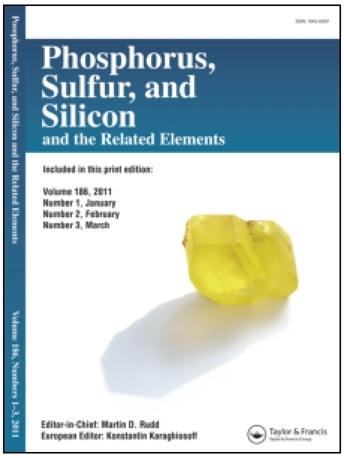

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NEW VERSATILE ORGANOPHOSPHORUS LIGANDS. CRYSTAL AND MOLECULAR STRUCTURES OF ISOMERIC P, P-DIMETHYL-P',P'-DIPHENYL-P-THIOIMIDODIPHOSPHINIC AND P,P-DIMETHYL-P',P'-DIPHENYL-P'-THIOIMIDODIPHOSPHINIC ACIDS

Roland Rösler[a]; Mihaela Stanciu[a]; Jincai Yang[b]; John E. Drake[b]; Cristian Silvestru[a]; Ionel Haiduc[a]
[a] Facultatea de Chimie, Universitatea "Babes-Bolyai", Cluj-Napoca, Romania [b] Department of Chemistry and Biochemistry, University of Windsor, Windsor, Canada

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ROLAND RÖSLER[a]*, MIHAELA STANCIU[a], JINCAI YANG[b], JOHN E. DRAKE[b], CRISTIAN SILVESTRU[a] and IONEL HAIDUC[a]

[a]*Facultatea de Chimie, Universitatea "Babes-Bolyai", RO-3400 Cluj-Napoca, Romania and* [b]*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada*

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The synthesis of isomeric $(SPMe_2)(OPPh_2)NH$ **1** and $(OPMe_2)(SPPh_2)NH$ **2** from $Li[HN(S)PR_2]$ and $R'_2P(O)Cl$, as well as of their K and Na salts, are presented. The compounds were characterized by means of IR and multinuclear NMR spectroscopy. The crystal and molecular structure of both free acids was determined using X-ray diffractometry. Compound **1** crystallizes in monoclinic space group $P2_1/n$, $a = 16.798(6)$ Å, $b = 17.526(8)$ Å, $c = 18.095(7)$ Å, $\beta = 114.72(2)°$, $Z = 12$, and the unit cell contains three independent molecules. Compound **2** crystallizes in orthorhombic space group Fdd2, $a = 15.072(7)$ Å, $b = 43.078(6)$ Å, $c = 9.912(8)$ Å, $Z = 16$. In both compounds the molecular units are associated into polymeric chains through N-H···O [1.96 Å (mean) in **1**, and 1.8 Å in **2**] hydrogen bonds, which involve only the oxygen atom of each molecule. The conformation of the SPNPO system is discussed.

Keywords: Organophosphorus ligands; Oxoimidodiphosphinic acids; Thioimidodiphosphinic acids; Crystal Structure; Conformation

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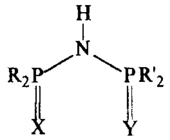
* Address to Author: Dr. R. Rösler, AK Prof. Dr. H. J. Breunig, Fachbereich 2 der Universität Bremen, Leobenerstr. NW2, D-28334 Bremen, Germany.

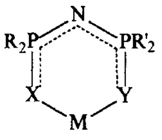
INTRODUCTION

Tetraorganodichalcogenoimidodiphosphinic acids (**A**) are versatile ligands which in the deprotonated form exhibit a high tendency to chelate symmetrically through both chalcogen atoms, thus leading to six-membered, carbon-free metallocycles (**B**).[1,2] Most of the research interest was so far concerned with compounds containing identical chalcogen atoms and phenyl groups attached to phosphorus atoms.[1,2]



X, Y = O, S, Se

A



B

However, asymmetric ligands of this type, *i.e.* containing different organic groups and/or chalcogen atoms, might provide interesting structural patterns and recently some research works on this topic have been published. Thus, the molecular structures of $(OPPh_2)(YPPh_2)NH$ ($Y = S$, Se)[3,4] and of some metal complexes containing deprotonated asymmetric ligands were determined by X-ray diffractometry and revealed interesting aspects concerning the coordination patterns and the conformation of the six-membered inorganic ring.[3–10] For example, in the sodium salt $[Na\{(OPPh_2)(SPPh_2)N\}.2THF]_2$ the ligand exhibits a bimetallic triconnective coordination pattern,[4] while the $Pd[\{OP(OPh)_2\}\{SP(OPh)_2\}N]_2$ complex provides the first example of coordination through nitrogen and sulfur for this type of ligand.[10]

We report here the synthesis of two new asymmetric ligands, namely isomeric $(SPMe_2)(OPPh_2)NH$ and $(OPMe_2)(SPPh_2)NH$, and their K and Na salts. The compounds were characterized by means of IR and multinuclear NMR spectroscopy, and the crystal and molecular structure of the two free acids was determined using X-ray diffractometry.

EXPERIMENTAL

The starting materials were prepared according to literature methods: $Me_2P(O)Cl$,[11] $Ph_2P(O)Cl$,[12] $Me_2P(S)NH_2$,[13] $Ph_2P(S)NH_2$.[12] IR spectra

(4000–400 cm^{-1}) were recorded on KBr discs using a SPECORD 75 IR Zeiss-Jena (Germany) spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained using a VARIAN GEMINI-300 spectrometer operating at 299.5, 75.4 and 121.4 MHz respectively. TMS and H_3PO_4 85% were used as external standards. The crystal and molecular structure of the free acids were determined using a Rigaku AFC6S X-ray diffractometer (prof. dr. John E. Drake, University of Windsor, Canada).

P,P-Dimethyl-P',P'-diphenyl-P-thioimidodiphosphinic acid, 1

A solution of *n*-BuLi in *n*-hexane (128 ml, 1.565 M) was added dropwise, at room temperature, to a stirred suspension of $Me_2P(S)NH_2$(21.8 g, 0.2 mol) in 200 ml of anhydrous diethyl ether, under argon atmosphere. The reaction mixture was cooled to room temperature, and then a solution of $Ph_2P(O)Cl$ (23.7 g, 0.1 mol) in 100 ml of anhydrous diethyl ether was added dropwise. About 150 ml of the solvent was distilled off from the reaction mixture, 200 ml of water was added to the resulted suspension, and the remaining organic solvent was removed under vacuum. The aqueous solution thus obtained was filtered and treated with HCl 10% until no solid product deposited. The white solid product was collected by suction filtration, dried in vacuum and recrystallized from acetonitrile to give $(SPMe_2)(OPPh_2)NH$ as colorless crystals. M.p. 179–181°C. Yield: 22.3 g (72%). Selected IR data (cm^{-1}): ν(NH) 2630m,br, ν(PO) 1180vs,br, $\nu_{as}(P_2NH)$ 940vs,br, ν(PS) 530vs. ^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.93 (d, 6H, $C\underline{H}_3$ $^{2}J_{PH}$ = 13.7 Hz), 5.03 (s,br, 1H, N$\underline{H}$), 7.43 (m, 4H, m-$\underline{H}$), 7.53 (m, 2H, p-$\underline{H}$), 7.75 (ddd, 4H, o-$\underline{H}$, $^{3}J_{PH}$ = 13.0 Hz, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.4 Hz). ^{13}C-NMR ($CDCl_3$): δ[ppm] = 25.47 (d, $\underline{C}H_3$, $^{1}J_{PC}$ = 66.5 Hz), 128.77 (d, m-$\underline{C}$, $^{3}J_{PC}$ = 13.0 Hz), 131.49 (d, o-$\underline{C}$, $^{2}J_{PC}$ = 10.9 Hz), 132.68 (d, p-$\underline{C}$, $^{4}J_{PC}$ = 2.5 Hz), 132.47 (d, i-$\underline{C}$, $^{1}J_{PC}$ = 126.3 Hz). ^{31}P-NMR ($CDCl_3$): 23.9 (d, $Ph_2\underline{P}$ = O, $^{2}J_{PP}$ = 19.5 Hz, $^{1}J_{PC}$ = 124.8 Hz), 63.0 (d, $Me_2\underline{P}$ = S, $^{2}J_{PP}$ = 19.5 Hz, $^{1}J_{PC}$ = 65.4 Hz).

Potassium P,P-dimethyl-P', P'-diphenyl-P-thioimidodiphosphinate

A reaction mixture of $(SPMe_2)(OPPh_2)NH$ (17 g, 0.055 mol) and *t*-BuOK (6.17 g, 0.055 mol) in 200 ml of anhydrous diethyl ether was stirred under reflux for 36 h. The solid product was collected by suction filtration, washed with benzene and dried at 120°C. M.p. 227–230°C. Yield: 18.7 g

(98%). Selected IR data (cm^{-1}): $\nu_{as}(P_2N)$ 1180vs, ν(PO) 1129s, ν(PS) 568s. ^{1}H-NMR (CD_3OD): δ[ppm] = 1.76 (d, 6H, C$\underline{H}_3$. $^2J_{PH}$ = 13.2 Hz), 7.42 (m, 6H, m/p-$\underline{H}$), 7.86 (ddd, 4H, o-$\underline{H}$, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.4 Hz). ^{13}C-NMR ($CDCl_3$): δ[ppm] = 28.05 (dd, $\underline{C}H_3$, $^1J_{PC}$ = 71.9 Hz, $^3J_{PC}$ = 3.5 Hz), 128.13 (d, m-$\underline{C}$, $^3J_{PC}$ = 12.7 Hz), 130.30 (s, p-$\underline{C}$), 131.87 (d, o-$\underline{C}$, $^2J_{PC}$ = 9.3 Hz), 139.92 (d, i-$\underline{C}$, $^1J_{PC}$ = 128.7 Hz). ^{31}P-NMR ($CDCl_3$): 21.2 (s, $Ph_2\underline{P}$ = O), 47.8 (s,br, $Me_2\underline{P}$ = S).

P,P-Dimethyl-P’,P’-diphenyl-P’-thioimidodiphosphinic acid, 2

A solution of *n*-BuLi in *n*-hexane (72 ml, 1.565 M) was added dropwise, at room temperature, to a stirred suspension of $Ph_2P(S)NH_2$ (26.9 g, 0.115 mol) in 200 ml of anhydrous diethyl ether, under argon atmosphere. The reaction mixture was cooled to room temperature, and then a solution of $Me_2P(O)Cl$ (6.5 g, 0.058 mol) in 100 ml of anhydrous benzene was added dropwise. About 200 ml of the solvent was distilled off from the reaction mixture, 250 ml of water was added to the resulted suspension, and the remaining organic solvent was removed under vacuum. The reaction mixture thus obtained was filtered and from the dried solid product $Ph_2P(S)NH_2$ was recovered (12.4 g, after recrystallization from toluene). The clear viscous filtrate containing the lithium salt of the title acid was treated with HCl 10% until no solid product deposited. The white solid product was collected by suction filtration, dried in vacuum and recrystallized from ethanol to give $(OPMe_2)(SPPh_2)NH$ as colorless crystals. M.p. 223–225°C. Yield: 14.7 g (82%). Selected IR data (cm^{-1}): ν(NH) 2680m,br, ν(PO) 1175vs,br, $\nu_{as}(P_2NH)$ 945vs,br, ν(PS) 635vs. ^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.61 (d, 6H, C$\underline{H}_3$, $^2J_{PH}$= 14.1 Hz), 4.6 (s,br, 1H, N$\underline{H}$), 7.44 (m, 6H, m/p-$\underline{H}$), 7.94 (ddd, 4H, o-$\underline{H}$, $^3J_{PH}$ = 14.3 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.2 Hz). ^{13}C-NMR ($CDCl_3$): δ[ppm] = 20.00 (d, $\underline{C}H_3$, $^1J_{PC}$ = 85.8 Hz), 128.51 (d, m-$\underline{C}$, $^3J_{PC}$ = 13.4 Hz), 131.25 (d, o-$\underline{C}$, $^2J_{PC}$ = 11.9 Hz), 131.80 (s, p-$\underline{C}$), 135.33 (d, i-$\underline{C}$, $^1J_{PC}$ = 102.1 Hz). ^{31}P-NMR ($CDCl_3$): 47.9 (s,br, $Ph_2\underline{P}$=S), 50.8 (d, $Me_2\underline{P}$=O, $^2J_{PP}$ = 6.9 Hz, $^1J_{PC}$ = 84.0 Hz).

Potassium P,P-dimethyl-P’, P’-diphenyl-P’-thioimidodiphosphinate

A reaction mixture of $(OPMe_2)(SPPh_2)NH$ (8 g, 0.023 mol) and *t*-BuOK (2.57 g, 0.023 mol) in 100 ml of anhydrous diethyl ether was stirred for 24 h. The mixture was filtered, and the solvent was completely removed from the clear filtrate under vacuum. The solid product thus obtained was solved in chloroform, filtered again, and then evaporated under vacuum over P_4O_{10}. The potassium salt was obtained quantitatively as a crystalline, hygroscopic solid. M.p. 138–140°C. ^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.16 (d, 6H, C<u>H</u>$_3$, $^2J_{PH}$ = 13.2 Hz), 7.31 (m, 6H, m/p-<u>H</u>), 7.94 (ddd, 4H, o-<u>H</u>, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 2.8 Hz). ^{13}C-NMR ($CDCl_3$): δ[ppm] = 20.20 (dd, <u>C</u>H$_3$, $^1J_{PC}$ = 90.7 Hz, $^3J_{PC}$ = 5.0 Hz), 127.94 (d, m-<u>C</u>, $^3J_{PC}$ = 12.6 Hz), 129.37 (s, p-<u>C</u>), 130.77 (d, o-<u>C</u>, $^2J_{PC}$ = 10.6 Hz), 141.31 (dd, i-<u>C</u>, $^1J_{PC}$ = 104.7 Hz, $^3J_{PC}$ = 5.1 Hz). ^{31}P-NMR ($CDCl_3$): 31.6 (s, Me$_2$<u>P</u>=O, $^1J_{PC}$= 88.8 Hz), 35.8 (s, Ph$_2$<u>P</u>=S, $^1J_{PC}$ = 104.9 Hz).

Sodium P,P-dimethyl-P', P'-diphenyl-P'-thioimidodiphosphinate

A reaction mixture of $(OPMe_2)(SPPh_2)NH$ (3 g, 0.001 mol) and NaOH (0.44 g, 0.0011 mol, 10% excess) in 50 ml of methanol was stirred for 24 h. The solvent was removed in open atmosphere, and the solid product was extracted with chloroform. After removal of the solvent in vacuum, the title compound was obtained quantitatively as a crystalline, non-hygroscopic solid. M.p. 138–140°C. Selected IR data (cm^{-1}): $\nu_{as}(P_2N)$ 1215vs, 1180vs, ν(PO) 1110vs,br, ν(PS) 590s. ^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.20 (d, 6H, C<u>H</u>$_3$, $^2J_{PH}$ = 13.5 Hz), 7.31 (m, 6H, m/p-<u>H</u>), 7.92 (ddd, 4H, o-<u>H</u>, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 2.9 Hz). ^{13}C-NMR ($CDCl_3$): δ[ppm] = 20.14 (dd, <u>C</u>H$_3$, $^1J_{PC}$ = 90.9 Hz, $^3J_{PC}$ = 5.0 Hz), 127.90 (d, m-<u>C</u>, $^3J_{PC}$ = 12.7 Hz), 129.96 (s, p-<u>C</u>), 130.74 (d, o-<u>C</u>, $^2J_{PC}$ = 10.6 Hz), 140.71 (dd, i-<u>C</u>, $^1J_{PC}$ = 105.0 Hz, $^3J_{PC}$ = 5.0 Hz). ^{31}P-NMR ($CDCl_3$): 35.8 (s, Me$_2$<u>P</u>=O, $^1J_{PC}$ = 86.6 Hz), 37.2 (s, Ph$_2$<u>P</u> = S, $^1J_{PC}$ = 105.3 Hz).

X-Ray crystal determinations

Colourless block crystals of $(SPMe_2)(OPPh_2)NH$ (**1**) and $(OPMe_2)(SPPh_2)NH$ (**2**) obtained from acetonitrile were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation, operating at 50 kV and 35 mA. Cell constants and an orientation matrix for data collection, obtained from 24 carefully centred reflections in the range $8.21 < 2\theta < 11.30°$ for **1** and $9.14 < 2\theta < 17.23°$ for **2**, corresponded to a monoclinic cell for **1** and an orthorhombic cell for **2**, whose dimensions are given in Table I. On the basis of the systematic absences (*h0l*, $h + l = 2n + 1$; *0k0*, $k = 2n + 1$ for **1**, and *hkl*, $h + k$, $k + l$, $h + l = 2n + 1$; *0kl*, $k + l = 4n + 1$; *h0l*, $h+ l = 4n + 1$ for **2**), packing considerations, statistical analyses of intensity distributions and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (no. 14) for **1** and *Fddd2* (No.43) for **2**.

TABLE I Crystallographic data for (**1**) and (**2**)

	$(SPMe_2)(OPPh_2)NH$ (1)	*$(OPMe_2)(SPPh_2)NH$ (2)*
Molecular formula	$C_{14}H_{17}ONP_2S$	$C_{14}H_{17}ONP_2S$
Formula weight	309.30	309.30
Crystall system	monoclinic	orthorhombic
Space group	$P2_1/n$	Fdd2
a (Å)	16.798(6)	15.072(7)
b (Å)	17.526(8)	43.078(6)
c (Å)	18.095(7)	9.912(8)
β (°)	114.72(2)	
V (Å^3)	4839(3)	6435(5)
Z	12	16
D_c (g cm^{-3})	1.27	1.28
μ(Mo-Kα) (cm^{-1})	3.91	3.92
2θ Range (°)	2–50	2–50
Reflections measured	$+h,+k,\pm l$, 8810	$-h,-k,-l$, 1593
Observed reflections, N_o	3114 $[F_o^2 \geq 3\sigma(F_o)^2]$	638 $[F_o^2 \geq 3\sigma(F_o)^2]$
Parameters refined, N_c	343	80
R[a]	0.0588	0.0662
R'[b]	0.0434	0.0505
Goodness of fit,[c] *S*	2.06	2.08

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ where $w = 1/\sigma^2(F_o)$; [c] $S = [\Sigma(|F_o| - |F_c|)/\sigma]/(N_o - N_c)$.

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.28° for **1** and 0.17° for **2** with a takeoff angle of 6.0°. Scans of (1.78 + 0.30tanθ)° for **1** and (1.31 + 0.30tanθ)° for **2** were made at speed of 32.0 and 8.0°/min (in ω) for **1** and **2**, respectively. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 4 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter ofthe incident beam collimator was 1.0 mm, and the crystal to detector distance was 285.0 mm.

Of the 8810 for **1** and 1593 for **2** reflections which were collected, 3114 and 638 were unique. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo-Kα is 3.91 for **1** and 3.92 cm^{-1} for **2**. An empirical absorption correction, using the program DIFABS[14] was applied which resulted in transmission factors ranging from 0.90 to 1.03 for **1**, and 0.82 to 1.08 for **2**. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods,[15] and expanded using Fourier techniques.[16] The non-hydrogen atoms, other than carbon, were refined anisotropically. The phenyl rings in **2** were constrained to a regular hexagon with C-C bond distances set at 1.40 Å and C-C-C angles at 120.0°. The hydrogen atoms, with the exception of that attached to nitrogen, were included in their idealized positions with C-H set at 0.95 Å. The hydrogen atoms attached to nitrogen were found from the difference map and their positions were refined. The isotropic thermal parameters were set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement[17] was based on 3114 and 638 for **1** and **2**, respectively, observed reflections ($I > 3.00\sigma(I)$) and 343 and 80 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0588$ for **1** and 0.0662 for **2**, and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.0434$ for **1** and 0.0505 for **2**.

The standard deviations of an observation of unit weight[18] were 2.06 and 2.08 for **1** and **2**, respectively. The weighting scheme was based on counting statistics and included a factor ($p = 0.004$) to downweight the intense reflections. Plots of $\sum w(|F_0| - |F_c|)^2$ versus $|F_0|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.48 and –0.39 for **1**, and 0.39 and –0.40 eÅ^{-3} for **2**.

Neutral-atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in F_c;[20] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[21] All calculations were performed using the TEXSAN[22] crystallographic software package of Molecular Structure Corp.

The final atomic coordinates of the non-hydrogen atoms are given in Tables II and III. Additional material available from the Cambridge Crystallographic Data Center comprises H-atom coordinates, thermal parameters and all of the bond lengths and angles. Structure factor tables are available from the authors.

TABLE II Atomic coordinates and *B*(eq) of non-hydrogen atoms and *H*-N atom for (1)

Atom	*x*	*y*	*z*	*B(eq)*
S(1)	0.6241(2)	0.0459(1)	-0.0336(1)	4.1(1)
S(2)	0.6444(2)	0.4811(1)	0.2457(2)	5.6(1)
S(3)	0.1642(2)	0.9111(2)	0.2588(2)	5.8(1)
P(1)	0.6738(1)	0.2740(1)	0.1018(1)	2.7(1)
P(2)	0.6056(1)	0.1189(1)	0.0386(1)	2.9(1)
P(3)	0.5703(1)	0.2543(1)	0.3281(1)	2.4(1)
P(4)	0.6560(2)	0.4052(1)	0.3265(1)	3.1(1)
P(5)	0.1165(2)	0.7824(1)	0.0217(1)	3.3(1)
P(6)	0.1896(2)	0.8862(1)	0.1663(1)	3.7(1)
0(1)	0.6174(3)	0.2693(3)	0.1463(3)	3.3(3)
0(2)	0.5390(3)	0.2795(3)	0.3892(3)	3.1(3)
0(3)	0.1940(4)	0.8050(3)	0.0079(3)	4.3(3)
N(1)	0.6793(4)	0.1899(4)	0.0618(4)	2.8(3)
N(2)	0.5982(4)	0.3263(4)	0.2837(4)	2.5(3)
N(3)	0.1200(5)	0.8207(5)	0.1074(5)	3.4(4)
C(1)	0.7858(5)	0.2990(5)	0.1646(5)	3.2(2)

Atom	*x*	*y*	*z*	*B(eq)*
C(2)	0.8483(6)	0.2437(6)	0.2040(6)	5.3(2)
C(3)	0.9354(7)	0.2645(7)	0.2590(7)	7.6(3)
C(4)	0.9518(7)	0.3400(7)	0.2691(6)	6.7(3)
C(5)	0.8927(7)	0.3964(6)	0.2341(6)	6.6(3)
C(6)	0.8069(6)	0.3765(6)	0.1793(6)	5.3(2)
C(7)	0.6341(5)	0.3416(5)	0.0210(5)	2.9(2)
C(8)	0.6768(6)	0.3525(5)	-0.0288(6)	4.8(2)
C(9)	0.6470(6)	0.4063(6)	-0.0928(6)	5.5(3)
C(10)	0.5701(6)	0.4452(5)	-0.1081(5)	4.9(2)
C(11)	0.5262(6)	0.4336(5)	-0.0616(5)	4.3(2)
C(12)	0.5578(5)	0.3827(5)	0.0043(5)	3.5(2)
C(13)	0.4981(6)	0.1604(5)	-0.0033(6)	5.0(5)
C(14)	0.6174(6)	0.0781(5)	0.1324(5)	4.7(5)
C(15)	0.6616(5)	0.1918(4)	0.3738(5)	2.5(2)
C(16)	0.7168(6)	0.1758(5)	0.3369(5)	4.4(2)
C(17)	0.7873(6)	0.1255(6)	0.3743(6)	5.5(3)
C(18)	0.8015(6)	0.0921(6)	0.4468(6)	6.0(3)
C(19)	0.7502(6)	0.1091(6)	0.4858(6)	5.8(3)
C(20)	0.6783(6)	0.1579(5)	0.4483(5)	4.6(2)
C(21)	0.4893(5)	0.2036(5)	0.2446(5)	2.7(2)
C(22)	0.4304(6)	0.2433(5)	0.1788(5)	3.7(2)
C(23)	0.3609(6)	0.2043(5)	0.1166(5)	4.5(2)
C(24)	0.3537(6)	0.1278(6)	0.1236(5)	4.7(2)
C(25)	0.4117(6)	0.0883(5)	0.1871(5)	4.6(2)
C(26)	0.4810(5)	0.1247(5)	0.2484(5)	3.6(2)
C(27)	0.6193(6)	0.4365(5)	0.4005(6)	6.3(6)
C(28)	0.7672(5)	0.3762(5)	0.3824(5)	5.2(5)
C(29)	0.0163(6)	0.8116(5)	-0.0613(5)	4.1(2)
C(30)	0.0222(7)	0.8643(6)	-0.1151(6)	6.3(3)
C(31)	-0.0545(8)	0.8902(7)	-0.1801(7)	8.2(3)
C(32)	-0.1299(8)	0.8617(7)	-0.1870(7)	7.6(3)
C(33)	-0.1411(8)	0.8069(7)	-0.1403(7)	7.8(3)
C(34)	-0.0627(7)	0.7803(6)	-0.0734(6)	5.7(3)
C(35)	0.1090(5)	0.6817(5)	0.0330(5)	3.3(2)
C(36)	0.0885(6)	0.6345(6)	-0.0347(6)	5.7(3)
C(37)	0.0924(7)	0.5563(7)	-0.0237(7)	7.3(3)

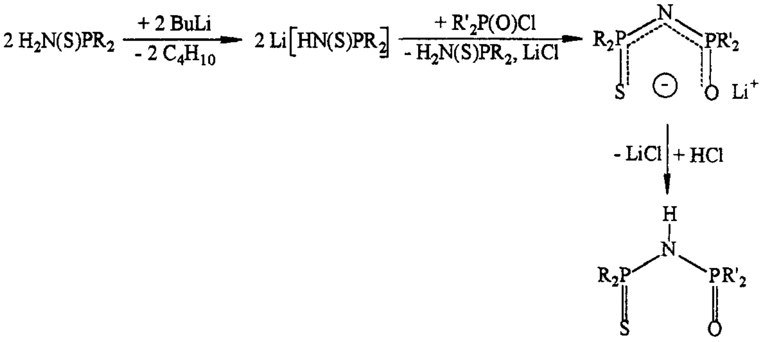
Atom	*x*	*y*	*z*	*B(eq)*
C(38)	0.1143(7)	0.5256(6)	0.0507(7)	6.7(3)
C(39)	0.1342(7)	0.5689(7)	0.1178(6)	6.6(3)
C(40)	0.1303(6)	0.6494(5)	0.1090(5)	4.5(2)
C(41)	0.2974(6)	0.8492(6)	0.1931(6)	6.6(6)
C(42)	0.1818(7)	0.9659(5)	0.1024(6)	6.0(6)
H(1)	0.726(5)	0.181(4)	0.044(5)	5.8
H(2)	0.604(5)	0.312(4)	0.236(5)	5.8
H(3)	0.081(5)	0.812(5)	0.117(5)	5.8

TABLE III Atomic coordinates and B(eq) of non-hydrogen atoms and $\underline{H}$-N atom for **(2)**

Atom	*x*	*y*	*z*	*B(eq)*
S(1)	0.0769(3)	0.1766(1)	0.0378	4.0(3)
P(1)	0.0131(4)	0.2595(1)	0.0916(7)	3.3(3)
P(2)	-0.0310(3)	0.1928(1)	0.1196(6)	2.8(2)
0(1)	-0.0077(8)	0.2574(2)	-0.054(1)	3.4(7)
N(1)	-0.028(1)	0.2301(3)	0.179(1)	2.6(7)
C(1)	0.129(1)	0.2600(4)	0.125(2)	6(1)
C(2)	-0.033(1)	0.2926(3)	0.172(2)	4(1)
C(3)	-0.0661(8)	0.1717(2)	0.268(1)	4.5
C(4)	-0.1443(7)	0.1796(2)	0.335(1)	4.5
C(5)	-0.1745(6)	0.1614(3)	0.441(1)	4.5
C(6)	-0.1264(8)	0.1353(2)	0.481(1)	4.5
C(7)	-0.0482(7)	0.1274(2)	0.414(1)	4.5
C(8)	-0.0181(6)	0.1456(3)	0.307(1)	4.5
C(9)	-0.1244(6)	0.1911(3)	0.007(1)	3.8
C(10)	-0.1282(6)	0.1673(2)	-0.088(1)	3.8
C(11)	-0.2023(8)	0.1644(2)	-0.171(1)	3.8
C(12)	-0.2727(6)	0.1853(2)	-0.159(1)	3.8
C(13)	-0.2689(6)	0.2090(2)	-0.063(1)	3.8
C(14)	-0.1948(8)	0.2119(2)	0.020(1)	3.8
H(1)	-0.02(1)	0.235(3)	0.27(2)	4.9

RESULTS AND DISCUSSION

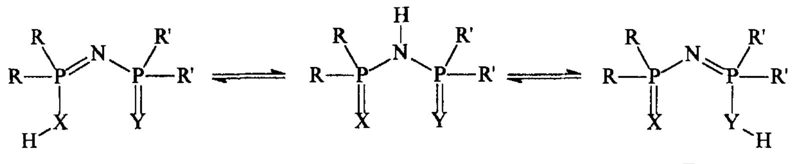
The isomeric acids were prepared according to the Scheme 1, by reacting the lithiated amide Li[HN(S)PR$_2$] with the diorganophosphinyl chloride R'$_2$P(O)Cl, followed by treatment of the reaction mixture with aqueous HCl solution:



(1)

This method is very versatile since various organophosphorus amides and halides might be used in the coupling reaction. Both (SPMe$_2$)(OPPh$_2$)NH and (OPMe$_2$)(SPPh$_2$)NH are colorless, crystalline solids, soluble in common organic solvents. The corresponding alkali salts were obtained by reacting the free acid with *t*-BuOK or NaOH in diethyl ether or methanol, respectively. It should be noted that K[(OPMe$_2$)(SPPh$_2$)N] is a highly hygroscopic compound, and therefore for synthetic purposes, *i.e.* preparation of metal complexes, the use of the sodium salt is recommended. Surprisingly, both K and Na salts of the (OPMe$_2$)(SPPh$_2$)NH acid are highly soluble in organic nonpolar solvents (for example in benzene or hexane). All these new compounds were characterized by IR and multinuclear NMR.

For asymmetric tetraorganodichalcogenoimidodiphosphinic acids several tautomeric formulae are possible, *i.e.* the acid proton might be attached to one of the chalcogen atoms (**C** or **E**) or to the nitrogen atom (**D**):



C **D** **E**

The infrared spectra of both acids exhibit absorptions of medium intensity around 2700 cm^{-1} which can be assigned to ν(NH) stretching vibrations. In addition, very strong absorptions at ca. 950 cm^{-1} were assigned to $\nu_{as}(P_2NH)$ stretching vibrations, thus suggesting the presence of the N-H group, and therefore a structure of type (**D**) can be assumed in solid state for the free acids (this was confirmed by the X-ray diffractometry studies; see subsequent discussion). The presence of the $S{=}PMe_2$ and $S{=}PPh_2$ groups in **1** and **2**, respectively, was proved by the wave numbers of the corresponding ν(PS) stretching vibrations, *i.e.* 530 and 635 cm^{-1}. In the IR spectra of the corresponding alkali salts, as expected, a shift of the strong absorptions observed in the free acids at 950 cm^{-1} [$\nu_{as}(P_2NH)$] and 1180 cm^{-1} [ν(PO)] to higher [ca. 1200 cm^{-1}, $\nu_{as}(P_2N)$], and lower [ca. 1120 cm^{-1}, ν(PO)] wave numbers, respectively, was noted.

The free acids and their alkali salts were investigated by solution NMR spectroscopy. Both the ^{1}H and ^{13}C NMR spectra showed the expected resonances for the organic groups attached to phosphorus; the resonance signals are split into two components, due to the phosphorus-proton and phosphorus-carbon couplings. The effect of the presence of different phosphorus atoms in the molecular unit is not observed in the ^{1}H and ^{13}C NMR spectra of the free acids, or in the ^{1}H NMR spectrum of the alkali salts. By contrast, the ^{13}C NMR spectra of all alkali salts show the expected doublet of doublets pattern of the resonance signal for the methyl carbons: $\delta = 28.05$dd, $^1J_{PC} = 71.9$ Hz, $^3J_{PC} = 3.5$ Hz for $K[(SPMe_2)(OPPh_2)N]$, $\delta = 20.20$dd, $^1J_{PC} = 90.7$ Hz, $^3J_{PC} = 5.0$ Hz for $K[(OPMe_2)(SPPh_2)N]$, and $\delta = 20.14$dd, $^1J_{PC} = 90.9$ Hz, $^3J_{PC} = 5.0$ Hz for $Na[(OPMe_2)(SPPh_2)N]$. Moreover, for the last two alkali salts the same pattern was observed for the resonance of the aromatic *ipso* carbon atoms: 141.31dd, $^1J_{PC} = 104.7$ Hz, $^3J_{PC} = 5.1$ Hz for the K salt, and 140.71dd, $^1J_{PC} = 105.0$ Hz, $^3J_{PC} = 5.0$ Hz for the Na salt, respectively. The non-equivalence of the two phosphorus atoms is also reflected in the presence of two ^{31}P resonances. In some cases, the expected doublet pattern due to phosphorus-phosphorus coupling is observed. The loss of the acidic proton is generally reflected in a significant shift to lower field of the ^{31}P resonances and their assignment was based up on the magnitude of the $^1J_{PC}$ coupling constant.

The solid state structures of the free acids $(SPMe_2)(OPPh_2)NH$ **1** and $(OPMe_2)(SPPh_2)NH$ **2** were determined by single-crystal X-ray diffraction. Compound **1** contains three independent, apparently very similar molecules in the unit cell (see the subsequent discussion). Selected bond distances and angles are listed in Table IV. Figure 1 shows an ORTEP-like view of the three independent molecules of **1**, with the coresponding atom numbering scheme. By contrast, the isomeric compound **2** contains only one independent molecule in the unit cell. Selected bond distances and angles for this compound are listed in Table V, and Figure 2 shows the ORTEP-like view of the molecular structure of **2**, with the atom numbering scheme.

TABLE IV Important bond lengths (Å) and angles (°) for the three independent molecules of **(1)**

N(1)-P(1)	1.662(7)	N(2)-P(3)	1.665(6)	N(3)-P(5)	1.666(7)
N(1)-P(2)	1.681(7)	N(2)-P(4)	1.681(6)	N(3)-P(6)	1.669(8)
P(1)-O(1)	1.480(5)	P(3)-0(2)	1.477(5)	P(5)-0(3)	1.479(5)
P(1)-C(1)	1.799(8)	P(3)-C(15)	1.782(8)	P(5)-C(29)	1.798(9)
P(1)-C(7)	1.780(8)	P(3)-C(21)	1.792(8)	P(5)-C(35)	1.788(8)
P(2)-S(1)	1.944(3)	P(4)-S(2)	1.925(3)	P(6)-S(3)	1.941(3)
P(2)-C(13)	1.795(9)	P(4)-C(27)	1.780(9)	P(6)-C(41)	1.789(9)
P(2)-C(14)	1.775(8)	P(4)-C(28)	1.786(8)	P(6)-C(42)	1.783(9)
N(1)-H(1)	0.97(7)	N(2)-H(2)	0.94(7)	N(3)-H(3)	0.77(7)
H(1)···O(3)[a]	1.96(7)	H(2)···O(1)	1.88(7)	H(3)···O(2)[b]	2.04(8)
N(1)···O(3)[a]	2.893(7)	N(2)···O(1)	2.820(7)	N(3)···O(2)[b]	2.793(8)
N(1)-P(1)-O(1)	110.7(3)	N(2)-P(3)-0(2)	113.2(3)	N(3)-P(5)-0(3)	111.0(3)
N(1)-P(1)-C(1)	104.9(4)	N(2)-P(3)-C(15)	109.2(3)	N(3)-P(5)-C(29)	108.6(4)
N(1)-P(1)-C(7)	107.6(4)	N(2)-P(3)-C(21)	103.7(3)	N(3)-P(5)-C(35)	105.5(4)
O(1)-P(1)-C(1)	114.1(3)	0(2)-P(3)-C(15)	110.1(3)	0(3)-P(5)-C(29)	111.4(4)
O(1)-P(1)-C(7)	112.3(4)	0(2)-P(3)-C(21)	113.4(3)	0(3)-P(5)-C(35)	113.1(4)
C(1)-P(1)-C(7)	106.9(4)	C(15)-P(3)-C(21)	106.8(4)	C(29)-P(5)-C(35)	106.9(4)
N(1)-P(2)-S(1)	110.2(2)	N(2)-P(4)-S(2)	111.3(3)	N(3)-P(6)-S(3)	111.0(3)
N(1)-P(2)-C(13)	108.1(4)	N(2)-P(4)-C(27)	106.6(4)	N(3)-P(6)-C(41)	106.4(4)
N(1)-P(2)-C(14)	106.5(4)	N(2)-P(4)-C(28)	107.1(40	N(3)-P(6)-C(42)	106.4(4)
S(1)-P(2)-C(13)	113.5(3)	S(2)-P(4)-C(27)	113.7(4)	S(3)-P(6)-C(41)	114.2(3)

S(1)-P(2)-C(14)	113.2(3)	S(2)-P(4)-C(28)	112.1(3)	S(3)-P(6)-C(42)	113.6(3)
C(13)-P(2)-(C14)	104.9(4)	C(27)-P(4)-C(28)	105.7(5)	C(41)-P(6)-C(42)	104.6(5)
P(1)-N(1)-P(2)	126.5(4)	P(3)-N(2)-P(4)	128.7(4)	P(5)-N(3)-P(6)	127.9(4)
P(1)-N(1)-H(1)	119(5)	P(3)-N(2)-H(2)	113(5)	P(5)-N(3)-H(3)	116(7)
P(2)-N(1)-H(1)	114(5)	P(4)-N(2)-H(2)	113(5)	P(6)-N(3)-H(3)	116(7)
N(1)-H(1)···O(3)[a]	161(7)	N(1)-H(2)···O(1)	173(7)	N(3)-H(3)···O(2)[b]	164(9)

[a] 1 - x, 1 - y, - z; [b] 1/2 - x, 1/2 + y, 1/2 -z.

TABLE V Important bond lengths (Å) and angles (°) for (**2**)

N(1)-P(1)	1.66(1)	N(1)-P(1)-O(1)	112.6(7)
N(1)-P(2)	1.71(1)	N(1)-P(1)-C(1)	106.2(9)
P(1)-O(1)	1.48(1)	N(1)-P(1)-C(2)	103.2(8)
P(1)-C(1)	1.78(2)	O(1)-P(1)-C(1)	113.1(9)
P(1)-C(2)	1.78(2)	O(1)-P(1)-C(2)	113.9(8)
P(2)-S(1)	1.946(5)	C(1)-P(1)-C(2)	107.0(9)
P(2)-C(3)	1.80(1)	N(1)-P(2)-S(1)	117.4(6)
P(2)-C(9)	1.80(1)	N(1)-P(2)-C(3)	101.4(6)
N(1)-H(1)	1.0(1)	N(1)-P(2)-C(9)	105.8(7)
H(1)···O(1)[a]	1.8(1)	S(1)-P(2)-C(3)	113.8(4)
N(1)···O(1)[a]	2.75(2)	S(1)-P(2)-C(9)	112.5(5)
		C(3)-P(2)-C(9)	104.6(6)
		P(1)-N(1)-P(2)	123.0(9)
		P(1)-N(1)-H(1)	107(9)
		P(2)-N(1)-H(1)	123(9)
		N(1)-H(1)···O(1)[a]	175(15)

[a] -x, 1/2-y, z-1/2.

The molecules of both compounds **1** and **2** contain an angular P-N-P system [av. 127.7(1.1)° in **1**, and 123.0(9)° in **2**, respectively] and the acid hydrogen atom is linked to the nitrogen atom [N-H av. 0.89(11) Å in **1**, and 1.0(1) Å in **2**]. The main difference was observed in the conformation of

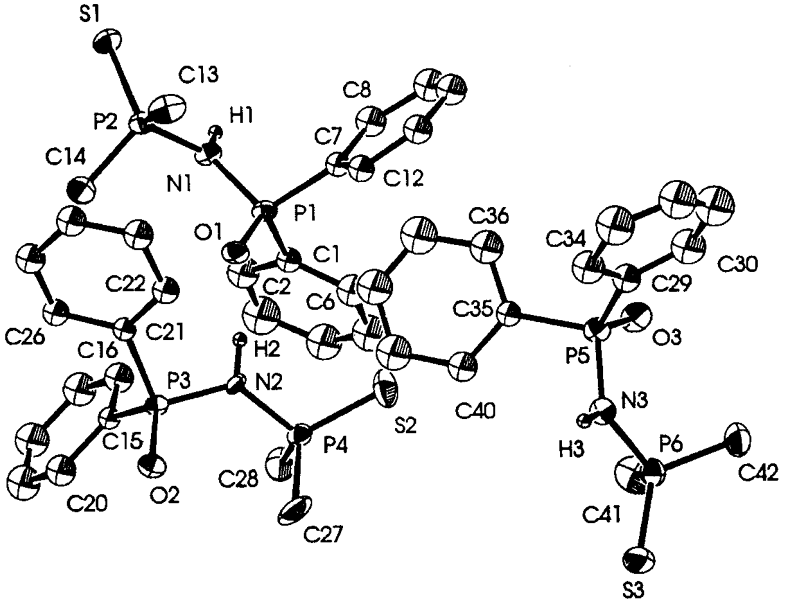


FIGURE 1 ORTEP-like plot of the three independent molecules in the asymmetric unit of $(SPMe_2)(OPPh_2)NH$ **1**. The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms, other than those attached to nitrogen, are omitted for clarity

the SPNPO skeleton and this is discussed bellow in comparison with that observed for the related $(OPPh_2)(SPPh_2)NH$ derivative.

The phosphorus-sulfur [av. 1.937(10) in **1**, and 1.946(5) Å in **2**] and phosphorus-oxygen [av. 1.479(2) in **1**, and 1.48(1) Å in **2**] bond lengths are typical for P=S and P=O double bonds, respectively [cf. $Ph_2P(=S)SH$:[23] P=S 1.954(1) Å, P-S 2.077(1) Å; $Ph_2P(O)OH$:[24] P=O 1.486(6) Å, P-O 1.526(6) Å]. The phosphorus-nitrogen bonds in a molecular unit are basically equivalent regardless the nature of the chalcogen atom or the organic groups attached to phosphorus atoms, and their magnitude [av. 1.671(8) in **1**, and av. 1.69(4) Å in **2**] is clearly consistent with P-N single bonds [cf. $(Me_3Si)_2N\text{-}P(=NBu^t)S]_2$:[25] P=N 1.529(2) Å, P-N 1.662(2) Å]. However, as observed for the symmetric analogs, $(SPPh_2)_2NH$,[26,27] and $(SePPh_2)_2NH$,[28] or the asymmetric $(OPPh_2)(SPPh_2)NH$ derivative,[4] the sum of the angles at the N atom is close to 360° (see the P-N-P and P-N-H angles in Table VI), thus suggesting considerable sp^2 character at nitrogen. The tetrahedral geometry

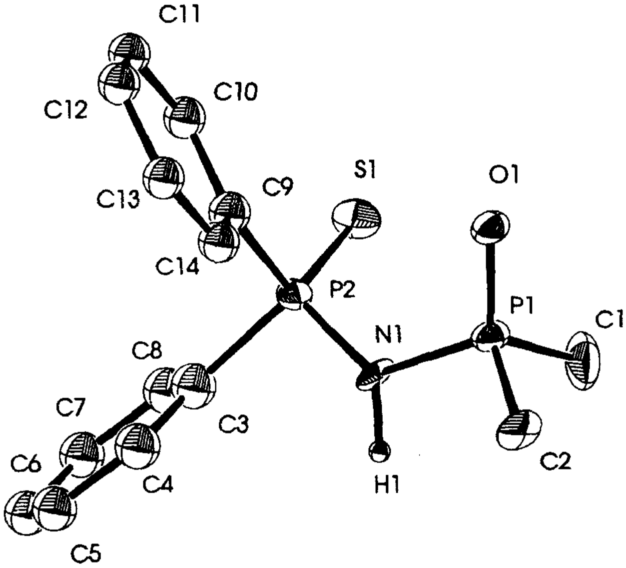


FIGURE 2 ORTEP-like plot of $(OPMe_2)(SPPh_2)NH$ **2**. The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms, other than those attached to nitrogen, are omitted for clarity

around both phosphorus atoms in the molecular units is distorted as reflected by the angles listed in Tables IVand V.

In the crystal of both compounds **1** and **2** the molecules are associated into polymeric chains through H bonds that involve only the O atoms of each molecular moiety (Fig 3 and 4).

A comparison of the molecular dimensions of **1**, **2** and the related $(OPPh_2)(SPPh_2)NH$ derivative, is presented in Table VI. One might note the smaller P-N-P angle in the molecules of compounds **1** and **2** *vs.* the compound containing only phenyl groups attached to phosphorus. However, the main difference is concerned with the conformation of the OPNPS skeleton as reflected by the torsion angles and deviations from the PNP plane (Table VI, Fig. 5). In previous works the conformation of this inorganic fragment was described only in terms of *anti* and *syn* with respect to the relative orientation of the phosphorus-chalcogen bonds. However, due to the high flexibility of the XPNPY fragment, it seems more convenient to use a combination of the conformations of the XPNP and PNPY systems (Fig. 5). Thus, both the molecules of

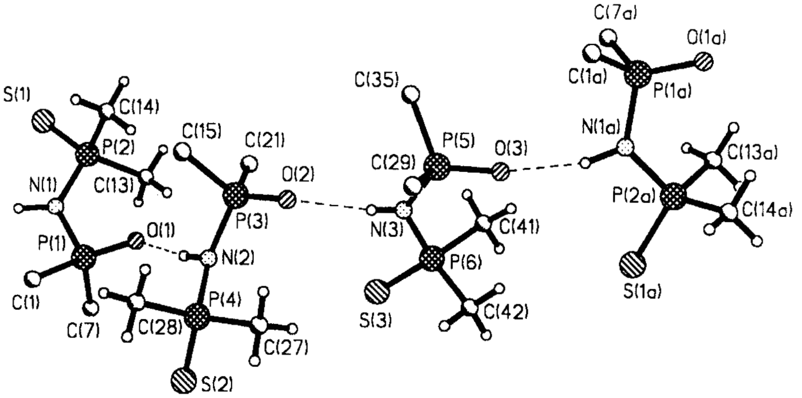


FIGURE 3 Chain polymeric association through H bonding in $[(SPMe_2)(OPPh_2)NH]_n$. For clarity, only the *ipso* carbons of the phenyl groups are shown

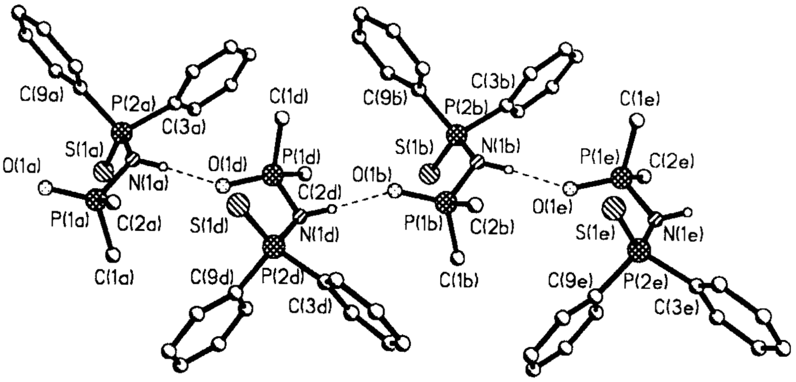


FIGURE 4 Chain polymeric association through H bonding in $[(OPMe_2)(SPPh_2)NH]_n$. For clarity, only the *ipso* carbons of the phenyl groups are shown

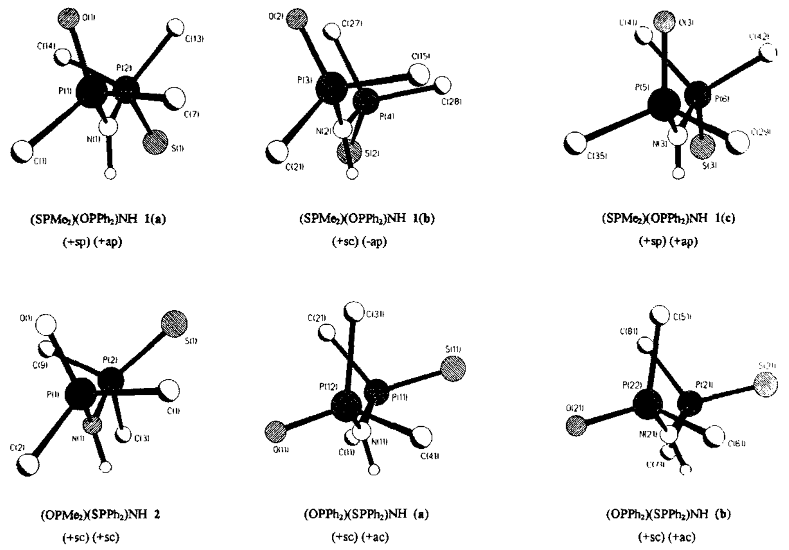
$(OPPh_2)(SPPh_2)NH$ and **1** might be simply described as *"anti"*, but some differences should be noted. For $(OPPh_2)(SPPh_2)NH$ the two independent molecules of the unit cell are very similar, with the chalcogen atoms placed on opposite sides of the PNP plane. The OP_2S system is planar [mean deviation: 0.019 Å for molecule (**a**), and 0.032 Å for molecule (**b**)], and the best OPPS plane is almost ortogonal to the PNP plane [dihedral angle: 71.2° for molecule (**a**), and 71.6° for molecule (**b**)]. In the molecules

1(a) and **1(c)**, the chalcogen atoms are also placed on opposite sides of the PNP plane, but the dihedral angle between the planar OP_2S system [mean deviation: 0.002 Å for molecule **1(a)**, and 0.041 Å for molecule **1(c)**] and the PNP plane is much smaller, *i.e.* 22.0° for molecule **1(a)**, and only 6.1° for molecule **1(c)**. The molecule **1(b)** is quite different, the chalcogen atoms lying on the same side of the PNP plane. For all these molecules the chalcogen atoms are pushed as far as posible, the non-bonding O···S distance being about 5.1–5.5 Å. In contrast, the molecule of **2** exhibits a "*syn*" orientation of the phosphorus-chalcogen bonds, with the chalcogen atoms placed on opposite sides of the PNP plane. This brings the chalcogen atoms at about only 3.8 Å, which compares with the non-bonding O···S distance in metal chelates containing the anionic form of such ligands.

TABLE VI Comparative molecular data for the monothioimidodiphosphinic acids

	$(OPPh_2)(SPPh_2)NH$[4]		$(SPMe_2)(OPPh_2)NH$			$(OPMe_2)(SPPh_2)NH$
	molecule (a)	*molecule (b)*	*(1a)*	*(1b)*	*(1c)*	*(2)*
P-S	1.935(2)	1.915(2)	1.944(3)	1.925(3)	1.941(3)	1.946(5)
(S)P-N	1.694(4)	1.673(5)	1.681(7)	1.681(6)	1.669(8)	1.71(1)
P-O	1.491(4)	1.514(4)	1.480(5)	1.477(5)	1.479(5)	1.48(1)
(O)P-N	1.668(5)	1.683(5)	1.662(7)	1.665(6)	1.666(7)	1.66(1)
O···S (non-bonding)	5.501	5.503	5.123	5.119	5.121	3.817
O···H	2.15(6)	2.03(6)	1.96(7)	1.88(7)	2.04(8)	1.8(1)
N-H	0.87(6)	0.86(6)	0.97(7)	0.94(7)	0.77(7)	1.0(1)
S-P-N	115.7(2)	115.2(2)	110.2(2)	111.3(3)	111.0(3)	117.4(6)
P-N-P	131.4(3)	132.9(3)	126.5(4)	128.7(4)	127.9(4)	123.0(9)
O-P-N	113.5(2)	112.6(2)	110.7(3)	113.2(3)	111.0(3)	112.6(7)
(S)P-N-H	111(4)	108(4)	114(5)	113(5)	116(7)	123(9)
(O)P-N-H	114(5)	113(4)	119(5)	113(5)	116(7)	107(9)
N-H···O	173(5)	175(5)	161(7)	173(7)	164(9)	175(15)
Deviations from PNP plane						
S	1.727	-1.719	-0.507	-0.451	0.007	1.265
O	-1.139	1.165	0.556	-0.933	-0.213	-0.839
H	0.291	-0.415	-0.105	0.411	0.127	0.430

	$(OPPh_2)(SPPh_2)NH^4$		$(SPMe_2)(OPPh_2)NH$			$(OPMe_2)(SPPh_2)NH$
	*molecule (**a**)*	*molecule (**b**)*	*(**1a**)*	*(**1b**)*	*(**1c**)*	*(**2**)*
Torsion angles						
SPNP	82.1	82.8	163.9	-165.4	179.8	47.0
OPNP	123.6	123.6	23.7	43.4	8.9	37.9
SPNH	-77.1	-66.7	-9.4	42.7	10.4	-99.7
OPNH	-77.8	-88.2	-163.3	-165.0	178.2	-170.8



(SPMe₂)(OPPh₂)NH 1(a)
(+sp) (+ap)

(SPMe₂)(OPPh₂)NH 1(b)
(+sc) (-ap)

(SPMe₂)(OPPh₂)NH 1(c)
(+sp) (+ap)

(OPMe₂)(SPPh₂)NH 2
(+sc) (+sc)

(OPPh₂)(SPPh₂)NH (a)
(+sc) (+ac)

(OPPh₂)(SPPh₂)NH (b)
(+sc) (+ac)

FIGURE 5 Conformation ofthe OPC_2NPC_2S skeleton in $(OPR_2)(SPR'_2)NH$ derivatives. [IUPAC abbreviations: (+sp) = + sinperiplanar; (±ap) = ± antiperiplanar; (+sc) = + sinclinal; (+ac) = + anticlinal]

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[18] Standard deviation of an observation of unit weight: $\sum w(|F_o| - |F_c|)^2/(N_o\text{-}N_c)^{1/2}$, where N_o = number of observations and N_c = number of variables.

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