First Structural Study of a Thiophosphorane Containing a Six-Membered Ring. Phosphorus-Sulfur vs Phosphorus-Oxygen Ligand Preferences[1,2]

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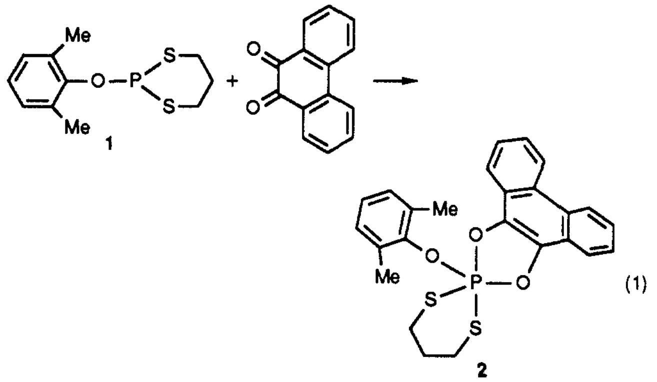
Received September 15, 1989. Revised Manuscript Received March 31, 1990

Abstract: Oxidative addition of phenanthrenequinone to the newly synthesized dithiaphosphorinane, $(\text{Xylyl-O})\overline{\text{P-S(CH}_2)_3\text{S}}$ (**1**), results in a new thiophosphorane containing a sulfur-bonded six-membered ring. X-ray analysis on separate crystals reveals both a monoclinic and triclinic modification. This represents the first structural study of a six-membered ring containing thiophosphorane. The structure which is a trigonal biyramid has the ring sulfur atoms located in apical-equatorial sites instead of the expected diequatorial arrangement. As a consequence, the more electronegative xylyloxy oxygen atom is relegated to an equatorial position. A slightly twisted boat conformation exists for the dithiaphosphorinane ring. ^{1}H NMR spectroscopy is consistent with the retention of the solid-state structure in solution which undergoes rapid intramolecular ligand exchange.

Although an abundance of structural studies indicating conformational preferences for phosphoranes containing five-membered rings has been performed,[3,4] little is known about corresponding six-membered ring systems.[5] In the case of analogous thiophosphoranes, no structural information appears to be available.[6] In this paper we report the first structural study of an unusual thiophosphorane containing a six-membered phosphorinane ring with ring sulfur atoms bonded to phosphorus. It is obtained in both a triclinic form, **2A**, and a monoclinic form, **2B**, from the oxidative addition reaction of phenanthrenequinone to **1** (eq 1), followed by recrystallization from dichloromethane.



X-ray analysis shows that the two crystalline modifications of **2** possess a trigonal-bipyramid structure with the principal difference between them being in the orientation of the *O*-xylyl group relative to the remainder of the molecule (Figure 1). Moreover, an apical-equatorial orientation for the sulfur-containing ring in both modifications arises in preference to a diequatorial ring placement that would allow the more electronegative oxygen atom of the xylyloxy group access to its preferred apical location. The observed structure is also unexpected on the basis of relative ring strain effects. In the diequatorial position, the six-membered ring suffers little strain, being accommodated with an ideal angle at phosphorus of 120°, whereas the actual structure contains the ring at a trigonal-bipyramidal angle at phosphorus of 90°.

In the monoclinic form, **2B**, the intermolecular packing includes stacking interactions between phenanthrene groups of inversion related pairs of molecules (Figure 2). The phenanthrene planes of such pairs, required by symmetry to be parallel, are separated by a distance of 3.524 Å. In the triclinic form, **2A**, inversion related pairs are in van der Waals' contact via atoms of the six-membered heterocylic rings and no stacking interactions are observed. The packing is apparently more efficient in the monoclinic form as evidenced by the densities: 1.405 g/cm^3 for **2B** versus 1.346 g/cm^3 for **2A**.

Despite the marked difference in the mode of packing for the two forms, the geometries of the spirocyclic systems are nearly identical and the only important difference in the molecular geometries involves the disposition of the xylyloxy group (Figure 1). This provides fairly compelling evidence that the apical-equatorial placement of the six-membered ring is in no way due to the energetics of packing, but rather reflects energy minimization within the molecule.

A further feature of the two forms of **2** is the presence of the six-membered ring in a near boat (or twist boat) conformation, with the axial sulfur atom, S1, and the opposing carbon atom, C2, at the prow and the stern of the boat (Figure 3). The five-membered ring is essentially planar and coplanar with the fused phenanthrene group (the 17 atom system is coplanar to within ±0.059 Å for **2B** and ±0.114 Å for **2A**).

The axial-equatorial orientation for the six-membered ring in a near boat conformation is of the type discussed by Trippett[5a,7] for phosphoranes that allows lone pairs of the equatorial ring atoms bonded to phosphorus to be placed near the equatorial plane for effective back-bonding.[8] The extent to which this effect might occur for sulfur atoms in a derivative of this type is not known with any certainty.[9] However, the preferred ring stabilization

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(5) Some X-ray studies of phosphoranes with six-membered rings in a boat or twist-boat conformation involving oxygen and nitrogen ring atoms attached to phosphorus are as follows: (a) Barlow, J. H.; Bone, S. A.; Russell, D. R.; Trippett, S.; Whittle, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 1031. (b) Schomburg, D.; Weferling, N.; Schmutzler, R. *Ibid.* **1981**, 810. (c) Pochlauer, P.; Petter, W.; Peringer, P.; Muller, E. P. *Ibid.* **1985**, 1760. (d) Schomburg, D.; Hacklin, H.; Röschenthaler, G. V. *Phosphorus Sulfur* **1988**, *35*, 241. (e) Yu, J. H.; Bentrude, W. G. *J. Am. Chem. Soc.* **1988**, *110*, 7987 (A report of a non-chair conformation for a six-membered oxygen-nitrogen ring bonded to pentacoordinated phosphorus apically and equatorially based on solution ^{1}H NMR evidence. More recently, these same workers reported a twist conformation for a model system closely related to cAMP: Yu, J. H.; Bentrude, W. G. *Tetrahedron Lett.* **1989**, *30*, 2195).

(6) A report of a phosphorane with a six-membered dithianaphthalene ring system is available but no structural information is given: Kimura, Y.; Kokura, T.; Saegusa, T. *J. Org. Chem.* **1983**, *48*, 3815.

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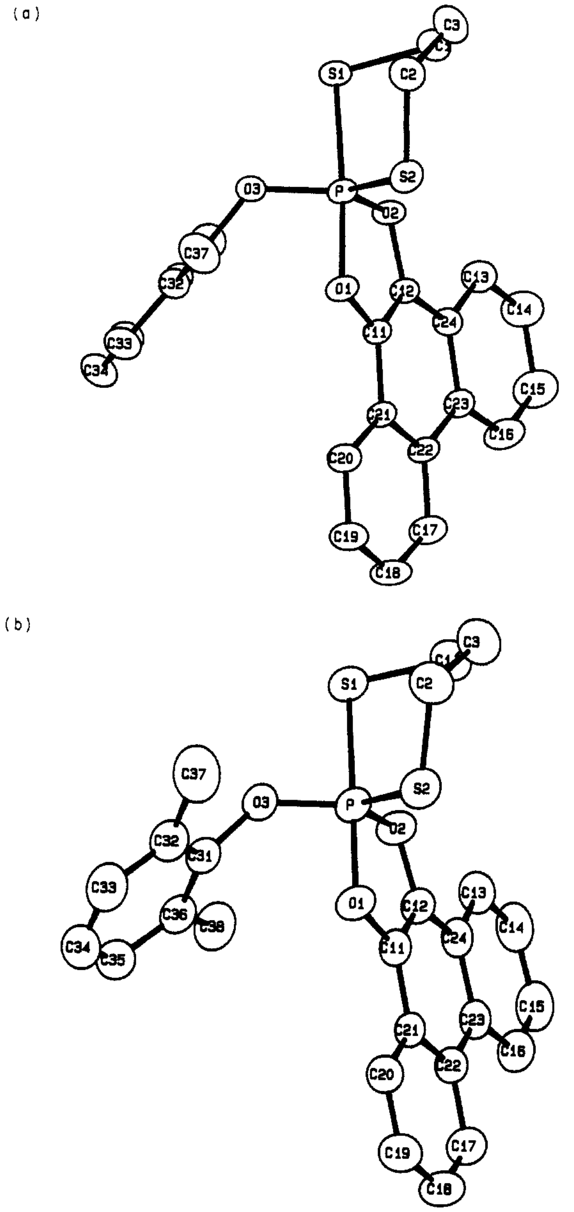
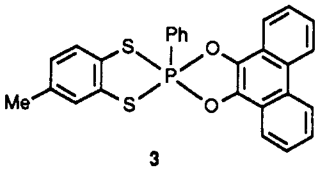


Figure 1. ORTEP plots showing the solid state molecular geometry of **2** in (a) the triclinic form, **2A**, and (b) the monoclinic form, **2B**. **Bond lengths (Å) for 2A,2B**: P–O1 = 1.746 (2), 1.753 (2); P–O2 = 1.649 (3), 1.645 (2); P–O3 = 1.607 (3), 1.598 (2); P–S1 = 2.151 (1), 2.145 (1); P–S2 = 2.090 (1), 2.092 (1). **Bond angles (deg) for 2A,2B**: P–S1–C1 = 99.4 (1), 99.2 (1); P–S2–C2 = 105.8 (1), 107.6 (1); S1–P–S2 = 98.94 (5), 97.81 (4); S1–P–O1 = 176.03 (9), 178.62 (7); S1–P–O2 = 89.78 (8), 89.92 (7); S1–P–O3 = 85.49 (8), 86.30 (7); S2–P–O1 = 84.78 (9), 83.51 (7); S2–P–O3 = 122.4 (1), 123.39 (8); O1–P–O2 = 89.7 (1), 89.76 (8); O1–P–O3 = 91.3 (1), 92.66 (9); O2–P–O3 = 120.2 (1), 117.2 (1).

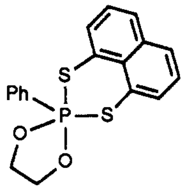
in apical–equatorial sites for **2** is sufficient to override the usual orientation observed for the more electronegative oxygen atom at an apical site of a trigonal bipyramid. It must be pointed out that Trippett's prediction is not universally obeyed, as related work on azoxyphosphoranes has shown.[10]

In a somewhat related phosphorane, **3**, containing a five-membered ring, X-ray analysis revealed an entirely different structure, that of a square-pyramidal geometry.[10] Here, ring strain effects for such unsaturated systems support a preference for the normally higher energy square-pyramidal structure compared to the trigonal bipyramid.[3,11,12] Presumably the presence of the more flexible saturated six-membered sulfur containing ring system in **2** inhibits the formation of a square-pyramidal structure.



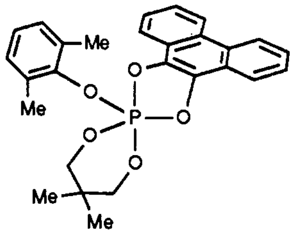
3

The ^{1}H NMR in CDCl$_3$ solution by itself does not differentiate between retention of the solid-state structure for **2** undergoing rapid Berry pseudorotation[13] and a structure having a diequatorial ring orientation. However, variable-temperature NMR studies[2,14,15] on related spirocyclic phosphoranes containing six-membered rings indicates nonrigid molecules with the presence of rapid permutational isomerization occurring at room temperature, e.g., in **4**.[15]



4

A variable-temperature ^{1}H NMR study of **2** in CD$_2$Cl$_2$ solution showed no significant change in the spectrum down to −90 °C similar to that found for **5**[16] and **6**.[14] Here, it was concluded[14,16] that a rapid, simple Berry exchange (a–e ⇌ e–a) was not slowed down to the lowest temperatures studied. By analogy, we presume that this also is occurring in **2** but the NMR data alone are not definitive.



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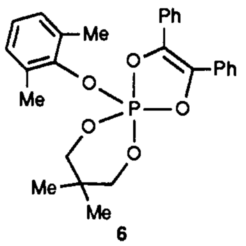

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In view of the present work on the cyclic thiophosphorane **2** and previous structural studies[2,5,14] on related phosphoranes with oxygen- and nitrogen-containing rings, it is concluded that the boat conformation positioned apically and equatorially in a trigonal bipyramid, energetically, is the generally preferred conformation for saturated six-membered rings in phosphoranes in the absence of perturbing influences, e.g., steric effects, hydrogen bonding,[10] and packing effects. It remains to learn the importance of this conformation in intermediates in enzymatic reactions of nucleoside cyclic 3′,5′-monophosphates.[17]

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, and Alfa and used without further purification. Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[18]

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(9) An estimate of P–S$_{eq}$ bond rotational barrier in a trigonal bipyramid of about 10 kcal/mol has been made.[5a]

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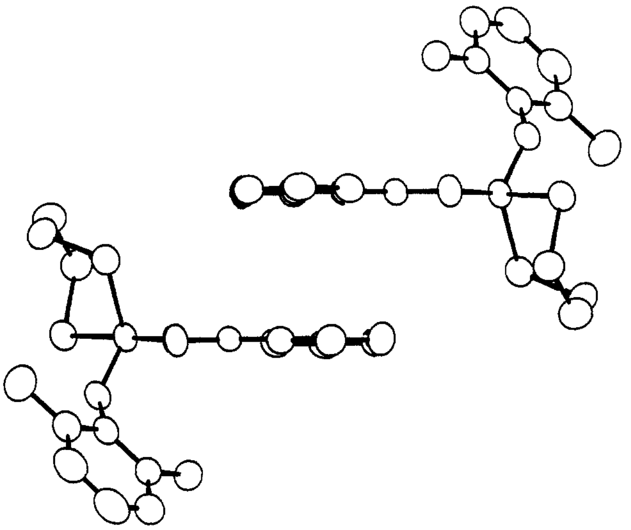

Figure 2. ORTEP plots showing the stacking interaction in the monoclinic form, **2B** viewed parallel to the stacked planes.

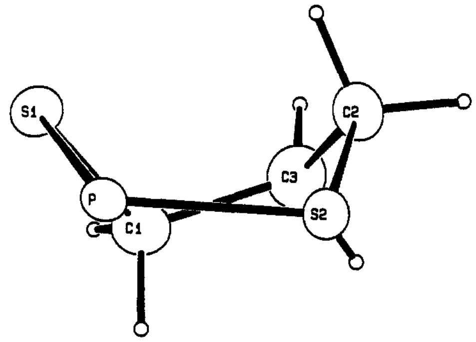

Figure 3. ORTEP plot showing the twist-boat conformation of the six-membered ring in **2A**. The ring conformation in **2B** is very similar.

^{1}H and ^{31}P NMR spectra were recorded on a Varian XL 300 FT/NMR spectrometer equipped with a multinuclear broad-band probe and operated at 300 and 121.4 MHz, respectively. Resonances are referenced versus tetramethylsilane (^{1}H) and 85% orthophosphoric acid (external standard, ^{31}P).

Preparation of 2-(2,6-Dimethylphenoxy)-1,3,2-dithiaphosphorinane, (Xylyl-O)$\overline{\mathrm{P\text{-}S(CH_2)_3S}}$ (1). To a solution of 2-chloro-1,3,2-dithiaphosphorinane (4.94 g, 28.6 mmol) (prepared from phosphorus trichloride, 1,3-propanedithiol, and triethylamine in diethyl ether and purified by distillation in vacuo: (^{31}P NMR δ = 136.7 ppm; lit.[19] δ 139.7 ppm) and 2,6-dimethylphenol (3.50 g, 28.6 mmol) in diethyl ether (150 mL) was added dropwise a solution of triethylamine (3.1 g, 30 mmol) in diethyl ether (15 mL) over a period of 20 min with continuous stirring at 0 °C under a nitrogen atmosphere. The mixture was stirred overnight and filtered under nitrogen. Diethyl ether and excess of triethylamine were distilled off, and the residue was redissolved in diethyl ether (50 mL) and filtered. The solvent was removed completely to obtain the new compound, 2-(2,6-dimethylphenoxy)-1,3,2-dithiaphosphorinane (**1**), as an oil (6.3 g, 85%): ^{1}H NMR ($CDCl_3$, ppm) 2.00–2.50 (m, CH_2C, 2 H), 2.42 (s, CH_3, 6 H), 2.65–2.85 (m, CH_2S, 2 H), 3.55–3.80 (m, CH_2S, 2 H), 6.90–7.10 (m, H_{Ar}, 3 H). ^{31}P NMR ($CDCl_3$, ppm) 150.45. anal. Calcd for $C_{11}H_{15}OPS_2$: C, 51.13; H, 5.81. Found: C, 50.44; H, 5.80.

Preparation of (Phenanthrenediyl-9,10-dioxy)(2,6-dimethylphenoxy)(propanediyl-1,3-dithio)phosphorane, $(C_{14}H_8O_2)$(Xylyl-O)P[S_2-$(CH_2)_3$] (2). **1** (1.82 g, 7.03 mmol) and phenanthrenequinone (1.47 g, 7.03 mmol) were heated together at 145 °C for 15 min under a nitrogen atmosphere. After cooling, the solidified mass was dissolved in dry dichloromethane (150 mL) at ca. 35 °C. Crystallization occurred upon slow evaporation of the solvent at 20 °C under nitrogen (10 h) to yield **2** (2.00 g, 61%). The triclinic form, **2A**, was obtained from the latter crop of crystals, mp 213–217 °C. A portion of this material (0.5 g) was recrystallized again from dichloromethane (80 mL) over a 48 h period. The monoclinic form, **2B**, was obtained from this crop of crystals, mp 208–213 °C. A mixture of **2A** and **2B** melted over the range 150–205 °C. The same proton NMR spectrum resulted from each: ^{1}H NMR at 20 °C ($CDCl_3$, ppm) 1.93 (m, 2 H, CH_2CH_2; shows an A**B** quartet upon decoupling from CH_2S protons, $^2J(H\text{–}H)_{\text{geminal}} \approx -14$ Hz), 2.33 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.99 (m, CH_2S (A), 2 H), 3.38 (m, CH_2S (**B**), 2 H) (upon decoupling CH_2S protons from CH_2C protons, a four line pattern with equal intensity for each of CH_2S (A) and CH_2S (B) was observed. This pattern has been analyzed for ^3J(P–SCH_2 (A)) = 35.4 Hz, ^3J(P–SCH_2 (**B**)) = 25.2 Hz, ^2J(CH_2S (A)–CH_2S (**B**)) = −13.5 Hz), 6.86 (br, H(phenoxy), 3 H), 7.45–7.60 (m, H (Ar), 4 H), 7.75–7.85 (m, H (Ar), 2 H), 8.55–8.65 (m, H (Ar), 2 H); ^{31}P NMR (C_6D_6, ppm) 3.96 ($^3J(P\text{–}H$(av) = 31.2 Hz). Anal. Calcd for $C_{25}H_{23}O_3PS_2$: C, 64.38; H, 4.93. Found: C, 64.23; H, 4.89.

X-ray Study. Crystals were mounted in thin-walled glass capillaries and sealed. $C_{25}H_{23}O_3S_2P$: triclinic form **2A**, colorless crystal (0.33 × 0.48 × 0.50 mm), space group $P\bar{1}$, a = 10.008 (6) Å, b = 10.149 (4) Å, c = 12.166 (5) Å, α = 81.99 (3)°, β = 87.19 (4)°, γ = 70.17 (4)°, Z = 2,$\mu_{\text{Mo K}\bar{\alpha}}$ = 3.132 cm^{-1}, V = 1151.1 Å^3, D_c = 1.346 g/cm^3; monoclinic form **2B**, colorless crystal (0.43 × 0.50 × 0.50 mm), space group $P2_1/n$, a = 10.083 (3) Å, b = 8.563 (3) Å, c = 25.885 (6) Å, β = 99.19 (2)°, Z = 4,$\mu_{\text{Mo K}\bar{\alpha}}$ = 3.268 cm^{-1}, V = 2206.3 Å^3, D_c = 1.405 g/cm^3. Data were collected on an Enraf-Nonius CAD4 diffractometer (23 ± 2 °C, graphite monochromated Mo K$\bar{\alpha}$ radiation, λ = 0.71073Å, $\theta - 2\theta$ scan mode).[20] For **2A**, $2\theta_{\max}$ = 43° (+h,±k,±l). For **2B**, $2\theta_{\max}$ = 50° (+-h,+k,±l). The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares (function minimized $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_1$, independent non-hydrogen atoms anisotropic (31), independent hydrogen atoms fixed isotropic(23)). The final agreement factors were as follows: **2A**, R = 0.041, R_w = 0.057 for the 2085 reflections having $I > 3\sigma_1$; **2B**, R = 0.037 and R_w = 0.055 for the 2950 reflections having $I > 3\sigma_1$.

Acknowledgment. The support of this research by the Army Research Office (Grant DAA03-88-K-0190) and the National Science Foundation (Grant CHE-8819152) is gratefully acknowledged.

Supplementary Material Available: Figures of the ORTEP plot showing the twist-boat conformation of the six-membered ring in **2B**, the ORTEP plot showing the stacking interaction in the monoclinic form, **2B**, viewed perpendicular to the stacked planes, (Figures S1 and S2, respectively), atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, and bond lengths and angles for **2A** (Tables S1–S4, respectively) and for **2B** (Tables S5–S8, respectively) (18 pages). Ordering information is given on any current masthead page.

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