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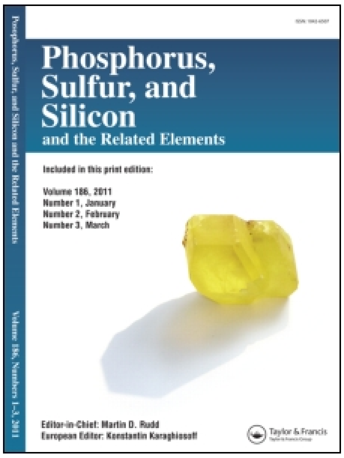

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Synthesis and Characterization of Toluene-3,4-dithiolatoarsenic(III) Derivatives of Dialkyldithiophosphates

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SYNTHESIS AND CHARACTERIZATION OF TOLUENE-3,4-DITHIOLATOARSENIC(III) DERIVATIVES OF DIALKYLDITHIOPHOSPHATES

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Replacement reactions of toluene-3,4-dithiolatoarsenic(III) chloride and sodium salts of dialkyldithiophosphoric acids in 1:1 molar ratio in refluxing anhydrous benzene yielded toluene-3,4-dithiolatoarsenic(III) dialkyldithiophosphate derivatives of the general formula $\overline{SC_6H_3(CH_3)SAs}S_2P(OR)_2$ *[where* R = Et, Pr^n, Pr^i, Bu^n *and* Bu^i*]. These newly synthesized derivatives are soluble in organic solvents like benzene, chloroform, and dichloromethane. These derivatives have been characterized by elemental analysis (C, H, S, and As) as well as IR and NMR (^1H, ^{13}C and ^{31}P) spectral studies.*

Keywords: Arsenic; dialkyldithiophosphates; dithiolates; IR spectra, ^1H, ^{13}C, and ^{31}P NMR spectra

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Diorganodithiophosphate ligands are known to exhibit remarkable diversities in their coordination pattern with transition as well as main group metals.[1–10] In most of the cases these ligands behave as chelating bidentate moieties. Several arsenic(III) *tris*, mixed halide, and organoarsenic(III) derivatives of these ligands are well studied and characterized.[7–16] The corresponding mixed dithiolatoarsenic(III) complexes with these ligands do not appear to have received much attention of chemists.[11] In view of the interesting results reported from our laboratories[14,17–21] on these ligands with group 15 metal derivatives has prompted us to synthesize some toluene-3,4-dithiolatoarsenic(III)

Financial assistance from U.G.C., New Delhi is gratefully acknowledged. The elemental analysis (C and H) and spectral [IR, NMR (^1H, ^{13}C, and ^{31}P) data were recorded at Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute (CDRI), Lucknow.

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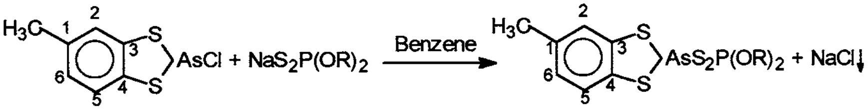
dialkyldithiophosphate derivatives and to characterized them by various spectroscopic (IR, ^{1}H, ^{13}C, and ^{31}P NMR) studies.

RESULTS AND DISCUSSION

Toluene-3,4-dithiolatoarsenic(III) dialkyldithiophosphate derivatives have been synthesized by reacting toluene-3,4-dithiolatoarsenic(III) chloride with sodium salts of dialkyldithiophosphoric acids in 1:1 molar ratio in refluxing benzene.



(where R= *Et, Pr^n^, Pr^i^, Bu^n^ and Bu^i^*)

All these newly synthesized derivatives are nonvolatile, yellow, viscous liquids and are soluble in common organic solvents like benzene, chloroform, and dichloromethane.

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Infrared Spectra

IR spectra of these compounds have been recorded in the range 4000–200 cm^{-1} and the characteristic bands have been assigned on the basis of earlier published work.[12–14,17–22]

The bands of medium to strong intensity observed in the region 1000–980 cm^{-1} and 890–860 cm^{-1} may be attributed to [(P)—O—C] and [P—O—(C)] stretching vibrations of dithiophosphate moieties respectively. A strong band due to (P=S) stretching vibrations present in the spectra of sodium salts of dialkyldithiophosphoric acids in the region 690–660 cm^{-1} is shifted toward lower frequencies (650–640 cm^{-1}) in all these derivatives. This shifting is indicating most probably a bidentate chelation of dialkyldithiophosphate ligands with arsenic.[12–14] Bands present in the region 550–500 cm^{-1} and 325–315 cm^{-1} are due to (P—S) and (As—S) stretching vibrations[12–14,22] respectively. In addition, the bands appearing in the region 730–660 cm^{-1} may be attributed to an asymmetrically trisubstituted benzene ring.[20,22]

^{1}H NMR Spectra

The ^{1}H NMR spectra of these derivatives have been recorded in C_6D_6 or $CDCl_3$ solutions using TMS as an internal standard. The spectra of these complexes exhibit the expected pattern without any appreciable shifts from the reported values.[12–14,20–22] In all these derivatives a sharp singlet have been observed in the region 1.86–2.32 δppm due to ring methyl protons. All these derivatives also show a sharp singlet in the region 6.95–7.25 δppm due to ring C_2 protons and two doublets in the region 6.50–6.91 δppm and 7.08–7.31 δppm due to ring C_6 and C_5 protons respectively. In addition these compounds also exhibit expected proton resonances due to the alkyl (ethyl, *n*-propyl, *i*-propyl, *n*-butyl, and *i*-butyl) protons of the dialkyldithiophosphate moieties (Table I).

^{13}C NMR Spectra

The ^{13}C NMR spectra of these derivatives have been recorded in $CDCl_3$ solutions using TMS as an internal standard. The ^{13}C NMR signals thus obtained are at reported values[20,22] without any appreciable shifts.

The ^{13}C NMR spectra of all these derivatives exhibit signals in the range 136.0–136.2 δppm; 137.6–137.9 δppm and at 141.2–141.6 δppm due to ring carbon number C_2, C_5,C_6; C_1 and C_3, C_4 resonances respectively. A signal in the region 20.6–20.8 δppm is observed due to ring methyl carbon. In addition these derivatives also exhibit the expected signals due to dialkyldithiophosphate moieties (Table I).

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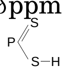
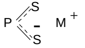
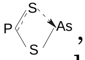
^{31}P NMR Spectra

The proton decoupled ^{31}P NMR spectra of the corresponding dialkyldithiophosphoric acids (LH) in $CDCl_3$ exhibit the resonances at ~81–83 δppm and of the sodium salts in Acetone d_6 at about 111 δppm and that of potassium and ammonium salts in D_2O at 107–108 δppm. In our toluene-3,4-dithiolatoarsenic(III) dialkyldithiophosphate complexes, we have obtained ^{31}P NMR chemical shift values in the range of 85.8 δppm to 90.2 δppm. These values are at lower field than the corresponding ligands  and higher than that of the corresponding ionic salts  indicating anisobidentate behaviour , of dithiophosphate moieties in these complexes Glidewell[23] also concluded that the values of proton decoupled ^{31}P NMR chemical shift ranging 83–101 δppm indicate bidentate behavior of the dialkyldithiophosphate ligands toward metals.

STRUCTURAL ELUCIDATION

In the corresponding IR spectra the (P=S) stretching vibrations ranging from 690–660 cm^{-1} in the free ligands are shifted toward lower

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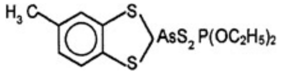
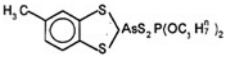
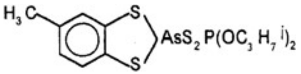
TABLE I ^{1}H, ^{13}C, and ^{31}P NMR Spectral Data of Toluene-3,4-Dithiolatoarsenic(III) Dialkyldithiophosphates

S. No.	Compounds	^{1}H NMR Chemical Shift (δppm)	^{13}C NMR Chemical Shift (δppm)	^{31}P NMR Chemical Shift (δppm)
1.		1.02, t, 6H (CH_3); J (OCH_2—CH_3) = 7.3 Hz	16.1 (CH_3)	
		1.87, s, 3H (ring CH_3)	20.8 (ring CH_3)	
		3.97, q, 4H (OCH_2); J (CH_3—OCH_2) = 7.3 Hz	64.2 (OCH_2)	
		6.50, d, 1H (ring CH(6)); J (ring protons) = 8.1 Hz	136.2 (C-2, 5, 6)	
		6.95, s, 1H (ring CH(2))	137.9 (C-1)	
		7.08, d, 1H (ring CH(5)); J (ring protons) = 8.1 Hz	141.4 (C-3, 4)	
2.		0.96, t, 6H (CH_3); J (CH_2—CH_3) = 7.3 Hz	10.2 (CH_3)	
		1.67–1.77, m, 4H (CH_2)	20.8 (ring CH_3)	
		2.32, s, 3H (ring CH_3)	23.5 (CH_2)	
		4.07, t, 4H (OCH_2); J (CH_2—OCH_2) = 7.3 Hz	69.7 (OCH_2)	
		6.98, d, 1H (ring CH(6)); J (ring protons) = 8.1 Hz	136.2 (C-2, 5, 6)	
		7.25, s, 1H (ring CH(2))	137.6 (C-1)	
		7.31, d, 1H (ring CH(5)); J (ring protons) = 8.1 Hz	140.6 (C-3, 4)	
3.		1.24, d, 12H (CH_3); J (OCH–$(CH_3)_2$) = 6.3 Hz	17.5 (CH_3)	85.8
		1.86, s, 3H (ring CH_3)	20.8 (ring CH_3)	
		4.84, sep., 2H (OCH); J ($(CH_3)_2$—OCH) = 6.3 Hz	73.6 (OCH)	
		6.49, d, 1H (ring CH(6)); J (ring protons) = 8.1 Hz	136.2 (C-2, 5, 6)	
		6.96, s, 1H (ring CH(2))	137.7 (C-1)	
		7.08, d, 1H (ring CH(5)); J (ring protons) = 8.1 Hz	141.5 (C-3, 4)	

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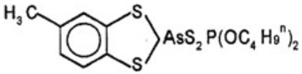
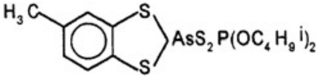
4.		0.90, t, 6H (CH_3); J (CH_2—CH_3) = 7.3 Hz 1.32–1.69, m, 8H (CH_2) 2.29, s, 3H (ring CH_3) 4.07, t, 4H (OCH_2); J (CH_2—OCH_2) = 7.3 Hz 6.91, d, 1H (ring CH(6)); J (ring protons) = 8.1 Hz 7.25, s, 1H (ring CH(2)) 7.31, d, 1H (ring CH(5)); J (ring protons) = 8.1 Hz	13.5 (CH_3) 18.6 (CH_2) 20.6 (ring CH_3) 31.6 (CH_2) 77.0 (OCH_2) 136.0 (C-2, 5, 6) 137.7 (C-1) 140.2 (C-3, 4)	89.8
5.		0.92, d, 12H (CH_3); J (CH—$(CH_3)_2$) = 6.6 Hz 1.87–2.07, m, 2H (CH) 2.29, s, 3H (ring CH_3) 3.83, d, 4H (OCH_2); J (CH—OCH_2) = 6.9 Hz 6.90, d, 1H (ring CH(6)); J (ring protons) = 8.1 Hz 7.24, s, 1H (ring CH(2)) 7.30, d, 1H (ring CH(5)); J (ring protons) = 8.1 Hz	18.7 (CH_3) 20.6 (ring CH_3) 28.6 (CH) 75.5 (OCH_2) 136.0 (C-2, 5, 6) 137.6 (C-1) 140.3 (C-3, 4)	90.2

s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = complex pattern.

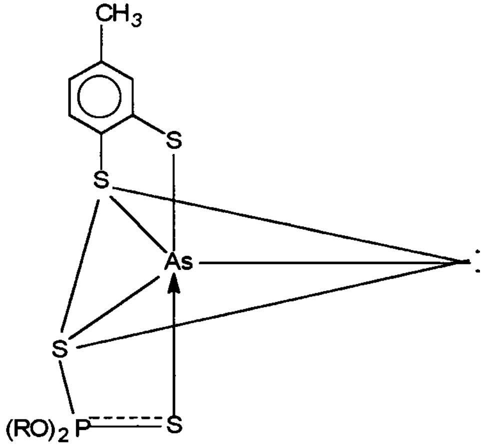


FIGURE 1 Proposed structure of the complexes.

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frequencies by ~20 cm^{-1} and are present in the range 650–640 cm^{-1} indicating weakening of P=S bond due to the coordination of the second sulphur atom to arsenic, indicating anisobidentate nature of the dialkyldithiophosphate moieties in these complexes. This has been further confirmed by the proton decoupled ^{31}P chemical shift values exhibited in the range of 85.8–90.2 δppm (Figure 1).

On the basis of the above spectral data it may be concluded tentatively that the dialkyldithiophosphate ligands behave as bidentate mode of attachment to the arsenic,[12–14] in all these derivatives, thus leading to distorted trigonal bipyramidal geometry, with a stereochemically active lone pair occupying one of the positions.

EXPERIMENTAL

All the experiments were carried out under moisture free conditions. Solvents (benzene, hexane and alcohols) were dried by standard methods,[24] P_2S_5 (Merck), Toluene-3,4-dithiol (Merck) were used as received without further purification. Dialkyldithiophosphoric acids and their sodium salts[1,2,14,28,29] were prepared by reported methods. Toluene-3,4-dithiolatoarsenic(III) chloride[22] was prepared by the reaction of arsenic trichloride and toluene-3,4-dithiol in equimolar ratio in anhydrous benzene. Arsenic was estimated iodometrically[12,13,25] and sulfur was estimated gravimetrically as barium sulfate.[26,27] Carbon and hydrogen were analyzed at RSIC, CDRI, Lucknow. The IR spectra

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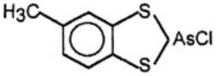
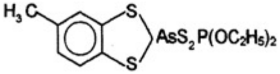
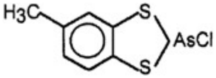
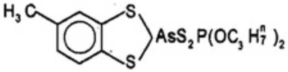
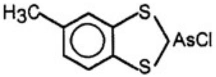
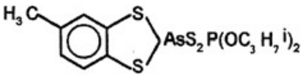
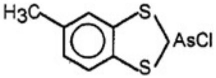
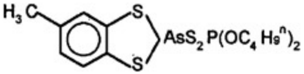
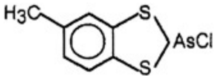
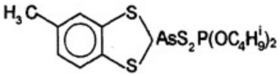
TABLE II Analytical and Physical Data for Toluene-3,4-Dithiolatoarsenic(III) Dialkyldithiophosphates

S. No	Reactants (grm)		Products[a] (yield(grm); %)	NaCl Found (Calcd.)	Found (Calcd.) %			
					As	S	C	H
1.	 (0.57)	$NaS_2P(OC_2H_5)_2$ (0.45)	 (0.81); 91	0.12 (0.12)	17.97 (18.08)	30.79 (31.00)	31.56 (31.89)	3.83 (3.86)
2.	 (0.56)	$NaS_2P(OC_3H_7^n)_2$ (0.51)	 (0.81); 86	0.11 (0.12)	15.37 (16.89)	25.51 (28.96)	35.60 (35.21)	4.42 (4.51)
3.	 (0.69)	$NaS_2P(OC_3H_7^i)_2$ (0.62)	 (0.95); 83	0.15 (0.15)	16.88 (16.89)	27.08 (28.96)	36.01 (35.21)	4.20 (4.51)
4.	 (0.41)	$NaS_2P(OC_4H_9^n)_2$ (0.41)	 (0.68); 93	0.09 (0.09)	15.75 (15.90)	26.31 (27.25)	38.51 (38.23)	4.89 (5.09)
5.	 (0.57)	$NaS_2P(OC_4H_9^i)_2$ (0.57)	 (0.97); 95	0.12 (0.12)	15.52 (15.90)	27.70 (27.25)	38.11 (38.23)	4.91 (5.09)

[a] All the products are yellow viscous liquids.

were recorded as Nujol mulls on a Perkin Elmer 577 spectrophotometer in the range 4000–200 cm^{-1}. The ^1H,^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX-300 NMR spectrophotometers. The chemical shift values ^1H and ^{13}C are expressed in δppm relative to TMS and that of ^{31}P relative to H_3PO_4.

Mixed toluene-3,4-dithiolato arsenic(III) dialkyldithiophosphate derivatives were synthesized (Table II) by the following method.

Reaction Between Toluene-3,4-dithiolatoarsenic(III) Chloride and Sodium Diethyldithiophosphate in 1:1 Molar Ratio

The solution of toluene-3,4-dithiolatoarsenic(III) chloride (0.57 g; 2.15 mmol) in benzene (~25 ml) was added dropwise to sodium diethyldithiophosphate (0.45 g; 2.15 mmol). The contents were heated under reflux for ~4 h. Precipitated sodium chloride (0.12 g) was removed by filtration. On removing the solvent from the filtrate nonvolatile, stable, yellow viscous liquid was obtained which was washed twice with hexane, dried and weighed. [Yield −0.81 g; 91%].

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