

This article was downloaded by:

On: 27 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

New Organic Derivatives of *O,O'*-(*o*-, *m*-, and *p*-Ditolyl)/Dibenzylthiophosphates: Synthesis and Characterization

Sangeeta Sharma^a; Suresh Magotra^a; Sushil K. Pandey^a

^a Department of Chemistry, University of Jammu, Jammu, India

To cite this Article Sharma, Sangeeta , Magotra, Suresh and Pandey, Sushil K.(2009) 'New Organic Derivatives of *O,O'*-(*o*-, *m*-, and *p*-Ditolyl)/Dibenzylthiophosphates: Synthesis and Characterization', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 8, 2140 — 2151

To link to this Article: DOI: 10.1080/10426500802445340

URL: <http://dx.doi.org/10.1080/10426500802445340>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

New Organic Derivatives of *O,O'*-(*o*-, *m*-, and *p*-Ditolyl)/Dibenzylidithiophosphates: Synthesis and Characterization

Sangeeta Sharma, Suresh Magotra, and Sushil K. Pandey

Department of Chemistry, University of Jammu, Jammu, India

*Reactions of (*m*- and *p*-ClC₆H₄NH₂), (*p*-BrC₆H₄NO₂), and (*p*-ClCOC₆H₄NO₂) with sodium *O,O'*-ditolyl/dibenzylphosphorodithionates, (ArO)₂PS₂Na, (Ar = *o*-, *m*-, and *p*-CH₃C₆H₄ or -C₆H₅CH₂) in 1:1 molar ratio in refluxing toluene under anhydrous conditions resulted in the formation of the compounds (ArO)₂PS₂C₆H₄L and (ArO)₂PS₂COC₆H₄L (L = NH₂ or NO₂) in 87–94% yield. These viscous compounds were characterized by elemental analyses, molecular weight determination, and IR and NMR (¹H, ¹³C, and ³¹P) spectroscopic studies, which revealed a monodentate mode of bonding of the dithiophosphate moiety with the carbon of the phenyl ring of the organic moiety leading to a P–S–C linkage.*

Keywords Dithiophosphate; organophosphorus; phosphorodithioate; phosphorus–sulfur

INTRODUCTION

Dialkylphosphonates [(RO)₂PO][–], dialkyldithiophosphonates [(RS)₂PO][–], dialkyldithiophosphates [(OR)₂PS₂][–], and *O, O'*-alkylenedithiophosphates, [OGOPS₂][–] (where G = –CHMeCMe₂–, –CMe₂CMe₂–, –CH₂CMe₂CH₂–, CH₂CEt₂CH₂–, and –CHMeCH₂CMe₂–), have attracted wide attention in academia, especially due to their versatile utility as active pesticides^{1–2} and also for providing various bonding aspects with several metals and metalloids.^{3–6} These derivatives find extensive applications in agriculture,^{7–8} industry,^{9–10} and analytical studies.^{11–12} A variety of complexes have been reported with these ligands, in which they have predominantly exhibited a bidentate mode of bonding.^{13–19} However, the less common monodentate

Received 13 May 2008; accepted 2 September 2008.

We are grateful to the Central Drug Research Institute, Lucknow, for providing spectral studies.

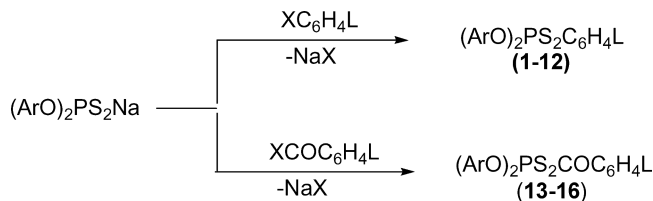
Address correspondence to Sushil K. Pandey, Department of Chemistry, University of Jammu, Baba Saheb Ambedkar Road, Jammu, 180 006 (J & K), India. E-mail: kpsushil@rediffmail.com

linkage has also been depicted by these ligands, such as in the case of nickel and tin.^{20–21} A literature survey revealed scant information on the derivatives of *O,O'*-ditolyldithiophosphate ligands compared to dialkyl- and alkylenedithiophosphates.^{22–26} We have recently reported a convenient synthesis of ditolyldithiophosphate ligands²⁷ and also a single crystal X-ray structure of $[\text{Et}_3\text{NH}]^+[(o\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]^-$.²⁸ These new ditolyldithiophosphate ligands appear to be potential chelating ligands to the metals, metalloids, and nonmetals. Recently, some metal complexes with the ditolyldithiophosphate ligands have been synthesized and characterized.^{29–30} Some interesting applications of ditolyldithiophosphates have also been reported such as rubber vulcanizers,³¹ aerofloats,³² polymerization catalysts,³³ oil additives,³⁴ and acaricides.³⁵ The nitrogen-containing organodithiophosphates are well known biologically active compounds, such as methyl/ethyl parathion, $(\text{RO})_2\text{P}(\text{S})\text{OC}_6\text{H}_4\text{NO}_2$ ($\text{R} = \text{Me}/\text{Et}$), and others such as malathion, $(\text{MeO})_2\text{PS}(\text{S})\text{CHCO}_2\text{EtCH}_2\text{CO}_2\text{Et}$, which is produced from dialkyldithiophosphoric acids, $(\text{RO})_2\text{PS}_2\text{H}$ ($\text{R} = \text{Me}/\text{Et}$) and widely used as effective pesticides.^{35–36} A review of the literature indicated no report of organic derivatives of ditolyl/dibenzylthiophosphates. In view of the above interesting facets of dithiophosphate chemistry, it was thought worthy to investigate the chemistry of organic derivatives of *O,O'*-(*o*-, *m*-, and *p*-ditolyl)/dibenzylthiophosphates. So, we report herein on the synthesis of some new nitrogen containing organic compounds of *O,O'*-ditolyl/dibenzylthiophosphates using *m*- and *p*-chloroaniline, *p*-bromonitrobenzene, and *p*-nitrobenzoylchloride.

RESULTS AND DISCUSSION

Reactions of *m*- $\text{ClC}_6\text{H}_4\text{NH}_2$, *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$, *p*- $\text{BrC}_6\text{H}_4\text{NO}_2$, and *p*- $\text{ClCOC}_6\text{H}_4\text{NO}_2$ with sodium *O,O'*-(*o*-, *m*- and *p*-ditolyl)/dibenzyl phosphorodithioates, $(\text{ArO})_2\text{PS}_2\text{Na}$ ($\text{Ar} = o$ -, *m*-, and *p*- $\text{CH}_3\text{C}_6\text{H}_4$ and – $\text{C}_6\text{H}_5\text{CH}_2$) in 1:1 molar ratio in toluene under refluxing conditions resulted in the formation of compounds of the type $(\text{ArO})_2\text{PS}_2\text{C}_6\text{H}_4\text{L}$ ($\text{L} = m\text{-NH}_2$ for **1–4**, *p*- NH_2 for **5–8**, and *p*- NO_2 for **9–12**) and $(\text{ArO})_2\text{PS}_2\text{COC}_6\text{H}_4\text{-}p\text{-NO}_2$ (**13–16**) in 87–94% yield (Scheme 1).

These reactions were found to be a bit sluggish and needed to be refluxed for 9–11 h. These compounds are viscous liquids; they appear to be moisture sensitive, since they became turbid when left open in humid atmosphere; and they are soluble in organic solvents such as toluene, benzene, and chloroform and insoluble in carbon tetrachloride and *n*-hexane. The micro-elemental analyses (C, H, N, and S) were found to be in agreement with the molecular weight of the compound.

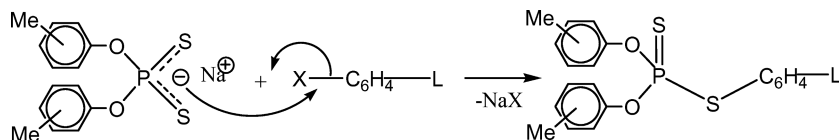


SCHEME 1 Where Ar = *o*-, *m*- and *p*-CH₃C₆H₄ or C₆H₅CH₂; L = *m*-NH₂ (**1-4**), *p*-NH₂ (**5-8**) and *p*-NO₂ (**9-12**) and *p*-NO₂ (**13-16**); X = Cl or Br.

These compounds are nonvolatile even under reduced pressure, and they decomposed to dark brown products, which could not be characterized. The monomeric nature of these compounds was confirmed by their molecular weight determination using a cryoscopic method (Table I).

Mechanistically, the reaction between dithiophosphate ligand and organic moiety might involve the nucleophilic displacement of the halide ion from the organic moiety with the dithiophosphate ligand (Scheme 2).

The IR spectral data (4000–400 cm⁻¹) were interpreted by comparison with relevant and related literature reports.^{22–25,34} The IR spectra of these compounds show the disappearance of the νC–X (X=Cl and Br) absorption band present in the range of 755–710 cm⁻¹ in the parent organic moiety and the appearance of a new absorption band in the region 680–608 cm⁻¹, which is assigned for νC–S vibrations. This fact has supported the cleavage of C–X bond thereby formation of P(S)–S–C linkage in these compounds. The bands of medium intensities in the region 780–681 cm⁻¹ and 598–506 cm⁻¹ are attributed to νP=S and νP–S (asymmetric and symmetric) vibrations of the dithiophosphate moiety, which indicated no shifting compared to the parent dithio ligand. The absorption bands of strong intensity present in the region 1195–1170 cm⁻¹ and 958–817 cm⁻¹ are assigned for ν(P)–O–C and νP–O–(C) stretching vibrations, respectively. A band for νN–H vibrations was observed in the region 3473–3339 cm⁻¹ in the compounds **1-8**. The absorption band for nitro group in the compounds **9-16** was observed



SCHEME 2 Nucleophilic displacement of halide ion with dithiophosphate moiety.

TABLE I Synthetic and Analytical Data of Organic Derivatives of Ditoly/dibenzylthiophosphates

S. No.	Reactants g (mmol)		Compound (Physical state)	Yield (%)	M.W Found (Calcd.)	Analysis (%) Found (Calcd.)			
	LX	(ArO) ₂ PS ₂ Na				C	H	N	S
1.	0.38 (3.0)	1.00 (3.0)	[(<i>o</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>m</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	94	399.00 (401.49)	58.99 (59.83)	4.87 (5.02)	3.21 (3.48)	15.70 (15.97)
2.	0.38 (3.0)	1.00 (3.0)	[(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>m</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	92	390.00 (401.49)	58.89 (59.83)	4.79 (5.02)	3.32 (3.48)	15.72 (15.97)
3.	0.38 (3.0)	1.00 (3.0)	[(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>m</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	92	390.00 (401.49)	58.83 (59.83)	4.76 (5.02)	3.21 (3.48)	15.51 (15.97)
4.	0.38 (3.0)	1.00 (3.0)	[(C ₆ H ₅ CH ₂ O) ₂ PS ₂ - <i>m</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	94	389.00 (401.49)	58.86 (59.83)	4.78 (5.02)	3.30 (3.48)	15.73 (15.97)
5.	0.38 (3.0)	1.00 (3.0)	[(<i>o</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	90	392.00 (401.49)	58.91 (59.83)	4.81 (5.02)	3.30 (3.48)	15.67 (15.97)
6.	0.38 (3.0)	1.00 (3.0)	[(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	94	392.00 (401.49)	58.80 (59.83)	4.81 (5.02)	3.23 (3.48)	15.87 (15.97)
7.	0.38 (3.0)	1.00 (3.0)	[(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	92	385.00 (401.49)	58.89 (59.83)	4.84 (5.02)	3.27 (3.48)	15.47 (15.97)
8.	0.38 (3.0)	1.00 (3.0)	[(C ₆ H ₅ CH ₂ O) ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NH ₂] (Light yellow viscous)	94	375.00 (401.49)	58.99 (59.83)	4.88 (5.02)	3.37 (3.48)	15.67 (15.97)

(Continued on next page)

TABLE I Synthetic and Analytical Data of Organic Derivatives of Ditolyl/dibenzylthiophosphates
(Continued)

S. No.	Reactants g (mmol)		Compound (Physical state)	Yield (%)	M.W Found (Calcd.)	Analysis (%) Found (Calcd.)			
	LX	(ArO) ₂ PS ₂ Na				C	H	N	S
9.	0.55 (3.0)	1.00 (3.0)	[<i>o</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NO ₂] (Greenish viscous)	89	425.50 (431.47)	55.09 (55.67)	4.33 (4.20)	3.01 (3.24)	14.82 (14.86)
10.	0.55 (3.0)	1.00 (3.0)	[<i>m</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NO ₂] (Greenish viscous)	88	424.00 (431.47)	55.29 (55.67)	4.35 (4.20)	3.12 (3.24)	14.67 (14.86)
11.	0.55 (3.0)	1.00 (3.0)	[<i>p</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NO ₂] (Greenish viscous)	88	422.50 (431.47)	55.27 (55.67)	4.45 (4.20)	3.07 (3.24)	14.80 (14.86)
12.	0.55 (3.0)	1.00 (3.0)	[(C ₆ H ₅ CH ₂ O) ₂ PS ₂ - <i>p</i> -C ₆ H ₄ NO ₂] (Greenish viscous)	87	422.50 (431.47)	55.29 (55.67)	4.35 (4.20)	3.19 (3.24)	14.99 (14.86)
13.	0.60 (3.0)	1.00 (3.0)	[<i>o</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -COC ₆ H ₄ NO ₂] (Reddish viscous)	90	451.00 (459.48)	54.27 (54.89)	3.45 (3.94)	2.97 (3.04)	13.90 (13.95)
14.	0.60 (3.0)	1.00 (3.0)	[<i>m</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -COC ₆ H ₄ NO ₂] (Reddish viscous)	93	450.00 (459.48)	54.29 (54.89)	3.85 (3.94)	2.78 (3.04)	13.79 (13.95)
15.	0.60 (3.0)	1.00 (3.0)	[<i>p</i> -CH ₃ C ₆ H ₄ O] ₂ PS ₂ - <i>p</i> -COC ₆ H ₄ NO ₂] (Reddish viscous)	94	448.00 (459.48)	54.39 (54.89)	3.88 (3.94)	2.91 (3.04)	13.27 (13.95)
16.	0.60 (3.0)	1.00 (3.0)	[(C ₆ H ₅ CH ₂ O) ₂ PS ₂ - <i>p</i> -COC ₆ H ₄ NO ₂] (Greenish violet viscous)	90	451.00 (459.48)	53.29 (54.89)	3.55 (3.94)	3.01 (3.04)	13.81 (13.95)

Where Ar = *o*-, *m*- or *p*-CH₃C₆H₄ or -C₆H₅CH₂, LX= *m*-ClC₆H₄NH₂ (**1-4**), *p*-ClC₆H₄NH₂ (**5-8**), *p*-BrC₆H₄NO₂ (**9-12**), and *p*-ClCOC₆H₄NO₂ (**13-16**).

TABLE II IR Spectral Data of Organic Derivatives of Ditolyl/dibenzylthiophosphates (in cm^{-1})

S. No.	Aromatic $\nu(\text{C—H})$	$\nu(\text{P})\text{—O—C}$	$\nu\text{P—O—(C)}$	$\nu\text{P= S}$	$\nu\text{P—S}$	$\nu\text{C—S}$	$\nu\text{N—H}$	νNO	$\nu\text{C=O}$
1.	2962, b	1174, s	889, s	682, m	563, m	608, m	3343, b	—	—
2.	2956, b	1174, s	887, s	681, m	559, m	632, m	3339, b	—	—
3.	3058, b	1195, s	888, s	681, m	527, m	630, m	3364, b	—	—
4.	2963, b	1170, s	889, s	682, m	561, m	668, m	3387, b	—	—
5.	2961, b	1191, s	896, s	688, m	562, m	640, m	3416, b	—	—
6.	2963, b	1177, s	877, s	681, m	566, m	635, m	3387, b	—	—
7.	2963, b	1181, s	820, s	697, m	506, m	639, m	3473, b	—	—
8.	2971, b	1174, s	817, s	698, m	585, m	637, m	3385, b	—	—
9.	2964, b	1188, s	870, s	780, m	510, m	665, m	—	1150, s	—
10.	2967, b	1190, s	885, s	775, m	514, m	665, m	—	1164, s	—
11.	2965, b	1177, s	880, s	760, m	511, m	640, m	—	1166, s	—
12.	2967, b	1188, s	885, s	766, m	513, m	680, m	—	1205, s	—
13.	2964, b	1181, s	951, s	705, m	598, m	669, m	—	1190, s	1580, s
14.	2963, b	1192, s	958, s	684, m	588, m	641, m	—	1234, s	1610, s
15.	2924, b	1189, s	942, s	730, m	591, m	631, m	—	1421, s	1609, s
16.	2963, b	1171, s	926, s	699, m	598, m	670, m	—	1478, s	1592, s

Where s = Strong, b = broad, and m = medium.

in the region $1478\text{--}1150\text{ cm}^{-1}$. The relevant IR spectral data are data are given in Table II.

In the ^1H NMR spectra (in CDCl_3), the chemical shifts for the $-\text{CH}_3$ and $-\text{CH}_2$ (benzyl ring) protons were observed in the regions δ 2.2–2.3 and δ 3.5–3.6 ppm as a singlet, whereas the chemical shift for the phenyl ring protons of the dithio moiety appeared in the region δ 7.0–7.5 ppm as a multiplet in all the compounds. This multiplet was due to long range coupling of these protons with a magnetically active phosphorus atom. The chemical shifts for the phenyl protons of organic moiety ($-\text{C}_6\text{H}_4\text{NH}_2$, $-\text{C}_6\text{H}_4\text{NO}_2$, and $-\text{COC}_6\text{H}_4\text{NO}_2$) also appeared as multiplet in the range δ 6.5–7.1 ppm. The resonance for $-\text{NH}_2$ protons in the compounds **1–8** was observed as a singlet in the region δ 3.0–3.5 ppm. The ^1H NMR spectral data of these compounds are summarized in Table III.

The ^{31}P NMR chemical shift occurred as singlet in the range δ 81.0–88.6 ppm for these compounds. The upfield shifting of ^{31}P chemical shift in range of δ 20–25 ppm compared to the parent dithiophosphate moiety ($\sim\delta$ 105 ppm) might be due to the formation of a covalent linkage between the carbon and sulfur atom of the dithiophosphate moiety in a unidentate manner. The occurrence of only one singlet in each case might be due to the equivalent nature of the phosphorus atom in these

TABLE III ^1H and ^{31}P NMR Spectral Data of Organic Derivatives of Ditolyl/dibenzylthiophosphates in CDCl_3 (δ ppm)

S. No.	^1H	^{31}P
1.	2.3 (s, 6H, $-\text{CH}_3$), 7.0–7.3 (m, 8H, $-\text{C}_6\text{H}_4$), 6.8–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.5 (s, 2H, $-\text{NH}_2$)	84.8, s
2.	2.3 (s, 6H, $-\text{CH}_3$), 7.1–7.2 (m, 8H, $-\text{C}_6\text{H}_4$), 6.5–6.6 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.5 (s, 2H, $-\text{NH}_2$)	81.0, s
3.	2.2 (s, 6H, $-\text{CH}_3$), 7.0–7.2 (m, 8H, $-\text{C}_6\text{H}_4$), 6.5–6.6 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.5 (s, 2H, $-\text{NH}_2$)	82.1, s
4.	3.5 (s, 6H, $-\text{CH}_2$), 7.2–7.3 (m, 10H, $-\text{C}_6\text{H}_5$), 6.7–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.5 (s, 2H, $-\text{NH}_2$)	84.1, s
5.	2.2 (s, 6H, $-\text{CH}_3$), 7.2–7.3 (m, 8H, $-\text{C}_6\text{H}_4$), 6.7–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.5 (s, 2H, $-\text{NH}_2$)	83.1, s
6.	2.2 (s, 6H, $-\text{CH}_3$), 7.1–7.2 (m, 8H, $-\text{C}_6\text{H}_4$), 6.7–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.4 (s, 2H, $-\text{NH}_2$)	81.0, s
7.	2.2 (s, 6H, $-\text{CH}_3$), 7.1–7.3 (m, 8H, $-\text{C}_6\text{H}_4$), 6.7–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.4 (s, 2H, $-\text{NH}_2$)	83.9, s
8.	3.5 (s, 6H, $-\text{CH}_2$), 7.1–7.3 (m, 10H, $-\text{C}_6\text{H}_5$), 6.7–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NH}_2$), 3.0 (s, 2H, $-\text{NH}_2$)	83.9, s
9.	2.2 (s, 6H, $-\text{CH}_3$), 7.0–7.4 (m, 8H, $-\text{C}_6\text{H}_4$), 6.6–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NO}_2$)	82.9, s
10.	2.2 (s, 6H, $-\text{CH}_3$), 7.1–7.3 (m, 8H, $-\text{C}_6\text{H}_4$), 6.6–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NO}_2$)	83.0, s
11.	2.3 (s, 6H, $-\text{CH}_3$), 7.2–7.5 (m, 8H, $-\text{C}_6\text{H}_4$), 6.6–6.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NO}_2$)	83.9, s
12.	3.5 (s, 6H, $-\text{CH}_2$), 7.1–7.3 (m, 10H, $-\text{C}_6\text{H}_5$), 6.6–6.8 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{C}_6\text{H}_5\text{NO}_2$)	84.1, s
13.	2.3 (s, 6H, $-\text{CH}_3$), 7.2–7.3 (m, 8H, $-\text{C}_6\text{H}_4$), 6.8–7.0 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{COC}_6\text{H}_5\text{NO}_2$)	88.6, s
14.	2.3 (s, 6H, $-\text{CH}_3$), 7.0–7.2 (m, 8H, $-\text{C}_6\text{H}_4$), 6.8–7.0 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{COC}_6\text{H}_5\text{NO}_2$)	87.1, s
15.	2.2 (s, 6H, $-\text{CH}_3$), 7.2–7.4 (m, 8H, $-\text{C}_6\text{H}_4$), 6.8–7.9 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{COC}_6\text{H}_5\text{NO}_2$)	88.2, s
16.	3.6 (s, 6H, $-\text{CH}_2$), 7.2–7.5 (m, 10H, $-\text{C}_6\text{H}_5$), 6.9–7.1 (m, 4H, $-\text{C}_6\text{H}_4$ of $\text{COC}_6\text{H}_5\text{NO}_2$)	87.9, s

Where s = singlet and m = multiplet.

compounds. The ^{31}P chemical shift values of these compounds are given in Table III.

The ^{13}C NMR spectra of these compounds did not show any appreciable deviation in the chemical shift value of the carbon nuclei compared to the parent moieties. The chemical shift for methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) carbon occurred in the range δ 22.0–22.9 and δ 42.9–43.2 ppm, respectively. The carbon nuclei of the phenyl groups ($-\text{C}_6\text{H}_5$ and $-\text{C}_6\text{H}_4$) have displayed their resonance in the

region δ 112.1–131.2 ppm. The chemical shift for C–O carbon in *meta*- and *para*-ditolyldithiophosphato derivatives (**2–3**, **6–7**, **10–11**, and **14–15**) was found in the region δ 152.1–154.9 ppm, which is indicative of intramolecular hydrogen bonding between a proton attached to one of the *ortho*-carbons of one tolyl ring with an oxygen atom (O–C) of the other tolyl ring. However, the shift for C–O carbon in *ortho*-ditolyldithiophosphato derivatives (**1**, **5**, **9**, and **13**) was found with an upfield shift in the range of δ 145.6–146.8 ppm, which shows the absence of intramolecular hydrogen bonding in *ortho*-derivatives. The presence of hydrogen bonding in the compounds (**2–3**, **6–7**, **10–11**, and **14–15**) is also supported by the chemical shift for the C–(CH₃) carbon in the range δ 115.2–116.9 ppm compared to the chemical shift in the compounds (**1**, **5**, **9**, and **13**), which lies in the normal region δ 122.6–122.9 ppm. This upfield swing for the chemical shift of C–(CH₃) carbon in the *meta*- and *para*- derivatives is possible because of hydrogen bonding between the proton attached to *ortho*-carbon of one tolyl ring with oxygen atom of other tolyl ring. In the ¹³C NMR spectra of the compounds (**1–16**), four signals for the phenyl carbons of the organic moiety have been observed in the region δ 115.1–153.1 ppm for C_{i(ips)}, C_{o(ortho)}, C_{m(meta)}, and C_{p(para)}, respectively. The corrected chemical shift values, δ' ($\delta' = C_{para} - C_{meta}$), are found to be positive in the range 22.6–30.0 for these compounds.³⁷ These positive δ' values do not appear in cases like metal dithiophosphates, for which δ' values are negative since the mode of attachment of the dithio ligand is referred to as bidentate. These positive values are suggestive of less polarity of carbon–sulfur bond compared to well established M–S linkages. The chemical shift of carbonyl carbon C(O) of organic moiety in the compounds (**13–16**) occurred in the region δ 190.2–192.4 ppm. The ¹³C NMR spectral data of these compounds are summarized in Table IV.

EXPERIMENTAL

General Procedure and Reagents

Benzene and toluene were freshly dried by refluxing over sodium metal and kept under a nitrogen atmosphere. Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk techniques. Elemental analyses (C, H, N, and S) were performed on a Vario EL III and CHNS-932 Leco elemental analyzer. *O,O'*-Ditolyldibenzylidithiophosphate ligands were prepared by a method in the literature.²⁷ Molecular weights were determined cryoscopically in freezing benzene. IR spectra were recorded either as nujol mulls or neat in the range of 4000–400 cm^{–1} on Perkin Elmer-577 and Shimadzu

TABLE IV ¹³C NMR Spectral Data of Organic Derivatives of Ditolyl/dibenzylthiophosphates in CDCl₃ (δ ppm)

S. No.	-CH _n n = 2/3	CH ₃ C ₆ H ₄ O/C ₆ H ₅ CH ₂ O						Organic moiety		
		Ring Carbon								
		-C(CH ₃)	C—O	C—O*	Ortho-	Meta-	Para-	C ₆ H ₄	-C(O)	
1.	22.7	122.9	146.8	—	121.8	126.7 and 131.2	125.7	115.1–147.1	—	—
2.	22.6	115.6	—	154.9	118.4 and 123.8	124.6	126.8	122.5–146.2	—	—
3.	22.9	116.3	—	152.6	112.1	124.3	—	117.0–145.1	—	—
4.	43.2	136.2	—	—	125.3	126.9	126.2	121.9–147.1	—	—
5.	22.9	122.7	145.6	—	121.5	126.8 and 131.2	125.6	115.5–146.9	—	—
6.	22.8	115.3	—	153.6	118.2 and 122.5	126.8	126.8	115.0–145.2	—	—
7.	22.9	116.2	—	152.6	119.8	124.3	—	115.9–147.1	—	—
8.	43.2	136.3	—	—	125.3	126.9	126.2	115.9–147.1	—	—
9.	22.1	122.9	145.6	—	120.8	126.7 and 130.2	125.2	122.6–145.1	—	—
10.	22.0	116.1	—	152.1	118.2 and 123.8	124.2	126.6	121.9–146.8	—	—
11.	22.9	115.6	—	153.6	119.8	124.7	—	123.0–146.1	—	—
12.	43.2	126.2	—	—	125.4	126.8	126.2	120.9–146.7	—	—
13.	22.9	122.6	145.6	—	123.8	124.9 and 129.2	126.6	122.6–153.1	190.9	190.9
14.	22.6	115.2	—	152.6	118.2 and 123.8	124.8	126.9	121.6–146.2	190.2	190.2
15.	22.1	116.9	—	153.6	118.2	124.7	—	121.0–146.2	192.4	192.4
16.	42.9	137.0	—	—	123.8	124.3	126.6	123.9–146.0	191.2	191.2

*Hydrogen bonded.

8201 PC spectrophotometers. The ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Bruker DRX 300 (300 MHz) and Bruker Avance 400 (400 MHz) spectrometer using TMS as an external reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR.

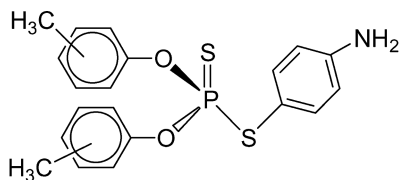
Synthesis of S-(3-Aminophenyl)-O,O'-di(2-tolyl)phosphorodithioate [(*o*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}$) $_2\text{PS}_2$ -*m*- $\text{C}_6\text{H}_4\text{NH}_2$] (1)

For the synthesis of (*o*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}$) $_2\text{PS}_2\text{C}_6\text{H}_4\text{NH}_2$ (1), an approximately 20 cm³ toluene solution of *m*-chloroaniline, *m*- $\text{ClC}_6\text{H}_4\text{NH}_2$ (0.38 g, 3.0 mmol) was added dropwise with constant stirring into a toluene suspension (~30 cm³) of sodium salt of O,O'-(*o*-ditolyl)dithiophosphoric acid, (*o*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}$) $_2\text{PS}_2\text{Na}$ (1.00 g, 3.0 mmol) in a 100 cm³ round-bottomed flask. The reaction mixture was refluxed for ~9 h and then was brought to room temperature. The precipitated sodium chloride was removed by filtration using a funnel fitted with a G-4 sintered disc. Subsequently, excess solvent from the filtrate was evaporated under reduced pressure. Final drying of the product in vacuo for ~3 h resulted the compound (*o*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}$) $_2\text{PS}_2\text{C}_6\text{H}_4\text{NH}_2$ (1) as light yellow viscous liquid in 94% yield.

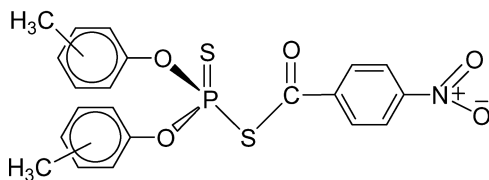
Similar methodology and stoichiometry was used for the synthesis of all other compounds (2–16). The synthetic and analytical data of these compounds are given in Table I.

STRUCTURAL FEATURES

It is not possible to predict the precise structure of these compounds, since we could not produce a single crystal, owing to viscous nature of the products. However, on the basis of analytical studies such as elemental analyses, molecular weight determination, IR, and multinuclear NMR (^1H , ^{31}P , and ^{13}C), a probable geometry may be assigned to these compounds. It is interesting to note that ^{31}P NMR spectra of the compounds have shown an upfield shift in the range δ 20–25 ppm compared to the parent dithio ligands, and this might be due to monodentate behavior of the ligand, since it is found that a low-field shift (high ppm) is usually observed in the cases when dithiophosphate ligand is bonded in bidentate manner.^{13–19} Hence only one sulfur atom of the ditolyl/dibenzyl dithiophosphate ligand is attached to the carbon atom of organic moiety, leaving another sulfur atom non-bonded. In conjunction with the reports in the literature,^{34–36} P–S–C linkage may be assigned in these compounds in which the phosphorus(V) atom might have a tetrahedral arrangement such as [(*o*-, *m*-, and



(a)



(b)

FIGURE 1

p -CH₃C₆H₄O)₂PS₂- p -C₆H₄NH₂] (Figure 1a) and [(o -, m -, and p -CH₃C₆H₄O)₂PS₂- p -COC₆H₄NO₂] (Figure 1b).

REFERENCES

- [1] C. Fest and K. J. Schimdt, *The Chemistry of Organophosphorus Pesticides*, 2nd ed. (Springer Verlag, New York, 1982).
- [2] M. Umemura, M. Konishi, A. Fukushima, J. Hisano, and T. Okamoto, EUR Pat EP 205, 165; *Chem. Abstr.*, **106**, 87468n (1987).
- [3] J. R. Wasson, G. M. Wolterman, and H. J. Stocklosa, *Top. Curr. Chem.*, **35**, 65 (1973).
- [4] B. P. S. Chauhan, G. Srivastava, and R. C. Mehrotra, *Coord. Chem. Rev.*, **55**, 207 (1984).
- [5] H. P. S. Chauhan, *Coord. Chem. Rev.*, **173**, 1 (1998).
- [6] I. Haiduc, *Rev. Inorg. Chem.*, **3**, 353 (1981).
- [7] A. Mihailovski, US Pat. 4071545 (1978); *Chem. Abstr.*, **88b**, 170295j (1978).
- [8] J. Kanazawa, H. Kubo, and R. Sato, *Agric. Boil. Chem.*, **29**, 43 (1965).
- [9] H. H. Farmer, B. W. Malone, and H. F. Tompkins, S. African Pat., 68, 02, 089 (1968); *Chem. Abstr.*, **71**, 23626f (1969).
- [10] C. L. Stewart (Ominitec Inc., USA), US Pat 200, 106, 04 (2002); *Chem. Abstr.*, **138**, 41800 (2002).
- [11] K. Hayashi, Y. Sasaki, S. Tagashira, Y. Soma, and S. Kato, *Anal. Sci.*, **105**, 237529d (1986).
- [12] A. Shishkov and D. Atanasova, *Nauchi. Tr. Plovdivski. Univ.*, **19**, 265 (1982); *Chem. Abstr.*, **98**, 190813 (1983).
- [13] S. K. Pandey, G. Srivastava, and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **19**, 795 (1989).
- [14] S. K. Pandey, G. Srivastava, and R. C. Mehrotra, *J. Ind. Chem. Soc.*, **66**, 558 (1989).
- [15] R. Chander, B. L. Kalsotra, and S. K. Pandey, *Ind. J. Chem.*, **43A**, 1134 (2004).

- [16] J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, M. Curtui, G. Gutal, and D. Ruse, *Inorg. Chem.*, **19**, 2861 (1980).
- [17] R. Chander, B. L. Kalsotra, and S. K. Pandey, *Transition. Met. Chem.*, **28**, 405 (2003).
- [18] U. N. Tripathi, *Phosphorus, Sulfur, and Silicon*, **159**, 47 (2000).
- [19] U. N. Tripathi, P. P. Bipin, R. Mirza, and A. Chaturvedi, *Pol. J. Chem.*, **73**, 1751 (1999).
- [20] P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, **92**, 3964 (1970).
- [21] K. C. Molloy, M. B. Hossain, D. V. Helm, J. J. Zuckerman, and I. Haiduc, *Inorg. Chem.*, **18**, 3507 (1980).
- [22] E. I. Markova, D. A. Akhmedzade, and N. F. Dzhanikbekov, *Azer. Khim. Zh.*, **1**, 135 (1984); *Chem. Abstr.*, **101**, 221365d (1984).
- [23] S. Wu, Z. Liu, and Y. Zhange, *Gazz. Chim. Ital.*, **123**, 647 (1993); *Chem. Abstr.*, **121**, 3580m (1994).
- [24] Q. Qie, X. Xu, D. Zhange, X. Xie, and C. Chen, *Huax Xue*, **51**, 96 (1993); *Chem. Abstr.*, **118**, 213207q (1993).
- [25] Q. Hao, H. K. Fun, S. I. Chantpromma, A. Razak, F. Jian, X. Yang, L. Lu, and X. Wang, *Acta Crystallogr.*, **57**, 717 (2001).
- [26] Q. Xie, N. Luo, J. Li, and X. Jing, *Youj. Haux.*, **12**, 159 (1992); *Chem. Abstr.*, **117**, 26650w (1992).
- [27] A. Kumar, K. R. Sharma, and S. K. Pandey, *Phosphorus, Sulfur, and Silicon*, **182**, 1023 (2007).
- [28] A. Kumar, J. E. Drake, C. L. B. Macdonald, R. Ratnani, and S. K. Pandey, *J. Chem. Crystallogr.*, **35**, 447 (2005).
- [29] J. E. Drake, C. Gurnani, M. B. Hursthouse, M. E. Light, M. Nirwan, and R. Ratnani, *App. Organomet. Chem.*, **21**, 539 (2007).
- [30] A. Kumar, D. Kumar, and S. K. Pandey, *Synth. React. Inorg. Met.-Org. Chem.*, **37**, 697 (2007).
- [31] J. A. McCleverty, R. S. Z. Kowalski, N. A. Bailey, R. Mulvaney, and D. A. O'Cleirigh, *J. Chem. Soc. Dalton. Trans.*, **4**, 627 (1983).
- [32] E. M. Idleson and A. K. Livshits, *Akad. Nauk.*, 61 (1956); *Chem. Abstr.*, **55**, 42553 (1961).
- [33] N. N. Glebova, O. K. Shrev, E. L. Tinyakova, and B. A. Dolgoplas, *Petrochem. Synth.*, **37**, 1145 (1995); *Chem. Abstr.*, **125**, 14337g (1996).
- [34] F. Yuan, Y. Haung, and Q. Xie, *App. Organomet. Chem.*, **16**, 660 (2002).
- [35] W. E. McEwen, V. C. Si, and B. J. Kalbacher, *Phosphorus, Sulfur, and Silicon.*, **11**, 191 (1981).
- [36] R. K. Gupta, A. K. Rai, R. C. Mehrotra, V. K. Jain, B. F. Hoskins, and E. R. T. Tiekink, *Inorg. Chem.*, **24**, 3280 (1985).