are consistent with only one type of alkyl or aryl group attached to phosphorus, which shows the expected multiplicity due to phosphorus–proton and -carbon couplings.

From the vicinal hydrogen coupling constants it is possible to calculate, in solution, the torsion angle formed by the fragment SCH_2CH_2X (see Table 4), through the R value of Lambert.[12] The assignment of the conformation of the eight-membered ring $X(CH_2CH_2S)_2M$ was made after comparison of the torsion angle with the mean torsion angle found by X-ray diffraction for different metallocanes. Dräger[13] proposed that with torsion angles shorter than 60° the chair–chair conformation would prevail and for those greater than 60° the boat–chair conformation. The Lambert R values and the

Table 5 Carbon-13 NMR data for the $X(CH_2CH_2S)_2AsS_2P(OR)_2$ derivatives

Compound		δ(*J*/Hz)			
X	R	CH_2X	CH_2SM	CH_2	CH_3
O	Me	73.71	33.39		29.27 [d, *J*(PC) = 55.35]
	Et	73.65	33.24	31.47 [d, *J*(PC) = 53.03]	7.04 [d, ^2J(PC) = 4.58]
	Ph[a]	73.71	33.21		
S	Me	40.77	32.93		29.64 [*J*(PC) = 55.36]
	Et	40.59	32.90	31.57 [d, *J*(PC) = 50.70]	6.94 [d, ^2J(PC) = 4.58]
	Ph[b]	40.68	32.83		

[a] δ 131.17 [d, ^2J(PC) 11.63, *o*-C], 128.33 [d, ^3J(PC) 13.90 Hz, *m*-C] and 131.49 (s, *p*-C). [b] δ 136.84 [d, *J*(PC) 85.35, *ipso*-C], 130.84 [d, ^2J(PC) 11.55, *o*-C], 128.15 [^3J(PC) 13.88 Hz, *m*-C] and 131.22 (s, *p*-C).

Table 6 The $^1H-^1H$ vicinal coupling constants (^3J/Hz), Lambert[12] *R* values and torsion angles of the fragment SCH_2CH_2X for the dithio arsocane derivatives

	$^3J_{trans}$		$^3J_{cis}$			
Compound	1,4	2,3	1,3	2,4	*R*	Ψ/°
X = O						
$O(CH_2CH_2S)_2AsS_2PMe_2$	3.30	10.20	3.45	2.90	2.13	60.70
$O(CH_2CH_2S)_2AsS_2PEt_2$	3.41	10.05	3.60	2.87	2.08	57.37
6 $O(CH_2CH_2S)_2AsS_2PPh_2$	3.98	9.80	3.15	2.70	2.35	59.15
X = S						
$S(CH_2CH_2S)_2AsS_2PMe_2$	8.18	7.70	2.93	2.70	2.82	61.62
$S(CH_2CH_2S)_2AsS_2PEt_2$						
7 $S(CH_2CH_2S)_2AsS_2PPh_2$	8.10	7.88	2.93	2.81	2.78	61.43

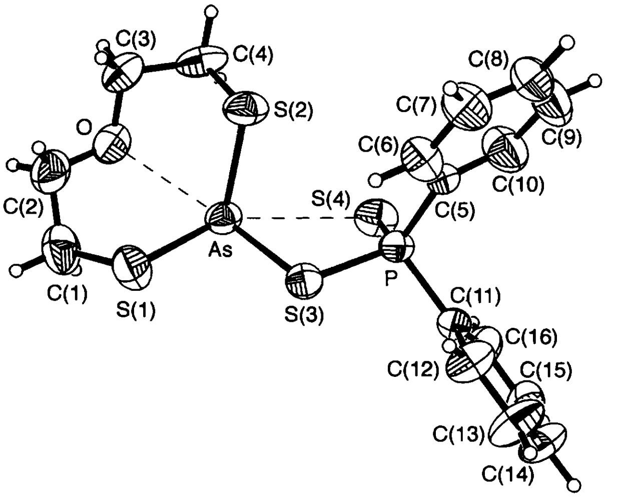


Fig. 2 An ORTEP[14] plot of $O(CH_2CH_2S)_2AsS_2PPh_2$ **6** with thermal ellipsoids at the 50% probability level

Table 7 Interatomic distances (Å) and angles (°) for $O(CH_2CH_2S)_2$-AsS_2PPh_2 **6**

As–S(1)	2.260(2)	C(7)–C(8)	1.323(12)
S(1)–C(1)	1.810(8)	C(8)–C(9)	1.364(13)
C(1)–C(2)	1.506(11)	C(9)–C(10)	1.387(13)
C(2)–O	1.388(9)	C(10)–C(5)	1.357(10)
As–S(2)	2.253(2)	P–C(11)	1.806(7)
S(2)–C(4)	1.826(7)	C(11)–C(12)	1.377(10)
C(4)–C(3)	1.511(11)	C(12)–C(13)	1.370(11)
C(3)–O	1.406(9)	C(13)–C(14)	1.339(13)
As–S(3)	2.286(2)	C(14)–C(15)	1.346(13)
P–S(3)	2.089(2)	C(15)–C(16)	1.402(12)
P–S(4)	1.945(3)	C(16)–C(11)	1.380(9)
P–C(5)	1.818(7)	As···O	2.678(5)
C(5)–C(6)	1.368(10)	As···S(4)	3.332(2)
C(6)–C(7)	1.381(11)		
S(1)–As–S(2)	106.3(1)	C(3)–C(4)–S(2)	111.1(5)
S(1)–As–S(3)	96.0(1)	C(4)–S(2)–As	96.8(3)
S(1)–As···S(4)	90.2(1)	As–S(3)–P	97.9(1)
S(1)–As···O	76.6(1)	S(3)–P–S(4)	113.7(1)
S(2)–As–S(3)	87.0(1)	P–C(5)–C(6)	122.6(5)
S(2)–As···S(4)	154.1(1)	C(5)–C(6)–C(7)	120.2(7)
S(2)–As···O	76.7(1)	C(6)–C(7)–C(8)	120.3(7)
S(3)–As···S(4)	71.6(1)	C(7)–C(8)–C(9)	121.0(8)
S(3)–As···O	159.1(1)	C(8)–C(9)–C(10)	118.9(8)
S(4)···As···O	127.5(1)	C(9)–C(10)–C(5)	120.6(8)
As–S(1)–C(1)	99.0(3)	P–C(11)–C(12)	121.0(5)
S(1)–C(1)–C(2)	110.8(6)	C(11)–C(12)–C(13)	120.8(7)
C(1)–C(2)–O	109.9(6)	C(12)–C(13)–C(14)	119.9(8)
C(2)–O–C(3)	114.9(6)	C(13)–C(14)–C(15)	121.9(9)
O–C(3)–C(4)	107.8(6)	C(14)–C(15)–C(16)	119.1(8)
C(4)–S(2)–As	96.8(3)	C(15)–C(16)–C(11)	119.8(7)

torsion angles Ψ found for the oxa- and thia-arsocanes are listed in Table 6. The Ψ angles for the oxaarsocanes suggest a predominance of the chair–chair conformation, but for the methyl and phenyl derivatives an equilibrium between boat–chair and chair–chair conformation could not be ruled out. The data for the thiaarsocanes suggest a predominance of the boat–chair conformation.

The decoupled ^{31}P NMR spectra show only one sharp singlet resonance for all compounds. The deshielding observed for the ethyl derivatives (around 20 ppm) suggests a greater π-electron-density delocalisation in the fragment PS_2.

Structures of $O(CH_2CH_2S)_2AsS_2PPh_2$ 6 and $S(CH_2CH_2S)_2AsS_2PPh_2$ 7

Fig. 2 shows the molecular structure of the oxaarsocane dithiophosphinate **6** and bond lengths and angles are listed in Table 7. Compound **6** displays both an endocyclic, transannular As···O interaction [2.678(5) Å] and an exocyclic As···S(4) secondary interaction [3.332(2) Å]. The transannular interaction is longer than that in the chlorooxa-arsocane $O(CH_2CH_2S)_2AsCl$ **4** [2.451(6) Å],[1] but shorter than that in the dithiocarbamate $O(CH_2CH_2S)_2AsS_2CN(CH_2CH_2)_2O$ **5** [2.957(4) Å].[6]

If secondary bonding is not neglected the arsenic atom is five-co-ordinate. For the arsocane **6** the co-ordination geometry about As could be described as ψ-trigonal bipyramidal (ψ-*TBPY*), with the O and S(3) atoms and the lone pair in axial positions and S(1) and S(2) in equatorial sites. The As···S(4) secondary bonding face caps the polyhedron formed by the ψ-*TBPY*.[15]

Fig. 3 shows the molecular structure of the thiaarsocane dithiophosphinate **7**, with the atom numbering scheme. Bond lengths and angles are listed in Table 8. Compound **7** also displays both an endocyclic, transannular As···S interaction [2.881(4) Å] and an exocyclic As···S(5) secondary interaction [3.267(4) Å]. The transannular interaction is longer than in $S(CH_2CH_2S)_2AsCl$ **1** [2.719(3) Å],[5] but shorter than that in the dithio derivatives $S(CH_2CH_2S)_2AsS_2CNEt_2$ **2** [2.957(4) Å][6] and $S(CH_2CH_2S)_2AsS_2P(OMe)_2$ **3** [2.911(1) Å].[7] When the strength of this interaction in the arsocanes **6** and **7** is compared (the As···S interaction is 22% longer than Σ_{cov} and the

As · · · O is 53% longer) it is found that it is stronger in the latter, in agreement with the results for the chloroarsocanes **1** and **4**.[1] The transannular secondary bonding in all the dithioarsocanes is weaker than that for the chloroarsocanes. One reason for this could be the competition between the two sulfur atoms of the ligand for co-ordination to arsenic. The phosphorus–sulfur bonds of the ligand in **6** and **7** are non-equivalent [2.089(2) and 1.945(3) for **6**; 2.071(4) and 1.961(5) Å for **7**]. These distances confirm the situation suggested by the IR spectra that, in the fragment PS_2, for the oxaarsocane derivatives there is less π-electron-density delocalisation than in the thiaarsocanes. The shorter P–S bond in **6** and **7** is intermediate between a double and a single bond.[16]

Similarly to **6**, the thiaarsocane **7** displays a ψ-*TBPY* co-ordination geometry about As. The S(3) and S(4) atoms and the lone pair are in axial positions and S(1) and S(2) in equatorial sites with the As · · · S(5) secondary bonding face capping the polyhedron formed by the ψ-*TBPY*. Five-co-ordinate compounds such as the arsocanes show a continuous series of geometries extending from the trigonal bipyramid (*TBPY*) to the square or rectangular pyramid (*SPY*).[17] Comparison of the dihedral angle sum for a compound of interest $\Sigma_i|\delta_i(M) - \delta_i(TBPY)|$ with the sum, $R = \Sigma_i|\delta_i(TBPY) - \delta_i(SPY)|$, for the two idealised geometries allows the calculations of a percentage displacement between these two geometries from *TBPY* to *SPY*.[18] A dihedral angle plot obtained from the application of this method on a common reference scale if the Berry coordinate is followed must go from 0 to 217°. For the arsocanes **1** and **4**–**7** the dihedral angles go from 206 to 388°. Clearly these arsocanes do not obey the Berry coordinate. For this reason we decided to exclude the intramolecular As · · · S interaction from the co-ordination polyhedron, and describe the geometry about the As atom as ψ-*TBPY*. In all these compounds the severe distortions from the idealised *TBPY* could be ascribed to the eight-membered ring constraints and the lone pair–bonding pair repulsion.

Table 8 Interatomic distances (Å) and angles (°) for $S(CH_2CH_2S)_2$-AsS_2PPh_2 **7**

As–S(1)	2.264(4)	C(6)–C(7)	1.429(24)
S(1)–C(1)	1.818(18)	C(7)–C(8)	1.348(24)
C(1)–C(2)	1.500(23)	C(8)–C(9)	1.373(27)
C(2)–S(3)	1.800(17)	C(9)–C(10)	1.402(23)
S(3)–C(3)	1.796(19)	C(10)–C(5)	1.399(17)
C(3)–C(4)	1.519(26)	C(11)–C(12)	1.405(22)
C(4)–S(2)	1.815(18)	C(12)–C(13)	1.321(29)
As–S(2)	2.252(5)	C(13)–C(14)	1.434(28)
As–S(4)	2.414(3)	C(14)–C(15)	1.386(27)
P–S(4)	2.071(4)	C(15)–C(16)	1.323(27)
P–S(5)	1.961(5)	C(16)–C(11)	1.388(21)
P–C(5)	1.808(13)	As · · · S(3)	2.881(4)
C(5)–C(6)	1.381(20)	As · · · S(5)	3.267(4)
S(1)–As–S(2)	101.2(2)	C(3)–C(4)–S(2)	111.5(14)
S(1)–As · · · S(3)	81.7(1)	C(4)–S(2)–As	103.4(7)
S(1)–As–S(4)	85.2(1)	As–S(4)–P	96.8(2)
S(1)–As · · · S(5)	155.1(1)	S(5)–P–S(4)	113.3(2)
S(2)–As · · · S(3)	80.4(1)	P–C(5)–C(6)	124.6(10)
S(2)–As–S(4)	98.9(1)	C(5)–C(6)–C(7)	118.8(13)
S(2)–As · · · S(5)	76.5(1)	C(6)–C(7)–C(8)	120.8(17)
S(3) · · · As–S(4)	166.5(1)	C(7)–C(8)–C(9)	120.4(17)
S(3) · · · As · · · S(5)	121.5(1)	C(8)–C(9)–C(10)	120.7(14)
S(4)–As · · · S(5)	70.9(1)	C(9)–C(10)–C(5)	119.2(14)
As–S(1)–C(1)	100.5(6)	P–C(11)–C(12)	121.1(12)
S(1)–C(1)–C(2)	113.7(14)	C(11)–C(12)–C(13)	118.9(15)
C(1)–C(2)–S(1)	113.7(14)	C(12)–C(13)–C(14)	123.7(17)
C(1)–C(2)–S(3)	112.5(12)	C(13)–C(14)–C(15)	114.1(18)
C(2)–S(3)–C(3)	102.4(10)	C(14)–C(15)–C(16)	123.6(17)
S(3)–C(3)–C(4)	113.0(12)	C(15)–C(16)–C(11)	120.5(15)

Table 9 presents a comparison between the torsion angles of the eight-membered heterocycle $X(CH_2CH_2S)_2As$ for the arsocanes **1** and **4**–**7**. Fig. 4 shows the conformation of the metallaarsocane moiety for **6** and **7**. The dithio thiaarsocane **7** shows the expected boat–chair conformation. The dithio oxaarsocane **6** which has a stronger As · · · O interaction than in **5** is the only example of an arsocane of the type $X(CH_2CH_2S)_2AsY$ with a chair–chair conformation, which is at first glance somewhat surprising. In fact, for these oxaarsocanes, it is clear that the endocyclic transannular interaction is not the main force which controls the conformation adopted by the eight-membered ring in the solid state and in solution. In other words, the As · · · O interaction in the oxaarsocanes **4**–**6** is significant enough to play an important role in the conformation of the heterocycle.

Experimental

General procedures

The starting compounds $O/S(CH_2CH_2SH)_2$ and $AsCl_3$ were obtained commercially and used as received. Solvents were dried before use. The chloroarsocanes were obtained using published procedures.[10] Sodium dialkyldithiophosphinates were synthesised according to literature methods.[19] Ammonium

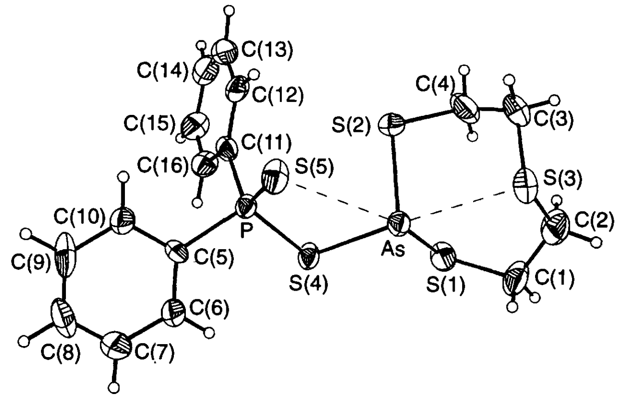


Fig. 3 An ORTEP plot of $S(CH_2CH_2S)_2AsS_2PPh_2$ **7** with thermal ellipsoids at the 50% probability level

Table 9 Comparative torsion angles (°) for $O(CH_2CH_2S)_2AsCl$ **4**, $O(CH_2CH_2S)_2AsS_2PPh_2$ **6**, $O(CH_2CH_2S)_2AsS_2CN(CH_2CH_2)_2O$ **5**, $S(CH_2CH_2S)_2AsS_2PPh_2$ **7** and $S(CH_2CH_2S)_2AsCl$ **1**

	4	**6**	**5**	**7**	**1**	
	boat–chair	chair–chair	boat–chair	boat–chair	boat–chair	
C(1)S(1)AsS(2)	70	101.4	38.4	45.6	56	C(4)S(2)AsS(1)
S(1)AsS(2)C(4)	−107	−104.5	−104.0	−111.6	−112	S(2)AsS(1)C(1)
AsS(2)C(4)C(3)	59	67.8	76.5	67.4	64	AsS(1)C(1)C(2)
S(2)C(4)C(3)O	−64	−64.1	−67	−63.1	−65	S(1)C(1)C(2)S(3)
C(4)C(3)OC(2)	155	147.3	135.6	122.5	130	C(1)C(2)S(3)C(3)
C(3)OC(2)C(1)	−78	−150.9	−83.5	−72.2	−72	C(2)S(3)C(3)C(4)
OC(2)C(1)S(1)	−57	63.8	−63.8	−60.8	−58	S(3)C(3)C(4)S(2)
C(2)C(1)S(1)As	36	−63.0	64.3	66.4	57	C(3)C(4)S(2)As

Table 10 Crystallographic and structure solution data for the arsocanes **6** and **7**[a]

	6	**7**
Compound formula	$C_{16}H_{18}AsOPS_4$	$C_{16}H_{18}AsPS_5$
M_r	460.4	476.5
a/Å	9.165(3)	8.818(1)
b/Å	12.091(4)	13.100(1)
c/Å	1.059(4)	17.246(2)
U/Å^3	2002.0(1)	1991.8(3)
θ Range for cell/°	5.31–11.40	6.2–12.28
D_c/g cm^{-3}	1.528	1.589
F(000)	836	968
μ(Mo-Kα)/mm^{-1}	2.196	2.307
Crystal size/mm	0.3 × 0.5 × 0.6	0.4 × 0.24 × 0.12
Transmission coefficients		0.5934–0.7682
No. data collected	3870	1995
No. unique data	2633	1515
hkl Ranges	−10 to 0, −14 to 0, −21 to 21	0–10, 0–15, 0–20
R_{merge}	0.0284	0.000
g In weighting scheme	0.0001	0.0008
No. refined parameters	209	209
Final R ('observed' data)[a]	0.0484	0.0672
Final R' (all data)	0.0413	0.0634
Goodness of fit, S[b]	1.36	1.22

[a] Details in common: orthorhombic, space group $P2_12_12_1$; $Z = 4$; θ range 1.5 – 25°; conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections having $F_o^2 > 1.5\sigma(F_o^2)$ (observed reflections); $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + gF^2$. [b] On F^2 values for all data.

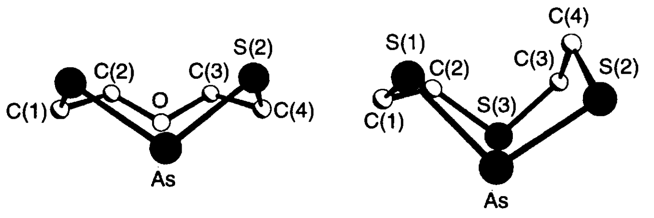


Fig. 4 Conformation of the eight-membered heterocycle $X(CH_2CH_2S)_2As$ of the dithioarsocanes **6** and **7**. In **6** the conformation is chair–chair and in **7** boat–chair

diphenyldithiophosphinate was obtained by bubbling gaseous ammonia into a benzene solution of the free acid.[20] Elemental analyses (C, H) were performed by commercial laboratories. Infrared spectra (4000–200 cm^{-1}) were recorded on KBr discs using a Perkin-Elmer 282B spectrometer, 70 eV EI mass spectra using a Hewlett-Packard MS-598 instrument, and ^1H, ^{13}C and ^{31}P NMR spectra in $CDCl_3$ solution using a Varian Gemini 300 spectrometer operating at 299.949, 50.29 and 121.4 MHz, respectively with $SiMe_4$ and H_3PO_4 (85%) as external standards.

Preparation of the arsocane dithiophosphinate compounds

Stoichiometric amounts of $O/S(CH_2CH_2S)_2AsCl$ and sodium or ammonium dithiophosphinates in CH_2Cl_2 or benzene (20 cm^3) were stirred for 12 h. The reaction mixture was filtered to remove the resulting NaCl or NH_4Cl and the clear filtrate was evaporated at low pressure. The resulting powder was recrystallised from a CH_2Cl_2–hexane mixture.

Crystallography

Single crystals suitable for X-ray diffraction of the oxa- and thia-arsocanes **6** and **7** were obtained by diffusion using a CH_2Cl_2–hexane mixture. The crystallographic and structure solution data are summarised in Table 10. A Siemens P4 diffractometer for both determinations was used. The data were collected at ω-scan speed 4.0–30.0° min^{-1} with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Corrections were applied for background and Lorentz-polarisation effects in both cases and a face-indexed absorption correction[21] was applied for **7**. The structures were solved by direct methods, with full-matrix least-squares refinement (on F)[22] and all non-hydrogen atoms anisotropic and hydrogens in idealised positions with a fixed U_{iso} = 0.06 Å^2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/184.

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