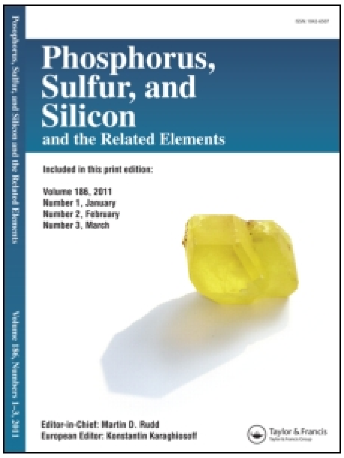

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SYNTHESIS AND STRUCTURAL ELUCIDATION OF SOME NEW PHENYLARSENIC(III) DERIVATIVES OF N(-SUBSTITUTED) S-BENZYL DITHIOCARBAZATES

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SYNTHESIS AND STRUCTURAL ELUCIDATION OF SOME NEW PHENYLARSENIC(III) DERIVATIVES OF N(-SUBSTITUTED) S-BENZYL DITHIOCARBAZATES

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Some new phenyl arsenic(III) derivatives of N(-substituted) S-benzyldithiocarbazate with the general formula $PhAsCl_{2-n}$ $[(X-C_6H_4)C(R)NNC(S)SCH_2C_6H_5]_n$ where n = 1 or 2; R = H, x = o-OH; R = CH_3; x = p- OCH_3, p-OH, p- Br, p- F, p- Cl have been synthesised by the reactions of phenylarsenic(III) dichloride with the sodium salt of the corresponding ligand in 1:1 and 1:2 molar ratios in refluxing benzene solution. All these compounds have been characterised by elemental analysis and molecular weight measurements and their plausible structure have been proposed on the basis of spectroscopic evidences. The compounds $PhAs[X-C_5H_4)C(R)NNC(S)SCH_2C_6H_5]_2$ appears to have distorted octahedral geometry whereas the compounds $PhAsCl[(X-C_6H_4)C(R)NNC(S)SCH_2C_6H_5)$ with trigonal bipyramidal geometry exist in two isomeric forms.

Keywords: Benzyl Dithiocarbazates; phenylarsenic derivatives; NMR spectra

INTRODUCTION

Organoarsenic (III) compounds have attracted attention due to their biological activity[1] and toxic effect.[2–4] Some organoarsenic (III) compounds also find chemotherapeutic[5] applications. Dithiocarbazic acid and its derivatives constitute an interesting class of dithioligands having four donor sites viz two sulphur and two nitrogen atoms. A number of metal complexes of these ligands have been prepared[6–10] and are found to be biologically active and carcinostatic[11]. In continuation to our work on phe-

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* Corresponding Author.

nylarsenic(III) derivatives[12–17] of various monofunctional bidentate ligands, we report the synthesis and characterisation of some new phenylarsenic(III) derivatives of N(-substituted)-S-benzyldithiocarbazates.

RESULTS AND DISCUSSION

Reactions of phenylarsenic(III) dichloride with sodium salt of N(-substituted)-S-benzyl dithiocarbazates in 1:1 and 1:2 molar ratios in refluxing benzene solution yield the corresponding derivatives.

$$\begin{gathered}\mathrm{PhAsCl_2 + nNa + n\,[X\text{-}C_6H_4)C(R)NNC(S)SCH_2C_6H_5]} \rightarrow \\ \mathrm{PhAs[(X\text{-}C_6H_4)C(R)NNC(S)SCH_2C_6H_4]_nCl_{2\text{-}n} + nNaCl}\downarrow \\ (\mathrm{n}{=}1 \text{ or } 2)\end{gathered}$$

Some of the chloroderivatives have also been prepared by the redistribution reactions between $PhAsCl_2$ and corresponding bis-derivatives:

$$\begin{gathered}\mathrm{PhAsCl_2 + PhAs[(X\text{-}C_6H_4)C(R)NNC(S)SCH_2C_6H_5]_2} \rightarrow \\ \mathrm{2PhAs[(X\text{-}C_6H_4)C(R)NNC(S)SCH_2C_6H_5]Cl}\end{gathered}$$

The resulting compounds are found to be yellow to brown viscous liquid, soluble in common organic solvents and monomeric in nature.

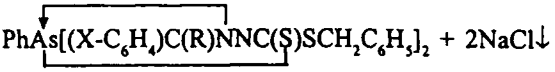
I.R. SPECTRA

IR spectra of these compounds have been recorded in region 4000–200 cm^{-1}. These ligands are found to exist in thione form, as the IR spectra displayed only νNH band at ~ 3000 cm^{-1}. Disappearance of this νNH band in complexes indicates the deprotonation of NH group. Although, a new band corresponding to νAs-N[18] at ~ 415 cm^{-1} has appeared, but a shift of ~ 40 cm^{-1} in the position of νC=N band indicates that the bonding is taking place through β-nitrogen[19]. This means that the α-nitrogen is not involved in bonding. This can be explained by considering the thione-thiol equilibrium in solution as exhibited in the ^1H NMR spectra of the ligands.

It appears that the sodium ion interact with the thiol form of the ligand and forms the corresponding sodium salt. Due to this reaction, the concentration of thione form deplets. This results in the formation of the sodium salt of thiol form which intereacts with $PhAsCl_2$ and forms the corresponding phenylarsenic(III) complexes:

$$\begin{tikzcd} (X\text{-}C_6H_4)C(R)NNHC(S)SCH_2C_6H_5 \arrow[r, shift left] & (X\text{-}C_6H_4)C(R)NNC(SH)SCH_2C_6H_5 \arrow[l, shift left] \arrow[d, "-H^+"', "+Na^+"] \\ & Na^+[(X\text{-}C_6H_4)C(R)NNC(S^-)SCH_2C_6H_5] \end{tikzcd}$$

$$2Na[(XC_6H_4)C(R)NNC(S)SCH_2C_6H_5] + PhAsCl_2 \longrightarrow$$



$$PhAs[(X\text{-}C_6H_4)C(R)NNC(S)SCH_2C_6H_5]_2 + 2NaCl\downarrow$$

The above mechanism is supported by the disappearance of νC=S band and the appearance of new bands in the region 1010–980, 380–365 and 355–340 cm^{-1} which may be assigned to νC-S, νAs-S[20] and νAs-Cl[20] modes. The νAs-C band was observed at 455 cm^{-1}. Thus, the IR spectral data suggest that the ligands bind the central arsenic atom through the β-nitrogen and sulphur atoms forming a five membered chelate ring.

^{1}H NMR SPECTRA

The ^{1}H NMR spectra of the ligands exhibit two sharp signals at δ 4.5 and 10.1 ppm which have been assigned to NH and SH proton, respectively. This indicates the presence of thione and thiol forms in the soution. In the spectra of corresponding phenylarsenic(III) complexes (table-I), both these signals are found to be absent. The proton signals of the R group ($R = H$ and CH_3) and the CH_2 protons undergo a downfield shift in comparison to their positions in parent ligands. The signals for the aromatic protons have been observed in the range δ 7.05–8.88 ppm as multiplet. The derivatives where x = o-OH. p-OH and p-OCH_3, no shift in the position of the methoxy and the hydroxy proton signals has been observed.

TABLE I ^{1}H NMR Spectral Data of Ph As[(XC$_6$H$_4$)C(R)NNC(S)SCH$_2$C$_6$H$_5$]$_n$ Cl$_{2-n}$ (δ ppm)

S.No.	*Complex X*	*R*	*n*	CH_3	CH_2	C_6H_5
1.	p-F,	CH_3	2	2.59(s)	3.65(s)	7.12–8.54(m)
2.	Br,	CH_3	2	2.60(s)	3.62(s)	7.15–8.65(m)
3.	p-Cl,	CH_3	2	2.62(s)	3.62(s)	7.15–8.62(m)
4.	OH^a,	CH_3	2	2.65(s)	3.58(s)	7.20–8.65(m)
5.	OCH^a,	CH_3	2	2.65(s)	3.65(s)	7.12–8.45(m)
6.	o-OH^a,	H	2	–	3.62(s)	7.21–8.65(m)
7.	p-F^b,	CH_3	1	2.62(s)	3.65(s)	7.05–8.21(m)
8.	p-Br,	CH_3	1	2.62(s)	3.62(s)	7.11–8.48(m)
9.	p-Cl,	CH_3	1	2.60(s)	3.62(s)	7.12–8.88(m)
10.	p-OH^a,	CH_3	1	2.68(s)	3.65(s)	7.15–8.61(m)
11.	OCH$_3^a$,	CH_3	1	2.60(s)	3.62(s)	7.21–8.35(m)
12.	OH^a,	H	1	–	3.65(s)	7.15–8.55(m)

a. The OH and OCH$_3$ proton signals appear at δ 11.19 and 3.86 ppm. respectively.
b. The ^{19}F signal appears at δ −107.2 ppm.

^{19}F NMR SPECTRA

The ^{19}F signal has been observed at δ −107.2 ppm in both the compounds. No shift has been observed in its position in comparison to its position in parent ligand.

^{13}C NMR SPECTRA

In the ^{13}C NMR spectra of these derivatives (table-II) the signals for CH$_3$ (R = CH$_3$) and CH$_2$ carbon atoms show a downfield shift in their positions compared to parent ligands and have been observed at ~δ 26.5 and δ 41.5 ppm, respectively. This downfield shift may be due to the change in the electronic environment around these carbon atoms. The CS carbon atom shows an upfield shift (2–4 ppm) while C = N carbon signal shifts (~ 2 ppm) towards downfield. The shift in the position of CN carbon signal indicates that the coordination occurs through β-nitrogen. The involvement of α-nitrogen is unfavourable because if the bonding would have been through α-nitrogen, a four membered ring will be formed which is expected to be less stable in comparison to a five membered ring formed by the involvement of β-nitrogen in bonding.

TABLE II ^{13}C NNR Spectral Data of Ph As(XC_6H_4)C(R)NNC(S)$SCH_2C_6H_5]_n$ Cl_{2-n}(δ ppm)

S.No	*Complex X*	*R*	*n*	*CH_3*	*CH_2*	*CS*	*CN*	*As-C_6H_5*[a]	*δ (σ R^o)*
1.	p-F	CH_3	2	26.11	41.01	196.06	170.92	137.17, 125.47	–5.75
								135.55, 129.80	(-0.26)
2.	p-Br	CH_3	2	26.28	43.07	196.71	170.54	138.25, 126.45	–5.27
								136.22, 130.95	(-0.24)
3.	p-Cl	CH_3	2	26.27	42.12	197.15	170.55	138.54, 126.24	–5.50
								135.42, 129.92	(-0.25)
4.	p-OH	CH_3	2	26.82	43.10	197.05	171.11	137.01, 126.57	(-0.25)
								135.27, 129.87	(-0.24)
5.	p-OCH	CH_3	2	25.88	42.25	196.72	170.22	136.82, 126.02	–6.70
				[b]55.11				135.05, 128.35	(-0.30)
6.	o-OH	H	2	–	42.85	196.88	169.95	136.75, 126.11	–6.70
								135.25, 128.55	(-0.30)
7.	p-F	CH_3	1	26.27	40.93	196.71	169.55	141.25, 140.02	–5.91
				27.11	43.13	197.23	170.23	127.24, 126.25	(-0.27)
								135.39, 135.36	
								129.48, 129.45	
8	p-Br	CH_3	1	26.35	42.21	197.15	169.23	142.24, 141.12	–5.40
				27.04	42.52	198.01	170.04	124.20, 128.51	(-0.24)
								135.35, 135.24	
								129.95, 129.84	
9.	p-Cl	CH_3	1	26.24	42.14	196.88	169.95	142.15, 141.75	–5.01
				26.55	43.05	197.04	170.22	127.64, 127.25	(-0.23)
								136.45, 135.25	
								131.25, 130.44	

S.No	Complex X	R	n	CH_3	CH_2	CS	CN	As-C_6H_5[a]	δ (σR^{o})
10.	p-OH	CH_3	1	25.82	42.25	196.52	169.85	141.75, 140.04	–5.59
				25.95	42.54	197.22	17.01	128.85, 127.25	(-0.25)
								135.40, 134.40	
								129.85, 129.42	
11.	p-OCH_3	CH_3	1	25.88	42.35	196.72	170.21	142.04, 141.15	–5.59
				25.98	42.44	196.88	170.24	128.85, 127.42	(-0.25)
				55.11				135.54, 135.43	
				54.95				129.95, 129.84	
12.	o-OH	H	1	–	42.75	197.05	169.95	140.42, 140.25	–4.49
					42.95	197.15	170.15	127.25, 128.15	(-0.21)
								134.84, 134.54	
								130.25, 129.95	

a. Values in the order of ipso, ortho, meta and para carbon atoms respectively
b. OCH_3 signals

The phenyl carbon signals have been observed in the range of δ 114.2 – 155.6 ppm. The phenyl group attached to the central arsenic atom exhibits distinct signal in the range δ 125.47 – 138.54 ppm in bis derivatives.

In chloro derivatives the signals for every carbon atom appears as doublets or two distinct signals. The CS and CN carbon signals show an upfield (3–4 ppm) and a downfield (1–2 ppm) shift in their positions, respectively. The signals for CH_3 and CH_2 carbons also show a downfield shift. Two sets of signals have also been observed for phenyl carbons in the range of δ 114.47 to 150.65 ppm. The appearance of splitted signal for every carbon including those for phenyl group indicates the presence of the ligand moiety and the phenyl group attached to the arsenic atom in two different environments. The carbon signals of the phenyl group attached to the metal atom appear as doublets in the range δ 126.25 – 142.24 ppm.

The corrected chemical shift values δ defined as[21,22] $\delta^1 = \delta Cp - \delta Cm$ (where δCp and δCm are the chemical shift values of para and meta carbon atoms of the phenyl ring respectively) have been found to be in the range of δ(-)5.27 to (-)6.70 ppm for bis derivatives and δ(-)4.59-(-)5.95

ppm for chloro derivatives. These negative values of δ are indicative of an electron release from arsenic atom towards phenyl ring. These δ values have been related to Hammett- Taft constant[23] σR° by the equation $\delta = 22.066R^\circ$. The value of σR° (-0.24 to –0.30) are also found to be negative indicating the poor donor capability of arsenic atom. The lower magnitude of the δ and σ R° in chloro derivatives may be due to the presence of electron withdrawing Cl atom on As atom. This decreases the electron release from metal to ligand.

On the basis of the spectral evidences discussed so far a structure in which arsenic atom is surrounded by two bidentate ligands and one phenyl group in pseudo octahederal geometry, may be proposed for bis-derivatives. Lone pair of electrons is expected to occupies the position trans to phenyl group.

In chloro derivatives arsenic atom acquires a four coordination with one bidenate ligand, one chlorine atom and one phenyl group. Taking into account, the presence of lone pair of electrons, a trigonal bipyramidal structure may be proposed for these derivatives.

EXPERIMENTAL

All the chemicals used were of reagent grade. Precaustions were taken to exclude moisture throughout the experiments. The ligands[24] and phenylarsenicdichloride[25] were prepared by literture method Arsenic sulphur and nitrogen were determined iodometrically[26], gravimetrically[26] and by Kjeldahls method[26] respectively. Molecular weights were determined on a Knauer vapour pressure osmomemeter in chloroform solution at 45°C. The IR spectra of the complexes were recorded on a cart-zeiss specord M-80 spectrophotometer as neat film in the range 4000–200 cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer in $CDCl_3$ solution using TMS as internal reference.

All these derivatives have been synthesised by following a similar route and therefore for brarity, the synthesis of a representative complex is being described here in detail and the data along with other compounds are being summarised in table III.

TABLE III Synthetic and Analytical Data for $PhAs[X\text{-}C_6H_4C(R)NNC(S)SCH_2C_6H_5]_nCl_{2\text{-}n}$

	Reactant (mM)			*Complex (Molecular formula) (% yield)*	*Elemental Analysis % Found (Calcd.)*				*M.Wt. Found (Calcd.)*
	LH	*Na*	*PhAsCl₂*		*As*	*Na*	*S*	*Cl*	
(1)	3.13	3.12	1.57	$PhAs[p\text{-}FC_6H_4\,C(CH_3)NNC(S)SCH_2C_6H_5]_2$	9.25	6.98	16.25	–	775
				$(C_{38}H_{33}N_4S_4F_2As)$ (90)	(9.53)	(7.13)	(16.29)		(785.9)
(2)	2.79	2.80	1.40	$PhAs[p\text{-}BrC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]_2$	8.15	6.05	14.00	–	900
				$C_{38}H_{33}N_4S_4Br_2As$ (90)	(8.25)	(6.17)	(14.10)	–	(907.7)
(3)	4.51	4.49	2.24	$PhAs[p\text{-}ClC_6H_4C(CH_3)NNC(S)\,SCH_2C_6H_5]_2$	9.11	6.75	15.24	–	810
				$C_{38}H_{33}N_4S_4Cl_2As$ (85)	(9.15)	(6.84)	(15.63)	–	(818.9)
(4)	3.54	3.52	1.76	$PhAs[p\text{-}OHC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]_2$	9.44	7.05	16.22	–	770
				$C_{38}H_{35}N_2O_2As$ (88)	(9.58)	(7.16)	(16.37)	–	(781.9)
(5)	3.15	3.15	1.57	$PhAs[p\text{-}OCH_3C_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]_2$	9.22	6.59	15.74	–	790
				$C_{40}H_{39}N_4S_4O_2As$ (92)	(9.25)	(6.91)	(15.80)	–	(809.9)
(6)	3.56	3.52	1.77	$PhAs[o\text{-}OHCH_3C_6H_4CHNNC(S)SCH_2C_6H_5]_2$	9.82	7.25	16.55	–	740
				$C_{38}H_{31}N_4S_4O_2As$ (89)	(9.94)	(7.43)	(16.98)	–	(753.9)
(7)	2.24	2.23	2.24	$PhAs[p\text{-}FC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]Cl$	14.58	5.32	12.42	7.00	495
				$C_{22}H_{19}N_2S_2FClAs$ (90)	(14.85)	(5.55)	(12.69)	(7.04)	(504.4)
(8)	3.11	3.12	3.14	$PhAs[p\text{-}BrC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]Cl$	13.05	4.82	11.05	5.98	550

	Reactant (mM)			*Complex (Molecular formula) (% yield)*	*Elemental Analysis % Found (Calcd.)*				*M.Wt. Found (Calcd.)*
	LH	*Na*	*$PhAsCl_2$*		*As*	*Na*	*S*	*Cl*	
				$C_{22}H_{19}N_2S_2BrClAs$ (95)	(13.25)	(4.95)	(11.32)	(6.28)	(565.3)
(9)	3.48	3.44	3.42	$PhAs[p\text{-}ClC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]Cl$	14.28	5.32	12.11	6.75	500
				$C_{22}H_{19}N_2S_2Cl_2As$ (95)	(14.38)	(5.38)	(12.29)	(6.82)	(520.9)
(10)	1.53	1.50	1.53	$PhAs[o\text{-}OHC_6H_4C(CH_3)NNC(S)SCH_2C_6H_5]Cl$	14.75	5.42	12.52	6.94	480
				$C_{22}H_{20}N_2S_2OClAs$ (94)	(14.91)	(5.57)	(12.74)	(7.07)	(502.4)
(11)	2.62	2.60	2.60	$PhAs[o\text{-}OCH_3CH_3C_6H_4CHNNC(S)SCH_2C_6H_5]Cl$	14.38	5.30	12.15	6.75	510
				$C_{23}H_{22}N_2S_2OClAs$ (90)	(14.50)	(5.42)	(12.39)	(6.87)	(516.4)
(12)	2.20	2.18	2.17	$PhAs[p\text{-}OHC_6H_5CHNNC(S)SCH_2C_6H_5]Cl$	15.25	5.45	12.98	7.12	480
				$C_{21}H_{18}N_2S_2OClAs$ (88)	(15.34)	(5.73)	(13.10)	(7.27)	(488.4)

Synthesis of PhAs[(p-FC_6H_4)C(CH_3)NNC(S)S$CH_2C_6H_5$]$_2$

A weighed amount of sodium metal (0.07 g., 3.04 mM) was reacted with a minimum quantity of methanol (~ 5 mL) and the benzene solution of the ligand p-$FC_6H_4C(CH_3)NNHC(S)SCH_2C_6H_5$(0.99 g., 3.08 mM) was added slowly. The reaction mixture was refluxed for ~ 2 hrs. After cooling the solution, a benzene solution of $PhAsCl_2$ (0.35g, 1.57 mM) was added and the reaction mixture was further refluxed for ~ 3 hours. After the completion of the reaction, NaCl was filtered off. After removing the volatile fraction under reduce of pressure, a light yellow coloured viscous product was obtained. For purification the compound was dissolved in minimum amount of $CHCl_3$ and the pet-ehter (40–60) was added dropwise till a visious solid just begin to separate out. The solution was stored overnight at −10°C. The excess solvent was decanted off and the product was dried under reduced pressure. The compound on analysis was found to have As, 9.25; N, 6.98 S, 16.25%. Calcd for $C_{38}H_{33}N_4F_2$, As, 9.53; N, 7.13 and S, 16.29%.

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