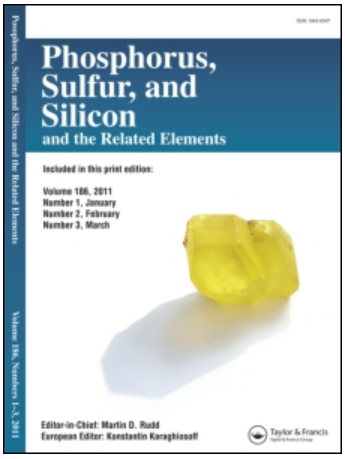

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kumar, Aran , Sharma, Kuldeep R. and Pandey, Sushil K.(2007) 'Synthesis and Characterization of *O,O'*-(*o*-, *m*-, or *p*-Ditolyl) Dithiophosphate Ligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 5, 1023 — 1031
To link to this Article: DOI: 10.1080/10426500601090917
URL: http://dx.doi.org/10.1080/10426500601090917

Phosphorus, Sulfur, and Silicon, 182:1023–1031, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601090917

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Synthesis and Characterization of *O,O′*-(*o*-, *m*-, or *p*-Ditolyl) Dithiophosphate Ligands

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O,O′-(ortho-, meta-, *or* para-*ditolyl) dithiophosphate ligands have been isolated as triethylammonium salts, (*o-, m- *or* p-$CH_3C_6H_4O)_2PS_2HNEt_3$, by an auto-catalytic reaction of cresols with P_2S_5 in the presence of Et_3N in a 4:1:2 molar ratio in toluene under anhydrous conditions. These triethylammonium salts could be converted into sodium/ammonium salts, (o-, m-, or p-$CH_3C_6H_4O)_2PS_2Na/NH_4$, by their direct reaction with sodium metal in equimolar ratio or passing dry ammonia gas in toluene. These salts were characterized by elemental analyses (C, H, N, and S) and mass, IR, and NMR (^1H, ^{13}C, and ^{31}P) spectroscopic studies.*

Keywords Cresyl; dithiophosphates; ditolyl; triethylammonium

INTRODUCTION

O,O′-dialkyl dithiophosphoric acids, $(RO)_2PS_2H$ (where R = Me, Et, Pr^n, Pr^i, or Bu^t), and cyclic analogous, *O,O′*-alkylene dithiophosphoric acids, $\overline{OGO}PS_2H$ (where G = 1,2- and 1,3-glycols), as well as their alkali metal salts have occupied a unique position as versatile chelating ligands in the last three decades.[1–4] These ligands are known to form a variety of complexes with transition and non-transition elements.[3–12] In general, a universal bi-dentate nature of these ligands has been established.[7–10,12] However, they have also depicted other bonding modes, e.g., monodentate, bridging, or chelating toward several metals and metalloids.[2,6,13] These ligands are known to form polymeric complexes.[10]Various dithiophosphate complexes find extensive applications in agriculture,[11] industries,[13,14] extraction,[15] and analytical processes.[16] A literature survey revealed that a substantial amount of

Received July 30, 2006; accepted October 6, 2006.
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work has been done with these ligands but scant information is available on the synthesis and characterization *O,O′*-ditolyl dithiophosphate ligands and their derivatives. The synthesis of $(p\text{-}CH_3C_6H_4O)_2PS_2H$ and its salts is reported; however, these have been characterized mainly on the basis of UV and IR spectroscopy.[17] Only a few reports are available on this subject, and they lack either the description of a convenient route to synthesis or proper characterization.[18–22] In addition, forced conditions, such as a higher temperature ranging 115–150°C, were applied for synthesis, and there also were difficulties in separation. Recently, some metal complexes with ditolyl dithiophosphate ligands have been synthesized and characterized.[23,24] Some derivatives of ditolyl dithiophosphates have found applications both in industries[25–27] and agriculture.[28] Therefore, it was thought worthy to investigate the chemistry of *O,O′*-(*o*-, *m*-, or *p*-ditolyl) dithiophosphates, and we report here on the convenient synthesis and characterization of *O,O′*-(*o*-, *m*-, or *p*−ditolyl) dithiophosphate ligands.

RESULTS AND DISCUSSION

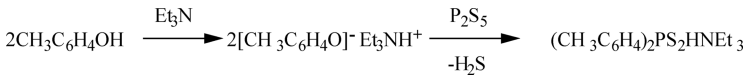
Reactions of P_2S_5 with *ortho*-, *meta*-, or *para*-hydroxytoluenes (cresols) in the presence of triethylamine, Et_3N, in a 4:1:2 stoichiometry in toluene were quite facile at 40–50°C and yielded sticky solid compounds corresponding to $(RO)_2PS_2HNEt_3$, where R = *o*—$CH_3C_6H_4O$ (**1**), *m*—$CH_3C_6H_4O$ (**2**), and *p*—$CH_3C_6H_4O$ (**3**) (Scheme 1).

$$4CH_3C_6H_4OH + P_2S_5 + 2Et_3N \xrightarrow[\sim 30\ \text{minutes}]{\text{Tol., } 40\text{–}50^\circ\text{C}} \underset{(\mathbf{1\text{-}3})}{2(CH_3C_6H_4O)_2PS_2HNEt_3} + H_2S$$

SCHEME 1

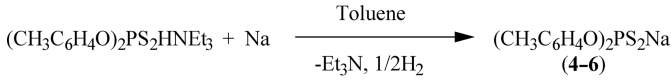
Zemlyanskii and Glushkova have obtained crude $(p\text{-}CH_3C_6H_4O)_2PS_2H$ by the reaction of P_2S_5 with cresol at 150°C, which on reaction with K_2CO_3 gave potassium salt in a 60% yield.[20] We have found that cresols do not show any reactivity with P_2S_5 in the absence of triethylamine even on refluxing in toluene over a week's time. It is to be noted also that the reactions of P_2S_5 with alcohols or glycols also are a bit sluggish and are completed usually in 4–6 h. Therefore, it is implicated that Et_3N has not only acted as a reactant but also played a catalytic role in these reactions. It may be presumed that an ionic species, $[CH_3C_6H_4O]^-Et_3NH^+$, initially formed, which then reacted with P_2S_5 in a rather facile way (Scheme 2).

Compounds (**1–3**) are fairly soluble in common organic solvents like toluene, chloroform, methylenedichloride, or benzene, and are insoluble



SCHEME 2

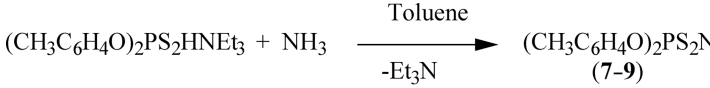
in carbon tetrachloride or *n*-hexane. These were obtained in a quantitative yield and appear to be moisture sensitive but sufficiently stable to handle if they are not directly exposed to moisture. These compounds get crystallized in 2–3 days just by leaving them at r.t. or by keeping the toluene-hexane solution at 0°C. These triethylammonium salts of *O,O′*-(*ortho-, meta-*, or *para*-ditolyl) dithiophosphates (**1–3**) were easily converted into sodium salts by their direct reaction with sodium metal in toluene in a 1:1 molar ratio (Scheme 3).



[*o*-$CH_3C_6H_4O$ **(4)**, *m*-$CH_3C_6H_4O$ **(5)**, and *p*-$CH_3C_6H_4O$ **(6)**]

SCHEME 3

Passing dry NH_3 gas through a toluene solution of triethylammonium salts (**1–3**) for 8–10 min resulted in the formation of ammonium salts of O,O′-ditolyl dithiophosphates (Scheme 4).



[*o*-$CH_3C_6H_4O$ **(7)**, *m*-$CH_3C_6H_4O$ **(8)**, and *p*-$CH_3C_6H_4O$ **(9)**]

SCHEME 4

Sodium and ammonium salts are soluble in CH_3OH or EtOH, sparingly soluble in chloroform, and insoluble in most of the hydrocarbon solvents. Efforts were made to convert triethylammonium salts of *O,O′*-(*o-*, *m-*, or *p*-ditolyl) dithiophosphates into *O,O′*-(*o-*, *m-*, or *p*-ditolyl) dithiophosphoric acids, $(CH_3C_6H_4O)_2PS_2H$, by their reaction with dry hydrochloric gas (HCl), but this was not successful to isolate because the final product was embedded with impurities, which could not be separated. However, this could be achieved by the reaction of triethylammonium salts of *O,O′*- (*o-*, *m-*, or *p*-ditolyl) dithiophosphates with acetic acid in toluene or benzene ,which results in the formation of a compound corresponding to $(CH_3C_6H_4O)_2PS_2H$ in a 50–60% yield

$$(CH_3C_6H_4O)_2PS_2Na + CH_3COOH \xrightarrow[CH_3COONa]{\text{Toluene/Benzene}} (CH_3C_6H_4O)_2PS_2H$$

SCHEME 5

(Scheme 5). This work is still under progress, especially in view of the characterization and optimization of yield.

The micro-elemental analyses (C, H, N, and S) of all the previously discussed compounds (**1–9**) were found consistent to their molecular composition. The monomeric nature of compounds (**1–3)** has been found by their molecular weight determinations in freezing benzene. All these compounds have shown the presence of the molecular ion peak in mass spectra.

IR spectra were recorded in the range 4000–200 cm^{-1}, and the tentative assignments were done on the basis of relevant literature reports.[1–5] IR spectra have shown a broad absorption for νNH vibrations in the region 3581–3425 cm^{-1} in compounds (**1–3**) and (**7–9**), while these absorptions were absent in compounds (**4–6**). In all the compounds ν(P)—O—C and νP—O—(C), stretching vibrations were found in the region 1189–1108 cm^{-1} and 950–860 cm^{-1}, respectively. Bands in region 563–540 cm^{-1} and 702–672 cm^{-1} may be assigned to νP—S and νP═S (symmetric and asymmetric) vibrations. The νCH stretching vibrations due to the tolyl group appeared in the region 2950–2910 cm^{-1}.

In ^{1}H NMR spectra, a triplet and quartet were observed for —CH_3 and —CH_2 protons of Et_3N moiety in the compounds (**1–3**) at δ 1.25–1.29 ppm ($J = 7.2$ Hz) and δ 3.09–3.11 ppm, respectively. The chemical shift for the —NH proton in compounds (**1–3**) and (**7–9)** appeared as a broad signal at δ 9.24–9.64 ppm. The chemical shifts of —CH_3 (attached to tolyl) and for tolyl ring protons were observed at δ 2.10–2.29 ppm and δ 6.82–7.44 ppm with a usual splitting pattern. The sodium and ammonium salts of the cresyl dithiophosphates have shown the chemical shifts for all the protons except the protons due to Et_3NH group.

The ^{13}C NMR spectral study of compounds (**4–9**) was not possible due to their poor solubility in $CDCl_3$. However, the ^{13}C NMR spectral data of compounds (**1–3**) have provided rather useful information. In ^{13}C spectra of compounds (**1–3**), the chemical shifts for —CH_3 and —CH_2 carbons of the Et_3NH moiety were observed in the regions δ 8.49–8.52 and δ 46.18–46.23 ppm, respectively. This upfield shift is due to the presence of a nitrogen atom bonded to it carrying a positive charge. For compound (**1**), chemical shifts for the —CH_3 carbons of both tolyl rings were found at δ 17.45–17.48 ppm. Chemical shifts for *para*- and *meta*-carbon were found in the regions δ 126.07–131.22 and δ 124.29–125.86 ppm, respectively. The shift for carbon, to which methyl groups are attached, was

found in the region δ 130.76–131.05 ppm, where a shift for *ortho*-carbon (unsubstituted ones) was found in the normal region δ 120.81–123.94 ppm, suggesting that none of the protons of these carbon atoms are involved in hydrogen bonding. The absence of hydrogen bonding is also confirmed by no significant change in the chemical shift for C—O. The ^{13}C spectrum of compound (**2**) has shown a chemical shift for the —CH_3 carbon of the two tolyl rings at δ 17.50 and δ 17.46 ppm. Chemical shifts for *ortho-*, *meta-,* and *para-* carbons were found in the regions δ 121.80–123.79, δ 124.37–126.04, and δ 126.26–130.99 ppm, respectively. Shifts for three *ortho*-carbons were found in the region δ 121.80–123.97 ppm, while one of the *ortho*-carbons was observed with an upfield shift at δ 115.17 ppm. This abnormal shift value might be due to intramolecular hydrogen bonding between protons attached to the carbon and oxygen atom. This hydrogen bonding is further supported by the chemical shift for C—O, which occurred at δ 154.73 ppm as compared to a shift for aromatic C—O without hydrogen bonding at 150–152 ppm.[29,30] In the ^{13}C spectrum of compound (**3**), chemical shifts for the —CH_3 carbon of both tolyl rings were found at δ 17.48 and δ 17.45 ppm. The chemical shift for *para*-carbon, to which methyl groups are attached, was found in the region δ 126.82–131.20 ppm. The shifts for *meta-* and *ortho*-carbon were found in the region δ 122.34–124.00 ppm and δ 124.38–126.62 ppm, while one of the *ortho*-carbons was observed with an upfield shift at δ 115.09 ppm, which is due to the presence of intramolecular hydrogen bonding akin to [(m—$CH_3C_6H_4O)_2PS_2HNEt_3$].

^{31}P NMR spectra (proton-decoupled) have shown the chemical shift as a singlet in each case in the downfield region. Chemical shifts for compounds (**1–9**) were found in the region δ 105.22–109.14 ppm, respectively. Occurrence of a singlet in each case indicated the equivalent nature of phosphorus nucleus in the molecule.

EXPERIMENTAL

General Procedures and Reagents

All the experimental manipulations were carried out strictly under anhydrous conditions, and a nitrogen atmosphere and also by using modified Schlenk techniques. Triethylamine (Thomas Baker, b.p. 88.8°C) and cresols (Highmedia, b.p. 191°C *ortho-*, 203°C *meta-*, and 202°C *para-*), were freshly distilled prior to use. P_2S_5(Spectrochem) was procured commercially and it was used as such. Toluene was dried by refluxing over sodium metal and kept under a nitrogen atmosphere. Micro-elemental analysis (C, H, and N) was done on a Vario EL III elemental analyzer, while sulfur was estimated as $BaSO_4$ by Messenger's

method. Infrared spectra were recorded in KBr on an FTIR Perkin Elmer-377 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on Jeol FX 90Q 90MHz using TMS as an external reference. ^{31}P NMR spectra were recorded by means of a Brucker DRX 300 (120 MHz) using 85% H_3PO_4 as an external reference. The mass spectrophotometeric analysis (EI) was carried out on ESQUIRE-300 (Brucker-Daltonics).

Synthesis

(o-$CH_3C_6H_4O)_2PS_2HNEt_3$ (1)

A toluene solution (~40 mL) of freshly distilled *ortho*-cresol (9.37 g, 8.99 mmol) was added dropwise to a toluene (~80 mL) suspension of P_2S_5 (5.0 g, 2.24 mmol). After stirring the contents for 5–7 min at ~50°C, a toluene solution (~40 mL) of Et_3N (4.55 g, 4.59 mmol) was added dropwise to it. All the P_2S_5 was dissolved in 15–20 min, resulting in a clear mixture. Evaporation of excess of toluene under reduced pressure resulted in the compound (*o*-$CH_3C_6H_4O)_2PS_2HNEt_3$ **(1)** in a quantitative yield as a colorless sticky solid. Yield 18.1 g (97.8%); m.p. 56–58°C; MS(EI, m/z): 410 (28%) (M^+); Anal. calcd. for $C_{20}H_{30}O_2PS_2N$ (411.54): C, 58.31; H, 7.28; S, 15.55% Found: C, 58.29; H, 7.30; S, 15.54; IR (KBr, cm^{-1}): 3581b, 2950b, 1615m, 1502s, 1488s, 1108s, 909s, 680s, 596s, and 540m; ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (t, 9H, —CH_3 of Et_3N, J = 7.2 Hz), 2.23 (s, 6H, —CH_3 of cresol), 3.09 (m, 6H, —CH_2 of Et_3N), 7.0–7.25 (m, 8H , —C_6H_4), 9.24 (s, 1H, -NH); ^{31}P NMR ($CDCl_3$, δ ppm): 105.65 (s).

(m-$CH_3C_6H_4O)_2PS_2HNEt_3$ (2)

The procedure adopted for the synthesis of (**2**) was similar to those used for (**1**). For the reaction, 7.49 g (6.9 mmol) of *meta*-cresol, 4 g (1.8 mmol) of P_2S_5, and 6.64 g (3.59 mmol) of Et_3N were used, and the product was a colorless sticky solid. Yield 14.5 g (98%); m.p. 55–57°C; MS(EI, m/z): 411.54 (31%, M^+); Anal. calcd. for $C_{20}H_{30}O_2PS_2N$ (411.54): C, 58.31; H, 7.28; S, 15.55%. Found: C, 58.29; H, 7.30; S, 15.55%; IR (KBr, cm^{-1}): 3513b, 2940b, 1585s, 1502s, 1139s, 950s, 687s, and 563m; ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (t, 9H , —CH_3 of Et_3N, J = 7.2 Hz), 2.29 (s, 6H, —CH_3 of cresol), 3.11 (m, 6H, —CH_2 of Et_3N), 6.92–7.25 (m, 8H , —C_6H_4), 9.25 (s, 1H, -NH); ^{31}P NMR ($CDCl_3$, δ ppm): 105.34 (s).

(p-$CH_3C_6H_4O)_2PS_2HNEt_3$(3)

A similar synthetic procedure as in the cases of (**1**) or (**2**) was used for the preparation of (**3**). The reaction of 6.20 g (5.80 mmol) *para*-cresol, 3.35 g (1.5 mmol) P_2S_5, and 3.04 g (3.01 mmol) of Et_3N was carried out, which resulted in compound (**3**) as a colorless sticky solid. Yield 12.16

g (98%); m.p. 57°C; MS(EI, m/z): 411.54 (27%, M^+); Anal. calcd. for $C_{20}H_{30}O_2PS_2N$ (411.54): C, 58.31; H, 7.28; S, 15.55%. Found: C, 58.30; H, 7.27; S, 15.53%; IR (KBr, cm^{-1}): 3543b, 2945b, 1608s, 1486s, 1189s, 1122s, 935s, 683s, and 550m; ^1H NMR ($CDCl_3$, δ ppm): 1.25 (t, 9H, $-CH_3$ of Et_3N, J = 7.2 Hz), 2.25 (s, 3H, $-CH_3$ of cresol), 3.11 (m, 6H, $-CH_2$ of Et_3N), 7.03–7.33 (m, 8H, $-C_6H_4$), 9.25 (s, 1H, -NH); ^{31}P NMR ($CDCl_3$, δ ppm): 105.6 (s).

(o-$CH_3C_6H_4O)_2PS_2Na$ (4)

A weighed amount of sodium metal (0.28 g, 1.2 mmol) was added to a toluene solution (~100 mL) of (o—$CH_3C_6H_4O)_2PS_2HNEt_3$ (**1**) (4.93 g, 1.2 mmol), and the mixture was stirred for 3 h at ~55°C, which resulted in white precipitates. The contents were cooled and then filtered by a funnel fitted with a G-4 sintered disc. Finally, the residue was dried under reduced pressure that gave compound (**4**) as a white solid. Yield 3.95 g (97.5%); m.p. 188°C; MS(EI, m/z): 333.35 (22%, M^+); Anal. calcd. for $C_{14}H_{14}O_2PS_2Na$ (333.35): C, 50.39; H, 4.20; S, 19.20%. Found: C, 50.40; H, 4.22; S, 19.18; IR (KBr, cm^{-1}): 2920b, 1618m, 1502s, 1211m, 1159s, 876s, 691s, 556m, and 520m; ^1H NMR ($CDCl_3$, δ ppm): 2.20 (s, 6H, $-CH_3$ of cresol), 6.82–7.30 (m, 8H, $-C_6H_4$); ^{31}P NMR (CH_3OH, δ ppm): 109.24 (s).

(m-$CH_3C_6H_4O)_2PS_2Na$ (5)

3.66 g (0.89 mmol) of (m-$CH_3C_6H_4O)_2PS_2HNEt_3$ (**2**) and 0.21 g (0.89 mmol) of sodium metal were used for the preparation of (**5**). All the experimental manipulations were similar as used for compound (**4**). Compound (**5**) was obtained as a white solid. Yield 2.35 g (97.1%); m.p. 188°C; MS(EI, m/z): 333.35 (24%, M^+); Anal. calcd. for $C_{14}H_{14}O_2PS_2Na$ (333.35): C, 50.39; H, 4.20; S, 19.20%. Found: C, 50.38; H, 4.20; S, 19.20%; IR (KBr, cm^{-1}): 2910b, 1622m, 1512s, 1217m, 1150s, 886s, 672s, and 550m; ^1H NMR ($CDCl_3$, δ ppm): 2.24 (s, 6H, $-CH_3$ of cresol), 6.95–7.44 (m, 8H, $-C_6H_4$); ^{31}P NMR (CH_3OH, δ ppm): 109.19 (s).

(p-$CH_3C_6H_4O)_2PS_2Na$ (6)

The method used for this synthesis was similar as used for compounds (**4–5**). 4.23 g (1.0 mmol) of (**3**) and 0.23 g (1.0 mmol) of sodium metal were used, which resulted in the formation of compound **(6)** as a white solid. Yield 3.38 g (98.8%); m.p. 188°C; MS(EI, m/z): 333.35 (20%, M^+); Anal. calcd. for $C_{14}H_{14}O_2PS_2Na$ (333.35): C, 50.39; H, 4.20; S, 19.20%. Found: C, 50.40; H, 4.20; S, 19.19%; IR (KBr, cm^{-1}): 2912w, 1620m, 1508s, 1214m, 1151s, 883s, 672s, and 552m; ^1H NMR ($CDCl_3$,

δ ppm): 2.24 (s, 6H, —CH_3 of cresol), 6.94–7.24 (m, 8H, —C_6H_4); ^{31}P NMR (CH_3OH, δ ppm): 109.11 (s).

(o-$CH_3C_6H_4O)_2PS_2NH_4$ (7)

Dry ammonia gas was passed through a toluene solution (~100 mL) of (o-$CH_3C_6H_4O)_2PS_2HNEt_3$ (**1**) (2.46 g, 0.60 mmol) for 8–10 minutes at r.t., which resulted in the formation of white precipitates. Compound (**7**) was obtained as a white powder after filtration by using a funnel fitted with a G-4 sintered disc and drying under reduced pressure. Yield 1.87 g (95.89%); m.p. 64°C; MS(EI, m/z): 327.41 (26%, M^+); Anal. calcd. for $C_{14}H_{14}O_2PS_2NH_4$ (327.41): C, 51.35; H, 5.54; S, 19.50; N, 4.27%. Found: C, 50.90; H, 4.21%; S, 19.10; N, 4.25%; IR (KBr, cm^{-1}): 3425b, 2920b, 1615m, 1500s, 1211m, 1158s, 860s, 688s, and 558m; ^{1}H NMR ($CDCl_3$, δ ppm): 2.23 (s, 6H, —CH_3 of cresol), 6.85–7.34 (m, 8H, —C_6H_4), 9.54 (s, 4H, NH_4); ^{31}P NMR (CH_3OH, δ ppm): 109.34 (s).

(m-$CH_3C_6H_4O)_2PS_2NH_4$ (8)

m-$CH_3C_6H_4O)_2PS_2HNEt_3$ (**2**) (1.23 g, 0.30 mmol) was used for the synthesis of compound (**8**), while using a similar method as for compound (**7**). Yield 1.05 g (85.36%); m.p. 68°C; MS(EI, m/z): 327.41 (23%, M^+); anal. calcd. for $C_{14}H_{14}O_2PS_2NH_4$ (327.41): C, 51.35; H, 5.54; S, 19.5; N, 4.27%. Found: C, 50.44; H, 4.15; S, 19.11; N, 4.24%; IR (KBr, cm^{-1}): 3431b, 2920b, 1618m, 1510s, 1212m, 1159s, 880s, 702s, and 556m; ^{1}H NMR ($CDCl_3$, δ ppm): 2.23 (s, 6H, —CH_3 of cresol), 6.83–7.33 (m, 8H, —C_6H_4), 9.64 (s, 4H, NH_4); ^{31}P NMR (CH_3OH, δ ppm): 109.60 (s).

(p-$CH_3C_6H_4O)_2PS_2NH_4$ (9)

p-$CH_3C_6H_4O)_2PS_2HNEt_3$ (**2**) (1.64 g, 0.4 mmol) was used for the synthesis of compound (**8**), while using a similar method as for compound (**7**). Yield 1.50 g (91.46%); m.p. 66°C; MS(EI, m/z): 327.41 (27%, M^+); anal. calcd. for $C_{14}H_{14}O_2PS_2NH_4$ (327.41): C, 51.35; H, 5.54; S, 19.5; N, 4.27%. Found: C, 50.80; H, 5.21; S, 19.00; N, 4.25%; IR (KBr, cm^{-1}): 3435b, 2933b, 1617m, 1508s, 1201m, 1166s, 878s, 700s, and 562m; ^{1}H NMR ($CDCl_3$, δ ppm): 2.21 (s, 6H, —CH_3 of cresol), 6.88–7.30 (m, 8H, —C_6H_4), 9.31 (s, 4H, NH_4); ^{31}P NMR (CH_3OH, δ ppm): 109.2 (s).

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