



Structural studies of organo-phosphorus (V) esters and thioesters
by Ronald Wade Warrant

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

The crystal and molecular structures of four organo-phosphorus (V) esters and thioesters were solved by X-ray diffraction methods.

S, S, S-tri-p-tolyl phosphorotriothioate crystallizes in space group $P2_1/n$ with $a = 9.489(4)$ Å, $b = 14.938(8)$ Å, $c = 14.916(8)$ Å, $\beta = 97.37(4)^\circ$, and $Z = 4$.

The structure was solved using symbolic addition procedures and all atoms lie in general positions. The structure is analyzed for features pertinent to the compound's ability to show long-range coupling effects in its 1H n.m.r. spectrum. The final R is 4.8% for 2144 observed intensities.

5-t-butyl-2-methoxy-2-oxo-1,3, 2-dioxaphosphorinane crystallizes in space group $Pnma$ with $a = 6.123(4)$ Å, $b = 10.02(1)$ Å, $c = 17.65(1)$ Å, and $Z = 4$. The structure was solved using the Patterson synthesis and the molecule lies on a mirror plane at $y = 1/4$ and $3/4$. The ring is a chair and the t-butyl and methoxy groups are trans to each other in axial positions. The final R is 5.9% for 585 observed intensities.

5-t-butyl-2-phenyl-2-thio-1, 3,2-dioxaphosphorinane crystallizes in space group $P2_1/n$ with $a = 6.150(2)$ Å, $b = 11.036(3)$ Å, $c = 20.823(5)$ Å, $\beta = 95.17(2)^\circ$, and $Z = 4$. The structure was solved using the Patterson synthesis and all atoms lie in general positions. The ring is a chair with the t-butyl and phenyl groups cis to each other on the ring. The t-butyl is equatorial and the phenyl axial.

The final R is 3.6% for 1259 observed intensities.

2, 5-t-butyl-1-thio-1, 3, 2-dioxaphosphorinane crystallizes in space group $Pmcn$ with $a = 10.077(3)$ Å, $b = 10.662(3)$ Å, $c = 12.703(3)$ Å, and $Z = 4$. The structure was solved using the Patterson synthesis and the molecule lies on a mirror plane at $x = 1/4$ and $3/4$. The ring is a chair and the t-butyl groups are cis to each other with the t-butyl group on the C (5) position axial and equatorial on the P(2) position. The final R is 4.8% for 763 observed intensities.

STRUCTURAL STUDIES OF
ORGANO-PHOSPHORUS(V) ESTERS AND THIOESTERS

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A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

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in

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ABSTRACT

The crystal and molecular structures of four organo-phosphorus(V) esters and thioesters were solved by X-ray diffraction methods.

S, S, S-tri-p-tolyl phosphorotrithioate crystallizes in space group $P2_1/n$ with $a = 9.489(4)$ Å, $b = 14.938(8)$ Å, $c = 14.916(8)$ Å, $\beta = 97.37(4)^\circ$, and $Z = 4$. The structure was solved using symbolic addition procedures and all atoms lie in general positions. The structure is analyzed for features pertinent to the compound's ability to show long-range coupling effects in its ^1H n. m. r. spectrum. The final R is 4.8% for 2144 observed intensities.

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5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane crystallizes in space group $P2_1/n$ with $a = 6.150(2)$ Å, $b = 11.036(3)$ Å, $c = 20.823(5)$ Å, $\beta = 95.17(2)^\circ$, and $Z = 4$. The structure was solved using the Patterson synthesis and all atoms lie in general positions. The ring is a chair with the t-butyl and phenyl groups cis to each other on the ring. The t-butyl is equatorial and the phenyl axial. The final R is 3.6% for 1259 observed intensities.

2,5-t-butyl-1-thio-1,3,2-dioxaphosphorinane crystallizes in space group $Pmcn$ with $a = 10.077(3)$ Å, $b = 10.662(3)$ Å, $c = 12.703(3)$ Å, and $Z = 4$. The structure was solved using the Patterson synthesis and the molecule lies on a mirror plane at $x = 1/4$ and $3/4$. The ring is a chair and the t-butyl groups are cis to each other with the t-butyl group on the C(5) position axial and equatorial on the P(2) position. The final R is 4.8% for 763 observed intensities.

INTRODUCTION

This dissertation is presented in two parts. Part I presents the crystal structure of S,S,S-tri-p-tolyl phosphorotrithioate, which contributes to an understanding of long range phosphorus-hydrogen coupling in aromatic esters and thioesters of phosphorus(V).

Part II presents three crystal structures: 1) 5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane, 2) 5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane, and 3) 2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane which contribute to the knowledge of conformations of six-membered phosphorus heterocyclic rings.

PART I

S,S,S-Tri-p-Tolyl Phosphorotrithioate

INTRODUCTION

Solution of the structure S,S,S-tri-p-tolyl phosphorotrithioate, shown in Figure 1, was undertaken in order to contribute to the explanation of long-range phosphorus-hydrogen coupling the compound shows in its n.m.r. spectrum.

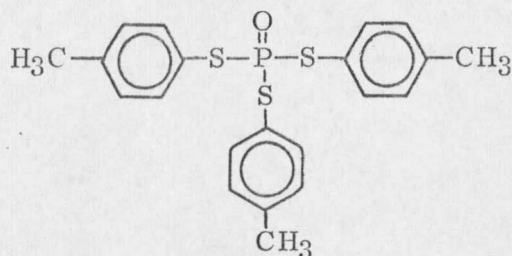


FIGURE 1

S,S,S-tri-p-tolyl phosphorotrithioate

R. A. Shaw (17) observed that the ^1H n.m.r. spectra of $\text{P}(\text{O})(\text{SC}_6\text{H}_4\text{-p-Me})_3$ shows some unusual long-range coupling effects. The n.m.r. spectrum of the p-methyl protons shows a doublet with a separation of 2.0 Hz in CCl_4 . Upon decoupling the phosphorus nucleus by irradiation with a second radio-frequency, the spectrum appears as a sharp singlet. Hence, the doublet must be the result of spin-spin coupling interaction over the seven bonds between the phosphorus nucleus and the p-methyl protons (P-S-C=C-C=C-C-H). This is believed to be the first example of spin-spin coupling over seven bonds in a phosphorus compound in which a sulfur atom is an intervening part of the

bonding system (17).

Several other compounds (of the type $P(Y)(XAr)_n(ZR)_m$; where $Y = O$ or S ; $X = O, C,$ or S ; and $R = \text{alkyl}$), also show long-range phosphorus-hydrogen coupling (11). In reviewing possible mechanisms which could explain the long-range spin-spin interactions for these compounds, Sternhell (19) concluded that, in general, a π -electron system is essential for transmission of long-range effects. Attempts were made to explain coupling between the phosphorus and the aromatic system by hyperconjugation thus imparting π -character into the $P-X-C$ bond, where $X = O, C,$ or S . This approach was discounted since tris-*p*-tolylmethylphosphonic dichloride (16), where hyperconjugation is not possible, also exhibits pronounced long-range coupling. Griffin and Gordon (11) explained the spin-spin coupling through the $P-X-C$ bond by using Fisher-Hirshfelder-Taylor models to show that for a benzyl phosphorus compound, the phosphorus atom lies over the inner circumference of the aromatic ring. This configuration may allow some overlap between the vacant d-orbitals of the phosphorus and the aromatic π -system and, therefore, enhance transmission of long-range coupling. Hence, the angle between phosphorus and the plane of the π -electron system ($P-X-C$), may be the key to the value of $^7J_{P-H}$.

In this dissertation the crystal and molecular structure of *S,S,S*-tri-*p*-tolyl phosphorotrithioate is presented and the features pertinent to the proposed overlap model are discussed.

THE CRYSTAL AND MOLECULAR STRUCTURE OF
S,S,S-TRI-para-TOLYL PHOSPHOROTRITHIOATE, $P(O)(SC_6H_4-p-Me)_3$

Preparation

Crystals of S,S,S-tri-p-tolyl phosphorotrithioate were supplied by R. A. Shaw and were prepared as described in the literature (18).

The crystal used for X-ray analysis is a colorless, transparent, well-shaped parallelepiped with approximate dimensions $(0.5 \text{ mm})^3$.

Density

The density of the crystals was measured by the flotation method using a solution of carbon tetrachloride and 2-methylbutane adjusted to just suspend a crystal. The calculated density was based on four molecules per unit cell, $d_{\text{exp}} = 1.310 \text{ g/cm}^3$ and $d_{\text{calc}} = 1.325 \text{ g/cm}^3$.

Determination of tentative cell dimensions and space group

Weissenberg photographs of the X-ray diffraction pattern of $P(O)(SC_6H_4-p-Me)_3$ indicated monoclinic symmetry. The axis along which the crystal was mounted was designated as a . The tentative cell dimensions calculated from the photographs were $a = 9$, $b = 14$, and $c = 17 \text{ \AA}$, β was not determined at this point. A unit cell of these dimensions would require four molecules to agree with its measured density.

The extinctions based on this cell were:

hkl: No conditions
 h0l: $l \neq 2n$
 0k0: $k \neq 2n$.

These extinctions correspond to the space group P_{21}/c with the b axis unique. However, for any unit cell of P_{21}/c symmetry, a new unit cell may be selected by choosing the diagonal of the a and c axes as the c axis for the new cell. In doing so, the new unit cell will be in the space group P_{21}/n . The convention for deciding which choice of space group to make, is to select the space group which minimizes the angle (β) between the a and c axes. Upon determination of more accurate cell dimensions, the β angle for P_{21}/c was found to be 117.12° and 97.37° for P_{21}/n . Hence, by convention the space group P_{21}/n was assigned. P_{21}/n has the extinctions:

hkl: No conditions
 h0l: $h + l \neq 2n$
 0k0: $k \neq 2n$.

Determination of accurate unit cell dimensions

The determination of accurate cell parameters was obtained by the following method which is standard for our General Electric XRD-5 Diffractometer; the crystal is mounted on the diffractometer and settings for several reciprocal lattice points are located. Twenty-four three-dimensional reflections were then selected for which precise measurements of the $+2\theta$ and -2θ

angles were made. Cell dimensions were then refined by least squares analysis of the 2θ 's using our standard crystallographic computing system. The crystal data are listed in Table 1.

Data collection

Data were collected on the General Electric XRD-5 Diffractometer equipped with a scintillation counter, pulse-height discriminator, and G. E. single crystal orienter, using θ - 2θ scan technique and zirconium filtered molybdenum K_{α} radiation. The crystal was mounted with the a axis parallel to the spindle axis. Each peak was scanned for 60 seconds and the backgrounds on each side of the peak were counted for 30 seconds. A chart recording of intensity vs. 2θ was monitored during the data collection as a check on the centering of the peak in the scan range and for general appearance of the peak and backgrounds. The scan rate was 2° per minute with a takeoff angle of 4° .

Intensities of 3518 unique reflections were measured of which 2144 were considered observed, using the criterion $I \geq 2.5 \sigma(I)$. Three standard reflections ($\bar{1}33$, 212, and 341 reflections) were checked approximately every two hours during data collection and remained constant with an average deviation of 1.6%, indicating no deterioration of the crystal.

Structure factors (F_o) were calculated from the intensities by applying the usual Lorentz-polarization correction, and weights were calculated from

TABLE 1

Crystal Data

S,S,S-tri-p-tolyl phosphorotrithioate

 $C_{21}PS_3OH_2$ F.W. 418.46 $F(000) = 872$ Monoclinic, space group $P2_1/n$ $a = 9.489(4) \text{ \AA}$ $\alpha = 90^\circ$ $b = 14.938(8)$ $\beta = 97.37(4)^\circ$ $c = 14.916(8)$ $\gamma = 90^\circ$ Volume of the unit cell =
 $2097 \text{ \AA}^3$ $D_{\text{exp}} = 1.310 \text{ g/cm}^3$

Molecules/unit cell = 4

 $D_{\text{calc}} = 1.325 \text{ g/cm}^3$

standard deviations as shown below. Each reflection was weighted according to the scheme described by Stout and Jensen for diffractometer data (20), where

$$w = 1/\sigma_F^2, \text{ and}$$

$$\sigma_F = k/2 \sqrt{Lp} \sqrt{\frac{N_T + N_{bg1} + N_{bg2} + (0.01N_{pk})^2}{N_T - N_{bg1} - N_{bg2}}}$$

where

w = the weight,

σ_F = the standard deviation in F_O ,

k = the scale constant

$1/\sqrt{Lp}$ = the Lorentz-polarization correction,

N_T = the total peak count,

N_{bg1} and N_{bg2} = the background counts on either side of the peak, and

N_{pk} = the net peak count.

The weighting is a measure of the reliability of an observation. If properly chosen, it has the effect of adjusting the contribution of each observation to a system of normal equations in such a way as to produce the most reliable results.

No absorption or extinction corrections were made. The linear absorption coefficient of P(O) (SC₆H₄-p-Me)₃ for MoK_α radiation ($\lambda = 0.71069$ Å) is $\mu = 4.27 \text{ cm}^{-1}$. The transmission factors for X-rays passing through the maximum and minimum dimensions of the crystal are approximately 0.69 and 0.79 respectively; this range corresponds to approximately 7% variation about a mean intensity value. Scattering factors for the non-hydrogen atoms and

anomalous scattering corrections ($\Delta f'$ and $\Delta f''$), for phosphorus and sulfur were taken from the International Tables (12). Scattering factors for hydrogen were taken from Steward, et. al. (20).

Structure determination

The structure was solved and refined in space group $P2_1/c$; data were then converted to the space group $P2_1/n$.

Efforts at solving the structure by Patterson analysis (2) failed; therefore, the method of "symbolic addition" (3) was used. The structure factors were normalized and Σ_2 relations were calculated for those reflections with E's greater than 1.50. There were 489 reflections with E's greater than 1.50 which were used in the Σ_2 calculations. The origin defining reflections selected were:

<u>H</u>	<u>K</u>	<u>L</u>	<u>sign</u>
-3	7	6	+
0	3	5	+
-1	1	0	+

Signs were determined for 483 reflections leaving only six arbitrary choices of sign.

Using this set of signs, an E-map (2) was calculated from which positions of the phosphorus, oxygen, and three sulfurs were readily found. Using these positions, the structure factor calculation gave an R-index of 0.39, where

$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$. A Fourier map revealed the positions of the remaining non-hydrogen atoms.

Refinement

Refinement was begun using the full matrix least squares method of refinement (9) with the R-index equal to 0.25 for the non-hydrogen structure along with isotropic temperature factors and a unit weighting scheme. After three cycles of refinement, the R-index dropped to 0.10. The temperature factors were then converted to anisotropic and the weighting scheme to that of Stout and Jensen (21). In two cycles the R-index dropped to 0.065 with a weighted R-index (R_{wtd}), of 0.071, where

$$R_{wtd} = \left[\frac{\sum (\sqrt{w} |F_o - F_c|)^2}{\sum (\sqrt{w} |F_o|)^2} \right]^{\frac{1}{2}}$$

and the function minimized during least squares refinement was

$$\sum w (|F_o| - 1/k |F_c|)^2.$$

A difference Fourier map (2) was then calculated to locate hydrogen positions. The twelve ring hydrogens were located and refinement of their positions along with the other atoms resulted in an $R = 0.048$ and $R_{wtd} = 0.050$. A second difference map was calculated in order to locate methyl hydrogens. The electron density around the methyl carbon atoms was a doughnut-shaped band, suggesting almost free rotation of the methyl groups around the C-Me bond. An attempt to refine hydrogen atoms in areas of slightly higher electron

density within the doughnut, resulted in temperature factors of approximately twenty and hydrogen positions making no chemical sense and hence, were not included in the final structure.

Refinement of the structure was continued including only those hydrogens on the phenyl rings until the shifts in the parameters were less than one half of their standard deviations. The R-index remained at 0.048 and an R_{wtd} of 0.050 during the final refinement. The observed and calculated structure factors are listed in Table 2. The positional parameters of the non-hydrogen atoms are listed in Table 3, the thermal parameters for the non-hydrogen atoms are listed in Table 4, and the hydrogen atom parameters are listed in Table 5.

Discussion of the structure

A drawing illustrating the thermal ellipsoids (13) for the molecule of S,S,S-tri-p-tolyl phosphorotrithioate is shown in Figure 2. The bond lengths are listed in Table 6 and bond angles in Table 7. The bond lengths and angles are also illustrated in Figure 3.

All atoms in the molecule lie in general positions. The coordination around the phosphorus is a distorted tetrahedron with the three sulfurs bent away from the oxygen at angles of 116.7, 116.9, and 116.2° for S(1), S(2), and S(3) respectively. The angles S(1)-P-S(3), S(2)-P-S(3), and S(1)-P-S(2) are 100.7, 101.4, and 102.3° respectively. The molecule has nearly C_3 symmetry

TABLE 3

Positional parameters of non-hydrogen atoms
in S,S,S-tri-p-tolyl phosphorotrithioate.

Atom	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
S(1)	0.0323(2) ^a	0.4718(1)	-0.3000(1)
S(2)	0.1606(2)	0.4600(1)	-0.0890(1)
S(3)	-0.0916(1)	0.3282(1)	-0.1714(1)
P	0.1018(1)	0.3792(1)	-0.2007(1)
O	0.2059(3)	0.3135(2)	-0.2228(2)
C(1)	0.0372(6)	0.4093(3)	-0.4007(3)
C(2)	0.1480(6)	0.4224(4)	-0.4506(4)
C(3)	0.1465(6)	0.3819(4)	-0.5334(4)
C(4)	0.0376(5)	0.3271(3)	-0.5699(3)
C(5)	-0.0698(6)	0.3144(4)	-0.5177(4)
C(6)	-0.0722(6)	0.3543(4)	-0.4342(4)
C(7)	0.0359(5)	0.2843(3)	-0.6632(3)
C(8)	0.3259(6)	0.5010(4)	-0.1164(3)
C(9)	0.3358(7)	0.5868(4)	-0.1486(4)
C(10)	0.4652(7)	0.6217(4)	-0.1636(3)
C(11)	0.5878(7)	0.5712(4)	-0.1486(3)
C(12)	0.5757(7)	0.4845(4)	-0.1171(3)
C(13)	0.4468(7)	0.4508(4)	-0.1012(4)
C(14)	0.7325(6)	0.6105(4)	-0.1657(4)
C(15)	-0.0394(5)	0.2582(3)	-0.0762(3)
C(16)	0.0277(6)	0.1782(4)	-0.0843(4)
C(17)	0.0576(6)	0.1249(4)	-0.0082(4)
C(18)	0.0201(6)	0.1483(4)	0.0756(3)
C(19)	-0.0478(7)	0.2285(4)	0.0811(4)
C(20)	-0.0766(7)	0.2839(4)	0.0059(4)
C(21)	0.0521(6)	0.0876(4)	0.1590(3)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 4

Thermal parameters of non-hydrogen atoms

in S,S,S-tri-p-tolyl phosphorotrithioate.

<u>Atom</u>	<u>β_{11}</u> ^{a,b}	<u>β_{22}</u>	<u>β_{33}</u>	<u>β_{12}</u>	<u>β_{13}</u>	<u>β_{23}</u>
S(1)	216(3) ^c	45(1)	47(1)	14(1)	7(1)	4(1)
S(2)	180(2)	69(1)	46(7)	-18(1)	20(1)	-13(1)
S(3)	135(2)	60(1)	58(1)	-1(1)	3(1)	11(1)
P	141(2)	45(1)	42(1)	3(1)	4(1)	0(1)
O	144(5)	56(2)	56(2)	19(3)	8(2)	0(2)
C(1)	131(8)	42(3)	45(3)	5(4)	-1(4)	8(2)
C(2)	118(9)	62(4)	57(3)	-25(5)	-1(5)	3(3)
C(3)	125(9)	70(4)	57(3)	-8(5)	33(5)	0(3)
C(4)	117(7)	40(3)	57(3)	5(4)	15(4)	8(2)
C(5)	129(9)	63(4)	66(4)	-30(5)	13(5)	-10(3)
C(6)	140(9)	66(4)	56(3)	-9(5)	30(5)	-3(3)
C(7)	206(9)	60(3)	46(3)	-1(5)	23(4)	-16(2)
C(8)	146(9)	47(3)	36(2)	-2(4)	5(4)	-6(2)
C(9)	171(10)	58(4)	52(3)	18(6)	2(5)	3(3)
C(10)	200(11)	58(4)	53(3)	-14(6)	16(5)	9(3)
C(11)	203(11)	64(4)	37(3)	1(6)	7(4)	-7(3)
C(12)	141(10)	63(4)	47(3)	13(6)	10(4)	-10(3)
C(13)	205(12)	40(3)	45(3)	-5(6)	7(5)	-4(3)
C(14)	155(9)	110(5)	88(4)	-43(7)	35(5)	5(4)
C(15)	129(8)	49(3)	46(3)	-5(4)	12(4)	0(2)

TABLE 4

(Continued)

<u>Atom</u>	<u>β_{11}</u>	<u>β_{22}</u>	<u>β_{33}</u>	<u>β_{12}</u>	<u>β_{13}</u>	<u>β_{23}</u>
C(16)	159(9)	56(3)	47(3)	9(4)	19(4)	1(3)
C(17)	160(9)	54(3)	62(4)	20(5)	14(4)	1(3)
C(18)	157(9)	57(3)	54(3)	-14(4)	-1(4)	-6(3)
C(19)	290(13)	61(4)	45(3)	7(6)	17(5)	-7(3)
C(20)	249(12)	52(4)	61(4)	9(5)	19(5)	-7(3)
C(21)	256(11)	74(4)	47(3)	-4(5)	-13(4)	22(3)

^aThe β_{ij} 's have been multiplied by 10^4 .

^bThe form of the anisotropic thermal ellipsoids is

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl).$$

^cThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 5

Hydrogen atom parameters in
S,S,S-tri-p-tolyl phosphorotrithioate.

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>Biso</u>
H(1)	0.222(4) ^a	0.455(2)	-0.433(2)	2.5(1.0)
H(2)	0.219(4)	0.394(3)	-0.564(3)	4.2(1.1)
H(3)	-0.139(4)	0.285(3)	-0.535(3)	4.0(1.3)
H(4)	-0.143(5)	0.347(3)	-0.395(3)	5.4(1.2)
H(5)	0.255(4)	0.622(2)	-0.163(2)	5.0(1.3)
H(6)	0.460(4)	0.687(3)	-0.194(2)	6.9(1.3)
H(7)	0.657(4)	0.448(2)	-0.109(2)	4.8(1.3)
H(8)	0.442(3)	0.403(2)	-0.078(2)	3.1(1.2)
H(9)	0.49(4)	0.160(3)	-0.147(3)	4.5(1.0)
H(10)	0.103(4)	0.072(3)	-0.015(3)	4.7(1.2)
H(11)	-0.076(5)	0.250(3)	0.142(3)	6.6(1.3)
H(12)	-0.123(6)	0.342(4)	0.007(3)	9.4(1.8)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

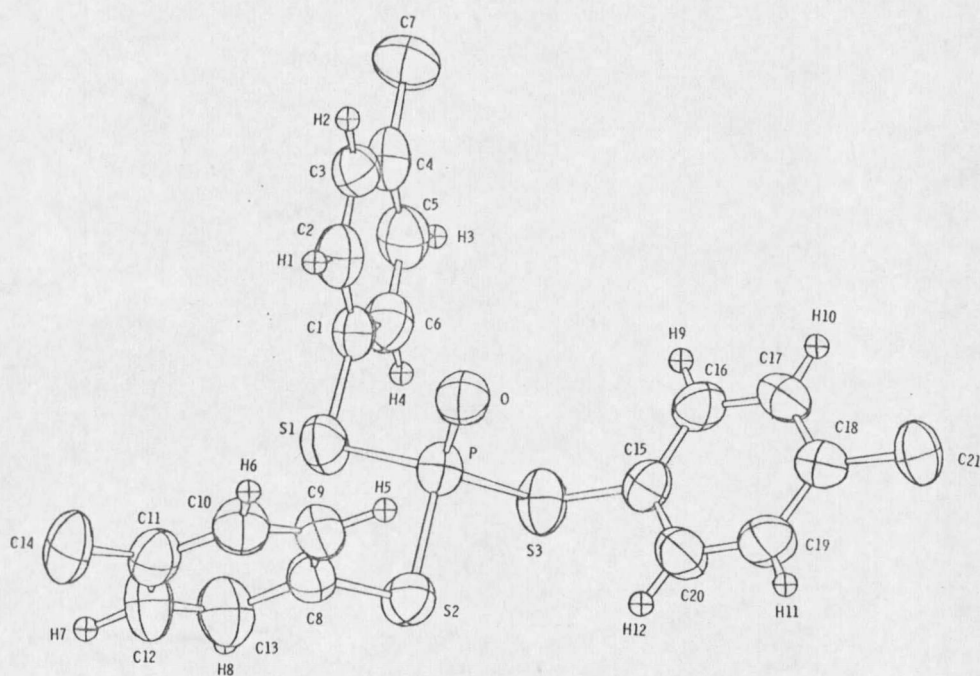


Figure 2.

Molecular structure of
S,S,S-tri-p-tolyl phosphorotrithioate
illustrating the thermal ellipsoids.

TABLE 6

Bond distances in
S,S,S-tri-p-tolyl phosphorotrithioate

<u>Bond</u>	<u>distance</u>	<u>Bond</u>	<u>distance</u>
S(1)-P	2.072(2) ^a	C(12)-C(13)	1.371(10)
S(1)-C(1)	1.774(5)	C(15)-C(16)	1.366(7)
S(2)-P	2.075(2)	C(15)-C(20)	1.373(8)
S(2)-C(8)	1.779(5)	C(16)-C(17)	1.386(8)
S(3)-P	2.084(2)	C(17)-C(18)	1.387(8)
S(3)-C(15)	1.781(5)	C(18)-C(19)	1.369(8)
P-O	1.459(3)	C(18)-C(21)	1.537(7)
C(1)-C(2)	1.379(8)	C(19)-C(20)	1.392(8)
C(1)-C(6)	1.367(8)	C(2)-H(1)	0.87(4)
C(2)-C(3)	1.374(8)	C(3)-H(2)	0.89(4)
C(3)-C(4)	1.375(8)	C(5)-H(3)	0.81(4)
C(4)-C(5)	1.372(8)	C(6)-H(4)	0.94(4)
C(4)-C(7)	1.529(7)	C(9)-H(5)	0.93(3)
C(5)-C(6)	1.385(8)	C(10)-H(6)	1.08(4)
C(8)-C(9)	1.376(8)	C(12)-H(7)	0.94(4)
C(8)-C(13)	1.365(9)	C(13)-H(8)	0.80(3)
C(9)-C(10)	1.378(10)	C(16)-H(9)	1.02(4)
C(10)-C(11)	1.381(9)	C(17)-H(10)	0.92(4)
C(11)-C(12)	1.387(9)	C(19)-H(11)	1.03(4)
C(11)-C(14)	1.544(8)	C(20)-H(12)	0.92(4)

^aThe number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE 7

Bond angles for S,S,S-tri-p-tolyl phosphorotrithioate.

Atoms	Degrees	Atoms	Degrees	Atoms	Degrees
P-S(1)-C(1)	102.3(2) ^a	C(9)-C(8)-C(13)	118.4(5)	C(4)-C(3)-H(2)	121.(3)
P-S(2)-C(8)	98.8(2)	C(8)-C(9)-C(10)	120.8(5)	C(4)-C(5)-H(3)	122.(3)
P-S(3)-C(15)	102.7(2)	C(9)-C(10)-C(11)	121.1(6)	C(6)-C(5)-H(3)	115.(3)
S(1)-P-S(2)	102.3(1)	C(10)-C(11)-C(12)	117.4(5)	C(5)-C(6)-H(4)	127.(3)
S(1)-P-S(3)	100.7(1)	C(10)-C(11)-C(14)	120.9(5)	C(1)-C(6)-H(4)	114.(3)
S(1)-P-O	116.7(1)	C(12)-C(11)-C(14)	121.7(5)	C(8)-C(9)-H(5)	121.(2)
S(2)-P-S(3)	101.4(1)	C(11)-C(12)-C(13)	121.0(6)	C(10)-C(9)-H(5)	119.(2)
S(2)-P-O	116.9(1)	C(12)-C(13)-C(14)	121.3(6)	C(9)-C(10)-H(6)	115.(2)
S(3)-P-O	116.2(1)	S(3)-C(15)-C(16)	121.9(4)	C(11)-C(10)-H(6)	124.(2)
S(1)-C(1)-C(2)	119.1(4)	S(3)-C(15)-C(20)	118.1(4)	C(11)-C(12)-H(7)	119.(2)
S(1)-C(1)-C(6)	121.7(4)	C(16)-C(15)-C(20)	119.9(5)	C(13)-C(12)-H(7)	120.(2)
C(2)-C(1)-C(6)	119.0(5)	C(15)-C(16)-C(17)	118.7(5)	C(12)-C(13)-H(8)	120.(2)
C(1)-C(2)-C(3)	120.2(5)	C(16)-C(17)-C(18)	123.0(5)	C(8)-C(13)-H(8)	118.(2)
C(2)-C(3)-C(4)	122.6(5)	C(17)-C(18)-C(19)	116.8(5)	C(15)-C(16)-H(9)	118.(2)
C(3)-C(4)-C(5)	115.7(5)	C(17)-C(18)-C(21)	122.3(5)	C(17)-C(16)-H(9)	123.(2)
C(3)-C(4)-C(7)	121.9(4)	C(19)-C(18)-C(21)	120.9(5)	C(16)-C(17)-H(10)	117.(3)
C(5)-C(4)-C(7)	122.5(5)	C(18)-C(19)-C(20)	121.2(6)	C(18)-C(17)-H(10)	120.(3)
C(4)-C(5)-C(6)	123.4(5)	C(19)-C(20)-C(15)	120.4(6)	C(18)-C(19)-H(11)	120.(3)
C(5)-C(6)-C(1)	119.2(5)	C(1)-C(2)-H(1)	124.(2)	C(20)-C(19)-H(11)	119.(3)
S(2)-C(8)-C(9)	120.2(4)	C(3)-C(2)-H(1)	116.(2)	C(19)-C(20)-H(12)	124.(3)
S(2)-C(8)-C(13)	121.4(4)	C(2)-C(3)-H(2)	117.(3)	C(15)-C(20)-H(12)	115.(3)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

Bond distances and angles for S,S,S-tri-p-tolyl phosphorotrithioate.

with the C_3 axis passing through the P=O bond.

An explanation for the sulfurs being bent away from the oxygen atom may be that the tolyl groups, being directed upward toward the oxygen atom, results in steric repulsion between the tolyl groups and the oxygen atom. The steric strain can be relieved by increasing the O-P-S angles.

The P-S(1), P-S(2), and P-S(3) bond distances are 2.072, 2.075, and 2.084 Å respectively. The P-S(3) bond length is 4-6 standard deviations longer than the P-S(1) and P-S(2) bond lengths, a difference which may be significant. The P-S(1) and P-S(2) bonds are not significantly different. All three P-S bond lengths may be considered normal. The P=O bond length of 1.459 Å is within the normal range, (1.42-1.52 Å).

Bond angles P-S(1)-C(1), P-S(2)-C(8), and P-S(3)-C(15) are 102.3, 99.8, and 102.7° respectively. These are normal P-S-C angles except when one considers that there are two bulky groups on either end of the bond. The oxygen atom is separated from the aromatic rings by only the sum of the van der Waals radii, approximately 3.27 Å. One might expect that the steric repulsion may be relieved by increasing the P-S-C angles which may have happened for the O-P-S angles. These seemingly small angles may result from overlap of orbitals between the phosphorus atom and the C(1), C(8), and C(15) atoms. The structure shows that these phosphorus to carbon atom distances are 2.954, 3.024, and 3.001 Å respectively, which are close enough to produce some overlap of orbitals

from phosphorus and the orbitals of the aromatic carbon atoms; however, the structure also shows that the phosphorus atom does not lie within the inner circumference of the aromatic ring as was suggested by R. A. Shaw (17) for this compound as in shown in figure 4. This arrangement may allow some type of bonding interaction between the phosphorus and carbon atoms to take place; however, the overlap model for the bonding proposed by Griffin and Gordon (11) does not seem to adequately describe the bonding. In their overlap model they attribute the observed long-range coupling between the phosphorus nucleus and the methyl protons to overlap between the vacant d-orbitals of the phosphorus and the aromatic π -system. However, it is believed that the Fermi contact term (23) is the dominant term in determining coupling in a liquid or gas, and is a measure of the probability of the bonding pair of electrons existing at both nuclei. Since d-orbitals have zero probability for electrons at the nucleus, they cannot contribute to the coupling; whereas, s-orbitals do have a finite probability at the nucleus and can contribute to coupling. Therefore, if some type of bonding does exist between the phosphorus and the aromatic π -system which enhances long-range coupling, then it should involve some s-orbital character.

The tolyl groups were found to be approximately perpendicular to the planes of the P-S-C bonds. The dihedral angles for the planes P, S(1), C(1) and C(2), C(1), C(6); P, S(2), C(8) and C(9), C(8), C(13); and P, S(3), C(15) and C(16), C(15), C(20) are 80.5, 78.5, and 70.4° respectively and are shown in

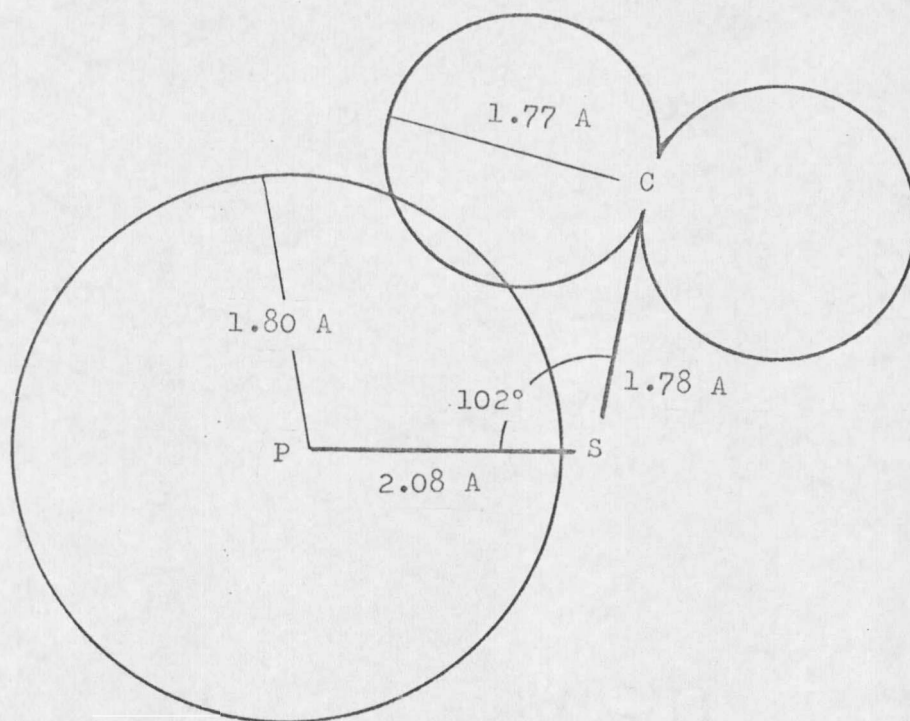


Figure 4.

Geometrical relationship of the P-S-C bonds showing the overlap of the vanderWaals radii for the phosphorus and carbon atoms.

Figure 5. The tolyl groups are planar within experimental error with the largest deviation 0.02 Å from planarity. The least squares equations for the planes of the tolyl groups are given in Table 8. The sulfurs are 0.10, 0.11, and 0.15 Å from the planes of the tolyl groups, indicating a bend in the C-S bond. The sulfurs are bent out of the plane 3.8, 4.2, and 5.8° for S(1), S(2), and S(3) respectively. Figure 6 shows the direction of distortion in the C-S bond. This distortion of the bond would indicate that the sp^2 hybridization of the carbon atom may have been slightly altered and the s-character of the bonding orbitals increased.

The aromatic C-C bonds are probably equivalent within experimental error and range from 1.365-1.392 Å and average 1.377 Å which are normal bond lengths for an aromatic ring. The bond angles for the tolyl groups range from 115.7-123.4° and average 120.0°. The bond angles are probably significantly different over this range. The C(3)-C(4)-C(5), C(10)-C(11)-C(12), and C(17)-C(18)-C(19) bonds appear to be the smallest angles in the rings and are located on the methyl end of the aromatic ring. The C-Me bonds are 1.529, 1.544, and 1.537 Å for C(4)-C(7), C(11)-C(14), and C(18)-C(21) respectively and are not significantly different.

A stereographic packing diagram (13) for the crystal is shown in Figure 7. It is unlikely that packing is responsible for the effects discussed here, since there are no intermolecular distances less than the sum of the van der Waals

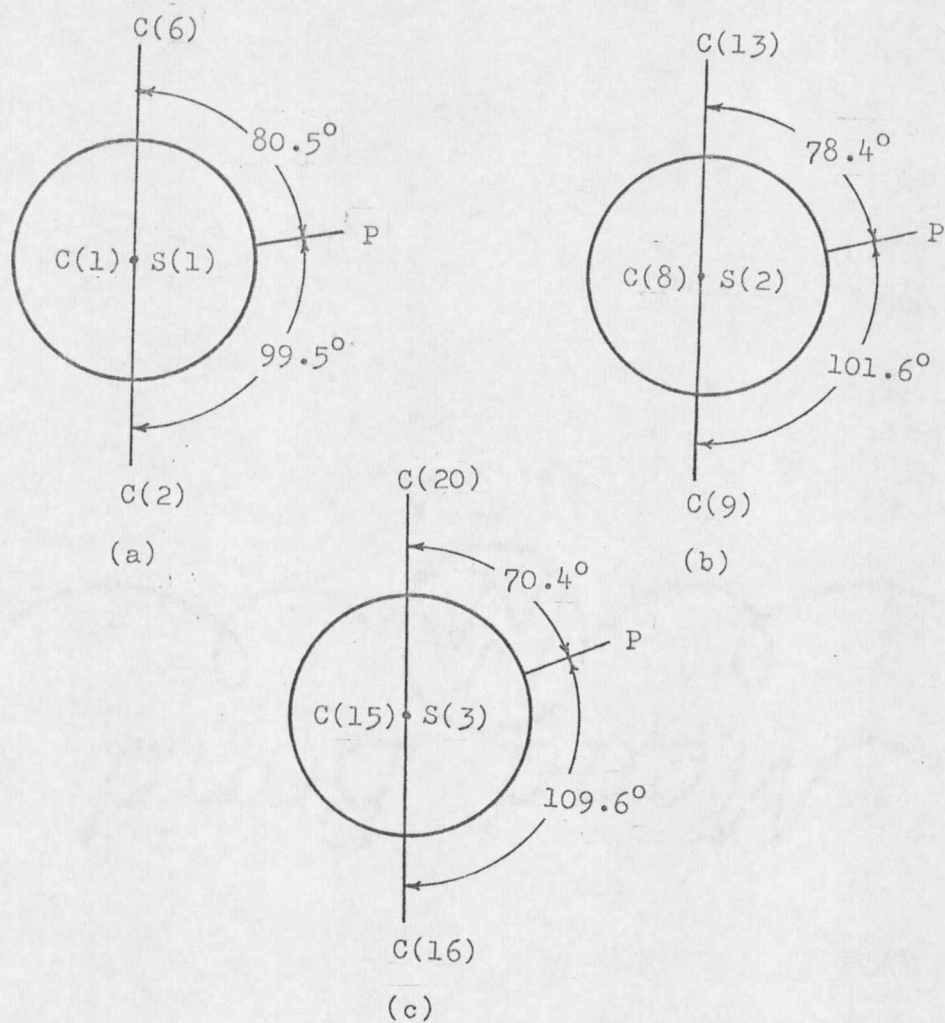


Figure 5.

- a) Dihedral angles between planes C(2), C(1), C(6) and P, S(1), C(1) looking down the C(1)-S(1) bond,
- b) planes C(9), C(8), C(13) and P, S(2), C(8) looking down the C(8)-S(2) bond, and
- c) planes C(16), C(15), C(20) and P, S(3), C(15) looking down the C(15)-S(3) bond.

TABLE 8

Equations of Least Squares Planes Referred to
Orthogonal Axes for P(O) (SC₆H₄-p-Me)₃^a

Atoms in the plane	ℓ	m	n	p(A)	$S(A^2) \times 10^4$
C(1), C(2), C(3), C(4), C(5), C(6)	-0.4489	0.8237	-0.3463	7.267	1.48
C(1), C(2), C(3), C(4), C(5), C(6), C(7)	-0.4496	0.8268	-0.3380	7.23	9.33
C(8), C(9), C(10), C(11), C(12), C(13)	0.0362	0.3399	0.9397	1.026	1.07
C(8), C(9), C(10), C(11), C(12), C(13), C(14)	0.0344	0.3391	0.9401	1.012	1.45
C(15), C(16), C(17), C(18), C(19), C(20)	0.8856	0.4644	0.0023	1.329	1.60
C(15), C(16), C(17), C(18), C(19), C(20), C(21)	0.8861	0.4635	0.0036	1.326	1.96
P-S(1)-C(1)	0.9559	0.2921	-0.03031	4.254	---
P-S(2)-C(8)	-0.4124	0.7744	-0.4798	5.254	---
P-S(3)-C(15)	-0.1713	0.7725	0.6114	2.329	---

$$^aX = x + z \cdot \cos \beta; \quad Y = y; \quad Z = x \cdot \sin \beta$$

$$\text{L.S. plane: } \ell X + mY + nZ - P = 0$$

S = sum of squares of deviations of atoms from the plane.

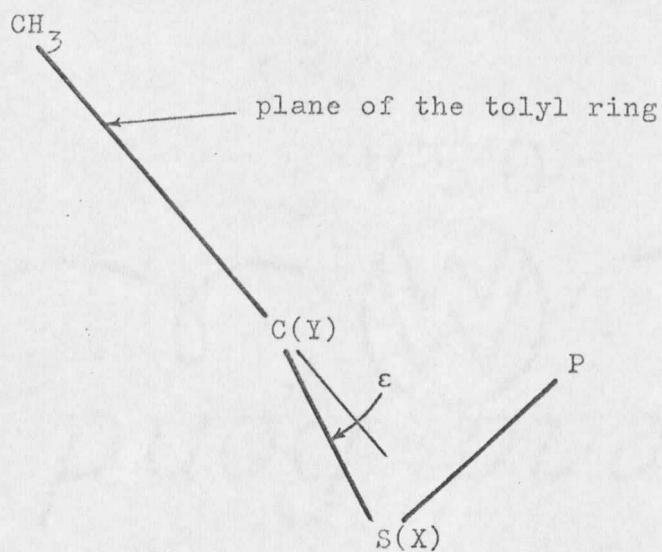


Figure 6.

Distortion of the three P-S bonds in
 $\text{PO}(\text{SC}_6\text{H}_4\text{-p-Me})_3$ where,

$$X = 1, Y = 1; \quad \epsilon = 3.8^\circ$$

$$X = 2, Y = 8; \quad \epsilon = 4.2^\circ$$

$$X = 3, Y = 15; \quad \epsilon = 5.8^\circ.$$

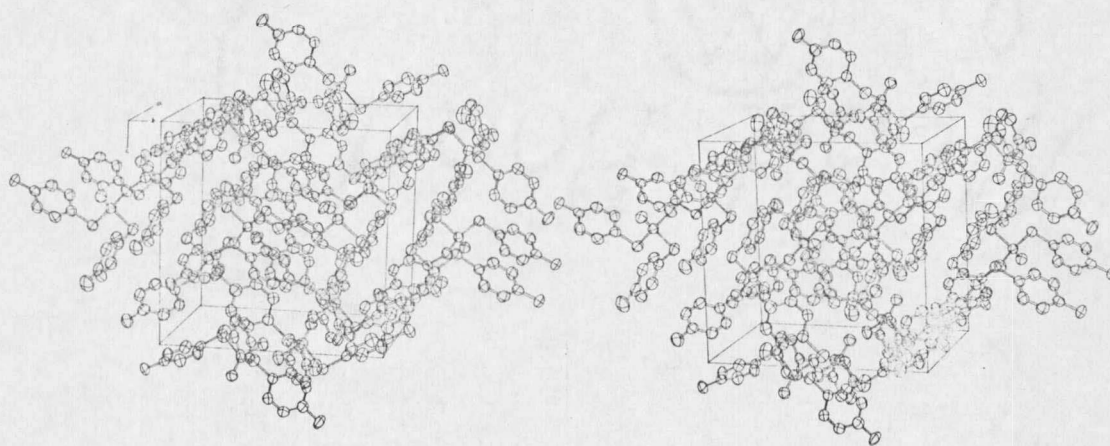


Figure 7.

Stereographic packing diagram of
S,S,S-tri-p-tolyl phosphorotrithioate.

radii. The pertinent van der Waals radii used are given by Bondi (8): P, 1.80; S, 1.80; double bonded O, 1.50; aromatic C, 1.77; aliphatic C, 1.70; and aromatic H, 1.0 Å.

SUMMARY AND CONCLUSIONS

The structure of S,S,S-tri-p-tolyl phosphorotrithioate provides facts which lead to a better understanding of the mechanism for long range phosphorus-hydrogen coupling in aromatic esters and thioesters of phosphorus(V).

The details of the structure appear to support, in general, the idea of a possible overlap between the phosphorus atom and the aromatic ring as proposed by Griffin and Gordon for the benzyl phosphorus compound (11); however, the structure shows that the phosphorus does not lie over the inner circumference of the aromatic ring as was proposed by Griffin and Gordon for the benzyl compound and by R. A. Shaw for the S,S,S-tri-p-tolyl phosphorotrithioate compound (17).

According to the proposed overlap model, the angle between phosphorus, the linking atom, and the plane of the π -electron system (P-X-C), may well be critical to the value of $^7J_{P-H}$. With oxygen being the linking heteroatom, as in P(O) (OC₆H₄-p-Me)₃, the P-X-C angles are approximately 120° and $^7J_{P-H}$ is 0.7 Hz in CCl₄ (17). The P-S-C angles in S,S,S-tri-p-tolyl phosphorotrithioate, P(O) (SC₆H₄-p-Me)₃, are 102.3, 98.8, and 102.7° which may facilitate a greater overlap of the orbitals involved and, in consequence, the largest values to date, $^7J_{P-H}$, 2.0 Hz for P(O) (SC₆H₄-p-Me)₃ in CCl₄, are obtained for compounds containing the P-S-C system.

PART II

1,3,2-Dioxaphosphorinanes

INTRODUCTION

The 2-oxo or thio-1,3,2-dioxaphosphorinanes, having lone substituents on the ring carbon atoms as shown in Figure 8(b) and (c), are of importance in considering the effects of substituents on the conformation of the ring, and those with a single substituent on the C(5) position are of interest in providing information about the preferred orientation of the groups on the ring. Steric effects of the C(5) substituent can be compared with those on the phosphorus atom.

Unsubstituted or 5,5-disubstituted 2-oxo-1,3,2-dioxaphosphorinanes, such as shown in Figure 8(a), have been studied by n.m.r. (10), dipole moment (14), and in a few cases X-ray crystallography (5). However, molecules having lone substituents on the ring carbon atoms have only recently been investigated (15).

The use of n.m.r. spectroscopy has been the most extensively used technique for these studies; however, n.m.r. does not permit an unambiguous assignment of the stereochemistry at phosphorus. X-ray crystallography does lend itself to unambiguously determining the stereochemistry.

The 2-oxo or thio-1,3,2-dioxaphosphorinanes present a unique opportunity for studies of six-membered ring systems since, unlike many other compounds containing six-membered rings, they tend to be crystalline solids

lending themselves to X-ray crystallographic studies.

Previously only one 2-oxo-1,3,2-dioxaphosphorinane with a lone substituent on the ring carbon atoms has been investigated using X-ray crystallography (15), which is shown in Figure 8(b). This investigation continues that study and contributes three additional crystal structures: 1) 5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane, 2) 5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane, and 3) 2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane, which are shown in Figure 8(c).

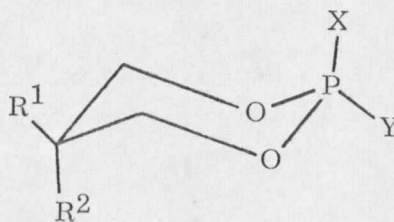


Figure 8.

- (a) $Y = O, R' = H, R^2 = H, X = OH$
 $Y = O, R' = H, R^2 = H, X = OPh$
 $Y = O, R' = Me, R^2 = CH_2Br, X = Br$
- (b) $Y = O, R' = t\text{-butyl}, R^2 = H, X = Me$
- (c) $Y = O, R' = H, R^2 = t\text{-butyl}, X = OMe$
 $Y = S, R' = t\text{-butyl}, R^2 = H, X = Ph$
 $Y = t\text{-butyl}, R' = H, R^2 = t\text{-butyl}, X = S$

THE CRYSTAL AND MOLECULAR STRUCTURE OF
5-t-BUTYL-2-METHOXY-2-OXO-1,3,2-DIOXAPHOSPHORINANE ($C_8PO_4H_{17}$)

Preparation

The crystals were supplied by Wesley G. Bentrude and were prepared as described in the literature (15).

The crystal used for X-ray analysis was a colorless, transparent, parallelepiped with approximate dimensions 0.3 x 0.5 x 1.0 mm. This was sealed in a Lindeman glass capillary to prevent loss by sublimation.

Density

The density of the crystals was measured by the flotation method, as described in Part I, page 5. The calculated density was based on four molecules per unit cell; $D_{\text{exp}} = 1.25 \text{ g/cm}^3$ and $D_{\text{calc}} = 1.277 \text{ g/cm}^3$.

Determination of tentative cell dimensions and space group

Weissenberg photographs of the X-ray diffraction pattern for the crystal $C_8PO_4H_{17}$, indicated orthorhombic symmetry. The axis along which the crystal was mounted was designated as a . The tentative unit cell dimensions were found to be $a = 6.13$, $b = 10.3$, and $c = 17.6 \text{ \AA}$ in accordance with the convention $a > b > c$. A unit cell of these dimensions would require four molecules to agree with its measured density. The extinctions based on this cell were:

hkl : no conditions
 $hk0$: $h \neq 2n$
 $0kl$: $k + l \neq 2n$
 $h0l$: no conditions
 $h00$: $h \neq 2n$
 $0k0$: $k \neq 2n$
 $00l$: $l \neq 2n$.

These extinctions corresponded to either space group $Pn2_1a$ or $Pnma$ where the former is a non-centrosymmetric space group and the latter is centrosymmetric. Solution of the structure showed the correct space group to be $Pnma$.

Determination of accurate unit cell dimensions

The determination of accurate cell parameters was obtained by the same procedure described in Part I, page 6. Twelve three-dimensional reflections were selected for which precise measurements of the $+2\theta$ and -2θ angles were made. The crystal data are listed in Table 9.

Data collection

Data were collected on the General Electric XRD-5 Diffractometer, equipped with a scintillation counter, pulse-height discriminator, and a G. E. single crystal orienter, using θ - 2θ scan technique and zirconium filtered molybdenum K_{α} radiation. The crystal was mounted with the a axis parallel to the spindle axis. Each peak was scanned for 100 seconds and the backgrounds on each side of the peak were counted for 50 seconds. The scan rate was 2° per minute with a takeoff angle of 4° .

TABLE 9

Crystal Data

5-t-Butyl-2-Methoxy-2-Oxo-1,3,2-Dioxaphosphorinane

 $C_8PO_4H_{17}$

F.W. 208.19

F(000) 448

Orthorhombic, space group Pnma

 $a = 6.123(4)$ $\alpha = 90^\circ$ $b = 10.02(1)$ $\beta = 90^\circ$ $c = 17.65(1)$ $\gamma = 90^\circ$ Volume of the unit cell =
1083. Å³ $D_{\text{exp}} =$
1.25 g/cm³Molecules/unit cell =
4 $D_{\text{calc}} =$
1.277 g/cm³

Intensities of 1008 unique reflections were measured of which 585 were considered observed, using the criterion $I \geq 2 \sigma(I)$. Three standard reflections (114, 121, and 131 reflections) were checked approximately every four hours during data collection and remained constant with an average deviation of 1.4%, indicating no deterioration of the crystal.

Structure factors (F_o) were calculated from the intensities by applying the usual Lorentz-polarization correction, weights were calculated from standard deviations as was described in Part I, page 7.

No absorption or extinction corrections were made. The linear absorption coefficient of $C_8PO_4H_{17}$ for $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) is $\mu = 2.41 \text{ cm}^{-1}$. The transmission factors for X-rays passing through the maximum and minimum dimensions of the crystal are approximately 0.73 and 0.93 respectively; this range corresponds to approximately 12% variation about a mean intensity value. Scattering factors for the non-hydrogen atoms and anomalous scattering corrections ($\Delta f'$ and $\Delta f''$), for phosphorus were taken from the International Tables (12). Scattering factors for hydrogen were taken from Steward, et. al. (20).

Structure determination

The space group was initially thought to be the non-centrosymmetric space group $Pn2_1a$, since there were four molecules per unit cell and $Pn2_1a$

has four general positions, which would indicate that each molecule would have to contain a symmetry element. Since there was no apparent symmetry element contained in the molecule, the centrosymmetric space group $Pn2_1a$ was used to solve the structure.

The positions of the phosphorus atoms were found from the Patterson synthesis (2). Using the phosphorus atom positions, the structure factor calculation (1) gave an R-index of 0.55, ($R = \sum |F_o - F_c| / \sum |F_o|$). A Fourier map (2) revealed the position of an oxygen and a structure factor calculation gave an R-index of 0.50. A subsequent Fourier synthesis revealed peaks for the remaining non-hydrogen atoms, plus, an additional peak. There were two peaks of equal intensity at the right distance from the methoxy oxygen to be bonded to it. The intensities were about one half that of the other carbons. This suggested that the methoxy carbon atom was disordered and to be found in one position or the other about 50% of the time.

Refinement

Refinement was begun using the block diagonal approximation to the least squares method (1) and phasing one half a methoxy carbon in each of the possible positions suggested by the Fourier map. Calculation of bond lengths revealed that the bonds were long on one side of the ring and short on the other. The atoms on a line through the center of the molecule, including the P(2),

O(13), O(14), C(5), C(7), and C(10), appeared to be shifted along the b axis. This was suggestive of some restriction imposed by the space group which prohibit atoms being located along the line bisecting the ring. Upon examination of the molecule, it was evident that the molecule could be placed on a mirror plane with the methoxy carbon atom located on either side of the mirror 50% of the time. Placing the molecule on the mirror plane allows it to be placed in a unit cell of symmetry Pnma rather than the non-centrosymmetric space group Pn2₁a.

Further refinement of the non-hydrogen atoms in space group Pnma along with anisotropic temperature factors was carried out using the full matrix least squares (9). An R of 0.086 and R_{wtd} of 0.083 were obtained, where $R_{wtd} = [\sum (\sqrt{w} |F_o - F_c|)^2 / \sum (\sqrt{w} |F_o|)^2]^{\frac{1}{2}}$ and the function minimized during least squares refinement was $\sum w (|F_o| - 1/k |F_c|)^2$.

A difference Fourier map was then calculated to location hydrogen atom positions, in which the quantities $|F_o - F_c|$ were used as coefficients of Fourier terms. The map showed that many of the hydrogens were apparently disordered and could not be unambiguously resolved. This is probably the result of the disordered methoxy group presenting a number of different possible environments and steric requirements about any particular molecule.

One hydrogen on each methyl carbon was found to refine with reasonable bond length, temperature factor, and bond angle with reference to the carbon

skeleton. Using the refinable hydrogen for a reference, positions of the remaining methyl hydrogens were calculated. Positions for the methylene hydrogens were also calculated. Isotropic temperature factors assigned to the hydrogens were those of the carbon atom to which they were bonded, plus 0.5; bond lengths were assigned as 1.00 Å. Refinement was then continued including the calculated hydrogen positions and assigned temperature factors, which were not allowed to vary.

Refinement was continued until the parameter shifts for the non-hydrogen atoms were less than half their calculated standard deviations. The final R-index is 0.059 and R_{wtd} equals 0.060. The observed and calculated structure factors are listed in Table 10. The positional parameters of the non-hydrogen atoms are listed in Table 11, the thermal parameters for the non-hydrogen atoms are listed in Table 12, and the calculated hydrogen atom parameters are listed in Table 13.

Discussion of the structure

The molecule of 5-*t*-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane with its thermal ellipsoids is shown in Figure 9. The bond lengths are listed in Table 14 and the bond angles in Table 15. Diagrams of the bond lengths and bond angles are shown in Figure 10.

The molecules lie on a crystallographic mirror plane with the P(2),

TABLE 11

Positional parameters of non-hydrogen atoms in
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
P(2)	0.0333(4) ^a	0.2500(0)	0.0925(1)
O(1)	-0.0519(7)	0.3744(4)	0.0474(2)
O(3)	-0.0519(7)	0.1256(4)	0.0474(2)
O(13)	-0.1027(10)	0.2500(0)	0.1676(3)
O(14)	0.2676(10)	0.2500(0)	0.1010(4)
C(4)	-0.2771(10)	0.1268(6)	0.0207(4)
C(5)	-0.3285(14)	0.2500(0)	-0.0253(5)
C(6)	-0.2771(10)	0.3732(6)	0.0207(4)
C(7)	-0.2444(15)	0.2500(0)	-0.1076(6)
C(8)	-0.3308(13)	0.3738(7)	-0.1513(4)
C(9)	-0.3308(13)	0.1262(7)	-0.1513(4)
C(10)	0.0040(17)	0.2500(0)	-0.1143(5)
C(11)	-0.0850(30)	0.3519(14)	0.2234(7)
C(12)	-0.0850(30)	0.1481(14)	0.2234(7)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 12

Thermal parameters of non-hydrogen atoms in
5-*t*-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

Atom	$\beta_{11}^{a,b}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(2)	225(7) ^c	94(3)	23(1)	0(0)	10(2)	0(0)
O(1)	280(11)	51(3)	29(1)	-2(5)	-3(3)	1(1)
O(3)	280(11)	51(3)	29(1)	2(5)	-3(3)	-1(1)
O(13)	280(19)	124(7)	25(2)	0(0)	27(5)	0(0)
O(14)	208(17)	185(8)	37(2)	0(0)	-12(5)	0(0)
C(4)	262(19)	83(7)	32(2)	-38(9)	-5(5)	12(3)
C(5)	144(21)	114(10)	31(3)	0(0)	11(7)	0(0)
C(6)	262(19)	83(7)	32(2)	38(9)	-5(5)	-12(3)
C(7)	245(25)	99(10)	37(4)	0(0)	-19(8)	0(0)
C(8)	501(25)	117(8)	42(2)	-3(13)	-28(7)	14(4)
C(9)	501(25)	117(8)	42(2)	3(13)	-28(7)	-14(4)
C(10)	369(36)	209(14)	28(3)	0(0)	46(9)	0(0)
C(11)	749(64)	127(15)	31(4)	15(29)	61(15)	-21(7)
C(12)	749(64)	127(15)	31(4)	-15(29)	61(15)	21(7)

^aThe β_{ij} 's have been multiplied by 10^4 .

^bThe expression for the anisotropic thermal parameters is of the form:

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl).$$

^cThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 13

Calculated hydrogen positional parameters and
assigned thermal parameters in
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>Biso</u>
H(1)	-0.268	0.468	-0.009	4.3
H(2)	-0.391	0.406	0.057	4.3
H(3)	-0.503	0.250	-0.030	4.0
H(4)	-0.266	0.380	-0.207	6.4
H(5)	-0.292	0.457	-0.121	6.4
H(6)	-0.496	0.368	-0.153	6.4
H(7)	0.065	0.349	-0.094	5.8
H(8)	0.050	0.250	-0.168	5.8
H(9)	-0.099	0.306	0.267	5.6
H(10)	-0.193	0.424	0.216	5.6
H(11)	0.069	0.394	0.220	5.6

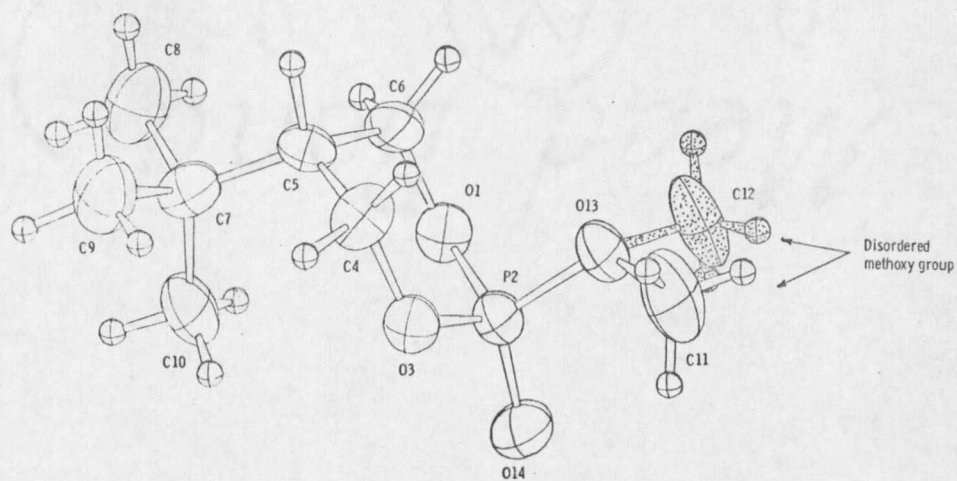


Figure 9.

Molecular structure of
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane
illustrating the thermal ellipsoids.

TABLE 14

Bond distances in

5-*t*-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

<u>Bond</u>	<u>distance, Å</u>	<u>Bond</u>	<u>distance, Å</u>
P(2)-O(1)	1.568(4) ^a	C(4)-C(5)	1.510(8)
P(2)-O(3)	1.568(4)	C(5)-C(6)	1.510(8)
P(2)-O(13)	1.567(6)	C(5)-C(7)	1.542(13)
P(2)-O(14)	1.443(6)	C(7)-C(8)	1.553(9)
O(1)-C(6)	1.457(7)	C(7)-C(9)	1.553(9)
O(3)-C(4)	1.457(7)	C(7)-C(10)	1.525(14)
O(13)-C(11)	1.422(14)		

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 15

Bond angles in

5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

<u>Atoms</u>	<u>angle, degrees</u>	<u>Atoms</u>	<u>angle, degrees</u>
O(1)-P(2)-O(3)	105.3(2) ^a	C(4)-C(5)-C(6)	109.6(6)
O(1)-P(2)-O(13)	104.6(3)	C(4)-C(5)-C(7)	115.9(6)
O(1)-P(2)-O(14)	112.6(3)	C(6)-C(5)-C(7)	115.9(6)
O(3)-P(2)-O(13)	104.6(3)	O(1)-C(6)-C(5)	112.2(5)
O(3)-P(2)-O(14)	112.6(3)	C(5)-C(7)-C(8)	110.7(6)
O(13)-P(2)-O(14)	116.1(3)	C(5)-C(7)-C(9)	110.7(6)
P(2)-O(1)-C(6)	118.2(4)	C(5)-C(7)-C(10)	114.0(6)
P(2)-O(3)-C(4)	118.2(4)	C(8)-C(7)-C(9)	106.0(6)
P(2)-O(13)-C(11)	123.1(7)	C(8)-C(7)-C(10)	107.5(6)
O(3)-C(4)-C(5)	112.2(5)	C(9)-C(7)-C(10)	107.5(6)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

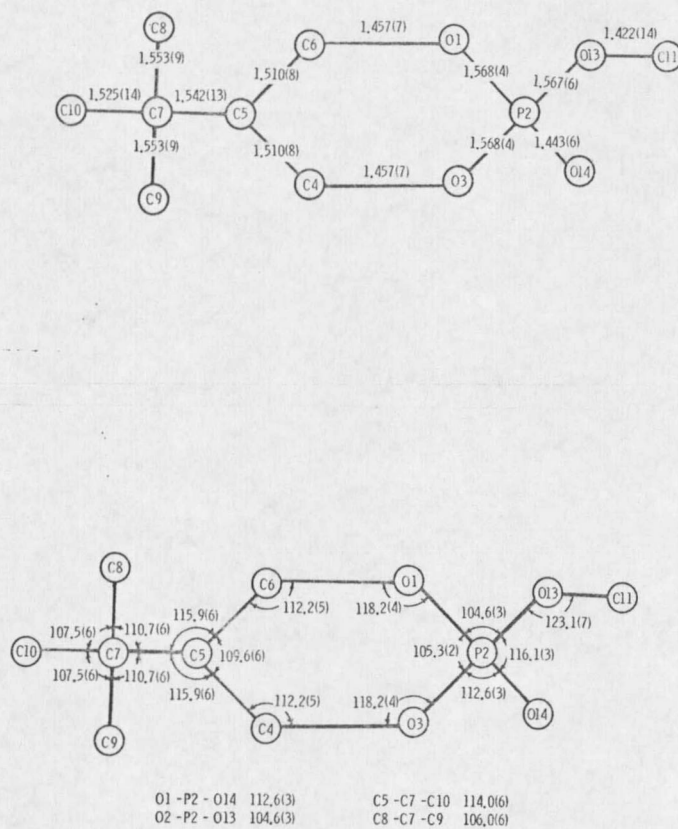


Figure 10.

Bond distances and bond angles of
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

O(13), O(14), C(5), C(7), and C(8) atoms located on the mirror in the special positions $y = 1/4$ and $3/4$. The methoxy carbon C(11), is found on either side of the mirror 50% of the time. The mirror requires that the bond lengths and bond angles are equal across the mirror plane.

The ring is a distorted chair with the t-butyl and methoxy groups trans to each other in axial positions. Dihedral angles between the ring plane O(1), O(3), C(4), C(6), and planes O(1), P(2), O(3), and C(4), C(5), C(6), are 37.9 and 49.9° respectively. The angles show a flattening of the ring as compared with 60° for an ideal chair. The equations of the planes are listed in Table 16. The torsional angles around the bonds of the ring are given in Table 17. The torsional angle about a bond is the dihedral angle between the planes defined by the two atoms involved in the bond plus the adjacent atom bonded on either end of the bond; e.g., the torsional angle about the P(2)-O(1) bond is the dihedral angle between the planes O(3), P(2), O(1) and P(2), O(1), C(6). These values show that the flattening of the ring is mostly on the phosphate end, with all other torsional angles near those expected for an ideal chair. More is said about the ring conformation later in the section comparing the 1,3,2-dioxaphosphorinanes on page 100.

P-O bond distances are 1.568 Å for the ring bonds. P(2)-O(1) or P(2)-O(3), and 1.567 Å for the phosphorus to methoxy bond, P(2)-O(13), and must be considered equal. The P=O bond of 1.44 Å is normal for tertiary organo-

TABLE 16

Equations of planes for

5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane^a

Atoms in plane	l	m	n	d
O(1), O(3), C(4), C(6)	-0.323	0.000	0.946	0.894
P(2), O(1), O(3)	-0.836	0.000	0.548	0.725
C(4), C(5), C(6)	-0.932	0.000	0.362	1.714

^aEquations of the plane: $lx + my + nz - d = 0.0$

TABLE 17

Torsional angles in the ring for
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane.

<u>Bond</u>	<u>Torsional angle, degrees</u>
P(2)-O(1)	44.1
O(1)-C(6)	53.4
C(6)-C(5)	55.7
C(5)-C(4)	55.7
C(4)-O(3)	53.4
O(3)-P(2)	44.1

phosphate esters. Bonding around the phosphorus forms a slightly distorted tetrahedron with angles ranging from 104.6 to 116.1° . The sum of the P-O bonds and the P=O bond is 6.15 ; most organo-phosphate esters have sums between 6.13 and 6.23 Å.

C-O bond distances in the ring of 1.46 are normal values for phosphate esters. The C-O bond of the methoxy group is somewhat shorter, 1.42 Å, than those in the ring. This distance is of the order of 3-4 standard deviations and may be significant. P-O-C bonds in the ring are 118° . The P-O-C bond angle for the methoxy group is 123° which is larger than the usual 120° , probably because of steric repulsions between the methyl and O(14) and O(1) or O(3).

C-C bonds in the ring are 1.51 Å and the C-C bonds in the t-butyl group range from 1.53 to 1.55 Å. The C(4)-C(5)-C(6) bond angle in the ring is 109.6° , a nearly perfect tetrahedral angle. The C-C-C bond angles of the t-butyl group range from 106.0 to 114.0° ; the largest angle C(5)-C(7)-C(10) is probably due to steric repulsions of the C(10) methyl with O(1), O(3), and O(14).

The disordered methoxy group, C(11) or C(12), is shown in a Newman projection along the P(2)-O(14) bond in Figure 11(a) and (b). The methyl is staggered and 6.7° closer to the O(14) atom than the ring oxygen. This agrees closely with the values found for the 2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane structure shown in Figure 11(c).

The packing diagram for the crystal is shown in the stereographic

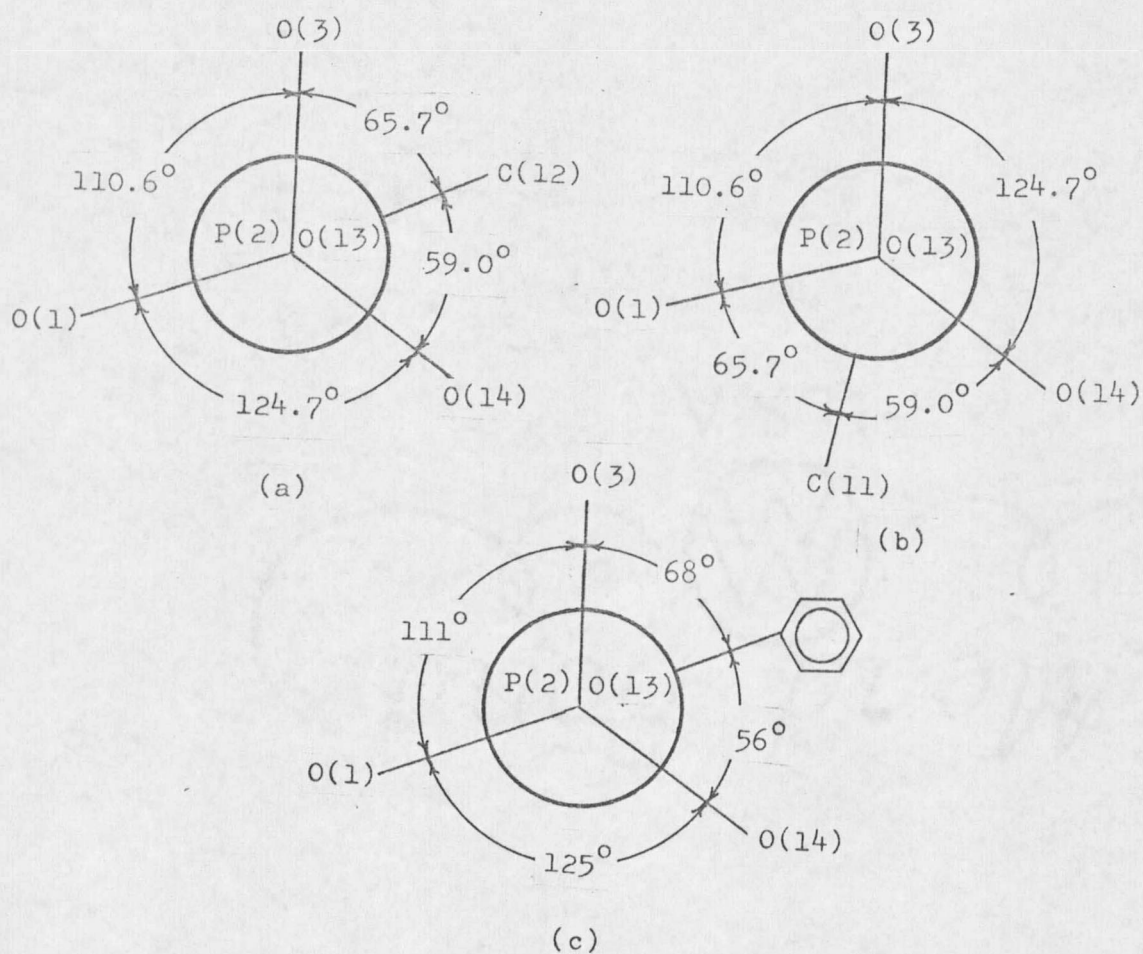


Figure 11.

Newman projections looking down the P(2)-O(13) bond for:

(a) and (b) the two possible configurations for

5-*t*-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane and

(c) 2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane.

diagram in Figure 12. Packing conditions are not likely to be an important factor in the conformation of the molecule since there are no intermolecular distances less than the sum of the van der Waals radii. Values of the van der Waals radii were obtained from Bondi (8), and the pertinent radii used were: P, 1.80; O, 1.52; C, 1.70; and H, 1.20 Å.

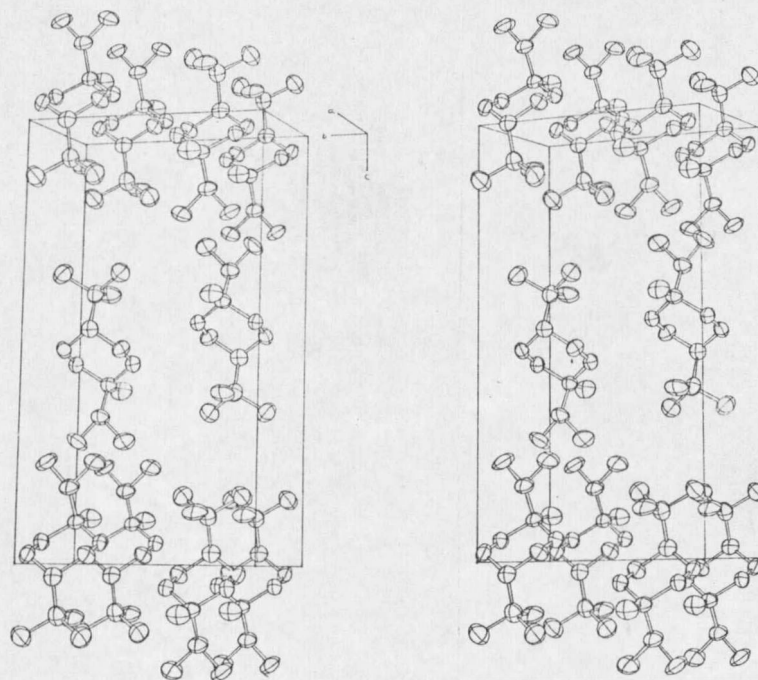


Figure 12.

Stereographic packing diagram of
5-t-butyl-2-methoxy-2-oxo-1,3,2-dioxaphosphorinane
with both the disordered methoxy carbon atoms drawn.

THE CRYSTAL AND MOLECULAR STRUCTURE OF
5-t-BUTYL-2-PHENYL-2-THIO-1,3,2-DIOXAPHOSPHORINANE ($C_{13}PSO_2H_{19}$)

Preparation

The crystals were supplied by Wesley G. Bentrude and were large, colorless, transparent, and needle-shaped in appearance.

The dimensions of the crystal used for X-ray analysis were approximately 0.2 x 0.3 x 0.4 mm.

Density

The density of the crystals was measured by the flotation method as described in Part I, page 5. The calculated density was based on four molecules per unit cell: $D_{exp} = 1.277 \text{ g/cm}^3$ and $D_{calc} = 1.275 \text{ g/cm}^3$.

Determination of tentative cell dimensions and space group

Weissenberg photographs of the X-ray diffraction pattern for the crystal $C_{13}PSO_2H_{19}$, indicated monoclinic symmetry. The axis along which the crystal was mounted was designated as a. The tentative unit cell dimensions were found to be $a = 11.30$, $b = 6.17$, and $c = 21.17 \text{ \AA}$. A unit cell of these dimensions would require four molecules to agree with its measured density. The extinctions based on this cell were:

hkl: no conditions

h0l: $l \neq 2n$

0k0: $k \neq 2n$.

These extinctions correspond to the space group $P2_1/c$ with the b axis unique.

However, $P2_1/n$ was found to be the space group with the smallest β angle.

Determination of accurate unit cell dimensions

The determination of accurate cell parameters was obtained by the same procedure used in Part I, page 6. Twenty-one three-dimensional reflections were selected for which precise measurements of the $+2\theta$ and -2θ angles were made. The crystal data are listed in Table 18.

Data collection

Data were collected on the General Electric XRD-5 Diffractometer equipped with a scintillation counter, pulse-height discriminator, and G. E. single crystal orienter, using θ - 2θ scan technique and zirconium filtered molybdenum $K\alpha$ radiation. The crystal was mounted with the a axis parallel to the spindle axis. Each peak was scanned for 60 seconds and the backgrounds on each side of the peak were counted for 10 seconds and later multiplied by three to speed data collection. A chart recording of peak intensity vs. 2θ was monitored during the data collection as a check on the centering of the peak in the scan range and for general appearance of the peak and backgrounds. The scan rate was 2° per minute with a takeoff angle of 4° .

Table 18

Crystal Data

5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane

 $C_{13}H_{19}PSO_2$ F.W. 270.31 $F(000) = 572$ Monoclinic, Space Group $P2_1/n$ $a = 6.150(2)$ $\alpha = 90^\circ$ $b = 11.036(3)$ $\beta = 95.17(2)^\circ$ $c = 20.823(5)$ $\gamma = 90^\circ$ Volume of the unit cell = 1408. $\text{\AA}^3$

Molecules/unit cell = 4

 $D_{\text{exp}} = 1.277 \text{ g/cm}^3$ $D_{\text{calc}} = 1.275 \text{ g/cm}^3$

Intensities of 1842 unique reflections were measured of which 1259 were considered observed, using the criterion $I \geq 2 \sigma(I)$. Three standard reflections (the 116, 132, and 115 reflections) were checked approximately every hour during data collection and remained constant with an average deviation of 1.6%, indicating no deterioration of the crystal.

Structure factors, (F_o) , were calculated from the intensities by applying the usual Lorentz-polarization correction, weights were calculated from standard deviations as was described in Part I, page 7.

No absorption or extinction corrections were made. The linear absorption coefficient of $C_{13}PSO_2H_{19}$ for $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) is $\mu = 3.29 \text{ cm}^{-1}$. The transmission factors for X-rays passing through the maximum and minimum dimensions of the crystal are approximately 0.83 and 0.93 respectively; this range corresponds to approximately 6% variation about a mean intensity value. Scattering factors for the non-hydrogen atoms and anomalous scattering corrections ($\Delta f'$ and $\Delta f''$) for phosphorus and sulfur were taken from the International Tables (12). Scattering factors for hydrogen were taken from Steward, et. al. (20).

Structure determination

The structure was solved in the space group $P2_1/n$. The positions of the phosphorus and sulfur atoms were found using the Patterson synthesis (2).

Using the phosphorus and sulfur atom positions; the structure factor calculation (9) gave an R-index of 0.45. A Fourier map (2) revealed the positions of the remaining non-hydrogen atoms.

Refinement

Refinement was begun using the full matrix least squares method of refinement (9) with the R-index equal to 0.26 for the non-hydrogen structure along with isotropic temperature factors and a unit weighting scheme. After three cycles of refinement, the R-index dropped to 0.098. The temperature factors were then converted to anisotropic and the weighting scheme to that of Stout and Jensen. In three cycles the R-index dropped to 0.081 with a weighted R-index, (R_{wtd}), of 0.089.

A difference Fourier map (2) was then calculated to locate hydrogen atom positions. Thirteen of the nineteen hydrogens were located from the map and the structure refined to an $R = 0.039$ and $R_{\text{wtd}} = 0.034$. A subsequent difference Fourier map was calculated and the remaining hydrogens were located.

Refinement of the complete structure was then continued until the shifts in the parameters were less than one half of their standard deviations. The final refinement gave an R of 0.036 and R_{wtd} of 0.031. The observed and calculated structure factors are listed in Table 19. The positional parameters of the non-hydrogen atoms are listed in Table 20, the thermal parameters for the

TABLE 20

Positional parameters of non-hydrogen atoms in
5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
S(17)	0.1624(2) ^a	0.0733(1)	0.1378(1)
P(2)	-0.0519(2)	0.1819(1)	0.0984(1)
O(1)	-0.2672(3)	0.1156(2)	0.0707(1)
O(3)	0.0341(3)	0.2511(2)	0.0388(1)
C(4)	-0.1275(6)	0.3098(4)	-0.0059(2)
C(5)	-0.3012(6)	0.2222(3)	-0.0325(2)
C(6)	-0.4193(6)	0.1751(4)	0.0227(2)
C(7)	-0.4550(6)	0.2758(3)	-0.0883(2)
C(8)	-0.6460(8)	0.1883(2)	-0.1051(2)
C(9)	-0.5479(10)	0.3990(4)	-0.0708(3)
C(10)	-0.3285(9)	0.2894(5)	-0.1480(2)
C(11)	-0.1353(5)	0.2979(3)	0.1518(2)
C(12)	-0.3329(6)	0.2896(4)	0.1788(2)
C(13)	-0.3868(7)	0.3752(4)	0.2235(2)
C(14)	-0.2452(9)	0.4666(5)	0.2412(2)
C(15)	-0.0482(8)	0.4760(4)	0.2149(2)
C(16)	0.0035(7)	0.3917(4)	0.1701(2)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

non-hydrogen atoms are listed in Table 21, and the hydrogen atom parameters are listed in Table 22.

Discussion of the structure

The molecule of 5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane with its thermal ellipsoids (13) is shown in Figure 13. The bond lengths are listed in Table 23 and bond angles in Table 24. Diagrams of the molecule showing bond lengths and angles are shown in Figure 14.

All atoms in the molecule lie in general positions. The ring is a distorted chair with the t-butyl and phenyl groups cis to each other on the ring. The t-butyl is equatorial and the phenyl axial. The dihedral angles between the best least squares plane through the O(1), O(3), C(4), C(6) plane and the planes O(1), P(2), O(3) and C(4), C(5), C(6) are 49.5 and 30.5° respectively, as compared to 60° for an ideal chair. The equations of the planes are listed in Table 25. The torsional angles for the ring bonds are given in Table 26. Both the dihedral and torsional angles show that most of the ring distortion is on the phosphate end of the ring. The aliphatic end of the ring has torsional angles near those normally occurring in six-membered rings. More is said about the conformation later in the section comparing the 1,3,2-dioxaphosphorinanes on page 100.

The mirror symmetry of the molecule is broken by the phenyl ring. The

TABLE 21

Thermal parameters of non-hydrogen atoms in
5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

Atom	$\beta_{11}^{a,b}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(17)	291(4) ^c	97(1)	31(1)	51(2)	2(1)	11(1)
P(2)	208(3)	73(1)	20(1)	8(2)	9(1)	5(1)
O(1)	237(8)	70(2)	22(1)	-15(3)	5(2)	7(1)
O(3)	198(7)	90(3)	20(1)	2(3)	13(2)	8(1)
C(4)	240(13)	78(4)	22(1)	-1(7)	19(3)	9(2)
C(5)	255(12)	56(4)	19(1)	13(6)	18(3)	-2(2)
C(6)	222(12)	80(4)	24(1)	-15(7)	4(3)	4(2)
C(7)	290(13)	73(4)	17(1)	22(6)	6(3)	-2(2)
C(8)	396(19)	119(6)	24(1)	-4(9)	-29(4)	-9(3)
C(9)	409(20)	87(5)	26(2)	53(9)	-13(5)	-1(2)
C(10)	485(23)	131(7)	23(1)	11(11)	14(4)	8(3)
C(11)	198(12)	76(4)	17(1)	13(6)	2(3)	8(2)
C(12)	244(14)	89(5)	21(1)	-8(7)	6(3)	3(2)
C(13)	301(16)	130(5)	20(1)	28(8)	18(4)	3(2)
C(14)	498(21)	113(6)	15(1)	59(9)	5(4)	-3(2)
C(15)	452(19)	96(5)	24(1)	-28(8)	1(4)	-7(2)
C(16)	247(15)	97(5)	23(1)	-6(7)	9(4)	5(2)

^aThe β_{ij} 's have been multiplied by 10^4 .

^bThe expression for the anisotropic thermal parameters is of the form:

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl).$$

^cThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 22

Hydrogen atom parameters in
5-t-butyl-2-phenyl-1-thio-1,3,2-dioxaphosphorinane.

Atom	x/a	y/b	z/c	Biso
H(1)	-0.192(4) ^a	0.377(2)	0.016(1)	2.6(6)
H(2)	-0.047(4)	0.344(2)	-0.036(1)	3.0(6)
H(3)	-0.228(3)	0.153(2)	-0.048(1)	1.9(5)
H(4)	-0.498(4)	0.241(2)	0.042(1)	3.6(7)
H(5)	-0.517(4)	0.107(3)	0.112(1)	5.0(7)
H(6)	-0.719(4)	0.215(3)	-0.142(1)	4.8(7)
H(7)	-0.589(5)	0.104(3)	-0.116(2)	8.4(1.0)
H(8)	-0.749(5)	0.180(3)	-0.067(2)	8.3(1.0)
H(9)	-0.644(5)	0.425(3)	-0.103(2)	6.2(8)
H(10)	-0.433(5)	0.456(3)	-0.069(1)	5.3(8)
H(11)	-0.622(4)	0.394(3)	-0.032(1)	4.8(7)
H(12)	-0.418(5)	0.330(3)	-0.184(2)	7.0(9)
H(13)	-0.217(5)	0.346(3)	-0.139(1)	5.0(7)
H(14)	-0.283(5)	0.202(3)	-0.163(2)	8.4(1.0)
H(15)	-0.420(4)	0.224(2)	0.168(1)	1.9(5)
H(16)	-0.531(4)	0.371(3)	0.243(1)	5.9(8)
H(17)	-0.275(4)	0.529(2)	0.272(1)	5.2(8)
H(18)	0.048(5)	0.543(3)	0.227(2)	7.7(9)
H(19)	0.136(4)	0.394(2)	0.155(1)	3.5(6)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

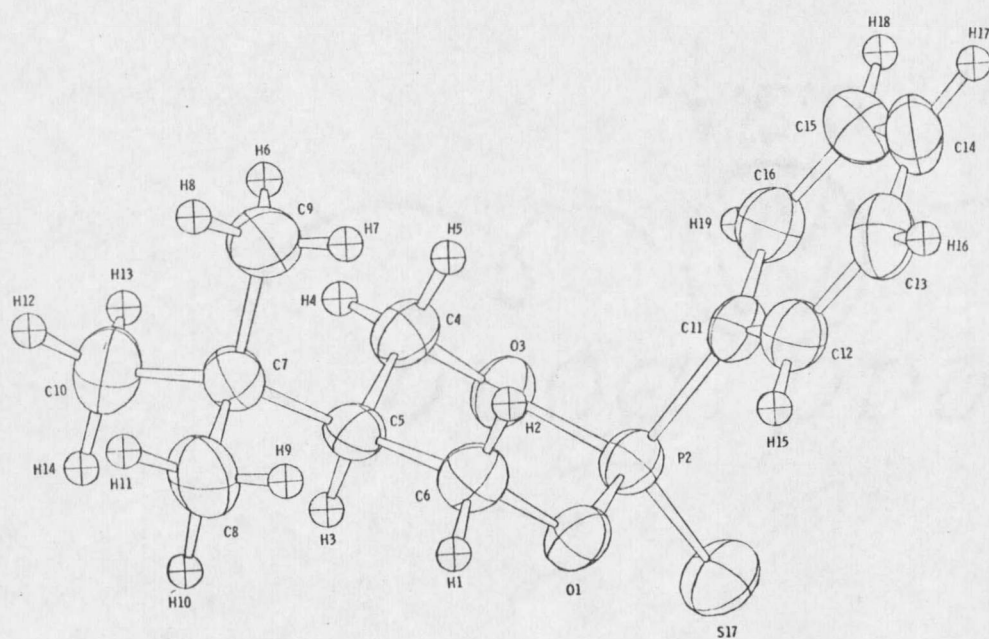


Figure 13.

Molecular structure of
5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane
illustrating the thermal ellipsoids.

TABLE 23

Bond distances for

5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Atoms</u>	<u>distance, Å</u>	<u>Atoms</u>	<u>distance, Å</u>
P(2)-S(17)	1.911(1) ^a	C(4)-H(2)	0.92(2)
P(2)-O(1)	1.576(2)	C(5)-H(3)	0.96(2)
P(2)-O(3)	1.587(2)	C(6)-H(4)	0.97(3)
P(2)-C(11)	1.801(3)	C(6)-H(5)	0.98(3)
O(1)-C(6)	1.462(4)	C(8)-H(6)	0.91(3)
O(3)-C(4)	1.452(4)	C(8)-H(7)	1.03(4)
C(4)-C(5)	1.508(5)	C(8)-H(8)	1.07(3)
C(5)-C(6)	1.507(5)	C(9)-H(9)	0.91(3)
C(5)-C(7)	1.547(5)	C(9)-H(10)	0.94(3)
C(7)-C(8)	1.537(6)	C(9)-H(11)	0.96(3)
C(7)-C(9)	1.531(6)	C(10)-H(12)	1.00(3)
C(7)-C(10)	1.532(6)	C(10)-H(13)	0.93(3)
C(11)-C(12)	1.386(5)	C(10)-H(14)	1.06(4)
C(11)-C(16)	1.374(5)	C(12)-H(15)	0.92(2)
C(12)-C(13)	1.386(6)	C(13)-H(16)	1.01(3)
C(13)-C(14)	1.362(7)	C(14)-H(17)	0.96(3)
C(14)-C(15)	1.374(6)	C(15)-H(18)	0.97(3)
C(4)-H(1)	0.98(2)	C(16)-H(19)	0.90(2)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 24

Bond angles of 5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Atoms</u>	<u>angles, °</u>	<u>Atoms</u>	<u>angles, °</u>	<u>Atoms</u>	<u>angles, °</u>
S(17)-P(2)-O(1)	113.0(1) ^a	C(14)-C(15)-C(16)	119.0(4)	C(7)-C(9)-H(10)	107.(2)
S(17)-P(2)-O(3)	111.8(1)	C(15)-C(16)-C(11)	121.5(4)	C(7)-C(9)-H(11)	111.(2)
S(17)-P(2)-C(11)	113.8(1)	O(3)-C(4)-H(1)	108.(1)	H(9)-C(9)-H(10)	104.(2)
O(1)-P(2)-O(3)	105.5(1)	O(3)-C(4)-H(2)	104.(2)	H(9)-C(9)-H(11)	109.(3)
O(1)-P(2)-C(11)	106.2(1)	C(5)-C(4)-H(1)	115.(2)	H(10)-C(9)-H(11)	115.(2)
O(3)-P(2)-C(11)	105.9(1)	C(5)-C(4)-H(2)	111.(1)	C(7)-C(10)-H(12)	112.(2)
P(2)-O(1)-C(6)	120.4(2)	H(1)-C(4)-H(2)	106.(2)	C(7)-C(10)-H(13)	109.(2)
P(2)-O(3)-C(4)	117.3(2)	C(4)-C(5)-H(3)	107.(1)	C(7)-C(10)-H(14)	108.(2)
O(3)-C(4)-C(5)	111.8(3)	C(6)-C(5)-H(3)	104.(1)	H(12)-C(10)-H(13)	102.(3)
C(4)-C(5)-C(6)	108.2(3)	C(7)-C(5)-H(3)	109.(1)	H(12)-C(10)-H(14)	109.(3)
C(4)-C(5)-C(7)	113.3(3)	O(1)-C(6)-H(4)	112.(2)	H(13)-C(10)-H(14)	117.(3)
C(6)-C(5)-C(7)	113.6(3)	O(1)-C(6)-H(5)	99.(2)	C(11)-C(12)-H(15)	118.1(1)
O(1)-C(6)-C(5)	110.8(3)	C(5)-C(6)-H(4)	110.(2)	C(13)-C(12)-H(15)	122.(1)
C(5)-C(7)-C(8)	109.5(3)	C(5)-C(6)-H(5)	114.(2)	C(12)-C(13)-H(16)	121.(2)
C(5)-C(7)-C(9)	112.1(3)	H(4)-C(6)-H(5)	111.(2)	C(14)-C(13)-H(16)	119.(2)
C(5)-C(7)-C(10)	109.0(3)	C(7)-C(8)-H(6)	108.(2)	C(13)-C(14)-H(17)	123.(2)
P(2)-C(11)-C(12)	120.8(3)	C(7)-C(8)-H(7)	111.(2)	C(15)-C(14)-H(17)	116.(2)
P(2)-C(11)-C(16)	120.2(3)	C(7)-C(8)-H(8)	112.(2)	C(14)-C(15)-H(18)	119.(2)
C(12)-C(11)-C(16)	118.9(3)	H(6)-C(8)-H(7)	105.(3)	C(16)-C(15)-H(18)	121.(2)
C(11)-C(12)-C(13)	119.9(4)	H(6)-C(8)-H(8)	113.(3)	C(15)-C(16)-H(19)	119.(2)
C(12)-C(13)-C(14)	120.1(4)	H(7)-C(8)-H(8)	109.(3)	C(11)-C(16)-H(19)	119.(2)
C(13)-C(14)-C(15)	120.7(4)	C(7)-C(9)-H(9)	110.(2)		

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

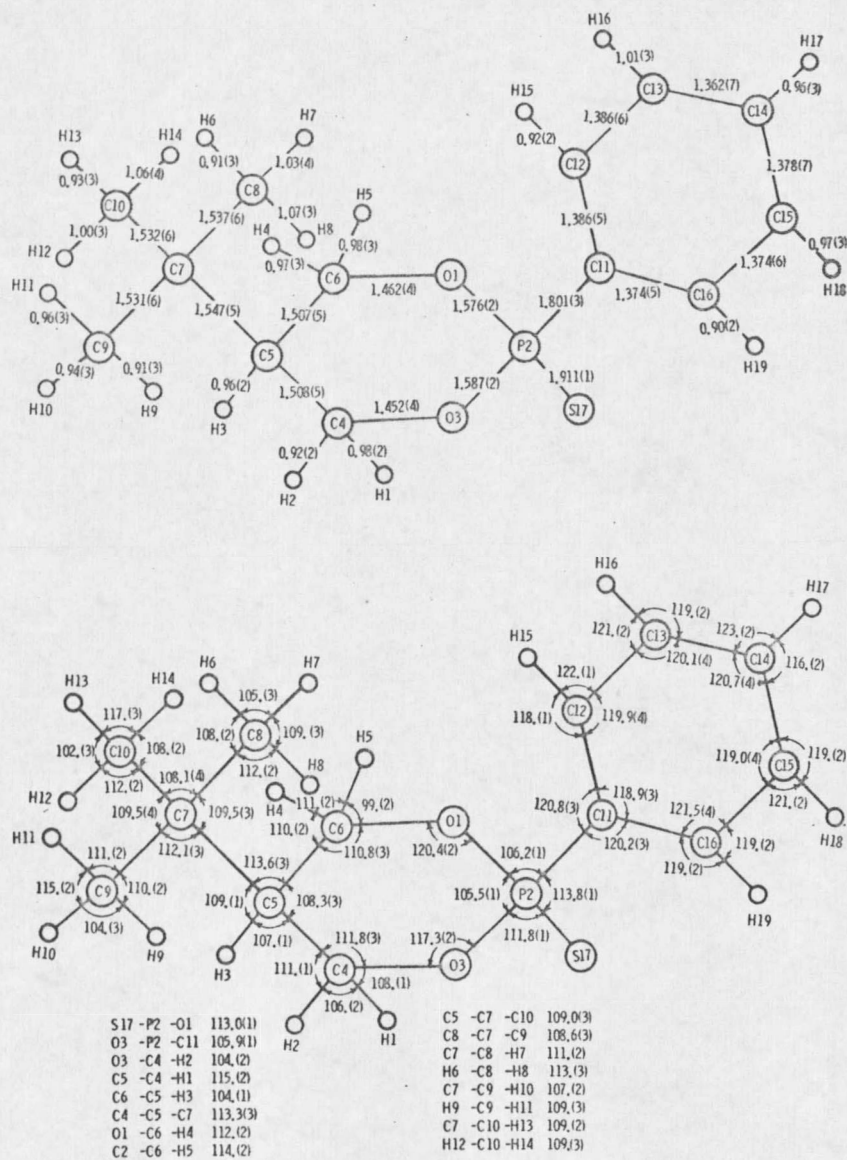


Figure 14.

Bond distances and bond angles of
5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

TABLE 25

Least squares planes referred to orthogonal axes in
5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane^a.

Atoms in plane	ℓ	m	n	$d(\text{\AA})$	$S(A^2)$
O(1), O(3), C(4), C(6)	-0.273	0.630	0.726	2.27	0.0084
O(1), P(2), O(3)	-0.556	0.804	0.209	2.32	---
C(4), C(5), C(6)	-0.646	0.753	-0.126	3.09	---
C(11), C(12), C(13), C(14), C(15), C(16)	0.385	-0.596	0.704	0.04	0.0007
C(11), P(2), S(17)	0.722	0.511	-0.391	0.25	---

$$^aX = x + z \cdot \cos \beta; \quad Y = y; \quad Z = z \cdot \sin \beta$$

$$\text{L.S. plane: } \ell X + mY + nZ - d = 0.0$$

S: sum of squares of deviations of atoms from plane.

TABLE 26

Torsional angles for

5-t-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Bond</u>	<u>torsional angle, degrees</u>
P(2)-O(1)	38.8°
O(1)-C(6)	51.0°
C(6)-C(5)	58.6°
C(5)-C(4)	62.2°
C(4)-O(3)	55.6°
O(3)-P(2)	40.2°

dihedral angle between the best least squares plane through the phenyl ring and the plane C(11), P(2), S(17) is 70.2° twisted around the P(2)-C(11) bond toward the O(1) side of the ring as shown in Figure 15. Steric repulsions are relieved between C(16) and H(19) and the lone pair of electrons on O(3) by the twist, and staggers C(16) and H(19) between O(3) and S(17).

The bonding around the phosphorus forms a slightly distorted tetrahedral with bond angles ranging from 105.5 to 113.8° . The P-O(3) bond distance is 5-6 standard deviations longer than the P-O(1) bond which may be a significant difference. The P-C(11) bond distance is 1.801 Å which is the same as found in 2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane. The P=S bond is 1.911 Å and can be considered a normal bond length.

The O(1)-C(3) bond distance is 2-3 standard deviations longer than the O(3)-C(4) distance which may be a significant difference. The C-C bonds in the ring are 1.507 and 1.508 Å.

The phenyl ring is planar with an average displacement from the best least squares plane of 0.003 Å, and the maximum displacement is 0.006 Å at the C(16) position. The equation of the plane is listed in Table 25. The C-C bond distances for the phenyl ring range from 1.362 to 1.386 Å and average 1.377 Å. The C-C-C bond angles range from 118.9 to 121.5° . These are normal values for a benzene ring.

The C-C bond distances in the t-butyl group range from 1.531 to 1.547 Å

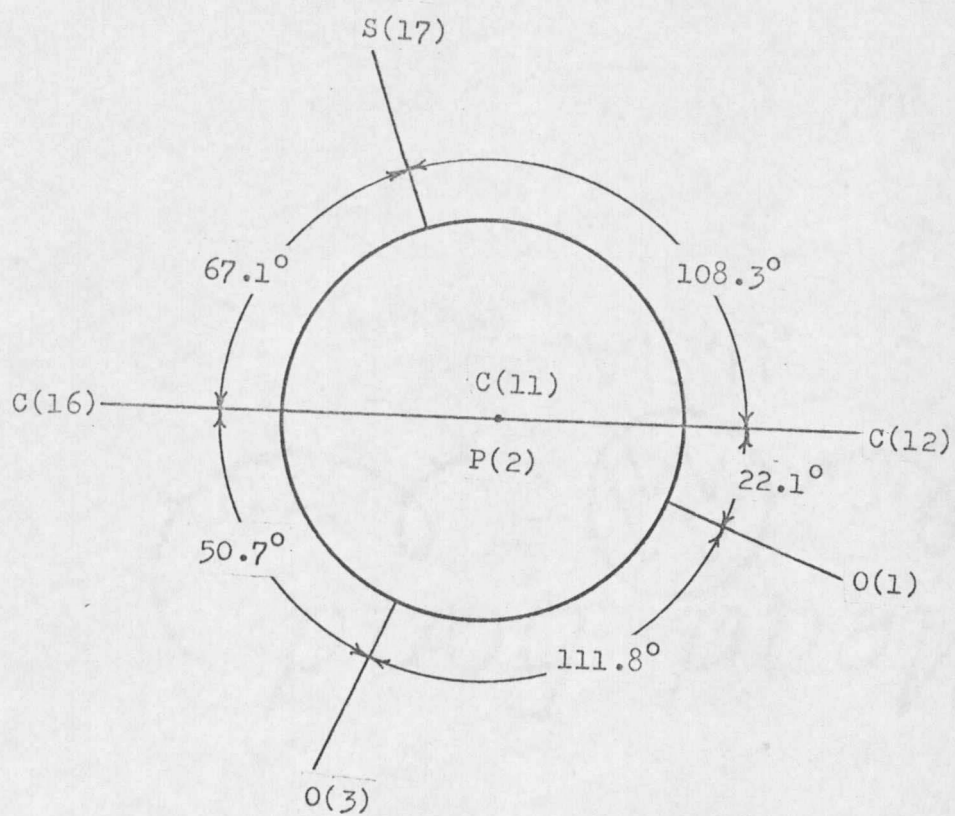


Figure 15.

Newman projection looking down the C(11)-P(2) bond.

and average 1.537 Å. The bond angles range from 108.1 to 112.1°. The largest angle C(5)-C(7)-C(9) is probably the result of steric repulsions between C(9) and the axial hydrogens on the ring, H(2) and H(5).

The stereographic packing diagram of the molecules in the unit cell is shown in Figure 16. Packing conditions are not likely to be an important factor in the conformation of the molecule since there are no intermolecular distances less than the sum of the van der Waals radii of the atoms in neighboring molecules. Values of the van der Waals radii were obtained from Bondi (8), and pertinent radii were: P, 1.80; O, 1.52; aliphatic C, 1.70; aromatic C, 1.77; double bonded S, 1.74; aliphatic H, 1.20; and aromatic H, 1.00 Å.

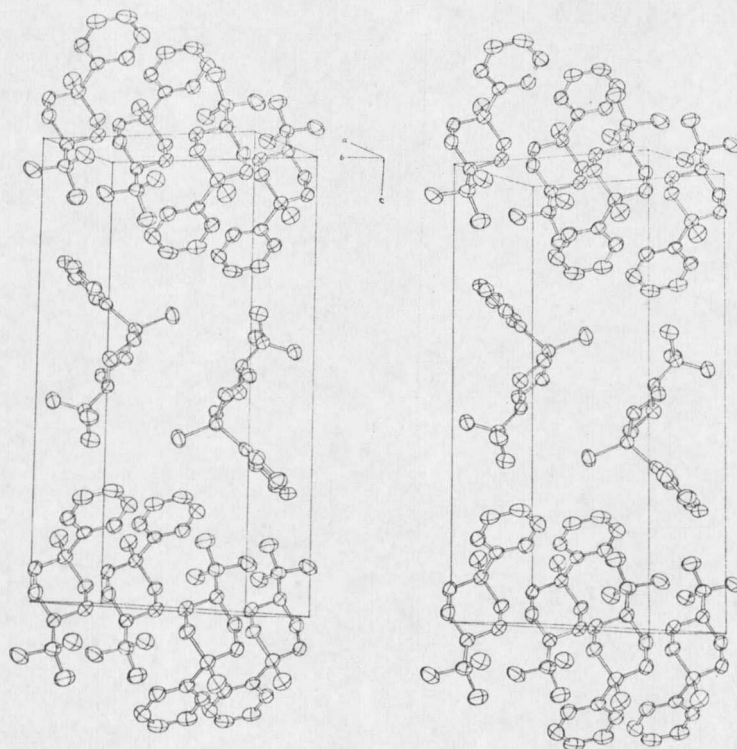


Figure 16.

Stereographic packing diagram for
5-t-butyl-1-phenyl-1-thio-1,3,2-dioxaphosphorinane.

THE CRYSTAL AND MOLECULAR STRUCTURE OF
2,5,-t-BUTYL-2-THIO-1,3,2-DIOXAPHOSPHORINANE (C₁₁PSO₂H₂₃)

Preparation

The crystals were supplied by Wesley G. Bentrude and were large, colorless, transparent, and needle-shaped in appearance. The dimensions of the crystal used for X-ray analysis were approximately 0.16 x 0.26 x 0.58 mm. The crystal was sealed in a Lindeman capillary to prevent loss by sublimation.

Density

The density of the crystals was measured by the flotation method as described in Part I, page 5. The calculated density was based on four molecules per unit cell; $D_{\text{exp}} = 1.210 \text{ g/cm}^3$ and $D_{\text{calc}} = 1.218 \text{ g/cm}^3$.

Determination of cell dimensions and space group

The crystal was placed on Oregon State University's Syntex P2₁ Automated Diffractometer equipped with a PDP-8 computer and polaroid cassette. A rotational photograph of the X-ray diffraction pattern for the crystal was made with the Polaroid cassette, and provided the Autocentering Program (22) with coordinates of fifteen reflections. The program refined the angular positions for the fifteen reflections by determining positions of the half-height peak intensity. The Autoindexing program (22) compiled a list of possible axial

vectors and the angles between these vectors. From this list an orthorhombic cell was chosen. The Least Squares Orientation Matrix Program (22) then calculated the orientation matrix and unit cell parameters. The cell dimensions obtained were $a = 10.135$, $b = 10.716$, and $c = 12.765$ Å. No standard deviations were given by the program.

The space group was determined by the extinctions in the intensity data, and was found to be $Pmcn$ with extinctions:

hkl : no conditions
 $h0l$: $l \neq 2n$
 $hk0$: $h + k \neq 2n$
 $0kl$: no conditions
 $h00$: $h \neq 2n$
 $0k0$: $k \neq 2n$
 $00l$: $l \neq 2n$.

Unit cell dimensions were again determined on our XRD-5 General Electric Diffractometer by the method described in Part I, page 6. Fifteen three-dimensional and three two-dimensional reflections were selected for which precise measurements of the $+2\theta$ and -2θ angles were made. The results were $a = 10.077(3)$, $b = 10.662(3)$, and $c = 12.703(3)$ Å, which are significantly different than those determined on the Syntex Diffractometer. The cell dimensions determined by the G.E. diffractometer were used for reporting since our program gives standard deviations, and I have more confidence in them. The crystal data are listed in Table 27.

TABLE 27

Crystal Data for

2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

C₁₁H₁₈PSO₂ F.W. 250.32 F(000) = 544

Orthorhombic, Space Group Pmcn

a = 10.077(3) α = 90°

b = 10.662(3) β = 90°

c = 12.703(3) γ = 90°

Volume of the unit cell = 1364.8 Å³

Molecules per unit cell = 4

D_{exp} = 1.210 g/cm³

D_{calc} = 1.218 g/cm³

Data collection

Two sets of data were taken from the crystal on two different diffractometers. The first set of data was collected on the Syntex P2₁ Diffractometer equipped with a PDP-8 computer, teletype, four-circle goniometer, scintillation counter, and a pulse-height discriminator. Intensities of 1303 unique reflections were measured of which 818 were considered observed, using the criterion $I \geq 2 \sigma(I)$. Standard reflections were checked after every 60 reflections during data collection and had an average deviation of 6.6%, which indicated a problem. The graph in Figure 17 shows that scale #3 starts to rise after approximately 18 hours and rises rapidly after 35 hours, indicating a rapid drop in intensity. Scales 1 and 2 remained relatively constant throughout the data collection. The problem could be explained by either crystal deterioration or by crystal slippage. In order to determine which case applied, the crystal was mounted on our General Electric XRD-5 diffractometer. Intensities of the three standard reflections were collected and their ratio's to those collected on the Syntex diffractometer were nearly equal. This suggested that the crystal had probably moved during data collection on the Syntex.

The 818 observed reflections were re-collected on the G.E. diffractometer. Each peak was scanned for 60 seconds and the backgrounds on each side of the peak were counted for 10 seconds and multiplied by 3. A chart recording of peak intensity vs. 2θ was monitored during the data collection as

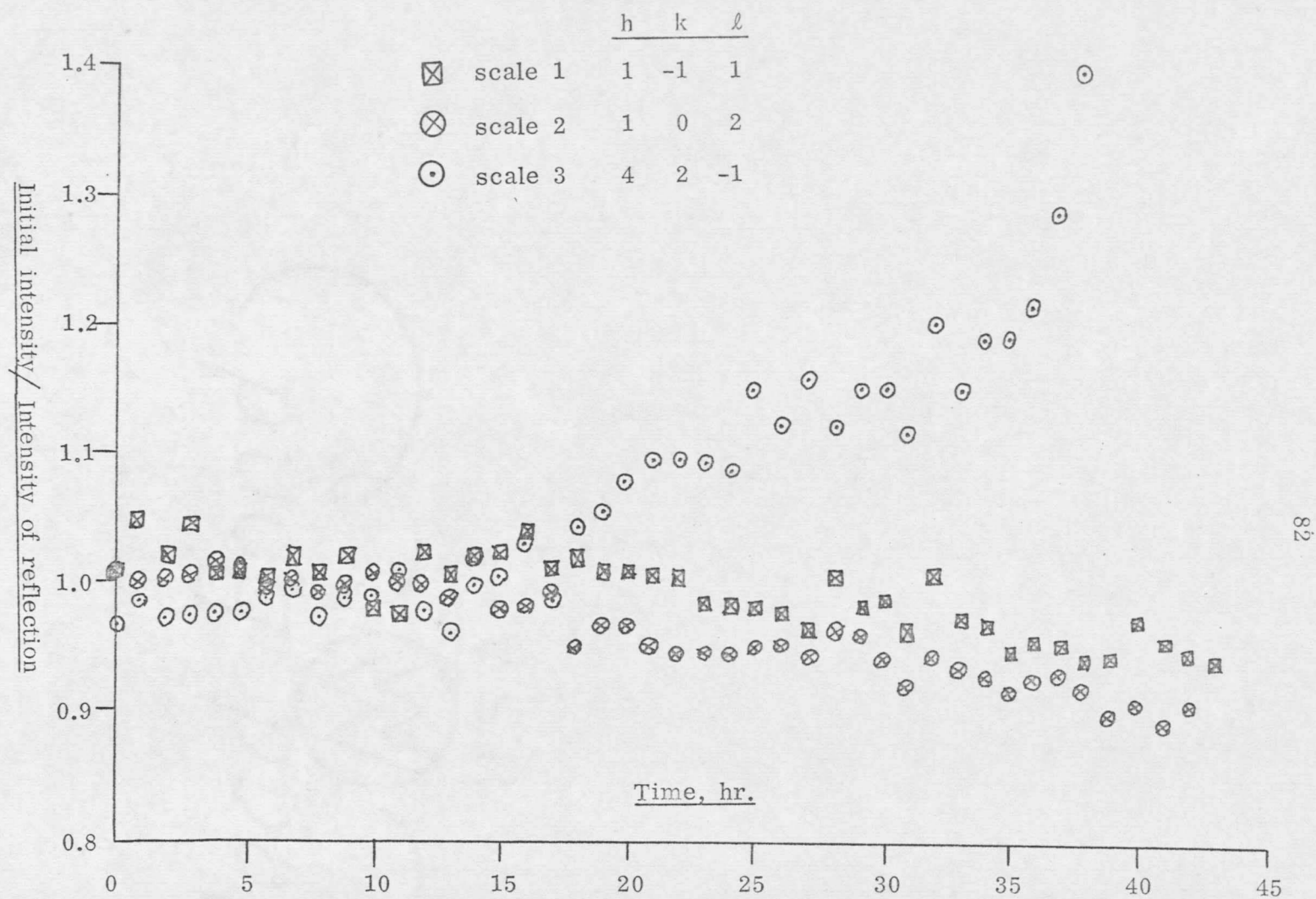


Figure 17.

Scale factors for data collected on the Syntex Diffractometer.

a check on the centering of the peak in the scan range and for general appearance of the peak and backgrounds. The scan rate was 2° per minute with a take-off angle of 4° .

Of the 818 observed reflections collected on the Syntex instrument, 763 were considered observed by the G. E. instrument. Three standard reflections (the 014, 330, and 421 reflections) were checked approximately every hour during data collection and remained constant with an average deviation of 1.1%, indicating no deterioration of the crystal.

Structure factors, (F_o), were calculated from the intensities by applying the usual Lorentz-polarization correction, and weights were calculated from standard deviations as was described in Part I, page 7.

No absorption or extinction corrections were made. The linear absorption coefficient of $C_{11}PSO_2H_{23}$ for $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) is $\mu = 3.33 \text{ cm}^{-1}$. The transmission factors for X-rays passing through the maximum and minimum dimensions of the crystal are approximately 0.80 and 0.95 respectively; this range corresponds to approximately 8% variation about a mean intensity value. Scattering factors for the non-hydrogen atoms and anomalous scattering corrections, ($\Delta f'$ and $\Delta f''$), for phosphorus and sulfur were taken from the International Tables (12). Scattering factors for hydrogen were taken from Steward, et. al. (20).

Structure determination

The structure was solved using the data collected on the Syntex diffractometer. The positions of the phosphorus and sulfur atoms were found from the Patterson synthesis (2). Using the phosphorus and sulfur atom positions, the structure factor calculation (9) gave an R-index of 0.46. A Fourier map (2) revealed positions of two oxygen atoms and three ring carbon atoms, giving an R-index of 0.31. A subsequent Fourier map showed the remaining non-hydrogen atom positions.

Refinement

Refinement was begun using the full matrix least squares method (9) of refinement with the R-index equal to 0.18 for the non-hydrogen structure along with isotropic temperature factors and a unit weighting scheme. After three cycles of refinement, the R-index dropped to 0.11. The temperature factors were then converted to anisotropic and the weighting scheme to that of Stout and Jensen. In three cycles the R-index dropped to 0.087 with a weighted R-index, (R_{wtd}), of 0.11.

A difference map was calculated to locate hydrogen atom positions, and all of the hydrogen atom positions were located from the map.

Refinement of the complete structure was then continued until the shifts in the parameters were less than one half of their standard deviations. The

final refinement of the Syntex data gave an R of 0.057 and an R_{wtd} of 0.066.

After the data were recollected on the G. E. diffractometer, the structure refined to an R of 0.048 and an R_{wtd} of 0.038. The observed and calculated structure factors are listed in Table 28. The positional parameters of the non-hydrogen atoms are listed in Table 29, the thermal parameters for the non-hydrogen atoms are listed in Table 30, and the hydrogen atom parameters are listed in Table 31.

Discussion of the structure

The molecule of 2,5 -*t*-butyl-2-thio-1,3,2-dioxaphosphorinane with its thermal ellipsoids is shown in Figure 18. The bond lengths are listed in Table 32 and bond angles in Table 33. Bond lengths and angles are diagrammed in Figure 19.

The molecule lies on a crystallographic mirror plane on which the atoms P(2), S(15), C(5), C(7), C(10), C(11), and C(14) lie on the special positions $x = 1/4$ and $3/4$. The ring is a distorted chair with the *t*-butyl groups cis to each other with the *t*-butyl group on the C(5) position axial and equatorial on the P(2) position. Bentrude had predicted that the thio group would be axial, but had also predicted a boat conformation for the ring (6).

The ring is flattened as shown by the dihedral angles between the plane O(1), O(3), C(4), C(6) and the planes O(1), P(2), O(3) and C(4), C(5), C(6); the

Observed and calculated structure factors.

TABLE 29

Positional parameters of non-hydrogen atoms in

2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Atom</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
S(15)	0.2500(0) ^a	0.1104(2)	0.2943(1)
P(2)	0.2500(0)	0.0193(1)	0.1633(1)
O(1)	0.3724(2)	-0.0730(2)	0.1490(2)
O(3)	0.1276(2)	-0.0730(2)	0.1490(2)
C(4)	0.1260(5)	-0.1789(4)	0.2230(4)
C(5)	0.2500(0)	-0.2607(6)	0.2155(5)
C(6)	0.3740(5)	-0.1789(4)	0.2230(4)
C(7)	0.2500(0)	-0.3604(5)	0.1275(4)
C(8)	0.3706(7)	-0.4449(6)	0.1381(5)
C(9)	0.1294(7)	-0.4449(6)	0.1381(5)
C(10)	0.2500(0)	-0.3039(7)	0.0176(6)
C(11)	0.2500(0)	0.1144(6)	0.0456(5)
C(12)	0.3742(6)	0.1961(6)	0.0485(5)
C(13)	0.1258(6)	0.1961(6)	0.0485(5)
C(14)	0.2500(0)	0.0329(8)	-0.0540(6)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 30

Thermal parameters of non-hydrogen atoms in
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

Atom	$\beta_{11}^{a,b}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(15)	131(2) ^c	101(2)	58(1)	0(0)	0(0)	-29(1)
P(2)	74(2)	61(2)	47(1)	0(0)	0(0)	6(1)
O(1)	68(3)	63(2)	56(2)	7(2)	1(2)	3(2)
O(3)	68(3)	63(2)	56(2)	-7(2)	-1(2)	3(2)
C(4)	86(6)	85(5)	57(3)	-7(5)	11(4)	1(3)
C(5)	88(7)	79(6)	41(4)	0(0)	0(0)	16(5)
C(6)	86(6)	85(5)	57(3)	7(5)	-11(4)	1(3)
C(7)	85(7)	56(6)	61(5)	0(0)	0(0)	2(4)
C(8)	143(8)	104(6)	112(6)	28(6)	-4(6)	-10(5)
C(9)	143(8)	104(6)	112(6)	-28(6)	4(6)	-10(5)
C(10)	162(12)	80(8)	58(5)	0(0)	0(0)	-8(5)
C(11)	92(7)	74(6)	57(5)	0(0)	0(0)	7(5)
C(12)	131(8)	99(6)	104(5)	-35(6)	8(5)	23(5)
C(13)	131(8)	99(6)	104(5)	35(6)	-8(5)	23(5)
C(14)	197(14)	107(9)	50(5)	0(0)	0(0)	5(6)

^aThe β_{ij} 's have been multiplied by 10^4 .

^bThe expression for the anisotropic thermal parameters is of the form:

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl).$$

^cThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 31

Hydrogen atom parameters in
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

Atom	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>Biso</u>
H(1)	0.047 (3) ^a	-0.227 (3)	0.201 (3)	3.8 (8)
H(2)	0.116 (3)	-0.150 (3)	0.298 (3)	3.7 (8)
H(3)	0.250 (0)	-0.312 (5)	0.285 (4)	4.8 (1.3)
H(4)	0.384 (3)	-0.150 (3)	0.298 (3)	3.7 (8)
H(5)	0.453 (3)	-0.227 (3)	0.201 (3)	3.8 (8)
H(6)	0.374 (4)	-0.515 (4)	0.075 (4)	7.9 (1.3)
H(7)	0.448 (5)	-0.405 (4)	0.117 (3)	6.8 (1.5)
H(8)	0.375 (5)	-0.477 (4)	0.207 (4)	7.4 (1.5)
H(9)	0.125 (5)	-0.477 (4)	0.207 (4)	7.4 (1.5)
H(10)	0.052 (5)	-0.405 (4)	0.117 (3)	6.8 (1.5)
H(11)	0.126 (4)	-0.515 (4)	0.075 (4)	7.9 (1.3)
H(12)	0.172 (4)	-0.255 (3)	0.005 (3)	5.2 (1.2)
H(13)	0.2500 (0)	-0.382 (5)	-0.035 (4)	5.8 (1.6)
H(14)	0.328 (4)	-0.255 (3)	0.005 (3)	5.2 (1.2)
H(15)	0.446 (5)	0.140 (4)	0.047 (4)	7.6 (1.6)
H(16)	0.366 (4)	0.249 (4)	0.122 (3)	8.3 (1.5)
H(17)	0.372 (4)	0.251 (4)	-0.016 (4)	7.3 (1.4)
H(18)	0.333 (4)	-0.018 (4)	-0.058 (4)	7.1 (1.4)
H(19)	0.250 (0)	0.080 (5)	-0.114 (5)	5.5 (1.7)
H(20)	0.167 (4)	-0.018 (4)	-0.058 (4)	7.1 (1.4)
H(21)	0.128 (4)	0.251 (4)	-0.016 (4)	7.3 (1.4)
H(22)	0.134 (4)	0.249 (4)	0.122 (3)	8.3 (1.5)
H(23)	0.054 (5)	0.140 (4)	0.047 (4)	7.6 (1.6)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

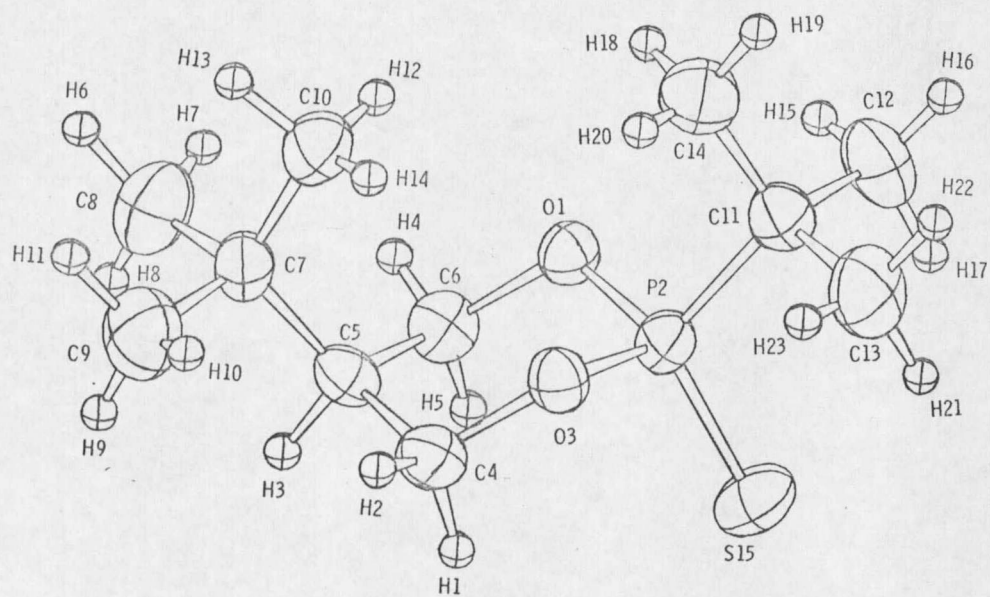


Figure 18.

Molecular structure of
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane
illustrating the thermal ellipsoids.

TABLE 32

Bond distances for

2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Bond</u>	<u>distance, Å</u>	<u>Bond</u>	<u>distance, Å</u>
S(15)-P(2)	1.927 (2) ^a	C(6)-H(5)	0.98 (3)
P(2)-O(1)	1.588 (3)	C(8)-H(6)	1.10 (5)
P(2)-O(3)	1.588 (3)	C(8)-H(7)	0.93 (5)
P(2)-C(11)	1.807 (6)	C(8)-H(8)	0.94 (5)
O(1)-C(6)	1.470 (5)	C(9)-H(9)	0.94 (5)
O(3)-C(4)	1.470 (5)	C(9)-H(10)	0.93 (5)
C(4)-C(5)	1.526 (6)	C(9)-H(11)	1.10 (5)
C(5)-C(6)	1.526 (6)	C(10)-H(12)	0.96 (4)
C(5)-C(7)	1.543 (8)	C(10)-H(13)	1.07 (6)
C(7)-C(8)	1.518 (7)	C(10)-H(14)	0.96 (4)
C(7)-C(9)	1.518 (7)	C(12)-H(15)	0.94 (5)
C(7)-C(10)	1.520 (9)	C(12)-H(16)	1.09 (4)
C(11)-C(12)	1.525 (7)	C(12)-H(17)	1.01 (4)
C(11)-C(13)	1.525 (7)	C(14)-H(18)	1.00 (4)
C(11)-C(14)	1.535 (10)	C(14)-H(19)	0.91 (6)
C(4)-H(1)	0.98 (3)	C(14)-H(20)	1.00 (4)
C(4)-H(2)	1.01 (3)	C(13)-H(21)	1.01 (4)
C(5)-H(3)	1.04 (5)	C(13)-H(22)	1.09 (4)
C(6)-H(4)	1.01 (3)	C(13)-H(23)	0.94 (5)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

TABLE 33

Bond angles for

2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Atoms</u>	<u>angle, °</u>	<u>Atoms</u>	<u>angle, °</u>
S(15)-P(2)-O(1)	114.3 (1) ^a	O(3)-C(4)-H(1)	103. (2)
S(15)-P(2)-O(3)	114.3 (1)	O(3)-C(4)-H(2)	112. (2)
S(15)-P(2)-C(11)	115.6 (2)	C(5)-C(4)-H(1)	110. (2)
O(1)-P(2)-O(3)	101.9 (1)	C(5)-C(4)-H(2)	108. (2)
O(1)-P(2)-C(11)	104.6 (2)	H(1)-C(4)-H(2)	110. (3)
O(3)-P(2)-C(11)	104.6 (2)	C(4)-C(5)-H(3)	104. (2)
P(2)-O(1)-C(6)	114.3 (2)	C(6)-C(5)-H(3)	104. (2)
P(2)-O(3)-C(4)	114.3 (2)	C(7)-C(5)-H(3)	105. (2)
O(3)-C(4)-C(5)	112.9 (3)	O(1)-C(6)-H(4)	112. (2)
C(4)-C(5)-C(6)	109.9 (4)	O(1)-C(6)-H(5)	103. (2)
C(4)-C(5)-C(7)	116.0 (4)	C(5)-C(6)-H(4)	108. (2)
C(6)-C(5)-C(7)	116.0 (4)	C(5)-C(6)-H(5)	110. (2)
O(1)-C(6)-C(5)	112.9 (3)	H(4)-C(6)-H(5)	110. (2)
C(5)-C(7)-C(8)	110.2 (4)	C(7)-C(8)-H(6)	111. (2)
C(5)-C(7)-C(9)	110.2 (4)	C(7)-C(8)-H(7)	112. (3)
C(5)-C(7)-C(10)	113.1 (4)	C(7)-C(8)-H(8)	110. (3)
C(8)-C(7)-C(9)	106.3 (4)	H(6)-C(8)-H(7)	94. (4)
C(8)-C(7)-C(10)	108.4 (4)	H(6)-C(8)-H(8)	116. (4)
C(9)-C(7)-C(10)	108.4 (4)	H(7)-C(8)-H(8)	113. (4)
P(2)-C(11)-C(12)	107.5 (4)	C(7)-C(9)-H(9)	110. (3)
P(2)-C(11)-C(13)	107.5 (4)	C(7)-C(9)-H(10)	112. (3)
P(2)-C(11)-C(14)	111.4 (4)	C(7)-C(9)-H(11)	111. (2)
C(12)-C(11)-C(13)	110.3 (4)	H(9)-C(9)-H(10)	113. (4)
C(12)-C(11)-C(14)	110.1 (4)	H(9)-C(9)-H(11)	116. (4)
C(13)-C(11)-C(14)	110.1 (4)	H(10)-C(9)-H(11)	94. (4)

TABLE 33

(Continued)

<u>Atoms</u>	<u>angle, °</u>	<u>Atoms</u>	<u>angle, °</u>
C(7)-C(10)-H(12)	112. (2)	C(11)-C(14)-H(18)	106. (3)
C(7)-C(10)-H(13)	105. (2)	C(11)-C(14)-H(19)	105. (2)
C(7)-C(10)-H(14)	112. (2)	C(11)-C(14)-H(20)	107. (3)
H(12)-C(10)-H(13)	109. (3)	H(18)-C(14)-H(19)	114. (4)
H(12)-C(10)-H(14)	110. (3)	H(18)-C(14)-H(20)	112. (4)
H(13)-C(10)-H(14)	109. (3)	H(19)-C(14)-H(20)	113. (3)
C(11)-C(12)-H(15)	106. (3)	C(11)-C(13)-H(21)	107. (3)
C(11)-C(12)-H(16)	105. (2)	C(11)-C(13)-H(22)	105. (2)
C(11)-C(12)-H(17)	107. (3)	C(11)-C(13)-H(23)	106. (3)
H(15)-C(12)-H(16)	114. (4)	H(21)-C(13)-H(22)	113. (3)
H(15)-C(12)-H(17)	112. (4)	H(21)-C(13)-H(23)	112. (4)
H(16)-C(12)-H(17)	113. (3)	H(22)-C(13)-H(23)	114. (4)

^aThe number in parentheses is the standard deviation and refers to the least significant digits.

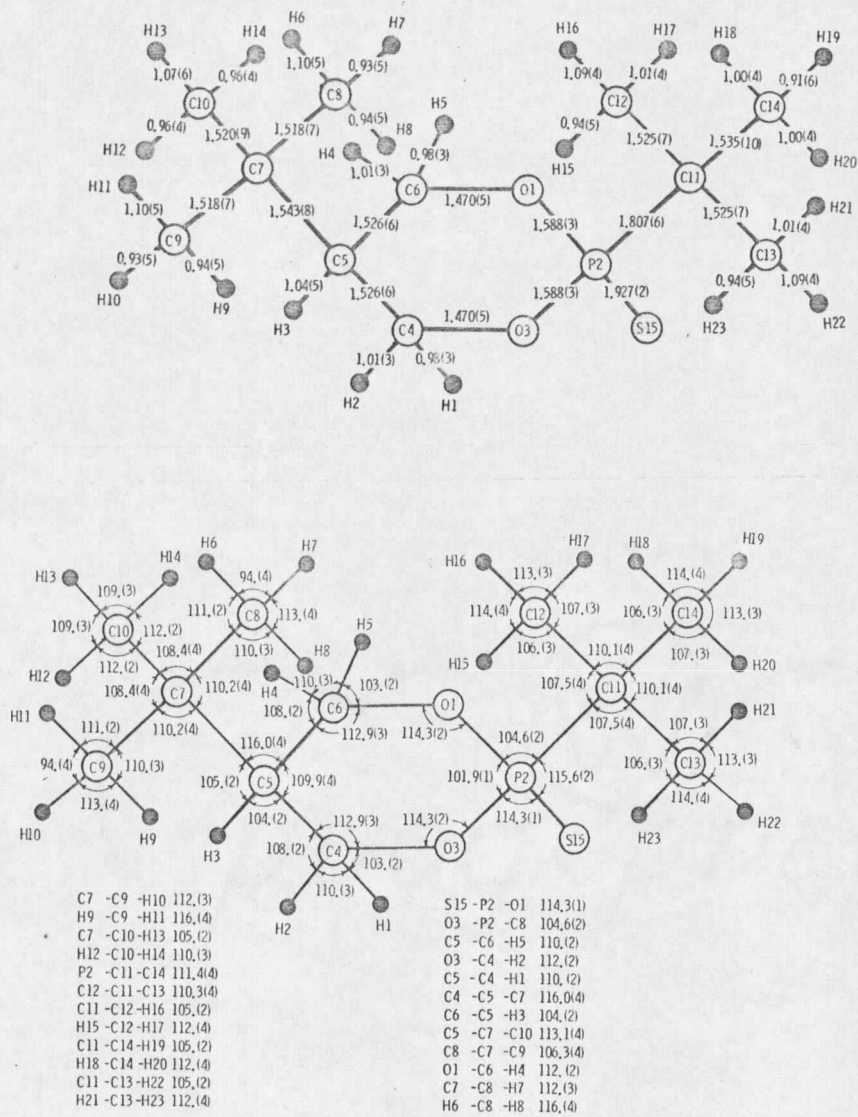


Figure 19.

Bond distances and bond angles for
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

dihedral angles are 50.3 and 46.0° respectively as compared to 60° for an ideal chair. The equations of the planes and the dihedral angles are listed in Table 34. The torsional angles about the ring bonds are given in Table 35. From the torsional angles, it can be seen that most of the flattening of the ring is on the carbon end of the ring, in contrast with the other 1,3,2-dioxaphosphorinanes that have been studied. More is said about the conformation later in the section comparing the 1,3,2-dioxaphosphorinanes on page 100.

The bond angles around the phosphorus form a distorted tetrahedral with bonds ranging from 101.9 to 115.6°. The P-C(11) bond is 1.807 Å which is the same as that found for the 5-*t*-butyl-2-phenyl-2-thio-1,3,2-dioxaphosphorinane. The P=S bond is 1.927 Å which is slightly longer than the 1.911 Å bond found in the 5-*t*-butyl-2-phenyl-2-thio- compound. The P-O bond distances are 1.588 Å which are normal bond lengths for phosphate esters. The C-O bonds are 1.470 Å and the C-C bonds in the ring are 1.526 Å, which are normal bond lengths.

The C-C bond distances of the *t*-butyl group on the phosphorus range from 1.525 to 1.535 Å and average 1.528 Å. The bond angles range from 107.5 to 111.4° which are nearly tetrahedral. The C-C bond distances of the *t*-butyl group on the C(5) position range from 1.518 to 1.543 Å and average 1.525 Å. The bond angles range from 106.3 to 113.1°. The angle C(5)-C(7)-C(10) appears to be increased by steric repulsions between C(10) and O(1) and O(3) on the ring.

TABLE 34

Equations of planes for
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane^a.

Atoms in plane	ℓ	m	n	$d(\text{\AA})$
O(1), O(3), C(4), C(6)	0.000	0.639	0.768	0.96
O(1), P(2), O(3)	0.000	-0.183	0.983	2.00
C(4), C(5), C(6)	0.000	-0.109	0.994	3.02

^aEquation of the plane: $\ell x + my + nz - d = 0.0$

TABLE 35

Torsional angles for
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

<u>Bond</u>	<u>angle, degrees</u>
P(2)-O(1)	57.6°
C(1)-C(6)	58.8°
C(6)-C(5)	51.4°
C(5)-C(4)	51.4°
C(4)-O(3)	58.8°
O(3)-P(2)	57.6°

The packing of the molecules in the unit cell is shown in the stereographic diagram in Figure 20. Packing conditions are not likely to be an important factor in the conformation of the molecule, since there are no intermolecular distances less than the sum of the van der Waals radii of neighboring molecules. Values of the van der Waals radii were obtained from Bondi (8). The pertinent radii were: P, 1.80; O, 1.52; C, 1.77; double bonded S, 1.74; and H, 1.20 Å.

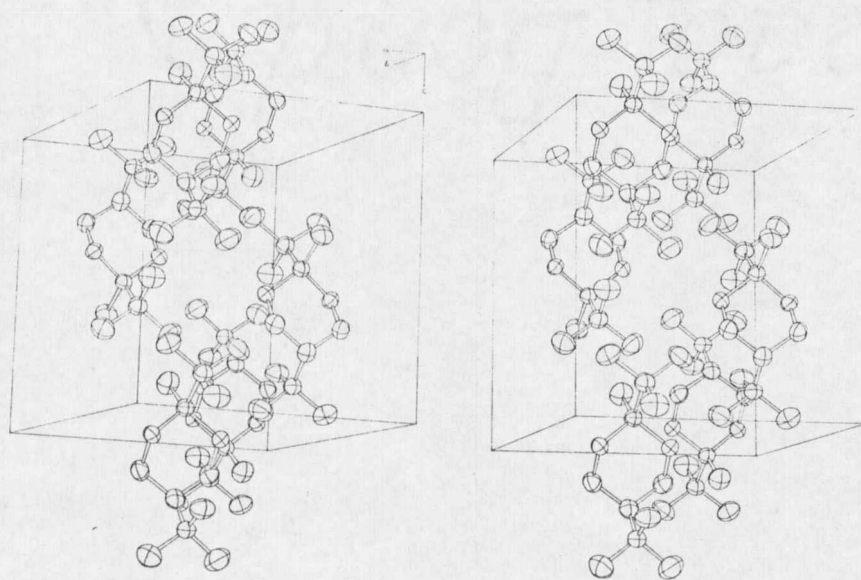


Figure 20.

Stereographic packing diagram for
2,5-t-butyl-2-thio-1,3,2-dioxaphosphorinane.

COMPARISON OF THE 1,3,2-DIOXAPHOSPHORINANES

A list of the 1,3,2-dioxaphosphorinanes for which crystal structures have been done is given in Table 36.

Points of comparison for the structures are: 1) the conformation of the ring, 2) comparison of size effects of various axial substituents bonded to the phosphorus atom, and 3) comparison of the effects of substituents bonded on the C(5) position. The bond angles and bond distances in the ring are not significantly different from those expected. Tables 37 and 38 show a comparison of the bond distances and bond angles of the 1,3,2-dioxaphosphorinanes.

2,5-*t*-butyl-2-thio-1,3,2-dioxaphosphorinane is unique in the series because the *t*-butyl on the phosphorus atom is equatorial rather than axial as the substituents for the rest of the series are. This may be due to the large steric repulsions between the bulky *t*-butyl and the 1,3- oxygen atoms and axial methylene hydrogens being greater than the 1-2 kcal preference for the substituent to be axial (7) causing the chair to invert.

All the 1,3,2-dioxaphosphorinane structures studied to this point have been found to be in the chair conformation. The dihedral angles between the planes O(1), O(3), C(4), C(6) and O(1), P(2), O(3) show a general flattening of the ring, as compared to the perfect chair with dihedral angles of 60°. The dihedral angles for the seven structures are listed in Table 36. There appears

TABLE 36

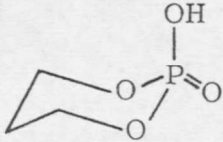
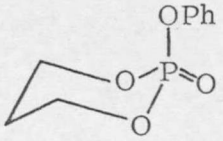
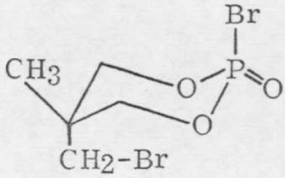
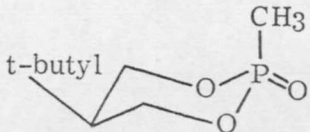
Compound	Ref.	R-index	Intensity collection	Dihedral angle O(1), O(3), C(4), C(6)- O(1), P(2), O(3)	Dihedral C(4), C(5), C(6)- O(1), O(3), C(4), C(6)
a) 	(5c)	0.108	Photographic	40.4°	54.2°
b) 	(5b)	0.115	Photographic	36.5°	53.1°
c) 	(5a)	0.045	Diffractionmeter	36.7°	52.5°
d) 	(15)	0.069	Diffractionmeter	33.5°	54.9°

TABLE 36

(Continued)

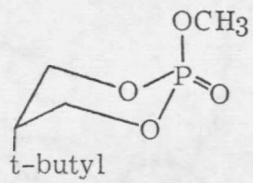
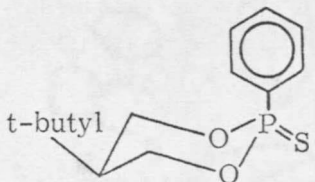
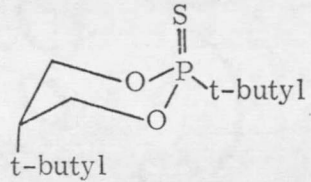
Compound	Ref.	R-index	Intensity collection	Dihedral angle O(1), O(3), C(4), C(6)- O(1), P(2), O(3)	Dihedral angle C(4), C(5), C(6)- O(1), O(3), C(4), C(6)
e) 		0.059	Diffractionmeter	37.9°	49.9°
f) 		0.036	Diffractionmeter	35.8°	56.0°
g) 		0.048	Diffractionmeter	50.3°	46.0°

TABLE 37

Comparison of bond distances for the
1,3,2-dioxaphosphorinanes.

Atoms	a ^a	b	c	d	e	f	g
P(2)-O(1)	1.56 ^b	1.56(1)	1.57(1)	1.56(1)	1.568(4)	1.576(2)	1.588(3)
P(2)-O(3)	1.58	1.57(1)	1.54(1)	1.58(1)	1.568(4)	1.587(2)	1.588(3)
P(2)=O	1.51	1.48(1)	1.44(2)	1.48(1)	1.443(6)	-----	-----
P(2)=S	---	---	---	---	----	1.911(1)	1.927(2)
P(2)-X	1.55	1.59(1)	2.171(6)	1.81(3)	1.567(6)	1.801(3)	1.807(6)
O(1)-C(6)	1.46	1.45(2)	1.47(2)	1.51(2)	1.457(7)	1.462(4)	1.470(5)
O(3)-C(4)	1.46	1.43(2)	1.49(3)	1.46(3)	1.457(7)	1.452(4)	1.470(5)
C(4)-C(5)	1.51	1.49(2)	1.50(3)	1.54(2)	1.510(8)	1.508(5)	1.526(6)
C(5)-C(6)	1.53	1.49(2)	1.59(3)	1.49(2)	1.510(8)	1.507(5)	1.526(6)

^aThe letters refer to the compounds shown in Table 36.

^bStandard deviations are 0.02-0.05 Å.

TABLE 38

Comparison of bond angles for the
1,3,2-dioxaphosphorinanes.

<u>Atoms</u>	<u>(a)^a</u>	<u>(b)</u>	<u>(c)</u>	<u>(d)</u>	<u>(e)</u>	<u>(f)</u>	<u>(g)</u>
O(1)-P(2)-O(3)	104.6(5) ^o	106.6(6) ^o	104.9(7) ^o	104.4(4) ^o	105.3(2) ^o	105.5(1) ^o	101.9(1) ^o
O(1)-P(2)-Y	110.1(5)	115.3(6)	113.8(8)	113.2(5)	112.6(3)	113.0(1)	114.3(1)
O(1)-P(2)-X	109.5(6)	101.7(6)	104.4(5)	110.0(5)	104.6(3)	106.2(1)	104.6(2)
O(3)-P(2)-Y	110.2(6)	111.8(6)	116.1(8)	112.9(4)	112.6(3)	111.8(1)	114.3(1)
O(3)-P(2)-X	105.1(7)	107.0(6)	105.1(5)	107.5(4)	104.6(3)	105.9(1)	104.6(2)
X-P(2)-Y	116.6(7)	113.7(6)	111.5(7)	108.7(5)	116.1(3)	113.8(1)	115.6(2)
P(2)-O(1)-C(6)	120.8(9)	117.7(9)	119.9(11)	119.7(7)	118.2(4)	120.4(2)	114.3(2)
O(1)-C(6)-C(5)	105.8(14)	110.5(13)	109.6(15)	110.5(10)	112.2(5)	110.8(3)	112.9(3)
C(6)-C(5)-C(4)	113.8(14)	109.9(14)	110.5(16)	107.7(10)	109.6(6)	108.3(3)	109.9(4)
C(5)-C(4)-O(3)	109.4(16)	112.0(13)	108.5(16)	110.7(9)	112.2(5)	111.8(3)	112.9(3)
C(4)-O(3)-P(2)	116.9(11)	117.5(9)	121.0(12)	120.2(8)	118.2(4)	117.3(2)	114.3(2)

^aThe letters refer to the compounds shown in Table 36.

to be a general correlation between the dihedral angle on the phosphate end of the ring and the size of the axial substituent with the exception of 2,5-*t*-butyl-2-thio-1,3,2-dioxaphosphorinane for which the *t*-butyl on the phosphorus atom is equatorial rather than axial. The correlation follows, in general, that the greater the flattening (smaller dihedral angle) the larger the substituent in the axial position, $\text{Me} > \text{Ph} > \text{Br} > \text{O}$. It is difficult to compare the Me and Ph groups as to size as far as what the 1,3-positions and axial hydrogens see. The phenyl ring is larger in overall dimensions, but the hydrogen on the methyl probably approaches the axial hydrogens much closer, making it appear larger sterically than the phenyl. The hydroxy, methoxy, and phenoxy groups are considered to be just an oxygen atom since the hydrogen, methyl, and phenyl groups bonded to the oxygen for the various compounds point away from the axial position. The size correlation may be explained by steric repulsions between the axial position of the phosphorus atom and the oxygen atoms in the ring plus the axial methylene hydrogens. These steric interactions may be relieved by flattening the phosphorus end of the ring, thus, decreasing the dihedral angle. The 2-phenoxy-2-oxo compound seems to be out of order. This may be because the data were photographic and refined to an R-index of 0.115, making the accuracy of the angle somewhat uncertain. The 2,5-*t*-butyl-2-thio compound does not fit into the correlation between Br and O where one would expect to find sulfur. However, for this compound, the phosphate end has been inverted compared to

the others in the series and the bulky t-butyl group in the equatorial position. The C(14) methyl on the t-butyl is in position to have steric interactions with the oxygens in the ring and the C(10) methyl on the axial t-butyl group bonded to the C(5) position. These steric interactions would tend to counter the flattening effect of the axial sulfur and increase the dihedral angle.

Another way in which the steric strain involving the axial substituents at phosphorus can be relieved is by bending the axial substituent toward the equatorial substituent. This angle decreases in the order OH, MeO, Ph, PhO, Br, Me being 116.6, 116.1, 113.8, 113.7, 111.5, and 108.7°, roughly as predicted by the increasing size of the group with the main exception of the phenyl group. The order of the phenyl may be due to the fact that the larger sulfur atom is in the equatorial position rather than oxygen, making the approach of the axial group more difficult. The mean value for the O(1)-P(2)-X and O(3)-P(2)-X angles vary little, (104.4-108.8°), over the series and show no firm size correlation. The O(1)-P(2)-O(3) angles remain almost constant, (104.4-106.6°), over the series. With the exception of the OH-compound, the mean angle of O(1)-P(2)-Y and O(3)-P(2)-Y remain almost constant over the series, (112.4-114.9°). The angles O(1)-P(2)-X, O(3)-P(2)-X, O(1)-P(2)-Y, and O(3)-P(2)-Y would not be expected to vary in any systematic method with the size of the axial substituent X.

The dihedral angles between the planes O(1), O(3), C(4), C(6), and C(4),

C(5), C(6) show little difference for the equatorial substituent, ($53.1 - 56.0^\circ$). For the compounds containing axial substituents on the C(5) position, there is some flattening of the ring with the disubstituted compound with the $-\text{CH}_2\text{-Br}$ group having less affect than the t-butyl groups. This is probably due to steric repulsion of the axial group with the 1,3-oxygens in the ring. In the $-\text{CH}_2\text{-Br}$ group, the Br points away from the ring making considerably less steric strain than the large t-butyl groups. In the case of the 2,5-t-butyl compound, there is also possible steric repulsion possible between the two t-butyl groups which could explain why the greatest amount of flattening of the carbon end of the ring occurs for this compound.

SUMMARY AND CONCLUSIONS

The three 1,3,2-dioxaphosphorinane structures reported in this dissertation continues the study of six-membered cyclic phosphorus compounds, and leads to a better understanding of the effects of substituents on the conformation of the ring (chair, boat, skew) as well as providing information about the orientational preferences of the groups. Comparison with other similar molecules is also made possible.

The conformations for the seven 1,3,2-dioxaphosphorinanes whose structures have been investigated have all been the chair. Also shown is an axial preference for the substituent on the phosphorus. Investigators have reported this axial preference to be 1-2 kilocalories (7). The exception in the series is the 2,5-*t*-butyl-2-thio-1,3,2-dioxaphosphorinane whose ring conformation is inverted on the phosphate end of the ring with respect to the rest of the 1,3,2-dioxaphosphorinanes and the *t*-butyl on the phosphorus is equatorial. For this compound, it appears that steric repulsions between the bulky *t*-butyl and the 1,3-oxygens and the axial methylene hydrogens are greater than the 1-2 kilocalorie preference for the axial conformation.

Another feature of this series of compounds, is that there is a general flattening of the ring, especially on the phosphate end. There appears to be a general correlation between the size of the axial substituent on the phosphorus

and the amount of flattening on the phosphate end of the ring. This effect can be seen in the decrease of the dihedral angle (ψ shown in Figure 21) between the planes of the chair as the size of the axial substituent on the phosphorus is increased, $\text{Me} > \text{Ph} > \text{Br} > \text{O}$. This same effect can also be seen with the axial substituents on the C(5) end of the ring, $t\text{-butyl} > \text{CH}_2\text{-Br} > \text{H}$.

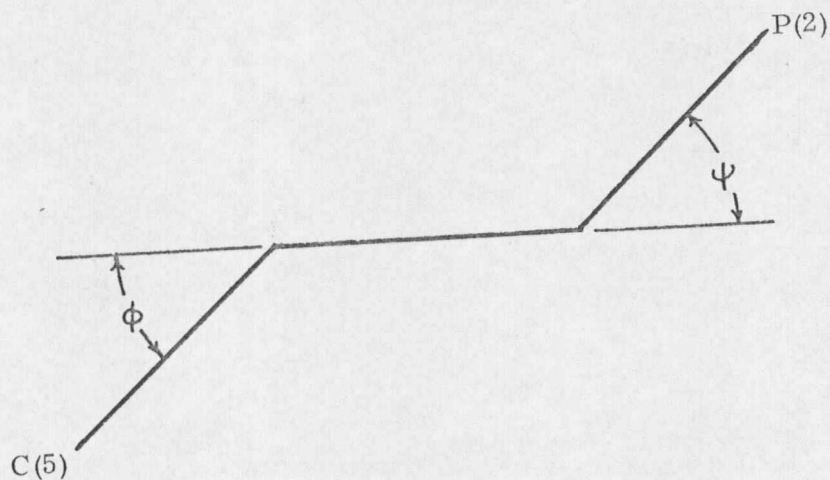


Figure 21.

Dihedral angles between the planes of the chair
for the 1,3,2-dioxaphosphorinanes.

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