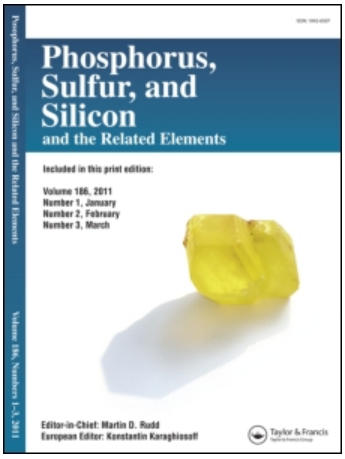

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

TETRAPHENYL PHOSPHONIUM AND ARSONIUM SALTS OF ALKYLENE DITHIOPHOSPHATO MOIETIES

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To cite this Article Tripathi, U. N. , Chaturvedi, A. , Singh, M. S. and Rao, R. J.(1997) 'TETRAPHENYL PHOSPHONIUM AND ARSONIUM SALTS OF ALKYLENE DITHIOPHOSPHATO MOIETIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 122: 1, 167 — 171
To link to this Article: DOI: 10.1080/10426509708043505
URL: http://dx.doi.org/10.1080/10426509708043505

Phosphorus, Sulfur, and Silicon, 1997, Vol. 122, pp. 167–171
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TETRAPHENYL PHOSPHONIUM AND ARSONIUM SALTS OF ALKYLENE DITHIOPHOSPHATO MOIETIES**

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(Received 24 September 1996; In final form 10 December 1996)

Complexes of the type $[Ph_4M]^+[S_2\overbrace{POGO}^{}]^-$ (M=P or As; G= $-CMe_2CH_2CHMe-$, $CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$, $-CMe_2CMe_2-$ and $-CH_2CH_2CHMe-$) have been synthesized by the reactions of tetraphenyl phosphonium and arsonium chloride with ammonium alkylene dithiophosphates. The derivatives have been chracterized by elemental analyses, molar conductance spectroscopic (IR, ^1H and ^{31}P NMR) studies.

Keywords: Tetraphenylphosphonium chloride; tetraphenylarsonium-chloride; alkylenedithiophosphates; molar conductance

In spite of extensive literature on dialkyl dithiphosphate derivatives[1–3] of phosphorous and arsenic; only a few alkylene dithiophosphato derivatives[4] of arsenic have been reported. Phosphonium and arsonium salts of dialkyl dithiophosphoric acids have also been reported[5]; but the alkylene dithiophosphato analogs are still unknown. In continuation of earlier investigations on dialkyl and alkylene dithiophosphato derivatives of main group elements[8–10]; it was of interest to extend these studies to the corresponding tetraphenyl phosphonium and arsonium and get a comparative study with their open chain derivatives.

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**This article is dedicated to (late) D. G. Srivastava, Associate Professor. Dept. of Chemistry, Rajasthan University, Jaipur.

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RESULTS AND DISCUSSION

Tetraphenylphosphonium and arsonium alkylenedithiophosphate were synthesized by the reactions of tetraphenylphosphonium and arsonium chloride with ammonium alkylenedithiophosphate in 1:1 molar ratio in isopropanol. These reactions are less facile compared to their O,O′-dialkyldithiophosphato counterparts[5].

$$Ph_4MCl + NH_4[S_2\overline{POGO}] \rightarrow [Ph_4M]^+[S_2\overline{POGO}]^+ NH_4Cl$$

[M = P, As; G = $-CMe_2CH_2CHMe-$, $CH_2CMe_2CH_2-$, $CH_2CEt_2CH_2$, $-CMe_2CMe_2$ and $-CH_2CH_2CHMe-$]

These derivatives are sharp melting, white crystalline solids, soluble in alcohol and water, whereas the open chain analogues are insoluble in water. The products show molar conductance in the range 18–25 $ohm^{-1}cm^2mole^{-1}$ in nitrobenzene, suggesting 1:1 electrolytic nature and these values are in accordance with their open chain derivatives having values5 in the range of 19–24 $ohm^{-1}cm^2mole^{-1}$.

In the IR spectra of these derivatives, bands in the range 1105-1075 cm^{-1}, 720–700cm^{-1}, 695–685cm^{-1} and 550–505cm^{-1} are due to different stretching and bending modes of the [P-C_6H_6 group][11,12] while the corresponding bands in tetraphenylarsonium[11] derivatives occur in the range 1095–1085cm^{-1}, 680–675cm^{-1}, 360–345cm^{-1} and 240–235cm^{-1}. A sharp band present in the region 710–670cm^{-1} is due to P=S stretching vibrations[1,13] which is overlapping with [P-C_6H_6] and [As-C_6H_6] vibrations. The bands present in the region 560–525cm^{-1} are due to [P-S] symmetric and asymmetric vibrations. In O,O′-dialkyldithiophosphato derivatives these bands are present at approximately the same positions[5].

The ^1H NMR spectra (Table I) show a minor upfield shift for all the resonance compared to the ligand acid spectra. In the case of tetraphenylarsonium derivatives a singlet due to phenyl protons is obtained while in tetraphenylphosphonium derivatives a multiplet is observed resulting from coupling of o-, m- and p-phenyl protons with phosphorous atom.

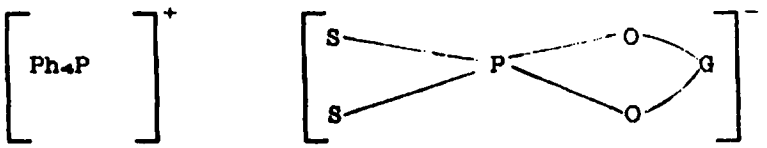
The ^{31}P NMR spectra shows the presence of a single resonance signal for tetraphenylarsonium derivatives, but two peaks are observed for tetraphenylphosphonium derivatives in which one corresponds to the dithiophosphate moiety and another is for the tetraphenylphosphonium cation's phosphorous. Although a usual feature of ^{31}P NMR spectra of these derivatives is that, in arsonium derivatives it should have an upfield shift compared to phosphonium

TABLE I IR and NMR (^1H and ^{31}P) spectral data of tetraphenyl phosphonium and arsonium alkylene dithiophosphates

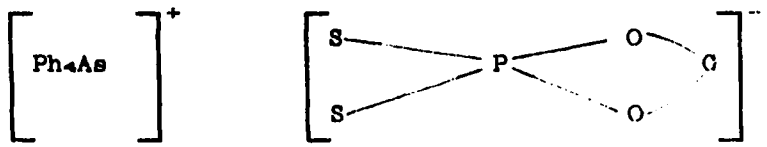
Compound	*IR* (cm^{-1}) (P=S)	*NMR* (δ *ppm*) ^1H	^{31}P
1. $[Ph_4P]^+[S_2\overline{POCMe_2CH_2CHMeO}]^-$	680	1.32, s, 6H(CH_3); 1.47, d, 3H(CH_3)J=7Hz;	88.02
		1.68,d,2H(CH_2)J=10Hz; 4.56–4.87, m, 1H(OCH); 7.26–7.95, m, 20H(C_6H_6)	21.09
2. $[Ph_4P]^+[S_2\overline{POCH_2CMe_2CH_2O}]^-$	670	1.38, s, 6H(CH_3); 3.61, d, 4H(OCH_2)J=16Hz	92.12
		7.36–7.92, m, 20H(C_6H_6)	20.80
3. $[Ph_4P]^+[S_2\overline{POCH_2CEt_2CH_2O}]^-$	695	0.78, t, 6H(CH_3) J=3Hz; 1.32, q, 4H(CH_2)	95.25
		4.07, d, 4H(OCH_2)J=15Hz; 7.28–7.98, m, 20(C_6H_6)	21.18
4. $[Ph_4P]^+[S_2\overline{POCMe_2CMe_2O}]^-$	710	1.31, s, 12H(CH_3); 8.15–9.00	103.46
		m, 20H(C_6H_6)	20.92
5. $[Ph_4P]^+[S_2\overline{POCH_2CH_2CHMeO}]^-$	700	1.42, d, 3H(CH_3) J=7Hz; 1.56, q, 2H(CH_2)	90.08
		3.67, d, 2H(OCH_2) J=17Hz; 4.51–4.83, m,1H(OCH); 7.32–7.91, m, 20H(C_6H_6)	21.00
6. $[Ph_4As]^+[S_2\overline{POCMe_2CH_2CHMeO}]^-$	685	1.20, s, 6H(CH_3); 1.38, d, 3H(CH_3) J=6Hz; 1.56, d, 2H(CH_2) J=9Hz; 4.50–4.93, m, 1H(OCH); 8.12, s, 20H(C_6H_6)	89.12
7. $[Ph_4As]^+[S_2\overline{POCH_2CMe_2CH_2O}]^-$	670	1.25, s, 6H(CH_3); 3.63, d, 4H (OCH_2) J=16Hz; 8.20, s, 20H (C_6H_6)	91.08
8. $[Ph_4As]^+[S_2\overline{POCH_2CEt_2CH_2O}]^-$	680	0.81, t, 6H(CH_3) J=3Hz; 1.40, q, 4H(CH_2); 4.18, d, 4H(OCH_2) J=15Hz; 8.08, s, 20H(C_6H_6)	94.87
9. $[Ph_4As]^+[S_2\overline{POCMe_2CMe_2O}]^-$	700	1.29, s, 12H(CH_3); 8.20, s, 20H(C_6H_6)	101.52
10. $[Ph_4As]^+[S_2\overline{POCH_2CH_2CHMeO}]^-$	695	1.42, d, 3H(CH_3) J=7Hz; 1.53, q, 2H(CH_2); 3.58, d, 2H(OCH_2) J=17Hz; 4.52–4.81, m, 1H(OCH) 8.06, s, 20H(C_6H_6)	92.02

salts as seen in most of these derivatives. However the anamalous behavior shown by a few of these derivatives may be due to the different chemical environment around the phosphorus atom of the dithiophosphato moiety, as the difference in chemical shift values is very small i.e. less than 2 ppm.

On the basis of the above studies and analogous with their open chain salts[5], an ionic nature have been proposed for these derivatives.



Tetraphenylphosphonium salt of alkylenedithiophosphates



Tetraphenylarsonium salt of alkylenedithiophosphates

EXPERIMENTAL

The tetraphenylphosphonium and arsonium chloride were used as supplied. Ammonium alkylenedithiophosphate were prepared as reported earlier14. The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer using Csl cells multinuclear NMR spectral measurements were recorded on a JEOL Fx 90Q spectrometer using TMS (for 1H) and H_3PO_4 (for 31P) as external references. Molar conductance were measured in nitrobenzene (10^{-3}M solution) on a Syntronics Digital Conductivity meter model 304 using a cell having a cell constant 1.0.

SYNTHESIS OF $[PH_4P]^+[\overline{S_2POCMeCH_2CHMeO}]^-$

Tetraphenylphosphonium chloride (1.82g; 4.8mmole) and $NH_4[S_2POCMeCH_2CHMeO]$ (1.11 g; 4.8 mmole) were reflexed in isopropanol for about 4 hours and left overnight. The NH_4Cl was filtered off. The volatiles were removed from filterate under pressure to get a white crystalline solid (2.71 g; 94% yield). The product recrystallized from ethanolic solution.

Other compounds were also prepared by the same procedure.

Acknowledgements

The authors (U.N. Tripathi and A. Chaturvedi) are highly grateful to Prof. R.C. Mehrotra and Dr. P.N. Nagar from Rajasthan University Jaipur for Valuable academic guidance.

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