Structures of Mixed Ligand Sulfur-Containing Spirocyclic Phosphoranes[1,2]

Roberta O. Day, Arjun C. Sau, and Robert R. Holmes*

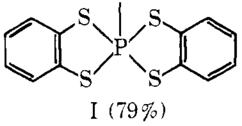
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received November 27, 1978*

Abstract: Single-crystal X-ray analysis of the sulfur-containing spirocyclic phosphorane $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III) revealed a geometry only slightly displaced from a rectangular pyramid. The X-ray analyses of the related thio spirocyclics, $(C_6H_4OS)_2PPh$ (IV) and $(C_6H_4S_2)_2PPh$ (V), showed geometries closer to the idealized trigonal pyramid. III crystallizes in the monoclinic space group $P2_1/n$, with a = 9.816 (2) Å, b = 14.047 (2) Å, c = 16.857 (3) Å, β = 100.19 (1)°, and Z = 4. IV crystallizes in the monoclinic space group $P2_1/c$, with a = 9.042 (4) Å, b = 10.119 (4) Å, c = 18.787 (4) Å, β = 96.63 (3)°, and Z = 4. V crystallizes in the monoclinic space group $P2_1/n$, with a = 16.701 (4) Å, b = 6.638 (1) Å, c = 16.994 (2) Å, β = 114.29 (2)°, and Z = 4. Data for all three compounds were collected, using an automated Enraf-Nonius CAD4 diffractometer, out to a maximum $2\theta_{\mathrm{MoK}\bar{\alpha}}$ of 55°. Full-matrix least-squares refinement techniques led to the final agreement factors of R = 0.043, R_w = 0.048 for III based on the 3171 reflections having $I \geq 2\sigma_I$, R = 0.034, R_w = 0.043 for IV for the 3025 reflections having $I \geq 2\sigma_I$, and R = 0.030 and R_w = 0.037 for V for the 2980 reflections having $I \geq 2\sigma_I$. The specific geometries obtained for III and IV are related to the different placement of the ring sulfur and oxygen atoms that constitute an identical set in each of the two structures. It is concluded that the general structural principles formulated for spirocyclic oxyphosphoranes thus far appear to apply to the related sulfur derivatives.

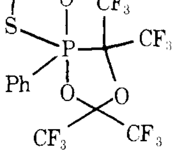
Introduction

In systematizing the stereochemistry of cyclic derivatives of pentacoordinated phosphorus,[3-5] most ring systems studied contain oxygen, nitrogen, and carbon atoms directly bonded to phosphorus. In these derivatives, oxygen is by far the most abundant atom. Crystallographic analyses have shown that the structures form a continuous series along a coordinate connecting the trigonal bipyramid with an idealized square (or rectangular) pyramid.[4]

However, the study of conformational preferences of cyclic phosphoranes is not complete without a knowledge of the role of directly bonded ring sulfur atoms, particularly in view of the importance of five-coordinated transition states proposed[6,7] for reactions of thio-containing cyclic phosphorus compounds. Two examples thus far appear to have been studied by X-ray diffraction, one containing sulfur atoms in an unsaturated spirocyclic system (I)[8] and another containing a single sulfur in a saturated ring system (II).[9] The former structure is not too far displaced from an ideal rectangular pyramid while the latter is not too far from the trigonal bipyramid. As measured by dihedral angles from polytopal faces, the percent displacements from the trigonal bipyramid (TP) toward the rectangular pyramid (RP) are 79[4] and 29%,[3] respectively (using actual bond distances).

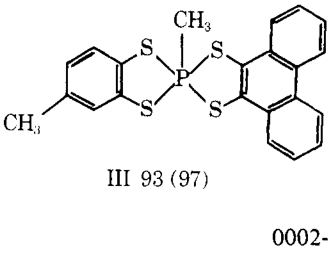


I (79%)

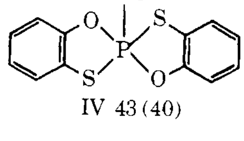


II (29%)

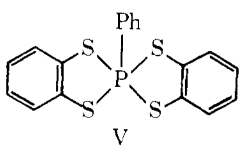
Although these structural forms are indicative of the type of distortions expected, it is of interest to ascertain if trends similar to that established with oxygen-containing derivatives apply to sulfur as well.[3,4,10] Accordingly, we synthesized the new thiophosphoranes III and IV, each containing the same set of heteroatoms bonded to phosphorus but at different sites. These were subjected to X-ray analysis, the results of which are reported here. The molecular structure of V, which contains a full set of directly bonded ring sulfur atoms as well as the phenyl substituent, was also determined.



III 93 (97)



IV 43 (40)



V

Experimental Section

5-Phenyl-2,3-phenanthro-7,8-(2′-methyl-5′,6′-benzo)-1,4-dioxa-6,9-dithia-5-phospha(V)spiro[4.4]nona-2,7-diene (III). Following a previous procedure,[11a] 9,10-phenanthrenequinone was reacted with 2-phenyl-2′-methyl-1,3,2-benzodithiaphospholane in toluene at 110 °C for 2 h to give III in 91% yield. Crystals suitable for X-ray analysis were grown by recrystallization from benzene at room temperature.

2-Phenyl-2,2′-spirobis(1,3,2-benzooxathiaphosphole) (IV). As detailed elsewhere,[11a] IV was prepared in 64% yield by the reaction of phenyltetrafluorophosphorane with 2 molar equiv of *o*-phenyleneoxathiabis(trimethylsilane) in toluene at 110 °C for 20 h. Crystals suitable for X-ray analysis were grown by cooling a saturated solution of IV in hexane at 0 °C.

Preparation of 2-Phenyl-2,2′-spirobis(1,3,2-benzodithiaphosphole) (V). The synthesis of V is based on a method given by Eisenhut[8a,11b] et al. with modifications detailed elsewhere.[11a] This involved the reaction of phenyltetrafluorophosphorane with 2 molar equiv of *o*-phenylenedithiobis(trimethylsilane) in benzene at reflux temperature. Crystals suitable for the X-ray study were obtained from the recrystallization of V from methyl cyanide at room temperature.

Space Group Determination and Data Collection for III. A slightly irregular crystal having approximate dimensions of 0.45 × 0.40 × 0.20 mm was cut from a larger polycrystalline mass and mounted in a thin-walled glass capillary tube which was sealed as a precaution against moisture sensitivity. Preliminary investigations using an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromated Mo Kα radiation (fine focus tube, 45 kV, 20 mA, takeoff angle = 3.1°, λ Kα_1 = 0.709 26 Å, λ Kα_2 = 0.713 54 Å) indicated monoclinic ($2/m$) symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, the space group was uniquely determined as $P2_1/n$ (alternate setting of $P2_1/c$-C_{2h}^5).[12] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.01° \leq \theta_{\mathrm{MoK}\bar{\alpha}} \leq 14.88°$ (λ K$\bar{\alpha}$ = 0.710 69) measured at an ambient laboratory temperature of 24 ± 2 °C are a = 9.816 (2) Å, b = 14.047 (2) Å, c = 16.857 (3)

0002-7863/79/1501-3790$01.00/0

Table I. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

atom	coordinates		
type[b]	10^4X	10^4Y	10^4Z
P	3249.5 (6)	493.3 (4)	7059.7 (4)
S1	4865.3 (7)	−405.4 (5)	6753.3 (4)
S2	4581.3 (7)	1726.8 (5)	7191.2 (4)
O9	2010 (2)	1335 (1)	6811 (1)
O10	2220 (2)	−312 (1)	6500 (1)
C1	−130 (3)	−1535 (2)	5755 (2)
C2	−1254 (4)	−2044 (2)	5393 (2)
C3	−2523 (4)	−1599 (2)	5164 (2)
C4	−2669 (3)	−649 (2)	5305 (2)
C5	−2897 (3)	1455 (2)	5587 (2)
C6	−2975 (3)	2414 (2)	5743 (2)
C7	−1825 (3)	2911 (2)	6145 (2)
C8	−600 (3)	2443 (2)	6390 (1)
C9	761 (2)	944 (2)	6449 (1)
C10	877 (2)	13 (2)	6284 (1)
C11	−249 (3)	−555 (2)	5903 (1)
C12	−1543 (3)	−84 (2)	5674 (1)
C13	−1660 (2)	938 (2)	5828 (1)
C14	−492 (2)	1460 (2)	6233 (1)
CD1	6302 (3)	192 (2)	7301 (1)
CD2	6176 (2)	1152 (2)	7508 (1)
CD3	7308 (3)	1637 (2)	7943 (2)
CD4	8574 (3)	1183 (2)	8171 (2)
CD5	8696 (3)	230 (2)	7965 (2)
CD6	7575 (3)	−258 (2)	7536 (2)
CM	9828 (4)	1739 (4)	8622 (3)
CP1	3079 (2)	144 (2)	8075 (1)
CP2	3485 (4)	729 (2)	8726 (2)
CP3	3312 (4)	447 (3)	9497 (2)
CP4	2721 (4)	−409 (3)	9610 (2)
CP5	2294 (4)	−1001 (3)	8968 (2)
CP6	2477 (3)	−740 (2)	8198 (2)

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Atoms labeled to agree with Figure 1.

Å, and $\beta = 100.19\ (1)°$. The calculated density for a unit cell content of four molecules is 1.366 g/cm^3. The density determined by flotation in aqueous KI was 1.364 g/cm^3.

Data was collected using the θ-2θ scan mode, with a θ scan range of $(0.85 + 0.35 \tan \theta)°$ centered about the calculated Mo $K\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on both sides of the aforementioned limits for the measurement of background radiation. The scan rates varied from 0.65°θ/min to 4.02°θ/min, the rate to be used for each reflection having been determined by a prescan. The intensity, I, for each reflection is thus given by $I = (FF/S)(P - 2(B1 + B2))$ where P are the counts accumulated during the peak scan, $B1$ and $B2$ are the left and right background counts, S is an integer inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = (FF^2/S^2)(P + 4(B1 + B2)) + 0.002I^2$.

A total of 5255 independent reflections $(+h, +k, \pm l)$ having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ were measured in two concentric shells of increasing 2θ containing approximately 2600 reflections each. Five standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No correction was made for absorption ($\mu_{MoK\bar{\alpha}} = 0.322\ mm^{-1}$) and the intensities were reduced to relative amplitudes, F_o, by means of standard Lorentz and polarization corrections. Reflections for which $I < 0.1\sigma_I$ were assigned $F_o = [c\sigma_I/Lp]^{1/2}$ and $\sigma_{F_o} = 0.5F_o/c$, where Lp is the Lorentz–polarization factor and $c = 0.1$.

Solution and Refinement of Structure for III. Initial coordinates for 26 of the 32 nonhydrogen atoms of the asymmetric unit were determined by direct methods (MULTAN). Coordinates for the remaining six independent atoms were determined by standard Fourier difference techniques. Unit weighted full-matrix least-squares isotropic refinement[13] of the parameters for the 32 independent nonhydrogen atoms and a scale factor gave a conventional residual $R = \Sigma|F_o - |F_c||/\Sigma F_o$ of 0.10 and a conventional weighted residual $R_w = \{\Sigma(w|F_o - |F_c||)^2/\Sigma wF_o^2\}^{1/2}$ of 0.09 for the 2128 reflections having $I \geq 2\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Anisotropic refinement gave $R = 0.059$ and $R_w = 0.060$ for 2128 reflections.

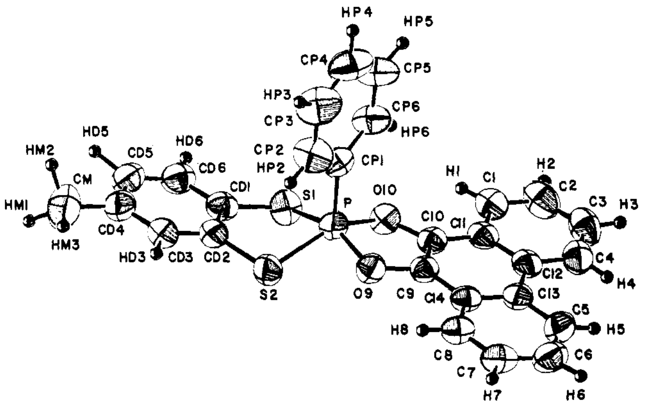


Figure 1. ORTEP plot of the $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ molecule (III) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

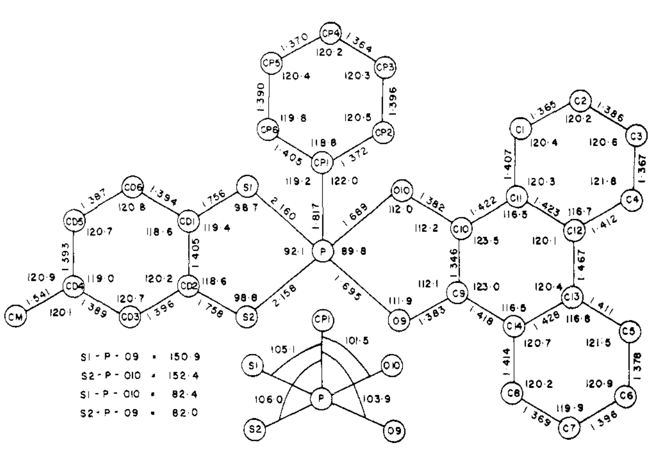


Figure 2. Selected bond lengths in ångstroms and angles in degrees for $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III).

Initial coordinates for the three independent methyl hydrogen atoms were then obtained from a difference Fourier synthesis, while initial coordinates for the 16 remaining independent hydrogen atoms were inferred from the required geometry of the molecule. Subsequent refinement including the hydrogen atoms as isotropic contributions gave $R = 0.032$ and $R_w = 0.030$ for 2128 reflections. Inclusion of the high-angle data in the unit-weighted refinement then gave $R = 0.043$ and $R_w = 0.038$ for the 3171 reflections having $I \geq 2\sigma_I$. The final cycles of refinement employed variable weights ($w^{1/2} = 2LpF_o/\sigma_I$) and led to $R = 0.043$, $R_w = 0.048$, and $S^{14} = 1.37$ for the 3171 reflections having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ and $I \geq 2\sigma_I$.

During the final cycle of refinement, the largest shift in any parameter was 0.06 times its estimated standard deviation. A final difference Fourier synthesis (3171 reflections) showed a maximum density of 0.26 e/Å^3. A structure factor calculation using the final parameters from the least-squares refinement, but including the weak data, gave $R = 0.085$ and $R_w = 0.052$ for the 5255 independent reflections, while a difference Fourier based on the above showed a maximum electron density of 0.37 e/Å^3.

Space-Group Determination and Data Collections for IV. A well-formed, nearly cubic crystal having dimensions of 0.33 × 0.35 × 0.45 mm was sealed in a thin-walled glass capillary for the X-ray diffraction studies. Conditions for space-group determination and data collection and reduction were the same as given for III except that the scan range used was $(0.75 \pm 0.35 \tan \theta)°$, six standard reflections were monitored, and reflections for which $I < 0.3\sigma_I$ were assigned F_o and σ_{F_o} using a value of 0.3 for c. Preliminary diffractometric investigations indicated monoclinic $(2/m)$ symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space group was uniquely determined as $P2_1/c$-C_{2h}^5.[12] The lattice constants as determined by

Table II. Thermal Parameters for Nonhydrogen Atoms in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

atom type[b]	anisotropic parameters B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	equivalent isotropic B, Å^2
P	4.34 (3)	3.65 (3)	4.18 (3)	0.08 (2)	0.80 (2)	−0.22 (2)	4.0
S1	5.08 (3)	5.02 (3)	5.94 (4)	0.38 (3)	1.63 (3)	−1.11 (3)	5.1
S2	4.38 (3)	3.92 (3)	7.11 (4)	−0.09 (2)	0.75 (3)	0.36 (3)	5.0
O9	4.6 (1)	4.0 (1)	5.0 (1)	0.1 (1)	0.2 (1)	−0.2 (1)	4.6
O10	5.0 (1)	4.1 (1)	4.6 (1)	0.1 (1)	0.6 (1)	−0.6 (1)	4.5
C1	6.0 (1)	5.0 (1)	4.4 (1)	−0.7 (1)	1.2 (1)	−0.5 (1)	5.0
C2	7.8 (2)	5.8 (2)	5.6 (1)	−2.0 (1)	1.8 (1)	−1.5 (1)	5.9
C3	6.4 (2)	7.1 (2)	5.6 (1)	−2.4 (1)	1.4 (1)	−1.5 (1)	6.0
C4	5.1 (1)	7.5 (2)	4.3 (1)	−1.1 (1)	1.1 (1)	−0.3 (1)	5.4
C5	4.9 (1)	7.4 (2)	5.1 (1)	0.2 (1)	0.7 (1)	1.1 (1)	5.6
C6	5.8 (2)	7.3 (2)	6.2 (2)	1.7 (1)	1.4 (1)	1.8 (1)	6.1
C7	6.8 (2)	5.2 (1)	5.4 (1)	1.1 (1)	2.1 (1)	1.0 (1)	5.5
C8	5.8 (1)	4.9 (1)	4.3 (1)	0.3 (1)	1.1 (1)	0.5 (1)	4.9
C9	4.5 (1)	4.4 (1)	3.5 (1)	−0.2 (1)	0.8 (1)	0.1 (1)	4.1
C10	4.7 (1)	4.3 (1)	3.4 (1)	−0.2 (1)	0.8 (1)	−0.1 (1)	4.1
C11	5.3 (1)	4.9 (1)	3.1 (1)	−0.6 (1)	1.2 (1)	0.0 (1)	4.2
C12	5.0 (1)	5.5 (1)	3.2 (1)	−0.8 (1)	1.3 (1)	0.1 (1)	4.3
C13	4.7 (1)	5.7 (1)	3.5 (1)	0.0 (1)	1.1 (1)	0.8 (1)	4.4
C14	4.9 (1)	4.6 (1)	3.5 (1)	0.1 (1)	1.2 (1)	0.5 (1)	4.2
CD1	5.2 (1)	5.1 (1)	4.6 (1)	0.3 (1)	1.7 (1)	0.5 (1)	4.8
CD2	4.3 (1)	5.1 (1)	5.1 (1)	0.1 (1)	1.2 (1)	0.8 (1)	4.7
CD3	5.0 (1)	5.6 (1)	5.3 (1)	−0.3 (1)	1.2 (1)	0.7 (1)	5.2
CD4	5.0 (1)	7.5 (2)	4.7 (1)	0.0 (1)	0.7 (1)	1.1 (1)	5.6
CD5	5.0 (1)	7.6 (2)	5.4 (1)	1.3 (1)	1.2 (1)	1.7 (1)	5.6
CD6	5.6 (1)	5.9 (2)	5.5 (1)	1.0 (1)	1.8 (1)	0.9 (1)	5.4
CM	5.8 (2)	11.5 (3)	8.9 (2)	−0.6 (2)	−0.1 (2)	−0.6 (2)	8.5
CP1	4.4 (1)	4.3 (1)	4.1 (1)	0.8 (1)	0.8 (1)	−0.2 (1)	4.2
CP2	8.7 (2)	5.7 (2)	5.3 (2)	−0.6 (1)	1.7 (1)	−1.0 (1)	6.3
CP3	11.0 (3)	7.8 (2)	4.6 (1)	0.5 (2)	1.5 (2)	−1.3 (2)	7.2
CP4	9.7 (2)	8.2 (2)	4.9 (2)	2.5 (2)	1.8 (1)	1.4 (2)	7.0
CP5	10.4 (2)	6.2 (2)	5.9 (2)	0.5 (2)	1.6 (2)	1.9 (1)	7.0
CP6	7.9 (2)	4.6 (1)	5.0 (1)	0.3 (1)	0.7 (1)	0.4 (1)	5.7

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Atoms are labeled in agreement with Figure 1. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

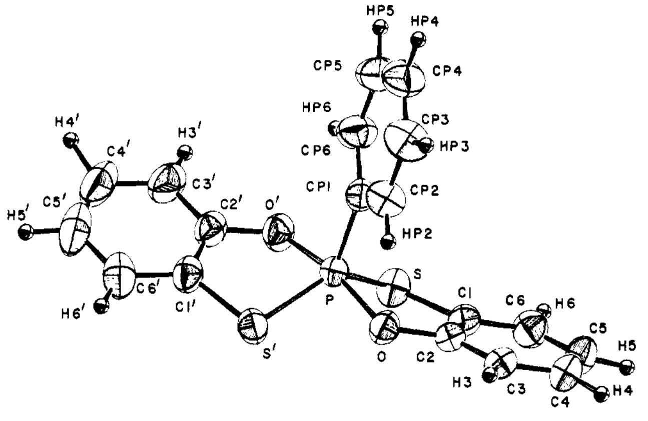


Figure 3. ORTEP plot of the $(C_6H_4OS)_2PPh$ molecule (IV) with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

Table III. Refined Parameters for Hydrogen Atoms in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

atom type[b]	coordinates 10^3X	10^3Y	10^3Z	isotropic thermal parameter B, Å^2
H1	73 (2)	−178 (2)	591 (1)	4 (1)
H2	−113 (3)	−268 (2)	525 (2)	6 (1)
H3	−332 (3)	−197 (2)	493 (2)	6 (1)
H4	−353 (3)	−34 (2)	513 (1)	6 (1)
H5	−368 (3)	116 (2)	529 (1)	6 (1)
H6	−386 (3)	268 (2)	554 (2)	8 (1)
H7	−188 (2)	359 (2)	628 (1)	6 (1)
H8	20 (2)	276 (2)	666 (1)	5 (1)
HD3	722 (2)	235 (2)	810 (1)	5 (1)
HD5	969 (2)	−19 (1)	820 (1)	4 (1)
HD6	763 (3)	−97 (2)	739 (2)	7 (1)
HP2	391 (3)	131 (2)	864 (2)	7 (1)
HP3	363 (4)	83 (2)	989 (2)	9 (1)
HP4	264 (3)	−57 (2)	1018 (2)	8 (1)
HP5	180 (3)	−162 (3)	905 (2)	9 (1)
HP6	218 (3)	−118 (2)	772 (2)	7 (1)
HM1	1076 (6)	182 (3)	842 (3)	16 (2)
HM2	1017 (5)	143 (4)	926 (4)	18 (2)
HM3	956 (6)	249 (4)	883 (3)	18 (2)

[a,b] Refer to footnotes of Table I.

the least-squares refinement of the diffraction geometry for 25 reflections having $12.16° \leq \theta_{\mathrm{Mo}K\bar{\alpha}} \leq 16.77°$ are $a = 9.042$ (4) Å, $b = 10.119$ (4) Å, $c = 18.787$ (4) Å, and $\beta = 96.63$ (3)°. A unit cell content of four molecules gives a calculated density of 1.386 g/cm^3, in good agreement with the value of 1.381 g/cm^3 which was determined by flotation in aqueous KI.

A total of 3918 independent reflections ($+h$, $+k$, $\pm l$) having $2° \leq 2\theta_{\mathrm{Mo}K\bar{\alpha}} \leq 55°$ were measured in three concentric shells of increasing 2θ, the first containing about 1960 reflections and the second and third containing about 980 reflections each. No corrections were made for absorption ($\mu_{\mathrm{Mo}K\bar{\alpha}} = 0.404$ mm^{-1}).

Solution and Refinement of Structure for IV. The conditions for refinement were the same as described for III. Initial coordinates for

Table IV. Bond Lengths and Selected Intramolecular Distances in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

type[b]	bond length, Å	type	bond length, Å
P-CP1	1.817 (2)	C12-C13	1.467 (4)
P-S1	2.160 (1)	C11-C1	1.407 (4)
P-S2	2.158 (1)	C14-C8	1.414 (3)
P-O9	1.695 (2)	C1-C2	1.365 (4)
P-O10	1.689 (2)	C8-C7	1.369 (4)
S1-CD1	1.756 (3)	C2-C3	1.386 (5)
S2-CD2	1.758 (2)	C7-C6	1.396 (4)
O9-C9	1.383 (2)	C3-C4	1.367 (5)
O10-C10	1.382 (3)	C6-C5	1.378 (5)
CD1-CD6	1.394 (4)	C4-C12	1.412 (4)
CD2-CD3	1.396 (4)	C5-C13	1.411 (4)
CD6-CD5	1.387 (4)	C12-C13	1.467 (4)
CD3-CD4	1.389 (4)	CP1-CP2	1.372 (4)
CD4-CD5	1.393 (4)	CP2-CP3	1.396 (5)
C9-C10	1.346 (3)	CP3-CP4	1.364 (6)
C9-C14	1.418 (3)	CP4-CP5	1.370 (5)
C10-C11	1.422 (3)	CP5-CP6	1.390 (5)
C14-C13	1.428 (3)	CP6-CP1	1.405 (4)
C11-C12	1.423 (3)	CD4-CM	1.541 (5)
C1-H1	0.91 (2)	CD6-HD6	1.03 (3)
C2-H2	0.94 (3)	CP2-HP2	0.94 (3)
C3-H3	0.96 (3)	CP3-HP3	0.87 (3)
C4-H4	0.95 (3)	CP4-HP4	1.00 (3)
C5-H5	0.93 (3)	CP5-HP5	1.01 (3)
C6-H6	0.95 (3)	CP6-HP6	1.01 (3)
C7-H7	0.98 (3)	CM-HM1	1.03 (5)
C8-H8	0.95 (2)	CM-HM2	1.15 (6)
CD3-HD3	1.04 (2)	CM-HM3	1.16 (6)
CD5-HD5	1.15 (2)		
Nonbonded Intramolecular Distances (Å)			
CP1-S1	3.165 (2)	CP1-O9	2.766 (3)
CP1-S2	3.181 (2)	CP1-O10	2.717 (3)
S1-O10	2.559 (2)	O9-O10	2.390 (2)
S2-O9	2.552 (2)	S1-S2	3.109 (1)

[a,b] Refer to footnotes of Table I.

the 23 nonhydrogen atoms of the asymmetric unit were determined by direct methods. Isotropic unit-weighted full-matrix least-squares refinement of the structural parameters for these atoms and a scale factor gave $R = 0.093$ and $R_w = 0.098$, for the 1739 reflections having $I \geq 3\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Anisotropic refinement gave $R = 0.059$ and $R_w = 0.072$ for 1739 reflections. Initial coordinates for the 13 independent hydrogen atoms were inferred from the required geometry of the molecule. Subsequent refinement (23 nonhydrogen atoms anisotropic, 13 hydrogen atoms isotropic) gave $R = 0.036$ and $R_w = 0.046$ for the 1778 reflections having $I \geq 2\sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$. Inclusion of the high-angle data in the unit-weighted refinement gave $R = 0.037$ and $R_w = 0.047$ for the 3025 reflections having $I \geq 2\sigma_I$. The final cycles of refinement employed variable weights and led to $R = 0.034$, $R_w = 0.043$, and $S = 1.36$ for the 3025 reflections having $2° \leq 2\theta_{\text{MoK}\alpha} \leq 55°$ and $I \geq 2\sigma_I$. During the final cycle of refinement the largest shift in any parameter was 0.04 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.20 e/Å^3. A structure factor calculation using the final parameters from the least-squares refinement, but including the weak data, gave $R = 0.050$ and $R_w = 0.045$ for the 3918 independent reflections, while a difference Fourier based on these showed a maximum density of 0.25 e/Å^3.

Space-Group Determination and Data Collection for V. A bright yellow, square platelet having dimensions of 0.38 × 0.38 × 0.20 mm was cut from the end of a longer crystal and mounted in a thin-walled glass capillary tube which was sealed as a precaution against moisture sensitivity. Conditions for space-group determination and data reduction were the same as given for III except that six standard reflections were monitored, and reflections for which $I < 0.2\sigma_I$ were assigned F_o and σ_{F_o} using a value of 0.2 for c. Preliminary diffractometric investigations indicated monoclinic ($2/m$) symmetry. From the observed extinctions $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, the space group was uniquely determined as $P2_1/n$ (alternate setting of $P2_1/c$-C_{2h}^5).[12] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.09° \leq \theta_{\text{MoK}\bar{\alpha}} \leq 14.92°$ measured at an ambient laboratory temperature of 24 ± 2 °C are $a = 16.701$ (4) Å, $b = 6.638$ (1) Å, $c = 16.994$ (2) Å, and $\beta = 114.29$ (2)°. A unit cell content of four molecules gives a calculated density of 1.501 g/cm^3, in agreement with the value of 1.496 g/cm^3 as measured by flotation in aqueous KI.

A total of 3936 independent reflections ($+h$, $+k$, $\pm l$) having $2° \leq 2\theta_{\text{MoK}\bar{\alpha}} \leq 55°$ were measured in three concentric shells of increasing 2θ, the first containing approximately 1970 reflections and the second

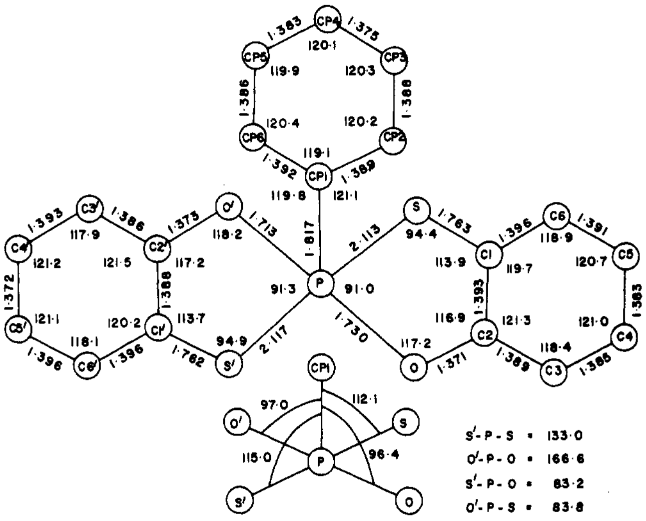


Figure 4. Selected bond lengths in ångstroms and angles in degrees for $(C_6H_4OS)_2PPh$ (IV).

Table V. Bond Angles for Nonhydrogen Atoms in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

type[b]	bond angle, deg	type	bond angle, deg
CP1-P-S1	105.1 (1)	C7-C6-C5	120.9 (3)
CP1-P-S2	106.0 (1)	C2-C3-C4	120.6 (3)
CP1-P-O9	103.9 (1)	C6-C5-C13	121.5 (3)
CP1-P-O10	101.5 (1)	C3-C4-C12	121.8 (2)
S1-P-O9	150.9 (1)	C5-C13-C14	116.8 (2)
S2-P-O10	152.4 (1)	C4-C12-C11	116.7 (2)
S1-P-O10	82.4 (1)	C5-C13-C12	122.9 (2)
S2-P-O9	82.0 (1)	C4-C12-C13	123.2 (2)
S1-P-S2	92.1 (1)	C9-C14-C8	122.7 (2)
O9-P-O10	89.8 (1)	C10-C11-C1	123.1 (2)
P-S1-CD1	98.7 (1)	C14-C9-O9	124.8 (2)
P-S2-CD2	98.8 (1)	C11-C10-O10	124.3 (2)
S1-CD1-CD2	119.4 (2)	CD6-CD1-CD2	118.6 (2)
S2-CD2-CD1	118.6 (2)	CD3-CD2-CD1	120.2 (2)
P-O9-C9	111.9 (1)	CD1-CD6-CD5	120.8 (3)
P-O10-C10	112.0 (1)	CD2-CD3-CD4	120.7 (2)
O9-C9-C10	112.1 (2)	CD6-CD5-CD4	120.7 (3)
O10-C10-C9	112.2 (2)	CD3-CD4-CD5	119.0 (2)
C10-C9-C14	123.0 (2)	CM-CD4-CD3	120.1 (3)
C9-C10-C11	123.5 (2)	CM-CD4-CD5	120.9 (3)
C9-C14-C13	116.5 (2)	S1-CD1-CD6	122.0 (2)
C10-C11-C12	116.5 (2)	S2-CD2-CD3	121.2 (2)
C14-C13-C12	120.4 (2)	P-CP1-CP2	122.0 (2)
C11-C12-C13	120.1 (2)	P-CP1-CP6	119.2 (2)
C13-C14-C8	120.7 (2)	CP1-CP2-CP3	120.5 (3)
C12-C11-C1	120.3 (2)	CP2-CP3-CP4	120.3 (3)
C14-C8-C7	120.2 (2)	CP3-CP4-CP5	120.2 (3)
C11-C1-C2	120.4 (2)	CP4-CP5-CP6	120.4 (3)
C8-C7-C6	119.9 (3)	CP5-CP6-CP1	119.8 (3)
C1-C2-C3	120.2 (3)	CP6-CP1-CP2	118.8 (2)

[a,b] Refer to footnotes of Table I.

Table VI. Bond Angles Involving Hydrogen Atoms in Crystalline $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)[a]

type[b]	bond angle, deg	type	bond angle, deg
H1-C1-C11	115 (1)	HP3-CP3-CP4	123 (2)
H1-C1-C2	125 (1)	HP4-CP4-CP3	116 (2)
H2-C2-C1	119 (2)	HP4-CP4-CP5	123 (2)
H2-C2-C3	121 (2)	HP5-CP5-CP4	120 (2)
H3-C3-C2	119 (1)	HP5-CP5-CP6	120 (2)
H3-C3-C4	120 (1)	HP6-CP6-CP5	121 (2)
H4-C4-C3	121 (1)	HP6-CP6-CP1	119 (2)
H4-C4-C12	118 (1)	HD3-CD3-CD2	121 (1)
H5-C5-C13	121 (2)	HD3-CD3-CD4	119 (1)
H5-C5-C6	117 (2)	HD5-CD5-CD4	121 (1)
H6-C6-C5	114 (2)	HD5-CD5-CD6	119 (1)
H6-C6-C7	125 (2)	HD6-CD6-CD5	122 (1)
H7-C7-C6	122 (1)	HD6-CD6-CD1	117 (1)
H7-C7-C8	119 (1)	HM1-CM-CD4	124 (3)
H8-C8-C7	122 (1)	HM2-CM-CD4	110 (3)
H8-C8-C14	118 (1)	HM3-CM-CD4	114 (3)
HP2-CP2-CP1	118 (2)	HM1-CM-HM2	103 (4)
HP2-CP2-CP3	121 (2)	HM1-CM-HM3	105 (4)
HP3-CP3-CP2	117 (2)	HM2-CM-HM3	95 (4)

[a,b] Refer to footnotes of Table I.

and third containing approximately 980 reflections each. No corrections were made for absorption ($\mu_{MoK\bar{\alpha}} = 0.622\ mm^{-1}$).

Solution and Refinement of the Structure of V. The conditions for refinement were the same as described for III. Initial coordinates for the 23 nonhydrogen atoms of the asymmetric unit were determined by direct methods. Isotropic unit-weighted full-matrix least-squares refinement[13] of the structural parameters for these atoms and a scale factor gave $R = 0.081$ and $R_w = 0.082$ for the 1727 reflections having $(\sin \theta)/\lambda \leq 0.52$ and $I \geq 2\sigma_I$. Anisotropic refinement led to $R = 0.046$ and $R_w = 0.056$ for 1727 reflections. Initial coordinates for the 13 independent hydrogen atoms were then inferred from the required geometry of the molecule. Subsequent refinement including the hydrogen atoms as isotropic contributions gave $R = 0.028$ and $R_w = 0.037$ for 1727 reflections. Inclusion of the high-angle data in the unit-weighted refinement then gave $R = 0.032$ and $R_w = 0.039$ for the 2980 reflections having $I \geq 2\sigma_I$.

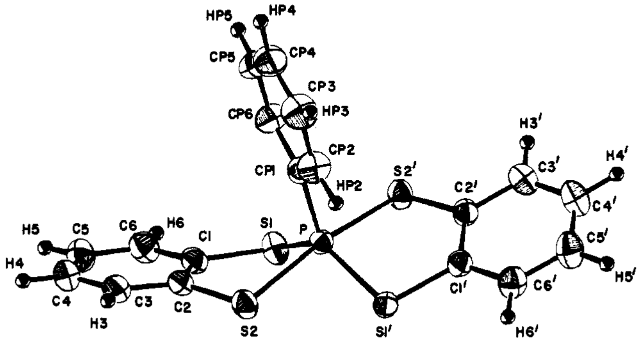


Figure 5. ORTEP plot of the $(C_6H_4S_2)_2PPh$ molecule (V), with thermal ellipsoids at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary radius.

The final cycles of refinement employed variable weights and led to $R = 0.030$, $R_w = 0.037$, and $S = 1.14$ for the 2980 reflections having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 55°$ and $I \geq 2\sigma_I$. During the final cycle of refinement the largest shift in any parameter was 0.04 times its estimated standard deviation. A final difference Fourier synthesis (2980 reflections) showed a maximum density of 0.32 e/Å^3. A structure factor calculation using the final parameters from the least-squares refinement, but including the weak data, gave $R = 0.047$ and $R_w = 0.039$ for 3936 reflections, while a difference Fourier based on these showed a maximum density of 0.44 e/Å^3.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) using the direct methods program, MULTAN, by Main, Germain and Woolfson; Zalkin's Fourier program, FORDAP; Prewitt's full-matrix least-squares program, SFLS; ORTEP, Johnson's thermal ellipsoid program; and several locally written programs.

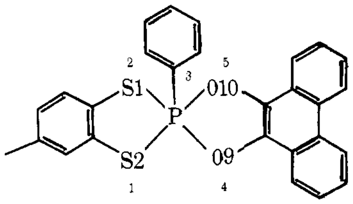
Table VII. Some Deviations (Å) from Selected Least-Square Mean Planes[a,b] in $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III)

	I	II	III	IV	V
P	0.020	0.016	(0.464)		
CP1	−0.004	0.002			
S1	−0.007		−0.011	0.003	
O9	−0.009		−0.014		0.004
S2		−0.008	0.011	−0.003	
O10		−0.011	0.014		−0.004
C9			(−0.246)		−0.007
C10			(−0.212)		0.007
CD1			(0.419)	−0.006	
CD2			(0.445)	0.006	

	VI	VIA		VII	VIIA		VIII	VIIIA
CP1	0.000	0.016	CD1	−0.001	0.005	C1	−0.020	0.001
CP2	−0.005	0.005	CD2	−0.002	0.012	C2	0.002	0.010
CP3	0.004	0.001	CD3	0.003	0.013	C3	0.021	0.014
CP4	0.003	−0.007	CD4	−0.003	−0.004	C4	0.030	0.020
CP5	−0.008	−0.010	CD5	0.000	−0.009	C5	−0.034	−0.050
CP6	0.005	0.014	CD6	0.001	−0.004	C6	−0.031	−0.048
P	(−0.049)	−0.018	S1	(−0.008)	0.003	C7	0.003	0.002
			S2	(−0.043)	−0.016	C8	0.035	0.045
			P	(0.801)	(0.827)	C9	0.013	0.041
			CM	(−0.051)	(−0.057)	C10	−0.029	0.000
						C11	−0.019	0.001
						C12	0.003	0.005
						C13	0.001	0.001
						C14	0.025	0.037
						O9	(−0.027)	0.015
						O10	(−0.133)	−0.087
						P	(0.113)	(0.170)

[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Selected dihedral angles between planes indicated: IV and V = 6.2°, I and II = 85.0°, III and VI = 84.8°, I and VI = 72.2°, II and VI = 13.0° VII and VIII = 4.7°, VIIA and VIIIA = 4.9°.

Table VIII. Dihedral Angles (δ) for $(CH_3C_6H_3S_2)(C_{14}H_8O_2)PPh$ (III) (deg)[a]



edge[b]	δ[c]	edge[b]	δ[c]
45	112.1 (116.2)	13	79.5 (76.8)
25	118.8 (118.6)	23	79.2 (76.3)
14	120.3 (120.0)	34	71.3 (75.6)
12	124.2 (118.3)	24	1.6 (1.6)
35	73.0 (77.6)		

$\Sigma_i|\delta_i(C) - \delta_i(TP)| = 215.7\ (212.9)$

$\Sigma_i|\delta_i(C) - \delta_i(RP)| = 29.6\ (7.8)$

$R^d - \Sigma_i|\delta_i(C) - \delta_i(RP)| = 188.1\ (209.9)$

av % along Berry coordinate = 92.8 (97.1)

[a] For purposes of comparison with other tabulations,[3,4] the atom numbering scheme shown above is used, where 1 and 5 refer to axial type atoms, 2 and 4 refer to equatorial type atoms, and 3 refers to the equatorial pivotal atom for a trigonal bipyramid in the Berry process. [b] The number pairs refer to the common edge connecting the two triangular faces of the coordination polyhedron of the P atom whose normals give the dihedral angles. [c] The numbers in parentheses are for a hypothetical coordination polyhedron defined by unit vectors along the bonds from the P atom to the five coordinated atoms. [d] $R = \Sigma_i|\delta_i(TP) - \delta_i(RP)| = 217.7°$.

Results and Discussion

Structural Distortions. For III the atom labeling scheme is given in Figure 1. Atomic coordinates and thermal parameters are given in Tables I–III. Bond lengths and angles are given in Tables IV–VI and are summarized pictorially in Figure 2.

The geometry about the phosphorus atom can best be described as a rectangular pyramid (RP) except that the base is trapezoidal owing to the difference in the P–O and P–S bond lengths. The atoms defining the basal plane (S1, S2, O9, and O10) are coplanar to within ±0.01 Å (plane III, Table VII), while the P atom is displaced 0.46 Å from this plane toward the apical atom, CP1.

The two trans basal angles are within 2.4° of the idealized value[4] of 150°, while the four apical to basal angles are within 4.5° of the idealized value of 105°. Based on the trans basal angles of 152.4 (1)° for S2–P–O10 and 150.9 (1)° for S1–P–O9, S2 and O10 can be said to be axial with respect to residual trigonal bipyramidal (TP) character. There is no concomitant residual TP character evident in the P–O and P–S bond lengths ($P–O_{ax}$ = 1.689 (2) Å, $P–O_{eq}$ = 1.695 (2) Å; $P–S_{ax}$ = 2.158 (1) Å, $P–S_{eq}$ = 2.160 (1) Å).

With respect to the Berry coordinate,[15] the molecular geometry is displaced 92.7 (based on actual bond distances) and 97.1% (based on unit bond vectors) from the TP toward the RP (Table VIII). In this case, considering the large difference in the covalent radii of S and O, the latter value obtained using unit vectors is preferable as evidenced by the closer fit to the Berry plot (212.9° against 210.1° using unit vectors vs. 188.3° against 215.7° using atomic positions).

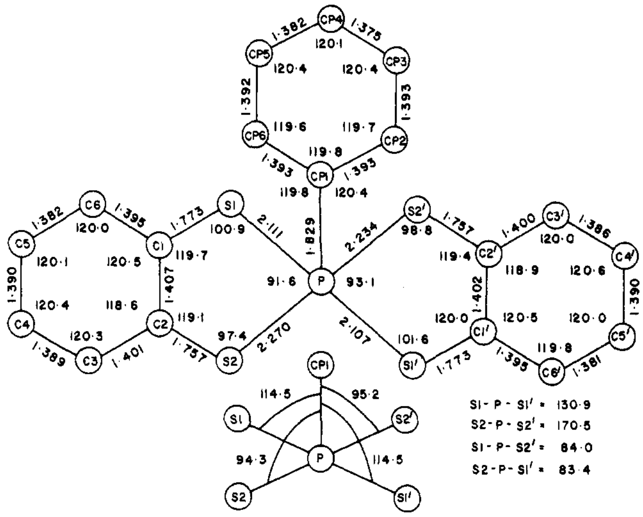


Figure 6. Selected bond lengths in ångstroms and angles in degrees for $(C_6H_4S_2)_2PPh$ (V).

Table IX. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

atom type[b]	coordinates 10^4X	10^4Y	10^4Z
P	233.3 (8)	7948.1 (7)	3307.6 (4)
S	−2005.1 (8)	7623.6 (8)	2884.5 (4)
S′	1736.7 (9)	9524.5 (8)	3210.8 (4)
O	−324 (2)	8917 (2)	3987 (1)
O′	618 (2)	7285 (2)	2510 (1)
C1	−2733 (3)	8051 (3)	3684 (2)
C2	−1716 (3)	8687 (3)	4183 (1)
C3	−2110 (4)	9095 (3)	4842 (2)
C4	−3548 (4)	8853 (3)	4995 (2)
C5	−4565 (4)	8208 (4)	4509 (2)
C6	−4173 (4)	7798 (3)	3849 (2)
C1′	2648 (3)	8753 (3)	2542 (1)
C2′	1938 (3)	7620 (3)	2262 (1)
C3′	2522 (5)	6868 (4)	1744 (2)
C4′	3845 (5)	7292 (6)	1506 (2)
C5′	4542 (5)	8424 (6)	1768 (2)
C6′	3962 (4)	9181 (4)	2292 (2)
CP1	973 (3)	6595 (3)	3877 (1)
CP2	1441 (4)	6794 (3)	4600 (2)
CP3	1975 (4)	5742 (4)	5029 (2)
CP4	2026 (4)	4493 (4)	4746 (2)
CP5	1551 (5)	4279 (4)	4028 (2)
CP6	1033 (4)	5327 (3)	3594 (2)

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Atoms are labeled to agree with Figure 3.

For IV the atom labeling scheme is given in the ORTEP plot of Figure 3. The molecule has a noncrystallographic pseudo-twofold axis which is roughly coincident with the P–CP1 bond. To facilitate the examination of this pseudosymmetry, nonphenyl atoms related by the pseudo-twofold axis have been given the same name and are distinguished from each other by a prime. Atomic coordinates and thermal parameters are given in Tables IX–XI. Bond lengths and angles are given in Table XII–XIV and are summarized pictorially in Figure 4.

The geometry about the phosphorus atom is between TP and RP, the displacement along the Berry coordinate being 43.0% (40.4%) from the TP toward the RP (Table XV). The near equality of the values of 93.6° (87.9°) for $\Sigma_i|\delta_i(C) - \delta_i(TP)|$ and 93.8° (88.1°) for $R - \Sigma_i|\delta_i(C) - \delta_i(RP)|$ shows that the displacement is well described by the Berry exchange coordinate.

The O′–P–O angle of 166.6 (1)° as compared to the S′–P–S angle of 133.0 (1)° places the oxygen atoms in axial positions with reference to TP geometry. S′, S, and CP1 are then equatorial, with CP1 occupying the pivotal position in the Berry exchange process. A comparison of the P–O bond lengths of 1.689 (2) and 1.695 (2) Å for III with 1.713 (2) and 1.730 (2)

Table X. Thermal Parameters for Nonhydrogen Atoms in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

atom type	anisotropic parameters B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	equivalent isotropic B, Å^2
P	3.06 (3)	3.10 (3)	2.83 (3)	0.02 (2)	0.62 (2)	0.00 (2)	3.0
S	3.24 (3)	5.12 (4)	3.22 (3)	−0.02 (3)	0.03 (2)	−0.04 (3)	3.8
S′	3.88 (4)	3.77 (3)	3.94 (3)	−0.67 (2)	1.20 (2)	0.02 (2)	3.7
O	3.5 (1)	3.7 (1)	3.9 (1)	−0.2 (1)	1.1 (1)	−0.6 (1)	3.6
O′	4.6 (1)	4.5 (1)	3.3 (1)	−0.3 (1)	1.3 (1)	−0.3 (1)	3.9
C1	3.2 (1)	3.7 (1)	3.8 (1)	0.5 (1)	0.5 (1)	0.6 (1)	3.5
C2	3.4 (1)	2.9 (1)	3.9 (1)	0.4 (1)	1.1 (1)	0.3 (1)	3.3
C3	4.3 (1)	3.5 (1)	4.6 (1)	0.2 (1)	1.6 (1)	−0.4 (1)	3.9
C4	4.7 (2)	4.8 (2)	5.5 (2)	0.6 (1)	2.4 (1)	−0.1 (1)	4.6
C5	3.6 (1)	5.7 (2)	6.5 (2)	0.7 (1)	1.9 (1)	0.8 (1)	4.8
C6	3.1 (1)	5.1 (2)	5.3 (2)	0.3 (1)	0.3 (1)	0.8 (1)	4.3
C1′	3.4 (1)	5.2 (1)	3.4 (1)	0.7 (1)	0.9 (1)	1.1 (1)	3.7
C2′	4.3 (1)	4.8 (1)	3.0 (1)	1.0 (1)	1.0 (1)	0.7 (1)	3.8
C3′	6.8 (2)	6.1 (2)	4.1 (1)	1.5 (2)	2.1 (1)	0.2 (1)	5.2
C4′	6.6 (2)	8.9 (3)	5.2 (2)	2.9 (2)	2.9 (2)	1.0 (2)	5.8
C5′	4.2 (2)	10.8 (3)	5.0 (2)	1.8 (2)	2.0 (1)	2.4 (2)	5.5
C6′	3.6 (1)	7.6 (2)	4.7 (2)	0.2 (1)	0.8 (1)	1.9 (2)	4.8
CP1	3.0 (1)	3.6 (1)	3.3 (1)	0.0 (1)	0.6 (1)	0.3 (1)	3.2
CP2	4.7 (1)	4.2 (1)	3.8 (1)	−0.3 (1)	−0.3 (1)	0.0 (1)	4.2
CP3	5.9 (1)	5.7 (2)	4.3 (2)	−0.1 (1)	−1.0 (1)	0.8 (1)	5.2
CP4	5.7 (2)	5.0 (2)	5.8 (2)	1.0 (1)	0.1 (1)	1.8 (1)	5.2
CP5	7.5 (2)	4.0 (2)	5.6 (2)	1.3 (1)	0.9 (2)	0.4 (1)	5.4
CP6	6.2 (2)	3.9 (1)	3.9 (1)	0.8 (1)	0.7 (1)	0.0 (1)	4.5

[a] Refer to footnotes of Table II except that atoms are labeled to agree with Figure 3.

Table XI. Refined Parameters for Hydrogen Atoms in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

atom type[b]	coordinates 10^3X	10^3Y	10^3Z	isotropic thermal parameter B, Å^2
H3	−142 (4)	953 (3)	516 (2)	4 (1)
H4	−383 (4)	920 (4)	547 (2)	5 (1)
H5	−559 (5)	814 (4)	463 (2)	7 (1)
H6	−486 (4)	724 (4)	354 (2)	5 (1)
H3′	199 (5)	609 (4)	156 (2)	7 (1)
H4′	430 (6)	653 (5)	116 (3)	10 (1)
H5′	543 (5)	875 (4)	157 (2)	8 (1)
H6′	451 (4)	996 (4)	248 (2)	5 (1)
HP2	139 (5)	765 (4)	478 (2)	6 (1)
HP3	225 (4)	591 (4)	553 (2)	6 (1)
HP4	238 (4)	380 (4)	504 (2)	6 (1)
HP5	151 (5)	332 (5)	383 (2)	8 (1)
HP6	79 (5)	519 (4)	309 (2)	7 (1)

[a,b] Refer to footnotes of Table IX.

Table XII. Bond Lengths and Selected Intramolecular Distances in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

type[b]	bond length, Å	type	bond length, Å
P–CP1	1.817 (3)	CP1–CP2	1.389 (4)
P–O	1.730 (2)	CP2–CP3	1.388 (5)
P–O′	1.713 (2)	CP3–CP4	1.375 (6)
P–S	2.113 (1)	CP4–CP5	1.383 (6)
P–S′	2.117 (1)	CP5–CP6	1.386 (5)
S–C1	1.763 (3)	CP6–CP1	1.392 (4)
S′–C1′	1.762 (3)		
O–C2	1.371 (3)		
O′–C2′	1.373 (4)	C3–H3	0.92 (3)
C1–C2	1.393 (4)	C4–H4	1.02 (4)
C1′–C2′	1.388 (4)	C5–H5	0.98 (4)
C2–C3	1.389 (4)	C6–H6	0.97 (4)
C2′–C3′	1.386 (5)	C3′–H3′	0.96 (4)
C3–C4	1.385 (5)	C4′–H4′	1.11 (5)
C3′–C4′	1.393 (6)	C5′–H5′	0.98 (4)
C4–C5	1.383 (5)	C6′–H6′	0.97 (4)
C4′–C5′	1.372 (8)	CP2–HP2	0.93 (4)
C5–C6	1.391 (5)	CP3–HP3	0.95 (4)
C5′–C6′	1.396 (6)	CP4–HP4	0.93 (4)
C6–C1	1.396 (4)	CP5–HP5	1.03 (5)
C6′–C1′	1.396 (5)	CP6–HP6	0.96 (4)
Nonbonded Intramolecular Distances (Å)			
O–S	2.754 (2)	O′–S	2.573 (2)
O′–S′	2.754 (2)	O–S′	2.570 (2)
CP1–O	2.644 (3)	CP1–S	3.264 (3)
CP1–O′	2.645 (3)	CP1–S′	3.322 (3)

[a,b] Refer to footnotes of Table IX.

Å for IV shows the elongation associated with axial character in the latter structure.

In compound IV, the atoms P, CP1, S, and S′, which would be strictly coplanar in an idealized TP, are coplanar to within ±0.008 Å (plane I, Table XVI). The atoms P, CP1, O, and O′ are coplanar to within ±0.001 Å (plane II, Table XVI). The dihedral angle between planes I and II should be in the range 85.9–90.0° if structural distortions lie along the TP-RP pathway. The observed dihedral angle between these planes for compound IV is 85.8°. The corresponding planes for compound III are defined by atoms P, CP1, S1, and 09 (coplanar to within ±0.02Å, plane I, Table VII) and P, CP1, S2, and O10 (±0.02Å, plane II, Table VII) while the corresponding dihedral angle has a value of 85.0°.

The pseudo-twofold axis in molecule IV can be visualized by examination of the bond lengths and angles in Figure 4 and is also seen in the roughly equal but opposite deviations of atoms related by the pseudo-twofold from the least-squares mean planes I and II (Table XVI) both of which contain the twofold axis (P–CP1).

Worth noting also is the compression below 120° in the endocyclic angles at C11 and C14 of the phenanthrene moiety for III. This is typically found for unsaturated rings in oxyphosphoranes[16a] and has been related to a secondary effect of

Table XIII. Bond Angles for Nonhydrogen Atoms in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

type[b]	bond angle, deg	type	bond angle, deg
CP1-P-O	96.4 (1)	C2′-C3′-C4′	117.9 (4)
CP1-P-O′	97.0 (1)	C3-C4-C5	121.0 (3)
CP1-P-S	112.1 (1)	C3′-C4′-C5′	121.2 (5)
CP1-P-S′	115.0 (1)	C4-C5-C6	120.7 (3)
S′-P-S	133.0 (1)	C4′-C5′-C6′	121.1 (4)
O′-P-O	166.6 (1)	C5-C6-C1	118.9 (3)
S′-P-O	83.2 (1)	C5′-C6′-C1′	118.1 (4)
O′-P-S	83.8 (1)	C6-C1-C2	119.7 (3)
O-P-S	91.0 (1)	C6′-C1′-C2′	120.2 (3)
O′-P-S′	91.3 (1)	S-C1-C6	126.5 (2)
P-O-C2	117.2 (2)	S′-C1′-C6′	126.1 (3)
P-O′-C2′	118.2 (2)	O-C2-C3	121.8 (2)
P-S-C1	94.4 (1)	O′-C2′-C3′	121.3 (3)
P-S′-C1′	94.9 (1)	P-CP1-CP2	121.1 (2)
O-C2-C1	116.9 (2)	P-CP1-CP6	119.8 (2)
O-C2′-C1′	117.2 (3)	CP1-CP2-CP3	120.2 (3)
S-C1-C2	113.9 (2)	CP2-CP3-CP4	120.3 (4)
S-C1′-C2′	113.7 (2)	CP3-CP4-CP5	120.1 (4)
C1-C2-C3	121.3 (3)	CP4-CP5-CP6	119.9 (4)
C1′-C2′-C3′	121.5 (3)	CP5-CP6-CP1	120.4 (3)
C2-C3-C4	118.4 (3)	CP6-CP1-CP2	119.1 (3)

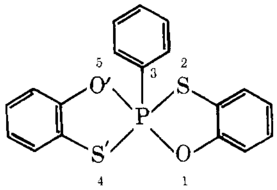
[a,b] Refer to footnotes of Table IX.

Table XIV. Bond Angles Involving Hydrogen Atoms in Crystalline $(C_6H_4OS)_2PPh$ (IV)[a]

type[b]	bond angle, deg	type	bond angle, deg
H3-C3-C2	120 (2)	H5′-C5′-C6′	119 (3)
H3-C3-C4	122 (2)	H6′-C6′-C5′	119 (2)
H4-C4-C3	117 (2)	H6′-C6′-C1′	123 (2)
H4-C4-C5	122 (2)	HP2-CP2-CP1	118 (2)
H5-C5-C4	117 (2)	HP2-CP2-CP3	122 (2)
H5-C5-C6	122 (2)	HP3-CP3-CP2	118 (2)
H6-C6-C5	119 (2)	HP3-CP3-CP4	122 (2)
H6-C6-C1	122 (2)	HP4-CP4-CP3	119 (2)
H3′-C3′-C2′	119 (3)	HP4-CP4-CP5	121 (2)
H3′-C3′-C4′	123 (3)	HP5-CP5-CP4	119 (2)
H4′-C4′-C3′	111 (3)	HP5-CP5-CP6	120 (2)
H4′-C4′-C5′	127 (3)	HP6-CP6-CP5	120 (3)
H5′-C5′-C4′	120 (3)	HP6-CP6-CP1	120 (3)

[a,b] Refer to footnotes of Table IX.

Table XV. Dihedral Angles (δ) for $(C_6H_4OS)_2PPh$ (IV) (deg)[a]



edge[b]	δ^c	edge[b]	δ^c
45	103.9 (107.3)	13	83.2 (90.8)
25	105.3 (108.5)	23	70.6 (64.2)
14	106.7 (109.7)	34	68.7 (62.4)
12	102.3 (105.4)	24	41.4 (31.8)
35	83.2 (90.9)		

$\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})| = 93.6\ (87.9)$

$\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})| = 124.1\ (129.8)$

$R^d - \Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})| = 93.6\ (87.9)$

av % along Berry coordinate = 43.0 (40.4)

[a-d] Refer to footnotes of Table VIII.

strain in the five-membered rings attached to phosphorus.[16a] With the thio derivatives containing longer P-S bonds, this effect appears to be nearly absent.

The atom labeling scheme for V is given in Figure 5. Atomic coordinates and thermal parameters are given in Tables XVII-XIX. Bond lengths and angles are given in Tables XX-XXII and are summarized pictorially in Figure 6.

The molecule has a noncrystallographic pseudo-twofold axis which is roughly coincident with the P-CP1 bond. To facilitate the examination of this pseudosymmetry, nonphenyl atoms related by the pseudo-twofold axis have been given the same name and are distinguished from each other by a prime.

The molecular geometry about the phosphorus atom is displaced somewhat from the idealized trigonal bipyramid (TP). In terms of the Berry coordinate[15] (Table XXIII), the displacement is 35.3 (31.1)% from the TP toward the RP. The angle between the axial atoms S2-P-S2′ is 170.50 (3)° as compared to the idealized value of 180°. The atoms defining the equatorial plane P, CP1, S1, and S1′ are coplanar to within ±0.01 Å (plane I, Table XXIV). The equatorial angles are S1-P-S1′ = 130.92 (3)°, CP1-P-S1 = 114.5 (1)°, and CP1-P-S1′ = 114.5 (1)° as compared to the idealized value of 120°.

The atoms P, CP1, S2, and S2′ are coplanar to within ±0.007 Å (plane II, Table XXIV). The dihedral angle between planes I and II should be in the range 85.9-90.0° if structural distortions are constrained along the coordinate connecting the idealized TP and RP configurations. The observed dihedral angle between these planes is 85.2°. The extent to which the molecule has C_2 symmetry can be visualized by examination of the bond lengths and angles in Figure 6 and is also seen in the roughly equal but opposite deviations of atoms related by the pseudo-twofold from planes I and II, both of which contain the twofold axis (P-CP1).

The P-S axial bond lengths of 2.270 (1) and 2.234 (1) Å are larger than the P-S equatorial bond lengths of 2.111 (1) and 2.107 (1) Å, in keeping with the trends previously observed with other atoms directly connected to phosphorus in spirocyclics.[3,4] The latter pair of values is comparable to the P-S "equatorial" bond lengths (2.117 (1) and 2.113 (1) Å) observed in the related molecule, IV, which is distorted only a few percent more from the TP than V. Also worth noting is the uniform presence of 120° internal ring angles in the benzo units. In all previously studied oxygen-containing spirocyclics, the angles at C3, C6, C3′, and C6′ were compressed significantly below 120°[16] (with reference to the labeling in Figure 6). The loss of this effect in V appears related to the relaxation of ring strain in the attached five-membered ring[17] containing larger sulfur atoms.

Bonding. The variation in conformation along the TP-RP coordinate for III and IV may be ascribable to the different positioning of the ring sulfur and oxygen atoms in unsaturated systems. In the phenanthro derivative III, having the same type of directly attached atom in a given ring, less ring strain is expected in the RP configuration. This has been attributed to the presence of basal bonds of equal character in the rectangular pyramid compared to bonds having different properties for atoms in rings spanning axial-equatorial sites of a trigonal bipyramid.[17] In IV, this type of ring constraint is reduced since the presence of different directly bonded ring atoms removes the possibility of attaining equivalency in the basal ligand bonds to phosphorus. Here, the equatorial site preference of sulfur, owing to its low electronegativity[18] relative to that for oxygen, appears to dominate and a structural form much less displaced from the trigonal bipyramid is observed.

This is analogous to the situation encountered for the structures of the spirocyclics VI and VII having ring oxygen

Table XVI. Deviations (Å) from Selected Least-Squares Mean Planes[a,b] in $(C_6H_4OS)_2PPh$ (IV)

	I	II	III	IV	V
P	−0.008	0.001	(0.519)	(0.529)	(0.436)
CP1	0.002	0.000	(2.328)		
S	0.003	(−1.952)	−0.338	0.003	
S′	0.003	(1.915)	−0.303		0.006
O	(1.705)	−0.001	0.485	−0.004	
O′	(−1.704)	−0.001	0.155		−0.008
C1	(1.723)	(−2.332)	(0.103)	0.006	
C2	(2.423)	(−1.219)	(0.508)	0.007	
C1′	(−1.735)	(2.291)	(−0.301)		−0.013
C2′	(−2.429)	(1.206)	(−0.021)		0.014

	VI	VIA		VII	VIIA		VIII	VIIIA
CP1	−0.002	−0.016	C1	−0.006	−0.002	C1′	0.009	−0.000
CP2	0.005	−0.002	C2	0.003	0.009	C2′	−0.008	0.003
CP3	−0.004	0.000	C3	0.003	0.006	C3′	−0.001	0.019
CP4	−0.001	0.008	C4	−0.006	−0.007	C4′	0.007	0.017
CP5	0.004	0.007	C5	0.003	−0.001	C5′	−0.005	−0.013
CP6	0.003	−0.011	C6	0.003	0.002	C6′	−0.003	−0.022
P	(0.044)	0.015	S	(−0.009)	−0.001	S′	(0.048)	0.029
			O	(−0.018)	−0.007	O′	(−0.049)	−0.032
			P	(0.505)	(0.520)	P	(0.420)	(0.426)

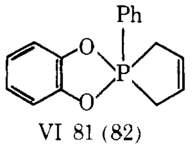
[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Selected dihedral angles between planes indicated: I and II = 94.2°, IV and V = 27.5°, I and VI = 60.9, III and VI = 90.7°, II and VI = 25.0°, VII and VIII = 29.2°, VIIA and VIIIA = 28.4°.

Table XVII. Atomic Coordinates in Crystalline $(C_6H_4S_2)_2PPh$ (V)[a]

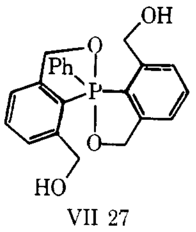
atom type[b]	coordinates 10^4X	10^4Y	10^4Z
P	6468.8 (3)	1276.6 (7)	9 618.2 (3)
S1	5815.4 (3)	−1061.9 (7)	8 749.0 (3)
S1′	5973.7 (3)	3773.7 (7)	10 041.7 (3)
S2	6346.0 (4)	3367.7 (7)	8 517.1 (3)
S2′	6346.6 (3)	−778.4 (7)	10 603.8 (3)
C1	6077 (1)	−458 (3)	7 866 (1)
C2	6352 (1)	1505 (3)	7 785 (1)
C3	6598 (1)	1916 (3)	7 107 (1)
C4	6539 (1)	428 (4)	6 511 (1)
C5	6239 (2)	−1487 (4)	6 582 (1)
C6	6017 (1)	−1937 (3)	7 261 (1)
C1′	6169 (1)	3043 (3)	11 109 (1)
C2′	6372 (1)	1033 (3)	11 367 (1)
C3′	6553 (1)	509 (3)	12 222 (1)
C4′	6494 (2)	1947 (4)	12 786 (1)
C5′	6265 (2)	3922 (4)	12 516 (1)
C6′	6111 (1)	4478 (3)	11 683 (1)
CP1	7668 (1)	1151 (3)	10 055 (1)
CP2	8175 (1)	2819 (3)	10 461 (1)
CP3	9088 (1)	2679 (4)	10 815 (2)
CP4	9490 (1)	919 (4)	10 748 (1)
CP5	8989 (1)	−732 (4)	10 335 (2)
CP6	8076 (1)	−634 (3)	9 993 (1)

[a] Numbers in parentheses following each entry are the estimated standard deviations in the last significant figure. [b] Atoms labeled to agree with Figure 5.

and carbon atoms directly attached to phosphorus. Here, the structures are 81 (82)[3] and 27%[4] displaced from a trigonal bipyramid toward a rectangular pyramid, respectively. The operation of the preference rule[18] in not positioning the less electronegative carbon and sulfur atoms in axial positions of a trigonal bipyramid is apparent.



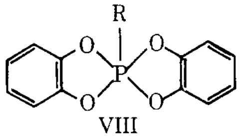
VI 81 (82)



VII 27

However, this must not be the only factor operating since the related bisdithiaphosphole V has a structure close to that of IV (displaced 35% from the TP based on actual bond distances). As commented earlier,[17,19] electron pair repulsion effects[20] are an important consideration in accounting for the location of a particular conformation along the TP–RP coordinate. On going from IV to V, the presence of additional sulfur atoms heightens electron pair repulsions among basal bonds which tends to favor the trigonal bipyramid. As far as the unique ligand is concerned in spirocyclic derivatives, enhanced electron pair repulsions between the apical and basal bonds of a RP tend to favor this structural type.[5,16,17,19] Thus, the structure of I, containing a methyl group of reduced electronegativity compared to the phenyl group in V, considerably displaced toward the RP (79%[21]), appears rationalized in a qualitative sense.

If this is so, the operation of the latter effect is certainly magnified compared to its presence in the related oxaphosphole series VIII. In this series, when R = Ph, the structure is 72% displaced toward the RP,[4,16] when R = CH_3, 82%.[4] This may be reasonable since the presence of highly electronegative oxygen atoms should cause electron-pair repulsions to be substantially reduced. Future work may therefore verify that thio-containing spirocyclic phosphoranes will be subject to greater structural changes with ligand substitutions at the unique position compared to corresponding changes in related oxyphosphoranes, partly as a result of a lesser role for ring strain as a structural determinant[17] in the thio series. This view is reinforced by the presence of longer P–S compared to P–O bond distances.



VIII

Table XVIII. Thermal Parameters in Crystalline $(C_6H_4S_2)_2PPh$ (V)[a]

atom	anisotropic parameters						equivalent isotropic
type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B, Å^2
P	2.26 (2)	2.09 (2)	2.16 (2)	−0.01 (1)	0.99 (1)	0.12 (1)	2.1
S1	3.15 (2)	3.01 (2)	2.37 (2)	−1.07 (2)	1.15 (2)	−0.23 (2)	2.7
S1′	3.57 (2)	2.46 (2)	2.69 (2)	0.79 (2)	1.76 (2)	0.50 (2)	2.6
S2	4.16 (2)	2.37 (2)	2.58 (2)	0.17 (2)	1.66 (2)	0.41 (2)	2.8
S2′	3.93 (2)	2.23 (2)	2.77 (1)	−0.04 (2)	1.88 (2)	0.31 (2)	2.7
C1	2.4 (1)	3.5 (1)	2.2 (1)	0.1 (1)	0.7 (1)	0.2 (1)	2.7
C2	2.5 (1)	3.1 (1)	2.2 (1)	0.3 (1)	0.8 (1)	0.4 (1)	2.6
C3	3.2 (1)	3.5 (1)	2.9 (1)	0.3 (1)	1.3 (1)	0.7 (1)	3.1
C4	4.0 (1)	4.7 (1)	2.8 (1)	0.7 (1)	1.8 (1)	0.7 (1)	3.5
C5	4.8 (1)	4.1 (1)	2.8 (1)	0.5 (1)	1.6 (1)	−0.2 (1)	3.7
C6	4.0 (1)	3.3 (1)	2.8 (1)	−0.1 (1)	1.1 (1)	0.0 (1)	3.4
C1′	2.4 (1)	3.0 (1)	2.5 (1)	0.0 (1)	1.1 (1)	0.1 (1)	2.6
C2′	2.7 (1)	2.9 (1)	2.5 (1)	−0.1 (1)	1.2 (1)	0.1 (1)	2.6
C3′	3.8 (1)	3.6 (1)	2.7 (1)	0.0 (1)	1.2 (1)	0.4 (1)	3.4
C4′	4.9 (1)	4.4 (1)	2.4 (1)	−0.4 (1)	1.4 (1)	0.2 (1)	3.8
C5′	5.0 (1)	4.0 (1)	3.0 (1)	−0.5 (1)	1.9 (1)	−0.7 (1)	3.7
C6′	3.9 (1)	2.9 (1)	3.3 (1)	−0.2 (1)	1.7 (1)	−0.2 (1)	3.3
CP1	2.3 (1)	2.8 (1)	2.3 (1)	−0.2 (1)	1.0 (1)	0.1 (1)	2.5
CP2	3.4 (1)	3.1 (1)	3.8 (1)	−0.4 (1)	1.2 (1)	−0.4 (1)	3.4
CP3	3.3 (1)	4.4 (1)	4.1 (1)	−1.2 (1)	0.9 (1)	−0.5 (1)	3.9
CP4	2.6 (1)	5.7 (1)	3.8 (1)	−0.2 (1)	1.1 (1)	0.3 (1)	3.9
CP5	3.3 (1)	4.5 (1)	4.5 (1)	0.9 (1)	1.7 (1)	−0.1 (1)	3.9
CP6	2.8 (1)	3.2 (1)	3.7 (1)	0.0 (1)	1.2 (1)	−0.5 (1)	3.2

[a] Refer to footnotes of Table II except that atoms are labeled to agree with Figure 5.

Table XIX. Refined Parameters for Hydrogen Atoms in Crystalline $(C_6H_4S_2)_2PPh$ (V)[a]

atom	coordinates			isotropic thermal parameter
type[b]	10^3X	10^3Y	10^3Z	B, Å^2
H3	685 (1)	326 (3)	710 (1)	4 (1)
H4	669 (2)	72 (4)	605 (2)	5 (1)
H5	618 (1)	−251 (4)	614 (2)	4 (1)
H6	581 (2)	−326 (4)	734 (2)	4 (1)
H3′	674 (2)	−79 (4)	1243 (2)	5 (1)
H4′	662 (2)	153 (3)	1339 (2)	5 (1)
H5′	622 (2)	492 (4)	1291 (2)	4 (1)
H6′	596 (2)	581 (4)	1149 (1)	4 (1)
HP2	787 (2)	398 (3)	1051 (1)	4 (1)
HP3	939 (2)	385 (4)	1108 (2)	5 (1)
HP4	1014 (2)	85 (4)	1101 (2)	6 (1)
HP5	924 (2)	−197 (4)	1030 (2)	5 (1)
HP6	771 (1)	−179 (3)	970 (1)	4 (1)

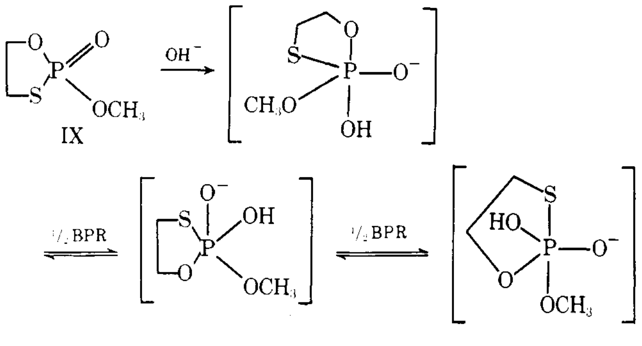
[a,b] See footnotes to Table XVII.

Table XX. Bond Lengths and Selected Nonbonded Distances in Crystalline $(C_6H_4S_2)_2PPh$ (V)

type[b]	bond length,[a] Å	type	bond length, Å
P-CP1	1.829 (2)	CP1-CP2	1.393 (3)
P-S1	2.111 (1)	CP1-CP6	1.393 (3)
P-S1′	2.107 (1)	CP2-CP3	1.393 (3)
P-S2	2.270 (1)	CP5-CP6	1.392 (3)
P-S2′	2.234 (1)	CP3-CP4	1.375 (4)
S1-C1	1.773 (2)	CP4-CP5	1.382 (4)
S1′-C1′	1.773 (2)		
S2-C2	1.757 (2)	C3-H3	0.99 (2)
S2′-C2′	1.757 (2)	C4-H4	0.95 (3)
C1-C2	1.407 (3)	C5-H5	0.99 (2)
C1′-C2′	1.402 (3)	C6-H6	0.97 (2)
C2-C3	1.401 (3)	C3′-H3′	0.93 (3)
C2′-C3′	1.400 (3)	C4′-H4′	1.00 (2)
C3-C4	1.389 (3)	C5′-H5′	0.97 (3)
C3′-C4′	1.386 (3)	C6′-H6′	0.94 (2)
C4-C5	1.390 (3)	CP2-HP2	0.95 (2)
C4′-C5′	1.390 (3)	CP3-HP3	0.94 (3)
C5-C6	1.382 (3)	CP4-HP4	1.00 (3)
C5′-C6′	1.381 (2)	CP5-HP5	0.93 (3)
C6-C1	1.395 (3)	CP6-HP6	0.98 (2)
C6′-C1′	1.395 (3)		
Selected Nonbonded Intramolecular Distances (Å)			
S1-S2	3.142 (1)	S1-S2′	2.908 (1)
S1′-S2′	3.153 (1)	S1′-S2	2.915 (1)
CP1-S1	3.317 (2)	CP1-S2	3.020 (2)
CP1-S1′	3.314 (2)	CP1-S2′	3.013 (2)

[a,b] See footnotes to Table XVII.

In view of the appearance of the structures of III–V at different points along the TP–RP coordinate, reaction mechanisms of ring-sulfur-containing phosphorus compounds for which pseudorotations are invoked appear likely. For example, alkaline hydrolysis of *O,S*-ethylene phosphorothioate (IX) results in almost exclusive P–S bond cleavage,[6] implying a Berry pseudorotation (BPR) to bring the ring sulfur atom into a leaving axial position of a trigonal bipyramid.



Structural Principles. Based on the available evidence covering the five sulfur-containing spirocyclic phosphoranes discussed here, three of the five principal factors that we previ-

Table XXI. Bond Angles for Nonhydrogen Atoms in Crystalline $(C_6H_4S_2)_2PPh$ (V)[a]

type[b]	bond angle, deg	type	bond angle, deg
S1-P-S1′	130.92 (3)	C6-C1-C2	120.5 (2)
S2-P-S2′	170.50 (3)	C6′-C1′-C2′	120.5 (2)
S1-P-S2′	83.98 (2)	C1-C2-C3	118.6 (2)
S2-P-S1′	83.42 (2)	C1′-C2′-C3′	118.9 (2)
S1-P-S2	91.57 (2)	C2-C3-C4	120.3 (2)
S1′-P-S2′	93.13 (3)	C2′-C3′-C4′	120.0 (2)
S1-P-CP1	114.5 (1)	C3-C4-C5	120.4 (2)
S1′-P-CP1	114.5 (1)	C3′-C4′-C5′	120.6 (2)
S2-P-CP1	94.3 (1)	C4-C5-C6	120.1 (2)
S2′-P-CP1	95.2 (1)	C4′-C5′-C6′	120.0 (2)
P-S1-C1	100.9 (1)	C5-C6-C1	120.0 (2)
P-S1′-C1′	101.6 (1)	C5′-C6′-C1′	119.8 (2)
P-S2-C2	97.4 (1)	P-CP1-CP2	120.4 (1)
P-S2′-C2′	98.8 (1)	P-CP1-CP6	119.8 (1)
S1-C1-C2	119.7 (1)	CP1-CP2-CP3	119.7 (2)
S1′-C1′-C2′	120.0 (1)	CP1-CP6-CP5	119.6 (2)
S2-C2-C1	119.1 (1)	CP2-CP3-CP4	120.4 (2)
S2′-C2′-C1′	119.4 (1)	CP6-CP5-CP4	120.4 (2)
S1-C1-C6	119.8 (1)	CP3-CP4-CP5	120.1 (2)
S1′-C1′-C6′	119.5 (1)	CP2-CP1-CP6	119.8 (2)
S2-C2-C3	122.3 (1)		
S2′-C2′-C3′	121.7 (1)		

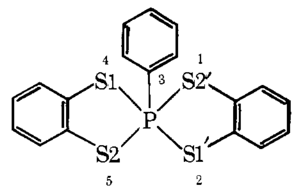
[a,b] See footnotes to Table XVII.

Table XXII. Bond Angles Involving Hydrogen Atoms in Crystalline $(C_6H_4S_2)_2PPh$ (V)[a]

type[b]	bond angle, deg	type	bond angle, deg
H3-C3-C2	117 (1)	H6′-C6′-C5′	121 (1)
H3-C3-C4	122 (1)	H6′-C6′-C1′	119 (1)
H4-C4-C3	120 (2)	HP2-CP2-CP1	117 (1)
H4-C4-C5	119 (2)	HP2-CP2-CP3	124 (1)
H5-C5-C4	119 (1)	HP3-CP3-CP2	116 (2)
H5-C5-C6	121 (1)	HP3-CP3-CP4	124 (2)
H6-C6-C5	123 (1)	HP4-CP4-CP3	119 (1)
H6-C6-C1	117 (1)	HP4-CP4-CP5	121 (1)
H3′-C3′-C2′	121 (2)	HP5-CP5-CP4	123 (2)
H3′-C3′-C4′	119 (2)	HP5-CP5-CP6	117 (2)
H4′-C4′-C3′	118 (1)	HP6-CP6-CP5	122 (1)
H4′-C4′-C5′	121 (1)	HP6-CP6-CP1	1119 (1)
H5′-C5′-C4′	120 (1)		
H5′-C5′-C6′	120 (1)		

[a,b] See footnotes to Table XVII.

Table XXIII. Dihedral Angles (δ) for $(C_6H_4S_2)_2PPh$ V (deg)[a]



edge[b]	δ[c]	edge[b]	δ[c]
45	109.2 (104.5)	13	92.9 (93.4)
25	112.4 (107.7)	23	55.2 (61.2)
14	112.5 (108.3)	34	54.6 (60.5)
12	108.9 (104.8)	24	34.3 (37.0)
35	92.8 (92.8)		
$\Sigma_i \lvert\delta_i(\mathrm{C}) - \delta_i(\mathrm{TP})\rvert$ = 76.7 (67.7)			
$\Sigma_i \lvert\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})\rvert$ = 141.0 (150.0)			
$R^d - \Sigma_i \lvert\delta_i(\mathrm{C}) - \delta_i(\mathrm{RP})\rvert$ = 76.7 (67.7)			
% along Berry coordinate = 35.2 (31.1)			

[a-d] Refer to footnotes of Table VIII.

Table XXIV. Deviations (Å) from Selected Least-Squares Mean Planes in $(C_6H_4S_2)_2PPh$ (V)[a,b]

	I	II	III	IV	V
P	0.014	0.007	(0.527)	(0.824)	(0.641)
CP1	−0.004	−0.001	(2.336)		
S1	−0.005	(−1.905)	−0.533	0.012	
S1′	−0.005	(1.918)	−0.148		0.009
S2	(−2.241)	−0.003	0.126	−0.010	
S2′	(2.231)	−0.003	0.555		−0.012
C1	(−1.630)	(−2.594)	(−0.319)	−0.025	
C2	(−2.613)	(−1.742)	(0.033)	0.024	
C1′	(1.668)	(2.581)	(0.332)		−0.023
C2′	(2.648)	(1.731)	(0.700)		0.026

	VI		VII		VIII
CP1	0.002	C1	0.011	C1′	0.009
CP2	−0.008	C2	−0.016	C2′	−0.017
CP3	0.007	C3	0.008	C3′	0.010
CP4	0.001	C4	0.006	C4′	0.005
CP5	−0.007	C5	−0.012	C5′	−0.011
CP6	0.006	C6	0.003	C6′	0.004
P	(0.040)	P	(0.779)	P	(0.538)
		S1	(0.070)	S1′	(0.035)
		S2	(−0.123)	S2′	(−0.156)

[a] Entries in parentheses are for atoms not included in the calculation of the plane. [b] Selected dihedral angles between planes indicated: I and II = 85.2°, IV and V = 29.5°, I and VI = 15.1°, II and VI = 70.2°.

ously established[3,4,10] which favor the formation of the rectangular pyramid for oxyphosphoranes appear to apply as well to the thio derivatives. Only I and III are markedly displaced toward the rectangular pyramid. These formulations contain unsaturated five-membered cyclic systems, the presence of two such rings, and the presence of like atoms bonded to phosphorus in any one ring, all factors observed in oxyphosphoranes with near-rectangular pyramidal structures. The two other structural features cited[10] for oxyphosphoranes to be conducive to the formation of a rectangular pyramid, namely, introduction of a more strained four-membered ring and the presence of an acyclic ligand in a spirocyclic derivative which is bulky and has low electronegativity,[4] go untested at present for related thio derivatives. The insight achieved here, however, is perhaps indicative of the general course to follow.

Acknowledgment. The support of this research by the National Institutes of Health (GM 21466) is gratefully acknowledged. We wish to thank the University of Massachusetts Computing Center for generous allocation of computer time.

Supplementary Material Available. A compilation of observed and calculated structure factor amplitudes (58 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, No. INOR-196.
(2) (a) Pentacoordinated Molecules. 35. (b) Previous paper in this series: T. E. Clark, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **18,** 1668 (1979).
(3) R. R. Holmes, *ACS Monogr.*, **No. 175,** in press.
(4) R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99,** 3318 (1977).
(5) R. R. Holmes, *J. Am. Chem. Soc.*, **100,** 433 (1978).
(6) (a) D. C. Gay and N. K. Hamer, *J. Chem. Soc., Perkin Trans. 2*, 929 (1972); (b) *Chem. Commun.*, 1564 (1970).
(7) (a) D. A. Usher, D. I. Richardson, Jr., and F. Eckstein, *Nature (London)*, **228,** 663 (1970); (b) D. A. Usher, E. S. Erenrich, and F. Eckstein, *Proc. Natl. Acad. Sci. U.S.A.*, **69,** 115 (1972).
(8) (a) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973); (b) W. S. Sheldrick, personal communication.

(9) E. Duff, D. R. Russell, and S. Trippett, *Phosphorus*, **4**, 203 (1974).

(10) (a) R. K. Brown, R. O. Day, S. Husebye, and R. R. Holmes, *Inorg. Chem.*, **17**, 3276 (1978); (b) P. F. Meunier, R. O. Day, J. R. Devillers, and R. R. Holmes, *ibid.*, **17**, 3270 (1978); (c) W. Althoff, R. O. Day, R. K. Brown, and R. R. Holmes, *ibid.*, **17**, 3265 (1978).

(11) (a) A. C. Sau and R. R. Holmes, *J. Organomet. Chem.*, **156**, 253 (1978); (b) M. Eisenhut, D.Sc. Thesis, Technical University, Braunschweig, West Germany, 1972.

(12) "International Tables for X-ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 99.

(13) The function minimized is $\sum w(F_o - |F_c|)^2$. Atomic form factors for nonhydrogen atoms were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); scattering factors for hydrogen atoms were taken from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(14) Goodness of fit, $S = [\sum w(F_o - |F_c|)^2/(N_o - N_v)]^{1/2}$; N_o = number of observations, N_v = number of variables.

(15) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(16) (a) R. K. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **99**, 3326 (1977); (b) *Inorg. Chem.*, **16**, 2294 (1977).

(17) R. R. Holmes, *J. Am. Chem. Soc.*, **97**, 5379 (1975).

(18) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(19) R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).

(20) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, Princeton, N.J., 1972, and references cited therein.

(21) In ref 17, the structural displacement was approximated as 57% from the trigonal bipyramid toward the square pyramid. This estimate was based on an erroneously reported[8a] trans basal S–P–S angle of 132.0°. This has been corrected to 143.5 (7)°.[8b]

Ethylene Complexes. Bonding, Rotational Barriers, and Conformational Preferences

Thomas A. Albright, Roald Hoffmann,* Jack C. Thibeault, and David L. Thorn

Contribution from the Departments of Chemistry, Cornell University,
Ithaca, New York 14853, and University of Houston, Houston, Texas 77004.

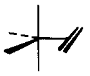
Received September 19, 1978

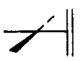
Abstract: Rotational barriers and conformational preferences are a primary probe of bonding in olefin complexes. Such barriers in ethylene-ML_{2-5} are analyzed in terms of differential interactions between the frontier orbitals of the ML_n fragment and the ethylene π and π^*. It is found that the large barrier to internal rotation about the M-ethylene axis in ethylene-ML_2 complexes, favoring the in-plane orientation, is due to loss of overlap between ethylene π^* and an ML_2 b_2 orbital—the dominant interaction in these compounds. An analogous situation exists for rigid rotation in ethylene-ML_4 within the trigonal-bipyramidal geometry. A much lower energy pathway for this complex is found if rotation is accompanied by pseudorotation. The barrier in square-planar ethylene-ML_3 compounds of the Zeise's salt type, on the other hand, is largely set by steric factors which favor the upright geometry. Various strategies are devised to lower the barrier or reverse the conformational preference in these complexes. This may be accomplished by changing the electronic or steric properties of the ligands on the metal or the ethylene. Finally unsymmetrically substituted olefin complexes are examined. In the ML_3 case the metal-carbon bond to the carbon bearing the weaker donor or weaker acceptor should be the stronger or shorter one. In the ML_2 and ML_4 complexes of ethylene the acceptor effect is accentuated, that of the donor less important.

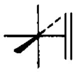
Few qualitative pictures have served the chemist as beautifully as the Dewar-Chatt-Duncanson model of metal-olefin bonding.[1] In the flowering of organometallic chemistry this model has proven a stimulus to much synthetic, structural, and mechanistic work. Not surprisingly, considerable theoretical effort has also been devoted to obtaining a detailed description of the electronic structure of transition metal-ethylene complexes.[2] One aspect of the chemistry of these complexes where the experimental information is relatively new, and yet provides the most direct evidence on the nature of the bonding, is the barrier to internal rotation about the metal-olefin axis. This is the primary focus of the present study,[3] which forms part of a general analysis of polyene-ML_n rotational barriers.[4]

The problem then that we will attack is the origin of the barrier to internal rotation in the molecules i–iv. The interrelationship between the various coordination geometries will prove to be illuminating. We will rationalize the observed equilibrium geometries and the magnitude of the rotational barriers in these complexes. The understanding obtained in the process will be used to explore ways in which these barriers may be modified by varying substituents on the ethylene or the metal, or by sterically imposed geometrical deformations. A specific problem of asymmetry in metal-olefin bonding will be studied at the end. The discussion presented in this paper will serve as an introduction and guide to a general analysis of polyene and cyclopolyene ML_2, ML_4, and ML_5 complexes.


i


ii


iii


iv

ML_{2-5} Fragments

A natural framework for the analysis of rotational barriers is found in the conceptual construction of the complex from ML_n and olefin fragments. The MOs of the ML_n fragments are first developed and then interacted with the levels of the ethylene in several extreme geometries which correspond to the end points of a rotational process. Standard perturbation theoretic arguments are used to pinpoint the differences in the conformations considered. Our actual calculations are of the extended Hückel type, with parameters specified in the Appendix.

Detailed discussions of the frontier orbitals of ML_n fragments have been given elsewhere.[5] Here we shall describe only their salient features, emphasizing those orbitals which eventually lead to a conformational distinction. The valence orbitals of four ML_{2-5} fragments are shown in Figure 1. Three of the fragments bear carbonyl ligands, the fourth a C_{2v} chloride intended as a precursor for the important class of olefin complexes of the Zeise's salt type. The C_{3v} pyramidal ML_3 fragment, and the barriers it engenders, has been discussed elsewhere.[4] The four fragments in Figure 1 are arranged not in order of coordination number, but to exploit a similarity to be discussed below, between ML_3 and ML_5 on one hand, and ML_2 and ML_4 on the other. The electron counts will also vary with the actual complex, but the typical situations are antici-

---

* Cornell University.

0002-7863/79/1501-3801$01.00/0