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Synthesis and Characterization of Phenoxarsin-10-yl 2-R_2N-Cyclopent-1-ene-1-carbodithioate ($R=H$, C_2H_5, cyclo-$C_6H_{11}CH_2$) and the Crystal and Molecular Structure of the 2-Amino ($R=H$) Derivative*

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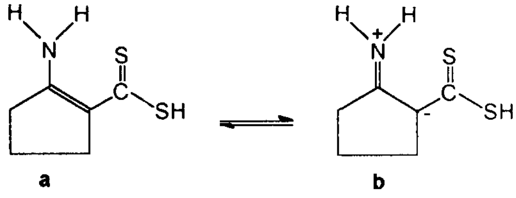
Phenoxarsin-10-yl derivatives of 2-aminocyclopent-1-ene-1-carbodithioic acid, (ACDA), and its *N*-alkyl derivatives $O(C_6H_4)_2AsS_2C—C_5H_6—NHR$-2 ($R=H$, CH_2CH_3, $CH_2C_6H_{11}$), have been prepared by reacting $O(C_6H_4)_2AsCl$ with the corresponding ACDA 1,1-dithioic acid. The compounds were obtained by stirring stoichiometric amounts of the reagents in ethanol, over 24 h, at room temperature. The scale of the preparations were in the order of 2 mmol and the yields of the compounds *ca* 75%. The reactions were carried out in absolute ethanol. The compounds were characterized by IR, mass and NMR (^1H, ^{13}C) spectroscopy. The molecular structure of $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2 was determined using X-ray diffractometry, achieving an *R*-value of 6.3%; this compound is monomeric and contains an asymmetric monometallic biconnective 1,1-dithiolato ligand [As—S(1) 2.272(2) Å, As · · · S(2) 3.125(2) Å]. An *intra*molecular hydrogen bond is established between one hydrogen atom of the NH_2 group and the sulfur [S(2)] atom involved in the secondary interaction to arsenic. The dihedral angle (150.3(3)°) of the phenoxarsine moiety is practically unaffected by substitution of chlorine on arsenic by the carbodithioato ligand.

Keywords: phenoxarsine; ACDA; carbodithioates; arsenic

INTRODUCTION

2-Aminocyclopent-1-ene-1-carbodithioic acid (ACDA) and its *N*- or *S*-alkyl derivatives have been reported to exhibit antifungal properties, and it was suggested that this biological behavior might be related to the ability of such compounds to form metal complexes.[1] The molecular structure of ACDA was investigated by X-ray diffractometry and an equilibrium between the mesomeric forms **a** and **b** (with a high contribution of **b**) has been proposed[2] (Eqn. [1]).



[1]

This ligand can exhibit various coordination patterns, e.g. monometallic monoconnective (monodentate—structure **c**), *S*,*S*-monometallic biconnective (bidentate—structure **d**) or *N*,*S*-monometallic biconnective (bidentate—structure **e**). Most of the studies on metal complexes of ACDA and its *N*-substituted derivatives reported so far have been concerned with transition metals, and either structure **d** or **e** was

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* Supplementary X-ray crystallographic data are lodged with the Cambridge Crystallographic Data Centre, UK.

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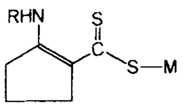

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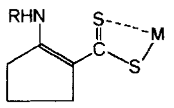

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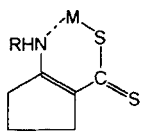


e

proposed on the basis of spectroscopic data (IR, ES, NMR).[3-6]

By contrast, knowledge of main group metal derivatives is scarce. Complexes of the type ML_3 [M = In(III),[7] As(III), Sb(III),[8] and Bi(III)[9,10]] containing *S,S*-monometallic biconnective ACDA ligands have been described, and an X-ray diffraction study of tris[2-ethylamino)-cyclopent-1-ene-1-carbodithioato]bismuth(III) supports this coordination pattern.[9] However, the spectral behavior of the diphenylantimony(III) derivatives of ACDA has suggested a monometallic monoconnective (monodentate) coordination of the 1,1-dithiolato ligand (structure **c**).[11] A similar coordination pattern was recently established by X-ray diffractometry for an inorganic As(III) complex $(CH_2S)_2AsS_2C—C_5H_6—NH_2$-2, and proposed for other analogous As(III) and Sb(III) complexes on the basis of IR and NMR (^1H and ^{13}C) data.[12]

We wish to report here the synthesis and spectroscopic characterization of some phenoxarsin-10-yl derivatives of ACDA and its *N*-alkyl (i.e. ethyl and methylcyclohexyl) analogue, as well as the crystal and molecular structure of $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2, containing a monometallic monoconnective ACDA-type ligand. The coupling of an organoarsenic moiety with a 1,1-dithiolato ligand, both exhibiting biological properties,[1,13] might result in interesting synergistic effects and useful applications.

EXPERIMENTAL

Materials and methods

The starting materials were of reagent or analytical grade and were used without further purification. 10-Chlorophenoxarsine was prepared from diphenyl ether and $AsCl_3$ in the presence of anhydrous $AlCl_3$.[14] ACDA and its *N*-alkyl derivatives, (i.e. ethyl and methylcyclohexyl) used in this work were obtained according to literature methods.[15]

Physical measurements

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 $CDCl_3$/DMSO-d_6 solutions using Varian VXR 300S and Varian Gemini 200 spectrometers, operating at 299.949 and 50.29 MHz, respectively. TMS was used as external standard. Electron-impact (70 eV) mass spectra were recorded using a Hewlett–Packard MS/GC 598 instrument.

General procedure for the preparation of phenoxarsin-10-yl derivatives

Stoichiometric amounts of 10-chlorophenoxarsine and the 1,1-dithioic acid were mixed in ethanol and stirred over 24 h. In a typical experiment, 557 mg of 10-chlorophenoxarsine (2 mmol) in 20 ml of absolute ethanol was added to 2 mmol of ACDA or the corresponding ACDA alkyl derivative, also in 20 ml of absolute ethanol. The reaction mixture was stirred at room temperature for 24 h and then filtered, yielding a solid. The solid obtained was washed with methanol and dried in a desiccator in the normal laboratory line vacuum over silica gel. Elemental analysis, yields and melting points are given in Table 1.

Crystal structure determination of $O(C_6H_4)_2AsS_2CC_5H_6—NH_2$-2

Crystal data

$C_{18}H_{16}AsNOS_2$, *M* 401.4, triclinic, $a = 8.028(3)$ Å, $b = 16.251(7)$ Å, $c = 6.900(3)$ Å, $\alpha = 93.63(3)°$, $\beta = 109.31(3)°$, $\gamma = 86.32(3)°$, $V = 846.9(4)$ Å^3, $Z = 2$, $D_c = 1.574\ g\ cm^{-3}$, $F(000) = 408$, space group *P*-1, CuKα radiation, $\lambda = 1.54178$ Å, μ(CuKα) 5.038 mm^{-1}, crystal size 0.40 mm × 0.24 mm × 0.08 mm.

Structure determination

Suitable crystals (yellowish plates) of the title compound were obtained by solvent diffusion in a $CHCl_3$–hexane mixture, at room temperature. Data were collected on a Nicolet P3/F four-cycle diffractometer with a nickel filter for 2190 reflections in the $2\theta/\theta$ scan mode, of which 1986 were independent ($R_{int} = 5.80\%$) and 1810 ($F > 3.0\sigma(F)$) were used in the full-matrix least-squares refinement.[16] The structure was solved by direct methods.

The final *R* values are $R = \Sigma|F_o - F_c|/\Sigma|F_o| =$ 6.30% and $wR = [\Sigma w(|F_o - F_c|)^2/\Sigma w|F_o|^2]^{1/2} =$

Table I Analytical data, physical properties and infrared spectra for phenoxarsin-10-yl complexes

		Elemental analysis (%)				Infrared data (cm^{-1})					
Compound	Formula[a]	C	H	Yield (%)	M.p. (°C)	ν(NH)	$\nu(NH_2 + C{=}C)$	$\nu(CN + C{=}S)$	$\nu(CS_2)$	ν(COC)	ν(AsC)
(1) $O(C_6H_4)_2AsS_2C—C_5H_6—(NH_2)$-2	$C_{18}H_{16}AsNOS_2$ (FW 401.2)	53.71 (53.86)	3.95 (4.02)	73	157d	3400 m, br	1610 vs	1460 s	905 w 875 w		375 m
(2) $O(C_6H_4)_2AsS_2C—C_5H_6—(NHEt)$-2	$C_{20}H_{20}AsNOS_2$ (FW 429.2)	55.20 (55.94)	4.56 (4.69)	80	179d		1590 vs	1430 m	910 mw 875 mw		390 w
(3) $O(C_6H_4)_2AsS_2C—C_5H_6—(NHCH_2C_6H_{11})$-2	$C_{25}H_{28}AsNOS_2$ (FW 497.2)	58.97 (60.35)	5.45 (5.63)	76	181d		1595 vs	1425 m	905 w 875 w		370 ws

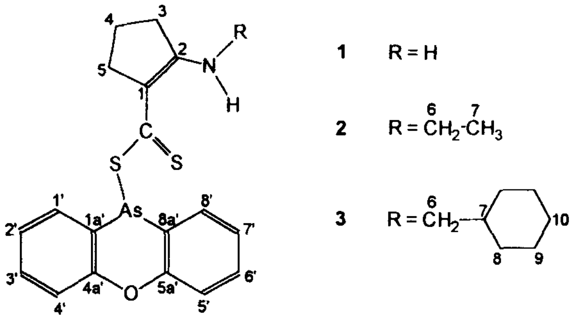
[a] Required values are given in parentheses. FW, formula weight.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $C_8H_{16}As\ NOS_2$

Atom	*x*	*y*	*z*	$u(eq)^a$
As	3196(1)	8031(1)	2137(1)	34(1)
S(1)	2814(2)	6905(1)	−64(3)	36(1)
S(2)	3010(3)	6365(1)	4065(3)	46(1)
O(1)	6156(7)	8312(3)	31(8)	41(2)
N(1)	2610(12)	4527(5)	3464(11)	54(3)
C(1)	2756(9)	6127(5)	1574(11)	30(3)
C(2)	2513(9)	5335(4)	627(11)	30(3)
C(3)	2506(10)	4603(5)	1569(13)	37(3)
C(4)	2268(13)	3870(5)	90(14)	50(4)
C(5)	2226(14)	4213(5)	−1913(14)	54(4)
C(6)	2353(12)	5147(5)	−1613(13)	44(3)
C(7)	5738(9)	7965(4)	3251(11)	30(3)
C(8)	6584(10)	7759(5)	5281(12)	37(3)
C(9)	8395(11)	7688(5)	6074(13)	47(3)
C(10)	9423(10)	7797(5)	4874(14)	45(3)
C(11)	8653(10)	8017(5)	2893(13)	42(3)
C(12)	6803(9)	8092(4)	2062(11)	32(3)
C(13)	4590(11)	8790(4)	−707(11)	38(3)
C(14)	4539(13)	9295(5)	−2268(13)	52(4)
C(15)	3009(16)	9785(5)	−3116(14)	63(4)
C(16)	1580(15)	9769(5)	−2416(15)	62(4)
C(17)	1666(12)	9258(5)	−908(14)	50(3)
C(18)	3176(10)	8751(4)	−10(13)	36(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

9.25% ($R = 6.73\%$ and $wR = 10.92\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.04585F^2$; goodness-of-fit 1.07. The residual electron density from a final difference Fourier synthesis was in the range of 0.71–0.69 e$Å^{-3}$. Refined values for the atomic coordinates are given in Table 2. The high value of $R = 6.30\%$ was due to the quality of the crystal and also to crystal-habit correction problems.



RESULTS AND DISCUSSION

The reaction of 10-chlorophenoxarsine with the corresponding 1,1-carbodithioic acid in ethanol at room temperature resulted in the formation of complexes **1–3** which have been isolated as yellow, crystalline solids. The compounds were investigated by means of IR, mass and NMR (^{1}H, ^{13}C) spectroscopy and in one case (compound **1**), the crystal and molecular structure was determined by single-crystal X-ray diffraction. (Carbon numbering generally is given as in structures 1–3. Carbon numbering for the *structure discussions* is as in Fig. 1 and carbon numbers are in *parentheses*.)

Important bands observed in the infrared spectra are listed in Table 1. The absence of a ν(SH) absorption around 2500 cm^{-1} and the presence of new bands in the 390–370 cm^{-1} region, assigned to As–S stretching vibrations,[17] indicate primary bonding of the ligand through sulfur. The exocyclic nitrogen atom seems to be not involved in the coordination to the central arsenic atom. The presence of two weak absorptions in the region 910–870 cm^{-1}, characteristic of carbon–sulfur stretching vibrations, might be indicative of monometallic biconnective (bidentate) behavior of the dithio ligand.[18] All complexes also exhibit

Table 3 Electron-impact (70 eV) mass spectra of phenoxarsin-10-yl derivatives (*m*/*z*, % intensity)

M^+	**1** R = H	**2** R = Et	**3** X = $CH_2C_6H_{11}$
$O(C_6H_4)_2AsS_2C—C_5H_6—(NHR)\text{-}2^+$	401 (13)	429 (18)	497 (1)
$O(C_6H_4)_2As^+$	243 (100)	243 (100)	243 (100)
$C_{12}H_8O^+$	168 (38)	168 (98)	168 (69)
$C_{11}H_7^+$	139 (18)	139 (57)	139 (43)
$S_2CC_5H_6(NHR)\text{-}2^+$	158 (10)	186 (21)	254 (20)
$SCC_5H_6(NHR)\text{-}2^+$	126 (23)	154 (52)	222 (25)
AsS^+	107 (1)	107 (11)	107 (5)

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

	Chemical shifts (ppm)																
Compound	C-4a′,5a′	C-1′,8′	C-3′,6′	C-2′,7′	C-1a′,8a′	C-4′,5′	CS_2	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1[b]	155.2	135.0	131.0	123.0	118.5	117.6	198.3	118.7	169.7	35.6	19.7	33.3					
2[c]	155.8	135.6	131.4	123.5	118.2	119.2	198.1	119.5	169.8	33.9	20.3	33.2	40.4	15.2			
3[c]	155.7	135.6	131.0	123.5	119.5	118.1	198.3	119.4	163.5	33.9	20.3	33.3	52.5	38.3	30.9	25.8	26.2

[a] For the numbering scheme see structures **1–3**. [b] In $CDCl_3/DMSO\text{-}d_6$. [c] In $CDCl_3$.

Table 5 Important bond distances (Å) and angles (°) in $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2[a]

As-S(1)	2.272 (2)	S(1)—As—C(7)	98.6 (2)
As· · ·S(2)	3.125 (3)	S(1)—As—C(18)	91.6 (2)
As—C(7)	1.927 (7)	S(1)—As· · ·S(2)	64.9 (1)
As—C(18)	1.940 (9)	C(7)—As· · ·S(2)	90.6 (2)
		C(18)—As· · ·S(2)	156.6 (3)
		C(7)—As—C(18)	93.2 (3)
C(7)—C(12)	1.397 (12)	As—C(7)—C(12)	122.2 (5)
C(12)—O(1)	1.386 (9)	C(7)—C(12)—O(1)	124.0 (6)
O(1)—C(13)	1.394 (9)	C(12)—O(1)—C(13)	121.2 (7)
C(13)—C(18)	1.378 (13)	O(1)—C(13)—C(18)	123.7 (7)
		C(13)—C(18)—As	122.8 (5)
C(1)—S(1)	1.759 (8)	As—S(1)—C(1)	100.7 (3)
C(1)—S(2)	1.685 (8)	S(1)—C(1)—S(2)	120.1 (4)
C(1)—C(2)	1.402 (10)	S(1)—C(1)—C(2)	114.4 (6)
C(2)—C(3)	1.392 (11)	S(2)—C(1)—C(2)	125.4 (6)
C(3)—C(4)	1.498 (11)	C(1)—C(2)—C(3)	126.8 (7)
C(4)—C(5)	1.512 (15)	C(1)—C(2)—C(6)	123.5 (7)
C(5)—C(6)	1.524 (12)	C(3)—C(2)—C(6)	109.6 (7)
C(6)—C(2)	1.521 (12)	N(1)—C(3)—C(2)	126.7 (8)
C(3)—N(1)	1.296 (12)	N(1)—C(3)—C(4)	121.2 (8)
N(1)—H(1A)	0.85 (11)	N(1)—H(1A)· · ·S(2)	133 (2)
N(1)· · ·S(2)	3.013 (9)		
H(1A)· · ·S(2)	2.37 (11)		

[a] For numbering scheme here, see Fig. 1.

other strong, characteristic absorptions for the dithio ligand and phenoxarsin-10-yl moiety, respectively (Table 1).

The 70 eV electron-impact mass spectra contain a low-intensity fragment corresponding to the molecular ion, as well as ion fragments resulting from the main fragmentation, i.e. $O(C_6H_4)_2As^+$ and $S_2C—C_5H_6—NHR$-2^+ (Table 3). Other characteristic ions arising from subsequent fragmentation of the phenoxarsin-10-yl[17, 19, 20] or carbodithiolato moieties were also identified.

The ^1H and ^{13}C NMR spectra are consistent with the formation of the title complexes and with their structural behavior suggested by IR data. In the ^1H NMR spectra none of the complexes exhibits a resonance for an S-*H* proton. At high field, multiplet signals at *ca* 2.4–2.5 ppm and 1.5–1.7 ppm are observed for the ACDA ring protons. Additionally, compound **2** shows a multiplet ($\delta = 3.4$ ppm) and a triplet ($\delta = 1.3$ ppm) corresponding to the CH_2 and CH_3 protons, respectively, of the ethyl group bound to nitrogen. For compound **3**, a triplet at 3.2 ppm was assigned to the CH_2 group bound to nitrogen (the protons of the cyclohexyl group exhibit a complex resonance at high field also). At lower field ($\delta = 7$–8 ppm) all compounds exhibit the expected resonance pat-

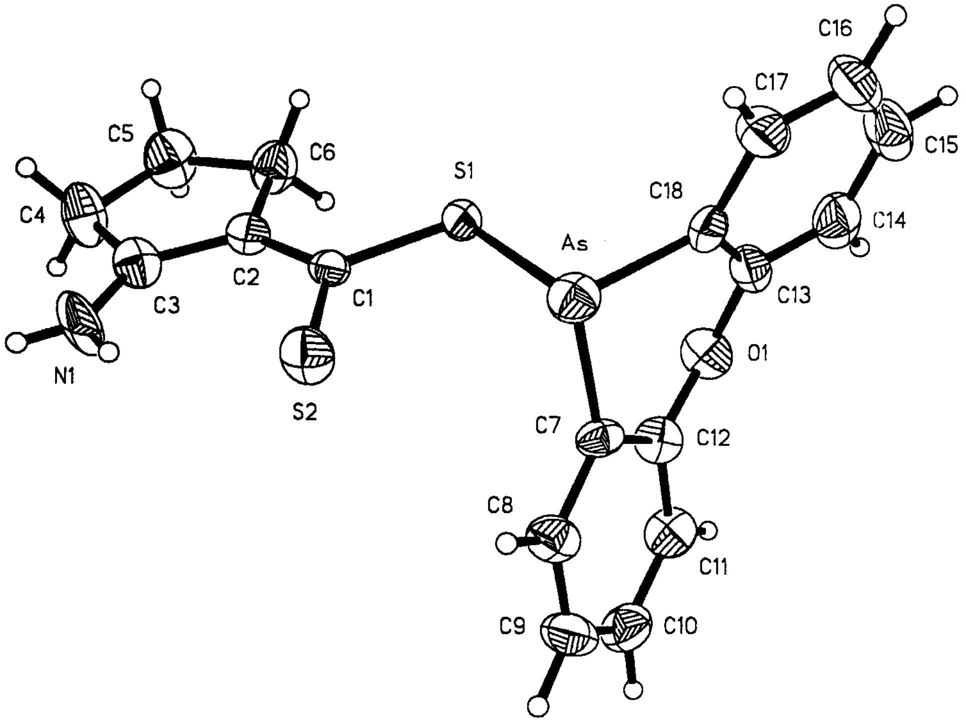


Figure 1 ORTEP-method drawing of the monomeric structure of $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2.

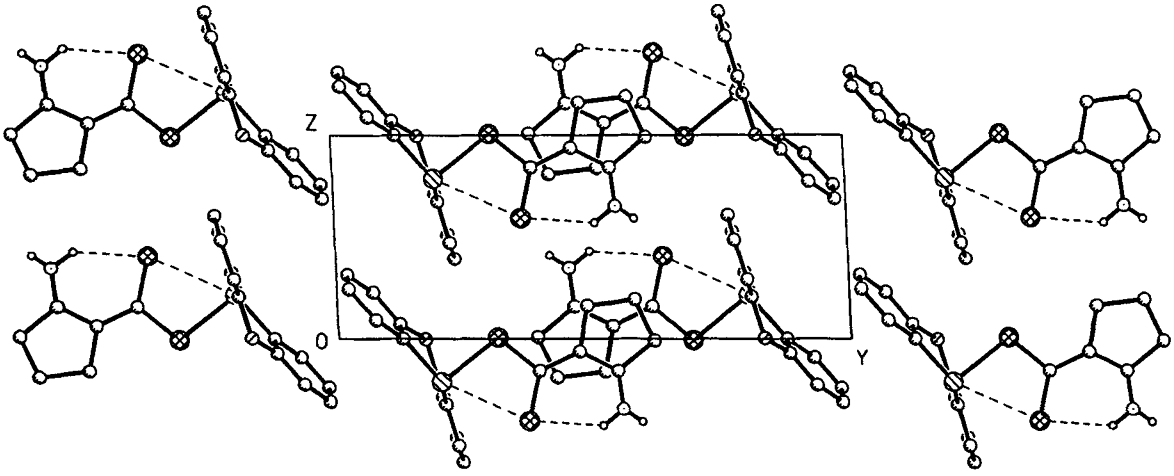


Figure 2 View of the unit cell of $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2.

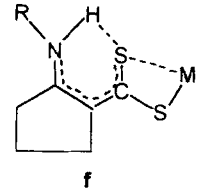
tern for the aromatic protons of the phenoxarsine moiety.[20,21] The title compounds also show a singlet resonance at 10.7 (**1**), 12.2 (**2**), and 12.3 ppm (**3**) for the N—*H* proton. Additionally, compound **1** exhibits a second N—*H* signal ($\delta = 4.6$ ppm), thus suggesting the non-equivalence of the amino group protons, due probably to a N—H· · ·S(=C) hydrogen bond. The ^{13}C NMR spectra (Table 4) of compounds **1–3** show the correct number of signals, thus reinforcing the identity of the compounds.

The crystal and molecular structure of $O(C_6H_4)_2AsS_2C—C_5H_6—NH_2$-2 (compound **1**) was determined by single-crystal X-ray diffraction. The lattice contains monomeric units with closest contacts of 3.490 Å and 3.783 Å between C(13)–C(18) rings ($1-x$, $2-y$, $-z$) and ACDA rings ($-x$, $1-y$, $-z$), respectively, of neighboring molecules. Important interatomic distances and angles are listed in Table 5, and the molecular structure with the numbering scheme is illustrated in Fig. 1. A view of the lattice is shown in Fig. 2.

The 1,1-dithio ligand exhibits an asymmetric monometallic biconnective coordination pattern. The short [As—S(1) 2.272(2) Å] and long (As· · ·S(2) 3.125(3) Å) arsenic–sulfur distances (cf the sum of van der Waals radii, $\Sigma_{vdW}(As, S) = 3.85$ Å[22]) are related to long and short carbon–sulfur bond lengths, i.e. C(1)–S(1) 1.759(8) Å and C(1)–S(2) 1.685(8) Å, respectively, the latter being indicative for single C—S and double C=S bonds. The system formed by the arsenic atom and the whole dithio ligand fragment is quasi-planar [deviations from the best plane: As −0.002, S(1) 0.002, C(1), 0.021, S(2) 0.000, C(2) 0.037, C(3) −0.014, C(4) −0.022, C(5) −0.049, C(6) 0.008, N(1) 0.000 Å], with the sp^3-hybridized C(5) atom exhibiting the largest deviation. This plane is almost perpendicular to the As–C(7)–C(18) plane [81.4(2)°].

The five-membered ring of the ACDA ligand contains, as expected, two sets of carbon–carbon bond distances. With the exception of C(2)–C(3) bond [1.392(11) Å], the length of which indicates a double-bond character, all the others exhibit a magnitude (average 1.514 Å) consistent with their single-bond nature. The exocyclic C(1)–C(2) [1.402(10) Å] and C(3)–N(1) [1.296(12) Å] bonds are significantly shorter than expected for single bonds (C—C 1.54, C=C 1.34, C—N 1.51, and C=N 1.32 Å[23]), thus suggesting their involvement in a hyperconjugated system (structure **f**). Similar behavior was observed in the free ligand,[2] as well as in $(CH_2S)_2AsS_2C—C_5H_6—NH_2$-2.[12] This is consistent with the planarity of the dithio ligand moiety, the As· · ·S(2) secondary interaction and the lack of coordinative interaction between N(1) and As in the title compound.

The coordination geometry of arsenic can be described as a slightly distorted trigonal pyramid, with arsenic in the apical position (C–As–X (X = C, S) average 94.5°). If the As· · ·S(2)



f

secondary interaction is taken into account, the coordination geometry of arsenic might be described as a distorted ψ-trigonal bipyramid, with S(2) and C(18) atoms in axial positions [C(18)–As–S(2) 156.6°]. The equatorial positions are occupied by S(1), by C(7) and supposedly by the electron lone pair of arsenic. This is supported by the angles at the arsenic atom (Table 5), and by the orientation of the S(1)–C(1)–S(2) fragment which brings the S(2) atom into a *trans* position to the C(18) atom, resulting in a large free space opposite the S(1)/C(7) atoms. The low value of the S(1)–As–S(2) angle (64.9°) is due to the small carbodithiolato ligand 'bite'.

The dihedral angle between the two halves of the phenoxarsine moiety [150.3(3)°] is slightly smaller than in 10-chlorophenoxarsine (156.3°).[24] This is consistent with the previous behavior of this folded system, which seems to be not affected by the substitution of the halogen by a 1,1-dithiolato ligand.[20,21]

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