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Synthesis and structural characterization of phenoxarsin-10-yl dithiocarbamates. $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$, a compound containing an asymmetric mononuclear biconnective 1,1-dithiolato ligand

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Abstract

Phenoxarsin-10-yl dithiocarbamates $O(C_6H_4)_2AsS_2CX$ ($X = NMe_2$, NEt_2, $N(CH_2CH)_2$, $N(CH_2CH_2)_2$ or $N[(CH_2)_3CH(CH_3)CH_2]$) have been prepared by the reaction between $O(C_6H_4)_2AsCl$ and sodium dithiocarbamates. The compounds were characterized by IR, mass and NMR (^1H and ^{13}C) spectroscopy. The molecular structure of $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$ was determined using single-crystal X-ray diffraction. The compound is monomeric and contains an asymmetric monometallic biconnective dithiocarbamato unit (As–S(1), 2.277(1), Å; As ··· S(2), 3.183(3) Å). The double-bond character of the C–N bond (1.318(5) Å) is in agreement with the NMR data. The dihedral angle (155.2°) of the phenoxarsine moiety is almost unaffected by substitution of chlorine by the dithiocarbamato ligand.

Keywords: Arsenic; Dithiocarbamates; Phenoxarsine; Group 15

1. Introduction

The development of the chemistry of metal dithiocarbamates has been continuously stimulated by either the potential applications (e.g. fungicides, herbicides and vulcanization accelerators) or their interesting structural behavior which results from the various coordination patterns of the 1,1-dithio ligands. Early results (until 1977) have been reviewed by Coucouvanis [1,2], and numerous other contributions to this topic have been added during the past 20 years. Our interest in the structure of main group metal derivatives of dithiolato ligands, mainly arsenic and antimony compounds [3–7], has prompted us to investigate organoarsenic dithiocarbamates. So far, several structures of inorganic arsenic(III) dithiocarbamates, e.g. $As(S_2CNEt_2)_3$ [8,9], $BrAs(S_2CNEt_2)_2$ [10], and $Br_2As(S_2CNEt_2)$ [11], containing mononuclear biconnective (bidentate) dithio ligand units have been described. In the solid state, the dibromoarsenic(III) derivative was found to be associated into dimers through halogen bridges. More recently the structures of $(CH_2S)_2AsS_2CN(CH_2CH_2)_2O$ [4] and $(CH_2S)_2AsS_2CN[(CH_2)_3C(O)]$ [5] have been described as containing mononuclear monoconnective dithio ligands. However, a reinvestigation of all the interatomic distances at arsenic has revealed As ··· S(=C) interactions (3.007 Å and 2.943 Å respectively), so that in both compounds the coordination pattern of the dithiocarbamate ligand should be described as asymmetric biconnective. Although several studies on organoarsenic dithiocarbamates have been reported [1,2], only two X-ray structure determinations have been performed, i.e. $PhAs(S_2CNEt_2)_2$ (monomeric) [12] and the unexpected complex $MeAs(S_2CNMe_2)I_2$, which contains a two-dimensional network built through iodine bridges [13]. Both of these monoorganoarsenic(III) derivatives contain biconnective dithiocarbamato ligands.

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Table 1
Analytical data, physical properties and IR spectra for phenoxarsin-10-yl dithiocarbamates

	Compound	Formula	C [a] (%)	H [a] (%)	Yield (%)	Melting point (°C)	IR data (cm^{-1}) ν(CN)	ν(CS$_2$)	ν(COC)	ν(AsS)
1	$O(C_6H_4)_2AsS_2CNMe_2$	$C_{15}H_{14}AsNOS_2$ (Formula weight 363.3)	48.88 (49.59)	3.81 (3.88)	89	162–164	1425s	970s	1260vs 1220vs 1060m	390mw 380mw
2	$O(C_6H_4)_2AsS_2CNEt_2$	$C_{17}H_{18}AsNOS_2$ (Formula weight 391.4)	51.93 (52.17)	4.52 (4.64)	90	121–123	1420vs	1000m 975m	1260vs 1225s 1060m	390ms
3	$O(C_6H_4)_2AsS_2CNC_4H_6$ [b]	$C_{17}H_{14}AsNOS_2$ (Formula weight 387.3)	53.01 (52.71)	3.38 (3.64)	87	171–173	1440vs	1000ms 940ms	1260s 1215s 1055m	385m 378m
4	$O(C_6H_4)_2AsS_2CNC_4H_8$ [c]	$C_{17}H_{16}AsNOS_2$ (Formula weight 389.3)	51.83 (52.44)	4.11 (4.14)	88	177–178	1440vs 1420s	1000m 952ms	1260s 1215s 1060m	385m 375m
5	$O(C_6H_4)_2AsS_2CNC_5H_{12}$ [d]	$C_{18}H_{20}AsNOS_2$ (Formula weight 405.4	52.95 (53.33)	5.08 (4.97)	89	184–186	1420vs	985m 950m	1260s 1220s 1060s	375m 370m

[a] Required values are given in parentheses.
[b] 3-Pyrrolinyl derivative.
[c] Pyrrolidinyl derivative.
[d] 3-Methyl-piperidinyl derivative.

In the present paper the synthesis and characterization of some phenoxarsin-10-yl dithiocarbamates is described in order to add to our knowledge concerning the coordination pattern of the ligands involving sulfur atoms in primary and secondary bonds, and to compare the molecular structure of the related $O(C_6H_4)_2AsS_2PPh_2$, which exists as a dimer with associations through binuclear triconnective dithiophosphinato units. The structural investigation of phenoxarsin-10-yl derivatives might also provide further insight concerning the geometry of the phenoxarsine moiety, i.e. the angular vs. planar behavior of the two halves of this system (for a review of the structural data already available see Ref. [7]).

2. Results and discussion

Phenoxarsin-10-yl dithiocarbamates $O(C_6H_4)_2AsS_2CX$ (**1–5**) were prepared by metathesis from $O(C_6H_4)_2AsCl$ and NaS_2CX.

All compounds are stable yellowish crystalline solids, sparingly soluble in MeOH and EtOH and soluble in $CHCl_3$. They were characterized by IR spectroscopy, mass spectroscopy (MS), and ^1H and ^{13}C NMR spectroscopy. The molecular structure of the phenoxarsin-10-yl pyrrolidinyldithiocarbamate was determined by single-crystal X-ray diffraction.

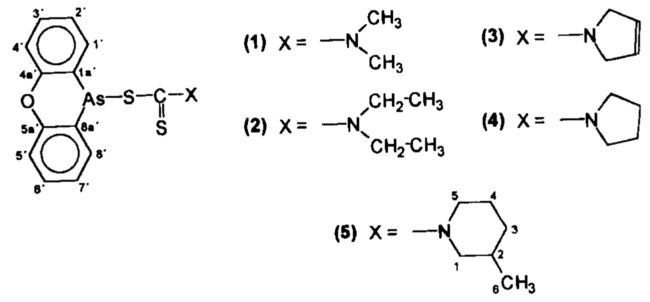


Table 2
70 eV electron impact mass spectra of phenoxarsin-10-yl dithiocarbamates

	m/z (intensity (%))			
	1 X ≡ NMe$_2$	2 X ≡ NEt$_2$	3 X ≡ NC$_4$H$_6$	4 X ≡ NC$_4$H$_8$
$O(C_6H_4)_2AsS_2CX^+$	363(13)	391(15)	387(4)	389(4)
$O(C_6H_4)_2As^+$	243(100)	243(100)	243(100)	243(100)
$C_{12}H_8O^+$	168(49)	168(67)	168(39)	168(99)
$C_{11}H_7^+$	139(28)	139(42)	139(25)	139(80)
S_2CX^+	120(8)	148(38)	144(30)	146(23)
SCX^+	88(41)	116(20)	112(8)	114(23)
AsS^+	107(1)	107(1)	107(1)	107(4)

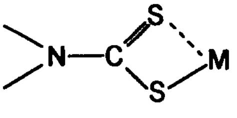
Table 3
^{1}H NMR data [a] (in $CDCl_3$)

Compound	Chemical shift [b] (ppm); coupling constants (Hz)							
	H(1′,8′)	H(3′,6′)	H(4′,5′)	H(2′,7′)	CH_3	NCH_2	NCH_2CH	NCH_2CH_2
1	8.00dd; $^{3}J = 7.4$, $^{4}J = 1.8$	7.44ddd; $^{3}J = 8.6$, $^{3}J = 7.2$, $^{4}J = 1.8$	7.28dd; $^{3}J = 8.6$, $^{4}J = 1.3$	7.17ddd; $^{3}J = 7.4$, $^{3}J = 7.2$, $^{4}J = 1.3$	3.45s 3.25s			
2	8.01dd; $^{3}J = 7.4$, 8u4$J = 1.7$	7.43ddd; $^{3}J = 8.4$ $^{3}J = 7.2$, $^{4}J = 1.7$	7.27dd; $^{3}J = 8.4$, $^{4}J = 1.3$	7.17ddd; $^{3}J = 7.4$, $^{3}J = 7.2$, 8u4$J = 1.3$	1.24t; $^{3}J = 7.1$, 1.15t; $^{3}J = 7.1$	3.94q; $^{3}J = 7.1$ 3.63q; $^{3}J = 7.1$		
3	7.99dd; $^{3}J = 7.3$, $^{4}J = 1.6$	7.43ddd; $^{3}J = 8.2$, $^{3}J = 7.1$, $^{4}J = 1.6$	7.27dd; $^{3}J = 8.2$, $^{4}J = 1.2$,	7.16ddd; $^{3}J = 7.3$, $^{3}J = 7.1$, $^{4}J = 1.2$		4.53m 4.23m	5.85m 5.74m	
4	7.99dd; $^{3}J = 7.5$ $^{4}J = 1.7$	7.42ddd; $^{3}J = 8.2$, $^{3}J = 7.0$, $^{4}J = 1.7$	7.26dd; $^{3}J = 8.2$, $^{4}J = 1.2$	7.16ddd; $^{3}J = 7.5$, $^{3}J = 7.0$, $^{4}J = 1.2$		3.82m 3.49m		1.93m

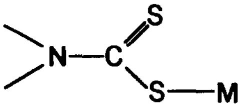
[a] For the numbering scheme see structures **1** and **2**.
[b] Abbreviations used: s, singlet; d, doublet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet; q, quartet.

2.1. IR spectra

Characteristic IR bands for compounds **1–5** are listed in Table 1. All compounds exhibit medium to strong absorptions in the 1440–1420 and 1000–950 cm^{-1} regions owing to carbon–nitrogen and carbon–sulfur stretching vibrations. In a previous study it was suggested that the number of $\nu(CS_2)$ absorptions is indicative of the coordination pattern of the dithiocarbamato moiety [14], i.e. one band for biconnective coordination (**6**), and two bands for monoconnective behavior (**7**):



(6)



(7)

On this basis, mononuclear monoconnective dithiocarbamato groups might be proposed for **2–5**, while biconnective coordination is expected for **1**. However, structural assignments using IR data only should be looked at cautiously because of the complexity of the spectra, and other spectroscopic studies are needed to confirm the proposed structures.

All the title compounds showed characteristic bands for ν(COC) vibrations of the phenoxarsine moiety, and medium to weak absorptions in the 390–370 cm^{-1} region assigned to the As–S stretching vibrations [15].

2.2. Mass spectra

The 70 electron impact (EI) mass spectra (Table 2) for **1–4** exhibit the corresponding molecular ion, while the base peak is always $O(C_6H_4)_2As^+$, resulting from

Table 4
^{13}C NMR data [a]

Compound	Chemical shift (ppm)												
	C(4a′,5a′)	C(1′,8′)	C(3′,6′)	C(2′,7′)	C(1a′,8a′)	C(4′,5′)	NCS_2	CH_3	NCH_2	NCH_2CH	NCH_2CH_2		
1 [b]	155.6	135.5	132.0	123.6	119.1	118.3	196.0	45.0 43.2					
2 [b]	155.7	135.5	131.9	123.6	119.2	118.2	194.8	12.7 11.6	49.1 48.3				
3 [b]	155.4	135.4	132.0	123.6	118.7	118.3	192.4		61.0 57.9	125.9 124.8			
4 [b]	155.4	135.4	131.8	123.5	118.9	118.1	191.7		54.8 52.1		26.39 24.95		
								C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
5 [c]	154.9	135.4	132.1	123.6	119.3	117.8	192.5	57.6	31.6	24.7	31.8	51.4	18.4

[a] For the numbering scheme see structures 1–5.
[b] In $CDCl_3$.
[c] In DMSO-d_6.

the first fragmentation of the phenoxarsin-10-yl dithiocarbamate molecule. Other fragments characteristic for phenoxarsin-10-yl derivatives [7,15,16], dithiocarbamato moiety as well as AsS^+, were also observed.

2.3. NMR spectra

The ^1H and ^{13}C NMR data for **1**–**5** are listed in Tables 3 and 4 respectively. The ^1H NMR spectra of **1**–**4** exhibit the expected pattern in the aromatic region for the phenoxarsin-10-yl moiety, i.e. four resonances in a 1 : 1 : 1 : 1 integral ratio, with a multiplicity determined by proton–proton couplings. Resonances assigned to non-equivalent organic groups bound to nitrogen are observed at a higher field, i.e. two singlets (CH_3) for **1**, and two quartets (NCH_2CH_3) and two triplets (NCH_2CH_3) for **2**. For the heterocyclic dithiocarbamates **3** and **4** this region is more complicated, but again the pattern of the observed resonances suggests the non-equivalence of the CH_2 and CH protons respectively. This is also supported by the number of resonances observed in the ^{13}C NMR data (Table 4). The non-equivalence of the organic groups attached to nitrogen atom is a common feature for some metal dithiocarbamates [2,17–19]. It was interpreted in terms of a higher contribution of structure **8** vs. structure **9**, the character of partial double bond between carbon and nitrogen atoms preventing the free rotation about this bond:

(8) **(9)**

2.4. Molecular structure of $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$

In order to gain greater insight into the structural details of the series of **1**–**5**, the structure of the heterocyclic dithiocarbamate derivative **4** was obtained by single crystal X-ray structural analysis.

Selected bond lengths and angles for $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$ are listed in Table 5, and the molecular structure with the numbering scheme is illustrated in Fig. 1.

The dithiocarbamato moiety is covalently bound to the arsenic atom through its S(1) atom (As–S(1), 2.277(1) Å) but exhibits a secondary interaction through the S(2) atom (As · · · S(2), 3.183(3) Å; cf. the sum of van der Waals radii, Σ_{vdW}(As, S) = 3.85 Å [20]). As a consequence, the coordination pattern of the 1,1-dithio ligand is best described as asymmetric mononuclear

Table 5
Selected bond distances (Å) and angles (°) in $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$

Bond distances	
As–S(1)	2.277(1)
As · · · S(2)	3.183(3)
As–C(1)	1.953(4)
As–C(12)	1.936(3)
C(1)–C(6)	1.381(5)
C(6)–O	1.381(4)
O–C(7)	1.387(5)
C(7)–C(12)	1.389(5)
C–S(1)	1.783(4)
C–S(2)	1.672(4)
C–N	1.318(5)
N–C(13)	1.464(5)
N–C(16)	1.486(6)
Bond angles	
S(1)–As–C(1)	89.7(1)
S(1)–As–C(12)	99.0(1)
S(1)–As · · · S(2)	64.9(1)
C(1)–As · · · S(2)	154.6(2)
C(12)–As · · · S(2)	89.7(1)
C(1)–As–C(12)	93.1(2)
As–C(1)–C(6)	123.1(3)
C(1)–C(6)–O	124.0(3)
C(6)–O–C(7)	122.3(3)
O–C(7)–C(12)	124.8(3)
C(7)–C(12)–As	122.4(3)
As–S(1)–C	100.0(1)
S(1)–C–S(2)	122.4(2)
S(1)–C–N	113.3(3)
S(2)–C–N	124.3(3)
C–N–C(13)	123.4(3)
C–N–C(16)	124.9(3)
C(13)–N–C(16)	111.7(3)

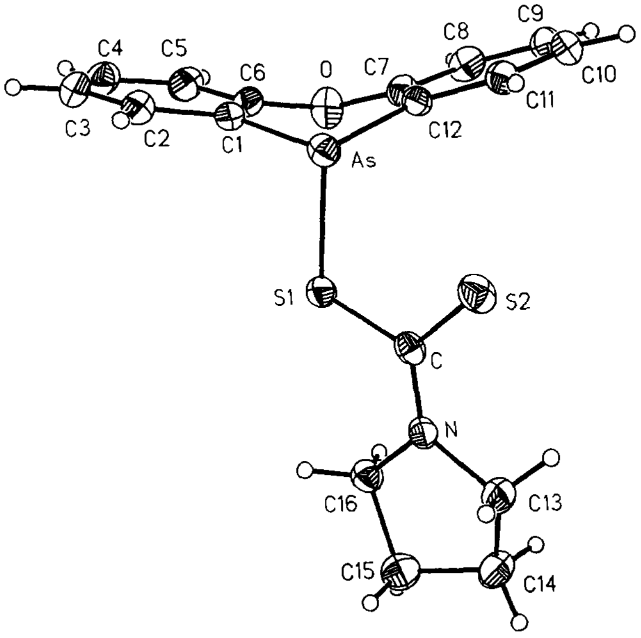


Fig. 1. ORTEP drawing of the monomeric structure of $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$.

biconnective. The described carbon–sulfur bond lengths, i.e. C–S(1), 1.783 Å and C–S(2), 1.672(4) Å, are indicative for single and double bonds respectively. Two different sets of nitrogen–carbon bonds are observed: the single N–C(13) and N–C(16) bonds (average, 1.475 Å) in the heterocycle are significantly longer than the exocyclic N–C bond (1.318(5) Å), suggesting a double-bond character for the latter (C=N, about 1.32 Å [21]). This is consistent with the NMR data. Similar C–N bond lengths have been reported for $As(S_2CNEt_2)_3$ [9], $Br_2As(S_2CNEt_2)$ [11] and $PhAs(S_2CNEt_2)_2$ [12] (1.33(2) (mean), 1.31(2) and 1.345(3) (mean) Å respectively), all of them having mononuclear biconnective dithio ligand units. The approximately sp^2 hybridization at the nitrogen atom is also supported by the angles at nitrogen (Σ(C–N–C) = 360°), and the planarity of the C(13)C(16)NCS(1)S(2) fragment (deviations from the best plane: C(13), −0.037; C(16), 0.030; N, 0.008; C, 0.013; S(1), −0.033; S(2), 0.020). The C–N bond length is not affected by the coordination pattern of the dithiocarbamato ligand, i.e. 1.33(2) (mean), 1.31(2) and 1.345(3) (mean) Å, for As-$(S_2CNEt_2)_3$ [9], $Br_2As(S_2CNEt_2)$ [11] and $PhAs(S_2CNEt_2)_2$ [12] respectively, all of them containing monometallic biconnective (bidentate) dithio ligand units.

The coordination geometry at the arsenic center can be described as a slightly distorted trigonal pyramid, with the arsenic atom in the apical position. However, if the As ··· S(2) secondary interaction is taken into account the coordination geometry at the arsenic center might be described as distorted trigonal bipiramid (Fig. 2). The S(2) and C(1) atoms are placed in axial positions (C(1)–As ··· S(2), 154.6(2)°), while the equatorial positions are occupied by S(1), C(12) and the electron lone pair of the arsenic atom. This is supported, not only by the angles at the arsenic center, but also by the orientation of the S(1)CS(2)N fragment which brings the atom S(2) into a *trans* position to the C(1) atom, leading to a large free space opposite to S(1) and C(12) atoms. The acute angle S(1)–As ··· S(2) (64.9(1)°) is due to the small dithocarbamate ligand "bite".

The dihedral angle (the angle between the two C_6 planes) in the phenoxarsine moiety (155.2(2)°) is almost not affected by the exchange of the chlorine atom (156.3° in 10-chlorophenoxarsine [22]) by the dithiocarbamate moiety. This indicates that the substitution of the halogen by our 1,1-dithiolato ligand does not result in a significant change in the phenoxarsine geometry. However, by contrast, $O(C_6H_4)_2As–S–As(C_6H_4)_2O$ contains two nearly planar (dihedral angles of 175.2 and 178.5°) phenoxarsine moieties [23].

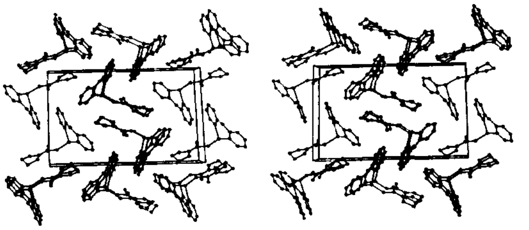


Fig. 2. Stereoscopic view of the unit cell of $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$. View from the *a* axis.

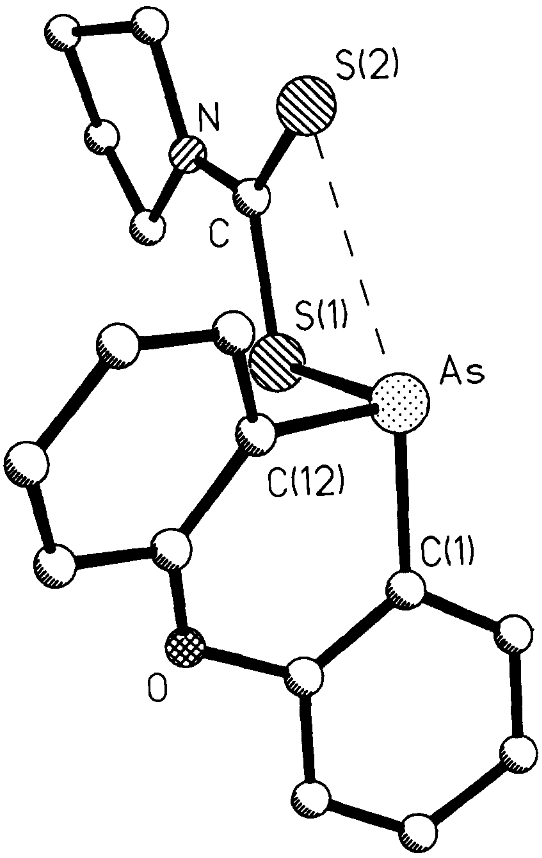


Fig. 3. View of the $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$ molecule showing the coordination geometry around the arsenic atom.

Large variations in dihedral angles in phenoxarsine derivatives are common. On the basis of the bending and stretching force constants, Meyers et al. [24] predicted easy flexing in the phenoxarsine rings since very large changes in dihedral angles can occur without large alterations in the energy of the compounds.

In comparison with the diphenyldithiophosphinato analogue, $O(C_6H_4)_2AsS_2PPh_2$, which was found to contain dimeric associations through weak intramolecular and intermolecular As ··· S secondary interactions, the unit cell of 4 contains discrete monomeric $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$ molecules (mean closest contacts of 3.629 and 3.765 Å between the AsS_2CN and phenyl (C(7)–C(12)) respectively, with their centrosymmetrically related counterparts). A stereoscopic view of the lattice is shown in Fig. 3.

3. Experimental details

3.1. Materials

10-Chlorophenoxarsine was prepared from diphenylether and $AsCl_3$ in the presence of anhydrous $AlCl_3$ [25]. The sodium dithiocarbamates used in this work were obtained according to literature methods [26]. IR spectra (4000–200 cm^{-1}) were obtained in KBr disks using a Perkin–Elmer 283B spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or $CDCl_3$–dimethysulfoxide-d_6 (DMSO-d_6) solutions using Varian VXR 300S and Varian Gemini 200 spectrometers, operating at 299.949 and 50.29 MHz respectively. Tetramethysilane was used as external standard. 70 eV EI mass spectra were recorded using a Hewlet–Packard MS–gas chromatography 598 instrument.

3.2. General procedure for the synthesis of phenoxarsin-10-yl dithiocarbamates

10-Chlorophenoxarsine and sodium dithiocarbamate (10% excess) in a 1 : 1 methanol : water mixture were stirred for 4 h at room temperature. The insoluble solid was filtered off, washed with methanol : water (2 : 1) and extracted with CH_2Cl_2. After evaporation of the solvent, the resulting solid was dried over silica gel. Elemental analysis, yields and melting points are given in Table 1.

3.3. Crystal structure determination of $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$

3.3.1. Crystal data

$C_{17}H_{16}AsNOS_2$; $M = 389.3$; monoclinic; $a = 6.723(2)$, $b = 19.893(5)$, $c = 12.718(3)$ Å; $\beta = 105.22(1)°$; $V = 1641.3(7)$ Å^3; $Z = 4$; $D_c = 1.576$ g cm^{-3}; $F(000) = 792$; space group, $P2_1/n$; Mo Kα radiation; $\lambda = 0.71073$ Å; μ(Mo Kα) = 2.309 mm^{-1}; crystal size, 0.35 × 0.35 × 1.05 mm.

3.3.2. Structure determination

Suitable crystals of the title compound were obtained from a $CHCl_3$–hexane mixture. Data were collected at room temperature on a Siemens P4 four-cycle diffractometer for 3719 reflections in the ω mode of which 2453 were independent ($R_{int} = 2.99\%$) and 2002 ($F > 3.0\sigma(F)$) were used in the full-matrix least-squares refinement [27]. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically and hydrogen atoms located and their coordinates refined with common fixed isotropic U values ($U = 0.05$ Å^2 (phenoxarsine), $U = 0.07$ Å^2 (pyrrolidinyl)). ψ-scan-based empirical absorption corrections were applied [27].

Table 6
Atomic coordinates (× 10^4) and equivalente isotropic displacement coefficients (Å^2 × 10^3)

	x	y	z	U(eq)
As	1736(1)	1330(1)	2351(1)	46(1)
S(1)	3265(2)	518(1)	1572(1)	46(1)
S(2)	−657(2)	−66(1)	1941(1)	58(1)
N	1959(5)	−700(1)	1049(2)	42(1)
O	6400(4)	1428(1)	3935(2)	62(1)
C	1446(5)	−146(2)	1483(3)	41(1)
C(1)	4020(6)	1937(2)	2352(3)	45(1)
C(2)	3773(8)	2436(2)	1552(3)	56(2)
C(3)	5360(9)	2853(2)	1489(4)	68(2)
C(4)	7236(9)	2782(2)	2237(4)	68(2)
C(5)	7520(7)	2313(2)	3049(4)	60(2)
C(6)	5921(6)	1894(2)	3101(3)	47(2)
C(7)	4923(6)	1163(2)	4400(3)	48(2)
C(8)	5667(8)	935(2)	5467(4)	61(2)
C(9)	4308(9)	665(2)	5999(3)	67(2)
C(10)	2252(8)	618(2)	5498(3)	59(2)
C(11)	1516(7)	825(2)	4439(3)	49(2)
C(12)	2850(6)	1089(2)	3867(3)	42(1)
C(13)	773(7)	−1324(2)	949(3)	54(2)
C(14)	2182(8)	−1840(2)	668(4)	65(2)
C(15)	3492(8)	−1457(2)	84(4)	64(2)
C(16)	3798(7)	−774(2)	618(3)	51(2)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The final R values are $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 3.45\%$ and $wR = [\Sigma w(|F_o - F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 2.92\%$ ($R = 4.58\%$ and $wR = 3.00\%$ for all data) with weights $w^{-1} = \sigma^2$(F); goodness of fit, 1.59. The residual electron density from a final difference Fourier synthesis was in the range 0.25–0.56 electrons Å^3. Refined values for the atomic coordinates are given in Table 6.

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