

Synthesis and characterisation of organoarsenic(III) xanthates and dithiocarbamates. X-ray crystal structures of $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$, $\text{R} = \text{Me}$ and Ph

Shivram S. Garje^{a,*}, Vimal K. Jain^a, Edward R.T. Tiekink^b

^a Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

^b Department of Chemistry, The University of Adelaide, Adelaide, S.A. 5005, Australia

Received 24 September 1996; revised 27 October 1996

Abstract

Organoarsenic(III) xanthates and dithiocarbamates of the types $[\text{RAs}(\text{S} \curvearrowright \text{S})_2]$ and $[\text{Me}_2\text{As}(\text{S} \curvearrowright \text{S})]$ [$\text{R} = \text{Me}, \text{Et}, \text{Ph}$; $(\text{S} \curvearrowright \text{S}) = \text{S}_2\text{COEt}, \text{S}_2\text{CNR}'_2$ ($\text{R}' = \text{Me}, \text{Et}$)] have been prepared and characterised by arsenic analysis, mass, IR and NMR (^1H and ^{13}C) spectral data. Crystal structure determinations for two of the compounds, $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$ [$\text{R} = \text{Me}$ or Ph], have also been determined and show that the arsenic atoms exist in pyramidal geometries and that the Lewis acidities of the RAs [$\text{R} = \text{Me}$ or Ph] centres are comparable.

Keywords: Arsenic(III); Xanthate; Dithiocarbamate; Crystal structure

1. Introduction

Both inorganic and organometallic 1,1-dithiolates of trivalent arsenic, antimony and bismuth have been the subject of considerable research in the last 15 years or so. The structural diversity in these molecules is quite remarkable and varies between monomeric [1–3], associated supramolecular dimers [4–7] or polymers [8,9]. The geometry of the molecule can also be influenced by the presence of a lone pair of electrons, which may be either stereochemically active [2] or inactive [3,10], and also by subtle changes in the nature of groups attached to the main group element centre and/or 1,1-dithiolate ligand [11,12].

Although a number of inorganic arsenic(III) dithiolates of the type $\text{As}(\text{S} \curvearrowright \text{S})_3$ [$\text{S} \curvearrowright \text{S} = \text{S}_2\text{PR}_2$ ($\text{R} = \text{OR}'$ or R'), S_2CNR_2 , S_2COR] have been isolated and several of them characterised fully by X-ray diffraction methods [13–17], relatively few studies have been made on organoarsenic(III) compounds and, of these, most deal with arylarsenic(III) derivatives [18–23]. There is a paucity of data on alkylarsenic(III) dithiolates [24]. In view of the above we have synthesised and characterised a number of alkylarsenic(III) xanthates and

dithiocarbamates and determined the crystal structures of $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$ [$\text{R} = \text{Me}$ and Ph]; the structure of the $\text{R} = \text{Ph}$ compound has been determined previously [23] but has been redetermined employing contemporary techniques.

2. Results and discussion

Reactions of organoarsenic halides with the sodium salts of dithiocarbamates or potassium salts of xanthates in benzene solutions gave organoarsenic dithiolate compounds (Eqs. (1) and (2)):



($\text{R} = \text{Me}, \text{Et}, \text{Ph}$; $\text{M} = \text{Na}, \text{K}$, $\text{S} \curvearrowright \text{S} = \text{S}_2\text{CNMe}_2$, S_2CNEt_2 , S_2COEt)

All of the compounds are air stable, colourless or pale-yellow liquids or crystalline solids that are soluble in common organic solvents. It is noteworthy that while the dimethylarsenic(III) compounds are stable at room temperature, their analogous dialkylantimony(III) compounds readily disproportionate at room temperature to $\text{RSb}(\text{S} \curvearrowright \text{S})_2$ and R_3Sb [25].

* Corresponding author.

Table 1
Analysis, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for organoarsenic compounds

Compound	% As Found (Calc.)	^1H NMR data δ (ppm)	$^{13}\text{C}\{^1\text{H}\}$ NMR data δ (ppm)
$[\text{Me}_2\text{As}(\text{S}_2\text{CNMe}_2)]$	32.8 (32.3)	1.47 (s, AsMe); 3.49 (s, NMe ₂)	12.4 (AsMe ₂); 45.0 (br, NMe ₂); 196.9 (S ₂ C)
$[\text{Me}_2\text{As}(\text{S}_2\text{CNEt}_2)]$	29.5 (29.6)	1.29 (t, 7.1 Hz, NCH ₂ Me); 1.46 (s, AsMe ₂); 3.92 (q, 7.1 Hz, NCH ₂ -)	12.0 (NCH ₂ Me); 12.5 (AsMe ₂); 48.5 (NCH ₂ -); 194.9 (S ₂ C)
$[\text{Me}_2\text{As}(\text{S}_2\text{COEt})]$	33.0 (33.1)	1.43 (t, 7.1 Hz, OCH ₂ Me); 1.44 (s, AsMe ₂); 4.60 (q, 7.1 Hz, OCH ₂ -)	12.1 (OCH ₂ Me); 13.6 (AsMe ₂); 70.5 (OCH ₂ -); 214.1 (S ₂ C)
$[\text{MeAs}(\text{S}_2\text{CNMe}_2)_2]$	22.4 (22.7)	2.05 (s, AsMe); 3.50 (s, NMe ₂)	23.2 (AsMe); 43.1 (NMe ₂); 198.5 (S ₂ C)
$[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$	19.2 (19.4)	1.30 (t, 7.1 Hz, NCH ₂ Me); 2.04 (s, AsMe); 3.90 (q, 7.1 Hz, NCH ₂ -)	12.1 (NCH ₂ Me); 23.3 (AsMe); 48.2 (NCH ₂ -); 196.2 (S ₂ C)
$[\text{MeAs}(\text{S}_2\text{COEt})_2]$	22.4 (22.5)	1.45 (t, 7.0 Hz, OCH ₂ Me); 1.93 (s, AsMe); 4.64 (q, 7.0 Hz, OCH ₂ -)	13.8 (OCH ₂ Me); 17.4 (AsMe); 71.3 (OCH ₂ -); 216.4 (S ₂ C)
$[\text{EtAs}(\text{S}_2\text{CNMe}_2)_2]$	21.5 (21.8)	1.39 (t, 7.6 Hz, AsCH ₂ Me); 2.48 (q, 7.6 Hz, AsCH ₂ -); 3.46 (s, NMe ₂)	11.4 (AsCH ₂ Me); 30.8 (AsCH ₂ -); 43.4 (NMe ₂); 198.5 (S ₂ C)
$[\text{EtAs}(\text{S}_2\text{CNEt}_2)_2]$	18.6 (18.7)	1.30 (t, 7.1 Hz, NCH ₂ Me); 1.42 (t, 7.6 Hz, AsCH ₂ Me); 2.34 (q, 7.6 Hz, AsCH ₂ -); 3.90 (q, 7.1 Hz, NCH ₂ -)	11.8 (AsCH ₂ Me); 12.1 (NCH ₂ Me); 31.7 (AsCH ₂ -); 48.2 (NCH ₂ -); 197.0 (S ₂ C)
$[\text{EtAs}(\text{S}_2\text{COEt})_2]$	21.7 (21.6)	1.38 (t, 7.6 Hz, AsCH ₂ Me); 1.44 (t, 7.1 Hz, NCH ₂ Me); 2.30 (q, 7.6 Hz, AsCH ₂ -); 4.63 (q, 7.1 Hz, NCH ₂ -)	11.5 (AsCH ₂ Me); 13.7 (NCH ₂ Me); 25.3 (AsCH ₂ -); 71.3 (NCH ₂ -); 216.2 (S ₂ C)
$[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$	16.6 (16.7)	1.25 (t, 7.1 Hz, NCH ₂ Me); 3.85 (q, 7.1 Hz, NCH ₂ -); 7.29–7.94 (m, Ph)	21.1 (NCH ₂ Me); 48.2 (NCH ₂ -); 127.7 (C-3,5); 128.5 (C-4); 133.3 (C-2,6); 144.5 (C-1); 195.5 (S ₂ C)

The organoarsenic 1,1-dithiolate compounds were characterised by arsenic analysis, IR, NMR (^1H , ^{13}C), mass spectral data and crystallography for two compounds. The IR spectra displayed a weak to medium intensity band in the region 340–380 cm^{-1} , assigned to $\nu(\text{As}-\text{S})$ stretching vibrations [21,26,27]. Bands in the region 555–580 cm^{-1} for the alkylarsenic compounds may be assigned to $\nu(\text{As}-\text{C})$ absorptions [28]. The ^1H and ^{13}C NMR data are summarised in Table 1. The ^1H NMR spectra showed the expected integration and peak multiplicities and the ^{13}C NMR spectra exhibited a single set of resonances for organoarsenic and ligand carbons. The C-1 resonance of the RAs group in the dithiocarbamate complexes is deshielded compared with the corresponding xanthate complexes, consistent with the tighter coordination of the former ligands (see later).

Mass spectra of some representative compounds were

recorded which indicated that fragmentation of these compounds takes place via both R and L dissociation routes. The most important fragment ions observed in the spectra have been tentatively assigned to the species indicated in brackets after each mass number; see Table 2.

Full characterisation of two compounds, i.e. $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$ [R = Me and Ph] has been afforded by a single crystal X-ray diffraction study.

The molecular structure of $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ is shown in Fig. 1 and selected interatomic parameters are collected in Table 3. The structure is molecular with the closest non-hydrogen intermolecular contact of 3.526(6) Å occurring between symmetry related S(4) atoms (symmetry operation: $1-x, -y, 2-z$). The arsenic atom forms three close contacts, one to the methyl carbon atom at 1.968(9) Å and two to sulphur

Table 2
Mass spectroscopic data (m/e) for selected compounds

$[\text{Me}_2\text{As}(\text{S}_2\text{CNMe}_2)]$:	225 [molecular ion] ⁺ ; 137 $[\text{Me}_2\text{AsS}]^+$; 120 $[\text{S}_2\text{CNMe}_2]^+$; 105 $[\text{Me}_2\text{As}]^+$.
$[\text{Me}_2\text{As}(\text{S}_2\text{COEt})]$:	211 $[\text{MeAs}(\text{S}_2\text{COEt})]^+$; 196 $[\text{As}(\text{S}_2\text{COEt})]^+$; 137 $[\text{Me}_2\text{AsS}]^+$; 121 $[\text{S}_2\text{COEt}]^+$; 105 $[\text{Me}_2\text{As}]^+$.
$[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$:	371 $[\text{As}(\text{S}_2\text{CNEt}_2)_2]^+$; 243 $[\text{As}(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{CNEt})]^+$; 239 $[\text{MeAs}(\text{S}_2\text{CNEt}_2)]^+$; 148 $[\text{S}_2\text{CNEt}_2]^+$; 107 $[\text{AsS}]^+$; 90 $[\text{MeAs}]^+$.
$[\text{MeAs}(\text{S}_2\text{COEt})_2]$:	211 $[\text{MeAs}(\text{S}_2\text{COEt})]^+$; 182 $[\text{MeAs}(\text{S}_2\text{CO})]^+$; 121 $[\text{S}_2\text{COEt}]^+$; 107 $[\text{AsS}]^+$.
$[\text{EtAs}(\text{S}_2\text{CNEt}_2)_2]$:	371 $[\text{As}(\text{S}_2\text{CNEt}_2)_2]^+$; 252 $[\text{EtAs}(\text{S}_2\text{CNEt}_2)]^+$; 223 $[\text{As}(\text{S}_2\text{CNEt}_2)]^+$; 148 $[\text{S}_2\text{CNEt}_2]^+$; 118 $[\text{SCNEt}_2]^+$; 107 $[\text{AsS}]^+$; 104 $[\text{EtAs}]^+$.
$[\text{EtAs}(\text{S}_2\text{COEt})_2]$:	317 $[\text{As}(\text{S}_2\text{COEt})_2]^+$; 225 $[\text{EtAs}(\text{S}_2\text{COEt})]^+$; 196 $[\text{As}(\text{S}_2\text{COEt})]^+$; 136 $[\text{EtAsS}]^+$; 121 $[\text{S}_2\text{COEt}]^+$; 107 $[\text{AsS}]^+$; 104 $[\text{EtAs}]^+$.
$[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$:	300 $[\text{PhAs}(\text{S}_2\text{CNEt}_2)]$; 152 $[\text{PhAs}]^+$; 116 $[\text{SCNEt}_2]^+$.

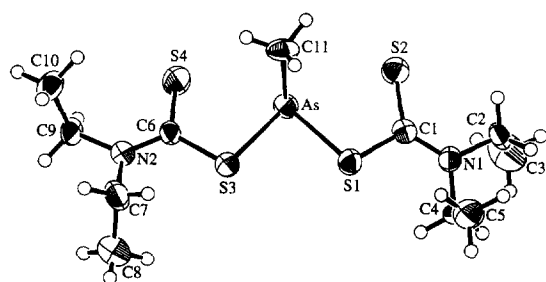


Fig. 1. ORTEP diagram of $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ showing the numbering scheme employed.

atoms, As–S(1) 2.337(2) Å and As–S(3) 2.326(3) Å. If these close contacts were considered to define the coordination geometry, i.e. the dithiocarbamate ligands are monodentate, then the environment about the arsenic atom would be best described as pyramidal with the lone pair of electrons being stereochemically active; the three pyramidal angles in this description range from 82.76(9)° to 98.2(3)°. The two remaining sulphur atoms are in close proximity to the arsenic atom, having As $\cdots$ S(2) and As $\cdots$ S(4) separations of 2.943(3) Å and 2.878(3) Å respectively, and may be responsible for some distortion from the ideal geometry. These distances are significantly within the sum of the van der Waals radii of arsenic and sulphur of 3.74 Å [29]. The disparity in the associated C–S distances, i.e. S(1)–C(1) 1.769(9) Å cf. S(2)–C(1) 1.675(9) Å and S(3)–C(6) 1.757(9) Å cf. 1.663(9) Å indicate, however, that any As $\cdots$ S interaction present would be weak. If the As $\cdots$ S interactions were considered significant, the

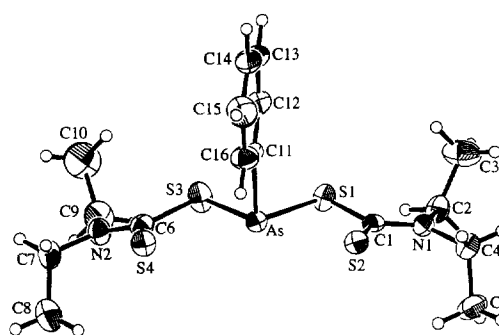


Fig. 2. ORTEP diagram of $[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$ showing the numbering scheme employed.

coordination geometry would be based on a skewed-trapezoidal bipyramidal geometry with one site vacant, i.e. occupied by a lone pair of electrons. Similar geometries have been found in $[\text{Me}_2\text{Sn}(\text{S}_2\text{COEt})_2]$ with the axial positions being occupied by the methyl substituents which lie over the weaker Sn $\cdots$ S interactions [30] and $[\text{Te}(\text{S}_2\text{CO}^i\text{Pr})_2]$ in which the two lone pairs of electrons are implied to lie over the weaker Te $\cdots$ S interactions [31]. A similar coordination geometry described for $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ is found in the structure of $[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$, which is illustrated in Fig. 2; selected interatomic parameters are listed in Table 3.

The unit cell of $[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$ is comprised of discrete molecules with the closest non-hydrogen contact occurring between the C(1) and C(5)' atoms of 3.579(9) Å (symmetry operation: $1 - x, -0.5 + y, 0.5 - z$). The arsenic atom is coordinated by the *ipso*-carbon atom of the phenyl group and two sulphur atoms derived from two essentially monodentate dithiocarbamate ligands. The As–C(11) distance is equal within experimental error to that in $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$. The As–S(1) and As–S(3) separations of 2.323(2) Å and 2.344(2) Å respectively are equivalent to the As–S(3) and As–S(1) separations in $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$, suggesting that the substitution of the arsenic-bound methyl group for a phenyl group does not have a profound influence on the immediate coordination geometry about the arsenic atom; the range of pyramidal angles is 84.59(7)° to 98.5(2)°. The intramolecular As $\cdots$ S interactions are also comparable to those in $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$, with As $\cdots$ S(2) 2.840(2) Å and As $\cdots$ S(4) 2.921(2) Å. There are two other $[\text{PhAs}(\text{1,1-dithiolate})_2]$ structures available in the literature for comparison.

Essentially similar coordination geometries as found in $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$ are evident in the structures of $[\text{PhAs}(\text{S}_2\text{CO}^i\text{Pr})_2]$ [20] and $[\text{PhAs}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_2]$ [19]. An examination of the arsenic to sulphur interactions in the three structures reveals a number of systematic trends. The average $d(\text{As} - \text{S})$ in each of the $[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$, $[\text{PhAs}(\text{S}_2\text{CO}^i\text{Pr})_2]$ and $[\text{PhAs}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_2]$ structures is 2.334(1) Å,

Table 3
Selected bond distances (Å) and angles (deg) for $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$, R = Me and Ph

	$[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$	$[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$
As–S(1)	2.337(2)	2.323(2)
As–S(3)	2.326(3)	2.344(2)
As–C(11)	1.968(9)	1.968(6)
S(1)–C(1)	1.769(9)	1.745(7)
S(2)–C(1)	1.675(9)	1.691(7)
S(3)–C(6)	1.757(9)	1.767(6)
S(4)–C(6)	1.663(9)	1.681(7)
S(1)–As–S(3)	82.76(9)	84.59(7)
S(1)–As–C(11)	98.2(3)	97.9(2)
S(3)–As–C(11)	95.4(3)	98.5(2)
As–S(1)–C(1)	94.7(3)	93.3(2)
As–S(3)–C(6)	93.9(3)	94.2(2)
As–C(11)–C(12)		125.0(6)
As–C(11)–C(16)		116.2(5)
C(12)–C(11)–C(16)		118.8(6)
S(1)–C(1)–S(2)	118.6(6)	118.8(4)
S(1)–C(1)–N(1)	116.7(7)	118.0(5)
S(2)–C(1)–N(1)	124.7(7)	123.2(5)
S(3)–C(6)–S(4)	119.8(6)	119.1(4)
S(3)–C(6)–N(2)	116.6(7)	116.7(5)
S(4)–C(6)–N(2)	123.7(7)	124.2(5)

2.2991(6) Å and 2.314(6) Å respectively and the average As...S separation is 2.881(1) Å, 3.0386(5) Å and 3.158(6) Å respectively. These results can be summarised by considering the average differences between the short and long As–S interactions which are 0.547 Å, 0.740 Å and 0.844 Å respectively. Hence, the relative coordinating abilities of these 1,1-dithiolate ligands can be ranked in the following order: $-\text{S}_2\text{CNEt}_2 > -\text{S}_2\text{CO}^i\text{Pr} > -\text{S}_2\text{P}(\text{O}^i\text{Pr})_2$; a similar observation has been reported previously for tin 1,1-dithiolate compounds [12].

3. Experimental

Infrared spectra were recorded as neat liquids or Nujol mulls between CsI plates on a Perkin–Elmer 783 spectrophotometer calibrated with polystyrene. The NMR spectra were obtained using a Varian XL-300 NMR spectrometer in 5 mm tubes in CDCl_3 solutions. Chemical shifts were referenced to the internal chloroform peak (δ 7.26 and 77.0 ppm) for ^1H and $^{13}\text{C}\{^1\text{H}\}$ respectively. Mass spectra were obtained on a VG Micromass 7070F mass spectrometer.

All reactions were carried out in analytical grade solvents under anhydrous conditions. Sodium ethylxanthate [32], MeAsI_2 , Me_2AsI , EtAsI_2 [33] and PhAsCl_2 [27] were prepared by the literature methods.

3.1. Synthesis of $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$

To a benzene solution of MeAsI_2 (817 mg, 2.37 mmol) was added $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ (1072 mg, 4.76 mmol) with constant stirring for 8 h at room temperature or under reflux conditions for 4 h. Precipitated sodium iodide was filtered through a G-3 filter funnel. The filtrate was evaporated in vacuo to give a pale-yellow paste. This was dissolved in a minimum quantity of benzene (ca. 5 ml) and hexane (20 ml) added, whereupon a pale-yellow crystalline solid deposited which was filtered and recrystallised from toluene–hexane as colourless crystals (636 mg, 69%). Similarly, all other organoarsenic compounds were prepared. Except $[\text{MeAs}(\text{S}_2\text{CNMe}_2)_2]$ (m.p. 120–122 °C), $[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$ (m.p. 76 °C), $\text{EtAs}(\text{S}_2\text{CNMe}_2)_2$ (m.p. 81–83 °C) and $[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$ (m.p. 140 °C), which are solids and were recrystallised from toluene–hexane, all other compounds are pale-yellow liquids.

3.2. Crystal structure determination of $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$ $\text{R} = \text{Me}$ and Ph

Intensity data for colourless crystals were collected at room temperature on a Rigaku AFC6R diffractometer employing $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and the $\omega:2\theta$ scan technique such that θ_{max} was 27.5° (25.0° for $\text{R} = \text{Ph}$); the data sets were corrected for Lorentz

Table 4
Crystal data and refinement details for $\text{RAs}(\text{S}_2\text{CNEt}_2)_2$, $\text{R} = \text{Me}$ and Ph

Compound	$[\text{MeAs}(\text{S}_2\text{CNEt}_2)_2]$	$[\text{PhAs}(\text{S}_2\text{CNEt}_2)_2]$
Formula	$\text{C}_{11}\text{H}_{23}\text{AsN}_2\text{S}_4$	$\text{C}_{16}\text{H}_{25}\text{AsN}_2\text{S}_4$
Formula weight	386.5	448.6
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.506(4)	14.861(3)
b (Å)	13.947(3)	9.535(4)
c (Å)	13.888(3)	16.637(4)
β (°)	103.03(2)	112.60(1)
V (Å ³)	1793.8(9)	2177(1)
Z	4	4
Crystal size (mm ³)	$0.07 \times 0.16 \times 0.32$	$0.05 \times 0.27 \times 0.29$
D_c (g cm ^{−3})	1.431	1.369
$F(000)$	800	928
μ (cm ^{−1})	23.48	19.46
Transmission factors	0.863–1	0.924–1
No. of data collected	4567	4272
θ_{max} (°)	27.5	25.0
No. of unique data	4317	4108
No. of reflections with $I \geq 3\sigma(I)$	1339	1727
R	0.053	0.042
R_w	0.043	0.034
Residual ρ_{max} (e Å ^{−3})	0.47	0.31

Table 5
Fractional atomic coordinates for [MeAs(S₂CNEt₂)₂]

Atom	x	y	z
As	0.3219(1)	0.02519(8)	−0.22341(7)
S(1)	0.2385(3)	0.0375(2)	−0.3946(2)
S(2)	0.3678(3)	0.2168(2)	−0.2996(2)
S(3)	0.2452(3)	−0.1327(2)	−0.2521(2)
S(4)	0.3578(3)	−0.0815(2)	−0.0422(2)
N(1)	0.1959(8)	0.2083(6)	−0.4804(6)
N(2)	0.2647(9)	−0.2541(6)	−0.1044(5)
C(1)	0.2623(10)	0.1632(7)	−0.3978(7)
C(2)	0.215(1)	0.3115(8)	−0.4941(7)
C(3)	0.100(1)	0.3709(8)	−0.4604(10)
C(4)	0.097(1)	0.1583(7)	−0.5627(7)
C(5)	0.174(1)	0.1179(8)	−0.6385(7)
C(6)	0.289(1)	−0.1638(7)	−0.1263(6)
C(7)	0.221(1)	−0.3290(7)	−0.1801(8)
C(8)	0.061(1)	−0.3433(9)	−0.2073(8)
C(9)	0.293(1)	−0.2889(8)	−0.0015(7)
C(10)	0.446(1)	−0.3227(9)	0.0351(8)
C(11)	0.5262(10)	−0.0016(7)	−0.2203(6)

and polarization effects [34] as well as for absorption employing an empirical procedure [35]. The structures were solved by direct methods [36] and refined by a full-matrix least-squares procedure based on F [34]. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions. The refinement was continued until convergence employing sigma weights [34]. Crystal data and final refinement details are given in Table 4. Fractional atomic coordinates are listed in Tables 5 and 6, selected interatomic

Table 6
Fractional atomic coordinates for [PhAs(S₂CNEt₂)₂]

Atom	x	y	z
As	0.28423(6)	0.02722(7)	−0.04301(4)
S(1)	0.2738(1)	0.1290(2)	0.0800(1)
S(2)	0.4715(1)	0.0515(2)	0.0926(1)
S(3)	0.1161(1)	0.0694(2)	−0.1067(1)
S(4)	0.2015(1)	−0.0456(2)	−0.2277(1)
N(1)	0.4353(4)	0.2039(5)	0.2110(3)
N(2)	0.0256(4)	0.0716(6)	−0.2781(3)
C(1)	0.4001(5)	0.1360(6)	0.1353(4)
C(2)	0.3723(5)	0.2783(7)	0.2473(4)
C(3)	0.3550(7)	0.1949(8)	0.3170(5)
C(4)	0.5408(5)	0.2152(7)	0.2618(4)
C(5)	0.5859(6)	0.3360(8)	0.2311(5)
C(6)	0.1074(5)	0.0329(7)	−0.2135(4)
C(7)	0.0101(5)	0.0442(8)	−0.3694(4)
C(8)	0.0459(6)	0.1665(9)	−0.4070(5)
C(9)	−0.0554(6)	0.1419(9)	−0.2648(5)
C(10)	−0.1282(7)	0.044(1)	−0.2549(6)
C(11)	0.2802(5)	−0.1704(6)	−0.0105(4)
C(12)	0.2238(6)	−0.2221(8)	0.0312(4)
C(13)	0.2272(7)	−0.365(1)	0.0529(5)
C(14)	0.2857(8)	−0.4526(9)	0.0316(5)
C(15)	0.3433(7)	−0.4034(8)	−0.0104(5)
C(16)	0.3399(6)	−0.2610(8)	−0.0312(4)

parameters are collected in Table 3 and the crystallographic numbering schemes are shown in Figs. 1 and 2, which were drawn with ORTEP [37] at 45 and 35% probability levels respectively. Copies of the CIFs and observed and calculated structure factors are available from E.R.T.T. (etiekink@chemistry.adelaide.edu.au).

Acknowledgements

One of the authors (S.S.G.) is grateful to DAE for the award of a Senior Research Fellowship. The authors thank Dr. J.P. Mittal, Director Chemistry Group and Dr. C. Gopinathan, Head Chemistry Division for encouragement. The facilities provided by RSIC, IIT Bombay for recording the NMR spectra and the financial support of the Australian Research Council for the crystallographic facility are gratefully acknowledged.

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