Synthesis and Characterization of Phenoxarsin-10-yl Diorganodithiophosphinates.† A Folded Phenoxarsine System in the First Dimeric Organoarsenic(III) 1,1-Dithiolate associated through As · · · S Secondary Bonding

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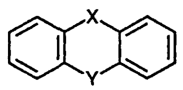
Some phenoxarsin-10-yl diorganodithiophosphinates, $O(C_6H_4)_2AsS_2PR_2$ (R = Me, Et or Ph), have been prepared by treating 10-chlorophenoxarsine with salts of the corresponding dithio compounds in CH_2Cl_2. The compounds were characterized by IR, mass spectrometry and ^1H, ^{13}C and ^{31}P NMR spectroscopy and the crystal structure of $O(C_6H_4)_2AsS_2PPh_2$ has been determined. The compound is monoclinic, space group $P2_1/n$, $a = 8.925(6)$, $b = 22.028(8)$, $c = 11.341(5)$ Å, $\beta = 100.70(2)°$ and $Z = 4$. It exhibits a dimeric, quasi-tricyclic structure based upon intra- and inter-molecular As···S secondary bonds (3.402 and 3.381 Å, respectively), which is unique in arsenic–sulfur chemistry. The phenoxarsine unit is non-planar with a dihedral angle of 154.4° between the planes of the two aromatic rings.

Several X-ray diffraction studies of 10-chlorophenoxarsine and related derivatives of structure **I** revealed differences in the dihedral angles between the phenyl ring planes. For Y = As–Cl and X = O, S or NH these angles are 156.3,[1] 152.7,[2] and 169.3°,[3] respectively. Surprisingly, the compound $O(C_6H_4)_2AsEAs(C_6H_4)_2O$ (E = S or Se) contains two nearly planar phenoxarsine moieties (175.2 and 178.5° for E = S,[4] and 173.9 and 176.0° for E = Se,[5] respectively). By contrast, in $O(C_6H_4)_2AsOAs(C_6H_4)_2O$, the two halves are very different (157.6 and 176.0°).[5] The dihedral angle in the $SbCl_5$ adduct $O(C_6H_4)_2As(O)Cl{\cdot}SbCl_5$[6] is significantly increased compared to 10-chlorophenoxarsine (167.7 *vs.* 156.3°). In all the phenoxarsine derivatives investigated so far by X-ray diffraction no *inter*molecular secondary interactions have been established.

On the other hand, dithiophosphinate ligands, $R_2PS_2^-$ (R = alkyl, aryl, alkoxy or aroxy), are known to exhibit different co-ordination patterns, basically due to their ability to involve both sulfur atoms in primary and secondary (intra- and/or inter-molecular) bonds.[7] Thus, for example, inorganic and organometallic antimony(III) derivatives with dithiophosphorus ligands exhibit a broad variety of structures in the solid state. Some of them are molecular monomeric compounds, *e.g.* $Sb(S_2PR_2)_3$ (R = Ph,[8] OEt,[9] OMe or OPr^i[10]) or $PhSb[S_2P(OPr^i)_2]_2$,[11] while others are supramolecular dimers, such as $[Ph_2SbS_2PPh_2]_2$[12] and $[(p\text{-}MeC_6H_4)_2SbS_2PEt_2]_2$,[13] or polymers, *e.g.* $[Ph_2SbS_2P(OPr^i)_2]_n$[14] and $[Me_2SbS_2PMe_2]_n$.[15] Small changes in the peripheral organic groups bound to phosphorus, quite far from the metal co-ordination centre, may drastically modify the co-ordination geometry around the metal, and can result in dimerization or polymerization.

The analogous arsenic(III) derivatives have been much less investigated. The crystal structure of $PhAs[S_2P(OPr^i)_2]_2$ was reported, the compound being monomeric with square-pyramidal co-ordination around the arsenic atom.[11] The synthesis and spectroscopic (IR, NMR) characterization of diorganoarsenic(III) dithiophosphinates, $R_2AsS_2PPh_2$ (R = Me or Ph),[16] and the synthesis of some phenoxarsin-10-yl dithiophosphates $O(C_6H_4)_2AsS_2P(OR)_2$,[17] have been reported, but no X-ray structural investigations have been carried out.



I

Taking into account the large range of dihedral angles reported so far for phenoxarsine derivatives, it is of interest to investigate compounds in which the chlorine atom on arsenic is substituted by dithiophosphinate groups, which may lead to secondary metal–sulfur interactions, and to see whether such interactions affect the folding dihedral angle of the phenoxarsine system.

We report here the synthesis and spectroscopic characterization of some phenoxarsin-10-yl diorganodithiophosphinates, $O(C_6H_4)_2AsS_2PR_2$ (R = Me, Et or Ph), and the crystal structure of the phenyl derivative.

Results and Discussion

The phenoxarsin-10-yl diorganodithiophosphinate compounds were prepared from 10-chlorophenoxarsine and sodium or ammonium salts of the appropriate dithiophosphinic acid in CH_2Cl_2 according to equation (1) (R = Me or Et, M = Na,

$$O(C_6H_4)_2AsCl + MS_2PR_2{\cdot}nH_2O \longrightarrow O(C_6H_4)_2AsS_2PR_2 + MCl + nH_2O \quad (1)$$

$n = 2$; R = Ph, M = NH_4, $n = 0$). All the compounds are air stable, colourless, crystalline solids, soluble in organic solvents (*e.g.* CH_2Cl_2 and $CHCl_3$). Experimental details, yields and melting points are given in Table 1. The compounds were characterized by IR, mass spectra and multinuclear NMR (^1H, ^{13}C, ^{31}P) spectra, and the crystal structure of $O(C_6H_4)_2AsS_2PPh_2$ has been determined.

Infrared Spectra.—Relevant infrared bands of the new compounds were assigned by comparison with the spectra of the starting materials and literature data,[5] and are listed in

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Preparation and analytical and physical data for $O(C_6H_4)_2AsS_2PR_2$

	Starting materials				Analyses (%)*	
Complex	$O(C_6H_4)_2AsCl$ (g, mmol)	Dithio derivative [(g, mmol)]	M.p./°C	Yield (%)	C	H
$O(C_6H_4)_2AsS_2PMe_2$	0.67, 2.41	$NaS_2PMe_2{\cdot}2H_2O$ (0.512, 2.78)	105–107	66	45.10 (45.65)	3.75 (3.85)
$O(C_6H_4)_2AsS_2PEt_2$	0.70, 2.52	$NaS_2PEt_2{\cdot}2H_2O$ (0.54, 2.55)	85–88	52	48.25 (48.50)	4.45 (4.60)
$O(C_6H_4)_2AsS_2PPh_2$	0.57, 2.05	$NH_4S_2PPh_2$ (0.54, 2.02)	140–141	88	58.20 (58.55)	3.60 (3.70)

* Required values are given in parentheses.

Table 2. The presence of two bands at *ca.* 370 and 340 cm^{-1} (assigned to As–S stretching vibrations[5]) in all the spectra are indicative of co-ordination of the dithio ligand to arsenic. Two medium-to-strong absorption bands were assigned to symmetrical and asymmetrical phosphorus–sulfur stretching vibrations; the difference $\Delta = \nu_{asym}(PS_2) - \nu_{sym}(PS_2) > 120$ cm^{-1} is consistent with an essentially monodentate co-ordination of the dithio ligand.[18] Characteristic absorption bands (at *ca.* 1260, 1220 and 1060 cm^{-1}) for the C–O–C group in 10-phenoxarsines[5] are present in all the compounds.

Mass Spectra.—The most important fragment ions observed in the 70 eV electron impact (EI) mass spectra are listed in Table 3. The molecular ion was observed for all compounds. The expected first fragmentation ion, *i.e.* $O(C_6H_4)_2As^+$ and $R_2PS_2^+$, was also present, the former always determining the base peak. Characteristic fragments for 10-phenoxarsine compounds, *i.e.* $C_{12}H_8O^+$, $C_{11}H_7As^+$ and $C_{11}H_7^+$,[5,19] were also observed, but no fragments were found with a mass higher than the molecular mass. This is consistent with the weak intermolecular As ··· S interactions established by X-ray diffraction for the phenyl derivative.

NMR Spectra.—Proton, ^{13}C and ^{31}P NMR data, listed in Table 4, confirm the identity of the compounds. The proton and carbon chemical shifts in the phenoxarsine moiety were assigned using literature data for the related 10-chlorophenarsazine[20,21] and a two-dimensional heteronuclear correlation spectroscopy NMR spectrum of 10-chlorophenoxarsine. The ^1H and ^{13}C NMR spectra are consistent with only one type of organic group bound to phosphorus, which gives resonances with the expected patterns due to phosphorus–proton and phosphorus–carbon couplings. This suggests a monomeric structure and monodentate behaviour of the dithiophosphinate group in solution. Only one sharp resonance was observed in the ^{31}P NMR spectra.

Structure of $O(C_6H_4)_2AsS_2PPh_2$.—The structure of the monomeric unit is shown in Fig. 1 and selected bond distances and angles are listed in Table 5. In the dithiophosphinate unit the two phosphorus–sulfur interatomic distances are in the range of single [2.091(2)] and double bonds [1.955(3) Å], respectively (*cf.* P–S 2.077 and P=S 1.954 Å in the free acid, $Ph_2P(S)SH$).[23] The As–S(1) bond distance [2.315(2) Å] is larger than the sum of the covalent radii (2.24 Å)[24] but in good agreement with the values of As–S single bonds reported for other compounds, *e.g.* 2.275 Å (av.) in $O(C_6H_4)_2AsSAs(C_6H_4)_2O$,[4] or 2.310(9) Å in $PhAs[S_2P(OPr^i)_2]_2$.[11] The co-ordination of the dithio ligand may be regarded as monodentate, leading to a pyramidal geometry with arsenic in the apical position and the S(1) and two carbons in the corners of the basal plane. The phenoxarsine system is folded over the As ··· O axis, with a dihedral angle of 154.4°, which is of the same magnitude as that of 10-chlorophenoxarsine (156.3°).[1]

Table 2 Infrared data (cm^{-1}) for $O(C_6H_4)_2AsS_2PR_2$

R	$\nu_{asym}(PS_2)$	$\nu_{sym}(PS_2)$	Δ*	ν(AsS)	ν(COC)
Me	588s	469m	128	364m, 340m	1260s, 1220s, 1060s
Et	578s	458m	120	370m, 340s	1260s, 1220s, 1060s
Ph	642s	520s	122	357m, 340m	1260s, 1213s, 1058s

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

Table 3 Mass spectra [*m*/*z* (% intensity)] of $O(C_6H_4)_2AsS_2PR_2$

R	Me	Et	Ph
$O(C_6H_4)_2AsS_2PR_2^{\cdot+}$	368 (10)	396 (2)	492 (8)
$O(C_6H_4)_2As^+$	243 (100)	243 (100)	243 (100)
$C_{11}H_7As^{\cdot+}$	214 (5)	214 (3)	214 (5)
$C_{12}H_8O^+$	168 (28)	168 (29)	168 (29)
$C_{11}H_7^{\cdot+}$	139 (16)	139 (18)	139 (23)
$R_2PS_2^+$	125 (7)	153 (2)	249 (11)
R_2PS^+	93 (6)	121 (3)	217 (8)
R_2P^+	61 (8)	89 (2)	185 (11)
PS^+	63 (7)	63 (6)	63 (5)

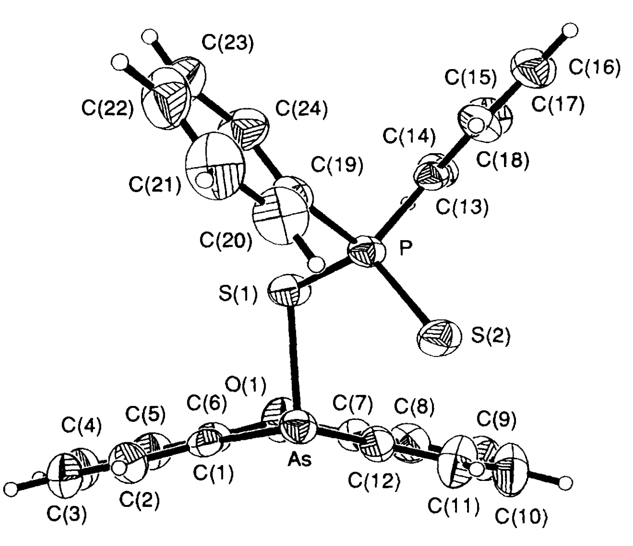
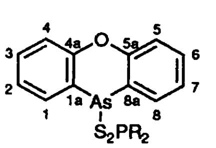


Fig. 1 ORTEP[22] view of the $O(C_6H_4)_2AsS_2PPh_2$ monomer

Differences in the structure of 10-chlorophenothiarsine and its antimony analogue have been reported. In the arsenic compound, the chlorine atom is in an axial position (structure **II**, E = S, X = Cl),[2] while in the antimony derivative the halogen atom occupies an equatorial position (structure **III**).[25] In all the structures of phenoxarsine derivatives previously reported,[1,4,5] as well as in $O(C_6H_4)_2AsS_2PPh_2$, the axial orientation of the As–X bond is preserved (structure **II**, E = O, X = Cl, O, S or Se).

Table 4 NMR data* for $O(C_6H_4)_2AsS_2PR_2$



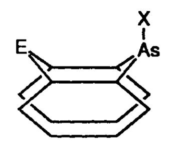
R		
Me	^{1}H:	1.96 [d, 6 H, PCH_3, ^2J(PH) = 12.9] 7.18 [ddd, 2 H^2,H^7; ^3J(HH) = ^4J(HH) = 7.21, ^5J(HH) = 0.34] 7.27 [ddd, 2 H^4, H^5; ^3J(HH) = 8.28, ^4J(HH) = ^5J(HH) = 0.34] 7.43 [ddd, 2 H^3, H^6; ^3J(HH) = ^4J(HH) = 7.71, ^5J(HH) = 1.68] 7.88 [dd, 2 H^1, H^8; ^3J(HH) = 7.5, ^4J(HH) = 1.46]
	^{13}C:	28.78[d, PCH$_3$, ^1J(PC) = 56.5] 118.23 (s, 2 C^{1a}, C^{8a}), 118.42 (s, 2 C^4, C^5), 123.95 (s, 2 C^2, C^7), 132.38 (s, 2 C^3, C^6), 135.18 (s, 2 C^1, C^8), 154.83 (s, 2 C^{4a}, C^{5a})
	^{31}P:	56.2
Et	^{1}H:	1.14 [dt, 6 H, PCH$_2$CH_3, ^3J(HH) = 7.5, ^3J(PH) = 21.6] 2.00 [dq, 4 H, PCH_2CH$_3$, ^3J(HH) = 7.5, ^2J(PH) = 10.2] 7.17 [dd, 2 H^2, H^7; ^3J(H^2-H^3) = ^3J(H^2-H^1) = 7.27] 7.27 [d, 2 H^4, H^5; ^3J(HH) = 8.1] 7.43 [ddd, 2 H^3, H^6; ^3J(H^3-H^4) = 8.32, ^3J(H^3-H^2) = 7.35, ^4J(HH) = 1.8] 7.88 [dd, 2 H^1, H^8; ^3J(HH) = 7.5, ^4J(HH) = 1.5]
	^{13}C:	6.92 [d, PCH$_2$$CH_3$, ^2J(PC) = 5.61] 31.34 [d, PCH$_2$CH$_3$,^1J(PC) = 51.9] 118.32 (s, 2 C^4, C^5), 118.71 (s, 2 C^{1a}, C^{8a}), 123.83 (s, 2 C^2, C^7), 132.21 (s, 2 C^3, C^6), 135.27 (s, 2 C^1, C^8), 154.92 (s, 2 C^{4a}, C^{5a})
	^{31}P:	77.9
Ph	^{1}H:	7.08 [ddd, 2 H^2, H^7; ^3J(H^2-H^3) = ^3J(H^2-H^1) = 7.34, ^4J(HH) = 1.34] 7.25 [dd, 2 H^4, H^5; ^3J(HH) = 8.29, ^4J(HH) = 1.3] 7.36–7.45 [m, 8 H^3, H^6 + PC$_6$H$_5$ (*m*- and *p*-H)] 7.63 [dd, 2H^1, H^8; ^3J(HH) = 7.5, ^4J(HH) = 1.73] 7.87 [ddd, 4 H, PC$_6$H$_5$ (*o*-H), ^3J(HH) = 7.9, ^4J(HH) = 1.61, ^3J(PH) = 14.5]
	^{13}C:	117.80 (s, 2 C^{1a}, C^{8a}), 118.25 (s, 2 C^4, C^5), 123.83 (s, 2 C^2, C^7), 132.26 (s, 2 C^3, C^6), 135.21 (s, 2 C^1, C^8), 154.69 (s, 2 C^{4a}, C^{5a}), 128.34 [d, 2 C, *m*-C, ^3J(PC) = 13.3], 131.27 [d, 2 C, *o*-C, ^2J(PC) = 11.8], 131.4 (s, 1 C, *p*-C), 136.05 [d, 1 C, *i*-C, ^1J(PC) = 83.9]
	^{31}P:	61.7

* Chemical shifts in δ, *J* in Hz; abbreviations used: s = singlet, d = doublet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, dq = doublet of quartets.

Table 5 Selected interatomic distances (Å) and angles (°) in $O(C_6H_4)_2AsS_2PPh_2$*

As–S(1)	2.315(2)	C(7)–C(12)	1.391(9)
As ··· S(2)	3.402(3)	P–S(1)	2.091(2)
As–C(1)	1.930(5)	P–S(2)	1.955(3)
As–C(12)	1.946(6)	P–C(13)	1.806(5)
C(1)–C(6)	1.398(9)	P–C(19)	1.814(6)
C(6)–O(1)	1.381(7)	As ··· S(2a)	3.381(3)
O(1)–C(7)	1.378(7)	As ··· As(a)	3.685(3)
S(1)–As–C(1)	93.2(2)	S(1)–P–S(2)	116.0(1)
S(1)–As–C(12)	98.1(2)	S(1)–P–C(13)	104.7(2)
S(1)–As ··· S(2)	70.9(1)	S(1)–P–C(19)	105.1(2)
C(1)–As–C(12)	93.7(3)	S(2)–P–C(13)	112.0(2)
C(1)–As ··· S(2)	161.4(2)	S(2)–P–C(19)	113.4(2)
C(12)–As ··· S(2)	98.0(2)	C(13)–P–C(19)	104.5(3)
As–C(1)–C(6)	123.3(4)	S(1)–As ··· S(2a)	167.9(1)
C(1)–C(6)–O(1)	123.5(5)	S(2a) ··· As ··· S(2)	114.2(1)
C(6)–O(1)–C(7)	123.1(5)	S(2a) ··· As–C(1)	79.6(2)
O(1)–C(7)–C(12)	124.8(6)	S(2a) ··· As–C(12)	92.1(2)
C(7)–C(12)–As	122.1(4)		

* Atoms a are derived from the transformation $x, y, z \longrightarrow -x, -y, -z$.



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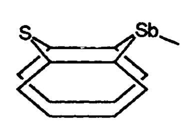

III

In addition to the three covalent As–S and As–C bonds, each arsenic atom exhibits two secondary interactions, one with the second sulfur atom (doubly bonded to phosphorus) of the same dithio ligand and one with a doubly bonded S atom of a neighbouring molecule, thus leading to dimeric associations in the crystal. The dimer (Fig. 2) contains a flattened-chair, eight-membered cyclic $As_2S_4P_2$ moiety (Fig. 3), with two long As ··· S interatomic distances [As ··· S(2a) 3.381 Å], of the same order of magnitude as the transannular As ··· S distances [As ··· S(2) 3.402 Å], but significantly shorter than the sum of van der Waals radii (*ca.* 3.65 Å).[26] This converts the molecular skeleton into a quasi-tricyclic system, which is novel in arsenic–sulfur chemistry. Taking into account these intra- and intermolecular interactions, it is tempting to describe the co-ordination geometry around the five-co-ordinated arsenic as a very distorted trigonal bipyramid, with S(1) and S(2a) in axial positions [S(1)–As ··· S(2a) 167.9(1)°], and S(2), C(1) and C(12) in equatorial positions, with the diphenyldithiophosphinate group acting as a bimetallic triconnective bridge.[7] However, with equatorial angles C(1)–As–C(12) 93.7°, C(12)–As ··· S(2) 98.0° and C(1)–As ··· S(2) 161.4°, deviating so markedly from the ideal value of 120°, this seems inappropriate. A better alternative is to consider the lone pair of arsenic as stereochemically active, occupying an equatorial position in the free space between C(1) and S(2). Consequently the co-ordination polyhedron around arsenic becomes a ψ octahedron. However, this is subject to discussion, since the S(1)–As ··· S(2a) angle [167.9(1)°] is opened through the 'free

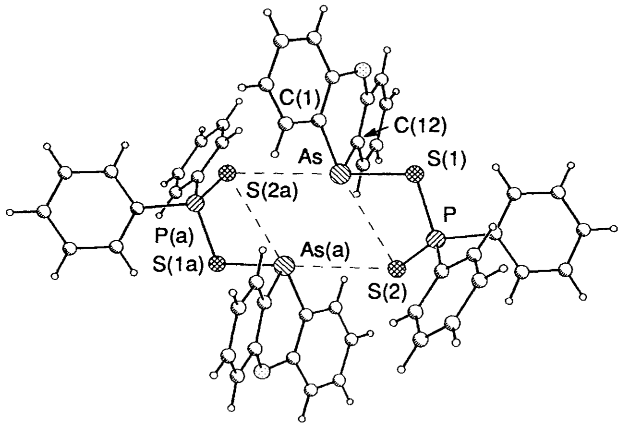

Fig. 2 View of the dimeric association in $[O(C_6H_4)_2AsS_2PPh_2]_2$

Table 6 Atomic coordinates (× 10^4) for $O(C_6H_4)_2AsS_2PPh_2$

Atom	*x*	*y*	*z*
As	363(1)	822(1)	153(1)
P	597(2)	873(1)	−2776(1)
S(1)	901(2)	1471(1)	−1319(1)
S(2)	−372(2)	97(1)	−2541(1)
O(1)	−882(5)	2052(2)	1236(4)
C(1)	1281(7)	1353(3)	1442(5)
C(2)	2722(7)	1220(3)	2080(5)
C(3)	3430(8)	1569(3)	3024(6)
C(4)	2666(9)	2069(3)	3352(6)
C(5)	1254(8)	2215(3)	2750(5)
C(6)	549(7)	1864(3)	1796(5)
C(7)	−1987(7)	1660(3)	668(5)
C(8)	−3475(8)	1859(3)	616(5)
C(9)	−4658(9)	1500(4)	67(6)
C(10)	−4396(8)	939(4)	−399(6)
C(11)	−2928(8)	750(4)	−345(6)
C(12)	−1698(7)	1102(3)	183(5)
C(13)	−486(6)	1300(3)	−4005(4)
C(14)	−1277(7)	1825(3)	−3855(5)
C(15)	−2140(7)	2113(3)	−4828(6)
C(16)	−2242(7)	1875(3)	−5953(6)
C(17)	−1469(8)	1350(3)	−6116(6)
C(18)	−588(7)	1067(3)	−5151(5)
C(19)	2471(7)	792(3)	−3160(5)
C(20)	3157(8)	235(3)	−3164(6)
C(21)	4619(9)	190(4)	−3462(7)
C(22)	5347(9)	699(5)	−3726(7)
C(23)	4678(8)	1249(4)	−3720(6)
C(24)	3241(7)	1306(3)	−3443(5)

equatorial' position and the same geometry could be achieved by involving pure p orbitals of arsenic.

In contrast to $O(C_6H_4)_2AsSAs(C_6H_4)_2O$,[4] which contains two nearly planar phenoxarsine moieties (175.2 and 178.5°), in $O(C_6H_4)_2AsS_2PPh_2$ the non-planarity of the phenoxarsine system (dihedral angle of 154.4°) is preserved [*cf.* 10-chlorophenoxarsine (156.3°)].[1] This suggests that neither the substitution of the halogen atom by the dithiophosphinate group, nor the intra- and inter-molecular interactions results in significant changes of the geometry of the phenoxarsine moiety.

The dimeric structure described above is unique for arsenic(III) 1,1-dithiolate derivatives; the dithiocarbamates and dithiocarbonates[27] which have been studied so far are monomeric. Even the crystal structure of the related phenoxarsin-10-yl tetramethylenedithiocarbamate contains discrete monomeric units.[28] Only halogenoarsenic(III) derivatives, *e.g.* $Br_2AsS_2CNEt_2$,[29] dimerize, however, this is through halogen bridging.

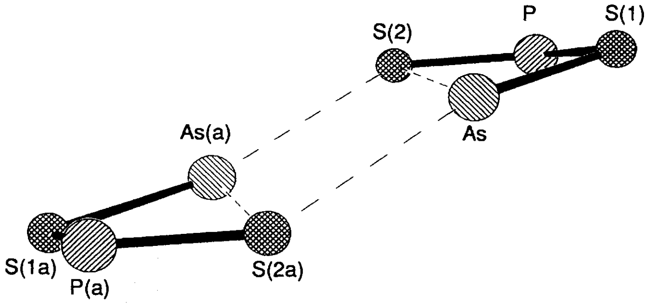

Fig. 3 Chair conformation of the eight-membered $As_2S_4P_2$ cyclic moiety

Experimental

10-Chlorophenoxarsine was prepared from diphenyl ether and $AsCl_3$, in the presence of $AlCl_3$.[30] Sodium dialkyldithiophosphinates were obtained according to literature methods[31,32] from $R_2P(S)P(S)R_2$, elemental sulfur and sodium sulfide. Ammonium diphenyldithiophosphinate was obtained by bubbling gaseous ammonia into the benzene solution of the free acid.[33] Elemental analyses (C, H) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). IR spectra (4000–200 cm^{-1}) were recorded on KBr discs using a Perkin-Elmer 282B spectrometer. 70 eV Electron-impact mass spectra were recorded using a Hewlett-Packard MS-598 instrument. Proton, ^{13}C and ^{31}P NMR spectra were obtained in $CDCl_3$ solution using a Varian Gemini 300 spectrometer operating at 299.949, 50.29 and 121.4 MHz, respectively. Tetramethylsilane and H_3PO_4 (85%) were used as external standards.

Preparation of Phenoxarsin-10-*yl Diorganodithiophosphinate*.—Stoichiometric amounts of $O(C_6H_4)_2$ AsCl and sodium or ammonium dithiophosphinates (an excess of *ca.* 15% of the dithio ligand salt was used for R = Me) in CH_2Cl_2 (20 cm^3) were stirred under reflux for 2 h. The reaction mixture was filtered to remove the resulting NaCl or NH_4Cl and the clear filtrate was evaporated *in vacuo*. The resulting oily products crystallized on addition of *n*-hexane. All the compounds were recrystallized from CH_2Cl_2 or $CHCl_3$–*n*-hexane. Experimental details are given in Table 1.

Crystal Structure of $O(C_6H_4)_2AsS_2PPh_2$.—Crystals suitable for X-ray diffraction were obtained from CH_2Cl_2–EtOH mixture.

Crystal data. $C_{24}H_{18}AsOPS_2$, $M = 492.4$, monoclinic, space group $P2_1/n$, $a = 8.925(6)$, $b = 22.028(8)$, $c = 11.341(5)$ Å, $\beta = 100.70(2)°$, $U = 2191(2)$ Å^3 (by least-squares refinement of 14 reflections in the range $9 < 2\theta < 14°$), $Z = 4$, $D_c = 1.493$ g cm^{-3}, $F(000) = 1000$, λ(Mo-Kα) = 0.710 71 Å, μ(Mo-Kα) = 18.28 cm^{-1}, crystal size 0.24 × 0.26 × 0.40 mm.

Data collection and processing. Siemens P4 diffractometer, ω mode, ω scan speed 4.00–30.00° min^{-1}, graphite-monochromated Mo-Kα radiation; 4918 reflections measured, 3863 unique ($R = 0.0222$), giving 2472 with $I > 2\sigma(I)$. Crystal decay and absorption negligible.

Structure analysis and refinement. The structure was solved by the Patterson method, with full-matrix least-squares refinement[34] with all non-hydrogen atoms anisotropic and hydrogens in idealized positions with a fixed $U_{iso} = 0.06$ Å^2. The weighting scheme $w = 1/[\sigma^2(F) + 0.0005F^2]$ gave satisfactory agreement analyses. Final R and R' $\{= [\Sigma(w|F_o - F_c|)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}\}$ values were 0.0533 and 0.0447. Refined atomic coordinates for the non-hydrogen atoms are collected in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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