



Structure-function relationships of some phosphorus compounds  
by Alvin Fitzgerald

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 two cyclic organophosphorus compounds were solved by the X-ray diffraction method. A hypothesis relating the free energy of hydrolysis of p-substituted monoaryl phosphates to the length of the P-O ester bonds has been presented. Huckel molecular orbital calculations were carried out as one test of the hypothesis. The structure of a sodium salt of phenyl phosphate was accurately determined as the initial work in a second test of the hypothesis.

2,2,3,3,4-Pentamethyl-1-phenylphosphetane-1-oxide crystallized in space group P21/c with  $a=17.165(16)\text{\AA}$ ,  $b=7.226(2)\text{\AA}$ ,  $c=11.365(10)\text{\AA}$ ,  $\beta=102.24(7)^\circ$ , and  $Z=4$ . This is the first unsymmetrical phosphetane oxide structure to be determined and indicates the reactivity of this group of compounds towards base is directly related to the amount of steric hindrance due to substitution on the  $\alpha$ -carbons. The final R is 6.5% for 1244 observed reflections.

1-Iodomethyl-3-methyl-1-phenylphospholanium iodide crystallizes in the space group P21 /c with  $a=7.217(3)\text{\AA}$ ,  $b=14.261(6)\text{\AA}$ ,  $c=14.778(6)\text{\AA}$ ,  $\beta=106.54(3)^\circ$ , and  $Z=4$ . The determination of this structure allowed workers in the field to assign structures to ten other compounds that are related to it through stereospecific reactions. The final R is 4.5% for 1434 observed reflections.

Data were presented indicating that the length of a P-O(Ar) bond, L, can be related to the equilibrium constant for the hydrolysis reaction by the equation.

$L=(k/\rho)\text{Log}(KArR/KO)$  Huckel molecular orbital calculations were carried out for para-substituted phenols, benzoic acids and phenyl phosphates. The results of these calculations are consistent with the proposed hypothesis.

Disodium phenylphosphate-2-methoxyethanol trihydrate molecular complex crystallizes in the space group P21/c with  $a=14.69(2)\text{\AA}$ ,  $b=7.960(6)\text{\AA}$ ,  $c=13.68(1)\text{\AA}$ ,  $\beta=107.3(2)^\circ$ , and  $Z=4$ . Comparison of the intramolecular distances in the phenylphosphate dianion with those of a previously determined structure showed significant differences in some of the non-bonded intramolecular distances. These differences were found to be due to a difference in the orientation of the phenyl ring with respect to the phosphate group. The final R is 5.6% for 969 observed reflections.

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A thesis submitted to the Graduate Faculty in partial  
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in

Chemistry

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## ABSTRACT

The crystal and molecular structures of two cyclic organophosphorus compounds were solved by the X-ray diffraction method. A hypothesis relating the free energy of hydrolysis of p-substituted monoaryl phosphates to the length of the P-O ester bonds has been presented. Hückel molecular orbital calculations were carried out as one test of the hypothesis. The structure of a sodium salt of phenyl phosphate was accurately determined as the initial work in a second test of the hypothesis.

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Data were presented indicating that the length of a P-O(Ar) bond, L, can be related to the equilibrium constant for the hydrolysis reaction by the equation.

$$L = \frac{k}{\rho} \text{Log} \left( \frac{K_{ArR}}{K_O} \right)$$

Hückel molecular orbital calculations were carried out for para-substituted phenols, benzoic acids and phenyl phosphates. The results of these calculations are consistent with the proposed hypothesis.

Disodium phenylphosphate-2-methoxyethanol trihydrate molecular complex crystallizes in the space group  $P2_1/c$  with  $a=14.69(2)\text{Å}$ ,  $b=7.960(6)\text{Å}$ ,  $c=13.68(1)\text{Å}$ ,  $\beta=107.3(2)^\circ$ , and  $Z=4$ . Comparison of the intramolecular distances in the phenylphosphate dianion with those of a previously determined structure showed significant differences in some of the non-bonded intramolecular distances. These differences were found to be due to a difference in the orientation of the phenyl ring with respect to the phosphate group. The final R is 5.6% for 969 observed reflections.

## INTRODUCTION

This dissertation is divided into five chapters which may be generally considered as two sections. The first section consists of the first two chapters which contain the structures of two compounds. The structures of 2,2,3,3,4-pentamethyl-1-phenylphosphetane 1-oxide and 1-iodomethyl-3-methyl-1-phenylphospholanium iodide were determined as a service to workers in the field of organophosphorus chemistry and as part of a long term study of the structures of phosphorus compounds carried on in this laboratory. Preliminary reports on these structures have appeared (22,23).

The second section of the thesis consists of the last three chapters. Chapter III consists of the evidence for and the derivation of a hypothesis relating the free energy of hydrolysis for monoaryl phosphates to the length of the P-O bond being hydrolyzed. A preliminary report of this hypothesis has been given (12). Huckel molecular orbital (HMO) calculations have been carried out as a preliminary test of the hypothesis and are presented in the fourth chapter. The structure of a sodium salt of phenyl phosphate has been determined as the initial structure analysis in a series of structures that must be accurately determined to test the validity of the hypothesis and is contained in the

fifth chapter.



## CHAPTER I

### THE CRYSTAL AND MOLECULAR STRUCTURE OF 2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE

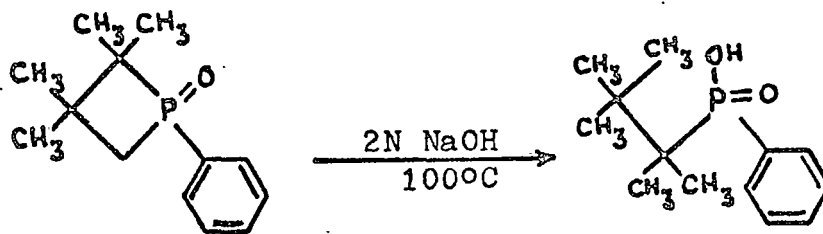
#### I. INTRODUCTION

The determination of the three-dimensional structure of 2,2,3,3,4-pentamethyl-1-phenylphosphetane 1-oxide is of interest for a number of reasons. Structures of compounds of this type have been studied in this laboratory for several years. Examples of other compounds in this series whose structures have been determined are shown in Figure I.

This is the first unsymmetrical phosphetane oxide whose structure has been determined. Dr. Sheldon Cremer of Marquette University synthesized the compound and supplied the sample. It is of particular interest in regard to organophosphorus chemistry to know if the methyl group on the mono-substituted  $\alpha$ -carbon is cis or trans to the phenyl group.

This class of compounds shows surprising stability when subjected to hydrolysis under basic conditions.

Corfield has reported the following two reactions (13):



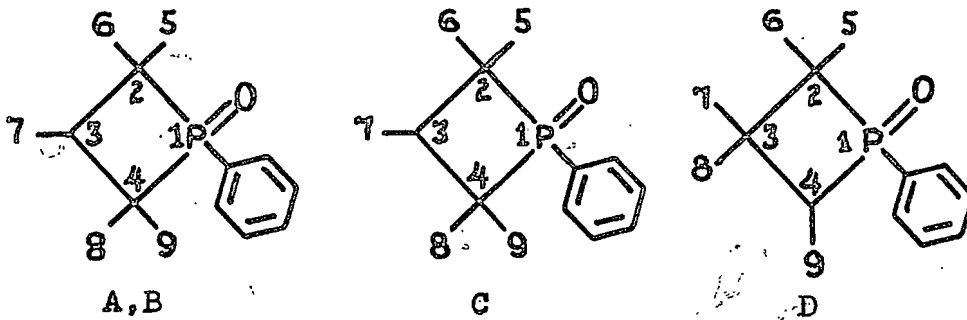
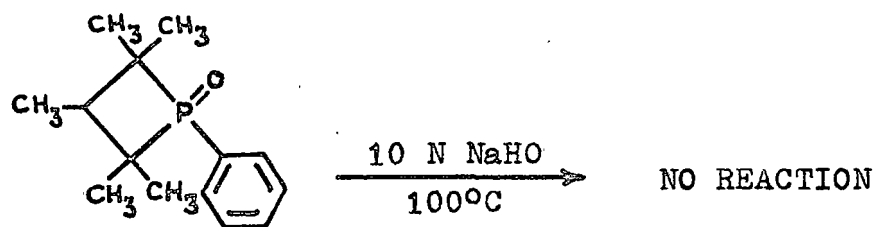
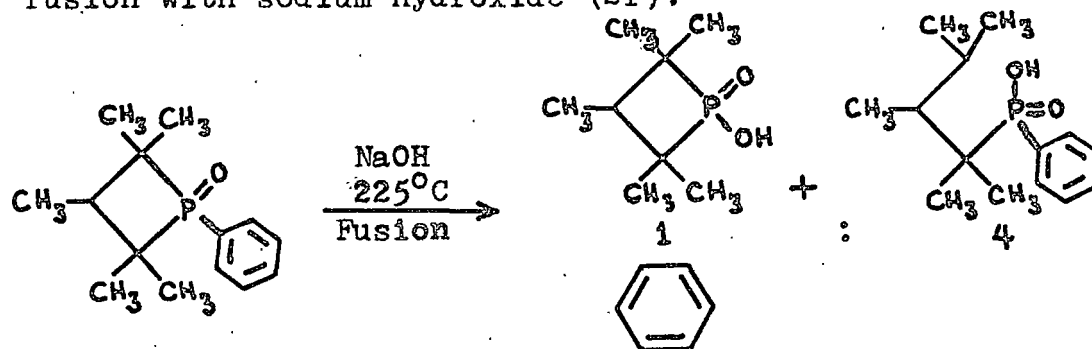


FIGURE I

ISOMERS FOR WHICH THREE-DIMENSIONAL STRUCTURES HAVE BEEN DETERMINED. A, B: METHYL-7 TRANS TO PHENYL (28); C: METHYL-7 CIS TO PHENYL (29); D: THIS WORK



Ezzel has observed that the P-C bond can be cleaved by fusion with sodium hydroxide (21):



These reactions clearly show the effect of  $\alpha$ -substitution on the reactivity of the compounds.

It has been suggested that the 1-4 bond may be longer in the unsymmetrical case than the 1-2 bond (37). Solution of this structure should adequately answer that question though ideally one would use a phosphetane-oxide that was disubstituted on a  $\alpha$ -carbon and unsubstituted on the other  $\alpha$ -carbon.

## II. PREPARATION OF CRYSTALS

The compound crystallized readily from solutions of

either benzene or cyclohexane when these were allowed to evaporate slowly. This was achieved by placing a Petri dish of the solution in a dessicator and opening the lid very briefly once a day until crystals formed. Two to three weeks were generally required for crystal growth to occur. The largest crystals were obtained from the cyclohexane solution and one of these was used for the data collection. The crystal was mounted on a glass fiber and sealed in a capillary in as much as the crystals turned opaque in air when exposed to X-rays.

### III. DENSITY DETERMINATION

The density of the compound was determined by flotation in a mixture of methanol and carbon tetrachloride. The observed density was  $1.12 \text{ gram/cm}^3$ , and the calculated density, assuming four molecules per unit cell, was  $1.14 \text{ gram/cm}^3$ .

### IV. DETERMINATION OF SPACE GROUP AND CELL PARAMETERS

The crystal was mounted coincident with the b-axis. An oscillation photograph contained a mirror plane perpendicular to the axis of rotation indicating a space group of monoclinic or higher symmetry. The space group extinct reflections, as determined on the General Electric XRD-5 diffractometer, were:

hkl: no conditions

Ok0:  $k = 2n + 1$

h0l:  $l = 2n + 1$

These extinctions uniquely determine the space group as  $P2_1/c$ . The unit cell dimensions were determined by least-squares refinement of the  $2\theta$  values of 12 general reflections using a General Electric XRD-5 diffractometer equipped with with a G.E. single crystal orienter.

Pertinent crystal data are listed in Table I. It was later discovered that a different cell still in space group  $P2_1/c$  could be chosen which would give a  $\beta$  angle nearer to  $90^\circ$ . The data were converted to this cell although the solution of the structure was obtained using the original cell parameters.

#### V. COLLECTION OF THE DATA

The unique intensity data were collected by the  $\theta$ - $2\theta$  scan method out to  $2\theta = 25.0^\circ$ , using zirconium-filtered  $\text{MoK}\alpha$  ( $\lambda = 0.71069\text{\AA}$ ) radiation. The General Electric XRD-5 diffractometer used was equipped with a scintillation counter, pulse-height discriminator, and a General Electric single crystal orientator. Each reflection was scanned over an angular width of  $2.0^\circ$  in  $2\theta$  at a rate of  $2^\circ$  per minute and background radiation was counted for ten

TABLE I  
CRYSTAL DATA

2,2,3,3,4-Pentamethyl-1-phenylphosphetane 1-oxide  
 $C_{14}POH_{21}$  F.W. 236.295 F(000) = 512  
 Monoclinic, space group  $P2_1/c$

ORIGINAL CELL

$$a = 18.50(4)\text{\AA}$$

$$b = 7.222(4)\text{\AA}$$

$$c = 11.36(2)\text{\AA}$$

$$\beta = 114.6(1)^\circ$$

$$\text{Volume of the unit cell} = 1379\text{\AA}^3$$

$$\text{Molecules/unit cell} = 4$$

$$\text{Linear absorption coefficient, } \mu(\text{MoK}\alpha) = 1.78\text{cm}^{-1}$$

Crystal dimensions: 0.18mm x 0.64mm x 0.65mm

Crystal was bound by faces {100}, {010}, and {001} respectively.

NEW CELL

$$a = 17.165(16)\text{\AA}$$

$$b = 7.226(2)\text{\AA}$$

$$c = 11.365(10)\text{\AA}$$

$$\beta = 102.24(7)^\circ$$

$$D_{\text{calc}} = 1.14 \text{ grams/cc.}$$

$$D_{\text{exp}} = 1.12 \text{ grams/cc.}$$

\*Unit cell dimensions and standard deviations are those determined for a second data set on a second crystal.

seconds at each end of the  $2\theta$  scan. The take-off angle was set at  $4.00^\circ$ . The intensities of the 020, 220, and 002 reflections were monitored during the data collection so that corrections could be made for such things as variations in room temperature, voltage supply, instrumental stability and also to check for decomposition of the crystal during the course of the data collection. A scale factor was calculated for each block of data using these standard reflections. The average value of the scale factor over the complete data collection was 1.08 with a standard deviation of 0.045.

#### VI. TREATMENT OF THE DATA

Structure factors ( $F_0$ ) were calculated from the intensities by applying the usual Lorentz-polarization correction for diffractometer data. The weights were calculated for each reflection assuming Poisson counting statistics and a correction factor,  $k_2$ , related to the instrument instability (45). The weight assigned to the individual  $F_0$  is related to the standard deviation,  $\sigma_F$ , as shown below.

$$w = \frac{1}{(\sigma_F)^2}$$

and

$$\sigma_F = \frac{k_1}{2\sqrt{L_p}} \sqrt{\frac{N_T + N_{Bg1} + N_{Bg2} + (k_2 N_{pk})^2}{N_{pk}}}$$

where

w = the weight

$\sigma_F$  = the standard deviation of  $F_o$

$k_1$  = the scale constant for the data set

$k_2$  = the instrument instability constant

p = the polarization factor

L = the Lorentz factor

$N_T$  = the total peak count

$N_{Bg1}$  and  $N_{Bg2}$  = the background counts at each end of the scan  
(corrected for time)

$N_{pk} = N_T - N_{Bg1} - N_{Bg2}$  = the net peak count

The data set consisted of 1712 reflections of which 1244 were considered observed at the three sigma level. The constant,  $k_2$ , was set at 0.07 based on the average standard deviation of the individual standard reflections (45). The data were corrected for absorption (35). The maximum and minimum transition factors were 0.96 and 0.98, respectively. Scattering factor curves for the non-hydrogen atoms were taken from the International Tables (31) as were the anomalous scattering corrections ( $\Delta f'$  and  $\Delta f''$ ) for phosphorus. The scattering factor curve for hydrogen was taken from Stewart,



et al. (44).

## VII. STRUCTURE DETERMINATION

Five possible phosphorus positions were located from a Patterson map and refinement was tried on each of them. The fifth peak proved to be the correct phosphorus position.

Refinement is taken to mean least squares refinement where the minimized function is

$$\sum w(|F_o| - \frac{1}{k_1} |F_c|)^2$$

There are several indicators which describe the fit of the model to the data. These will be defined here for use in this chapter and the remaining two structural chapters. The residual index, summed over the observed data only is

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

The residual index summed over all data collected is

$$R_{\text{obs} + \text{unobs}} = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

The weighted residual index summed over the observed data only is defined as

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

A fourth indicator, S, the standard deviation of an observation of unit weight summed over the observed data only is

$$S = \left[ \frac{\sum w (|F_o| - |F_c|)^2}{N_{\text{obs}} - N_{\text{var}}} \right]^{\frac{1}{2}}$$

where

$N_{\text{obs}}$  = the number of observed data

and

$N_{\text{var}}$  = the number of variables that are refined in the model

Full matrix least squares refinement of the positional and anisotropic thermal parameters for the 16 heavy atoms produced an R of 0.084 (8). A series of difference Fourier maps were needed to determine the positions of all the hydrogen atoms. The methyl groups appear to be somewhat disordered.

Positional and anisotropic thermal parameters of the 16 non-hydrogen atoms were refined. The positional and

isotropic temperature factors for the 21 hydrogen atoms were included in the refinement. At the completion of the refinement  $R = 0.065$ ,  $R'' = 0.080$ ,  $R_{\text{obs} + \text{unobs}} = 0.123$  and  $S = 1.70$ . The largest shift divided by the standard deviation was less than 0.2 at the end of the refinement.

A final difference map was calculated. The largest peaks on this map were less than  $\pm 0.26 \text{e}\text{\AA}^{-3}$  and were found near the phosphorus atom.

#### VIII. DISCUSSION OF THE STRUCTURE

The positional parameters of the non-hydrogen atoms are listed in Table II. The thermal parameters of the non-hydrogen atoms are listed in Table III. The hydrogen atom parameters are listed in Table IV. Table V contains the observed and calculated structure factors.

Figure II shows an ORTEP drawing of the structure with the thermal ellipsoids calculated at the 50% probability level (32). The bond lengths and angles are presented in Figure III.

The ORTEP drawing clearly shows that the single  $\alpha$ -methyl group is trans to the phenyl group. Figure III shows that the two P-C bonds in the ring differ by about eight standard deviations. Moret and Trefonas have suggested that the P-C bond to the least substituted

TABLE II

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN  
2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE

<u>ATOM</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
P	.74713(7) <sup>a</sup>	.23726(16)	.76522(10)
C(2)	.7405(3)	.0113( 6)	.7293(5)
C(3)	.6518(3)	.0276( 7)	.6599(5)
C(4)	.6633(2)	.2419( 7)	.6398(4)
C(5)	.5958(4)	.3776(10)	.6375(7)
C(6)	.6253(4)	.0767( 9)	.5422(5)
C(7)	.5923(4)	.0058( 9)	.7400(6)
C(8)	.7512(4)	.1382( 8)	.8377(6)
C(9)	.7942(3)	.0669( 7)	.6439(5)
C(10)	.8344(2)	.3594( 6)	.7384(4)
C(11)	.8516(3)	.3804( 7)	.6287(5)
C(12)	.9187(4)	.4772( 8)	.6143(7)
C(13)	.9679(3)	.5536( 8)	.7160(7)
C(14)	.9509(3)	.5353( 9)	.8243(7)
C(15)	.8849(3)	.4378( 8)	.8386(5)
O	.7327(2)	.2904( 5)	.8843(3)

<sup>a</sup>The number in parentheses is the standard deviation and refers to the least significant digits.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN

2,2,3,3,4-PENTAMETHYL-1-PHOSPHETANE 1-OXIDE

ATOM	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
P	.00258( 4)	.01508(24)	.00692(11)	.00017( 9)	.00095( 4)	-.00007(14)
C(2)	.0033( 2)	.0139( 9)	.0093( 5)	.0005( 3)	.0005( 2)	-.0012( 5)
C(3)	.0030( 2)	.0178(10)	.0078( 5)	.0006( 3)	.0011( 2)	-.0009( 5)
C(4)	.0023( 1)	.0177(10)	.0088( 4)	.0003( 3)	.0013( 2)	-.0005( 6)
C(5)	.0030( 2)	.0289(17)	.0199(10)	-.0030( 5)	.0002( 3)	.0001(10)
C(6)	.0048( 3)	.0254(14)	.0107( 6)	.0033( 5)	-.0002( 3)	.0025( 7)
C(7)	.0038( 2)	.0305(17)	.0141( 8)	.0027( 5)	.0026( 3)	-.0033( 8)
C(8)	.0063( 3)	.0174(13)	.0156( 8)	.0017( 5)	-.0002( 4)	-.0080( 8)
C(9)	.0037( 2)	.0154(11)	.0127( 6)	-.0011( 4)	.0012( 3)	.0040( 6)
C(10)	.0018( 2)	.0155(10)	.0093( 5)	-.0001( 3)	.0004( 2)	-.0004( 5)
C(11)	.0027( 2)	.0228(12)	.0095( 5)	.0004( 4)	.0012( 2)	-.0021( 6)
C(12)	.0038( 2)	.0260(15)	.0152( 8)	-.0003( 5)	.0023( 3)	-.0051( 8)

TABLE III (CONTINUED)

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN

2,2,3,3,4-PENTAMETHYL-1-PHOSPHETANE 1-OXIDE

ATOM	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(13)	•0027( 2)	•0190(12)	•0184( 8)	•0014( 4)	•0001( 3)	•0032( 8)
C(14)	•0036( 2)	•0260(15)	•0138( 8)	•0015( 5)	•0001( 3)	•0007( 8)
C(15)	•0030( 2)	•0193(12)	•0112( 6)	•0006( 4)	•0003( 3)	•0025( 6)
O	•0041( 2)	•0244( 9)	•0096( 4)	•0019( 3)	•0019( 2)	•0016( 4)

(e.s.d.'s in parentheses)

The expression for the anisotropic thermal parameters is of the form:

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

TABLE IV

HYDROGEN ATOM POSITIONS AND THERMAL PARAMETERS FOR  
2,2,3,3,4-PENTAMETHYL-1-PHOSPHETANE 1-OXIDE

ATOM	$x/a$	$y/b$	$z/c$	$B_{iso}$
H(1)	•690(3) <sup>a</sup>	•258( 7)	•585( 4)	4•(1)
H(2)	•556(5)	•343(12)	•604( 8)	9•(2)
H(3)	•574(5)	•386(11)	•716( 7)	9•(2)
H(4)	•614(9)	•538(18)	•651(13)	15•(4)
H(5)	•571(5)	•044(11)	•492( 7)	8•(2)
H(6)	•651(4)	•069( 8)	•481( 6)	6•(1)
H(7)	•616(4)	•178(10)	•565( 6)	7•(2)
H(8)	•545(4)	•042( 9)	•701( 6)	7•(2)
H(9)	•598(4)	•126(11)	•772( 7)	8•(2)
H(10)	•604(5)	•056(12)	•824( 8)	9•(2)
H(11)	•733(4)	•246( 9)	•809( 6)	6•(1)
H(12)	•799(4)	•154( 9)	•872( 6)	6•(1)
H(13)	•721(6)	•091(15)	•890( 9)	12•(3)
H(14)	•788(3)	•193( 8)	•615( 5)	5•(1)
H(15)	•783(6)	•006(12)	•574( 9)	11•(3)
H(16)	•857(4)	•078( 9)	•711( 6)	7•(2)
H(17)	•827(4)	•334( 8)	•564( 5)	6•(1)

<sup>a</sup>The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE IV (CONTINUED)  
HYDROGEN ATOM POSITIONS AND THERMAL PARAMETERS FOR  
2,2,3,3,4-PENTAMETHYL-1-PHOSPHETANE 1-OXIDE

<u>ATOM</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>B<sub>iso</sub></u>
H(18)	.928(4)	-.515( 8)	.544( 6)	5.(1)
H(19)	1.011(7)	-.612(15)	.702(11)	14.(3)
H(20)	.987(4)	-.563( 9)	.919( 7)	7.(2)
H(21)	.875(4)	-.427( 9)	.912( 6)	7.(1)



TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS

Table with multiple columns containing numerical data representing structure factors. The data is organized in rows and columns, with some cells containing labels like 'L', 'h', 'k', 'l' and numerical values.

19

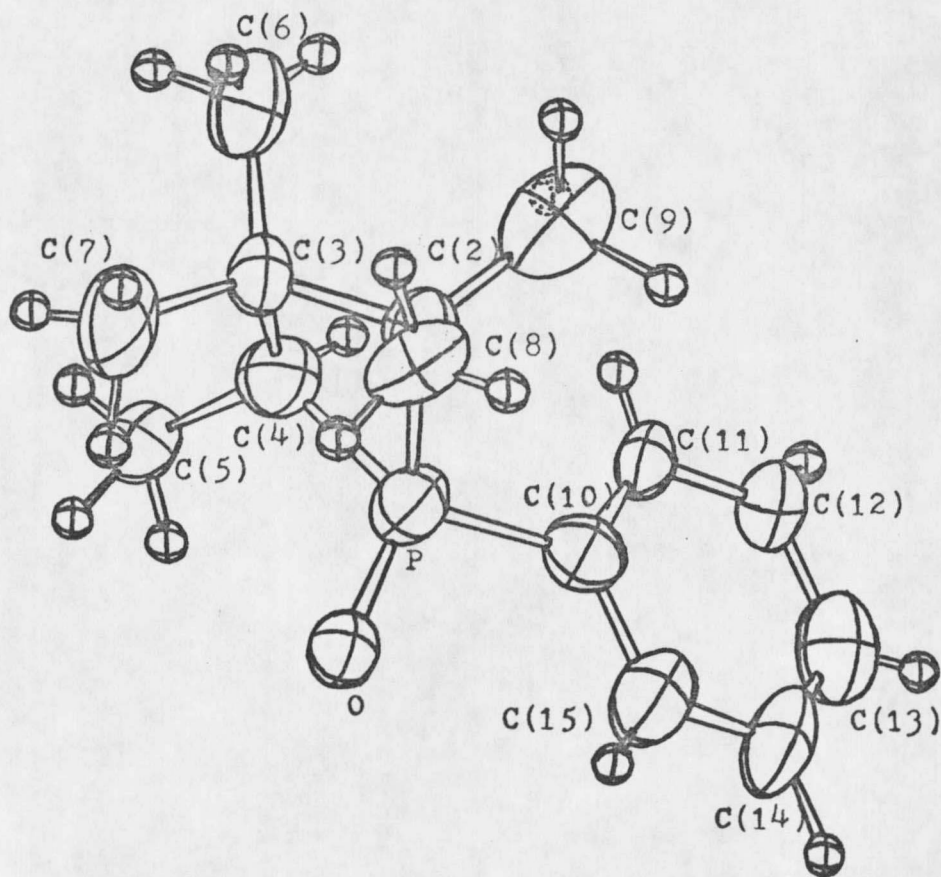


FIGURE II

MOLECULAR STRUCTURE OF  
2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE  
AT THE 50% PROBABILITY LEVEL

The hydrogen atoms were arbitrarily assigned isotropic temperature factors of 1.0 in this illustration.

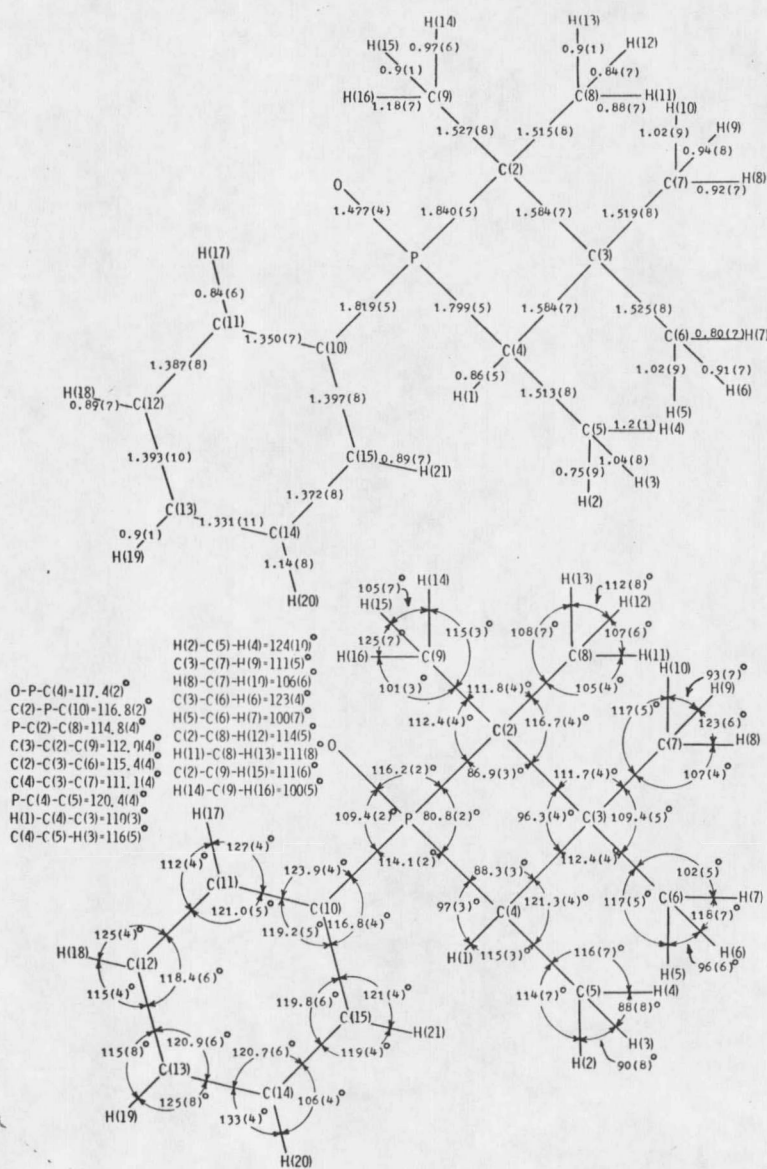


FIGURE III

BOND DISTANCES AND ANGLES FOR  
 2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE

$\alpha$ -carbon will be longer than the other P-C bond (37). They based this suggestion on the ring opening reactions of this class of compounds. In fact, the P-C bond to the least substituted  $\alpha$ -carbon is shorter than the other P-C bond. The observed result is reasonable since increased  $\alpha$ -carbon substitution causes an increased number of steric interactions (30). As steric repulsion between groups attached to bonded atoms increases, the distance between the bonded atoms increases. Other than the P-C(4) bond distance, the bond angles and distances are not significantly different from previously reported values for phosphetane oxides (28, 29).

Corfield has proposed a trigonal-bipyramid transition state for basic hydrolysis in which the ring carbons are axial-equatorial (13). Steric hindrance apparently is responsible for the differences in reactivity of this class of compounds. The symmetrical  $\alpha$ -disubstituted compounds would provide a great deal of hindrance to the approach of the hydroxide ion. The mono-substituted  $\alpha$ -carbon would offer a less hindered approach for the hydroxide ion. A transition state involving a pseudo-rotation (36) must be invoked to explain the cleavage of the P-C bond to the least substituted  $\alpha$ -carbon. This is illustrated in Figure IV.

Four-membered rings of this type are expected to be puckered. A comparison of the ring pucker in these three

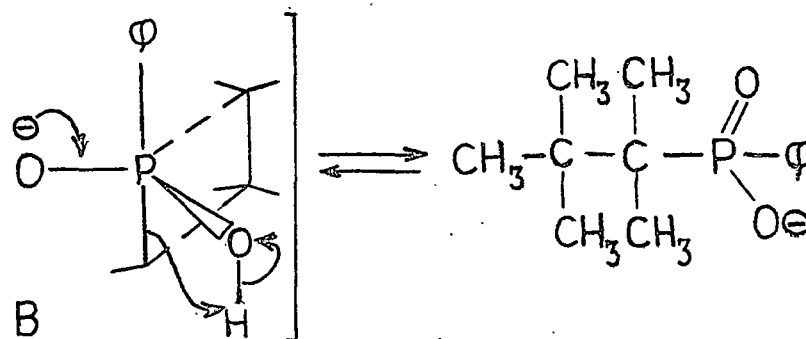
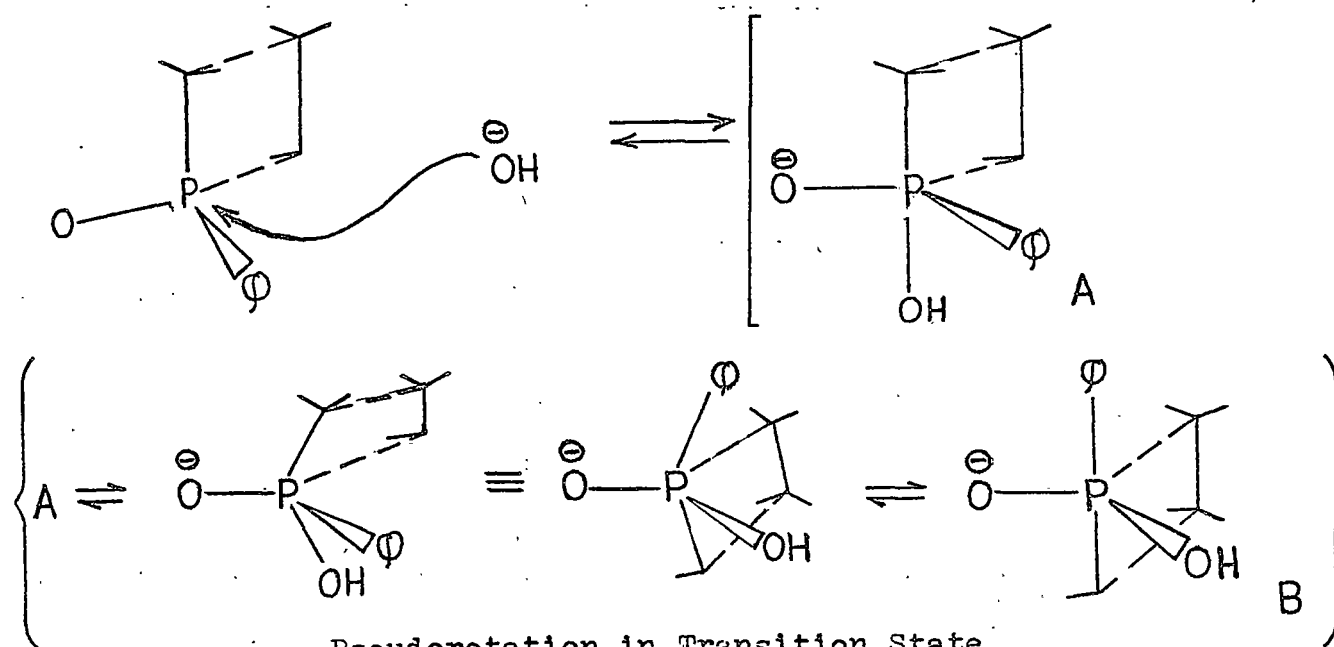


FIGURE IV

PROPOSED REACTION MECHANISM FOR ALKALINE HYDROLYSIS OF  
2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE

isomers is shown in Figure V. The angle between the planes C(2)-P-C(4) and C(2)-C(3)-C(4) is larger in this compound than in the other compounds. The phenyl group is tilted  $12^\circ$  away from being perpendicular to the C(2)-P-C(4) plane as is illustrated in Figure VI.

The phenyl group is planar with an average displacement from the least squares plane of  $0.0034\text{\AA}$ . The maximum displacement from the plane is  $0.0062\text{\AA}$  at the C(14) position. The equations for the various planes of interest are given in Table VI.

A stereographic packing diagram is shown in Figure VII. The closest intermolecular contact is  $3.1(1)\text{\AA}$  and occurs between H(4) and C(6). There are no intermolecular distances that are significantly less than the sum of the van der Waal radii (38).

A  $\bar{\sigma}_R$  plot was constructed for this structure and is shown in Figure VIII (1). The slope of the least squares line through the data points was 1.60 with an intercept of 0.01. This indicates underestimation of the standard deviations by a factor of about 1.60. Further discussion of the  $\bar{\sigma}_R$  plot is contained in Chapter V.

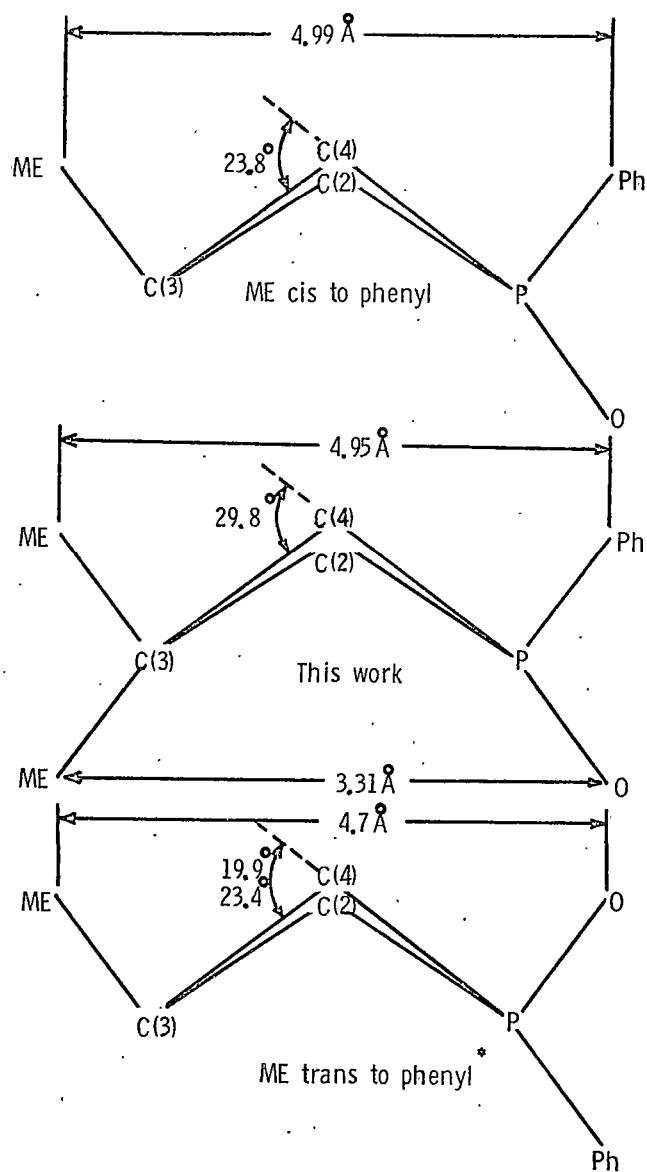


FIGURE V

COMPARISON OF RING PUCKERING IN THE THREE ISOMERIC PHOSPHETANE OXIDES

\*Two molecules in the asymmetric unit.

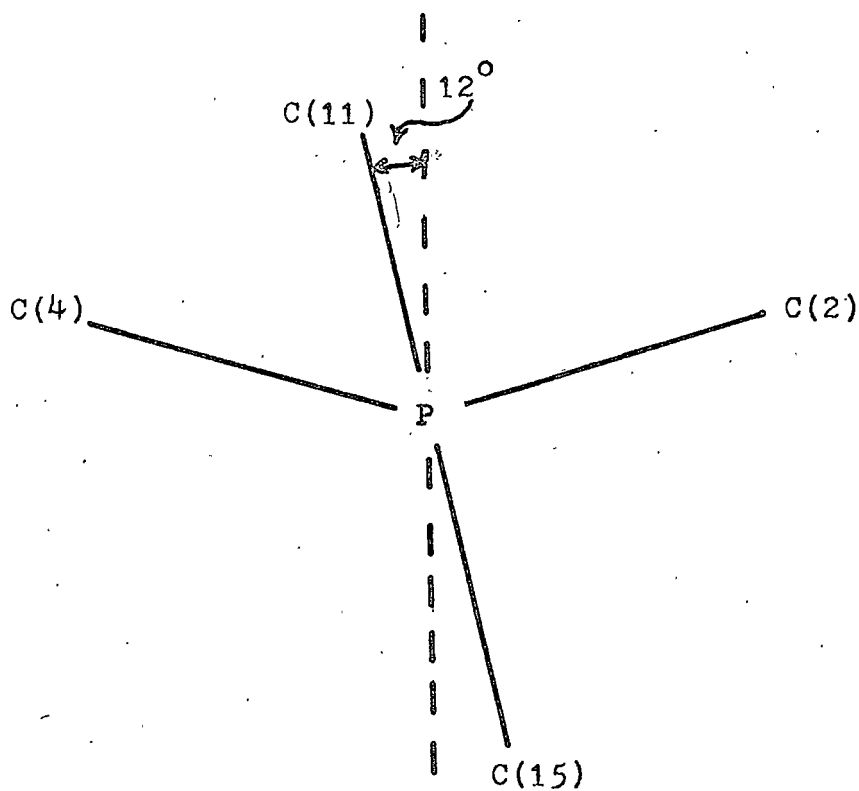


FIGURE VI

TILT OF PHENYL GROUP RELATIVE TO THE C(2)-P-C(4) PLANE



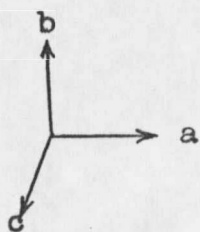
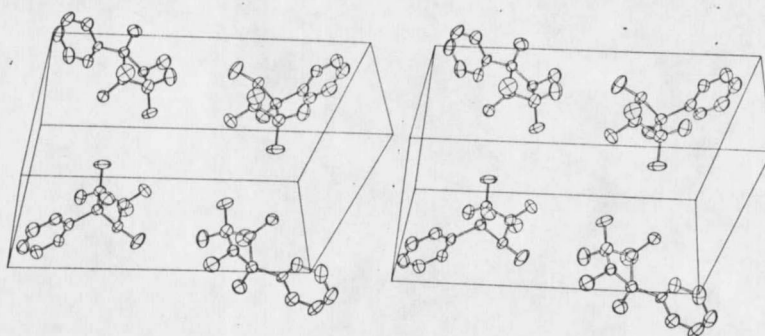
TABLE VI  
 EQUATIONS OF PLANES<sup>a.)</sup> REFERRED TO ORTHOGONAL AXES IN  
 2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE<sup>b.)</sup>

<u>ATOMS IN PLANE</u>	<u>l</u>	<u>m</u>	<u>n</u>	<u>p</u>	<u>S(<math>\Delta^2</math>)<sup>c.)</sup></u>
C(10), C(11), C(12), C(13), C(14), C(15)	0.520	0.843	0.138	5.461	0.00009
C(2), P, C(4)	0.770	-0.127	-0.626	3.353	————
C(2), C(3), C(4)	-0.454	-0.197	0.869	2.052	————

a.) Least squares plane:  $lX + mY + nZ - p = 0.0$

b.) Coordinate system for plane is: X along a, Y in a-b plane,  
z along c.

c.)  $S(\Delta^2)$  is the sum of the squares of the deviations of atoms  
from the planes.



Orientation of unit cell

FIGURE VII  
STEREOGRAPHIC PACKING DIAGRAM FOR  
2,2,3,3,4-PENTAMETHYL-1-PHENYLPHOSPHETANE 1-OXIDE

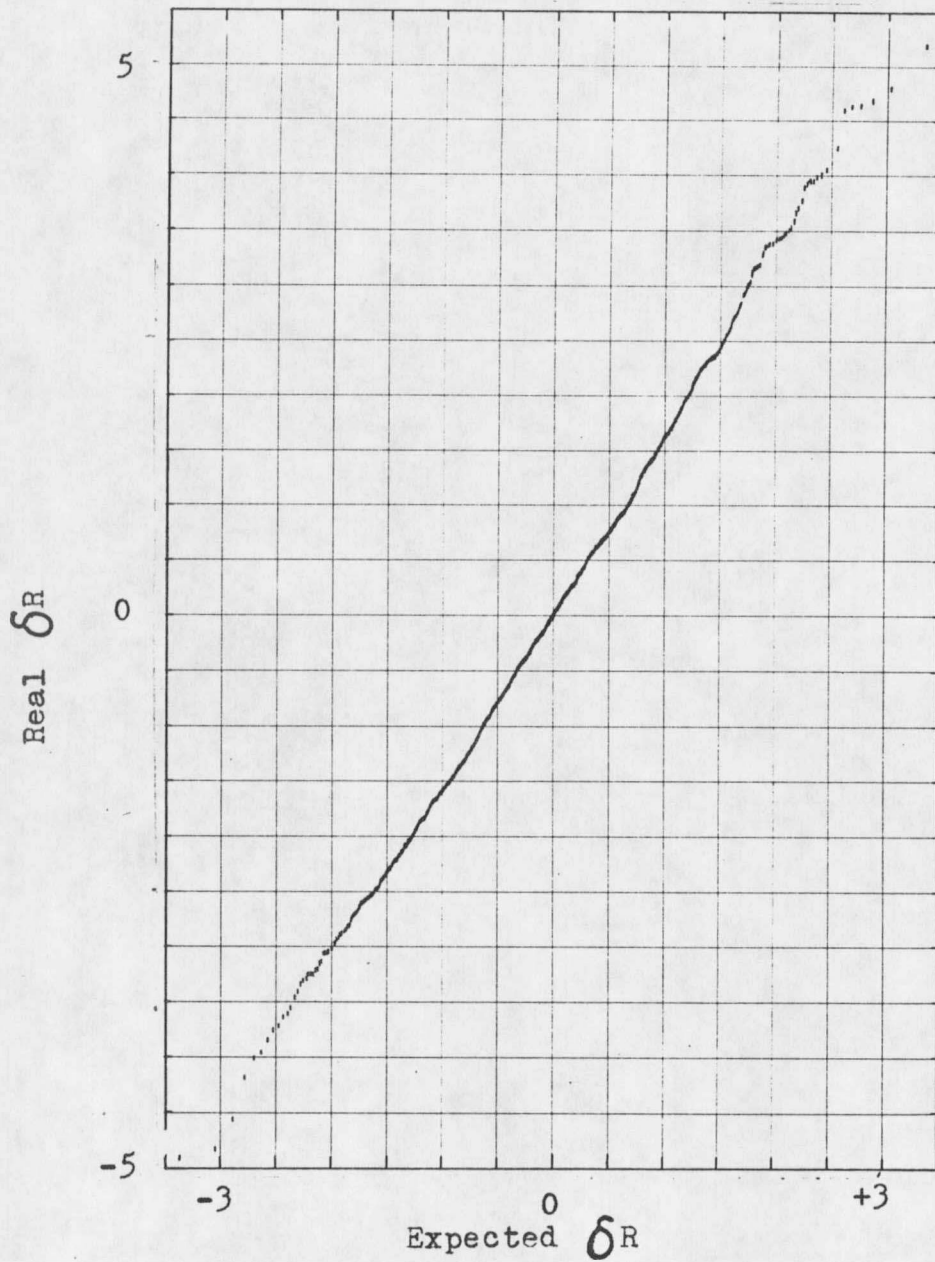


FIGURE VIII

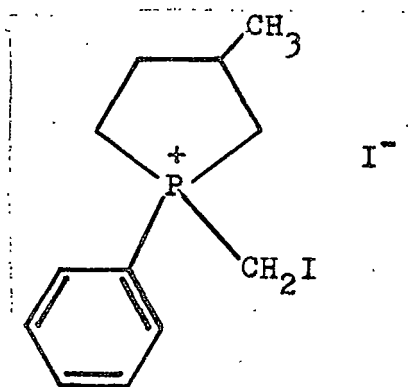
NORMAL PROBABILITY PLOT OF 1244  $\delta_R$  BASED ON  $F_0$

## CHAPTER II

### THE CRYSTAL AND MOLECULAR STRUCTURE OF 1-IODOMETHYL-3-METHYL-1-PHENYLPHOSPHOLANIUM IODIDE

#### I. INTRODUCTION

The primary purpose for determining the three-dimensional structure of this compound was to correlate structural results with those of others in a series of phosphorus organic compounds. Dr. Kenneth L. Marsi of California State College, Long Beach, prepared the compound and supplied the crystals. It was known that the crystals were a racemic mixture of either the cis or the trans isomer of this structure:



Attempts to determine the configuration of this compound by the use of NMR spectroscopy had proved fruitless. A crystal structure analysis seemed the logical method for obtaining

the desired answers.

## II. CHOICE OF A CRYSTAL

The crystal used for the X-ray analysis was chosen because of its small size and well-defined faces. It was a colorless, transparent parallelepiped of dimensions  $0.486 \times 0.076 \times 0.064 \text{ mm}^3$ . Since the compound could be somewhat hygroscopic, the crystal was mounted on a glass fiber and sealed in a Lindemann glass capillary tube.

## III. DENSITY

The density was determined experimentally by the flotation method, using a mixture of carbon tetrachloride and bromoform that would just suspend a crystal. The experimental density,  $D_{\text{exp}}$ , is  $2.12 \text{ g/cm}^3$  and the calculated density,  $D_{\text{calc}}$ , based on four molecules per unit cell, is  $2.03 \text{ g/cm}^3$ .

## IV. DETERMINATION OF SPACE GROUP AND UNIT CELL DIMENSIONS

A combination of Weissenberg and oscillation photographs indicated that the compound crystallized in a monoclinic space group and that the crystal was mounted along the a-axis. The precession camera was used to determine the  $\beta$ -angle. Initial unit cell dimensions were

chosen as  $a \approx 7.7\text{\AA}$ ,  $b \approx 15.3\text{\AA}$ ,  $c \approx 15.7\text{\AA}$ , and  $\beta \approx 106.5^\circ$ . Using this unit cell the following extinctions were observed.

hkl: no conditions

Ok0:  $k = 2n + 1$

h0l:  $l = 2n + 1$

These extinctions uniquely determine the space group as  $P2_1/c$ . In addition, the Weissenberg photographs exhibited a pseudo-A-centering condition which was of some value in the interpretation of the Patterson map.

#### V. DETERMINATION OF ACCURATE UNIT CELL DIMENSIONS

Accurate unit cell dimensions were determined from a least squares analysis of the  $2\theta$  values for eighteen independent reflections. Both  $+2\theta$  and  $-2\theta$  were carefully determined for each reflection and the average  $2\theta$  value for the reflection was used in the refinement. The crystal data are listed in Table VII.

#### VI. DATA COLLECTION

The intensities of the 1946 reflections were measured out to  $\theta \approx 22.5^\circ$ . The method of data collection was the same as in Chapter I. Three standard reflections (060, 121,  $\bar{2}12$

TABLE VII  
CRYSTAL DATA

1-Iodomethyl-3-methyl-1-phenylphospholanium Iodide

C PI H F. W. 446.051 F(000)=840

Monoclinic, space group  $P2_1/c$

$$a' = 7.217(3)\text{\AA}$$

$$b = 14.261(6)\text{\AA}$$

$$c = 14.778(6)\text{\AA}$$

$$\beta = 106.54^\circ(3)$$

Volume of the unit cell =  $1458\text{\AA}^3$   $D_{\text{calc}} = 2.03$  grams/cc.

Molecules/unit cell = 4  $D_{\text{exp}} = 2.12$  grams/cc.

Linear absorption coefficient,  $\mu(\text{MoK}\alpha) = 44.473\text{cm}^{-1}$

Crystal dimensions: 0.486mm x 0.076mm x 0.064mm

Crystal was bound by faces  $\{100\}$ ,  $\{0\bar{1}1\}$ , and  $\{011\}$ , respectively.

reflections) were measured at about two hour intervals during the course of the data collection. A scale factor calculated from these was used to scale each block of data to the same scale as the initial data block. The average value of the scale factor over the complete data collection was 1.006 with a standard deviation of 0.026. This indicates little deterioration of the crystal or deviation of conditions over the course of the data collection. The crystal did change to a yellowish-brown color in the course of the data collection.

#### VII. TREATMENT OF DATA

The intensities were converted to structure factors ( $F_o$ ) in the usual manner. The weights for each reflection were determined as in Chapter I with an instrument instability constant ( $k_2$ ) of 0.05 (45).

#### VIII. STRUCTURE DETERMINATION

The structure was solved from the Patterson map and subsequent Fourier maps. The pseudo-A-centering condition indicated that if one iodine atom was located at  $x, y, z$  in the unit cell the other iodine atom was at  $x, y + \frac{1}{2}, z + \frac{1}{2}$ . The positions determined from the Patterson map were  $x, y, z$  and  $x - 0.2, y + 0.5, z + 0.5$ . Refinement of the iodine positional parameters and isotropic temperature



factors produced an R of 0.23. A Fourier map(2) revealed the positions of all the remaining heavy atoms. All atomic positions except those of the ring-methyl group were included in the full matrix refinement with isotropic temperature factors. Another Fourier map was calculated and the ring-methyl group was clearly shown to be trans to the phenyl group. The heavy atom positional parameters and isotropic temperature factors refined to an R of 0.07 using a unit weighting scheme. Further refinement of the positions and anisotropic thermal parameters using the weighting scheme of Stout and Jensen (45) produced an R of 0.047. A difference map(2) revealed the tentative positions of all the hydrogen atoms except those on the ring-methyl group. Refinement of the positional parameters of all atoms, anisotropic thermal parameters for the heavy atoms and isotropic temperature factors for the hydrogen atoms produced an R of 0.042. It was discovered at this point that the data had been used as decacounts which is roughly the same as considering the data to be observed at the 6-sigma cut-off level.

The data were converted to counts, reduced in the usual manner with 1434 of the 1904 reflections considered observed at the 3-sigma level. Hydrogen atom positions were calculated (42) but not refined at this point as they were not readily observable on a difference map. Refinement of the

heavy atom positions and anisotropic thermal parameters produced an R of 0.066.

The data were very carefully inspected at this point since certain aspects of the model that best fit the data were not reasonable. One of the carbon-carbon single bond distances calculated to be 1.403Å in this model. Some 39 reflections (2.8% of the observed data) were found to be in poor agreement with the rest of the data. The reflections removed all had  $|\Delta F|/\sigma_F \geq 6.0$ ; all data with  $|\Delta F|/\sigma_F < 6.0$  at this point were assumed to be in reasonable agreement. The data removed were classified roughly into four groups: obvious error in instrument setting, 5; irregularly shaped backgrounds, 4; high peak count due to short-term variation, 23 (all very low intensity reflections); no obvious error, 7. At the completion of the refinement 5 pieces of data were found to have  $|\Delta F|/\sigma_F \geq 6.0$ . These were considered to be statistically in agreement with the rest of the data set as will be discussed later in the chapter.

All hydrogen atoms were located from a difference map. Four additional cycles of full matrix refinement of positional parameters of all atoms, anisotropic thermal parameters of the heavy atoms and isotropic temperature factors of the hydrogen atoms completed the refinement. At completion,  $R = 0.045$ ,  $R'' = 0.059$ ,  $R_{\text{obs} + \text{unobs}} = 0.085$ ,

and  $S = 1.87$ . Final shifts in heavy atom parameters were less than 10% of their standard deviations. Corresponding shifts in the hydrogen atom parameters were less than 25% of their standard deviations.

Maximum and minimum transmission coefficients were 0.77 and 0.72 respectively. When the data were corrected for absorption (35) and refined as above, no significant differences between the two refinements were found. The various indicators were:  $R = 0.046$ ,  $R'' = 0.060$ ,  $R_{\text{obs}} + u_{\text{obs}} = 0.086$ , and  $S = 1.89$ .

The observed and calculated structure factors are listed in Table VIII. The positional and thermal parameters for the non-hydrogen atoms are listed in Tables IX and X respectively. The positional and thermal parameters for the hydrogen atoms are listed in Table XI. The bond angles and bond distances are indicated in Figure IX.

The scattering factor curve for the iodide ion was taken from Cromer and Mann (15), the curve for hydrogen from Stewart, et al. (44), and all other curves were from the International Tables (31). The normal phosphorus curve was used since there is no reported curve for a phosphorus with a formal positive charge. Anomalous scattering corrections ( $\Delta f'$  and  $\Delta f''$ ) were assumed to be the same for both iodine and iodide ion and were taken from the International Tables (31).

TABLE VIII

OBSERVED AND CALCULATED STRUCTURE FACTORS

Table with multiple columns containing numerical data, likely representing structure factors. The table is organized into several vertical sections, each with its own header and data rows. The data includes observed and calculated values for various structure factors.

TABLE IX

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN  
1-IODOMETHYL-3-METHYL-1-PHENYLPHOSPHOLANIUM IODIDE

<u>ATOM</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>
I(1)	.90818(10) <sup>a</sup>	.88611(5)	.22996(5)
I(2)	.30387( 9)	.61494(5)	.24359(4)
PA *	.3556( 3)	.7580(2)	.0815(2)
C(2)	.1005(12)	.7451(7)	.0187(6)
C(3)	.0556(13)	.8258(8)	-.0483(7)
C(4)	.1750(15)	.9089(7)	-.0017(7)
C(5)	.3791(13)	.8767(6)	.0427(7)
C(6)	-.1623(16)	.8452(9)	-.0486(8)
C(7)	.3939(14)	.7515(7)	.2060(7)
C(8)	.5047(12)	.6768(6)	.0426(5)
C(9)	.4522(16)	.6515(7)	-.0516(7)
C(10)	.5658(17)	.5905(7)	-.0825(6)
C(11)	.7267(14)	.5531(7)	-.0230(8)
C(12)	.7787(14)	.5771(7)	.0691(8)
C(13)	.6677(13)	.6387(6)	.1052(7)

<sup>a</sup>The number in parentheses is the standard deviation and refers to the least significant digits.

TABLE X

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN

1-IODOMETHYL-3-METHYL-1-PHENYLPHOSPHOLANIUM IODIDE

<u>ATOM</u>	<u><math>\beta_{11}</math></u>	<u><math>\beta_{22}</math></u>	<u><math>\beta_{33}</math></u>	<u><math>\beta_{12}</math></u>	<u><math>\beta_{13}</math></u>	<u><math>\beta_{23}</math></u>
I(1)	.02025(20)	.00576( 5)	.00565( 5)	.00011( 7)	.00348( 7)	-.00087( 3)
I(2)	.01933(18)	.00569( 5)	.00376( 4)	.00044( 7)	.00286( 6)	.00012( 3)
P	.0127( 5)	.0034( 1)	.0042( 1)	.0004( 2)	.0022( 2)	.0000( 1)
C(2)	.0165(23)	.0045( 6)	.0047( 6)	.0011( 9)	.0036( 9)	.0006( 4)
C(3)	.0137(22)	.0057( 7)	.0065( 6)	.0020(10)	.0033(10)	.0011( 5)
C(4)	.0193(24)	.0042( 6)	.0064( 7)	.0018(10)	.0049(11)	.0009( 5)
C(5)	.0155(23)	.0034( 5)	.0057( 6)	.0000( 8)	.0029( 9)	-.0004( 4)
C(6)	.0195(28)	.0072( 7)	.0075( 8)	-.0005(12)	-.0019(12)	-.0003( 7)
C(7)	.0193(25)	.0046( 6)	.0048( 6)	-.0005( 9)	.0027( 9)	-.0016( 5)
C(8)	.0126(20)	.0041( 5)	.0030( 5)	-.0014( 8)	.0025( 8)	.0003( 4)
C(9)	.0275(29)	.0038( 6)	.0048( 6)	.0010(11)	.0040(11)	.0004( 5)
C(10)	.0348(35)	.0056( 7)	.0027( 5)	.0022(12)	.0063(11)	-.0005( 5)

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TABLE X (CONTINUED)

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN

1-IODOMETHYL-3-METHYL-1-PHENYLPHOSPHOLANIUM IODIDE

ATOM	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(11)	.0187(26)	.0033( 6)	.0072( 8)	-.0025( 9)	.0042(12)	-.0017( 5)
C(12)	.0148(23)	.0048( 6)	.0068( 7)	-.0001(10)	-.0004(10)	-.0002( 6)
C(13)	.0147(23)	.0047( 6)	.0050( 6)	-.0006( 9)	.0023( 9)	-.0001( 5)

(e.s.d.'s in parentheses)

The expression for the anisotropic thermal parameters is of the form:

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

TABLE XI

HYDROGEN ATOM POSITIONS AND THERMAL PARAMETERS FOR  
1-IODOMETHYL-3-METHYL-1-PHENYLPHOSPHOLANIUM IODIDE

<u>ATOM</u>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>B<sub>iso</sub></u>
H(1)	.057(16) <sup>a</sup>	.670(9)	-.013(7)	8.(3)
H(2)	.017(13)	.736(6)	.055(6)	5.(2)
H(3)	.097(11)	.843(6)	-.091(5)	3.(2)
H(4)	.119(11)	.929(6)	.037(6)	4.(2)
H(5)	.171(14)	.970(7)	-.051(7)	6.(3)
H(6)	.440(13)	.875(6)	-.002(6)	4.(2)
H(7)	.449( 8)	.907(4)	.094(4)	0.(1)
H(8)	-.234(14)	.791(7)	-.112(7)	6.(3)
H(9)	-.233(18)	.868(7)	-.032(8)	7.(3)
H(10)	-.213(15)	.893(7)	-.129(7)	8.(3)
H(11)	.510(15)	.758(6)	.234(6)	5.(2)
H(12)	.310( 8)	.805(4)	.222(4)	0.(1)
H(13)	.351(11)	.678(6)	-.093(5)	4.(2)
H(14)	.536( 8)	.576(4)	-.144(4)	0.(1)
H(15)	.774(12)	.502(6)	-.045(6)	5.(2)
H(16)	.874(10)	.550(5)	.114(5)	3.(2)
H(17)	.714( 9)	.662(4)	.178(4)	1.(1)

<sup>a</sup>The number in parentheses is the standard deviation and refers to the least significant digits.































































































































































































