STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 2, TOM II, 2010

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

AMMONIUM SALTS OF ORGANOPHOSPHORUS ACIDS. CRYSTAL AND MOLECULAR STRUCTURE OF $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ AND $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$

ANA MARIA PREDA[a], MONIKA KULCSAR[b], RICHARD A. VARGA[a], DRAGOS MARGINEANU[a], ANCA SILVESTRU[a,*]

ABSTRACT. The ammonium salts $[Et_3NH]^+L^-$ {$L^- = [(SPMe_2)(SPPh_2)N]^-$ (**1**), $Ph_2PS_2^-$ (**2**)} were obtained in the reaction between triethylamine and the corresponding organophosphorus acid in a 1:1 molar ratio, while $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ (**3**) resulted as hydrolysis product in the process of growing crystals of $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4SeS_2P(OPr^i)_2$. Compounds **1** and **2** were characterized by ^1H and ^{31}P NMR spectroscopy. Single-crystal X-ray diffraction studies revealed the presence of short intermolecular S···H contacts which result in the formation of dimeric units in **1** and of a layered supramolecular structure in **3**.

Keywords*: onium salts, intermolecular interactions, supramolecular network, dimeric units*

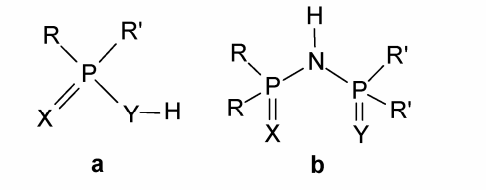
INTRODUCTION

Organophosphorus acids of type **a** (diorganodichalcogeno-phosphinic acids, diorganodichalcogenophosphonic acids and diorgano-dichalcogeno-phosphoric acids) or of type **b** (tetraorganodichalcogeno-imidodiphosphinic acids) (Scheme 1) have attracted a considerable interest in last three decades. They proved a high capacity to build metal complexes both with main group or transition metals by displaying a large variety of coordination patterns and their metal complexes found applications in biology, catalysis or electronics.[1-12]

On the other hand, onium salts melting at low temperatures was observed to be suitable as ionic liquids.[13,14]

[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 400028 Cluj-Napoca, Romania; * ancas@chem.ubbcluj.ro*

[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain*



R = alkyl, aryl, alkoxy, aryloxy; X, Y = O, S.

Scheme 1

We report here about the new ammonium salts

$[Et_3NH]^+L^-$ {L^- = $[(SPMe_2)(SPPh_2)N]^-$ (**1**), $[Ph_2PS_2]^-$ (**2**)} and

$[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ (**3**).

RESULTS AND DISCUSSION

The ionic compounds $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ (**1**) and $[Et_3NH]^+[S_2PPh_2]^-$ (**2**) were prepared according to eq. *(1)*, by reacting triethylamine either with the dimethyldiphenyldithioimidodiphosphinic acid or the diphenyldithiophosphinic acid, in a 1:1 molar ratio, in benzene, at room temperature.

$$Et_3N + LH \longrightarrow [Et_3NH]^+L^- \qquad (1)$$

$L^- = (Me_2PS)(Ph_2PS)N^-$ (**1**), $Ph_2PS_2^-$ (**2**)

$[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ (**3**) resulted as a hydrolysis product in the attempts to grow crystals of

$[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4SeS_2P(OPr^i)_2$.

Compounds **1** and **2** were isolated in quantitative yields as microcrystalline solid species and were characterized by ^1H and ^{31}P NMR spectroscopy.

The ^1H NMR spectra display the expected resonances for the organic groups attached to phosphorus and nitrogen, respectively. The multiplicity of the ^1H resonances is determined by proton–proton and phosphorus–proton couplings. The N*H* protons in the triethylammonium cation give large singlet resonances at δ 10.02 and 10.22 ppm for **1** and **2**, respectively. The ^{31}P NMR spectra of the two compounds display two resonances in a 1:1 ratio for **1** and only one resonance for **2**, shifted in comparison with the corresponding free acids, due to the interaction with the cationic species.

Single-crystals suitable for X-ray diffraction studies were obtained for compounds **1** and **3** by slow diffusion from a mixture of CH_2Cl_2 and n-hexane (1:4, v/v). The ORTEP diagrams of the molecular structures of **1** and **3** with the atom numbering schemes are depicted in Figures 1 and 2, respectively, while selected interatomic distances and angles are listed in Table 1.

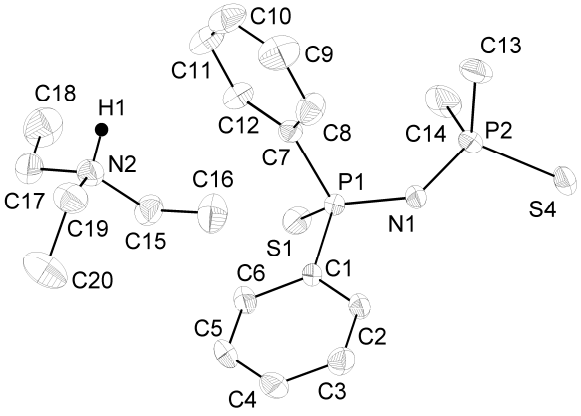


Figure 1. ORTEP plot of $[Et_3NH]^+$ $[(SPMe_2)(SPPh_2)N]^-$ (**1**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms, except the one attached to nitrogen, are omitted for clarity.

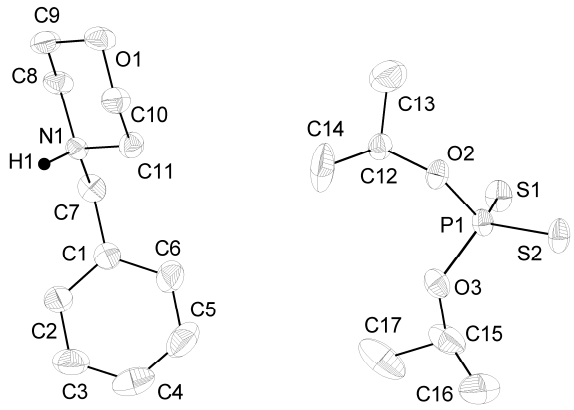


Figure 2. ORTEP plot of $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ (**3**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms, except the one attached to nitrogen, are omitted for clarity.

Both compounds are ionic species in which the ammonium cations and the organophosphorus anions are held together by electrostatic interactions. The central atoms N2 and N1, respectively, in the ammonium

cations in compounds **1** and **3** have a distorted tetrahedral coordination geometry, with angles ranging between 104(2) and 114.8(3)° in **1** and 107.1(2) and 112.9(2)° in **3**, respectively. The N–H distance is similar with those found in other ionic species containing $[Et_3NH]^+$ or $[Bu_3NH]^+$ cations.[15,16]

The organophosphorus ligands display almost equal P-S [1.971(1) and 1.985(1) Å in **1** and 1.968(1) and 1.980(2) Å in **3**] and P–N interatomic distances [1.594(3) and 1.596(3) Å in **1**], thus suggesting a symmetrical delocalization of the π electrons over the SPNPS system in **1** and the PS_2 system in **3**, respectively. However, these values are intermediate between those observed for single P–E and double P=E (E = S, N) bonds in the free acid $Ph_2P(S)SH$: P–S 2.077(1) and P=S 1.954(1) Å [17] and $Ph_2P(=S)–N=PPh_2(–SMe)$: P=S 1.954(1), P–S 2.071(1), P=N 1.562(2) and P–N 1.610(2) Å [18].

Table 1. Interatomic bond distances (Å) and angles (°) for compounds **1** and **3**

1		**3**	
N(1)–P(1)	1.594(3)	P(1)–S(1)	1.968(1)
N(1)–P(2)	1.596(3)	P(2)–S(2)	1.980(2)
P(1)–S(1)	1.971(1)	N(2)–H(1)	0.87(3)
P(2)–S(2)	1.985(1)	N(1)–C(7)	1.514(6)
N(2)–H(1)	0.87(2)	N(1)–C(8)	1.496(5)
N(2)–C(15)	1.488(4)	N(1)–C(5)	1.497(11)
N(2)–C(17)	1.501(5)		
N(2)–C(19)	1.489(5)		
P(1)–N(1)–P(2)	132.94(17)	S(1)–P(1)–S(2)	116.69(5)
C(15)–N(2)–C(19)	114.8(3)	C(7)–N(1)–C(8)	110.5(2)
C(15)–N(2)–C(17)	111.6(3)	C(7)–N(1)–C(11)	112.9(2)
C(19)–N(2)–C(17)	112.0(3)	C(8)–N(1)–C(11)	109.3(2)
C(15)–N(2)–H(1)	110(2)	C(7)–N(1)–H(1)	109.2(2)
C(17)–N(2)–H(1)	104(2)	C(8)–N(1)–H(1)	107.1(2)
C(19)–N(2)–H(1)	104(2)	C(11)–N(1)–H(1)	107.7(2)

A closer check of the crystal structures of **1** and **3** revealed intermolecular S···H contacts between cations and anions [cf. Σr_{vdW}(S,H) ca. 3.05 Å] [19]. In compound **1** dimeric associations are formed both by strong cation – anion hydrogen bonding [H1···S2''' 2.351(3) Å] and week inter-anions interactions [H13B"···S2''' 2.967(3) Å] (Figure 3).

By contrast, in the crystal of **3** a layered network is formed both by cation – anion hydrogen bonding [H1···S2'' 2.53(3), H8A···S1' 2.901(7) and S2'···H7B 2.981(2) Å] and inter–anions H···S interactions [H14B···S2' 2.984(1) Å] (Figure 4). While in compound **1** only one sulfur atom is involved

in hydrogen bonding, in compound **3** both sulfur atoms are involved, probably due to the small byte of the dithiophosphinato group in comparison with the highly flexible tetraorganoimidodiphosphinato moiety.

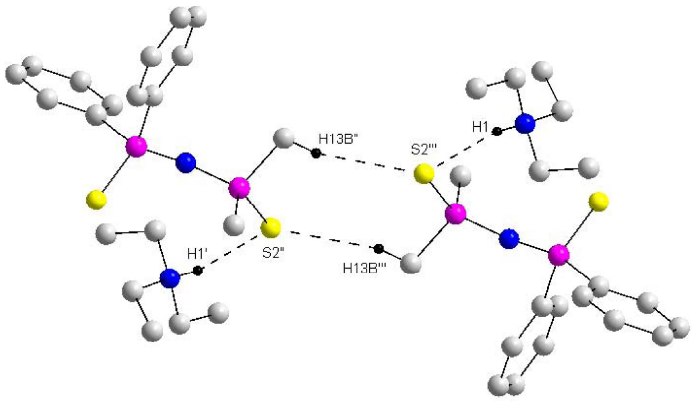


Figure 3. Dimeric association in the crystal of compound **1**.
[symmetry equivalent atoms (–*x*, 1 – *y*, 1 – *z*) are given by “prime”].

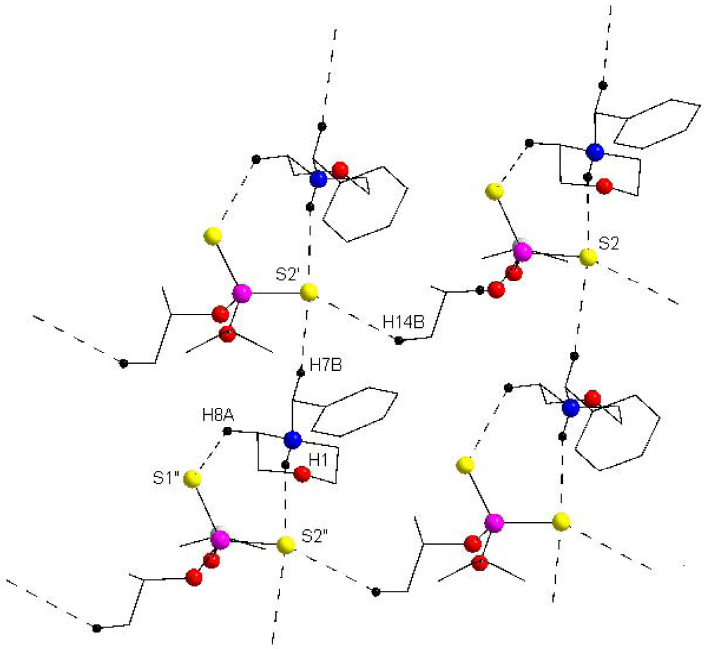


Figure 4. Polymeric association in the crystal of compound **3**.
[symmetry equivalent atoms (–0.5 + *x*, -0.5 + *y*, 0.5 + *z*) and (x, y, 1 + z)
are given by “prime” and “second”, respectively].

The conformation of the S-P-N-P-S skeleton in compound **1** can be described as *syn* [S1-P1···P2-S2 torsion angle 89.2(8)^o] [12], with both phosphorus-sulfur bonds oriented on the same side of the PNP plane at 1.54 and 0.85 Å, respectively.

CONCLUSIONS

New ammonium salts of organophosphorus ligands, *e.g*. $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ and $[Et_3NH]^+[S_2PPh_2]^-$ were isolated as colorless, microcrystalline solids and were characterized in solution by ^1H and ^{31}P NMR. X-Ray diffraction studies on $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ and the ammonium salt $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ revealed different association patterns in the crystals of the two compounds, *e.g*. dimeric units in the case of the tetraorganodithioimidodiphosphinato species and a polymeric layered structure in the case of the dithiophosphato derivative.

EXPERIMENTAL SECTION

Starting materials were commercially available (Fluka), or prepared following a published procedure: Ph_2PS_2H [17], $(Me_2PS)(Ph_2PS)NH$ [20]. ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance 500 instrument using $CDCl_3$ solutions. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. $CHCl_3$: ^1H 7.26 ppm) for ^1H NMR and H_3PO_4 85% for ^{31}P NMR.

Preparation of $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ (1)

A mixture of triethylamine (0.14 mL, 1 mmol) and $[(Me_2PS)(Ph_2PS)N]H$ (0.325 g, 0.1 mmol) in benzene (30 mL) was stirred for 12 h at room temperature. Then the solvent was removed in vacuum to give the title compound as a colorless powder. Yield: 0.4 g (94%), m.p. 172^{o}C. ^1H NMR: δ 1.31t [9H, CH_2CH_3, $^3J_{HH}$ 7.4 Hz], 1,64d (6H, PCH_3, $^2J_{PH}$ 13,2 Hz), 3.29q (6H, CH_2CH_3, $^3J_{HH}$ 7.4 Hz), 7.24m (6H P-C_6H_5-*meta+para*), 8.02ddd (4H, P-C_6H_5-*ortho*, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.8, $^3J_{PH}$ 12.8 Hz), 10.02s (br., 1H, N*H*). ^{31}P NMR (121.4 MHz): 37.1s, br., Ph_2PS, 45.3s, br., Me_2PS.

*$[Et_3NH]^+[S_2PPh_2]^-$ (**2**)* was similarly obtained from triethylamine (0.14 mL, 1 mmol) and Ph_2PS_2H (0.375 g, 0.1 mmol). Yield: 0.44 g (92%), m.p. 81^{o}C. ^1H NMR: δ 1.32t [9H, CH_2CH_3, $^3J_{HH}$ 7.3 Hz], 3.26q (6H, CH_2CH_3, $^3J_{HH}$ 7.3 Hz), 7.30 – 7.36m (6H P-C_6H_5-*meta+para*), 8.15ddd (4H, P-C_6H_5-*ortho*, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.6, $^3J_{PH}$ 13.9 Hz), 10.22s (br., 1H, N*H*). ^{31}P NMR (121.4 MHz): 61.4s.

X-ray Crystallographic Study

Block crystals of $[Et_3NH]^+[(SPMe_2)(SPPh_2)N]^-$ (**1**) and $[2\text{-}\{O(CH_2CH_2)_2N(H)CH_2\}C_6H_4]^+[S_2P(OPr^i)_2]^-$ (**3**) were attached with Paratone N oil on cryoloops. The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The details of the crystal structure determination and refinement are given in Table 2.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The hydrogen atoms bonded to the nitrogen in compounds **1** and **3** were found in a difference map and refined with a restrained N–H distance of 0.87(2) Å for **1** and 0.87(3) Å for **3**, respectively. For structure solving and refinement the software package SHELX-97 was used [21]. The drawings were created with the Diamond program [22].

Table 2. Crystallographic data for compounds **1** and **2**.

	1	**3**
chemical formula	$C_{20}H_{32}N_2P_2S_2$	$C_{17}H_{30}NO_3PS_2$
crystal habit	colorless block	colorless block
crystal size [mm]	0.25 x 0.22 x 0.2	0.38 x 0.33 x 0.18
crystal system	triclinic	monoclinic
space group	*P-1*	*P2(1)/n*
a [Å]	9.7823(11)	10.048(10)
b [Å]	10.7488(12)	17.246(17)
c [Å]	11.3737(13)	12.500(12)
α [deg]	91.951(2)	90
β [deg]	95.651(2)	92.469(17)
γ [deg]	93.647(2)	90
U [Å^3]	1186.7(2)	2164(4)
Z	2	4
D_c [g cm^{-3}]	1.194	1.202
M	426.54	391.53
F(000)	456	840
θ range [deg]	1.90 to 25.00	2.35 to 25.00
μ(Mo Kα) [mm^{-1}]	0.366	0.334
no. of reflections collected	11545	20438
no. of independent reflections	4177 (R_{int} = 0.0470)	3816 (R_{int} = 0.0491)
R_1 [$I > 2\sigma(I)$]	0.0616,	0.0611
wR_2	0.1270	0.1416
no. of parameters	244	225
no. of restraints	1	0
GOF on F^2	1.093	1.167
largest difference electron density [e Å^{-3}]	0.418 and -0.262	0.413 and -0.296

ACKNOWLEDGEMENTS

This work was supported by the National University Research Council of Romania (CNCSIS, Research Project No. ID-2404/2008). A. M. P. thanks the European Social Fund for a Scholarship (Education and Training Program 2008-2013, POSDRU/6/1.5/S/3).

SUPPLEMENTARY MATERIAL

CCDC 753670 and 753671 contain the supplementary crystallographic data for compounds **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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