



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
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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.

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 P21/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
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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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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.

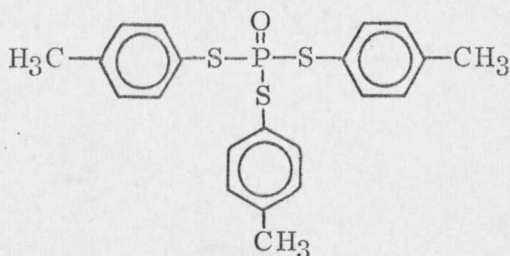


FIGURE 1

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 ${}^7J_{\text{P-H}}$.

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_0) 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 \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_0 ,

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

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

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 $R_{\text{wtd}} = 0.050$. 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

