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Phosphorus, Sulfur, and Silicon and the Related Elements

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

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

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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 $-C_6H_5CH_2$) 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.

 $\label{eq:keywords} {\bf Keywords} \quad {\rm Dithiophosphate; \ organophosphorus; \ phosphorodithioate; \ phosphorus-sulfur}$

INTRODUCTION

Dialkylphosphonates $[(RO)_2PO]^-$, dialkyldithiophosphonates $[(RS)_2 PO]^-$, dialkyldithiophosphates $[(OR)_2PS_2]^-$, and O, O'-alkylenedithiophosphates, $[OGOPS_2]^-$ (where G = -CHMeCMMe-, $-CMe_2CMe_2$ -, $-CH_2CMe_2CH_2$ -, $CH_2CEt_2CH_2$ -, and $-CHMeCH_2CMe_2$ -), have attracted wide attention in academia, especially due to their versatile utility as active pesticides¹⁻² 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

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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 [Et₃NH]⁺[(o-MeC₆H₄O)₂PS₂]^{-.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, $(RO)_2P(S)OC_6H_4NO_2$ (R = Me/Et), and others such as malathion, (MeO)₂PS(S)CHCO₂EtCH₂CO₂Et, which is produced from dialkyldithiophosphoric acids, $(RO)_2PS_2H$ (R = Me/Et) and widely used as effective pesticides.³⁵⁻³⁶ A review of the literature indicated no report of organic derivatives of ditolyl/dibenzyldithiophosphates. 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)/dibenzyldithiophosphates. So, we report herein on the synthesis of some new nitrogen containing organic compounds of O,O'-ditolyl/dibenzyldithiophosphates using m- and pchloroaniline, *p*-bromonitrobenzene, and *p*-nitrobenzoylchloride.

RESULTS AND DISCUSSION

Reactions of m-ClC₆H₄NH₂, p-ClC₆H₄NH₂, p-BrC₆H₄NO₂, and p-ClCOC₆H₄NO₂ with sodium O,O'-(o-, m- and p-ditolyl)/dibenzyl phosphorodithioates, (ArO)₂PS₂Na (Ar = o-, m-, and p-CH₃C₆H₄ and -C₆H₅CH₂) in 1:1 molar ratio in toluene under refluxing conditions resulted in the formation of compounds of the type (ArO)₂PS₂C₆H₄L (L = m-NH₂ for **1-4**, p-NH₂ for **5-8**, and p-NO₂ for **9-12**) and (ArO)₂PS₂COC₆H₄-p-NO₂ (**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 $Ar = 0^-$, 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 ν C–X (X=CI and Br) absorption band present in the range of $755-710 \text{ cm}^{-1}$ in the parent organic moiety and the appearance of a new absorption band in the region 680–608 cm⁻¹, which is assigned for ν C–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 ν P=S and ν P–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 $\nu(P)$ –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.

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	Reactar	tts g (mmol)		Yield	M.W Found	Aı	nalysis (%) F	ound (Calcd	(.
S. No.	ΓX	$(ArO)_2PS_2Na$	Compound (Physical state)	(%)	(Calcd.)	C	Н	Z	s
1.	0.38~(3.0)	1.00(3.0)	$[(o-CH_3C_6H_4O)_2PS_2-m-C_6H_4NH_2]$	94	399.00 (401.49)	58.99 (59.83)	4.87(5.02)	3.21(3.48)	$15.70\ (15.97)$
5	0.38~(3.0)	1.00 (3.0)	(Light yellow viscous) [(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>m</i> - C ₆ H ₄ NH ₂]	92	390.00 (401.49)	58.89 (59.83)	4.79(5.02)	3.32~(3.48)	15.72~(15.97)
ы.	0.38~(3.0)	1.00(3.0)	(Light yellow viscous) [(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ - <i>m</i> - C ₆ H ₄ NH ₂]	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)	(Light yellow viscous) [(C ₆ H ₅ CH ₂ O) ₂ PS ₂ -m- C ₆ H ₄ NH ₂]	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)	$\begin{array}{l} (Light\ yellow\ viscous) \\ [(o-CH_3C_6H_4O)_2PS_{2}\text{-}p\text{-}\\ C_6H_4NH_2] \end{array}$	06	392.00 (401.49)	58.91~(59.83)	4.81(5.02)	3.30(3.48)	15.67~(15.97)
.9	0.38(3.0)	1.00(3.0)	(Light yellow viscous) $[(m-CH_3C_6H_4O)_2PS_2-p-C_6H_4NH_2]$	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)	(Light yellow viscous) $[(p-CH_3C_6H_4O)_2PS_{2}-p-C_6H_4NH_2]$	92	$385.00\ (401.49)$	58.89 (59.83)	4.84(5.02)	3.27~(3.48)	$15.47\ (15.97)$
ò.	0.38 (3.0)	1.00 (3.0)	(Light yellow viscous) $[(C_6H_5CH_2O)_2PS_2-p-C_6H_4NH_2]$ (Light yellow viscous)	94	375.00 (401.49)	58.99 (59.83)	4.88 (5.02)	3.37 (3.48)	15.67 (15.97)

TABLE I Synthetic and Analytical Data of Organic Derivatives of Ditolyl/dibenzyldithiophosphates

(Continued on next page)

100	manin								
	Reactai	nts g (mmol)		Yield	M.W Found	An	alysis (%) F	ound (Calco	1.)
S. No.	LX.	$(ArO)_2PS_2Na$	Compound (Physical state)	(%)	(Calcd.)	С	Η	Ν	S
9.	0.55(3.0)	1.00(3.0)	$[(o-CH_3C_6H_4O)_2PS_2-p-C_6H_4NO_2]$	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)	(Greenish viscous) $[(m-CH_3C_6H_4O)_2PS_2-p-C_6H_4NO_2]$	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)	(Greenish viscous) $[(p-CH_3C_6H_4O)_2PS_2-p-C_6H_4NO_2]$	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)	(Greentsh viscous) $[(C_6H_5CH_2O)_2PS_2$ - p - $C_6H_4NO_2]$ (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)	$(o-CH_3C_6H_4O)_2PS_2 \cdot p - COC_6H_4NO_2]$ $(OCC_6H_4NO_2]$ (Roddish viscous)	06	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)	(medden Mecous) $[(m-CH_3C_6H_4O)_2PS_2-p-COC_6H_4O)_2]$ $(COC_6H_4NO_2]$ (Roddish 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)	$[(p-CtH_3C_6H_4O)_2PS_{2}-p-CoC_6H_4O)_2PS_{2}-p-CoC_6H_4NO_2]$	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)	(Greensn vioue viscous) $[(C_6H_5CH_2O)_2PS_2-p-COC_6H_4NO_2]$ (Reddish viscous)	06	451.00 (459.48)	53.29 (54.89)	3.55 (3.94)	3.01 (3.04)	13.81 (13.95)
p-CIC	here $Ar = c$ OC_6H_4NC	-, <i>m</i> - or <i>p</i> -CH ₃ λ ₂ (13-16).	C_6H_4 or $-C_6H_5CH_2$, $LX=m$ -Cl C_6H_3	$[_4NH_2$	(1–4), <i>p</i> -ClC ₆ H ₄]	NH ₂ (5–8), <i>p</i> -F	$^{\rm h}{ m C_6}{ m H_4}{ m NO_2}$	(9–12), and	

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S. No.	Aromatic v(C—H)	ν(P)—O—C	ν Ρ—Ο— (C)	vP=S	vP—S	vC—S	νN —H	νNO	vC=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		$1478,\mathrm{s}$	$1592,\mathrm{s}$

TABLE II IR Spectral Data of Organic Derivatives of Ditolyl/ dibenzyldithiophosphates (in cm⁻¹)

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

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

In the ¹H NMR spectra (in CDCl₃), the chemical shifts for the $-CH_3$ and $-CH_2$ (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 ($-C_6H_4NH_2$, $-C_6H_4NO_2$, and $-COC_6H_4NO_2$) also appeared as multiplet in the range δ 6.5–7.1 ppm. The resonance for $-NH_2$ 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 ³¹P NMR chemical shift occurred as singlet in the range δ 81.0– 88.6 ppm for these compounds. The upfield shifting of ³¹P 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

S. No.	$^{1}\mathrm{H}$	^{31}P
1.	2.3 (s, 6H, -CH ₃), 7.0-7.3 (m, 8H, -C ₆ H ₄), 6.8-6.9 (m, 4H, -C ₆ H ₄ of C ₆ H ₅ NH ₂), 3.5 (s, 2H, -NH ₂)	84.8, s
2.	2.3 (s, 6H, -CH ₃), 7.1–7.2 (m, 8H, -C ₆ H ₄), 6.5–6.6 (m, 4H, -C ₆ H ₄) of C ₆ H ₅ NH ₂), 3.5 (s, 2H, -NH ₂)	81.0, s
3.	2.2 (s, 6H, $-CH_3$), 7.0–7.2 (m, 8H, $-C_6H_4$), 6.5–6.6 (m, 4H, $-C_6H_4$ of $C_6H_5NH_2$), 3.5 (s, 2H, $-NH_2$)	82.1, s
4.	3.5 (s, 6H, $-CH_2$), 7.2–7.3 (m, 10H, $-C_6H_5$), 6.7–6.9 (m, 4H, $-C_6H_4$ of C_6H_5 NH ₂), 3.5 (s, 2H –NH ₂)	84.1, s
5.	2.2 (s, 6H, $-CH_3$), 7.2–7.3 (m, 8H, $-C_6H_4$), 6.7–6.9 (m, 4H, $-C_6H_4$ of $C_6H_5NH_9$), 3.5 (s, 2H – NH_9)	83.1, s
6.	2.2 (s, 6H, $-CH_3$), 7.1–7.2 (m, 8H, $-C_6H_4$), 6.7–6.9 (m, 4H, $-C_6H_4$ of $C_6H_5NH_9$), 3.4 (s, 2H, $-NH_9$)	81.0, s
7.	2.2 (s, 6H, $-CH_3$), 7.1–7.3 (m, 8H, $-C_6H_4$), 6.7–6.9 (m, 4H, $-C_6H_4$ of $C_6H_7NH_9$), 3.4 (s, 2H, $-NH_9$)	83.9, s
8.	3.5 (s, 6H, $-CH_2$), 7.1–7.3 (m, 10H, $-C_6H_5$), 6.7–6.9 (m, 4H, $-C_6H_4$ of $C_2H_2NH_2$), 3.0 (s, 2H, $-NH_2$)	83.9, s
9.	(1, 1) $(2, 1)$ $(3, 1)$ $(3, 1)$ $(4, 1)$ $(4, 1)$ $(4, 2)$ $(4, 1)$ $(4, 2)$ $($	82.9, s
10.	2.2 (s, 6H, $-CH_3$), 7.1–7.3 (m, 8H, $-C_6H_4$), 6.6–6.9 (m, 4H, $-C_6H_4$ of $C_2H_2NO_3$)	83.0, s
11.	2.3 (s, 6H, $-CH_3$), 7.2–7.5 (m, 8H, $-C_6H_4$), 6.6–6.9 (m, 4H, $-C_6H_4$ of $C_2H_2NO_3$)	83.9, s
12.	3.5 (s, 6H, $-CH_2$), 7.1–7.3 (m, 10H, $-C_6H_5$), 6.6–6.8 (m, 4H, $-C_6H_4$	84.1, s
13.	2.3 (s, 6H, $-CH_3$), 7.2–7.3 (m, 8H, $-C_6H_4$), 6.8–7.0 (m, 4H, $-C_6H_4$)	88.6, s
14.	2.3 (s, 6H, -CH ₃), 7.0–7.2 (m, 8H, -C ₆ H ₄), 6.8–7.0 (m, 4H, -C ₆ H ₄)	87.1, s
15.	2.2 (s, 6H, -CH ₃), 7.2–7.4 (m, 8H, -C ₆ H ₄), 6.8–7.9 (m, 4H, -C ₆ H ₄)	88.2, s
16.	3.6 (s, 6H, -CH ₂), 7.2–7.5 (m, 10H, -C ₆ H ₅), 6.9–7.1 (m, 4H, -C ₆ H ₄ of COC ₆ H ₅ NO ₂)	87.9, s

TABLE III ¹H and ³¹P NMR Spectral Data of Organic Derivatives of Ditolyl/dibenzyldithiophosphates in CDCl₃ (δ ppm)

Where s = singlet and m = multiplet.

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

The ¹³C 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 (-CH₃) and methylene (-CH₂) 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 (-C₆H₅ and -C₆H₄) have displayed their resonance in the

region δ 112.1–131.2 ppm. The chemical shift for C–O carbon in metaand *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 orthoditolyldithiophosphato 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 $C-(CH_3)$ 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 $C_{i(ipso)}$, $C_{o(ortho)}$, $C_{m(meta)}$, and $C_{p(para)}$, respectively. The corrected chemical shift values, $\delta' (\delta' = C_{para} - C_{meta})$, 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 13 C 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'-Ditolyl/dibenzyldithiophosphate 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

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TABLE IV ¹³C NMR Spectral Data of Organic Derivatives of Ditolyl/dibenzyldithiophosphates in CDCl₃ (**% ppm**)

			0	$H_{3}C_{6}H_{4}O_{1}$	$C_6H_5CH_2O$				
					R	ing Carbon		Organic moi	ety
S. No.	-CH _n n = 2/3	-C(CH ₃)	C-0	C—0*	Ortho-	Meta-	Para-	C_6H_4	-C(O)
1.	22.7	122.9	146.8	I	121.8	126.7 and 131.2	125.7	115.1 - 147.1	I
2.	22.6	115.6	I	154.9	118.4 and 123.8	124.6	126.8	122.5 - 146.2	I
с.	22.9	116.3		152.6	112.1	124.3		117.0 - 145.1	I
4.	43.2	136.2	I	Ι	125.3	126.9	126.2	121.9 - 147.1	I
5.	22.9	122.7	145.6	I	121.5	126.8 and 131.2	125.6	115.5 - 146.9	
.9	22.8	115.3	I	153.6	118.2 and 122.5	126.8	126.8	115.0 - 145.2	I
7.	22.9	116.2		152.6	119.8	124.3		115.9 - 147.1	
œ.	43.2	136.3		I	125.3	126.9	126.2	115.9 - 147.1	I
9.	22.1	122.9	145.6	Ι	120.8	126.7 and 130.2	125.2	122.6 - 145.1	I
10.	22.0	116.1	I	152.1	118.2 and 123.8	124.2	126.6	121.9 - 146.8	I
11.	22.9	115.6		153.6	119.8	124.7		123.0 - 146.1	I
12.	43.2	126.2			125.4	126.8	126.2	120.9 - 146.7	I
13.	22.9	122.6	145.6	Ι	123.8	124.9 and 129.2	126.6	122.6 - 153.1	190.9
14.	22.6	115.2	I	152.6	118.2 and 123.8	124.8	126.9	121.6 - 146.2	190.2
15.	22.1	116.9	I	153.6	118.2	124.7	I	121.0 - 146.2	192.4
16.	42.9	137.0			123.8	124.3	126.6	123.9 - 146.0	191.2
*Hyd	rogen bonded.								

8201 PC spectrophotometers. The ¹H, ¹³C, and ³¹P 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 ³¹P NMR.

Synthesis of S-(3-Aminophenyl)-O,O'-di(2tolyl)phosphorodithioate) [(o-CH₃C₆H₄O)₂PS₂-m-C₆H₄NH₂] (1)

For the synthesis of $(o\text{-}CH_3C_6H_4O)_2PS_2C_6H_4NH_2(1)$, an approximately 20 cm³ toluene solution of *m*-chloroaniline, *m*-ClC₆H₄NH₂(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, $(o\text{-}CH_3C_6H_4O)_2PS_2Na$ (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 $(o\text{-}CH_3C_6H_4O)_2PS_2C_6H_4NH_2(1)$ 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, ³¹P, and ¹³C), a probable geometry may be assigned to these compounds. It is interesting to note that ³¹P 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 ditotyl/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)



FIGURE 1

 $p-CH_3C_6H_4O_2PS_2-p-C_6H_4NH_2$] (Figure 1a) and [(o-, m-, and $p-CH_3C_6H_4O_2PS_2-p-COC_6H_4NO_2$] (Figure 1b).

REFERENCES

- 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).
- 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. Chantrpromma, 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. Dolgoplask, *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).

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