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The Crystal and Molecular Structure of a Versatile Bidentate Ligand: Tetraphenyldithioimidodiphosphinate, $Ph_2(S)P–NH–P(S)Ph_2$

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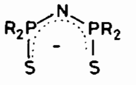
Abstract

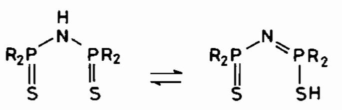
The crystal and molecular structure of tetraphenyldithioimidodiphosphinate, $Ph_2(S)P–NH–P(S)$-Ph_2 has been determined by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, a = 10.644(2), b = 10.840(2), c = 11.205(2) Å, α = 64.76(2), β = 74.96(2), γ = 80.79(2)°, Z = 2; R = 0.16 for 1673 unique reflections. The short P–S bonds (1.915(3) and 1.917(3) Å) and long P–N bonds (1.652(7) and 1.700(7) Å) suggest the tautomeric form $\mathrm{Ph_2\overset{\overset{S}{\|}}{P}–NH–\overset{\overset{S}{\|}}{P}Ph_2}$, although the hydrogen atom could not be located. The P–N–P angle is 131.7(5)°. The S–P–N–P–S framework is nearly planar with the two sulphur atoms in a *trans* position relative to the P–N–P skeleton.

Introduction

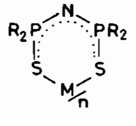
The anion (**I**) of tetraorganyldithioimidodiphosphinates (**II**) (R = Me, Ph) is an extremely versatile bidentate ligand and several metal complexes (**III**) containing iron [1], nickel [2], manganese [2] and bismuth [3], have been prepared. In addition, the protonated form of the ligand, under mild conditions, is also able to form transition metal complexes, which probably have structure (**IV**) [4], but no diffraction study has yet been performed on any such complexes.



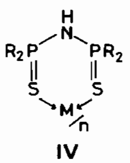
I



IIa **IIb**



III

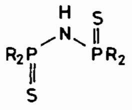


IV

The free ligand may occur in two tautomeric forms, **IIa** and **IIb**. Spectrosocpic data (IR and NMR) suggest structure **IIa** [5–7], whereas treatment with diazomethane produces an S-methyl ester derived from (**IIb**) [5].

Although the molecular structures of several metal complexes, (**III**), were established by X-ray diffraction [2, 3], the structure of the free ligand (**II**) has not been determined. Such an investigation is of double interest, since it can establish which of the forms (**IIa**) or (**IIb**) is present in the solid state and also affords the possibility to compare the bonding in the free ligand and its complexes.

The work described here establishes that the free ligand (R = Ph) has structure (**IIa**) in solid state and surprisingly, the two sulfur atoms adopt a *trans*-configuration (**IIc**) in the solid state. Formation of type (**IV**) complexes therefore requires a rotation about the P–N bond, which seems to be not hindered in solution.



IIc

Experimental

The compound was prepared according to literature data [8], and was recrystallized from toluene, m.p. 220–1 °C.

Crystal data. $C_{24}H_{21}NP_2S_2$, M = 449.5, triclinic, a = 10.644(2), b = 10.840(2), c = 11.205(2) Å, α = 64.76(2), β = 74.96(2), γ = 80.79(2)°, U = 1127.5 Å^3, Z = 2, D_c = 1.32 g cm^{-3}, F(000) = 468. Monochromated MoKα radiation, λ = 0.71069 Å, μ = 3.8 cm^{-1}. Space group $P\bar{1}$ from successful structure refinement.

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Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal *ca.* 0.3 × 0.2 × 0.2 mm. Preliminary investigation using the SEARCH and INDEX routines of the CAD4 suggested that the crystal was twinned. However it proved possible to separate out reflections which could be indexed on the basis of a triclinic unit cell and final cell parameters were calculated from the setting angles for 25 reflections with $\theta \approx 12^\circ$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 22^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 120 seconds. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lp effects but not for absorption and after averaging any equivalent reflections 1673 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + 0.02\, I)^2]^{1/2}/\mathrm{Lp}$. No attempt was made to correct intensities of reflections which might be affected by overlap from the twin data.

The structure was solved by routine heavy atom methods. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least squares. Refinement converged at $R = 0.16$, $R' = 0.20$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map showed peaks of up to 1.5 e Å^{-3} but none seemed to correspond to chemically reasonable atom sites. Hydrogen atom sites could not be located.

The structure solution and refinement were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 9. Final atom co-ordinates are listed in Table I, and lists of temperature factors and structure factors are available for the authors.

TABLE I. Fractional Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses.

	x	*y*	*z*
S(1)	–32(5)	4188(6)	3502(5)
S(2)	4796(5)	2723(7)	5193(7)
P(1)	1733(5)	4353(5)	3501(5)
P(2)	2963(5)	2748(6)	5954(6)
N	1996(15)	3984(17)	5010(14)
C(1)	2213(19)	6094(18)	2499(17)
C(2)	1628(26)	6884(24)	1402(20)
C(3)	2001(24)	8225(23)	603(23)
C(4)	2984(25)	8744(23)	836(23)
C(5)	3509(26)	7936(23)	1968(24)
C(6)	3183(23)	6594(20)	2737(24)
C(7)	2865(20)	3255(21)	2833(21)
C(8)	4006(21)	3700(21)	1941(22)
C(9)	4830(25)	2794(23)	1395(23)
C(10)	4484(26)	1503(24)	1801(27)
C(11)	3289(25)	1050(22)	2701(23)
C(12)	2419(25)	1922(22)	3262(19)
C(13)	2585(18)	3156(22)	7444(20)
C(14)	3133(20)	4318(21)	7306(19)
C(15)	2808(23)	4728(23)	8392(22)
C(16)	1952(27)	3858(28)	9630(26)
C(17)	1447(24)	2744(25)	9777(21)
C(18)	1774(20)	2343(23)	8653(21)
C(19)	2232(19)	1245(19)	6425(19)
C(20)	854(24)	1175(23)	6709(24)
C(21)	307(26)	89(24)	6852(25)
C(22)	1098(38)	–1169(24)	6907(24)
C(23)	2471(25)	–1102(23)	6651(26)
C(24)	2980(26)	4(23)	6451(23)

Results and Discussion

Bond distances and bond angles are listed in Table II. The atom numbering scheme and the overall molecular structure are illustrated in Fig. 1.

The molecule adopts a twisted conformation, with the two sulfur atoms adopting mutually *trans*-positions, relative to the P–N–P skeleton. This is a somewhat unexpected result, in view of the ability of this ligand to form transition metal complexes even in protonated form (*i.e.* (**IV**)), in which the sulfur atoms are obviously *cis*. The torsion angles, which give an image of the molecular conformation are listed in Table III.

The phosphorus–sulfur bond distances of 1.916 Å (average) are clearly indicative of double bond character and are of the same order of magnitude as P=S bonds in P_4S_{10} (1.96 Å) [10], but are significantly shorter than values found in the metal complexes *e.g.* P–S 2.009–2.025 Å in the bismuth complex [3], and 2.013 Å in the manganese complex [2].

The P–N–P bond angle of 131.7(5)° compares well with the value of 138.5° found in the $[Ph_3PNPPh_3]^+$ cation [11] (although a linear variety of the cation has also been observed [12]). This angle is approximately preserved by coordination in the manganese and bismuth complexes, where the MS_2P_2N ring adopts a twisted boat conformation with the P–N–P angle of 133° [2, 3]. In most of the cyclophosphazane compounds, however a smaller P–N–P bond angle is determined by the ring strain *e.g.* 96° for $[ClP(S)N(Me)]_2$ [13] or 121° in $[MeOP(O)NMe]_3$ [14].

TABLE II. Intramolecular Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

a) Bonds			
S(1)–P(1)	1.915(3)	S(2)–P(2)	1.917(3)
P(1)–N	1.652(7)	P(1)–C(1)	1.813(9)
P(1)–C(7)	1.807(10)	P(2)–N	1.700(7)
P(2)–C(13)	1.835(10)	P(2)–C(19)	1.732(9)
C(1)–C(2)	1.400(12)	C(1)–C(6)	1.370(12)
C(2)–C(3)	1.402(14)	C(3)–C(4)	1.390(14)
C(4)–C(5)	1.397(15)	C(5)–C(6)	1.385(14)
C(7)–C(8)	1.361(13)	C(7)–C(12)	1.433(14)
C(8)–C(9)	1.438(14)	C(9)–C(10)	1.355(14)
C(10)–C(11)	1.41(2)	C(11)–C(12)	1.439(14)
C(13)–C(14)	1.405(12)	C(13)–C(18)	1.405(12)
C(14)–C(15)	1.411(14)	C(15)–C(16)	1.47(2)
C(16)–C(17)	1.33(2)	C(17)–C(18)	1.444(14)
C(19)–C(20)	1.424(13)	C(19)–C(24)	1.443(13)
C(20)–C(21)	1.327(14)	C(21)–C(22)	1.47(2)
C(22)–C(23)	1.42(2)	C(23)–C(24)	1.302(14)
b) Angles			
S(1)–P(1)–N	114.1(3)	S(1)–P(1)–C(1)	111.1(3)
S(1)–P(1)–C(7)	112.2(3)	N–P(1)–C(1)	104.8(4)
N–P(1)–C(7)	106.3(4)	C(1)–P(1)–C(7)	107.9(4)
S(2)–P(2)–N	117.4(3)	S(2)–P(2)–C(13)	112.2(3)
S(2)–P(2)–C(19)	115.0(3)	N–P(2)–C(13)	99.2(4)
N–P(2)–C(19)	104.3(4)	C(13)–P(2)–C(19)	107.0(4)
P(1)–N–P(2)	131.7(5)	P(1)–C(1)–C(2)	117.6(7)
P(1)–C(1)–C(6)	121.5(7)	C(2)–C(1)–C(6)	120.7(9)
C(1)–C(2)–C(3)	118(1)	C(2)–C(3)–C(4)	121.2(9)
C(3)–C(4)–C(5)	118(1)	C(4)–C(5)–C(6)	121(1)
C(1)–C(6)–C(5)	120(1)	P(1)–C(7)–C(8)	122.0(8)
P(1)–C(7)–C(12)	114.1(8)	C(8)–C(7)–C(12)	124(1)
C(7)–C(8)–C(9)	119.1(9)	C(8)–C(9)–C(10)	120(1)
C(9)–C(10)–C(11)	121(1)	C(10)–C(11)–C(12)	121(1)
C(7)–C(12)–C(11)	115(1)	P(2)–C(13)–C(14)	116.8(7)
P(2)–C(13)–C(18)	121.0(8)	C(14)–C(13)–C(18)	122(1)
C(13)–C(14)–C(15)	119(1)	C(14)–C(15)–C(16)	117(1)
C(15)–C(16)–C(17)	124(1)	C(16)–C(17)–C(18)	118(1)
C(13)–C(18)–C(17)	119(1)	P(2)–C(19)–C(20)	122.4(7)
P(2)–C(19)–C(24)	122.1(8)	C(20)–C(19)–C(24)	115.3(8)
C(19)–C(20)–C(21)	122(1)	C(20)–C(21)–C(22)	121(1)
C(21)–C(22)–C(23)	117(1)	C(22)–C(23)–C(24)	121(1)
C(19)–C(24)–C(23)	124(1)		

TABLE III. Selected Torsion Angles (°).

S(1)–P(1)–N–P(2)	118(1)
P(1)–N–P(2)–S(2)	60(2)
C(1)–P(1)–N–P(2)	−121(1)
C(7)–P(1)–N–P(2)	−7(2)
P(1)–N–P(2)–C(13)	−179(1)
P(1)–N–P(2)–C(19)	−69(2)
S(1)–P(1)–C(1)–C(2)	−30(2)
S(1)–P(1)–C(7)–C(8)	136(2)
N–P(2)–C(13)–C(14)	−74(2)
N–P(2)–C(19)–C(20)	−35(2)

The P–N bonds in the free ligand (P(1)–N 1.652(7) and P(2)–N 1.700(7) Å) are longer than in the metal complexes of the same ligand (1.586–1.595 Å in the bismuth complexes [3] and 1.588 Å in the manganese complexes [2]) but are comparable with the P–N bonds in [ClP(S)N(Me)]$_2$ 1.67 Å [13], Me$_4$(S)$_3$P$_4$N$_4$Me$_4$ 1.73–1.74 Å [15] and (H$_2$N)$_2$(S)P–NMe–P(S)NH$_2$NHMe 1.73 Å [16], suggesting typical single P–N bonds.

Both the P=S and P–N bond lengths clearly indicate that the free ligand has structure (**IIa**) in solid state. Although the position of the hydrogen atoms could not be located, these data suggest that a proton must be present at the nitrogen site. The comparison

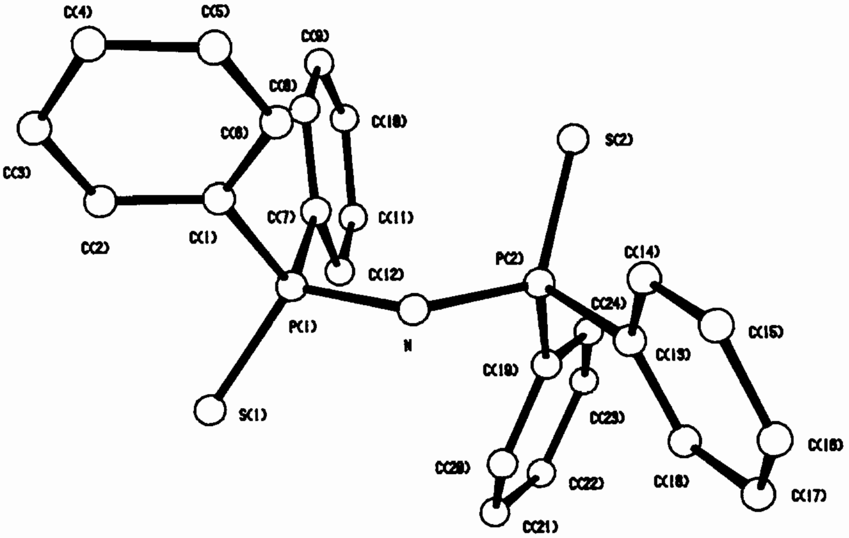

Fig. 1. The atom numbering scheme and overall molecular structure.

of data supports the conclusion that some π-electron delocalization occurs in the inorganic chelate ring (**III**) which results in longer P–S bonds and shorter P–N bonds in the complexes than in the free ligand.

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