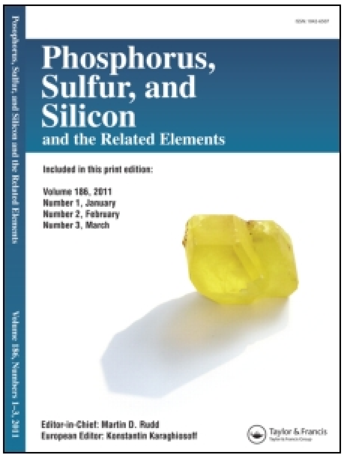

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHENYLARSENIC(III) DERIVATIVES OF SOME THIOSEMICARBAZONES

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To cite this Article Gupta, Rita , Singh, Yashpal and Rai, Audhesh Kumar(1992) 'PHENYLARSENIC(III) DERIVATIVES OF SOME THIOSEMICARBAZONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 70: 1, 235 — 241

To link to this Article: DOI: 10.1080/10426509208049172

URL: http://dx.doi.org/10.1080/10426509208049172

Phosphorus, Sulfur, and Silicon, 1992, Vol. 70, pp. 235–241
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PHENYLARSENIC(III) DERIVATIVES OF SOME THIOSEMICARBAZONES

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(Received December 6, 1991; in final form April 28, 1992)

Complexes having the general formula $PhAs[SC(NH_2):NN:C(R)R']_nCl_{2-n}$ where (n = 1 or 2) have been synthesized by the reaction of phenylarsenic(III) dichloride with thiosemicarbazones in the presence of triethylamine in stoichiometric ratios in refluxing THF solution. These complexes have been characterized by elemental analyses and molecular weight measurements. Their plausible structure has been assigned on the basis of spectral (IR, ^1H and ^{13}C NMR) studies.

Key words: Thiosemicarbazones, phenylarsenic(III) dichloride, IR and NMR spectra, bidentate ligand.

INTRODUCTION

During the past few decades a variety of organic derivatives of organoarsenic(III) have been synthesized and characterized according to their potential pharmacological[1,2] and biological applications.[3,4] Some of these derivatives are powerful skin irritants and capable of producing health hazards.[5]

In continuation of our work on phenylarsenic (III) derivatives of β-diketones,[6] β-ketoamines,[7] monothio-β-diketones[6] etc., the synthesis and characterization of phenylarsenic(III) derivatives of thiosemicarbazones is reported in this work.

RESULTS AND DISCUSSION

The interaction of phenylarsenic(III) dichloride with thiosemicarbazones in the presence of triethylamine in THF solution in 1:1 and 1:2 molar ratios, respectively lead to the formation of corresponding phenylarsenic(III) derivatives of thiosemicarbazones.

$$PhAsCl_2 + nNH_2CS(H){:}NN{:}C(R)R' + nEt_3N \rightarrow PhAs[SC(NH_2){:}NN{:}C(R)R']_nCl_{2-n} + nEt_3NHCl \downarrow$$

where n = 1(**Ia–If**) or 2(**IIa–IIf**)
R = H, R′ = C_6H_5(a), C_6H_5CHCH(b), $C_6H_4OCH_3$(c)
R = CH_3, R′ = C_6H_5(d), $C_6H_4CH_3$(e), $C_6H_4OCH_3$(f)

Filtration of precipitated Et_3NHCl and removal of excess solvent from the filtrate yield yellow to brown colored solids with sharp melting points and good solubility in common organic solvents. These derivatives have been further purified by recrystallization from chloroform/pet. ether solution. Osmometric molecular weight measurements in chloroform solution show their monomeric nature.

IR SPECTRA

Infrared spectra of these derivatives Table I (recorded in the range 4000–200 cm^{-1}) shows the disappearance of a broad band in the region 2900–2800 cm^{-1} (νNH)[8] observed in parent ligands and the appearance of a new band in the region 413–405 cm^{-1} (νAs—N)[9] indicating the deprotonation of the NH nitrogen and formation of a new As—N bond.

Two medium intensity bands observed in the region 1610–1600 cm^{-1} (νC═N)[10] and 1090–1080 cm^{-1} (νC═S)[11] in parent ligands are shifted towards a lower wave number by ~40 cm^{-1}. This shift is due to the involvement of both nitrogen and sulfur in bonding. The bonding of the sulfur atom with the central arsenic atom is further supported by the appearance of a band in the region 380–372 cm^{-1} (νAs—S).[12] The band for νAs—C[13] has been observed in the region 470–462 cm^{-1}.

In the spectra of the chloro derivatives PhAsCl[SC(NH$_2$):NN:C(R)R′], the As—Cl[14] band has been observed in the region 364–347 cm^{-1}.

The absorption bands (3407–3240 cm^{-1}) assigned to symmetric and asymmetric NH$_2$ bands[15] in the ligands do not show any significant shift in their positions in phenylarsenic(III) derivatives, indicating the noninvolvement of this particular group in bonding.

TABLE I

IR data of phenylarsenic(III) derivatives of thiosemicarbazones (cm^{-1})

Derivative	CN	CS	As-C	As-N	As-S	As-Cl	NH$_2$
Ia	1550 m	1030 m	470 m	405 m	372 m	360 m	3400 m
IIa	1570 m	1011 m	454 m	405 m	388 m	--	3400 m
Ib	1553 m	1040 m	462 m	405 m	380 m	355 m	3390 m
IIb	1570 m	961 m	454 m	405 m	388 m	--	3390 m
Ic	1586 m	1027 m	470 s	413 m	372 m	347 m	3407 w
IIc	1537 m	1027 m	460 m	405 m	380 m	--	3407 m
Id	1570 m	1040 m	462 m	413 m	380 m	355 m	3362 m
IId	1570 m	994 m	465 m	413 m	396 m	--	3362 m
Ie	1570 m	1044 m	462 s	405 m	380 m	355 s	3427 m
IIe	1537 m	1011 m	468 m	405 m	380 m	--	3387 m
If	1520 m	1011 m	470 m	405 m	380 m	364 m	3380 w
IIf	1540 m	1018 m	454 m	410 m	390 m	--	3400 m

^{1}H NMR SPECTRA

Two singlets observed in the region 10.0–8.80 ppm and 1.84–1.55 ppm in the ligands are assigned to the NH and SH proton signals indicating the presence of these ligands in two isomeric forms in solution. Disappearance of these singlets from the spectra of corresponding derivatives indicates the deprotonation of the ligands. No shift in the position of NH_2 protons signals (Table II; 6.94–6.55 ppm) supports the nonparticipation of the NH_2 groups in bonding as evidenced by IR spectra.

Signals in the region 3.98–2.23 ppm and 8.13–6.92 ppm may be assigned to methyl and methine protons. All phenyl protons appear as a complex multiplet in the region 8.04–6.79 ppm.

^{13}C NMR SPECTRA

A comparison of the ^{13}C NMR spectra of these derivatives (Table III) with those of the corresponding ligands shows a shift in the position of the C=S and C=N carbon signals, confirming the involvement of both these groups in bonding. Methyl

TABLE II

^{1}H NMR data of phenylarsenic(III) derivatives of thiosemicarbazones (ppm)

Derivative	CH	CH_3	NH_2	Phenyl
Ia	8.09 s	--	6.78 b	7.37-8.00 m
IIa	8.09 s	--	6.78 b	7.31-8.00 m
Ib	a,7.95 d b,mixed in phenyl c,6.92 d	--	6.55 b	7.28-7.64 m
IIb	a,7.95 d b,mixed in phenyl c,6.90 d	--	6.59 b	7.30-7.68 m
Ic	8.04 s	3.88 s	6.60 b	6.92-7.91 m
IIc	8.13 s	3.38 s	6.59 b	6.79-7.95 m
Id	---	2.27 s	6.90 b	7.37-7.99 m
IId	---	2.27 s	6.94 b	7.50-8.04 m
Ie	---	a,2.45 s b,2.32 s	6.56 b	7.28-8.04 m
IIe	---	a,2.36 s b,2.27 s	6.57 b	7.15-7.91 m
If	---	a,3.98 s	6.60 b	6.92-7.86 m
IIf	---	a,3.84 s	6.66 b	6.83-8.00 m

TABLE III

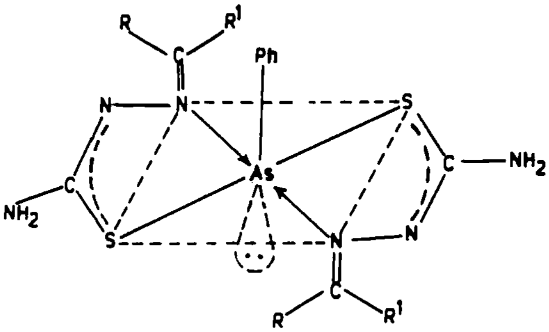
^{13}C NMR data of phenylarsenic(III) derivatives of thiosemicarbazones (δppm)

Derivative	CH_3	CN	CS	C_6H_5*	δ	σ_R°
Ia	--	147.5 144.8	183.1 178.5	143.0,133.0 130.6,128.8; 141.0,132.3 129.9,127.9	-2.4	-0.10
IIa	--	144.0	178.3	132.9,130.8 128.8,127.4	-2.0	-0.09
Ib	--	149.2,148.3 144.8,139.5 127.9,125.2	180.1 178.0	136.8,132.4 129.7,128.8; 136.2,130.6 128.0,127.6	-2.7	-0.12
IIb	--	146.9 140.8 125.3	178.9	136.7,131.6 128.7,127.5	-2.9	-0.13
Ic	55.2 51.3	148.4 146.5	179.3 178.5	136.3,132.3 129.6,127.9; 135.4,131.3 128.6,127.3	-2.7	-0.12
IIc	55.1	148.4	178.5	136.1,132.3 129.7,127.5	-2.6	-0.11
Id	16.6 13.0	150.1 146.8	180.4 182.2	137.7,132.3 129.7,127.9; 136.2,130.6 128.1,127.0	-2.6	-0.11
IId	13.6	148.2	178.4	133.5,132.1 129.3,128.1	-2.8	-0.12
Ie	24.6,20.2 14.8,12.2	148.4 144.8	183.5 181.0	139.5,133.3 130.6,128.8; 138.3,132.4 129.8,127.9	-2.7	-0.12
IIe	20.9 13.8	150.0	175.7	133.6,132.1 129.9,127.2	-2.2	-0.10
If	55.2,51.0 21.1,19.8	148.4 146.3	180.1 177.7	136.7,134.3 131.3,129.8; 135.8,133.8 130.8,128.6	-3.0	-0.13
IIf	55.2 21.1	148.4	177.4	133.5,131.2 128.8,127.2	-2.4	-0.10

*Values are given in the order of ipso, meta, para and ortho, respectively.

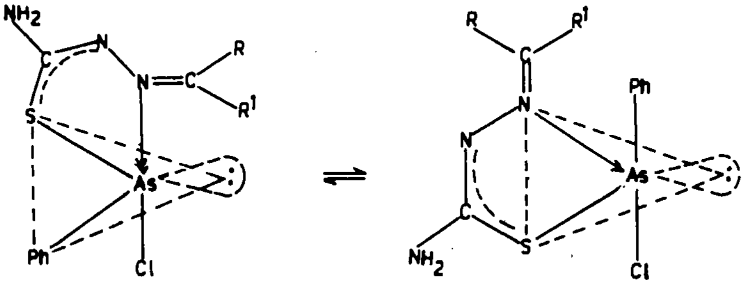
carbon signals observed at 55.2–13.0 ppm in these derivatives also show a down field shift.

In view of the monomeric nature of these derivatives and the bidentate behaviour of ligands, the following structure in which the central arsenic atom acquires a pseudo-octahedral geometry is being proposed:



The corrected chemical shift values[16,17] for these complexes defined as $\delta' = \delta C_p - \delta C_m$ (where δC_p and δC_m denote the chemical shift values of para and meta carbon atoms of the phenyl ring) and $\sigma R^{\circ 18}$ are found to be in the range of -2.9 to -2.0 ppm and -0.13 to -0.09 ppm. These negative values indicate an electron release from the arsenic atom towards the phenyl ring through dA-pA conjugation and poor donor capability of the arsenic atom in these derivatives.

In the spectra of mixed chloro phenylarsenic(III) derivatives PhAsCl[SC-(NH_2):NN:C(R)R′], a shift in the position of C=S and C=N carbon signals as compared with the spectra of the corresponding ligands confirms the bonding of the ligand moiety with phenylarsenic(III) through the nitrogen and sulfur atoms. All ^{13}C signals are observed to be splitted in these derivatives. This splitting may be due to the existence of chloro derivatives in two geometrical isomeric forms in approximately equal ratio.



The presence of these two geometrical forms could not be detected by IR and ^1H NMR spectra.

In these derivatives also, the negative values for δ' (-3.0 to -2.4) and σR° (-0.13 to -0.10 ppm) indicates the similar trend in electron release and donor capability of arsenic as described earlier in case of PhAs[SC(NH_2):NN:C(R)R′$]_2$ complexes.

EXPERIMENTAL

All reactions were carried out under anhydrous conditions. The chemicals used were of reagent grade. Phenylarsenic(III) dichloride[19] was synthesized by reported method. Thiosemicarbazones[20] were prepared by the condensation of aldehyde or ketone with thiosemicarbazide in a 1:1 molar ratio in ethanol and were recrystallized. Arsenic, sulfur, nitrogen and chlorine were estimated by iodometric, gravimetric, Kjeldahl's and Volhard's methods, respectively.[21] Molecular weights were determined on a Knauer Vapour Pressure Osmometer in $CHCl_3$ solutions at 45°. IR spectra were recorded on a Perkin

TABLE IV

Synthetic and analytical data of phenylarsenic(III) derivatives of thiosemicarbazone

Derivative	Reactants (g)			Molar ratio	m.p. °C	% Found (calcd.)			
	PhAsCl$_2$	R'(R)C:NN(H)SCNH$_2$	Et$_3$N			As	N	S	Cl
Ia.	0.75	R=H, R'=C_6H_5 0.43	0.24	1:1:1	81	20.12 (20.51)	11.13 (11.49)	8.38 (8.75)	9.34 (9.71)
IIa.	0.21	R=H, R'=C_6H_5 0.33	0.19	1:2:2	132	14.50 (14.76)	16.26 (16.53)	12.19 (12.59)	--
Ib.	0.22	R=H, R'=C_6H_5CHCH 0.36	0.16	1:1:1	71	18.92 (19.15)	10.10 (10.72)	8.00 (8.17)	8.98 (9.06)
IIb.	0.35	R=H, R'=C_6H_5CHCH 0.65	0.32	1:2:2	110	13.18 (13.39)	14.95 (15.00)	11.16 (11.42)	--
Ic.	0.23	R=H, R'=$C_6H_4OCH_3$ 0.22	0.10	1:1:1	75	18.12 (18.96)	10.32 (10.61)	7.95 (8.09)	8.12 (8.97)
IIc.	0.38	R=H, R'=$C_6H_4OCH_3$ 0.71	0.35	1:2:2	150	12.99 (13.20)	14.16 (14.78)	11.00 (11.26)	--
Id.	0.47	R=CH_3, R'=C_6H_5 0.41	0.21	1:1:1	85	19.01 (19.76)	10.89 (11.06)	8.09 (8.43)	9.03 (9.35)
IId.	0.33	R=CH_3, R'=C_6H_5 0.58	0.30	1:2:2	121	13.40 (13.99)	14.90 (15.67)	11.83 (11.94)	--
Ie.	0.37	R=CH_3, R'=$C_6H_4CH_3$ 0.35	0.17	1:1:1	72	18.85 (19.05)	10.24 (10.67)	7.95 (8.13)	8.98 (9.02)
IIe.	0.45	R=CH_3, R'=$C_6H_4CH_3$ 0.84	0.41	1:2:2	130	12.95 (13.29)	14.38 (14.89)	11.00 (11.34)	--
If.	0.39	R=CH_3, R'=$C_6H_4OCH_3$ 0.39	0.18	1:1:1	65	18.00 (18.31)	9.91 (10.25)	7.60 (7.81)	8.12 (8.66)
IIf.	0.63	R=CH_3, R'=$C_6H_4OCH_3$ 1.26	0.57	1:2:2	140	12.18 (12.58)	13.96 (14.09)	10.15 (10.73)	--

Elmer Spectrophotometer using KBr films. NMR spectra (^{1}H and ^{13}C) were recorded on a JEOL FX 90Q (90 MHz) spectrometer in $CDCl_3$ solutions using TMS as an internal standard. All the complexes have been synthesized by a similar route and therefore for brevity the synthetic procedure for a representative complex is described below and the analytical details of all the complexes are summarized in Table IV.

Synthesis of $PhAs[SC(NH_2):NN:C(H)C_6H_5]_2$: To a THF solution (10 ml) of $PhAsCl_2$ (0.21 g, 0.95 mM) was added drop by drop with constant stirring the THF solution (20 ml) of a 1:1 mixture of the ligand $C_6H_5CHNNCSH(NH_2)$ (0.33 g, 1.84 mM) and Et_3N (0.19 g, 1.88 mM). The reaction mixture was refluxed for ~4 hours. Et_3NHCl thus formed was filtered and the excess solvent was removed under reduced pressure. The resultant yellow solid was recrystallized from chloroform/pet. ether mixture and dried under vacuum. The compound has been analyzed for As, N and S. Found: As = 14.40, N = 16.26 and S = 12.19%; calcd. for $C_{22}H_{21}N_6S_2As$; As = 14.76, N = 16.53 and S = 12.59%.

ACKNOWLEDGEMENT

One of the authors, Rita Gupta, is thankful to CSIR, New Delhi for financial assistance.

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