Structural studies of cyclic organic phosphorus compounds
by Duane Douglas Swank

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


Abstract:
Using the Patterson synthesis and the "Symbolic Addition Procedure" the structures of three cyclic organic compounds of phosphorus were solved by x-ray diffraction.

Acetionenediol cyclophosphate crystallizes in space group P2 /n with a = 7.755A, b = 9.446A, c = 10.345A, β = 99.65° The ring system is planar and the methoxy group lies directly above the ring with the carbon atom centered between the two ring oxygens. There appears to be some electron delocalization around the double bond. The O-P-O ring angle is 97.3° thus allowing for the formation of a trigonal-bipyramidal intermediate.

P03(C6H5)4(C6H4Br)C5H2 crystallizes in space group P21/C a = 9.432A, b = 15.854, c = 19.094A, β - 102.01°. The five-membered ring is planar and the trigonal bipyramid is little distorted. The more electronegative atoms occupy axial positions, while the carbon atoms occupy the equatorial positions. The yellow color is apparently due to the conjugation in the 1,4-dipheny butadiene portion of the molecule.

2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate crystallizes in space group C2/c with a = 13.251A, b = 6.511A, c = 26.387A, β= 101.46° The four-membered ring is slightly bent to form a very shallow V and is very highly strained. The phosphoryl oxygen is hydrogen bound to a water molecule across the two-fold screw axis and to the screw related water.

The screw related water is also hydrogen bound to the hydroxyl group of the phosphinic acid. This hydrogen bonding forms a network of zig-zag chains in the y-direction of the unit cell.

# STRUCTURAL STUDIES OF CYCLIC ORGANIC PHOSPHORUS COMPOUNDS

by

DUANE DOUGLAS SWANK

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

of

DOCTOR OF PHILOSOPHY

in

Chemistry

Approved:

Charles N. Caughlan
Head, Major Department

Charles N. Caughlan
Chairman, Examining Committee

K. Goering
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1969

## ACKNOWLEDGEMENTS

The author is deeply indebted to Professor Charles N. Caughlan for his advice and guidance, to the other members of the faculty of Montana State University, and to Dr. Lyle Jensen and Dr. Verner Schomaker of the University of Washington for their invaluable help.

I wish to acknowledge the United States Department of Health, Education and Welfare for a fellowship (NDEA) while working on the research. I also wish to thank the Computing Centers of Montana State University, the University of Washington and Western Data Processing Center of the University of California at Los Angeles for the granting of computing time.

Finally, I wish to thank my wife, Barbara, for her understanding, patience and inspiration, while the research was in progress.

TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

## ABSTRACT

Using the Patterson synthesis and the "Symbolic Addition Procedure" the structures of three cyclic organic compounds of phosphorus were solved by x-ray diffraction.

Acetionenediol cyclophosphate crystallizes in space group $P2_1/n$ with a = 7.755A, b = 9.446A, c = 10.345A, $\beta = 99.65^\circ$. The ring system is planar and the methoxy group lies directly above the ring with the carbon atom centered between the two ring oxygens. There appears to be some electron delocalization around the double bond. The O-P-O ring angle is $97.3^\circ$ thus allowing for the formation of a trigonal-bipyramidal intermediate.

$PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ crystallizes in space group $P2_1/c$ with a = 9.432A, b = 15.854A, c = 19.094A, $\beta = 102.01^\circ$. The five-membered ring is planar and the trigonal bipyramid is little distorted. The more electronegative atoms occupy axial positions, while the carbon atoms occupy the equatorial positions. The yellow color is apparently due to the conjugation in the 1,4-diphenyl butadiene portion of the molecule.

2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate crystallizes in space group C2/c with a = 13.251A, b = 6.511A, c = 26.387A, $\beta = 101.46^\circ$. The four-membered ring is slightly bent to form a very shallow V and is very highly strained. The phosphoryl oxygen is hydrogen bound to a water molecule across the two-fold screw axis and to the screw related water. The screw related water is also hydrogen bound to the hydroxyl group of the phosphinic acid. This hydrogen bonding forms a network of zig-zag chains in the y-direction of the unit cell.

# INTRODUCTION

In 1905, Harden and Young demonstrated the dependence of alcoholic fermentation on the presence of inorganic phosphates. Since that time, biochemical research has revealed an amazing dependence of most biological systems on organic phosphates.

Dialkyl phosphate groups are the structural units in deoxyribonucleic acids (DNA) and ribonucleic acids (RNA). The hydrolysis of the latter material under alkaline conditions proceeds through an intermediate which is formulated as a five-membered cyclic phosphate. This cyclization involves the neighboring hydroxyl group on the 2' position of the ribose ring and results in the cleavage of the phosphorus-oxygen bond attached to the 5' carbon of the ribose of the next nucleotide moiety (1). This is illustrated in Figure 1. Subsequent reactions of the cyclic esters with water produce a mixture of 2' and 3' phosphates. The cyclic esters are very reactive (42,43,44), in contrast to dialkyl phosphates and it is, therefore, instructive to investigate some of the simple cyclic phosphates. Previous to this work, the structures of two five-membered cyclic phosphates have been determined (2,3). The main conclusion of these investigations is that the rapid rate of hydrolysis of the five-membered cyclic phosphates compared to the open chain analogs is due primarily to the strain in the cyclic esters (58). This conclusion was subject to question when it was discovered that the acid-catalyzed hydrolysis of ethylene hydrogen phosphate in water enriched with $O^{18}$ was accompanied by exchange of heavy oxygen into the unreacted ester (4). The exchange reaction was accelerated just as the hydrolysis was in the presence of a five-membered

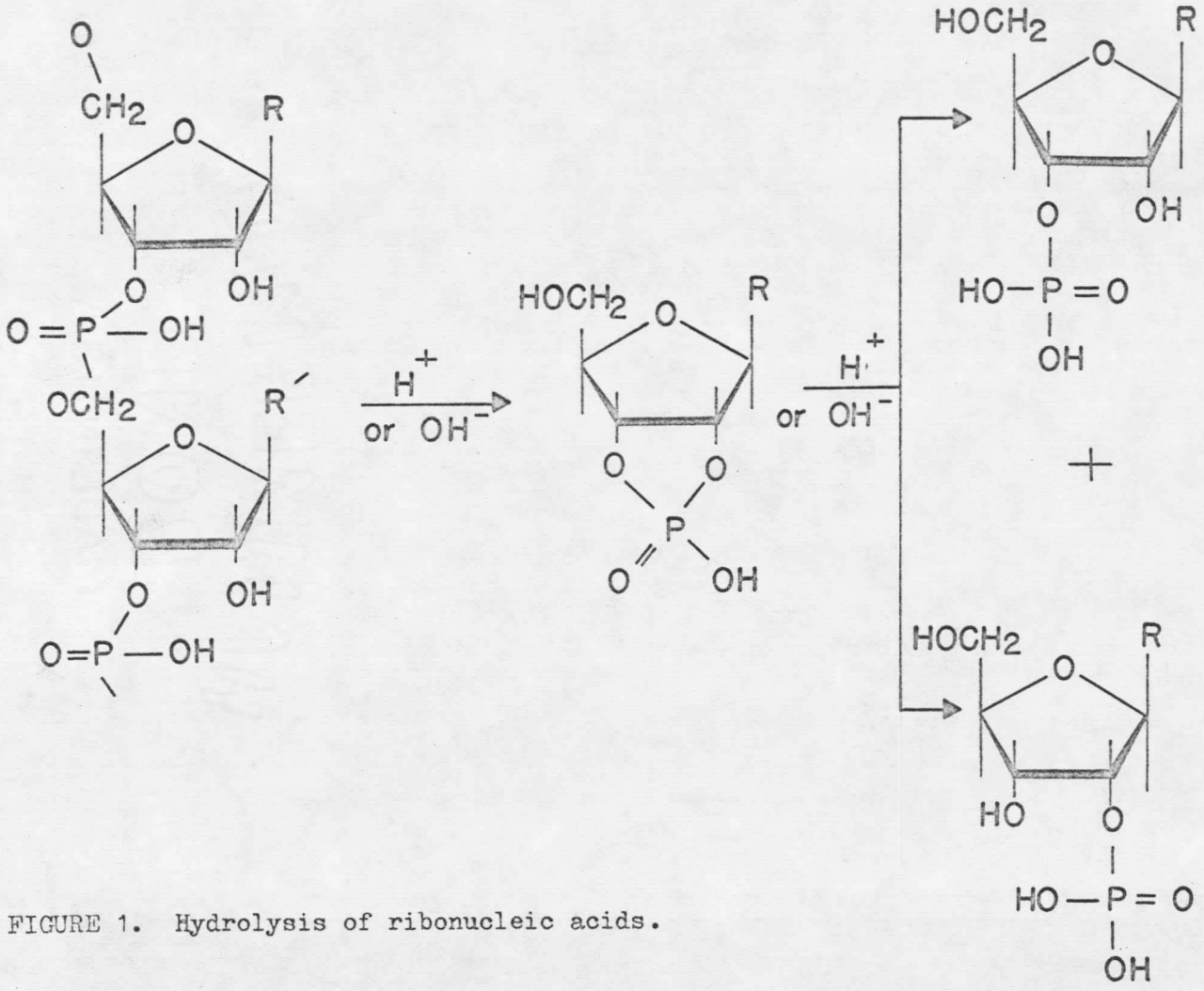



FIGURE 1. Hydrolysis of ribonucleic acids.

ring. Both of the structures reported were saturated rings and, therefore, it was of great interest to see if an unsaturated five-membered cyclic phosphate would exhibit the same properties in regards to the hydrolysis as the saturated systems. The structure of acetionenediol cyclophosphate was, therefore, undertaken in hopes of obtaining more information about the hydrolysis of five-membered cyclic phosphates.

With the discovery of the $O^{18}$ exchange phenomena thus leading to the conclusion that strain alone would not answer the question of the rapid hydrolysis, it was postulated that the hydrolysis of five-membered cyclic phosphates proceeded via intermediates with pentacoordinated phosphorus (5). This conclusion was based on certain considerations dealing with the phenomenon of pseudo-rotation in the trigonal-bipyramidal structure of the pentaoxyphosphoranes (45). Pseudo-rotation for trigonal bipyramids can be understood as being the intramolecular process whereby the molecule is transformed by deforming bond angles in such a way that it appears to have been rotated $90^{\circ}$ about one of the interatomic bonds.

The ring opening hydrolysis does not require pseudo-rotation since it proceeds through an intermediate which resembles that of an $S_N2$ process.

The structure of a five-membered cyclic pentaoxyphosphorane was recently established by x-ray studies (6,7,8). The unsaturated five-membered ring occupies an apical-equatorial position in a trigonal bipyramid just as Haake and Westheimer (4) had postulated for the transition state in the acid-catalyzed hydrolysis of ethylene hydrogen phosphate where the ring is saturated. It seems reasonable that (a) if a five-membered cyclic phosphate ester is strained relative to an open chain

phosphate ester or an unstrained cyclic phosphate and (b) if the pentaoxyphosphorane which is derived by addition of water or another nucleophile to the phosphorus is less strained when it has a five-membered ring than when it lacks it, due to intramolecular crowding in the trigonal bipyramid (6,7,8), the hydrolysis of cyclic phosphotriesters (24) and cyclic phosphodiesters could occur by the phosphoryl addition mechanism, at least under certain experimental conditions. This view has been recently expressed by several investigators (5,25,26,27,28). The mechanism is given in Figure 2.

This mechanism allows for (a) a path where the ring is apical-equatorial, (b) a ring angle of $90^{\circ}$, for intermediates leading to ring opening or hydrolysis external to the ring, and (c) a mechanism consistent with the principle of microscopic reversibility. The mechanism also allows the ring to occupy one apical position, while one group enters and another leaves from the second apical position.

Since the pentacoordinated complexes that have been determined were all pentaoxyphosphoranes, it was of interest to look at a complex with fewer oxygens attached to the phosphorus. The complex studied was $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$, a heterocyclic fused five- and six-membered ring system with two P-O oxygens. This would be a test case for two postulates, first that the more electronegative atoms should be found in the axial positions and, secondly, the five-membered ring should occupy the apical-equatorial position with the oxygens in the apical position. If this is true then the rings would both be apical-equatorial, fused at the equatorial carbon. If both oxygens are not apical then the six-membered ring

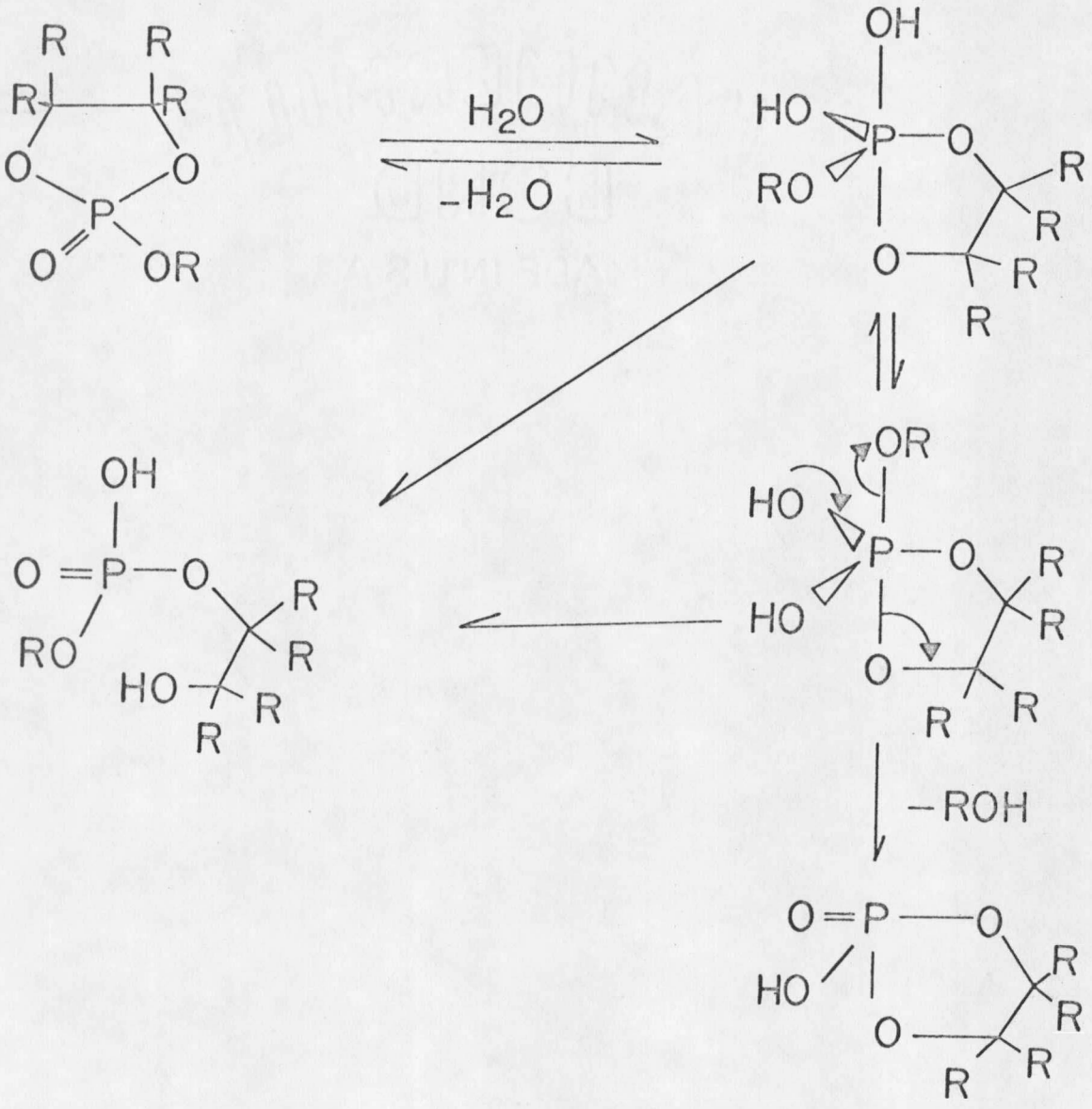



FIGURE 2. Proposed mechanism for the hydrolysis of five-membered cyclic phosphates.

could be apical-equatorial fused at the axial carbon which would be a less stable configuration since it is expected that the axial bonds will be stabilized when the ligands are highly electronegative and have a tendency to draw electrons away from the central atom. Finally, it must be mentioned that the phenyl groups and the double bond conjugation in the two rings should lead to a very high degree of stability in the molecule and effect the carbon bonds in this region extensively.

While engaged in the study of five-membered cyclic phosphates, it was discovered that no structural information exists on four-membered cyclic phosphorus compounds. Although no known biological systems exist where four-membered phosphates are involved, the structure of these compounds would further our knowledge of the role of the 3-d orbitals in phosphorus chemistry. The structure of a four-membered cyclic phosphinic acid was thus undertaken.

This dissertation contains the study and discussion of the crystal and molecular structures of acetionenediol cyclophosphate, $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$, and 2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate. The structures of the first two were solved by the use of the Patterson map while the third was solved using a combination of direct methods (Symbolic Addition procedure of I. Karle and J. Karle) and the Patterson map. The theory of both methods will be presented in some detail in the body of the dissertation.

PART I

GENERAL THEORY

Introduction to the Phase Problem

Diffraction can be briefly described as the scattering of waves by various parts of an object and the recombination of these scattered waves in various directions. Since a crystal is a three-dimensional ordered array, it will act as a three-dimensional grating capable of diffracting x-rays. The complex resultant of the sum of these scattered waves can be expressed as

$$F_m = \sum_j f_j \exp\left[ i m \left\{ x_j / a \right\} 2\pi \right]$$

where $f_j$ = the scattering factor of the $j^{th}$ atom,

$x_j$ = position of the $j^{th}$ scatterer,

$a$ = translation periodicity,

$m$ = order of the resultant scattering.

This can be simplified if we refer to the scattering points as a fraction of the period "a". Then $x = X/a$, so we can define $F_m$ as

$$F_m = \sum_j f_j \exp 2\pi i m x_j .$$

The amplitude of the resultant is a complex function which has a magnitude $|F_m|$ and a phase angle, $\phi$ .

In a simple lattice array, all maxima have the same magnitude since

$$|F_m| = |f \exp 2\pi i m x| = f \quad .$$

However, for a general pattern, various maxima have different magnitudes due to the differnet angles between vectors, which are dependent on $\phi$ . It can be seen from this that the amplitude of the maxima are dependent on relative arrangements of the scattering points in the unit cell, but not on the dimension of the cell.

As stated above, a crystal is a three-dimensional grating so we can expand the one-dimensional ideas to three dimensions. If we let a, b, and c be the translational periodicities in the three dimensions, i.e., the unit cell dimensions, then we can define any given plane hkl (the reciprocal of the Weiss indices) to the diffracted wave front for the rows a , b, c, respectively, i.e., the Bragg reflection. Given this and the coordinates of the scattering atoms, we can define the structure factor as

$$F\{hkl\} = \sum_{j=1}^{N} f_j \exp 2\pi i \{hx_j + ky_j + lz_j\}$$

$$= |F\{hkl\}| \exp i\phi(hkl)$$

where $f_j$ = scattering factor of the $j^{th}$ atom for the particular diffraction angle,

$h, k, l$ = Miller indices describing a particular set of planes,

$x_j, y_j, z_j$ = position of the $j^{th}$ atom in the unit cell,

$\phi(hkl)$ = phase angle of the diffracted beam relative to the incident beam.

The intensity of the diffracted maxima is proportional to the square of the structure factor $F(hkl)$. Thus we can determine the magnitude of $F(hkl)$, but not the phase angle of the diffracted maxima

$$I(hkl) \propto |F(hkl)|^2 .$$

The results of interference effects within the scattering atoms arising from the finite extent of the atoms in relation to the wavelength will affect the intensity of the diffracted beam. The function defining this interference is called the atomic scattering factor or form factor and in its approximate classical form is given as

$$f_o = \int_0^\infty \left\{ U(r) \sin \mu r / \mu r \right\} dr$$

where $U(r)$ = the probability that an electron lies between radii $r$ and $r + dr$ is $4\pi r^2 \rho(r)$ ,

$\mu = 4\pi \sin\theta / \lambda$,

$r$ = arbitrary coordinate of integration in the scattering sphere,

$\rho(r)$ = probability that an electron lies in volume element $d\tau$.

The following condition must hold

$$\int_0^\infty U(r)\, dr = Z \quad \text{(the atomic number of the atom).}$$

$U(r)$ can be determined from quantum mechanical arguments by replacing $\rho(r)$, the classical probability, with $\psi^* \psi$ and has been calculated by

Hartree and others for many atoms. It can be seen that the expression is dependent on the scattering angle $\theta$. The normal assumption as expressed above is that the frequency of the incident radiation is large in comparison with any natural absorption frequency $\omega$ of the scattering atom. This is generally the case for light atoms, but not often true for the heavy atoms. For the latter case, there will be an anomalous phase change during scattering by the electrons associated with the absorption edge. The scattering becomes a complex function and is known as anomalous scattering or anomalous dispersion. The term being defined as

$$f = f_o + \Delta f' + i\Delta f'' = f' + i\Delta f''$$

where $f' = f + \Delta f'$

and

$$\Delta f'_k = \left\{ mc/2\pi^2 e^2 \right\} \mu(\omega_k)\ \omega_k^n \int_{\omega_k}^{\infty} \left[ \omega^2 / (\omega_i^2 - \omega^2)\, \omega^n \right] d\omega$$

$$\Delta f''_k = \left\{ mc/4\pi e^2 \right\} \omega_i \left[ \omega_k / \omega_i \right]^n \mu(\omega_k)$$

where $\omega$ = oscillator frequency,

$\omega_k$ = frequency of the absorption edge,

$\omega_i$ = frequency of the incident radiation,

$\mu(\omega_k)$ = absorption coefficient at the edge,

$n \simeq 3$, but varies with the edge and atomic number. Uncertainty in $n$ is a serious defect in present-day anomalous dispersion theory,

$m$, $c$, and $e$ have their usual meanings.

The dispersion terms depend on $\lambda$ and the diffraction angle $\theta$, but are less sensitive relative to $\theta$ than $f_o$ since the tightly bound electrons responsible for these effects are concentrated in a small volume near the nucleus.

X-rays as they come from their source are unpolarized, that is, they assume all directions in space. When they are diffracted from a crystal the parallel component of the beam is unaffected by the diffraction angle, but the perpendicular component is reduced, thus creating a partial polarization of the diffracted beam. This reduces the intensity by the factor $p$ where $p$ is known as the polarization factor. It is a function of the diffraction angle only, and is given by

$$p = \left[1 + \text{Cos}^2 2\theta\right] \Big/ 2 \quad .$$

When using equi-inclination Weissenberg techniques to collect data one must also consider the variation in the rotational velocity of the planes with respect to the x-ray beam. A correction factor, $L$, must be applied to allow for the fact that planes inclined to the rotation axis pass through the Bragg angle at a smaller velocity $\omega$ than those perpendicular to the beam. This rotational factor is known as the Lorentz factor and is a function of the Bragg angle $\theta$ as well as the equi-inclination angle $\mu$. The Lorentz correction is defined by

$$L = 1 \Big/ 2 \,\text{Cos}\theta \sqrt{\text{Cos}^2\mu - \text{Cos}^2\theta} \quad .$$

The observed intensities from the film must, therefore, be corrected for

these factors and diffractometer data, as taken in this laboratory, must be corrected using an equi-inclination angle of zero. When these corrections are applied the intensities are converted to observed structure factors. The conversion is given by

$$|F(hkl)|^2 = KI/Lp$$

where K = the scale factor.

Indirect Methods of Solving Crystal Structures

In the early stages of x-ray structure analysis, crystal structures were solved by the method of trial and error. The object was to deduce a trial structure from which a set of structure factors could be calculated. These calculated structure factors were then compared with the experimentally measured structure factors. A measure of correctness of the structure is given by the reliability index or R-factor and is defined as

$$R = \sum \Big| |F_o| - |F_c| \Big| \Big/ \sum |F_o|$$

where $F_o$ = observed structure factor,

$F_c$ = calculated structure factor.

The summation is over all of the reflections (hkl).

This method has its limitations since large structures would have so many orientations in crystal space and would be far too complicated to solve by this method. It soon became evident that a more comprehensive method was needed to solve crystal structures.

In 1934, Patterson (9) described a totally new method of determining the crystal structure of a material. The method involved use of the function known as the Patterson function, given by

$$P(uvw) = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz)\, \rho(x+u, y+v, z+w)\, dx\, dy\, dz$$

where $\rho(xyz)$ = the electron density at $(x,y,z)$,

$V$ = unit cell volume,

$\rho(x+u, y+v, z+w)$ = the electron density at some distance $(u,v,w)$ from $(x,y,z)$.

Fourier's theory states that any periodic function can be reproduced by superimposing a sufficient number of sinusoidal waves with the same periodicity. Each wave contributes an appropriate amplitude and phase to the total function. Since crystals are built on a repeated pattern of atoms and molecules, the repeating unit being the unit cell, and since the electrons which scatter the x-rays repeat in the same manner, Fourier synthesis can be used to calculate the electron density within the crystal. Each Miller indice has associated with it a particular magnitude and phase of diffraction. Thus, summing these at discrete points $x, y, z$ throughout the unique portion of the unit cell will yield the electron density and, hence, the atomic positions. We can define the electron density $\rho$ as

$$\rho(xyz) = 1/V \sum_h \sum_k \sum_l \left|F(hkl)\right| e^{-\phi_{hkl}}\, e^{2\pi i(hx + ky + lz)}$$

where $V$ = volume of the unit cell,

$h, k, l$ = indices of reflecting planes,

$\phi_{hkl}$ = phase angle of the given $F(h,k,l)$,

$|F(hkl)|$ = absolute value of the structure factor,

$x, y, z$ = factional unit cell coordinates.

Thus, the Patterson can be redefined as

$$P(uvw) = V/V^2 \int_0^1 \int_0^1 \int_0^1 \left\{ \sum_h \sum_k \sum_l |F(hkl)| \, e^{-2\pi i (hx + ky + lz)} \right.$$

$$\left. \sum_{h'} \sum_{k'} \sum_{l'} |F(h'k'l')| \, e^{-2\pi i \{h'[x+u] + k'[y+v] + l'[z+w]\}} \right\}$$

$$dx \; dy \; dz$$

or

$$P(uvw) = 1/V \sum_h \sum_k \sum_l |F(hkl)|^2 \, e^{-2\pi i [hu + kv + lw]} .$$

It will be noted that the phase angle $\phi(hkl)$ does not appear in the function. The value of the Patterson function at $(u, v, w)$ is just the average value of the product of the electron density at the ends of a vector of length $(u, v, w)$, all originating at the origin. There will be $n(n-1)$ non-origin peaks resulting from n atoms in the unit cell since n of the peaks will be at the origin. The complexity of a Patterson map will be further be increased by the fact that the atoms are not point scatterers and, thus, different atoms with similar interatomic vectors may be superimposed.

Since the Patterson function is a function of the electron densities

heavier atoms, that is, atoms with high atomic numbers and therefore, many scattering electrons, will contribute more to the Patterson function than light atoms. The heavy atom position can generally be determined from the Patterson map by using certain sections or lines characteristic of the symmetry of the space group. These sections and lines have a higher concentration of peaks and are known as Harker sections and lines, respectively. The heavy atom technique is by far the most common method of solving crystal structures at the present time. A detailed discussion of the Patterson method is given by M. Buerger in Vector Space (10).

Direct Methods of Solving Crystal Structures

In 1945, Harker and Kasper (11, 46) reported that, although the phase of the structure factor could not be determined directly, there exists explicit relationships between the amplitudes of structure factors and their phases for centrosymmetric crystals. To determine the specific relations they made use of the well-known Cauchy's inequality

$$\left| \sum_{j=1}^{N} a_j b_j \right|^2 \leq \sum_{j=1}^{N} \left| a_j \right|^2 \sum_{j=1}^{N} \left| b_j \right|^2$$

and Schwartz's inequality

$$\left| \int f g \, d\tau \right|^2 \leq \int \left| f \right|^2 d\tau \int \left| g \right|^2 d\tau .$$

By allowing $a$ and $b$ to be the structure factor, it can easily be shown that

$$\left| F(hkl) \right|^2 \leq Z^2$$

which is just what one would expect, that is, no atom can scatter with an amplitude greater than the number of scattering electrons. This relation is not startling since it arises from other considerations. However, the application of these inequalities to amplitudes arising from symmetrical sets of atoms gives rise to many relationships. Additional relationships have been developed by Okaya and Nitta (12), Karle and Hauptman (13), and Hauptman and Karle (14).

Using a statistical approach to the phase problem, Hauptman and Karle (15) derived several relationships which can be used to determine the sign of a reflection for centric crystals. The most significant result of their work is the $\sum_2$ relationship given by

$$sE_H \sim s \sum_{H1} E_{H1} E_{H-H1}$$

where $E_H$ is the normalized structure factor given as

$$\left|E_H\right|^2 = F_H^2 \Big/ \varepsilon \sum_{j=1} f_j^2$$

where $\varepsilon$ = the degeneracy of $F_H$,

$sE_H$ refers to the "sign of $E_H$".

Not all of the phases are determined by the structure for some are based uniquely on the choice of origin. For a centrosymmetric crystal, we can define the structure factor as

$$F(hkl) = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi \left\{ hx_j + ky_j + lz_j \right\} .$$

If instead we choose the point (1/2, 1/2, 1/2) as our origin, rather than (0,0,0), then

$$F'(hkl) = 2\sum_{j=1}^{N/2} f_j \cos 2\pi \left\{ h(x_j + 1/2) + k(y_j + 1/2) + l(z_j + 1/2) \right\}$$

$$= 2\sum_{j=1}^{N/2} f_j \left[ \cos 2\pi \left\{ hx_j + ky_j + lz_j \right\} \cos \pi \left\{ h + k + l \right\} \right.$$

$$\left. + \sin 2\pi \left\{ hx_j + ky_j + lz_j \right\} \sin \pi \left\{ h + k + l \right\} \right]$$

$$= 2\sum_{j=1}^{N/2} f_j \cos 2\pi \left\{ hx_j + ky_j + lz_j \right\} \cos \pi \left\{ h + k + l \right\}$$

$$= \{-1\}^{h+k+l} F(hkl)$$

The change, therefore, does not alter the sign of $F(hkl)$ as long as $h+k+l = 2n$. Reflections of this type are known as "structure invariants". However, when $h+k+l = 2n+1$, the sign of $F(hkl)$ is dependent on the choice of the origin and the phase is said to be "structure semivariant". Hauptman and Karle (15) have shown that it is possible to assign arbitrary phases to the "structure semivariants" if they are linearly independent. Thus, it is possible to assign three "origin determining" signs for a primitive cell, two for a face centered cell and one for a body centered cell.

In general, the "origin determining" signs are not enough to allow one to assign signs to all of the remaining reflections using the $\sum_2$ relationship. Karle and Karle (16) employed the method of "symbolic

addition" which had been suggested earlier by Zachariasen (17). The method involves choosing a set of origin determining reflections and a set of "symbolic" signs for several other reflections. These signs can then be used in the $\sum_2$ relationship to arrive at the signs of the other reflections. The expression derived by Karle and Karle (16) for the probability of a sign, determined by the $\sum_2$ relationship, being positive is given as

$$P_+\{E_H\} = 1/2 + 1/2 \tanh\left\{\left\{1/2\, N^{1/2}\right\} E_H \sum E_{H_1} E_{H-H_1}\right\}.$$

This expression assumes that all of the atoms in the unit cell are identical which is generally not true. However, the actual probability expression for the non-equivalent atom case is far too complicated to be of use and the above expression can be used for approximate results. If we require the sign to have a high probability of being correct before we use it in the $\sum_2$ relationship to obtain the signs of other reflections, then the assignment of incorrect signs can be minimized.

Proceeding with the sign determination, it usually becomes obvious that some of the symbolic signs are related to one another or to the origin determining signs. Thus, one can slowly eliminate "symbolic signs" until, in the end, there are generally only one or two "symbolic signs" left. If this elimination were not possible the number of sign combinations for the "symbolic signs" would be unacceptably large since there are $2^N$ possible for N signs.

When all possible signs have been determined and all combinations of phases established E-maps can be calculated. An E-map is simply a Fourier

(electron density map) calculated with normalized structure factors. Thus, an E-map is a point atom Fourier map. Generally, the validity of an E-map can be established on chemical grounds. The correct E-map, generally, indicates only the heavier atoms in the unit cell. However, if these are refined and used to determine phases for a Fourier map, then the other atoms in the structure can frequently be located. The method described was used for the solution of 2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate which belongs to the space group C2/c.

Refinement and Weighting

Once the solution of the structure is completed, it becomes necessary to obtain the best fit of the parameters to the data. The most powerful method of refining a structure, i.e., of obtaining the best fit of the variable parameters to the data, is the method of least squares. We can define an observable quantity L as a linear function of a set of variables $x_1, x_2, \ldots, x_n$ where

$$L = a_1x_1 + a_2x_2 + \ldots + a_nx_n.$$

If the values of L are measured at m points where $m > n$, the least squares principle says that the best values for the parameters $a_1, a_2, \ldots, a_n$ are those which minimize the sums of the squares of the properly weighted differences between observed and calculated values of the function for all measured points m. Thus, one needs to minimize Q which is defined as

$$Q = \sum_{j=1}^{m} w_j \left\{ g_j^o - g_j^c \right\}^2$$

where $w_j$ = the weight of the $j^{th}$ observable,

$g^o_j$ = the $j^{th}$ observable value,

$g^c_j$ = the value calculated for the $j^{th}$ observable.

The best fit is obtained by varing the parameters $a_1, a_2, \ldots, a_n$ to minimize $Q$, thus

$$a'_j = a_j + \Delta a_j .$$

The parameters refined in crystallographic refinement are the atomic positional parameters, the isotropic or anisotropic thermal parameters, and the data scaling parameters. The process of refining is continued until there is no significant changes in the parameters between two successive cycles. This iteration is necessary since the observational equations L are not truly linear in the a's, but are made linear to satisfy the least squares requirement by approximating the function as a Taylor series. A full description of least squares refinement can be found in M. Buerger (47) or G. Stout and L. Jensen (35).

In the least squares refinement a weight which was dependent on the precision of the measurement was used for each observation. The appropriate weight of an observation is given by the reciprocal of the variance $\sigma^2$ of the observation where $\sigma$ is the standard deviation.

$$\omega_j = 1 / \sigma_j^2$$

For photographic data the following scheme was suggested by Hughes (48).

$$\sqrt{\omega} = 1 \qquad F_{obs} < 4F_{min}$$

$$\sqrt{\omega} = 4F_{min} / F_{obs} \qquad F_{obs} > 4F_{min} .$$

The less intense reflections are thus given unit weights while the more intense reflections are given weights less than unity.

For diffractometer data, the standard deviation in the counts is (49)

$$\sigma_{counts} = \sqrt{N}$$

where $N$ = the total counts.

Since the x-ray measurement involves both the peak counts and background counts

$$N = N_T + N_{bkg1} + N_{bkg2}$$

where $N_T$ = total peak count.

This expression does not involve any instability in the instrument itself. Inclusion of the machine stability yields a final expression for the relative intensity.

$$\sigma_{I_{rel}} = \sqrt{\sigma_{pk}^2 + \{a N_{pk}\}^2}$$

where $\sigma_{pk} = \sqrt{N_T + N_{bkg1} + N_{bkg2}}$

$$N_{pk} = N_T - \{N_{bkg1} + N_{bkg2}\}$$

$a$ = machine stability constant, usually 0.01 - 0.03.

The value of $a$ is determined from the average deviation of the standard reflections used in the data collection. The standard deviation of $F_{obs}$ can be determined from $\sigma_{I_{rel}}$ and the relationship between $I_{rel}$ and $F_{obs}$.

PART II

# THE CRYSTAL STRUCTURE OF ACETIONENEDIOL CYCLOPHOSPHATE

## Preparation of the Crystals

Crystals were furnished by F. Ramirez and prepared according to methods described in the literature (50). The crystals are extremely sensitive to moisture and it was necessary to seal them in pyrex glass capillaries. The crystal chosen for the x-ray study had dimensions of 0.30 x 0.50 x 0.55 mm.

## Density Determination of $PO_4C_2(CH_3)_3$

The density of the crystal was determined by measuring the density of a solution of mineral oil and carbon tetrachloride in which the crystal remained suspended. The density of $PO_4C_2(CH_3)_3$ was determined to be 1.417 $g/cm^3$.

## Collection of the Data

The linear absorption coefficient for Cu $K_\alpha$ radiation is 20.18 $cm^{-1}$. For the size and shape of the crystal used, the absorption for Cu $K_\alpha$ would be negligible.

Intensity data were collected on a Supper Weissenberg camera using nickel-filtered Cu $K_\alpha$ radiation (1.5418A) and a combination of multiple film and timed exposure techniques. Levels zero through four were recorded while rotating about the $\langle 100 \rangle$ direction. The conditions for reflection, k=2n for the 0k0 reflections and h+l=2n for the h0l zone, indicates space group $P2_1/n$. The intensities of 479 independent

reflections were estimated visually by comparison with a set of standard intensities and converted to structure factors in the usual manner using a program from the crystallographic library (32). The crystal was originally mounted on a General Electric XRD-5 diffractometer for data collection, but small crystal-movement due to the results of slight hydrolysis made diffractometer usage unacceptable.

The cell constants were determined on a General Electric XRD-5 diffractometer equipped with a General Electric single crystal orienter and scintillation counter for a detector. Using the cell dimensions and assuming four molecules per unit cell, the calculated density is 1.464 $g/cm^3$. Table I gives a summary of the unit cell data.

Structural Determination

The structure was solved from the three-dimensional Patterson map. For the crystal symmetry $P2_1/n$, the following equivalent positions exist

$$\begin{aligned} &x, && y, && z;\\ &-x, && -y, && -z;\\ &\tfrac{1}{2}+x, && \tfrac{1}{2}-y, && \tfrac{1}{2}+z;\\ &\tfrac{1}{2}-x, && \tfrac{1}{2}+y, && \tfrac{1}{2}-z. \end{aligned}$$

Considering the vector between an atom at $(x,y,z)$ and $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$, we obtain $u=\frac{1}{2}-2x$, $v=\frac{1}{2}$, $w=\frac{1}{2}-2z$. Thus, we have a Harker section at $v=\frac{1}{2}$ due to the $2_1$ screw in the y-direction. This means that for every atom in the unit cell a peak is obtained on the $v=\frac{1}{2}$ section of the Patterson map. Due to the other symmetry transformations of the equivalent atoms the

TABLE I

Summary of Crystal Data for $PO_4C_2(CH_3)_3$

$a = 7.755(5)A$

$b = 9.446(5)A$

$c = 10.345(5)A$

$\beta = 99.65(5)^\circ$

| | |
|---|---|
| Space Group | $P2_1/n$ |
| Molecules per unit cell | 4 |
| Calculated density | $= 1.417\ g/cm^3$ |
| Measured density | $= 1.464\ g/cm^3$ |

following vectors also arise; $2x, 2y, 2z$ due to the center of symmetry and $\frac{1}{2}, \frac{1}{2}-2y, \frac{1}{2}$ due to the n (diagonal) glide. This last vector set is known as the Harker line.

The major peak on the Harker section was at (0.1875, 0.5000, 0.8625) and the major peak on the Harker line was at v=0.075. From these positions it is possible to determine the position of the centrosymmetric peak which is calculated to be (0.6875, 0.4250, 0.3625). A peak was found at this position on the Patterson map and was of the appropriate height for a P-P vector. Table II gives a summary of the atomic position, Patterson vectors, and peak heights.

Using this phosphorus position, the structure factor calculation gave an R-index of 56% which though high is not totally unreasonable since the phosphorus is near the $y=1/4$ section thus causing many of the structure factors to calculate low or zero. Scattering factors for the individual atoms were taken from the International Tables for Crystallography (18). A Fourier map showed the position of all four oxygen atoms. With these new positions from the Fourier map the R-index dropped to 48%. A second Fourier using structure factors from the previous calculation gave positions for all of the carbon atoms.

Refinement of the Structure

Refinement started with the atomic positions from the Fourier which gave an R-index of 35%. The block diagonal least squares program of G.A. Mair (19) was used. Several cycles varing positional parameters and individual isotropic temperature factors reduced the R-index to 13.8% and

TABLE II

Coordinates and Vector Assignments for the Structure $PO_4C_2(CH_3)_3$

| ATOM | x | y | z |
|---|---|---|---|
| P | 0.3440 | 0.2125 | 0.1812 |

| ASSIGNMENT | POSITION | HEIGHT | |
|---|---|---|---|
| P-P ($2_1$) | 0.1875, 0.5000, 0.8625 | 93[a] | 60[b] |
| P-P (n) | 0.5000, 0.0750, 0.5000 | 82 | 60 |
| P-P (i) | 0.6875, 0.4250, 0.3625 | 32 | 30 |

[a] Observed peak height on the Patterson map.

[b] Calculated peak height for the vector.

eight cycles varing positional parameters and anisotropic temperature factors brought the R-index to 11.8%. While using the block diagonal least squares program, a parameter shift damping factor of 0.25 was used initially, but increased to 0.80 as the refinement progressed. The last two cycles of refinement used the full matrix refinement program of Busing, Martin, and Levy (20) modified by J.M. Steward (21) to refine positional and anisotropic parameters and five scale constants for level to level scaling. The final R-index is 10.7%.

The weighting scheme used during the block diagonal refinement was the third form suggested by Mair.

$$w = 1 \Big/ \left\{ 1 + [(KF_o - b)/a]^2 \right\}^{1/2}$$

where $a = 8F_{min}$,

$b = 5F_{min}$,

$K$ = scale constant.

This scheme is a modified Hughes scheme. The weighting scheme used during the full matrix refinement was another modified Hughes weighting scheme (22) where $K_1$ was chosed as the average intensity for each layer and $K_2$ as twice the minimum observable intensity. The scheme is given as

$$\sigma = F_{obs} \quad : \quad F_{obs} > \left\{ I_{ave} \right\}^{1/2},$$

$$\sigma = \left\{ I_{ave} \right\}^{1/2} \quad : \quad \left\{ 2I_{min} \right\}^{1/2} < F_{obs} < \left\{ I_{ave} \right\}^{1/2},$$

$$\sigma = \left\{ 2I_{ave}\, I_{min} \right\}^{1/2} \Big/ F_{obs} \quad : \quad F_{obs} < \left\{ 2I_{min} \right\}^{1/2}.$$

Final positional parameters are listed in Table III. Table IV lists the anisotropic temperature factors and Table V lists the anisotropic thermal parameters in terms of the mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids. For calculation of these an orthogonal coordinate system was used in which the x-axis coincided with a and the y-axis coincided with b. Table VI shows the equations for the best least squares planes for the phosphorus ring system with and without the methyl groups and for the phosphorus, phosphoryl oxygen, methoxy plane. The least squares planes are calculated according to the method described by V. Schomaker, et al. (23). Table IX contains the observed and calculated structure factors.

Discussion of the Structure

The results obtained from the crystallographic analysis are shown in Figures 3 and 4. The bond distances are listed in Table VII and the bond angles in Table VIII.

The dioxyaphospholene ring is planar. The plane of the ring includes the two exocyclic methyl groups, C(3) and C(4). This plane forms a dihedral angle close to $90^{\circ}$ with another plane which includes the atoms C(5), O(2), P, and O(4). The carbon of the methyl group, C(5), points directly back over the ring and is centered between the two oxygens of the ring, O(1) and O(3), to within the accuracy of this determination, this carbon is 2.61A above the plane of the ring. The orientation of the methoxy group is identical with that found in methyl ethylene phosphate (2), but differs by $180^{\circ}$ from that found in methyl pinacol phosphate (3).

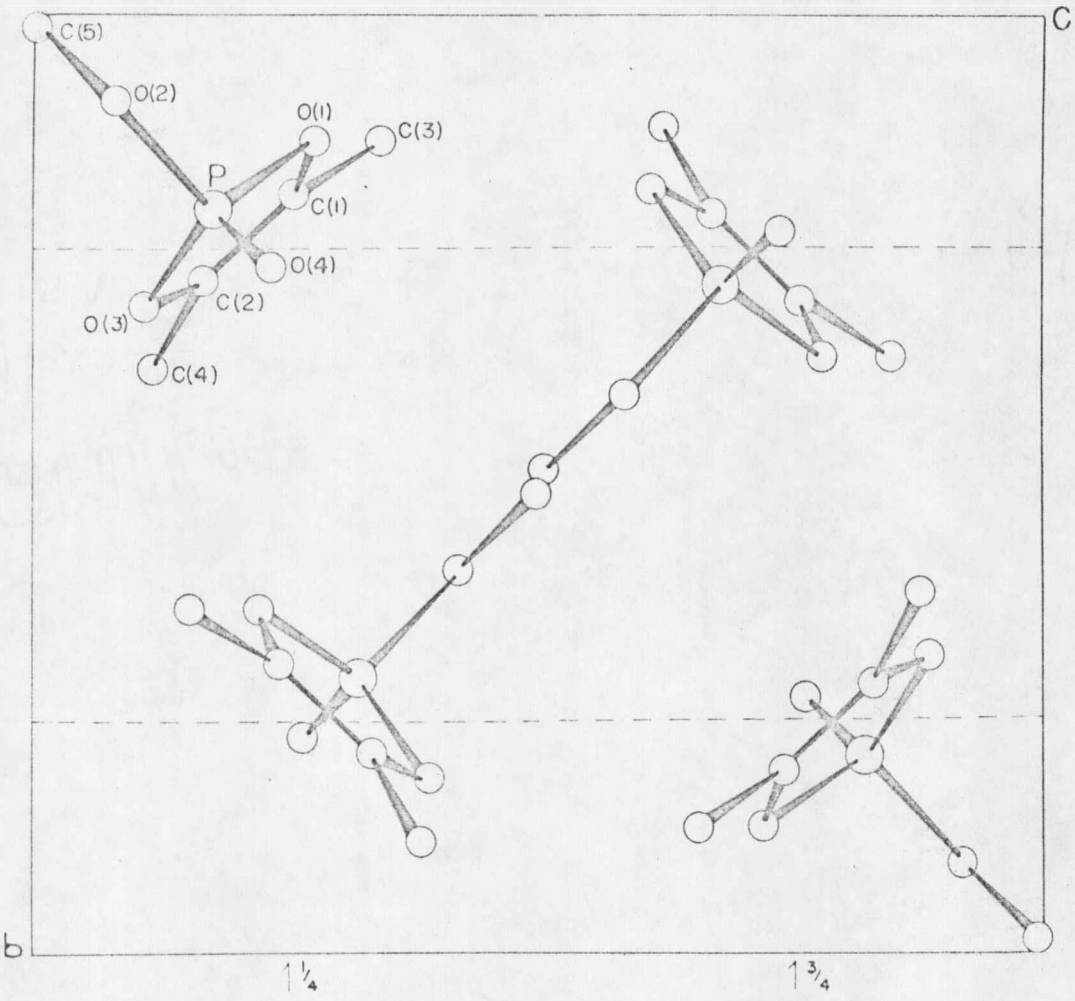



FIGURE 3. Projection of the Crystal Structure of Acetionenediol Cyclophosphate onto the bc plane.

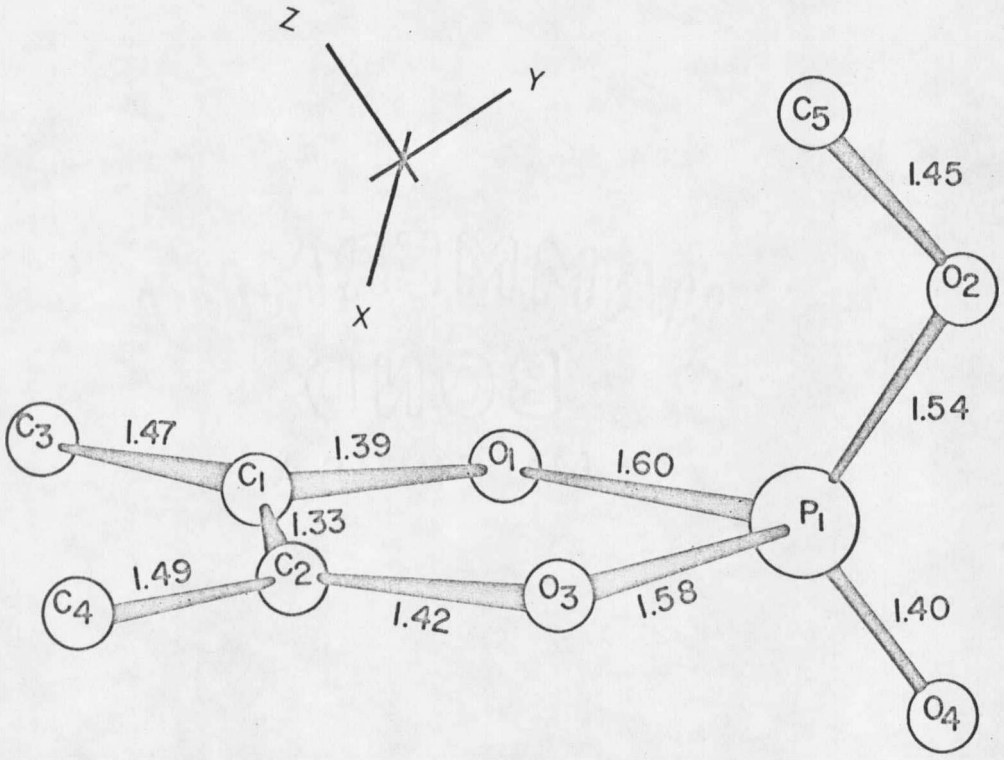



FIGURE 4. Molecular Structure of Acetionenediol Cyclophosphate.

TABLE III

Final Atomic Coordinates for $PO_4C_2(CH_3)_3$

| ATOM | | | |
|---|---|---|---|
| P | 0.3475(8)[a] | 0.2092(5) | 0.1791(4) |
| O(1) | 0.2344(22) | 0.1359(14) | 0.2766(10) |
| O(2) | 0.3818(16) | 0.0958(14) | 0.0803(12) |
| O(3) | 0.2008(17) | 0.3141(11) | 0.1100(11) |
| O(4) | 0.5079(21) | 0.2705(17) | 0.2344(14) |
| C(1) | 0.0670(32) | 0.1923(18) | 0.2600(15) |
| C(2) | 0.0483(25) | 0.2888(18) | 0.1656(16) |
| C(3) | -0.0470(26) | 0.1366(20) | 0.3483(17) |
| C(4) | -0.1033(26) | 0.3834(20) | 0.1179(17) |
| C(5) | 0.2407(31) | 0.0140(26) | 0.0051(21) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE IV

Thermal Parameters for $PO_4C_2(CH_3)_3$

| ATOM | $B_{11}$[b,c] | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| P | 1.51 | 1.48 | 2.30 | -0.08 | 0.00 | 0.74 |
| O(1) | 3.20 | 3.53 | 2.58 | -0.05 | 0.16 | 2.01 |
| O(2) | 2.20 | 4.04 | 4.16 | 0.82 | 1.29 | -0.61 |
| O(3) | 1.20 | 1.62 | 3.24 | 1.35 | 0.82 | 1.44 |
| O(4) | 4.05 | 6.12 | 6.48 | 0.26 | 0.99 | 1.75 |
| C(1) | 3.85 | 2.58 | 1.64 | -0.63 | -1.62 | -0.83 |
| C(2)[a] | -2.47 | 5.04 | 4.31 | -0.18 | 0.36 | -2.65 |
| C(3)[a] | 2.43 | 3.36 | 4.22 | -0.43 | 3.78 | 0.77 |
| C(4) | 2.93 | 4.33 | 3.13 | 2.49 | -0.20 | 0.56 |
| C(5) | 2.50 | 5.16 | 4.85 | 0.63 | 1.25 | -2.10 |

[a] The anisotropic temperature factors for these atoms are non-positive definite.

[b] Standard deviations of the $B_{ij}$'s are approximately 0.2 for the phosphorus and 0.5 for the carbon and oxygen atoms.

[c] These are given as $B_{ij}$'s rather than $\beta_{ij}$'s.

TABLE V

Principal Axes of the Thermal Ellipsoids for $PO_4C_2(CH_3)_3$

| | Mean Square Displacement in $A^2$ | | |
|---|---|---|---|
| ATOM | MAX | MED | MIN |
| P | 0.04 | 0.02 | 0.01 |
| O(1) | 0.07 | 0.04 | 0.01 |
| O(2) | 0.06 | 0.05 | 0.01 |
| O(3) | 0.06 | 0.02 | 0.01 |
| O(4) | 0.09 | 0.05 | 0.05 |
| C(1) | 0.05 | 0.03 | 0.00 |
| C(2)[a] | 0.05 | 0.03 | 0.02 |
| C(3)[a] | 0.14 | 0.05 | 0.03 |
| C(4) | 0.07 | 0.04 | 0.02 |
| C(5) | 0.09 | 0.06 | 0.01 |

[a] For mean square displacement, $\beta_{11}$ of C(2) and $\beta_{13}$ and $\beta_{23}$ of C(3) were set equal to 0.0001 which was less than the standard deviation.

TABLE VI

Equations of Least Squares Planes Referred to Orthogonal Axes for $PO_4C_2(CH_3)_3$[a]

| ATOM | a | b | c | D(A) | S($A^2$) |
|---|---|---|---|---|---|
| PO(2)O(4)C(5) | -0.0142 | -0.6870 | 0.7265 | -0.076 | $63.0 \times 10^{-6}$ |
| PO(1)O(3)C(1)C(2) C(3)C(4) | 0.2206 | 0.7307 | 0.6460 | 3.271 | $30.9 \times 10^{-4}$ |
| PO(1)O(3)C(1)C(2) | 0.1999 | 0.7312 | 0.6522 | 3.241 | $39.1 \times 10^{-5}$ |

[a] $\bar{X} = x + z\cos\beta$ ; $Y = y$; $Z = z\sin\beta$,

$D = a\bar{X} + b\bar{Y} + c\bar{Z}$

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

D = origin to plane distance in angstroms,

All atoms are given equal weight.

TABLE VII

Bond Distances in Acetionenediol Cyclophosphate

| ATOMS | DISTANCE |
|---|---|
| P-O(1) | 1.60(2)[a] |
| P-O(2) | 1.54(2) |
| P-O(3) | 1.58(2) |
| P-O(4) | 1.40(3) |
| P-C(1) | 2.46(3) |
| P-C(2) | 2.42(2) |
| P-C(3) | 3.83(3) |
| P-C(4) | 3.82(3) |
| P-C(5) | 2.61(4) |
| O(1)-C(1) | 1.39(4) |
| O(1)-C(2) | 2.22(4) |
| O(1)-O(3) | 2.39(2) |
| O(2)-C(5) | 1.45(5) |
| O(2)-O(1) | 2.52(2) |
| O(2)-O(3) | 2.54(2) |
| O(2)-O(4) | 2.39(4) |
| O(3)-C(2) | 1.42(3) |
| O(3)-C(1) | 2.31(4) |
| C(1)-C(2) | 1.33(4) |
| C(1)-C(3) | 1.47(4) |
| C(2)-C(4) | 1.49(4) |
| C(5)-O(1) | 3.04(3) |
| C(5)-O(3) | 3.07(4) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE VIII

Bond Angles for Acetionenediol Cyclophosphate

| ATOMS | DEGREES |
|---|---|
| O(1)-P-O(2) | 107.0(6)[a] |
| O(2)-P-O(3) | 109.1(7) |
| P-O(1)-C(1) | 110.8(11) |
| O(3)-C(2)-C(1) | 114.7(16) |
| C(3)-C(1)-C(2) | 134.4(18) |
| O(1)-P-O(3) | 97.3(6) |
| O(2)-P-O(4) | 108.6(8) |
| P-O(3)-C(2) | 107.2(11) |
| O(1)-C(1)-C(3) | 115.7(16) |
| C(4)-C(2)-C(1) | 129.6(17) |
| O(1)-P-O(4) | 117.6(6) |
| O(3)-P-O(4) | 116.5(6) |
| O(1)-C(1)-C(2) | 109.9(17) |
| O(3)-C(2)-C(4) | 115.4(14) |
| P-O(2)-C(5) | 121.9(9) |
| O(2)-P-C(1) | 116.3(7) |
| O(2)-P-C(2) | 116.7(7) |
| O(2)-P-C(3) | 114.8(6) |
| O(2)-P-C(4) | 116.5(6) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 0 L | | | 5 | 140 | 137 | - 7 | 139 | -166 | | 1 7 L | | - 3 | 85 | 103 | - 9 | 109 | 108 | | 2 11 L | | | 3 4 L | | 2 | 455 | 494 |
| * 2 | 364 | -814 | | 6 | 74 | 59 | - 8 | 94 | 66 | 0 | 185 | 187 | - 3 | 268 | -336 | -11 | 85 | -86 | - 3 | 67 | -105 | 0 | 80 | 72 | 3 | 142 | 120 |
| 4 | 72 | -53 | | 7 | 157 | -159 | - 9 | 75 | 90 | 1 | 162 | -151 | 4 | 104 | -106 | | 2 5 L | | | 3 0 L | | 1 | 191 | -198 | - 3 | 236 | 212 |
| 12 | 129 | 92 | | 8 | 80 | 75 | | 1 3 L | | - 2 | 145 | -156 | - 4 | 337 | -290 | 1 | 217 | 211 | 1 | 139 | 178 | - 1 | 321 | 301 | 4 | 264 | -266 |
| | 0 1 L | | | 9 | 83 | 67 | 0 | 118 | 107 | 3 | 106 | 110 | - 5 | 91 | -49 | 2 | 118 | -138 | - 3 | 271 | -290 | - 2 | 292 | -276 | 7 | 107 | 114 |
| 1 | 162 | 116 | | | 0 7 L | | 1 | 156 | -155 | 4 | 267 | -315 | - 5 | 91 | -49 | 2 | 73 | 29 | 5 | 254 | 217 | 3 | 66 | -90 | - 7 | 78 | 128 |
| * 2 | 409 | -856 | | 1 | 147 | -93 | - 1 | 361 | 300 | 5 | 75 | -68 | 6 | 101 | 98 | - 2 | 96 | 60 | - 5 | 343 | 243 | - 3 | 340 | -331 | - 8 | 105 | 127 |
| 3 | 436 | 369 | | 3 | 260 | 254 | 2 | 162 | 173 | - 5 | 109 | 125 | - 6 | 404 | 406 | - 3 | 72 | 59 | 7 | 168 | -142 | 4 | 119 | -101 | 10 | 117 | 106 |
| 4 | 176 | 158 | | 4 | 94 | 53 | - 2 | 187 | 147 | 6 | 240 | 269 | - 7 | 219 | -223 | - 4 | | | - 7 | 79 | 49 | - 4 | 301 | 278 | | 4 2 L | |
| 6 | 75 | 47 | | 5 | 146 | -135 | 3 | 122 | -113 | - 7 | 145 | -125 | 8 | 156 | -148 | 5 | 379 | -441 | - 9 | 260 | -298 | 5 | 156 | 147 | 0 | 46 | 49 |
| 9 | 96 | -85 | | 9 | 73 | 57 | - 3 | 538 | -544 | 8 | 131 | -107 | - 8 | 258 | -282 | 6 | 84 | 82 | -11 | 129 | 56 | - 5 | 98 | -37 | 1 | 98 | -134 |
| 10 | 174 | 176 | | | 0 8 L | | 4 | 307 | -329 | - 8 | 137 | -105 | - 9 | 119 | 124 | - 6 | 90 | -102 | | 3 1 L | | - 7 | 100 | 102 | - 1 | 193 | -194 |
| 11 | 107 | 100 | | 0 | 95 | -80 | - 4 | 158 | -117 | | 1 8 L | | -10 | 84 | 97 | 7 | 163 | 172 | | | | | | | | | | |
| 12 | 143 | -137 | | 1 | 74 | 88 | 5 | 215 | 214 | 0 | 143 | 154 | | 2 2 L | | - 7 | 132 | -136 | 0 | 366 | 333 | 9 | 98 | -94 | 2 | 165 | 83 |
| | 0 2 L | | | 4 | 96 | 87 | - 5 | 85 | 73 | 1 | 121 | 111 | 0 | 306 | -185 | 8 | 101 | -84 | 1 | 283 | -144 | | 3 5 L | | - 2 | 87 | 1 |
| * 0 | 441 | -979 | | 7 | 94 | 94 | 6 | 168 | 156 | - 1 | 121 | -115 | 1 | 315 | 333 | - 9 | 100 | 94 | - 1 | 77 | 75 | 0 | 307 | 280 | 3 | 217 | 306 |
| 1 | 370 | -475 | | | 0 9 L | | - 6 | 142 | 129 | 2 | 192 | -209 | 2 | 76 | 78 | | 2 6 L | | 2 | 346 | -328 | 2 | 167 | -136 | - 3 | 86 | 56 |
| * 2 | 446 | 866 | | 2 | 228 | 208 | - 8 | 235 | -256 | 3 | 75 | 72 | - 2 | 137 | 129 | 0 | 175 | -185 | - 2 | 368 | 274 | - 2 | 333 | -327 | 4 | 192 | -219 |
| 3 | 361 | 242 | | 4 | 142 | -90 | -10 | 229 | 208 | - 3 | 109 | -104 | 3 | 367 | -375 | 1 | 242 | 238 | 3 | 182 | 178 | 5 | 126 | 126 | - 4 | 265 | 249 |
| 4 | 61 | 54 | | 5 | 96 | 75 | -11 | 80 | 61 | - 4 | 140 | -140 | - 3 | 230 | 174 | - 1 | 147 | 130 | - 3 | 302 | 98 | | 3 6 L | | - 5 | 59 | 39 |
| 5 | 173 | -145 | | | 0 10 L | | | 1 4 L | | 5 | 116 | -86 | - 4 | 437 | -439 | 2 | 131 | -114 | 4 | 143 | -136 | 0 | 131 | -104 | 6 | 201 | 251 |
| 6 | 80 | -80 | 0 | | 236 | 215 | 1 | 55 | 46 | - 5 | 121 | 136 | 5 | 140 | 140 | - 2 | 155 | 132 | - 4 | 173 | -82 | - 1 | 158 | -163 | - 6 | 144 | 111 |
| 7 | 147 | -129 | | | 1 0 L | | - 1 | 107 | 73 | - 6 | 112 | 102 | - 5 | 102 | -66 | 3 | 305 | -318 | - 5 | 498 | -474 | - 2 | 369 | 380 | - 7 | 126 | -118 |
| 8 | 83 | 109 | * 1 | | 786 | -1123 | 2 | 434 | -511 | 8 | 79 | -73 | 6 | 139 | -117 | - 3 | 328 | -330 | 7 | 288 | -261 | 3 | 99 | 104 | - 8 | 185 | -202 |
| 9 | 74 | 55 | * - 1 | | 720 | 966 | - 2 | 139 | -110 | | 1 9 L | | - 6 | 203 | 177 | - 5 | 267 | 271 | - 7 | 399 | 396 | - 4 | 258 | -256 | -10 | 127 | 145 |
| 11 | 84 | 84 | 3 | | 323 | 280 | 3 | 62 | -16 | 0 | 121 | -113 | - 7 | 176 | -173 | 7 | 195 | 175 | - 8 | 109 | -99 | - 6 | 90 | 76 | | 4 3 L | |
| 12 | 66 | -53 | - 3 | | 177 | 177 | - 3 | 153 | 124 | 1 | 85 | 77 | 8 | 139 | -145 | - 7 | 120 | -102 | 9 | 180 | 187 | | 3 7 L | | 0 | 321 | 328 |
| | 0 3 L | | 5 | | 263 | -260 | 4 | 350 | 387 | - 1 | 121 | 129 | 9 | 84 | -63 | 9 | 84 | -90 | -11 | 128 | -103 | 0 | 224 | -256 | 1 | 308 | 376 |
| 1 | 420 | 361 | - 5 | | 178 | -180 | - 4 | 111 | -100 | 2 | 103 | -101 | | 2 3 L | | -11 | 90 | 127 | | 3 2 L | | - 1 | 79 | -90 | - 1 | 68 | 102 |
| 2 | 261 | 230 | 7 | | 107 | 74 | 5 | 116 | 98 | - 2 | 165 | 163 | 0 | 278 | 208 | | 2 7 L | | 0 | 182 | -184 | 2 | 102 | 108 | 2 | 100 | -142 |
| 3 | 68 | -70 | - 7 | | 204 | 213 | - 5 | 271 | -263 | 3 | 214 | -174 | 1 | 376 | -359 | 0 | 133 | -140 | 1 | 135 | 44 | - 2 | 163 | 166 | - 2 | 304 | -282 |
| 4 | 486 | -504 | 9 | | 175 | 146 | 6 | 124 | 132 | - 3 | 116 | -105 | - 1 | 151 | 129 | 1 | 233 | -224 | - 1 | 216 | -109 | 3 | 103 | 110 | 3 | 138 | -151 |
| 5 | 57 | -74 | | | 1 1 L | | - 6 | 192 | 208 | 4 | 156 | 128 | 2 | 114 | 145 | - 1 | 241 | 245 | 2 | 431 | -363 | - 4 | 102 | -103 | - 3 | 202 | -246 |
| 6 | 172 | 170 | 0 | | 220 | -202 | 7 | 94 | -89 | 6 | 75 | -77 | - 2 | 259 | 240 | - 2 | 128 | -133 | - 2 | 77 | 162 | | 3 8 L | | 4 | 140 | 136 |
| 8 | 45 | 65 | 1 | | 386 | -431 | - 7 | 175 | 171 | 7 | 75 | -88 | 3 | 244 | -271 | 3 | 159 | -157 | 3 | 102 | 91 | 0 | 114 | 115 | - 4 | 176 | -234 |
| 9 | 199 | 216 | - 1 | | 319 | -435 | 8 | 184 | -197 | - 8 | 57 | 64 | 4 | 148 | -133 | - 3 | 104 | -128 | - 3 | 421 | 267 | 1 | 103 | 84 | 5 | 114 | 170 |
| 10 | 101 | -67 | 2 | | 352 | -313 | - 9 | 86 | -87 | | 1 10 L | | - 4 | 96 | -82 | 5 | 195 | 217 | 4 | 189 | 175 | - 1 | 151 | -144 | - 5 | 176 | 219 |
| 11 | 116 | -119 | 3 | | 152 | 161 | | 1 5 L | | 0 | 136 | -130 | 5 | 229 | 239 | - 6 | 107 | 128 | - 4 | 218 | 188 | 2 | 102 | 107 | - 6 | 162 | 133 |
| | 0 4 L | | - 3 | | 482 | 527 | 1 | 175 | 179 | 1 | 122 | -125 | - 5 | 188 | -188 | 7 | 183 | -173 | 5 | 270 | -266 | - 2 | 140 | -140 | -10 | 98 | -111 |
| 1 | 164 | 140 | 4 | | 121 | 98 | - 1 | 369 | -295 | - 1 | 107 | 104 | 6 | 223 | -233 | 9 | 61 | 87 | - 5 | 262 | -204 | - 3 | 151 | 165 | | 4 4 L | |
| 2 | 125 | -84 | - 4 | | 303 | 285 | 2 | 117 | 118 | 2 | 120 | 103 | - 6 | 225 | -212 | - 9 | 94 | -109 | 6 | 84 | 80 | - 4 | 125 | 108 | 1 | 94 | -68 |
| 3 | 355 | -326 | 5 | | 182 | 130 | - 3 | 142 | 113 | - 4 | 76 | 73 | 7 | 135 | -133 | | 2 8 L | | - 6 | 215 | 194 | - 5 | 96 | -91 | - 1 | 332 | 357 |
| 4 | 206 | 188 | - 5 | | 143 | -121 | 4 | 370 | 412 | - 5 | 70 | -90 | - 7 | 219 | 240 | 1 | 220 | -226 | - 7 | 174 | -162 | | 3 9 L | | 2 | 81 | 106 |
| 5 | 72 | -81 | - 7 | | 156 | -184 | - 4 | 133 | -134 | | 1 11 L | | 8 | 180 | -178 | 3 | 173 | 162 | - 8 | 100 | -83 | 0 | 122 | 119 | - 2 | 274 | 279 |
| 6 | 197 | 187 | - 8 | | 128 | 128 | 5 | 139 | -141 | 2 | 64 | 16 | - 9 | 221 | -234 | - 3 | 152 | 160 | 9 | 193 | 173 | 1 | 121 | 122 | - 3 | 736 | -289 |
| 7 | 211 | 214 | - 9 | | 252 | 266 | - 5 | 178 | -152 | - 2 | 76 | -75 | | 2 4 L | | - 4 | 213 | -236 | - 9 | 140 | 147 | 2 | 93 | -97 | - 5 | 141 | -137 |
| 8 | 86 | -105 | -10 | | 136 | -127 | 6 | 377 | -416 | 3 | 59 | 71 | 0 | 102 | 85 | - 5 | 190 | -162 | | 3 3 L | | | 3 10 L | | - 7 | 96 | 96 |
| | 0 5 L | | -11 | | 173 | -159 | - 6 | 140 | -109 | | 2 0 L | | 1 | 266 | -213 | - 6 | 98 | 87 | 0 | 494 | -459 | - 1 | 132 | 128 | | 4 5 L | |
| 1 | 54 | 46 | | | 1 2 L | | - 7 | 108 | 120 | 2 | 93 | 111 | 2 | 338 | -329 | - 7 | 80 | 70 | - 1 | 120 | -60 | - 3 | 127 | -148 | 0 | 150 | -190 |
| 2 | 158 | -127 | 0 | | 520 | -546 | - 8 | 223 | 234 | - 2 | 713 | -759 | - 2 | 286 | -258 | - 9 | 68 | 98 | 2 | 350 | 346 | | 4 0 L | | 1 | 167 | 219 |
| 3 | 157 | -149 | 1 | | 431 | 476 | -10 | 93 | -91 | 4 | 134 | -144 | 3 | 401 | 460 | | 2 9 L | | - 2 | 142 | -207 | 2 | 219 | -117 | - 1 | 200 | 234 |
| 4 | 276 | 236 | - 1 | | 433 | -499 | | 1 6 L | | - 4 | 68 | 78 | - 3 | 191 | 184 | - 1 | 184 | -183 | 3 | 164 | -162 | 4 | 524 | 592 | - 2 | 103 | 55 |
| 5 | 305 | 287 | 2 | | 636 | 854 | - 1 | 153 | 131 | 6 | 101 | 95 | 4 | 70 | -62 | - 3 | 142 | 133 | - 3 | 96 | 67 | - 4 | 106 | -7 | - 3 | 198 | 248 |
| 6 | 189 | -180 | - 2 | | 427 | -377 | 2 | 166 | 170 | - 6 | 213 | -232 | - 4 | 428 | 393 | - 7 | 99 | -124 | 4 | 65 | 83 | 6 | 203 | -213 | - 5 | 102 | -116 |
| 7 | 86 | 83 | 3 | | 196 | -201 | 4 | 190 | -184 | | 2 1 L | | 5 | 148 | -121 | | 2 10 L | | - 4 | 160 | 174 | - 6 | 70 | 102 | | 4 6 L | |
| 9 | 113 | -90 | - 3 | | 110 | -96 | - 4 | 159 | 141 | 0 | 410 | 432 | - 5 | 226 | -209 | 1 | 91 | 92 | 5 | 135 | -120 | - 8 | 315 | 437 | 0 | 80 | 116 |
| 11 | 65 | 65 | 4 | | 255 | -266 | 6 | 140 | -142 | 1 | 99 | -26 | - 6 | 236 | -231 | - 1 | 103 | -101 | - 5 | 305 | 271 | -10 | 102 | -183 | 1 | 126 | 240 |
| | 0 6 L | | - 4 | | 174 | -113 | - 6 | 264 | -304 | - 1 | 463 | -280 | 7 | 162 | -179 | - 2 | 116 | -113 | 7 | 282 | 274 | | 4 1 L | | - 1 | 302 | -354 |
| 0 | 138 | 61 | - 5 | | 368 | 400 | - 7 | 75 | -87 | 2 | 135 | 111 | - 7 | 135 | 135 | - 4 | 94 | 117 | - 7 | 120 | -93 | 0 | 125 | -76 | - 3 | 153 | 137 |
| 3 | 85 | 63 | - 6 | | 108 | 104 | 8 | 170 | 161 | - 2 | 219 | -193 | 8 | 84 | 100 | 5 | 88 | 95 | 9 | 103 | -98 | 1 | 122 | -69 | | 4 7 L | |
| | | | | | | | | | | | | | | | | | | | | | | | | | - 2 | 83 | 111 |

TABLE IX

Observed and Calculated Structure Factors for Acetionenediol Cyclophosphate.

The C(5)-O(1) and the C(5)-O(3) distances are 3.04 and 3.07A, respectively, very similar to those found in methyl ethylene phosphate (3.01 and 2.89A, respectively) (2,3). These distances are within the range of possible hydrogen bonding, however, it seems very unlikely that a hydrogen bond as weak as this could account for the orientation of the methoxy group. Unfortunately, the hydrogen positions could not be found on a difference map.

The P-O distances in the ring are slightly longer than the P-$OCH_3$ distances. This distance is of the order of 2-3 standard deviations and could be considered as significant. The P-O distance of the phosphoryl oxygen (1.40A) is somewhat shorter than the corresponding distance in other phosphotriesters (1.44A). Again, this is probably significant. It should be noted that the phosphoryl group gives rise to strong bands in the infrared spectrum of this substance in carbon tetrachloride solutions at 1316 $cm^{-1}$ and 1300 $cm^{-1}$ (7.60 and 7.69 $\mu$). These bands are at a slightly higher frequency than those found in open chain phosphotriesters (23).

The C-O distances are of considerable interest. The methoxy distance, C(5)-O(2) is normal (1.45A), but the two C-O distances in the ring are shortened (1.39 and 1.42A). The C-C distances between the methyl groups and the ring, C(1)-C(3) and C(2)-C(4), are somewhat shorter than those of a normal C-C single bond (1.54A). This is probably due to the $sp^3$ orbital interaction with the $sp^2$ $\pi$ bonds in the ring. Concerning the bond angles, several significant features should be noted: (a) the two P-O-C angles in the ring, P-O(1)-C(1) and P-O(3)-C(2), are somewhat smaller than those found in methyl ethylene phosphate (2) and methyl pinacol phosphate (3);

(b) apparently the repulsion between the two methyl groups on the ring, C(3) and C(4), led to an increase in the angles, C(3)-C(1)-C(2) and C(4)-C(2)-C(1), to 134.4 and 129.6°, respectively, and the corresponding angles to oxygen, C(3)-C(1)-O(1) and C(4)-C(2)-O(3), have decreased to 115.7 and 115.4°, respectively; and (c), finally, the ring angle at phosphorus, O(1)-P-O(3), is essentially the same as that found in the other five-membered cyclic phosphates (2,3).

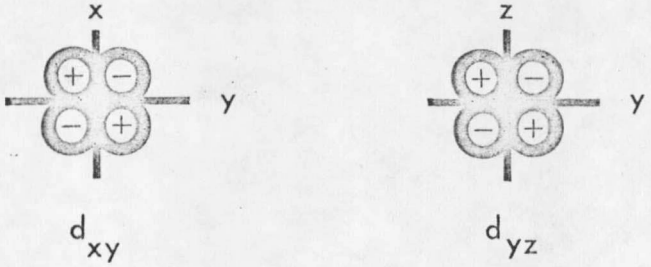
The relationship between the molecular structure of saturated cyclic phosphotriesters and the reactivity of these compounds have been extensively discussed (2,3,5,29). The present work provides data for an unsaturated five-membered cyclic phosphate. The data shows that there is considerable ring strain in the molecule of acetionenediol cyclophosphate. Assuming the following normal bond angles, (O-P-O, 109°; P-O-C, 120°; O-C-C, 120°; C-C-C, 120°), it can be seen that there is considerable strain in the P-O-C bonds and the bonds adjacent to the C-C double bond. A rough calculation of this strain indicates several kilocalories in excess of that in methyl ethylene phosphate. The force constants used for this calculation were the midrange constants given by Usher, Dennis, and Westheimer (30) and a value of 50 kcal/radian$^2$ for the bending force constant around the C-C bond was calculated from an approximate value of $0.32 \times 10^{-11}$ erg/radian$^2$ (31). Using these values and calculating the strain energy by

$$E = \sum \tfrac{1}{2} K \left\{ \Delta \nu \right\}^2$$

where K = the force constant

a value of about 5 kcal/mole was obtained for methyl ethylene phosphate while that for acetionenediol cyclophosphate is about 10 kcal/mole. The major contribution towards this greater strain is the P-O-C angles around the C-C double bond.

The strain resulting from the fact that the ring is planar appears to be one of the most important factors in determining the reactivity of acetionenediol cyclophosphate. The molecular structure of the unsaturated phosphate also suggests considerable delocalization of the electrons around the C-C double bond. This delocalization appears as bonding to O(1) and O(3), thus shortening these bonds. There seems to be a slight decrease in the bonding of the phosphorus to O(1) and O(3) producing a lengthening of these bonds. There could also be an increase in $\pi$ bonding to O(2) with a corresponding decrease in the bond length. The orientation of C(5) directly over the ring could be taken as indicative of the importance of the oxygen orientation for proper overlap of the p-orbitals of the oxygen atom with the 3d-orbitals of the phosphorus atom in the formation of d-p $\pi$ bonds (3,29). The d-p $\pi$ bonding could be described as follows: If we use the coordinate system shown in Figure 4, that is, one in which the z-axis coincides with the P=O axis, then the filled lone




$d_{xy}$ $d_{yz}$

pair $p_y$ orbital on O(2) can overlap considerably with the empty $d_{xy}$ orbital and to a lesser degree with the $d_{yz}$ orbital on the phosphorus atom. If these considerations are valid, it can be seen that the withdrawl of electrons associated with O(1) and O(3) from the phosphorus would tend to increase the positive charge on the phosphorus atom. Collin (29) calculated a charge of 0.5085 for methyl ethylene phosphate, which is higher than any of the open chain phosphotriesters. This would effect the shortening of a phosphoryl oxygen distance and should also account for part of the increase in the reactivity of acetionenediol cyclophosphate towards nucleophiles.

PART III

# THE CRYSTAL STRUCTURE OF $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

## Preparation of the Crystals

Crystals were furnished by F. Ramirez and prepared according to methods described in a private communication.

## Density Determination of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

The density of the crystal was determined by measuring the density of a solution of carbon tetrachloride and benzene in which the crystals remained suspended. The density of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ was determined to be 1.409 $g/cm^3$.

## Collection of the Data

The linear absorption coefficient for Cu $K_\alpha$ radiation is 21.08 $cm^{-1}$. For the uniform size of crystal used in the x-ray study (0.50 x 0.50 x 0.65 mm) the absorption for Cu $K_\alpha$ would be negligible.

Intensity data were collected on a General Electric XRD-5 diffractometer equipped with a General Electric single crystal orienter and scintillation counter for a detector. Independent reflections were collected by the theta-two theta scan technique (moving crystal-moving counter method) using 100 second scans and counting the background for 50 seconds on either side of the peak. The scan rate in two theta was two degrees per minute and the take-off angle of the x-ray tube was four degrees. Nickel-filtered copper radiation (1.5418A) was used for the data collection. The diffractometer settings for the individual

reflections were calculated using a computer program by R. Witters (32). The crystal was mounted about the a-axis. A total of 4142 reflections were collected of which 3277 were treated as observed, that is, greater than $2\sigma$, where $\sigma$ was defined in the general theory. The machine stability constant used was 0.01. The conditions for reflection, k=2n for 0k0 and l=2n for h0l, indicates the space group $P2_1/c$.

The intensity data was corrected for the Lorentz-polarization factor using a computer program from the crystallographic library (33). Scattering factors for each reflection were also calculated by this program. Real and imaginary anomalous scattering terms were used for the bromine atom where $\Delta f' = -0.9$ and $\Delta f'' = 1.5$ at $\sin\theta/\lambda = 0$. Scattering factor tables were taken from the International Tables for Crystallography (18).

Using the cell dimensions and assuming four molecules per unit cell, the density was calculated to be 1.441 $g/cm^3$. Table X gives a summary of the unit cell data.

Structural Determination

The structure was solved from the three dimensional Patterson map. For the crystal symmetry $P2_1/c$, the following equivalent positions exist

$$x, \quad y, \quad z;$$

$$-x, \quad -y, \quad -z;$$

$$x, \quad \frac{1}{2}-y, \quad \frac{1}{2}+z;$$

$$-x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z.$$

Considering the vectors between an atom at $(x,y,z)$ and $(-x,\frac{1}{2}+y,\frac{1}{2}-z)$ the

TABLE X

Summary of Crystal Data for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| | |
|---|---|
| a = | 9.432(5)A |
| b = | 15.854(5)A |
| c = | 19.094(6)A |
| $\beta$ = | 102.01(7)° |
| Space Group | $P2_1/c$ |
| Molecules per unit cell | 4 |
| Calculated density | = 1.441 $g/cm^3$ |
| Measured density | = 1.409 $g/cm^3$ |

following is obtained u=2x, v=$\frac{1}{2}$, w=$\frac{1}{2}$+2z indicating that a Harker section exists at v=$\frac{1}{2}$, due to the $2_1$ screw axis in the y-direction. Due to the other symmetry transformations of the equivalent atoms, the following vectors also arise; 2x, 2y, 2z, due to the center of symmetry, and 0, $\frac{1}{2}$-2y, $\frac{1}{2}$, due to the c glide. This last vector set is known as the Harker line.

The major peak on the Harker section was at (0.9100, 0.5000, 0.8100) and the major peak on the Harker line was at v=0.0125. From these positions it is possible to determine the position of the centrosymmetric peak which is (0.9100, 0.4875, 0.3100). A peak was found at this position on the Patterson map and was of the appropriate height for a Br-Br vector. Table XI gives a summary of the atomic position, Patterson vectors, and peak heights.

Using the bromine position, the structure factor calculation gave an R-index of 77.1% which is rather high, but since the bromine is very near the y =1/4 section, many of the structure factors calculated as zero. Since the bromine was such a large scatterer in the cell, it was decided that its positional parameters should be refined as far as possible before calculating a Fourier map. The full matrix least squares program of Busing, Martin, and Levy (20) modified by Steward (21) was used. The R-factor dropped to 56.1% in three cycles. At this point a Fourier map was calculated using the program of Steward (21). From the Fourier map it was possible to determine the positional parameters of all of the remaining atoms. With all atoms used in a structure factor calculation the R-index was 30%.

TABLE XI

Coordinates and Vector Assignments for the Structure $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | x | y | z |
|---|---|---|---|
| Br | 0.4550 | 0.2438 | 0.1550 |

| ASSIGNMENT | POSITIONS | HEIGHT | |
|---|---|---|---|
| Br-Br ($2_1$) | 0.9100, 0.5000, 0.8100 | 176[a] | 186[b] |
| Br-Br (c) | 0.0000, 0.0125, 0.5000 | 307 | 186[c] |
| Br-Br (i) | 0.9100, 0.4875, 0.3100 | 117 | 93 |

[a] Observed peak height on the Patterson map.

[b] Calculated peak height for the vector.

[c] The calculated height is about half of what it should be due to the fact that the Br is near the quarter section in y. This makes the Harker line appear to be four weighted rather than double weighted.

Refinement of the Structure

Refinement, using the block diagonal least squares program of G.A. Mair (19), started with the R-index at 30%. Several cycles, varing positional parameters and individual isotropic temperature factors, reduced the R-index to 14.6%. In using the block diagonal least squares program, a parameter shift damping factor of 0.25 was used initially, but increased to 0.60 as the refinement progressed. The final cycles of refinement used the block diagonal least squares program of F.R. Ahmed (34) refining positional and anisotropic thermal parameters. A parameter shift damping factor of 0.50 was used. A total of 3254 reflections were included in the least squares refinement, 23 being excluded from the refinement since they suffered from secondary extinction. The final R-index is 5.59%.

Unit weights were used during the Mair portion of the refinement and the weighting scheme suggested by Stout and Jensen (35) was used during the final cycles. Final positional parameters are listed in Table XII. Table XIII lists the anisotropic temperature factors and Table XIV lists the anisotropic thermal parameters in terms of the mean-square amplitude of vibration along the principal axes of the thermal ellipsoids. For calculation of these, an orthogonal coordinate system was used in which the x-axis coincided with a and the y-axis coincided with b. Table XV shows the equations for the best least squares planes for the five-membered ring, the equatorial plane of the trigonal bipyramid, and for the carbon atoms of the chromophore portion of the molecule. The least

squares planes are calculated according to the method described by V. Schomaker et al. (23). Table XVIII contains the observed and the calculated structure factors.

Discussion of the Structure

The results obtained from the crystallographic analysis are shown in Figures 5 and 6. The bond distances are listed in Table XVI and the bond angles in Table XVII.

Again, as in acetionenediol cyclophosphate, the dioxyphospholene ring is planar (the deviation being $11.2 \times 10^{-4} A^2$ in this structure verus $39.1 \times 10^{-5} A^2$ in acetionenediol cyclophosphate for the sum of the squares of the deviations of the atoms from the best least squares plane). The equatorial plane of the trigonal bipyramid atoms is also planar and the axial oxygens form an angle of $176.88^\circ$ with the phosphorus. The five-membered ring is axial-equatorial as predicted by Dennis and Westheimer (5) and as found in the crystal structure of 2,2,2-triisopropyl-4,5-(2',2"-biphenyleno)-1,3,2-dioxaphospholene (7,8). This orientation of the five-membered ring is the most energetically favorable since it accommodates the O-P-O ring angle ($97.3^\circ$ in acetionenediol cyclophosphate) better than the equatorial-equatorial ($120^\circ$) position would. The six-membered ring is puckered at C(1), as expected, since it is prevented from doing so at C(8) due to the double bond in this position. The geometry of the molecule is particularly interesting since two orientations for the six-membered ring are possible. The geometry found is that with both oxygens axial which indicates, as Muetterties and coworkers

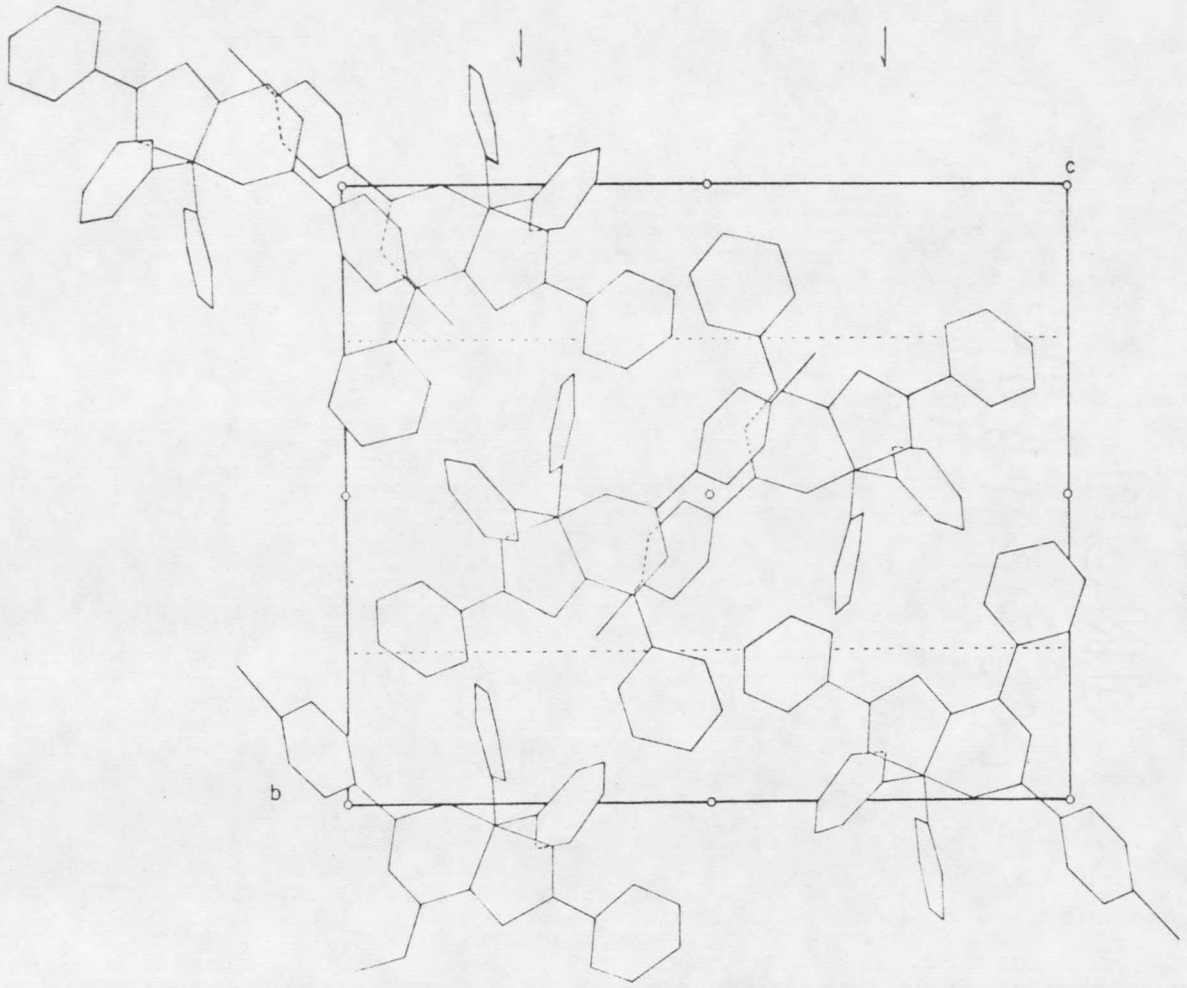



FIGURE 5. Projection of the Crystal Structure of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ onto the bc Plane.

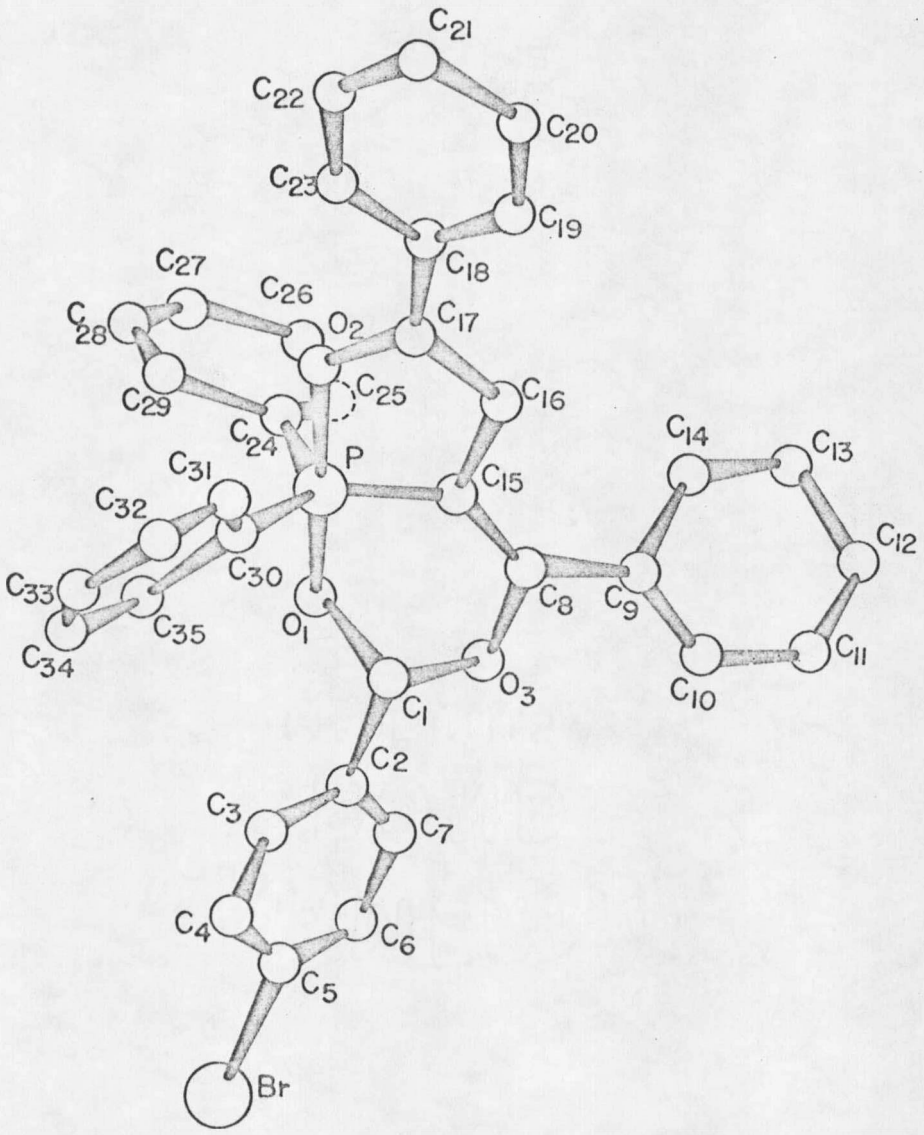



FIGURE 6. Molecular Structure of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

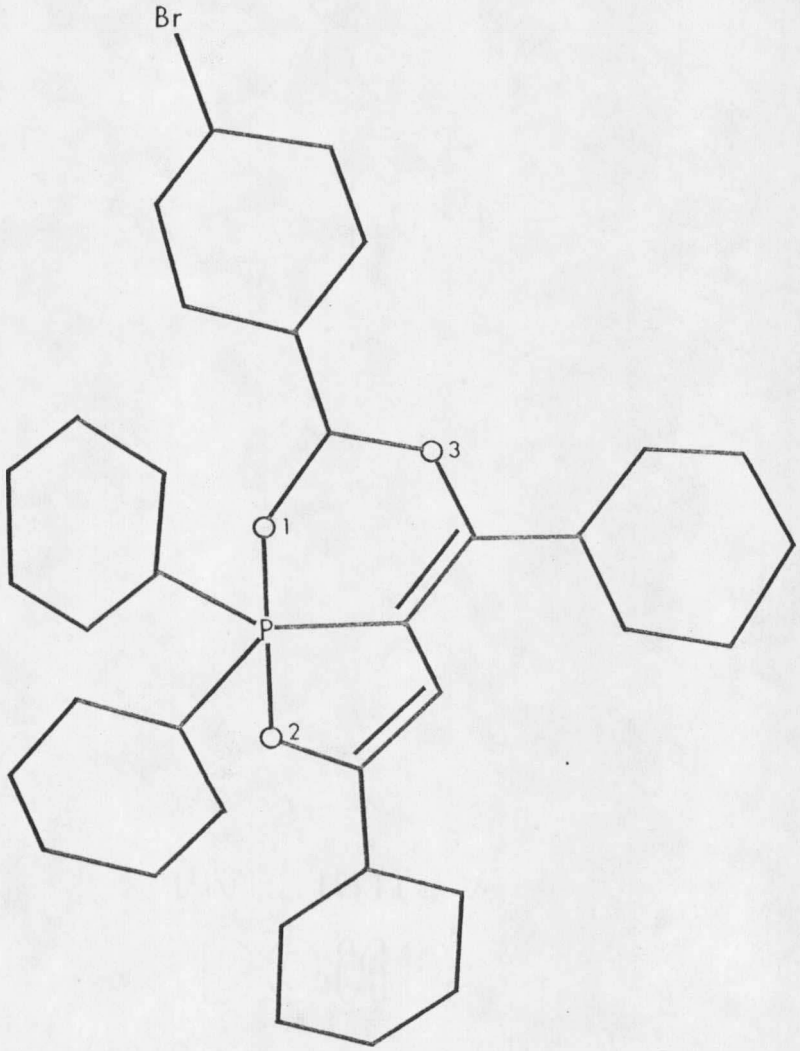



FIGURE 6a. Diagram of the Molecule $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

TABLE XII

Final Atomic Coordinates for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | x | y | z |
|---|---|---|---|
| Br | -0.45453(8)[a] | -0.22962(4) | -0.15446(3) |
| P | -0.03874(14) | 0.03996(7) | 0.20729(6) |
| O(1) | -0.16758(34) | 0.00355(18) | 0.13501(15) |
| O(2) | 0.08588(37) | 0.07947(19) | 0.28373(15) |
| O(3) | -0.18095(37) | 0.10914(18) | 0.05175(15) |
| C(1) | -0.13784(54) | 0.02423(27) | 0.06861(22) |
| C(2) | -0.21582(52) | -0.03391(28) | 0.01067(23) |
| C(3) | -0.15527(63) | -0.11210(32) | 0.00337(28) |
| C(4) | -0.22421(59) | -0.16942(33) | -0.04629(27) |
| C(5) | -0.35619(59) | -0.14776(31) | -0.08879(25) |
| C(6) | -0.41906(67) | -0.07055(34) | -0.08348(28) |
| C(7) | -0.34650(62) | -0.01283(33) | -0.03318(28) |
| C(8) | -0.11363(53) | 0.16586(28) | 0.10123(24) |
| C(9) | -0.13770(53) | 0.25305(27) | 0.07535(23) |
| C(10) | -0.13111(65) | 0.27310(36) | 0.00519(26) |
| C(11) | -0.15675(85) | 0.35531(38) | -0.01877(30) |
| C(12) | -0.19105(92) | 0.41711(38) | 0.02522(33) |
| C(13) | -0.20056(85) | 0.39702(34) | 0.09501(30) |
| C(14) | -0.17399(69) | 0.31576(33) | 0.11924(27) |
| C(15) | -0.02989(53) | 0.14286(27) | 0.16678(22) |
| C(16) | 0.06877(56) | 0.19750(29) | 0.21330(24) |
| C(17) | 0.13097(51) | 0.15921(27) | 0.27557(23) |
| C(18) | 0.24419(52) | 0.19148(30) | 0.33482(24) |
| C(19) | 0.30926(58) | 0.26987(36) | 0.33107(28) |
| C(20) | 0.41417(65) | 0.29865(42) | 0.38720(31) |
| C(21) | 0.46185(69) | 0.24876(44) | 0.44726(33) |
| C(22) | 0.39821(78) | 0.17122(45) | 0.45142(32) |
| C(23) | 0.28833(69) | 0.14219(36) | 0.39562(28) |

TABLE XII (Continued)

Final Atomic Coordinates for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | x | y | z |
|---|---|---|---|
| C(24) | -0.16978(52) | 0.02249(28) | 0.26363(23) |
| C(25) | -0.28598(63) | 0.07780(37) | 0.25906(28) |
| C(26) | -0.38731(72) | 0.06691(46) | 0.30217(33) |
| C(27) | -0.37138(80) | -0.00074(44) | 0.35012(33) |
| C(28) | -0.25657(83) | -0.05577(39) | 0.35463(32) |
| C(29) | -0.15488(70) | -0.04419(34) | 0.31151(29) |
| C(30) | 0.08691(54) | -0.04599(29) | 0.20166(22) |
| C(31) | 0.23793(61) | -0.03236(35) | 0.21620(28) |
| C(32) | 0.33239(68) | -0.09829(40) | 0.21011(33) |
| C(33) | 0.27885(68) | -0.17831(38) | 0.19139(29) |
| C(34) | 0.13072(67) | -0.19282(32) | 0.17755(26) |
| C(35) | 0.03538(59) | -0.12682(29) | 0.18165(25) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XIII

Thermal Parameters for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | $\beta_{11}$ [a,b] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Br | 1685(9)[c] | 0393(2) | 0327(2) | 0014(4) | 0378(6) | -310(9) |
| P | 0976(16) | 0204(4) | 0135(3) | -077(6) | -031(11) | -010(14) |
| O(1) | 1002(43) | 0278(13) | 0139(8) | -204(17) | -001(30) | -047(38) |
| O(2) | 1309(50) | 0250(13) | 0158(9) | -200(17) | 0139(34) | 0013(40) |
| O(3) | 1314(50) | 0220(13) | 1154(9) | -068(16) | 0078(33) | 0048(39) |
| C(1) | 1141(67) | 0235(18) | 0135(12) | -078(24) | -040(46) | -022(56) |
| C(2) | 1057(65) | 0258(19) | 0150(12) | -080(25) | 0084(46) | -043(57) |
| C(3) | 1372(82) | 0307(21) | 0251(17) | -076(30) | 0026(58) | -139(65) |
| C(4) | 1147(76) | 0372(23) | 0253(16) | 0013(31) | 0032(55) | -185(65) |
| C(5) | 1212(73) | 0323(21) | 0187(14) | -102(28) | 0044(51) | -065(63) |
| C(6) | 1663(92) | 0343(23) | 0231(16) | 0123(31) | -250(62) | -139(72) |
| C(7) | 1345(79) | 0336(23) | 0241(16) | 0168(30) | -209(58) | -090(67) |
| C(8) | 0951(65) | 0246(19) | 0194(13) | -032(25) | 0016(47) | -019(55) |
| C(9) | 1054(65) | 0242(20) | 0173(13) | -030(24) | -135(46) | 0017(53) |
| C(10) | 1666(87) | 0383(23) | 0202(15) | 0166(32) | 0062(56) | 0127(79) |
| C(11) | 2586(131) | 0413(27) | 0241(18) | 0355(35) | 0142(76) | 0163(95) |
| C(12) | 2953(144) | 0328(25) | 0286(19) | 0288(35) | -021(83) | 0092(95) |
| C(13) | 2724(130) | 0261(22) | 0249(18) | 0326(31) | -051(75) | -018(84) |
| C(14) | 1828(95) | 0289(22) | 0223(16) | 0122(29) | -013(61) | -038(72) |
| C(15) | 1027(66) | 0228(18) | 0155(13) | -016(24) | 0009(46) | 0044(56) |
| C(16) | 1202(72) | 0249(19) | 0186(14) | 0116(26) | 0092(50) | -049(58) |
| C(17) | 0908(63) | 0225(18) | 0184(13) | 0011(25) | 0019(46) | -074(53) |
| C(18) | 0892(65) | 0312(20) | 0202(14) | 0046(27) | 0103(48) | -140(58) |
| C(19) | 1150(72) | 0419(23) | 0279(17) | -292(35) | 0270(55) | -269(73) |
| C(20) | 1151(80) | 0636(33) | 0309(19) | -455(40) | 0239(62) | -349(80) |
| C(21) | 1345(85) | 0675(37) | 0328(20) | -075(42) | -032(64) | -374(86) |
| C(22) | 1815(106) | 0624(34) | 0271(19) | 0207(40) | -437(72) | -170(95) |
| C(23) | 1645(91) | 0415(25) | 0215(16) | 0159(33) | -284(61) | -072(77) |

TABLE XIII (Continued)

Thermal Parameters for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| C(24) | 1065(66) | 0257(19) | 0154(13) | -183(25) | 0072(46) | 0085(56) |
| C(25) | 1218(78) | 0483(27) | 0235(16) | 0094(33) | 0106(57) | -014(73) |
| C(26) | 1419(92) | 0685(36) | 0313(20) | -222(43) | 0381(68) | -098(92) |
| C(27) | 1979(108) | 0600(33) | 0292(20) | -741(40) | 0527(73) | -192(98) |
| C(28) | 2364(119) | 0426(28) | 0292(19) | -506(36) | 0644(77) | -041(91) |
| C(29) | 1819(94) | 0343(23) | 0256(16) | -179(32) | 0412(63) | 0064(76) |
| C(30) | 1152(68) | 0273(19) | 0142(12) | 0011(25) | 0092(46) | 0058(58) |
| C(31) | 1152(74) | 0429(25) | 0263(16) | 0025(33) | 0101(56) | -056(70) |
| C(32) | 1377(91) | 0518(30) | 0335(20) | 0202(38) | 0126(68) | -136(81) |
| C(33) | 1547(91) | 0477(28) | 0247(17) | 0188(35) | 0158(63) | 0038(80) |
| C(34) | 1805(93) | 0308(21) | 0187(15) | 0117(28) | 0316(59) | 0046(72) |
| C(35) | 1346(77) | 0258(20) | 0192(14) | -001(27) | 0207(54) | 0018(61) |

[a] The $\beta_{ij}$'s have been multiplied by $10^5$.

[b] The form of the anisotropic ellipsoids is

$$T = \exp\left[-\left\{\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl\right\}\right].$$

[c] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XIV

Principal Axes of the Thermal Ellipsoids for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | Mean Square Displacement in $A^2$ | | |
|---|---|---|---|
| | MAX | MED | MIN |
| Br | 0.10 | 0.07 | 0.01 |
| P | 0.05 | 0.03 | 0.02 |
| O(1) | 0.05 | 0.04 | 0.02 |
| O(2) | 0.07 | 0.03 | 0.02 |
| O(3) | 0.06 | 0.03 | 0.02 |
| C(1) | 0.06 | 0.03 | 0.02 |
| C(2) | 0.05 | 0.03 | 0.03 |
| C(3) | 0.07 | 0.05 | 0.03 |
| C(4) | 0.06 | 0.05 | 0.03 |
| C(5) | 0.06 | 0.04 | 0.03 |
| C(6) | 0.09 | 0.04 | 0.03 |
| C(7) | 0.08 | 0.04 | 0.03 |
| C(8) | 0.05 | 0.03 | 0.03 |
| C(9) | 0.06 | 0.03 | 0.02 |
| C(10) | 0.08 | 0.05 | 0.03 |
| C(11) | 0.12 | 0.06 | 0.03 |
| C(12) | 0.13 | 0.05 | 0.04 |
| C(13) | 0.13 | 0.04 | 0.03 |
| C(14) | 0.09 | 0.04 | 0.04 |
| C(15) | 0.05 | 0.04 | 0.02 |
| C(16) | 0.06 | 0.04 | 0.03 |
| C(17) | 0.05 | 0.03 | 0.02 |
| C(18) | 0.05 | 0.04 | 0.03 |
| C(19) | 0.07 | 0.05 | 0.03 |
| C(20) | 0.10 | 0.05 | 0.04 |
| C(21) | 0.11 | 0.06 | 0.04 |
| C(22) | 0.11 | 0.07 | 0.03 |
| C(23) | 0.09 | 0.05 | 0.03 |

TABLE XIV (Continued)

Principal Axes of the Thermal Ellipsoids for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | Mean Square Displacement in $A^2$ | | |
|---|---|---|---|
| | MAX | MED | MIN |
| C(24) | 0.06 | 0.03 | 0.02 |
| C(25) | 0.06 | 0.05 | 0.04 |
| C(26) | 0.09 | 0.06 | 0.05 |
| C(27) | 0.11 | 0.05 | 0.04 |
| C(28) | 0.11 | 0.05 | 0.04 |
| C(29) | 0.08 | 0.05 | 0.04 |
| C(30) | 0.05 | 0.04 | 0.02 |
| C(31) | 0.06 | 0.05 | 0.04 |
| C(32) | 0.08 | 0.06 | 0.05 |
| C(33) | 0.08 | 0.05 | 0.04 |
| C(34) | 0.08 | 0.04 | 0.03 |
| C(35) | 0.06 | 0.04 | 0.03 |

TABLE XV

Equations of Least Squares Planes Referred to Orthogonal Axes for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ [a]

| ATOMS | a | b | c | D(A) | S($A^2$) |
|---|---|---|---|---|---|
| PO(2)C(15)C(16)C(17) | -0.7156 | 0.2743 | 0.6424 | 2.339 | $6.9\times10^{-4}$ |
| PC(15)C(24)C(30) | 0.5778 | 0.3951 | 0.7142 | 3.326 | $2.6\times10^{-3}$ |
| C(8)C(9)C(15)C(16) C(17)C(18) | -0.7089 | 0.1305 | 0.6931 | 2.167 | $1.3\times10^{-2}$ |
| C(8)C(9)C(10)C(14) | 0.9719 | 0.2163 | -0.0925 | -0.248 | $3.8\times10^{-4}$ |
| C(17)C(18)C(19)C(23) | -0.6797 | 0.3600 | 0.6391 | 2.609 | $1.3\times10^{-5}$ |

[a] $X = x + z\cos\beta$ ; $Y = y$; $Z = z\sin\beta$ ,

$D = a\overline{X} + b\overline{Y} + c\overline{Z}$,

S = sum of squares of deviations of atoms from plane,

D = origin to plane distance in angstroms,

All atoms are given equal weight.

TABLE XVI

Bond Distances for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOMS | DISTANCE |
|---|---|
| Br-C(5) | 1.905(9)[a] |
| P-O(1) | 1.737(6) |
| P-O(2) | 1.786(6) |
| P-C(24) | 1.821(7) |
| P-C(15) | 1.815(6) |
| P-C(30) | 1.824(7) |
| O(1)-C(1) | 1.402(7) |
| O(2)-C(17) | 1.354(7) |
| O(3)-C(1) | 1.430(8) |
| O(3)-C(8) | 1.362(10) |
| C(1)-C(2) | 1.514(12) |
| C(2)-C(3) | 1.384(10) |
| C(2)-C(7) | 1.380(13) |
| C(3)-C(4) | 1.375(14) |
| C(4)-C(5) | 1.380(13) |
| C(5)-C(6) | 1.374(11) |
| C(6)-C(7) | 1.398(14) |
| C(8)-C(9) | 1.470(9) |
| C(8)-C(15) | 1.383(11) |
| C(9)-C(10) | 1.390(8) |
| C(9)-C(14) | 1.388(11) |
| C(10)-C(11) | 1.386(12) |
| C(11)-C(12) | 1.373(14) |
| C(12)-C(13) | 1.392(11) |
| C(13)-C(14) | 1.374(12) |
| C(15)-C(16) | 1.436(12) |
| C(16)-C(17) | 1.356(12) |
| C(17)-C(18) | 1.476(12) |
| C(18)-C(19) | 1.395(10) |
| C(18)-C(23) | 1.389(12) |
| C(19)-C(20) | 1.376(15) |

TABLE XVI (Continued)

Bond Distances for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOM | DISTANCE |
|---|---|
| C(20)-C(21) | 1.389(16) |
| C(21)-C(22) | 1.378(14) |
| C(22)-C(23) | 1.402(16) |
| C(24)-C(25) | 1.392(11) |
| C(24)-C(29) | 1.386(11) |
| C(25)-C(26) | 1.396(12) |
| C(26)-C(27) | 1.399(15) |
| C(27)-C(28) | 1.379(15) |
| C(28)-C(29) | 1.400(13) |
| C(30)-C(31) | 1.410(10) |
| C(30)-C(35) | 1.396(10) |
| C(31)-C(32) | 1.394(12) |
| C(32)-C(33) | 1.389(14) |
| C(33)-C(34) | 1.386(12) |
| C(34)-C(35) | 1.393(11) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XVII

Bond Angles for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOMS | DEGREES |
|---|---|
| O(1)-P-O(2) | 176.88(9)[a] |
| O(1)-P-C(24) | 88.31(11) |
| O(1)-P-C(15) | 92.68(16) |
| O(1)-P-C(30) | 93.48(15) |
| O(2)-P-C(24) | 89.01(12) |
| O(2)-P-C(15) | 87.26(16) |
| O(2)-P-C(30) | 89.14(16) |
| C(15)-P-C(24) | 119.06(19) |
| C(24)-P-C(30) | 116.78(18) |
| C(15)-P-C(30) | 123.95(21) |
| P-O(1)-C(1) | 113.29(22) |
| P-O(2)-C(17) | 113.75(24) |
| P-C(15)-C(8) | 123.68(35) |
| P-C(15)-C(18) | 111.10(32) |
| P-C(30)-C(31) | 121.07(34) |
| P-C(30)-C(35) | 120.58(35) |
| O(1)-C(1)-O(3) | 108.35(32) |
| O(1)-C(1)-C(2) | 110.54(34) |
| O(2)-C(17)-C(16) | 115.50(35) |
| O(2)-C(17)-C(18) | 115.47(34) |
| O(3)-C(1)-C(2) | 109.22(36) |
| C(1)-O(3)-C(8) | 113.08(27) |
| C(1)-C(2)-C(3) | 117.73(38) |
| C(1)-C(2)-C(7) | 122.83(39) |
| C(3)-C(2)-C(7) | 119.42(42) |
| C(4)-C(3)-C(2) | 121.03(43) |
| C(3)-C(4)-C(5) | 118.69(40) |
| C(4)-C(5)-C(6) | 121.93(42) |
| C(5)-C(6)-C(7) | 118.49(45) |
| C(2)-C(7)-C(6) | 120.42(47) |
| C(8)-C(9)-C(10) | 120.27(36) |
| C(8)-C(9)-C(14) | 120.72(39) |
| C(10)-C(9)-C(14) | 118.94(40) |
| C(9)-C(10)-C(11) | 119.55(44) |

TABLE XVII (Continued)

Bond Angles for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| ATOMS | DEGREES |
|---|---|
| C(10)-C(11)-C(12) | 121.10(50) |
| C(11)-C(12)-C(13) | 119.56(53) |
| C(14)-C(13)-C(12) | 119.58(49) |
| C(9)-C(14)-C(13) | 121.25(47) |
| C(8)-C(15)-C(16) | 125.14(42) |
| C(15)-C(16)-C(17) | 112.28(37) |
| C(16)-C(17)-C(18) | 129.00(37) |
| C(17)-C(18)-C(19) | 121.70(36) |
| C(17)-C(18)-C(23) | 119.25(36) |
| C(19)-C(18)-C(23) | 119.05(38) |
| C(18)-C(19)-C(20) | 120.54(46) |
| C(19)-C(20)-C(21) | 120.73(47) |
| C(22)-C(21)-C(20) | 119.06(50) |
| C(21)-C(22)-C(23) | 120.78(52) |
| C(18)-C(23)-C(22) | 119.77(45) |
| C(25)-C(24)-C(29) | 119.50(42) |
| C(24)-C(25)-C(26) | 120.79(44) |
| C(25)-C(26)-C(27) | 119.19(50) |
| C(26)-C(27)-C(28) | 120.15(53) |
| C(27)-C(28)-C(29) | 120.36(51) |
| C(24)-C(29)-C(28) | 120.02(48) |
| C(31)-C(30)-C(35) | 118.34(42) |
| C(30)-C(31)-C(32) | 120.38(43) |
| C(31)-C(32)-C(33) | 120.23(47) |
| C(32)-C(33)-C(34) | 120.02(46) |
| C(35)-C(34)-C(33) | 120.11(43) |
| C(30)-C(35)-C(34) | 120.88(42) |
| Br-C(5)-C(6) | 119.81(37) |
| Br-C(5)-C(4) | 118.24(32) |
| Br-C(5)-C(2) | 177.55(27) |
| Br-C(5)-C(3) | 148.77(28) |
| Br-C(5)-C(7) | 150.84(28) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H= | 0 K= | 0 | 13 | 18 | 17 | 18 | 13 | 13 | 6 | 27 | 29 |
| 2 | 90 | 113 | 14 | 25 | 25 | 20 | 10 | 10 | 7 | 23 | 23 |
| 4 | 23 | 24 | 15 | 22 | 21 | H= | 0 K= | 5 | 8 | 58 | 59 |
| 6 | 117 | 117 | 16 | 22 | 20 | 1 | 72 | 66 | 9 | 25 | 26 |
| 8 | 57 | 54 | 17 | 40 | 41 | 2 | 97 | 99 | 10 | 16 | 15 |
| 10 | 8 | 2 | 18 | 34 | 34 | 3 | 94 | 102 | 12 | 27 | 28 |
| 14 | 51 | 52 | H= | 0 K= | 3 | 4 | 49 | 53 | 13 | 28 | 27 |
| 16 | 46 | 46 | 1 | 6 | 8 | 5 | 29 | 27 | 14 | 34 | 34 |
| 18 | 18 | 16 | 2 | 22 | 23 | 6 | 19 | 15 | 15 | 18 | 19 |
| 20 | 26 | 27 | 3 | 101 | 114 | 8 | 57 | 57 | 17 | 10 | 10 |
| H= | 0 K= | 1 | 4 | 111 | 135 | 9 | 8 | 5 | 18 | 5 | 6 |
| 1 | 74 | 107 | 5 | 10 | 6 | 10 | 10 | 8 | 19 | 20 | 21 |
| 2 | 82 | 110 | 6 | 15 | 15 | 11 | 9 | 8 | H= | 0 K= | 8 |
| 3 | 12 | 12 | 7 | 29 | 24 | 12 | 26 | 24 | 0 | 23 | 18 |
| 4 | 48 | 47 | 8 | 13 | 14 | 13 | 6 | 6 | 1 | 5 | 9 |
| 5 | 51 | 44 | 9 | 77 | 78 | 14 | 12 | 13 | 2 | 68 | 64 |
| 6 | 97 | 91 | 10 | 34 | 31 | 15 | 10 | 10 | 3 | 29 | 28 |
| 7 | 55 | 46 | 11 | 33 | 32 | 16 | 42 | 41 | 4 | 43 | 45 |
| 8 | 58 | 60 | 12 | 45 | 43 | 17 | 31 | 31 | 5 | 74 | 74 |
| 9 | 16 | 13 | 13 | 16 | 16 | 18 | 16 | 16 | 6 | 30 | 28 |
| 10 | 24 | 22 | 14 | 43 | 42 | 19 | 8 | 8 | 7 | 35 | 36 |
| 11 | 9 | 12 | 15 | 39 | 37 | 20 | 7 | 5 | 8 | 30 | 28 |
| 12 | 57 | 54 | 16 | 18 | 17 | H= | 0 K= | 6 | 9 | 31 | 31 |
| 13 | 13 | 11 | 17 | 15 | 16 | 0 | 26 | 21 | 10 | 59 | 60 |
| 14 | 34 | 35 | 20 | 9 | 9 | 1 | 52 | 57 | 11 | 50 | 51 |
| 15 | 39 | 41 | H= | 0 K= | 4 | 2 | 21 | 15 | 12 | 34 | 33 |
| 16 | 26 | 27 | 0 | 95 | 112 | 3 | 46 | 46 | 13 | 7 | 6 |
| 17 | 19 | 18 | 1 | 13 | 17 | 4 | 8 | 5 | 14 | 19 | 18 |
| 18 | 36 | 37 | 2 | 64 | 67 | 5 | 20 | 21 | 15 | 6 | 8 |
| 19 | 21 | 21 | 3 | 56 | 54 | 6 | 31 | 28 | 17 | 6 | 4 |
| 20 | 7 | 7 | 4 | 69 | 73 | 7 | 17 | 20 | H= | 0 K= | 9 |
| H= | 0 K= | 2 | 5 | 47 | 47 | 8 | 13 | 9 | 1 | 50 | 49 |
| 0 | 23 | 23 | 6 | 94 | 95 | 10 | 24 | 25 | 2 | 53 | 54 |
| 1 | 77 | 101 | 7 | 54 | 50 | 11 | 33 | 30 | 3 | 60 | 61 |
| 2 | 56 | 60 | 8 | 16 | 15 | 12 | 29 | 28 | 4 | 52 | 52 |
| 3 | 35 | 35 | 9 | 51 | 47 | 13 | 19 | 18 | 5 | 18 | 17 |
| 4 | 115 | 153 | 10 | 75 | 73 | 14 | 38 | 38 | 7 | 64 | 64 |
| 5 | 93 | 91 | 11 | 34 | 33 | 15 | 33 | 36 | 9 | 59 | 57 |
| 6 | 89 | 83 | 12 | 9 | 9 | 16 | 16 | 14 | 10 | 20 | 21 |
| 8 | 14 | 5 | 13 | 28 | 28 | 17 | 18 | 18 | 11 | 38 | 36 |
| 9 | 9 | 8 | 14 | 58 | 59 | 19 | 11 | 11 | 12 | 29 | 27 |
| 10 | 75 | 76 | 15 | 27 | 26 | H= | 0 K= | 7 | 13 | 27 | 26 |
| 11 | 35 | 31 | 16 | 14 | 15 | 2 | 27 | 30 | 14 | 7 | 8 |
| 12 | 76 | 75 | 17 | 28 | 29 | 3 | 53 | 61 | 15 | 16 | 15 |

TABLE XVIII

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 19 | 18 | 11 | 8 | 7 | 5 | 16 | 15 | 7 | 19 | 19 |
| 17 | 8 | 9 | 13 | 18 | 19 | 7 | 12 | 12 | -7 | 14 | 13 |
| 18 | 17 | 16 | 15 | 23 | 23 | 9 | 16 | 17 | 8 | 81 | 75 |
| H= | 0 K= | 10 | H= | 0 K= | 13 | H= | 0 K= | 17 | -8 | 87 | 83 |
| 0 | 38 | 35 | 2 | 11 | 11 | 1 | 12 | 10 | 9 | 35 | 36 |
| 1 | 36 | 36 | 3 | 39 | 40 | 2 | 22 | 21 | -9 | 63 | 58 |
| 2 | 17 | 18 | 4 | 41 | 39 | 3 | 9 | 9 | 10 | 16 | 15 |
| 3 | 20 | 21 | 5 | 62 | 62 | 4 | 26 | 24 | -10 | 63 | 62 |
| 5 | 53 | 55 | 6 | 12 | 13 | 6 | 9 | 9 | 11 | 34 | 32 |
| 7 | 27 | 28 | 7 | 65 | 63 | H= | 1 K= | 0 | -11 | 36 | 33 |
| 8 | 13 | 12 | 9 | 58 | 56 | 0 | 67 | 72 | 12 | 52 | 51 |
| 9 | 30 | 31 | 10 | 5 | 5 | 2 | 35 | 32 | -12 | 28 | 24 |
| 10 | 13 | 13 | 12 | 9 | 9 | -2 | 81 | 90 | 13 | 32 | 31 |
| 11 | 30 | 27 | 13 | 25 | 24 | 4 | 167 | 295 | 14 | 46 | 45 |
| 13 | 9 | 8 | 14 | 12 | 13 | -4 | 15 | 13 | -14 | 59 | 58 |
| 14 | 24 | 24 | H= | 0 K= | 14 | 6 | 97 | 95 | 15 | 28 | 26 |
| 15 | 14 | 12 | 0 | 20 | 20 | -6 | 38 | 24 | -15 | 43 | 44 |
| 16 | 13 | 12 | 1 | 46 | 45 | 8 | 49 | 38 | 16 | 37 | 38 |
| 17 | 7 | 7 | 3 | 17 | 15 | -8 | 23 | 11 | -16 | 15 | 15 |
| H= | 0 K= | 11 | 4 | 22 | 20 | 10 | 123 | 132 | 17 | 18 | 19 |
| 1 | 33 | 30 | 5 | 26 | 24 | -10 | 100 | 107 | -17 | 37 | 37 |
| 2 | 9 | 10 | 6 | 12 | 14 | 12 | 44 | 44 | 18 | 26 | 25 |
| 3 | 76 | 80 | 7 | 6 | 6 | -12 | 58 | 60 | -18 | 5 | 4 |
| 5 | 33 | 33 | 8 | 15 | 13 | -14 | 22 | 23 | 19 | 18 | 19 |
| 6 | 44 | 44 | 9 | 25 | 24 | 16 | 19 | 20 | -19 | 19 | 18 |
| 7 | 10 | 9 | 10 | 17 | 16 | -16 | 39 | 38 | 20 | 8 | 9 |
| 8 | 15 | 13 | 11 | 23 | 23 | 18 | 15 | 16 | H= | 1 K= | 2 |
| 9 | 21 | 20 | 12 | 27 | 27 | -18 | 6 | 2 | 0 | 108 | 172 |
| 10 | 12 | 12 | H= | 0 K= | 15 | 20 | 7 | 7 | 1 | 40 | 45 |
| 11 | 8 | 6 | 1 | 24 | 24 | -20 | 42 | 42 | -1 | 25 | 21 |
| 13 | 33 | 32 | 2 | 5 | 4 | H= | 1 K= | 1 | 2 | 88 | 111 |
| 14 | 17 | 18 | 3 | 28 | 27 | 0 | 16 | 16 | -2 | 37 | 39 |
| 15 | 13 | 13 | 5 | 20 | 19 | 1 | 42 | 41 | 3 | 54 | 51 |
| 16 | 6 | 5 | 6 | 7 | 7 | -1 | 17 | 18 | -3 | 119 | 169 |
| H= | 0 K= | 12 | 7 | 9 | 9 | 2 | 44 | 45 | -4 | 77 | 81 |
| 1 | 45 | 46 | 8 | 34 | 33 | -2 | 12 | 13 | 5 | 18 | 13 |
| 2 | 30 | 31 | 9 | 8 | 8 | 3 | 60 | 62 | -5 | 69 | 68 |
| 3 | 13 | 12 | 10 | 29 | 28 | -3 | 55 | 58 | 6 | 52 | 51 |
| 4 | 22 | 21 | 11 | 13 | 13 | 4 | 60 | 63 | -6 | 71 | 73 |
| 5 | 54 | 53 | H= | 0 K= | 16 | -4 | 125 | 161 | 7 | 30 | 33 |
| 6 | 31 | 31 | 0 | 21 | 20 | -5 | 83 | 85 | -7 | 84 | 79 |
| 8 | 26 | 28 | 2 | 8 | 9 | 6 | 86 | 84 | 8 | 17 | 15 |
| 9 | 9 | 7 | 3 | 8 | 7 | -6 | 35 | 25 | -8 | 53 | 47 |
| 10 | 39 | 39 | 4 | 19 | 19 | | | | 9 | 23 | 22 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -9 | 25 | 27 | -12 | 46 | 44 | -15 | 40 | 41 | H= | 1 K= | 6 |
| 10 | 49 | 49 | 13 | 18 | 16 | 16 | 53 | 53 | 0 | 78 | 88 |
| -10 | 47 | 45 | -13 | 29 | 29 | -16 | 7 | 5 | 1 | 7 | 6 |
| 11 | 50 | 50 | 14 | 25 | 25 | -17 | 27 | 28 | -1 | 35 | 34 |
| -11 | 7 | 7 | 15 | 25 | 25 | 18 | 5 | 5 | 2 | 31 | 32 |
| 12 | 14 | 17 | -15 | 25 | 23 | -18 | 39 | 38 | -2 | 68 | 70 |
| -12 | 8 | 9 | 16 | 25 | 25 | 19 | 13 | 13 | 3 | 11 | 8 |
| 13 | 18 | 17 | -16 | 7 | 5 | -19 | 16 | 16 | -3 | 49 | 53 |
| -13 | 53 | 51 | 17 | 19 | 20 | -20 | 10 | 9 | 4 | 94 | 100 |
| 14 | 32 | 31 | -17 | 30 | 32 | H= | 1 K= | 5 | -4 | 18 | 24 |
| -14 | 46 | 44 | 18 | 35 | 35 | 0 | 17 | 11 | 5 | 49 | 44 |
| 15 | 5 | 4 | -18 | 26 | 26 | 1 | 36 | 30 | -5 | 68 | 71 |
| -15 | 17 | 18 | 19 | 12 | 13 | -1 | 6 | 11 | -6 | 90 | 105 |
| 16 | 6 | 6 | -19 | 13 | 13 | -2 | 50 | 57 | 7 | 30 | 31 |
| -16 | 44 | 43 | -20 | 17 | 17 | 3 | 30 | 31 | -7 | 62 | 68 |
| 17 | 16 | 16 | H= | 1 K= | 4 | 4 | 30 | 28 | -8 | 17 | 17 |
| -17 | 13 | 13 | 0 | 89 | 107 | -4 | 69 | 74 | 9 | 45 | 47 |
| -18 | 8 | 6 | 1 | 22 | 27 | 5 | 22 | 14 | -9 | 47 | 42 |
| 20 | 29 | 30 | -1 | 50 | 49 | -5 | 10 | 10 | 10 | 31 | 31 |
| -20 | 19 | 19 | 2 | 30 | 21 | 6 | 132 | 151 | -10 | 51 | 50 |
| H= | 1 K= | 3 | -2 | 28 | 26 | 7 | 120 | 122 | 11 | 38 | 39 |
| 0 | 76 | 87 | 3 | 30 | 26 | -7 | 11 | 13 | -11 | 66 | 67 |
| 1 | 119 | 178 | -3 | 52 | 50 | 8 | 64 | 62 | -12 | 33 | 33 |
| -1 | 91 | 117 | 4 | 79 | 79 | -8 | 68 | 73 | 13 | 24 | 26 |
| 2 | 108 | 135 | -4 | 52 | 55 | 9 | 33 | 32 | -13 | 32 | 31 |
| -2 | 8 | 2 | 5 | 24 | 26 | -9 | 51 | 52 | 14 | 10 | 10 |
| 3 | 51 | 46 | -5 | 26 | 28 | 10 | 16 | 12 | -14 | 17 | 16 |
| -3 | 84 | 88 | 6 | 101 | 104 | -10 | 17 | 19 | 15 | 20 | 22 |
| 4 | 103 | 108 | -6 | 84 | 95 | 11 | 5 | 5 | -15 | 14 | 13 |
| -4 | 79 | 90 | 7 | 50 | 43 | -11 | 29 | 28 | 16 | 14 | 12 |
| 5 | 43 | 29 | 8 | 18 | 16 | 12 | 48 | 47 | -16 | 17 | 17 |
| -5 | 44 | 47 | -8 | 5 | 1 | -12 | 22 | 22 | 17 | 24 | 24 |
| 6 | 31 | 32 | 9 | 16 | 14 | 13 | 17 | 16 | -19 | 9 | 7 |
| -6 | 42 | 38 | -9 | 12 | 12 | -13 | 12 | 13 | H= | 1 K= | 7 |
| 7 | 20 | 20 | 10 | 60 | 61 | 14 | 41 | 42 | 0 | 14 | 14 |
| -7 | 6 | 12 | -10 | 90 | 93 | -14 | 25 | 24 | 1 | 93 | 91 |
| 8 | 102 | 104 | 11 | 6 | 7 | 15 | 41 | 41 | -1 | 51 | 49 |
| -8 | 46 | 48 | -11 | 56 | 55 | 16 | 10 | 10 | 2 | 106 | 125 |
| 9 | 23 | 21 | 12 | 26 | 25 | -16 | 18 | 16 | -2 | 8 | 6 |
| -9 | 24 | 22 | -12 | 42 | 42 | -17 | 29 | 29 | 3 | 66 | 69 |
| 10 | 28 | 24 | 13 | 20 | 19 | 18 | 16 | 15 | -3 | 86 | 90 |
| -10 | 56 | 53 | -13 | 27 | 26 | -18 | 17 | 18 | 4 | 38 | 44 |
| 11 | 32 | 28 | -14 | 21 | 20 | 19 | 7 | 6 | -4 | 75 | 83 |
| 12 | 18 | 19 | 15 | 6 | 5 | | | | 5 | 30 | 32 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -5 | 17 | 15 | 13 | 5 | 5 | 2 | 52 | 49 | 10 | 34 | 37 |
| 6 | 26 | 23 | -13 | 15 | 13 | 3 | 13 | 17 | 11 | 22 | 24 |
| 7 | 79 | 78 | 14 | 34 | 36 | -3 | 13 | 11 | -11 | 14 | 15 |
| -7 | 37 | 39 | -14 | 6 | 4 | 4 | 16 | 16 | 12 | 7 | 5 |
| -8 | 20 | 16 | 15 | 30 | 31 | -4 | 33 | 35 | -12 | 32 | 33 |
| 9 | 24 | 25 | -15 | 31 | 31 | 5 | 74 | 78 | 13 | 30 | 31 |
| -9 | 62 | 64 | 16 | 30 | 31 | -5 | 29 | 29 | -13 | 44 | 44 |
| -10 | 27 | 26 | -16 | 23 | 23 | 6 | 15 | 16 | 14 | 13 | 14 |
| 11 | 6 | 4 | 17 | 5 | 6 | -6 | 12 | 15 | -14 | 6 | 4 |
| -11 | 10 | 9 | -17 | 18 | 18 | 7 | 10 | 8 | 15 | 11 | 12 |
| 12 | 15 | 14 | 18 | 7 | 7 | -7 | 51 | 51 | -15 | 21 | 20 |
| -12 | 16 | 16 | H= | 1 K= | 9 | 8 | 39 | 38 | -16 | 17 | 16 |
| 13 | 34 | 33 | 0 | 9 | 10 | 9 | 30 | 28 | H= | 1 K= | 12 |
| -13 | 38 | 38 | 1 | 26 | 30 | -9 | 28 | 27 | 0 | 32 | 34 |
| 14 | 10 | 13 | -1 | 38 | 38 | 10 | 28 | 29 | 1 | 29 | 28 |
| -15 | 34 | 35 | 2 | 6 | 7 | -10 | 31 | 33 | -1 | 57 | 58 |
| 16 | 20 | 20 | 3 | 71 | 71 | 11 | 41 | 41 | 2 | 25 | 26 |
| -16 | 24 | 25 | 4 | 13 | 14 | -11 | 7 | 9 | -2 | 7 | 7 |
| 18 | 23 | 23 | -4 | 14 | 12 | -12 | 11 | 9 | 3 | 30 | 28 |
| -18 | 27 | 27 | 5 | 9 | 6 | 13 | 8 | 8 | 4 | 24 | 25 |
| -19 | 6 | 5 | -5 | 46 | 47 | -13 | 38 | 36 | -4 | 6 | 2 |
| H= | 1 K= | 8 | 6 | 49 | 49 | -14 | 11 | 11 | 5 | 35 | 35 |
| 0 | 38 | 43 | -6 | 16 | 18 | 15 | 29 | 30 | -5 | 15 | 12 |
| 1 | 43 | 42 | 7 | 22 | 20 | -15 | 7 | 7 | 6 | 19 | 19 |
| -1 | 86 | 98 | -7 | 17 | 19 | 16 | 7 | 7 | -6 | 9 | 10 |
| 2 | 61 | 64 | 8 | 17 | 14 | -17 | 15 | 15 | 7 | 12 | 12 |
| -2 | 25 | 20 | -8 | 42 | 41 | H= | 1 K= | 11 | -7 | 6 | 6 |
| 3 | 59 | 57 | -9 | 15 | 15 | 0 | 25 | 25 | 8 | 10 | 10 |
| -3 | 50 | 53 | 10 | 23 | 21 | 1 | 17 | 17 | -8 | 28 | 28 |
| 4 | 19 | 18 | -10 | 25 | 27 | -1 | 36 | 34 | 9 | 43 | 43 |
| -4 | 6 | 8 | -11 | 5 | 4 | 2 | 27 | 28 | -9 | 24 | 24 |
| -5 | 41 | 43 | 12 | 9 | 8 | 3 | 11 | 11 | 10 | 7 | 8 |
| -6 | 39 | 37 | 13 | 39 | 37 | -3 | 28 | 28 | -10 | 12 | 12 |
| 7 | 24 | 24 | 14 | 28 | 28 | -4 | 14 | 15 | 11 | 28 | 27 |
| -7 | 28 | 28 | -14 | 8 | 9 | 5 | 39 | 38 | -11 | 19 | 18 |
| 8 | 16 | 13 | 15 | 6 | 6 | -5 | 11 | 9 | 12 | 17 | 17 |
| 9 | 13 | 11 | -15 | 25 | 25 | 6 | 23 | 24 | -12 | 23 | 23 |
| -9 | 23 | 25 | 17 | 19 | 20 | -6 | 25 | 26 | 13 | 18 | 19 |
| 10 | 8 | 6 | -17 | 20 | 21 | 7 | 37 | 37 | 14 | 15 | 14 |
| -10 | 30 | 32 | -18 | 7 | 6 | -7 | 85 | 89 | -14 | 20 | 19 |
| 11 | 42 | 45 | H= | 1 K= | 10 | 8 | 7 | 9 | -15 | 23 | 23 |
| -11 | 16 | 17 | 0 | 7 | 3 | -8 | 35 | 33 | H= | 1 K= | 13 |
| 12 | 20 | 22 | 1 | 23 | 24 | 9 | 32 | 33 | 0 | 24 | 26 |
| -12 | 22 | 23 | -1 | 46 | 45 | -9 | 51 | 51 | 1 | 40 | 41 |
| | | | | | | | | | -1 | 40 | 40 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 23 | 23 | -4 | 19 | 17 | -10 | 30 | 29 | -2 | 52 | 44 |
| -2 | 6 | 6 | 5 | 5 | 7 | 12 | 45 | 44 | 3 | 83 | 80 |
| 3 | 30 | 32 | -5 | 9 | 11 | -12 | 42 | 43 | -3 | 117 | 142 |
| -3 | 53 | 53 | 6 | 26 | 26 | 14 | 72 | 71 | 4 | 75 | 76 |
| 4 | 30 | 30 | -6 | 8 | 8 | -16 | 70 | 72 | -4 | 5 | 11 |
| -4 | 6 | 6 | 7 | 32 | 31 | 18 | 17 | 18 | 5 | 42 | 39 |
| 5 | 65 | 65 | -7 | 40 | 39 | -18 | 29 | 28 | -5 | 50 | 42 |
| -5 | 23 | 23 | 8 | 8 | 7 | H= | 2 K= | 1 | -6 | 97 | 97 |
| 6 | 24 | 24 | -8 | 23 | 23 | 0 | 136 | 201 | 7 | 76 | 74 |
| -6 | 12 | 14 | 9 | 12 | 11 | 1 | 51 | 36 | -7 | 48 | 46 |
| -7 | 19 | 17 | -9 | 37 | 35 | 2 | 7 | 6 | 8 | 64 | 59 |
| 8 | 7 | 6 | 10 | 6 | 7 | -2 | 126 | 178 | -8 | 60 | 50 |
| -9 | 5 | 4 | -10 | 12 | 11 | 3 | 11 | 11 | 9 | 9 | 5 |
| 10 | 29 | 28 | H= | 1 K= | 16 | -3 | 138 | 180 | -9 | 42 | 41 |
| -10 | 13 | 12 | 1 | 15 | 13 | 4 | 38 | 35 | 10 | 105 | 108 |
| 11 | 8 | 7 | -1 | 16 | 16 | -4 | 178 | 271 | -10 | 51 | 54 |
| -11 | 9 | 8 | 3 | 9 | 9 | 5 | 41 | 41 | 11 | 13 | 12 |
| -12 | 14 | 11 | 4 | 15 | 15 | 6 | 69 | 64 | -11 | 22 | 21 |
| 13 | 20 | 20 | -4 | 14 | 14 | -6 | 6 | 2 | 12 | 22 | 21 |
| H= | 1 K= | 14 | 5 | 14 | 15 | -7 | 22 | 19 | -12 | 37 | 37 |
| 0 | 34 | 34 | -5 | 34 | 31 | 8 | 57 | 60 | 13 | 16 | 15 |
| -1 | 32 | 31 | 6 | 8 | 8 | -8 | 42 | 40 | -13 | 10 | 7 |
| -2 | 21 | 21 | -6 | 24 | 23 | 9 | 13 | 11 | 14 | 44 | 44 |
| 3 | 19 | 20 | 7 | 12 | 12 | 10 | 8 | 8 | -14 | 12 | 12 |
| 4 | 22 | 22 | -7 | 21 | 22 | -10 | 55 | 50 | 15 | 40 | 41 |
| -4 | 21 | 21 | -8 | 8 | 7 | 11 | 9 | 8 | -15 | 26 | 28 |
| 5 | 39 | 38 | -9 | 13 | 13 | -11 | 29 | 25 | 16 | 24 | 24 |
| -5 | 8 | 9 | H= | 1 K= | 17 | 12 | 65 | 63 | -16 | 8 | 6 |
| -6 | 7 | 6 | 1 | 8 | 7 | -12 | 20 | 16 | -17 | 10 | 8 |
| -7 | 25 | 24 | -1 | 8 | 8 | 14 | 57 | 58 | -20 | 11 | 11 |
| 8 | 17 | 17 | 3 | 22 | 20 | -14 | 35 | 35 | H= | 2 K= | 3 |
| -8 | 22 | 21 | -3 | 20 | 19 | 15 | 7 | 7 | 0 | 82 | 84 |
| 9 | 43 | 42 | -6 | 7 | 5 | -15 | 10 | 10 | 1 | 6 | 6 |
| 10 | 8 | 7 | H= | 2 K= | 0 | 16 | 21 | 21 | -1 | 76 | 81 |
| -10 | 29 | 27 | 0 | 33 | 32 | 17 | 8 | 7 | 2 | 119 | 137 |
| 11 | 18 | 18 | 2 | 78 | 72 | -17 | 25 | 26 | -2 | 41 | 44 |
| -11 | 9 | 8 | -2 | 162 | 273 | 18 | 25 | 25 | 3 | 16 | 12 |
| H= | 1 K= | 15 | 4 | 59 | 53 | -18 | 13 | 13 | -3 | 84 | 85 |
| 0 | 7 | 7 | -4 | 77 | 77 | -19 | 9 | 8 | 4 | 57 | 46 |
| 1 | 15 | 13 | 6 | 53 | 49 | -20 | 24 | 23 | -4 | 76 | 76 |
| 2 | 19 | 20 | -6 | 68 | 58 | H= | 2 K= | 2 | 5 | 44 | 37 |
| -2 | 9 | 10 | 8 | 48 | 46 | 0 | 100 | 115 | 6 | 103 | 108 |
| 3 | 31 | 32 | -8 | 51 | 42 | 1 | 57 | 48 | -6 | 37 | 29 |
| -3 | 33 | 32 | 10 | 8 | 6 | -1 | 66 | 78 | 7 | 85 | 82 |
| | | | | | | 2 | 25 | 18 | | | |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -7 | 57 | 56 | 13 | 9 | 8 | 18 | 18 | 18 | 2 | 15 | 6 |
| 8 | 69 | 70 | -13 | 45 | 44 | -18 | 18 | 18 | -2 | 24 | 24 |
| 9 | 13 | 9 | 14 | 27 | 26 | -19 | 35 | 36 | 3 | 59 | 56 |
| 10 | 9 | 11 | -14 | 13 | 13 | -20 | 12 | 11 | -3 | 16 | 21 |
| -10 | 40 | 42 | 15 | 19 | 19 | H= | 2 K= | 6 | 4 | 22 | 20 |
| 11 | 8 | 7 | -15 | 58 | 60 | 0 | 72 | 75 | -4 | 12 | 12 |
| -11 | 32 | 31 | -16 | 54 | 53 | 1 | 56 | 53 | 5 | 44 | 40 |
| 12 | 57 | 55 | 17 | 12 | 13 | -1 | 115 | 135 | -5 | 42 | 42 |
| 13 | 44 | 44 | -17 | 10 | 13 | -2 | 27 | 28 | 6 | 95 | 97 |
| -13 | 7 | 6 | -20 | 23 | 24 | 3 | 58 | 58 | -6 | 50 | 49 |
| 14 | 9 | 7 | H= | 2 K= | 5 | -3 | 66 | 73 | 7 | 46 | 45 |
| -14 | 39 | 41 | 0 | 51 | 54 | 4 | 45 | 53 | -7 | 21 | 19 |
| 15 | 19 | 18 | 1 | 23 | 29 | -4 | 27 | 32 | 8 | 63 | 63 |
| -15 | 36 | 35 | -1 | 18 | 18 | 5 | 66 | 63 | -8 | 44 | 45 |
| 17 | 8 | 8 | 2 | 69 | 66 | -5 | 7 | 6 | 9 | 21 | 22 |
| -17 | 26 | 26 | -2 | 31 | 29 | 6 | 73 | 72 | -9 | 19 | 23 |
| 18 | 30 | 29 | 3 | 58 | 59 | -6 | 12 | 14 | 10 | 29 | 28 |
| 19 | 10 | 11 | -3 | 45 | 52 | 7 | 44 | 41 | -10 | 42 | 40 |
| -19 | 16 | 17 | 4 | 51 | 49 | -7 | 41 | 46 | 11 | 56 | 58 |
| H= | 2 K= | 4 | -4 | 39 | 40 | 8 | 9 | 10 | -11 | 17 | 18 |
| 0 | 80 | 87 | 5 | 22 | 17 | -8 | 8 | 0 | 12 | 49 | 49 |
| 1 | 16 | 14 | -5 | 21 | 19 | 9 | 5 | 4 | 13 | 21 | 21 |
| -1 | 26 | 27 | 6 | 9 | 8 | -9 | 15 | 14 | -13 | 29 | 29 |
| 2 | 57 | 54 | -6 | 27 | 28 | 10 | 30 | 30 | 14 | 7 | 6 |
| -2 | 25 | 26 | 7 | 18 | 16 | -10 | 25 | 24 | -14 | 14 | 13 |
| 3 | 8 | 5 | -7 | 9 | 2 | 11 | 9 | 10 | -16 | 8 | 7 |
| -3 | 26 | 22 | 8 | 19 | 20 | -11 | 27 | 26 | 17 | 26 | 28 |
| 4 | 37 | 35 | -8 | 9 | 7 | 12 | 17 | 17 | -17 | 6 | 7 |
| -4 | 38 | 30 | -9 | 29 | 28 | -12 | 8 | 5 | -19 | 12 | 13 |
| 5 | 7 | 3 | 10 | 38 | 35 | 13 | 22 | 19 | H= | 2 K= | 8 |
| -5 | 78 | 82 | -10 | 25 | 22 | -13 | 20 | 21 | 0 | 27 | 23 |
| 6 | 43 | 34 | 11 | 27 | 27 | 14 | 31 | 29 | -1 | 21 | 19 |
| -6 | 45 | 49 | -11 | 6 | 7 | -14 | 7 | 7 | 2 | 25 | 27 |
| 7 | 64 | 62 | 12 | 39 | 39 | 15 | 22 | 22 | -2 | 54 | 56 |
| -7 | 72 | 74 | -12 | 20 | 21 | -15 | 31 | 30 | 3 | 47 | 51 |
| 8 | 67 | 69 | 13 | 25 | 24 | 16 | 6 | 7 | -3 | 18 | 17 |
| -8 | 75 | 80 | -13 | 21 | 21 | -16 | 17 | 15 | 4 | 27 | 26 |
| 9 | 41 | 44 | 14 | 28 | 28 | 17 | 5 | 3 | -4 | 38 | 36 |
| 10 | 27 | 29 | -14 | 50 | 51 | -17 | 25 | 24 | 5 | 28 | 29 |
| -10 | 18 | 20 | 15 | 9 | 9 | 18 | 9 | 9 | -5 | 44 | 44 |
| 11 | 64 | 67 | -15 | 14 | 14 | H= | 2 K= | 7 | 6 | 34 | 32 |
| -11 | 30 | 29 | 16 | 27 | 27 | 0 | 11 | 3 | -6 | 61 | 59 |
| 12 | 28 | 27 | 17 | 5 | 6 | 1 | 17 | 18 | 7 | 29 | 27 |
| -12 | 13 | 11 | -17 | 6 | 7 | -1 | 75 | 75 | -7 | 47 | 48 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 40 | 41 | -17 | 8 | 7 | 7 | 19 | 17 | 4 | 8 | 6 |
| -8 | 35 | 34 | -18 | 23 | 21 | -8 | 22 | 22 | -4 | 21 | 19 |
| 9 | 66 | 69 | H= | 2 K= | 10 | 9 | 16 | 15 | 5 | 49 | 47 |
| -9 | 13 | 13 | 0 | 48 | 47 | -9 | 25 | 25 | -5 | 27 | 25 |
| 10 | 47 | 50 | 1 | 20 | 19 | 11 | 17 | 15 | 6 | 10 | 11 |
| -10 | 33 | 33 | -1 | 54 | 61 | -11 | 7 | 7 | -6 | 26 | 26 |
| 11 | 18 | 18 | 2 | 13 | 12 | 12 | 14 | 16 | 7 | 34 | 35 |
| -11 | 53 | 54 | -2 | 15 | 16 | -12 | 14 | 14 | -7 | 44 | 43 |
| -12 | 41 | 41 | 3 | 24 | 22 | 13 | 15 | 16 | 8 | 7 | 6 |
| 13 | 9 | 8 | -3 | 37 | 39 | 14 | 7 | 8 | -8 | 6 | 5 |
| -13 | 30 | 29 | 4 | 23 | 22 | -14 | 7 | 7 | 9 | 13 | 13 |
| 14 | 7 | 9 | 5 | 39 | 39 | 15 | 23 | 23 | -9 | 34 | 33 |
| 15 | 31 | 32 | -5 | 40 | 38 | -15 | 8 | 7 | 10 | 20 | 21 |
| -15 | 10 | 9 | 6 | 9 | 8 | -16 | 9 | 7 | -10 | 7 | 4 |
| 16 | 6 | 8 | -6 | 20 | 19 | H= | 2 K= | 12 | 11 | 16 | 15 |
| -16 | 8 | 7 | 7 | 12 | 12 | 0 | 24 | 23 | -11 | 10 | 8 |
| 17 | 22 | 24 | -7 | 37 | 39 | 1 | 21 | 20 | 12 | 5 | 3 |
| H= | 2 K= | 9 | 8 | 33 | 33 | -1 | 35 | 37 | -12 | 9 | 10 |
| 0 | 67 | 70 | -8 | 16 | 16 | -2 | 10 | 7 | -13 | 15 | 14 |
| 1 | 38 | 38 | 9 | 65 | 68 | 3 | 56 | 57 | H= | 2 K= | 14 |
| -1 | 18 | 16 | -9 | 28 | 29 | -3 | 29 | 30 | 0 | 12 | 12 |
| 2 | 54 | 58 | 10 | 16 | 16 | 4 | 18 | 19 | 1 | 8 | 9 |
| 3 | 33 | 33 | 11 | 12 | 12 | 5 | 48 | 47 | -1 | 27 | 28 |
| -3 | 6 | 12 | -11 | 38 | 37 | -5 | 34 | 31 | 2 | 12 | 11 |
| 4 | 30 | 31 | 12 | 21 | 20 | 6 | 12 | 12 | 3 | 24 | 23 |
| 5 | 19 | 18 | -12 | 7 | 7 | 7 | 23 | 24 | 4 | 19 | 19 |
| -5 | 9 | 7 | -13 | 8 | 8 | -7 | 33 | 32 | -4 | 12 | 11 |
| -6 | 15 | 11 | 14 | 24 | 25 | -8 | 35 | 34 | 5 | 22 | 21 |
| 7 | 48 | 49 | 15 | 27 | 27 | 9 | 26 | 25 | -5 | 43 | 41 |
| -7 | 13 | 12 | -15 | 24 | 23 | -9 | 38 | 35 | 6 | 11 | 10 |
| 8 | 8 | 9 | -16 | 9 | 7 | -10 | 23 | 22 | -6 | 13 | 12 |
| -9 | 62 | 65 | -17 | 26 | 25 | 11 | 41 | 43 | 7 | 6 | 6 |
| 10 | 32 | 34 | H= | 2 K= | 11 | -11 | 44 | 43 | -7 | 28 | 26 |
| -10 | 30 | 32 | 0 | 13 | 11 | 12 | 8 | 8 | -8 | 18 | 17 |
| 11 | 12 | 12 | 1 | 71 | 71 | -12 | 14 | 12 | 9 | 17 | 16 |
| -11 | 27 | 25 | 2 | 21 | 20 | -13 | 23 | 21 | -9 | 6 | 5 |
| -12 | 14 | 14 | -2 | 37 | 37 | 14 | 8 | 8 | 10 | 13 | 12 |
| 13 | 9 | 6 | 3 | 67 | 68 | H= | 2 K= | 13 | 11 | 7 | 6 |
| -13 | 44 | 42 | -3 | 59 | 63 | 0 | 9 | 9 | -11 | 32 | 30 |
| 14 | 21 | 21 | 4 | 33 | 32 | 1 | 28 | 26 | -12 | 26 | 26 |
| -14 | 37 | 37 | 5 | 7 | 8 | -1 | 7 | 8 | H= | 2 K= | 15 |
| 15 | 15 | 15 | -5 | 50 | 51 | 2 | 22 | 24 | 1 | 27 | 26 |
| -15 | 23 | 22 | 6 | 36 | 37 | -2 | 6 | 3 | -1 | 23 | 22 |
| 16 | 28 | 29 | -6 | 24 | 24 | 3 | 30 | 32 | -2 | 27 | 25 |
| | | | | | | -3 | 22 | 21 | 3 | 30 | 29 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -3 | 18 | 18 | H= | 3 K= | 1 | 4 | 120 | 126 | 9 | 22 | 21 |
| 5 | 9 | 7 | 0 | 67 | 72 | -4 | 97 | 97 | -9 | 5 | 4 |
| -5 | 7 | 6 | -1 | 16 | 14 | 5 | 49 | 39 | 10 | 23 | 25 |
| 6 | 17 | 17 | 2 | 124 | 131 | -5 | 26 | 21 | -10 | 18 | 17 |
| 7 | 21 | 21 | -2 | 65 | 67 | 6 | 29 | 26 | 11 | 22 | 22 |
| 8 | 7 | 6 | 3 | 12 | 15 | -6 | 47 | 50 | -11 | 8 | 9 |
| -10 | 16 | 16 | -3 | 42 | 37 | 7 | 9 | 12 | 12 | 15 | 16 |
| -11 | 9 | 8 | -4 | 36 | 31 | -7 | 69 | 65 | -12 | 35 | 34 |
| H= | 2 K= | 16 | 5 | 44 | 43 | 8 | 16 | 18 | 13 | 36 | 35 |
| 0 | 10 | 10 | -5 | 86 | 78 | -8 | 35 | 32 | -13 | 12 | 11 |
| 1 | 28 | 26 | 6 | 38 | 38 | 9 | 32 | 30 | 14 | 15 | 15 |
| -1 | 28 | 26 | -6 | 35 | 33 | 10 | 22 | 20 | -14 | 48 | 48 |
| 2 | 8 | 7 | 7 | 53 | 47 | -10 | 16 | 13 | 15 | 6 | 4 |
| -2 | 21 | 20 | -7 | 66 | 58 | 11 | 37 | 35 | -15 | 31 | 32 |
| 3 | 17 | 17 | 8 | 34 | 30 | -11 | 11 | 10 | 16 | 32 | 33 |
| -3 | 19 | 17 | -8 | 53 | 51 | 12 | 46 | 46 | -16 | 10 | 11 |
| 4 | 23 | 22 | 9 | 7 | 9 | -12 | 45 | 42 | 17 | 13 | 13 |
| 5 | 29 | 28 | -9 | 61 | 56 | 13 | 26 | 26 | 18 | 12 | 13 |
| -5 | 12 | 10 | 10 | 28 | 28 | -13 | 5 | 3 | -18 | 14 | 15 |
| 6 | 25 | 25 | -10 | 58 | 53 | 14 | 45 | 45 | -19 | 13 | 13 |
| H= | 2 K= | 17 | 11 | 31 | 31 | -14 | 11 | 6 | -20 | 34 | 34 |
| 2 | 20 | 19 | 12 | 17 | 17 | 16 | 19 | 20 | H= | 3 K= | 4 |
| 3 | 7 | 6 | -12 | 22 | 22 | -16 | 34 | 33 | 0 | 71 | 70 |
| -3 | 12 | 9 | 13 | 23 | 24 | -17 | 10 | 11 | 1 | 28 | 26 |
| -4 | 18 | 17 | -13 | 12 | 12 | 18 | 20 | 21 | -1 | 67 | 66 |
| H= | 3 K= | 0 | 14 | 15 | 15 | -18 | 26 | 25 | -2 | 81 | 80 |
| 0 | 132 | 135 | -14 | 23 | 23 | H= | 3 K= | 3 | 3 | 30 | 28 |
| 2 | 143 | 150 | 15 | 17 | 16 | 0 | 56 | 57 | -3 | 85 | 89 |
| -2 | 51 | 45 | -15 | 8 | 11 | 1 | 25 | 19 | 4 | 118 | 127 |
| 4 | 87 | 77 | 16 | 20 | 23 | -1 | 50 | 48 | 5 | 65 | 64 |
| -4 | 48 | 40 | -16 | 24 | 23 | 2 | 79 | 72 | -5 | 53 | 51 |
| 6 | 30 | 34 | 17 | 19 | 20 | 3 | 27 | 26 | 6 | 11 | 7 |
| -6 | 84 | 87 | -17 | 11 | 11 | -3 | 75 | 69 | -6 | 41 | 38 |
| 8 | 124 | 127 | 18 | 14 | 14 | 4 | 4 | 6 | 7 | 35 | 33 |
| -8 | 32 | 34 | -18 | 6 | 7 | -4 | 105 | 111 | -7 | 31 | 33 |
| 10 | 100 | 105 | -20 | 8 | 7 | 5 | 28 | 25 | 8 | 73 | 70 |
| 12 | 37 | 34 | H= | 3 K= | 2 | -5 | 10 | 15 | -8 | 58 | 57 |
| -12 | 14 | 15 | 0 | 77 | 74 | 6 | 96 | 106 | 9 | 20 | 17 |
| 14 | 63 | 64 | 1 | 8 | 4 | -6 | 29 | 30 | -9 | 23 | 24 |
| -14 | 21 | 19 | 2 | 44 | 37 | 7 | 4 | 5 | 10 | 31 | 32 |
| 16 | 15 | 14 | -2 | 58 | 63 | -7 | 50 | 54 | -10 | 29 | 28 |
| -16 | 11 | 11 | 3 | 11 | 7 | 8 | 39 | 39 | 11 | 9 | 8 |
| -18 | 14 | 13 | -3 | 25 | 25 | -8 | 20 | 23 | -11 | 22 | 23 |
| | | | | | | | | | -12 | 52 | 57 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 9 | 8 | -17 | 12 | 11 | 5 | 9 | 10 | -14 | 33 | 34 |
| -13 | 14 | 14 | -18 | 21 | 20 | -5 | 47 | 50 | 15 | 8 | 8 |
| 14 | 41 | 42 | H= | 3 K= | 6 | -6 | 62 | 62 | -15 | 16 | 17 |
| -14 | 12 | 10 | 0 | 36 | 35 | 7 | 21 | 20 | -17 | 21 | 23 |
| 15 | 13 | 13 | 1 | 19 | 25 | 8 | 9 | 7 | -18 | 7 | 7 |
| -15 | 26 | 26 | 2 | 92 | 90 | 9 | 13 | 15 | H= | 3 K= | 9 |
| -16 | 10 | 10 | 3 | 80 | 85 | -9 | 40 | 40 | 0 | 35 | 35 |
| 17 | 5 | 6 | -3 | 22 | 23 | 10 | 22 | 23 | 1 | 64 | 67 |
| -17 | 15 | 16 | 4 | 23 | 23 | 11 | 27 | 27 | -1 | 8 | 7 |
| 18 | 17 | 18 | -4 | 14 | 17 | -11 | 35 | 35 | 2 | 7 | 5 |
| -19 | 6 | 6 | 5 | 39 | 38 | 12 | 20 | 21 | -2 | 7 | 8 |
| -20 | 7 | 6 | -5 | 54 | 53 | -12 | 21 | 20 | 3 | 43 | 45 |
| H= | 3 K= | 5 | 6 | 17 | 17 | 13 | 25 | 26 | -3 | 41 | 44 |
| 0 | 24 | 30 | -6 | 27 | 31 | -13 | 15 | 17 | 4 | 24 | 24 |
| 1 | 9 | 5 | 7 | 64 | 62 | -14 | 38 | 37 | -4 | 28 | 27 |
| -1 | 28 | 25 | -7 | 15 | 17 | -15 | 48 | 49 | 5 | 25 | 23 |
| 2 | 55 | 45 | 8 | 11 | 11 | 16 | 31 | 31 | -5 | 40 | 41 |
| -2 | 39 | 36 | -8 | 44 | 43 | 17 | 18 | 17 | 6 | 56 | 57 |
| 3 | 53 | 54 | 9 | 56 | 56 | -17 | 14 | 13 | -6 | 13 | 13 |
| -3 | 59 | 62 | -9 | 4 | 2 | -18 | 17 | 17 | 7 | 54 | 54 |
| 4 | 34 | 30 | 10 | 30 | 30 | H= | 3 K= | 8 | -7 | 12 | 13 |
| -4 | 70 | 73 | 11 | 52 | 53 | 0 | 34 | 34 | 8 | 7 | 6 |
| 5 | 46 | 44 | -11 | 57 | 59 | -1 | 88 | 91 | -8 | 28 | 27 |
| -5 | 6 | 6 | 12 | 6 | 6 | 2 | 39 | 38 | 9 | 9 | 8 |
| 6 | 43 | 44 | -12 | 20 | 19 | -2 | 22 | 25 | -9 | 18 | 17 |
| -6 | 19 | 18 | -13 | 49 | 50 | 3 | 33 | 34 | 10 | 8 | 9 |
| 7 | 64 | 61 | 14 | 15 | 13 | -3 | 28 | 32 | -10 | 65 | 68 |
| 8 | 29 | 28 | -14 | 10 | 9 | 4 | 9 | 10 | 11 | 32 | 32 |
| -8 | 60 | 61 | 15 | 32 | 33 | -4 | 20 | 17 | -11 | 13 | 10 |
| 9 | 10 | 8 | -15 | 15 | 15 | 5 | 59 | 63 | 12 | 22 | 24 |
| -9 | 45 | 45 | 16 | 14 | 15 | -5 | 19 | 15 | 13 | 19 | 20 |
| 10 | 20 | 18 | -16 | 16 | 15 | 6 | 18 | 17 | -13 | 13 | 13 |
| -10 | 75 | 77 | 17 | 14 | 13 | -6 | 9 | 11 | -14 | 11 | 11 |
| 11 | 12 | 12 | -17 | 11 | 9 | 7 | 25 | 26 | 15 | 17 | 16 |
| -11 | 15 | 16 | -18 | 9 | 8 | -7 | 50 | 51 | -15 | 10 | 10 |
| 12 | 48 | 49 | H= | 3 K= | 7 | 8 | 23 | 24 | -16 | 7 | 5 |
| -12 | 8 | 7 | 0 | 70 | 71 | -8 | 7 | 1 | H= | 3 K= | 10 |
| 13 | 33 | 33 | 1 | 67 | 64 | 9 | 13 | 14 | 0 | 17 | 16 |
| -14 | 19 | 18 | -1 | 59 | 60 | -9 | 27 | 29 | 1 | 6 | 4 |
| 15 | 5 | 6 | 2 | 54 | 55 | -10 | 34 | 37 | -1 | 51 | 52 |
| -15 | 15 | 13 | -2 | 42 | 44 | 12 | 19 | 20 | 2 | 7 | 6 |
| 16 | 30 | 32 | 3 | 19 | 20 | -12 | 7 | 6 | -2 | 15 | 15 |
| -16 | 12 | 12 | -3 | 28 | 31 | 13 | 26 | 25 | 3 | 30 | 29 |
| 17 | 20 | 20 | 4 | 19 | 17 | 14 | 35 | 37 | 4 | 21 | 20 |
| | | | -4 | 49 | 56 | | | | | | |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -4 | 6 | 2 | -16 | 10 | 10 | -13 | 7 | 6 | -5 | 11 | 10 |
| 5 | 27 | 28 | H= | 3 K= | 12 | H= | 3 K= | 14 | -6 | 15 | 15 |
| -5 | 29 | 27 | 0 | 21 | 21 | 0 | 12 | 13 | -7 | 31 | 30 |
| 6 | 26 | 26 | 1 | 10 | 12 | 1 | 32 | 30 | -8 | 16 | 14 |
| -6 | 26 | 25 | -1 | 38 | 38 | -1 | 34 | 35 | H= | 3 K= | 17 |
| 7 | 10 | 11 | 2 | 15 | 17 | -2 | 33 | 35 | 0 | 6 | 4 |
| -7 | 31 | 31 | -2 | 6 | 4 | 3 | 12 | 14 | -2 | 7 | 6 |
| 8 | 13 | 12 | 3 | 14 | 13 | -3 | 25 | 24 | -3 | 19 | 18 |
| 9 | 37 | 37 | -3 | 12 | 11 | -4 | 10 | 9 | H= | 4 K= | 0 |
| -9 | 17 | 18 | 4 | 13 | 12 | 5 | 25 | 25 | 0 | 40 | 39 |
| 10 | 8 | 8 | -4 | 7 | 8 | -5 | 13 | 9 | 2 | 18 | 15 |
| -10 | 15 | 15 | 5 | 19 | 19 | 6 | 27 | 27 | -2 | 82 | 77 |
| 11 | 16 | 17 | -5 | 45 | 45 | 7 | 16 | 14 | 4 | 118 | 121 |
| -11 | 61 | 58 | 6 | 25 | 24 | -7 | 20 | 20 | -4 | 76 | 77 |
| -12 | 7 | 6 | -6 | 8 | 7 | 8 | 7 | 7 | 6 | 30 | 30 |
| 13 | 14 | 14 | 7 | 5 | 8 | -8 | 8 | 7 | -6 | 60 | 66 |
| -13 | 22 | 22 | -7 | 38 | 36 | 9 | 22 | 21 | 8 | 23 | 20 |
| 14 | 6 | 6 | 9 | 30 | 30 | -9 | 9 | 9 | -8 | 22 | 26 |
| -14 | 7 | 7 | 10 | 15 | 16 | -10 | 14 | 14 | 10 | 55 | 55 |
| 15 | 17 | 18 | 11 | 6 | 6 | -12 | 17 | 16 | -10 | 13 | 11 |
| -15 | 25 | 25 | -11 | 6 | 5 | H= | 3 K= | 15 | 12 | 27 | 24 |
| -16 | 10 | 8 | 12 | 24 | 25 | 0 | 21 | 22 | -12 | 26 | 24 |
| H= | 3 K= | 11 | -12 | 12 | 12 | 1 | 10 | 11 | 14 | 39 | 39 |
| 0 | 10 | 10 | 13 | 15 | 14 | -1 | 10 | 9 | -14 | 42 | 41 |
| 1 | 17 | 17 | -13 | 24 | 23 | 2 | 16 | 16 | 16 | 7 | 9 |
| -1 | 15 | 18 | -14 | 19 | 17 | -2 | 20 | 21 | -16 | 17 | 18 |
| 2 | 11 | 10 | -15 | 9 | 12 | 3 | 16 | 15 | -18 | 32 | 31 |
| -2 | 6 | 5 | H= | 3 K= | 13 | 4 | 16 | 15 | H= | 4 K= | 1 |
| 3 | 24 | 23 | 0 | 9 | 10 | -4 | 7 | 7 | 0 | 69 | 70 |
| -3 | 29 | 28 | 1 | 40 | 39 | 5 | 32 | 31 | 1 | 29 | 27 |
| 4 | 18 | 19 | -1 | 36 | 39 | -5 | 15 | 14 | 2 | 47 | 46 |
| 5 | 61 | 62 | 2 | 22 | 25 | 6 | 5 | 5 | -2 | 17 | 20 |
| -5 | 24 | 25 | 3 | 57 | 58 | -6 | 7 | 6 | 3 | 35 | 30 |
| 7 | 44 | 44 | -3 | 45 | 46 | 7 | 27 | 27 | -3 | 32 | 31 |
| 9 | 15 | 15 | 4 | 9 | 10 | -7 | 11 | 9 | 4 | 5 | 3 |
| -9 | 33 | 30 | -4 | 21 | 19 | 8 | 12 | 12 | -4 | 83 | 83 |
| 10 | 21 | 21 | 5 | 19 | 18 | -8 | 6 | 5 | 5 | 61 | 54 |
| -10 | 9 | 7 | -5 | 12 | 12 | -9 | 44 | 41 | -5 | 89 | 88 |
| 11 | 37 | 38 | 6 | 12 | 12 | H= | 3 K= | 16 | 6 | 58 | 56 |
| -11 | 17 | 17 | -6 | 6 | 4 | 1 | 8 | 7 | -6 | 69 | 68 |
| 13 | 29 | 30 | 7 | 12 | 11 | -1 | 7 | 6 | 7 | 23 | 23 |
| -13 | 8 | 6 | 8 | 8 | 9 | 3 | 20 | 19 | -7 | 21 | 12 |
| 14 | 9 | 9 | 9 | 6 | 5 | -3 | 6 | 6 | 8 | 43 | 39 |
| -14 | 15 | 14 | 11 | 25 | 25 | 4 | 12 | 11 | -8 | 28 | 24 |
| -15 | 18 | 18 | -12 | 16 | 15 | 5 | 11 | 10 | -9 | 22 | 22 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 61 | 60 | -15 | 10 | 10 | 3 | 39 | 38 | -7 | 38 | 36 |
| -10 | 18 | 16 | 16 | 7 | 6 | -3 | 19 | 18 | 8 | 10 | 11 |
| 11 | 18 | 16 | 17 | 9 | 9 | 4 | 44 | 46 | -8 | 13 | 10 |
| -11 | 6 | 4 | -17 | 13 | 15 | -4 | 67 | 72 | 9 | 5 | 4 |
| 12 | 44 | 44 | -19 | 11 | 12 | 5 | 17 | 15 | -9 | 19 | 16 |
| -12 | 5 | 3 | -20 | 5 | 6 | -5 | 79 | 80 | 10 | 8 | 4 |
| -13 | 11 | 12 | H= | 4 K= | 3 | 6 | 15 | 17 | -10 | 6 | 5 |
| 14 | 10 | 10 | 0 | 47 | 46 | -6 | 5 | 4 | 11 | 25 | 25 |
| -14 | 10 | 10 | 1 | 34 | 29 | 7 | 40 | 39 | -11 | 9 | 8 |
| 15 | 15 | 14 | -1 | 12 | 8 | -7 | 77 | 78 | 12 | 7 | 6 |
| -15 | 6 | 6 | 2 | 21 | 16 | 8 | 36 | 35 | 13 | 7 | 7 |
| 16 | 15 | 15 | -2 | 31 | 32 | -8 | 14 | 12 | -13 | 25 | 26 |
| -16 | 10 | 9 | 3 | 49 | 45 | 9 | 63 | 63 | 14 | 26 | 27 |
| 17 | 11 | 13 | 4 | 63 | 60 | -9 | 18 | 19 | -14 | 15 | 16 |
| -17 | 10 | 9 | -4 | 43 | 41 | 10 | 14 | 13 | 15 | 7 | 6 |
| -18 | 9 | 10 | 5 | 31 | 29 | -10 | 27 | 27 | 16 | 28 | 28 |
| -19 | 13 | 14 | -5 | 37 | 36 | 11 | 22 | 22 | -17 | 16 | 15 |
| -20 | 19 | 19 | 6 | 59 | 58 | -11 | 27 | 27 | -18 | 34 | 34 |
| H= | 4 K= | 2 | -6 | 19 | 21 | 12 | 34 | 34 | -19 | 5 | 5 |
| 0 | 27 | 31 | 7 | 31 | 27 | -12 | 7 | 7 | -20 | 18 | 18 |
| 1 | 61 | 58 | 8 | 20 | 17 | 13 | 6 | 5 | H= | 4 K= | 6 |
| -1 | 54 | 50 | -8 | 39 | 41 | -13 | 8 | 7 | 0 | 30 | 31 |
| 2 | 40 | 39 | 9 | 10 | 7 | 14 | 33 | 34 | -1 | 59 | 58 |
| -2 | 63 | 67 | -9 | 72 | 75 | 15 | 24 | 25 | 2 | 47 | 49 |
| 3 | 41 | 36 | 10 | 56 | 55 | -15 | 16 | 15 | -2 | 46 | 49 |
| -3 | 65 | 62 | -10 | 76 | 76 | 16 | 17 | 19 | 3 | 34 | 32 |
| 4 | 58 | 59 | 11 | 57 | 57 | -16 | 14 | 15 | -3 | 33 | 38 |
| -4 | 23 | 22 | -11 | 11 | 9 | 17 | 22 | 23 | 4 | 76 | 76 |
| 5 | 61 | 59 | 12 | 18 | 19 | -17 | 19 | 17 | -4 | 12 | 16 |
| 6 | 23 | 23 | 13 | 15 | 15 | -18 | 23 | 22 | 5 | 35 | 35 |
| -6 | 93 | 95 | -13 | 13 | 12 | -20 | 6 | 7 | -5 | 12 | 14 |
| 7 | 8 | 6 | 14 | 14 | 11 | H= | 4 K= | 5 | 6 | 37 | 35 |
| -7 | 23 | 22 | -14 | 10 | 11 | 0 | 63 | 64 | -6 | 27 | 29 |
| 8 | 87 | 88 | -15 | 12 | 10 | 1 | 47 | 46 | 7 | 13 | 12 |
| -8 | 121 | 126 | 16 | 15 | 15 | -1 | 13 | 16 | -7 | 21 | 20 |
| 9 | 16 | 15 | -16 | 36 | 36 | 2 | 44 | 42 | 8 | 50 | 49 |
| -9 | 42 | 43 | -17 | 8 | 6 | -2 | 18 | 14 | -8 | 8 | 2 |
| 10 | 62 | 63 | -18 | 13 | 13 | -3 | 7 | 10 | 9 | 6 | 3 |
| -10 | 32 | 31 | -19 | 16 | 15 | 4 | 21 | 20 | -9 | 18 | 15 |
| -11 | 11 | 10 | H= | 4 K= | 4 | -4 | 75 | 77 | 10 | 30 | 30 |
| 12 | 16 | 17 | 0 | 11 | 12 | 5 | 13 | 11 | -10 | 34 | 33 |
| -12 | 27 | 25 | 1 | 9 | 9 | -5 | 43 | 42 | 11 | 17 | 19 |
| 14 | 32 | 32 | -1 | 24 | 25 | 6 | 48 | 48 | 12 | 24 | 25 |
| -14 | 38 | 36 | 2 | 34 | 32 | -6 | 14 | 13 | -12 | 23 | 22 |
| 15 | 7 | 4 | -2 | 56 | 61 | 7 | 48 | 47 | | | |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 11 | 11 | 2 | 7 | 8 | 11 | 18 | 18 | -3 | 9 | 8 |
| -13 | 15 | 15 | -2 | 26 | 26 | -11 | 38 | 37 | -4 | 18 | 19 |
| 14 | 6 | 6 | 3 | 40 | 40 | 12 | 13 | 12 | 5 | 10 | 10 |
| -14 | 9 | 7 | -3 | 6 | 5 | -12 | 31 | 30 | -5 | 56 | 60 |
| -15 | 6 | 6 | 4 | 37 | 37 | 13 | 42 | 43 | 6 | 26 | 26 |
| 16 | 7 | 8 | -4 | 10 | 9 | 14 | 18 | 18 | 7 | 38 | 37 |
| -16 | 27 | 26 | 5 | 13 | 14 | -14 | 24 | 24 | -7 | 11 | 11 |
| -17 | 20 | 20 | -5 | 14 | 16 | -15 | 22 | 21 | -8 | 19 | 17 |
| -19 | 13 | 13 | 6 | 30 | 30 | -16 | 9 | 7 | 9 | 9 | 6 |
| H= | 4 K= | 7 | -6 | 29 | 29 | H= | 4 K= | 10 | -9 | 12 | 11 |
| 1 | 59 | 60 | 7 | 36 | 37 | 0 | 18 | 18 | 10 | 34 | 36 |
| -1 | 33 | 28 | -7 | 26 | 26 | 1 | 10 | 9 | -10 | 18 | 16 |
| 2 | 19 | 19 | 8 | 15 | 14 | -1 | 33 | 32 | 11 | 14 | 13 |
| 3 | 29 | 28 | -8 | 28 | 28 | 2 | 38 | 38 | -11 | 20 | 20 |
| -3 | 30 | 30 | 9 | 43 | 44 | -2 | 51 | 52 | 12 | 5 | 5 |
| 4 | 27 | 28 | 10 | 9 | 10 | 3 | 33 | 34 | -12 | 16 | 17 |
| -4 | 33 | 34 | 11 | 19 | 19 | -3 | 42 | 41 | -13 | 31 | 30 |
| 5 | 43 | 42 | -11 | 11 | 13 | 4 | 19 | 19 | -15 | 22 | 21 |
| -5 | 19 | 20 | 12 | 14 | 14 | -4 | 8 | 9 | H= | 4 K= | 12 |
| 6 | 48 | 46 | 13 | 13 | 12 | 5 | 37 | 37 | 0 | 28 | 30 |
| -6 | 13 | 10 | -13 | 39 | 38 | 6 | 17 | 16 | 1 | 17 | 16 |
| 7 | 25 | 23 | 14 | 7 | 6 | -6 | 17 | 17 | -1 | 29 | 27 |
| -7 | 14 | 15 | -14 | 29 | 29 | 7 | 22 | 23 | 2 | 8 | 9 |
| 8 | 20 | 20 | 15 | 24 | 25 | -7 | 27 | 27 | -2 | 21 | 19 |
| -8 | 47 | 47 | -18 | 5 | 5 | 8 | 13 | 10 | 3 | 30 | 30 |
| 9 | 32 | 33 | H= | 4 K= | 9 | -8 | 11 | 9 | -3 | 17 | 16 |
| -9 | 19 | 21 | 0 | 34 | 34 | 9 | 8 | 8 | 4 | 12 | 12 |
| 10 | 38 | 38 | 1 | 11 | 11 | -9 | 14 | 13 | -4 | 11 | 9 |
| -10 | 40 | 40 | -1 | 9 | 10 | 10 | 10 | 9 | 5 | 6 | 5 |
| 11 | 25 | 25 | 2 | 20 | 17 | -10 | 32 | 31 | 6 | 10 | 7 |
| -11 | 33 | 33 | -2 | 28 | 27 | -11 | 7 | 7 | -6 | 17 | 14 |
| 12 | 19 | 20 | 3 | 20 | 20 | 12 | 21 | 21 | 7 | 10 | 9 |
| -12 | 25 | 26 | -3 | 16 | 16 | -12 | 8 | 9 | -7 | 20 | 20 |
| 13 | 24 | 24 | 4 | 27 | 27 | 13 | 33 | 34 | 8 | 6 | 8 |
| -13 | 20 | 20 | -4 | 25 | 25 | -13 | 20 | 20 | 9 | 39 | 39 |
| 14 | 10 | 10 | 5 | 67 | 69 | -14 | 19 | 18 | -9 | 19 | 20 |
| -14 | 20 | 20 | -5 | 24 | 25 | -15 | 9 | 8 | -10 | 10 | 10 |
| 15 | 18 | 19 | 6 | 35 | 35 | -16 | 9 | 8 | -11 | 20 | 19 |
| -17 | 11 | 12 | -6 | 21 | 20 | -17 | 12 | 11 | -12 | 9 | 7 |
| -19 | 8 | 9 | 7 | 46 | 45 | H= | 4 K= | 11 | -13 | 12 | 10 |
| H= | 4 K= | 8 | -7 | 14 | 14 | 0 | 15 | 14 | -14 | 15 | 13 |
| 0 | 6 | 2 | 8 | 19 | 20 | 1 | 67 | 68 | H= | 4 K= | 13 |
| 1 | 6 | 5 | -9 | 19 | 19 | -1 | 24 | 24 | 0 | 17 | 17 |
| -1 | 36 | 34 | 10 | 6 | 4 | -2 | 5 | 6 | 1 | 25 | 25 |
| | | | -10 | 18 | 19 | 3 | 38 | 37 | | | |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -1 | 5 | 5 | -2 | 21 | 19 | -15 | 7 | 9 | -3 | 12 | 9 |
| 2 | 18 | 18 | 3 | 17 | 16 | 16 | 26 | 26 | 4 | 33 | 32 |
| -3 | 18 | 19 | -3 | 19 | 19 | -17 | 10 | 11 | -4 | 15 | 16 |
| 5 | 12 | 10 | -4 | 18 | 18 | -18 | 9 | 9 | -5 | 9 | 9 |
| -5 | 21 | 21 | -5 | 12 | 11 | -19 | 8 | 8 | 6 | 38 | 37 |
| 7 | 38 | 37 | H= | 5 K= | 0 | -20 | 7 | 8 | -6 | 62 | 64 |
| 8 | 9 | 10 | 0 | 15 | 14 | H= | 5 K= | 2 | 7 | 45 | 45 |
| -9 | 33 | 31 | 2 | 26 | 12 | 0 | 56 | 49 | -7 | 36 | 37 |
| 10 | 6 | 6 | -2 | 109 | 101 | 1 | 15 | 12 | 8 | 16 | 15 |
| -10 | 7 | 8 | -4 | 12 | 5 | -1 | 9 | 6 | -8 | 35 | 32 |
| -11 | 28 | 26 | 6 | 54 | 52 | 2 | 50 | 47 | 9 | 9 | 10 |
| -12 | 8 | 7 | -6 | 47 | 42 | -2 | 58 | 59 | -9 | 8 | 8 |
| H= | 4 K= | 14 | 8 | 51 | 51 | 3 | 10 | 6 | 10 | 29 | 29 |
| 0 | 11 | 10 | -8 | 49 | 46 | -3 | 4 | 4 | -10 | 9 | 8 |
| 1 | 19 | 18 | -10 | 19 | 17 | 4 | 66 | 64 | 11 | 10 | 9 |
| -1 | 5 | 3 | 12 | 37 | 37 | -4 | 57 | 58 | -11 | 6 | 6 |
| 2 | 13 | 14 | -12 | 58 | 58 | 5 | 15 | 13 | 12 | 24 | 23 |
| -2 | 5 | 4 | 14 | 24 | 24 | -5 | 24 | 24 | -12 | 6 | 4 |
| 3 | 17 | 17 | -14 | 8 | 5 | 6 | 36 | 33 | -13 | 6 | 5 |
| -3 | 9 | 9 | H= | 5 K= | 1 | -6 | 5 | 2 | 14 | 19 | 18 |
| -4 | 18 | 18 | 0 | 98 | 95 | 7 | 38 | 36 | -14 | 13 | 15 |
| 5 | 17 | 17 | 1 | 6 | 5 | -7 | 59 | 55 | 15 | 15 | 15 |
| -5 | 10 | 11 | 2 | 24 | 19 | 8 | 23 | 25 | 16 | 24 | 25 |
| 7 | 10 | 10 | -2 | 9 | 3 | -8 | 16 | 13 | -18 | 7 | 8 |
| -7 | 15 | 13 | 3 | 10 | 15 | 9 | 29 | 27 | -19 | 7 | 7 |
| 8 | 7 | 5 | -3 | 23 | 23 | 10 | 12 | 11 | H= | 5 K= | 4 |
| -8 | 12 | 12 | 4 | 58 | 55 | 11 | 30 | 29 | 0 | 12 | 11 |
| -10 | 5 | 5 | -4 | 38 | 36 | -11 | 7 | 6 | -1 | 24 | 23 |
| -11 | 19 | 19 | 5 | 14 | 15 | 12 | 8 | 8 | 2 | 78 | 78 |
| H= | 4 K= | 15 | -5 | 7 | 8 | -12 | 18 | 18 | -2 | 20 | 18 |
| 0 | 13 | 12 | 6 | 62 | 59 | 13 | 6 | 5 | 3 | 53 | 49 |
| 1 | 41 | 40 | -6 | 12 | 11 | -13 | 15 | 16 | -3 | 40 | 37 |
| -1 | 17 | 16 | 7 | 5 | 4 | 14 | 32 | 32 | 4 | 31 | 30 |
| -2 | 5 | 6 | -7 | 4 | 4 | -14 | 6 | 3 | -4 | 13 | 15 |
| 3 | 11 | 10 | -9 | 18 | 18 | 15 | 15 | 15 | 5 | 53 | 50 |
| -3 | 10 | 14 | 10 | 50 | 49 | 16 | 9 | 9 | -5 | 23 | 23 |
| 4 | 5 | 6 | -10 | 38 | 38 | -16 | 18 | 17 | 6 | 36 | 35 |
| -4 | 24 | 23 | 11 | 17 | 15 | -18 | 18 | 18 | -6 | 60 | 61 |
| 5 | 11 | 11 | -11 | 39 | 36 | -19 | 6 | 7 | 7 | 11 | 12 |
| -5 | 30 | 31 | 12 | 19 | 20 | -20 | 8 | 6 | -7 | 38 | 37 |
| -9 | 4 | 2 | -12 | 12 | 11 | H= | 5 K= | 3 | 8 | 11 | 8 |
| H= | 4 K= | 16 | -13 | 11 | 12 | 0 | 91 | 93 | -8 | 53 | 55 |
| 0 | 7 | 6 | 14 | 13 | 13 | 1 | 13 | 13 | 9 | 23 | 20 |
| -1 | 19 | 19 | -14 | 14 | 15 | 2 | 64 | 60 | -9 | 5 | 1 |
| 2 | 15 | 13 | 15 | 10 | 10 | 3 | 14 | 14 | 10 | 34 | 36 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 31 | 33 | -19 | 5 | 5 | 7 | 35 | 35 | -1 | 51 | 53 |
| -11 | 8 | 9 | H= | 5 K= | 6 | -7 | 10 | 12 | 2 | 32 | 31 |
| 12 | 17 | 19 | 0 | 24 | 22 | 8 | 15 | 14 | -2 | 35 | 35 |
| -12 | 36 | 36 | 1 | 34 | 35 | -8 | 25 | 23 | 3 | 8 | 8 |
| 13 | 17 | 17 | -1 | 10 | 9 | 9 | 9 | 10 | -3 | 8 | 10 |
| -13 | 11 | 10 | 2 | 20 | 20 | -9 | 10 | 8 | 4 | 18 | 20 |
| 14 | 24 | 25 | -2 | 49 | 49 | 11 | 24 | 24 | 5 | 34 | 34 |
| -14 | 30 | 29 | 3 | 29 | 29 | -11 | 24 | 24 | -5 | 39 | 40 |
| 15 | 4 | 5 | 4 | 8 | 7 | 12 | 21 | 22 | 6 | 10 | 9 |
| -16 | 11 | 13 | -4 | 13 | 12 | -12 | 20 | 20 | 7 | 16 | 14 |
| -17 | 23 | 22 | 5 | 19 | 20 | -13 | 16 | 17 | -7 | 11 | 12 |
| -18 | 8 | 8 | -5 | 10 | 7 | 14 | 35 | 38 | 8 | 22 | 21 |
| -19 | 11 | 10 | 6 | 6 | 7 | -14 | 14 | 14 | -8 | 28 | 28 |
| H= | 5 K= | 5 | -6 | 33 | 33 | -17 | 19 | 20 | 9 | 19 | 18 |
| 0 | 48 | 48 | 7 | 48 | 46 | -18 | 8 | 8 | -9 | 19 | 19 |
| 1 | 54 | 52 | -7 | 37 | 39 | H= | 5 K= | 8 | 10 | 34 | 33 |
| -1 | 31 | 31 | 8 | 50 | 51 | 1 | 5 | 6 | -10 | 28 | 27 |
| 2 | 7 | 7 | -8 | 32 | 30 | -1 | 38 | 40 | 11 | 24 | 25 |
| -2 | 13 | 15 | 9 | 52 | 52 | 2 | 44 | 47 | -11 | 17 | 16 |
| 3 | 22 | 19 | -9 | 13 | 14 | -2 | 8 | 7 | 12 | 20 | 21 |
| -3 | 16 | 14 | 10 | 38 | 39 | 3 | 45 | 45 | -12 | 13 | 13 |
| 4 | 48 | 48 | 11 | 27 | 27 | -3 | 68 | 70 | -13 | 27 | 26 |
| -4 | 33 | 32 | -11 | 19 | 19 | 4 | 37 | 36 | -14 | 16 | 15 |
| 5 | 34 | 35 | 12 | 17 | 18 | -4 | 19 | 20 | -15 | 29 | 26 |
| -5 | 48 | 48 | -12 | 7 | 7 | 5 | 20 | 21 | -16 | 14 | 14 |
| 6 | 36 | 35 | 13 | 28 | 28 | -5 | 18 | 20 | H= | 5 K= | 10 |
| -6 | 9 | 9 | -13 | 15 | 14 | 6 | 11 | 12 | 0 | 13 | 11 |
| -7 | 26 | 23 | 14 | 40 | 41 | -6 | 5 | 3 | 1 | 20 | 21 |
| -8 | 22 | 24 | -14 | 24 | 22 | 8 | 15 | 18 | 2 | 10 | 12 |
| -9 | 38 | 39 | -15 | 16 | 14 | -8 | 12 | 13 | -2 | 9 | 9 |
| 10 | 42 | 42 | -17 | 10 | 9 | 9 | 17 | 18 | 3 | 42 | 42 |
| -10 | 42 | 43 | -18 | 8 | 8 | -9 | 8 | 4 | -3 | 16 | 12 |
| 11 | 39 | 39 | H= | 5 K= | 7 | 10 | 8 | 9 | 4 | 19 | 17 |
| -11 | 28 | 29 | 0 | 47 | 48 | -10 | 13 | 13 | -4 | 22 | 20 |
| 12 | 48 | 49 | 1 | 31 | 30 | 11 | 14 | 12 | 5 | 9 | 10 |
| -12 | 40 | 39 | -1 | 16 | 16 | -11 | 8 | 7 | -5 | 21 | 22 |
| 13 | 7 | 6 | 2 | 21 | 23 | 12 | 15 | 15 | 6 | 25 | 25 |
| -13 | 8 | 9 | -2 | 35 | 34 | -12 | 6 | 6 | -6 | 10 | 9 |
| 14 | 8 | 8 | 3 | 22 | 20 | 13 | 20 | 19 | 7 | 24 | 24 |
| -14 | 18 | 18 | -3 | 17 | 16 | -15 | 6 | 3 | -7 | 43 | 45 |
| 15 | 7 | 7 | 4 | 21 | 21 | -16 | 10 | 10 | 8 | 22 | 23 |
| -15 | 23 | 23 | -4 | 24 | 24 | -17 | 22 | 23 | -8 | 6 | 4 |
| -16 | 8 | 6 | 5 | 19 | 18 | H= | 5 K= | 9 | 9 | 29 | 29 |
| -17 | 17 | 16 | -5 | 29 | 30 | 0 | 22 | 21 | -9 | 37 | 37 |
| -18 | 10 | 9 | 6 | 13 | 13 | 1 | 43 | 45 | 10 | 6 | 6 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -11 | 8 | 10 | -13 | 5 | 4 | -10 | 12 | 13 | -6 | 32 | 33 |
| 12 | 15 | 17 | -14 | 5 | 6 | 12 | 12 | 12 | 7 | 13 | 13 |
| -12 | 14 | 12 | H= | 5 K= | 13 | -12 | 10 | 12 | -7 | 13 | 12 |
| -13 | 17 | 16 | 0 | 12 | 12 | 14 | 7 | 7 | 8 | 51 | 50 |
| -14 | 16 | 14 | 1 | 28 | 27 | H= | 6 K= | 1 | -8 | 56 | 55 |
| -15 | 5 | 2 | -1 | 16 | 17 | 0 | 48 | 48 | 9 | 27 | 27 |
| -16 | 7 | 6 | 3 | 8 | 7 | 1 | 45 | 39 | -9 | 13 | 12 |
| H= | 5 K= | 11 | 4 | 6 | 6 | -1 | 11 | 11 | -10 | 35 | 34 |
| 0 | 8 | 7 | 5 | 26 | 26 | 2 | 48 | 44 | -11 | 9 | 11 |
| -1 | 14 | 16 | -5 | 31 | 30 | 3 | 26 | 25 | 12 | 19 | 20 |
| 2 | 12 | 10 | 6 | 9 | 8 | -3 | 22 | 20 | -12 | 24 | 24 |
| -2 | 9 | 10 | -6 | 16 | 15 | 4 | 49 | 45 | 13 | 9 | 8 |
| -3 | 10 | 8 | 7 | 16 | 16 | -4 | 24 | 24 | -13 | 8 | 8 |
| 4 | 10 | 8 | -7 | 5 | 4 | 5 | 15 | 12 | 14 | 25 | 26 |
| 5 | 27 | 27 | -8 | 9 | 9 | -5 | 13 | 15 | -16 | 6 | 3 |
| -5 | 19 | 18 | -9 | 19 | 18 | 6 | 46 | 44 | -17 | 5 | 6 |
| 6 | 13 | 12 | -10 | 5 | 5 | -6 | 39 | 38 | H= | 6 K= | 3 |
| 7 | 15 | 16 | -12 | 4 | 3 | 7 | 23 | 20 | 0 | 7 | 6 |
| -7 | 9 | 9 | H= | 5 K= | 14 | -7 | 7 | 5 | 1 | 8 | 5 |
| -8 | 6 | 7 | 0 | 10 | 10 | -8 | 9 | 8 | -1 | 10 | 11 |
| 9 | 11 | 11 | 1 | 9 | 9 | 9 | 17 | 18 | 2 | 9 | 10 |
| -9 | 22 | 22 | -1 | 19 | 20 | 10 | 34 | 34 | -2 | 12 | 10 |
| 10 | 8 | 8 | 3 | 26 | 27 | -10 | 32 | 31 | 3 | 7 | 4 |
| 11 | 32 | 33 | -3 | 28 | 27 | -11 | 30 | 31 | 4 | 53 | 50 |
| -11 | 8 | 6 | 4 | 10 | 10 | 12 | 7 | 6 | -4 | 14 | 16 |
| -12 | 5 | 5 | -4 | 35 | 35 | -12 | 8 | 7 | -5 | 33 | 33 |
| -13 | 15 | 13 | 6 | 5 | 5 | 13 | 15 | 14 | 6 | 48 | 48 |
| -15 | 8 | 8 | -6 | 12 | 11 | -13 | 21 | 21 | -6 | 8 | 6 |
| H= | 5 K= | 12 | -7 | 11 | 11 | 14 | 18 | 19 | -7 | 20 | 20 |
| 0 | 13 | 12 | -8 | 5 | 4 | -15 | 7 | 7 | 8 | 20 | 21 |
| -1 | 8 | 7 | -9 | 16 | 15 | -16 | 19 | 19 | -8 | 24 | 22 |
| 2 | 6 | 5 | H= | 5 K= | 15 | -18 | 11 | 10 | 9 | 6 | 4 |
| -2 | 28 | 27 | 0 | 11 | 10 | -19 | 6 | 5 | -9 | 22 | 21 |
| 3 | 22 | 21 | 1 | 6 | 5 | H= | 6 K= | 2 | 10 | 46 | 47 |
| -3 | 30 | 31 | 2 | 12 | 12 | 0 | 22 | 22 | -10 | 49 | 51 |
| -4 | 12 | 13 | -2 | 11 | 11 | 1 | 10 | 10 | 11 | 16 | 16 |
| -5 | 8 | 10 | -3 | 24 | 24 | -1 | 17 | 18 | -11 | 39 | 40 |
| 6 | 8 | 8 | -4 | 9 | 10 | 2 | 27 | 26 | 12 | 19 | 19 |
| -6 | 8 | 6 | -6 | 12 | 12 | -2 | 26 | 26 | -12 | 25 | 24 |
| 7 | 19 | 19 | H= | 6 K= | 0 | 3 | 21 | 19 | 13 | 19 | 18 |
| -7 | 18 | 18 | 4 | 58 | 56 | 4 | 20 | 18 | -16 | 7 | 7 |
| 8 | 8 | 9 | -4 | 71 | 66 | -4 | 35 | 34 | -18 | 10 | 9 |
| -8 | 11 | 12 | 8 | 54 | 53 | 5 | 21 | 21 | H= | 6 K= | 4 |
| 9 | 18 | 17 | -8 | 29 | 27 | -5 | 24 | 25 | 1 | 18 | 18 |
| -11 | 12 | 12 | 10 | 8 | 8 | 6 | 49 | 48 | -1 | 5 | 1 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 25 | 25 | -12 | 9 | 10 | 7 | 15 | 14 | 7 | 6 | 6 |
| -2 | 30 | 32 | 13 | 10 | 10 | -7 | 24 | 25 | -7 | 9 | 8 |
| 3 | 6 | 6 | -13 | 11 | 10 | 8 | 6 | 7 | -8 | 11 | 13 |
| 4 | 51 | 49 | -16 | 7 | 7 | -9 | 8 | 6 | 9 | 29 | 29 |
| -4 | 31 | 33 | -17 | 7 | 7 | 10 | 32 | 31 | -9 | 23 | 21 |
| 5 | 7 | 6 | -18 | 5 | 6 | -10 | 22 | 22 | -10 | 12 | 11 |
| 6 | 30 | 28 | H= | 6 K= | 6 | 11 | 16 | 17 | 11 | 34 | 33 |
| -6 | 5 | 6 | 0 | 12 | 12 | 12 | 22 | 23 | -11 | 26 | 25 |
| 7 | 53 | 53 | 1 | 10 | 9 | -12 | 9 | 8 | -12 | 9 | 10 |
| -7 | 31 | 32 | -1 | 6 | 7 | -14 | 7 | 7 | -13 | 18 | 16 |
| 8 | 13 | 14 | 2 | 44 | 44 | H= | 6 K= | 8 | H= | 6 K= | 10 |
| 9 | 23 | 24 | -2 | 13 | 13 | 0 | 48 | 48 | 0 | 7 | 5 |
| -9 | 41 | 43 | 3 | 29 | 28 | 1 | 57 | 60 | 1 | 8 | 8 |
| -10 | 18 | 19 | -3 | 43 | 45 | 3 | 28 | 27 | -1 | 40 | 41 |
| -11 | 18 | 19 | 4 | 6 | 3 | -3 | 9 | 10 | -2 | 7 | 8 |
| 12 | 11 | 12 | -4 | 11 | 9 | 5 | 6 | 5 | 3 | 46 | 44 |
| -12 | 5 | 4 | -5 | 11 | 10 | -5 | 14 | 15 | -3 | 38 | 40 |
| 13 | 13 | 14 | 6 | 12 | 14 | 6 | 18 | 17 | 4 | 25 | 23 |
| -13 | 23 | 24 | -6 | 18 | 19 | -6 | 18 | 20 | -4 | 26 | 26 |
| 14 | 12 | 12 | 7 | 14 | 13 | 7 | 31 | 31 | -5 | 43 | 44 |
| -17 | 11 | 11 | -7 | 18 | 15 | -7 | 22 | 22 | 7 | 15 | 15 |
| -19 | 5 | 4 | -8 | 20 | 21 | 8 | 10 | 11 | -8 | 15 | 16 |
| H= | 6 K= | 5 | -9 | 10 | 10 | -8 | 15 | 14 | 9 | 11 | 11 |
| 0 | 50 | 49 | 10 | 12 | 11 | 9 | 23 | 24 | -9 | 9 | 9 |
| 1 | 20 | 21 | -10 | 8 | 7 | -9 | 13 | 13 | 10 | 16 | 16 |
| -1 | 38 | 38 | 11 | 18 | 18 | 10 | 6 | 6 | -11 | 9 | 8 |
| 2 | 29 | 27 | 12 | 16 | 16 | -10 | 9 | 11 | -12 | 16 | 15 |
| -2 | 32 | 31 | -12 | 21 | 20 | 11 | 7 | 6 | -13 | 5 | 4 |
| 3 | 5 | 4 | 13 | 20 | 19 | -12 | 8 | 8 | H= | 6 K= | 11 |
| -3 | 19 | 19 | -14 | 23 | 21 | -13 | 23 | 23 | 1 | 25 | 25 |
| 4 | 18 | 17 | -17 | 12 | 13 | -15 | 29 | 29 | -1 | 36 | 37 |
| -4 | 26 | 30 | -18 | 21 | 21 | -17 | 11 | 11 | 2 | 10 | 10 |
| 5 | 47 | 46 | H= | 6 K= | 7 | H= | 6 K= | 9 | -2 | 11 | 11 |
| 6 | 5 | 3 | 0 | 29 | 31 | 0 | 33 | 33 | 3 | 5 | 5 |
| -6 | 47 | 48 | -1 | 33 | 33 | 1 | 21 | 21 | -3 | 6 | 5 |
| 7 | 29 | 29 | 2 | 42 | 42 | -1 | 13 | 10 | 4 | 8 | 7 |
| -7 | 8 | 10 | -2 | 12 | 11 | 2 | 40 | 38 | -4 | 9 | 9 |
| -8 | 34 | 33 | 3 | 14 | 16 | -2 | 37 | 39 | 5 | 24 | 24 |
| 9 | 10 | 8 | -3 | 11 | 10 | 3 | 29 | 28 | -5 | 5 | 5 |
| -9 | 31 | 31 | 4 | 47 | 46 | -3 | 25 | 24 | -6 | 14 | 14 |
| 10 | 24 | 25 | -4 | 5 | 4 | 4 | 12 | 11 | 7 | 11 | 10 |
| -10 | 9 | 8 | 5 | 5 | 5 | 5 | 17 | 18 | -7 | 6 | 6 |
| 11 | 7 | 6 | -5 | 28 | 29 | -5 | 26 | 26 | 8 | 16 | 16 |
| -11 | 13 | 13 | 6 | 22 | 21 | 6 | 8 | 8 | -9 | 8 | 8 |
| 12 | 22 | 23 | -6 | 20 | 20 | -6 | 23 | 23 | -10 | 6 | 5 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -13 | 5 | 4 | 12 | 40 | 40 | -12 | 8 | 9 | 8 | 40 | 40 |
| H= | 6 K= | 12 | -12 | 22 | 20 | -13 | 7 | 7 | -8 | 15 | 17 |
| 0 | 6 | 4 | -14 | 22 | 22 | -15 | 14 | 15 | 9 | 5 | 3 |
| 1 | 21 | 22 | -18 | 10 | 10 | -16 | 13 | 15 | -9 | 12 | 13 |
| -1 | 16 | 15 | H= | 7 K= | 1 | -18 | 15 | 15 | -10 | 20 | 21 |
| 2 | 14 | 14 | 0 | 15 | 14 | H= | 7 K= | 3 | -11 | 7 | 7 |
| -2 | 12 | 12 | 1 | 29 | 26 | 0 | 63 | 62 | -11 | 7 | 7 |
| 3 | 20 | 19 | -1 | 30 | 29 | 1 | 31 | 30 | 12 | 23 | 23 |
| -3 | 20 | 19 | 3 | 26 | 26 | -1 | 26 | 27 | -14 | 17 | 18 |
| -4 | 12 | 13 | -3 | 10 | 13 | 2 | 14 | 11 | -16 | 9 | 7 |
| 5 | 14 | 15 | 4 | 32 | 31 | -2 | 22 | 21 | H= | 7 K= | 5 |
| 6 | 14 | 13 | -4 | 14 | 15 | -3 | 19 | 19 | 0 | 27 | 28 |
| -6 | 19 | 19 | -5 | 32 | 32 | 4 | 7 | 6 | -1 | 6 | 6 |
| 7 | 23 | 24 | 6 | 15 | 14 | -4 | 19 | 19 | 2 | 31 | 32 |
| -7 | 21 | 20 | -6 | 31 | 31 | 5 | 30 | 31 | -2 | 27 | 25 |
| -9 | 19 | 18 | 7 | 12 | 12 | -5 | 10 | 9 | 3 | 42 | 42 |
| -11 | 7 | 6 | 8 | 21 | 21 | 6 | 6 | 8 | 4 | 20 | 20 |
| H= | 6 K= | 13 | -8 | 9 | 8 | -6 | 32 | 33 | -4 | 18 | 18 |
| 0 | 14 | 15 | 9 | 17 | 17 | 7 | 26 | 26 | -5 | 18 | 17 |
| -1 | 8 | 9 | -9 | 5 | 6 | -7 | 8 | 8 | 6 | 37 | 37 |
| -2 | 7 | 7 | 10 | 29 | 28 | -8 | 24 | 23 | -6 | 13 | 14 |
| -3 | 21 | 21 | 11 | 14 | 14 | -9 | 11 | 11 | 7 | 10 | 9 |
| -4 | 10 | 8 | -11 | 9 | 7 | 10 | 24 | 24 | -7 | 8 | 8 |
| 5 | 21 | 22 | 12 | 8 | 8 | -10 | 14 | 16 | 8 | 10 | 8 |
| -5 | 27 | 26 | -12 | 27 | 26 | 11 | 5 | 4 | 9 | 27 | 26 |
| -7 | 8 | 7 | -13 | 26 | 24 | -11 | 34 | 35 | -9 | 9 | 7 |
| -8 | 20 | 19 | -16 | 12 | 13 | -12 | 7 | 8 | 10 | 38 | 38 |
| H= | 6 K= | 14 | H= | 7 K= | 2 | -13 | 20 | 19 | -10 | 23 | 23 |
| 2 | 6 | 5 | 0 | 32 | 33 | -16 | 10 | 10 | 11 | 15 | 16 |
| -2 | 8 | 7 | 1 | 5 | 5 | -17 | 7 | 7 | -12 | 15 | 14 |
| -3 | 19 | 18 | 2 | 51 | 50 | H= | 7 K= | 4 | -14 | 10 | 8 |
| -4 | 13 | 12 | -2 | 45 | 44 | 0 | 15 | 14 | -16 | 9 | 9 |
| -5 | 4 | 3 | 4 | 33 | 33 | 1 | 11 | 10 | H= | 7 K= | 6 |
| -6 | 15 | 15 | -4 | 36 | 37 | -1 | 27 | 27 | 0 | 8 | 8 |
| -7 | 19 | 18 | 5 | 5 | 5 | 2 | 10 | 12 | 1 | 9 | 10 |
| H= | 7 K= | 0 | -5 | 13 | 12 | -2 | 6 | 8 | -1 | 18 | 18 |
| 0 | 29 | 28 | 6 | 29 | 29 | 3 | 40 | 38 | -2 | 27 | 26 |
| 2 | 24 | 10 | -6 | 19 | 16 | -3 | 27 | 26 | 3 | 19 | 18 |
| 4 | 15 | 17 | 7 | 8 | 6 | 4 | 26 | 25 | -3 | 27 | 27 |
| -4 | 27 | 25 | -7 | 27 | 27 | -4 | 12 | 11 | 4 | 22 | 22 |
| 6 | 32 | 32 | 8 | 13 | 12 | -5 | 25 | 25 | -4 | 25 | 26 |
| -6 | 22 | 19 | 9 | 8 | 8 | 6 | 17 | 16 | 6 | 25 | 25 |
| 8 | 18 | 18 | -10 | 14 | 16 | -6 | 20 | 19 | -6 | 10 | 12 |
| -8 | 24 | 24 | 11 | 7 | 6 | -7 | 9 | 7 | 7 | 20 | 20 |
| -10 | 21 | 19 | 12 | 16 | 19 | | | | -7 | 18 | 18 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 13 | 13 | 9 | 10 | 10 | H= | 7 K= | 12 | -13 | 18 | 20 |
| -8 | 13 | 12 | -9 | 15 | 15 | 0 | 5 | 6 | -15 | 15 | 16 |
| 9 | 27 | 27 | -11 | 13 | 13 | 1 | 15 | 14 | -17 | 8 | 9 |
| -9 | 35 | 37 | -14 | 11 | 11 | 2 | 10 | 10 | H= | 8 K= | 2 |
| 10 | 13 | 14 | -15 | 6 | 6 | 3 | 14 | 14 | 0 | 8 | 5 |
| -10 | 10 | 8 | H= | 7 K= | 9 | -3 | 8 | 8 | 1 | 9 | 10 |
| 11 | 17 | 17 | 0 | 11 | 7 | -5 | 8 | 8 | -1 | 12 | 8 |
| -11 | 9 | 9 | 1 | 13 | 11 | -6 | 7 | 7 | 2 | 16 | 16 |
| -13 | 12 | 13 | -1 | 38 | 38 | -8 | 13 | 13 | 3 | 13 | 13 |
| -15 | 24 | 24 | 2 | 19 | 19 | -9 | 12 | 11 | -3 | 7 | 5 |
| -16 | 6 | 7 | -3 | 27 | 27 | H= | 7 K= | 13 | 4 | 15 | 16 |
| -17 | 8 | 7 | 4 | 19 | 18 | -1 | 22 | 21 | -4 | 14 | 14 |
| H= | 7 K= | 7 | -4 | 11 | 11 | -3 | 17 | 16 | 6 | 33 | 34 |
| 0 | 30 | 30 | 5 | 15 | 14 | -4 | 11 | 11 | -7 | 7 | 8 |
| -1 | 28 | 28 | 7 | 11 | 11 | -6 | 5 | 5 | 8 | 17 | 17 |
| -2 | 19 | 21 | -7 | 22 | 22 | H= | 8 K= | 0 | -8 | 12 | 12 |
| 3 | 14 | 13 | 8 | 13 | 12 | 0 | 21 | 18 | 9 | 13 | 12 |
| 4 | 15 | 14 | -9 | 8 | 6 | -2 | 25 | 24 | -9 | 19 | 21 |
| 5 | 16 | 16 | -10 | 8 | 8 | 4 | 8 | 5 | 10 | 7 | 8 |
| -5 | 17 | 20 | H= | 7 K= | 10 | -4 | 17 | 16 | -10 | 20 | 18 |
| 6 | 19 | 19 | -1 | 10 | 10 | 6 | 12 | 13 | -11 | 8 | 7 |
| -6 | 7 | 8 | 3 | 9 | 8 | -6 | 9 | 7 | -14 | 20 | 21 |
| 7 | 7 | 7 | 4 | 16 | 16 | 8 | 8 | 7 | -16 | 15 | 15 |
| 8 | 8 | 9 | -4 | 14 | 15 | 10 | 14 | 15 | H= | 8 K= | 3 |
| -8 | 9 | 10 | 5 | 9 | 11 | -12 | 24 | 25 | 0 | 8 | 7 |
| 9 | 24 | 23 | 6 | 16 | 17 | -14 | 5 | 5 | 1 | 18 | 17 |
| -9 | 15 | 17 | -6 | 22 | 21 | -16 | 8 | 8 | -1 | 15 | 16 |
| 10 | 9 | 9 | 7 | 24 | 25 | H= | 8 K= | 1 | 2 | 18 | 16 |
| -10 | 13 | 13 | -8 | 10 | 8 | 0 | 35 | 36 | 3 | 13 | 13 |
| -14 | 13 | 14 | -9 | 10 | 10 | 1 | 32 | 32 | -3 | 13 | 14 |
| -15 | 7 | 7 | -13 | 17 | 17 | -1 | 46 | 45 | 4 | 36 | 38 |
| H= | 7 K= | 8 | H= | 7 K= | 11 | -2 | 24 | 24 | 5 | 21 | 21 |
| 0 | 13 | 13 | 0 | 11 | 12 | 4 | 30 | 29 | -6 | 21 | 23 |
| 1 | 8 | 8 | 1 | 6 | 5 | -4 | 13 | 15 | 7 | 6 | 7 |
| -1 | 11 | 9 | -1 | 8 | 7 | -5 | 20 | 20 | 8 | 14 | 15 |
| 2 | 7 | 7 | -2 | 8 | 8 | 6 | 20 | 20 | -8 | 9 | 9 |
| -2 | 6 | 6 | 3 | 13 | 13 | 7 | 6 | 5 | 9 | 18 | 18 |
| 3 | 28 | 28 | -3 | 12 | 12 | -7 | 10 | 11 | -9 | 8 | 6 |
| -3 | 36 | 38 | 4 | 8 | 9 | 8 | 6 | 7 | -10 | 8 | 9 |
| 4 | 18 | 16 | 5 | 14 | 16 | -8 | 24 | 23 | -11 | 20 | 22 |
| -4 | 11 | 11 | -5 | 22 | 22 | -9 | 10 | 9 | -13 | 24 | 25 |
| 5 | 6 | 6 | 6 | 6 | 7 | 10 | 18 | 18 | H= | 8 K= | 4 |
| -5 | 25 | 25 | -7 | 8 | 8 | -10 | 15 | 17 | 0 | 10 | 12 |
| -6 | 10 | 11 | -9 | 6 | 6 | -11 | 5 | 5 | -1 | 9 | 10 |
| 7 | 21 | 22 | -11 | 31 | 31 | -12 | 14 | 14 | 2 | 36 | 37 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

| | | |
|---|---|---|
| -2 | 8 | 6 |
| 3 | 9 | 9 |
| -3 | 7 | 8 |
| 4 | 7 | 7 |
| -4 | 27 | 29 |
| 5 | 5 | 4 |
| -5 | 10 | 10 |
| 6 | 14 | 16 |
| -6 | 7 | 8 |
| 7 | 8 | 9 |
| -7 | 13 | 13 |
| -8 | 10 | 10 |
| 9 | 7 | 8 |
| -15 | 6 | 6 |
| -16 | 5 | 5 |
| H= | 8 K= | 5 |
| 0 | 27 | 28 |
| 1 | 10 | 8 |
| -1 | 17 | 17 |
| -2 | 15 | 14 |
| 3 | 23 | 22 |
| -3 | 8 | 8 |
| 4 | 7 | 8 |
| -4 | 15 | 14 |
| 5 | 20 | 20 |
| 7 | 7 | 7 |
| -7 | 19 | 19 |
| 8 | 9 | 10 |
| -8 | 9 | 10 |
| 9 | 8 | 8 |
| -12 | 10 | 11 |
| -13 | 7 | 6 |
| -14 | 16 | 17 |
| H= | 8 K= | 6 |
| 0 | 25 | 25 |
| 1 | 25 | 25 |
| -1 | 9 | 8 |
| -2 | 7 | 7 |
| 3 | 15 | 15 |
| -3 | 11 | 9 |
| 4 | 6 | 4 |
| -4 | 16 | 16 |
| 5 | 12 | 12 |
| -5 | 22 | 24 |
| 6 | 14 | 15 |
| 7 | 6 | 6 |
| 8 | 15 | 14 |
| -10 | 15 | 15 |
| -12 | 8 | 8 |
| H= | 8 K= | 7 |
| 0 | 5 | 4 |
| 1 | 5 | 4 |
| -1 | 28 | 29 |
| -3 | 22 | 22 |
| 4 | 5 | 5 |
| -4 | 32 | 33 |
| 5 | 11 | 12 |
| 6 | 10 | 9 |
| -6 | 9 | 10 |
| -8 | 9 | 9 |
| -9 | 8 | 9 |
| -10 | 11 | 12 |
| -11 | 11 | 12 |
| -12 | 9 | 8 |
| -14 | 6 | 6 |
| H= | 8 K= | 8 |
| 0 | 8 | 8 |
| -1 | 17 | 16 |
| 2 | 15 | 15 |
| -2 | 8 | 8 |
| -3 | 12 | 12 |
| 4 | 6 | 7 |
| -4 | 10 | 11 |
| 5 | 14 | 14 |
| -5 | 13 | 14 |
| -7 | 11 | 12 |
| -8 | 7 | 7 |
| -9 | 12 | 13 |
| -10 | 13 | 14 |
| H= | 8 K= | 9 |
| 0 | 21 | 21 |
| 1 | 9 | 8 |
| -1 | 17 | 17 |
| -2 | 12 | 11 |
| 3 | 21 | 21 |
| -3 | 7 | 6 |
| 4 | 11 | 10 |
| 5 | 8 | 7 |
| -5 | 14 | 15 |
| -6 | 7 | 7 |
| -7 | 8 | 9 |
| -9 | 5 | 5 |
| -10 | 10 | 11 |
| -11 | 8 | 7 |
| -12 | 7 | 6 |
| H= | 8 K= | 10 |
| 1 | 23 | 25 |
| 2 | 9 | 10 |
| 3 | 19 | 19 |
| -3 | 16 | 18 |
| -4 | 12 | 12 |
| -5 | 7 | 9 |
| -6 | 20 | 20 |
| -8 | 10 | 11 |
| -9 | 6 | 7 |
| -10 | 5 | 6 |
| H= | 8 K= | 11 |
| 1 | 7 | 8 |
| -1 | 23 | 24 |
| -2 | 8 | 9 |
| -3 | 14 | 14 |
| -7 | 13 | 12 |
| H= | 9 K= | 0 |
| -2 | 16 | 18 |
| 4 | 12 | 12 |
| -4 | 9 | 7 |
| 6 | 26 | 28 |
| -6 | 9 | 9 |
| -8 | 17 | 17 |
| -10 | 7 | 8 |
| H= | 9 K= | 1 |
| 1 | 14 | 15 |
| -1 | 8 | 6 |
| 2 | 15 | 15 |
| -2 | 11 | 13 |
| -3 | 7 | 8 |
| 4 | 7 | 7 |
| -6 | 9 | 10 |
| -10 | 6 | 8 |
| -11 | 5 | 5 |
| -13 | 13 | 14 |
| H= | 9 K= | 2 |
| 0 | 26 | 27 |
| 2 | 24 | 26 |
| 3 | 19 | 20 |
| -4 | 19 | 22 |
| 5 | 14 | 15 |
| 6 | 13 | 14 |
| -6 | 7 | 6 |
| -10 | 13 | 14 |
| -12 | 5 | 5 |
| -13 | 6 | 6 |
| H= | 9 K= | 3 |
| 0 | 8 | 8 |
| 1 | 12 | 11 |
| -2 | 21 | 24 |
| 3 | 8 | 7 |
| -3 | 8 | 8 |
| 4 | 17 | 16 |
| -4 | 7 | 8 |
| 5 | 6 | 7 |
| -5 | 14 | 16 |
| 6 | 6 | 7 |
| -7 | 7 | 9 |
| -8 | 10 | 10 |
| -9 | 10 | 10 |
| -13 | 7 | 8 |
| -14 | 4 | 6 |
| H= | 9 K= | 4 |
| 0 | 10 | 10 |
| 1 | 25 | 25 |
| -1 | 18 | 18 |
| 2 | 6 | 7 |
| -2 | 9 | 10 |
| -3 | 7 | 7 |
| 4 | 9 | 8 |
| -4 | 12 | 13 |
| 6 | 27 | 27 |
| -7 | 6 | 5 |
| -8 | 12 | 13 |
| -11 | 5 | 4 |
| -12 | 6 | 5 |
| H= | 9 K= | 5 |
| 0 | 7 | 7 |
| -1 | 15 | 17 |
| -3 | 6 | 6 |
| 4 | 17 | 17 |
| -4 | 6 | 6 |
| 5 | 8 | 8 |
| -5 | 8 | 10 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

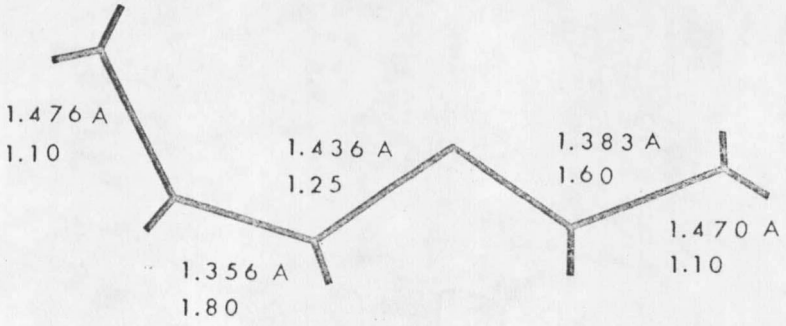
| | | |
|---|---|---|
| -6 | 22 | 24 |
| -7 | 10 | 9 |
| -10 | 9 | 11 |
| -12 | 14 | 14 |
| -13 | 12 | 13 |
| H= | 9 K= | 6 |
| 0 | 9 | 9 |
| 1 | 10 | 8 |
| -1 | 6 | 5 |
| 2 | 12 | 13 |
| 3 | 13 | 14 |
| -4 | 24 | 26 |
| -5 | 6 | 6 |
| -6 | 9 | 11 |
| -7 | 8 | 8 |
| -9 | 13 | 14 |
| -11 | 10 | 11 |
| -12 | 5 | 7 |
| H= | 9 K= | 7 |
| 0 | 10 | 10 |
| 2 | 6 | 5 |
| -2 | 6 | 7 |
| 3 | 18 | 19 |
| -3 | 6 | 8 |
| -4 | 17 | 19 |
| -5 | 8 | 10 |
| H= | 9 K= | 8 |
| 0 | 5 | 5 |
| 1 | 14 | 14 |
| 2 | 13 | 12 |
| -4 | 7 | 7 |
| -5 | 19 | 21 |
| -7 | 9 | 9 |
| H= | 9 K= | 9 |
| -1 | 8 | 8 |
| -3 | 11 | 11 |
| -6 | 4 | 3 |
| H= | 10 K= | 0 |
| 0 | 23 | 25 |
| -8 | 11 | 13 |
| H= | 10 K= | 1 |
| 1 | 7 | 6 |
| 2 | 10 | 12 |
| -2 | 13 | 15 |
| -5 | 6 | 6 |
| -7 | 6 | 6 |
| H= | 10 K= | 2 |
| -5 | 9 | 10 |
| H= | 10 K= | 3 |
| -2 | 16 | 1 |
| -3 | 6 | 7 |
| H= | 10 K= | 4 |
| 0 | 15 | 18 |
| -1 | 5 | 5 |
| -4 | 6 | 6 |
| -9 | 5 | 6 |
| H= | 10 K= | 5 |
| -1 | 5 | 5 |
| -2 | 14 | 16 |
| -4 | 15 | 18 |
| -6 | 8 | 9 |

TABLE XVIII (Continued)

Observed and Calculated Structure Factors for $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$.

(36) suggest, that the more electronegative atoms preferentially occupy the apical positions, whereas, the less electronegative groups preferentially occupy equatorial positions in a trigonal bipyramid. The argument for placing the more polar substituents in the apical positions is that the $p_z$ and $d_z2$ orbitals are directed in space and, therefore, can provide good overlap with polar atoms that pull electrons away from the phosphorus. However, the equatorial $sp^2$ orbitals will bond best with electrons close to the phosphorus, i.e., with substituents that are electron donating. Pseudo-rotation of the molecule would satisfy the ring angle requirements, but would place both oxygens equatorial and, therefore, unfavorable positions for the stable molecule. This does not, of course, rule out pseudo-rotation for the hydrolysis reaction, since the transition state will be of higher energy than the ground state molecule.

The yellow color of these crystals is apparently due to the chromophore composed of the 1,4-diphenyl butadiene portion of the molecule. The conjugation of this unit is very strongly reflected in the bond lengths as illustrated below. The bond orders are those of L. Pauling (51).



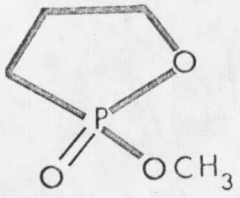
The distances differ considerably from normal single bond (1.54A) and double bond (1.33A) distances. The fact that the conjugation is so great is surprising since the phenyl rings are twisted with respect to the double bond portion of the molecule; the angles being 136°32' for the phenyl group on the six-membered ring and 13°40' for the phenyl group on the five-membered ring. This indicates that the p-p $\pi$ overlap can be considerably reduced and still retain a great deal of $\pi$ bond character.

The trigonal-bipyramidal phosphorus portion of the molecule is, essentially, undistorted with bond angles ranging from 87.36 to 93.48° for the axial-equatorial angles and 116.78 to 123.95° for the equatorial-equatorial angles. It is very interesting to note that the C(5)-P-O(2) angle, the five-membered ring phosphorus angle, has changed from 97.3° in acetionenediol cyclophosphate to 87.26° in this complex.

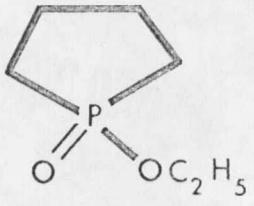
The phosphorus-carbon distances are all 1.82A and can be considered as normal for a P-C single bond (1.82A). The P-O distances are 1.74A for the six-membered ring oxygens and 1.79A for the five-membered ring oxygen which compare with 1.76A for the five-membered ring oxygen and 1.63A for the isopropyl oxygen in 2,2,2-triisopropyl-4,5-(2',2"-biphenyleno)-1,3,2-dioxaphospholene (7,8). The apical bonds are essentially that predicted by Cruickshank (37) for a P-O single bond (1.76A). Thus the $\pi$ bond character of these bonds is very small, if not zero.

It is interesting to note that *I* (the methyl ester of propylphostonic acid) undergoes hydrolysis rapidly with ring opening, but not with loss of the external methoxy group. The trigonal-bipyramidal intermediate cannot readily undergo pseudo-rotation, for pseudo-rotation

about the equatorial carbon atom as a pivot would expand the ring angle to 120°, whereas pseudo-rotation about either of the other two equatorial substituents as a pivot would push the alkyl substituent into an apical position. It, therefore, cannot undergo pseudo-rotation easily to place the methoxy group in the appropriate apical leaving position. In addition, the reaction rate of cyclic phosphinates 2 should be low for there is no way to form a trigonal-bipyramidal intermediate of low energy since the ring angle must be 120° or else an alkyl group must replace an oxygen atom in an apical position. Either one of these would have a high energy of formation.




1




2

PART IV

# THE CRYSTAL STRUCTURE OF 2,3,4-TRIMETHYLPENTANE-2,4-PHOSPHINIC ACID MONOHYDRATE (38)

## Preparation of the Crystals

Crystals were furnished by Paul Haake and Prepared according to methods described in the literature (39). A crystal of suitable size for x-ray studies was enclosed in a Lindemann capillary along with a small amount of mother liquor since the crystals tend to lose water of hydration if not so treated.

## Density Determination of $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

The density of the crystal was determined by measuring the density of a solution of water and bromoethyl acetate in which the crystal remained suspended. The density of $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$ was determined to be 1.156 $g/cm^3$.

## Collection of the Data

The linear absorption coefficient for Cu $K_\alpha$ radiation is 18.52 $cm^{-1}$ and that for Mo $K_\alpha$ is 2.00 $cm^{-1}$. Even though the absorption is small for Cu $K_\alpha$ radiation, the extreme differences in two of the crystals dimensions (0.20 x 0.02 x 0.40 mm) would make absorption a problem. It was, therefore, decided that Mo $K_\alpha$ radiation would be best for data collection.

Intensity data were collected on a General Electric XRD-5 diffractometer equipped with a General Electric single crystal orienter and scintillation counter for a detector. Independent reflections were

collected by the theta-two theta scan technique (moving crystal-moving counter method) using 100 second scans counting the background for 50 seconds on either side of the peak. The scan rate in two theta was two degrees per minute and the take-off angle of the x-ray tube was four degrees. Zirconium-filtered molybdenum radiation (0.7107A) was used. The diffractometer settings for the individual reflections were calculated using a computer program by E. Enwall (40). The crystal was mounted about the b-axis. A total of 1237 reflections were recorded of which 763 were treated as observed, that is, greater than $2\sigma$. The machine stability constant used was 0.02. The conditions for reflection, l=2n for h0l and h+k=2n for hkl, indicates the space group C2/c or Cc. The statistical test of Howell, Phillips, and Rogers (41), the results of which are given in Figure 7, indicates the centrosymmetric space group.

The intensity data was corrected for the Lorentz-polarization factor using a computer program from the crystallographic library (33). Scattering factors for each reflection were also calculated by this program. The scattering factor tables were taken from the International Tables for Crystallography (18).

Using the cell dimensions and assuming eight molecules per unit cell, the density was calculated to be 1.152 $g/cm^3$. Table XIX gives a summary of the unit cell data.

Structural Determination

The structure was solved using a combination of the "symbolic sign" determination and a three-dimensional Patterson map. For the crystal

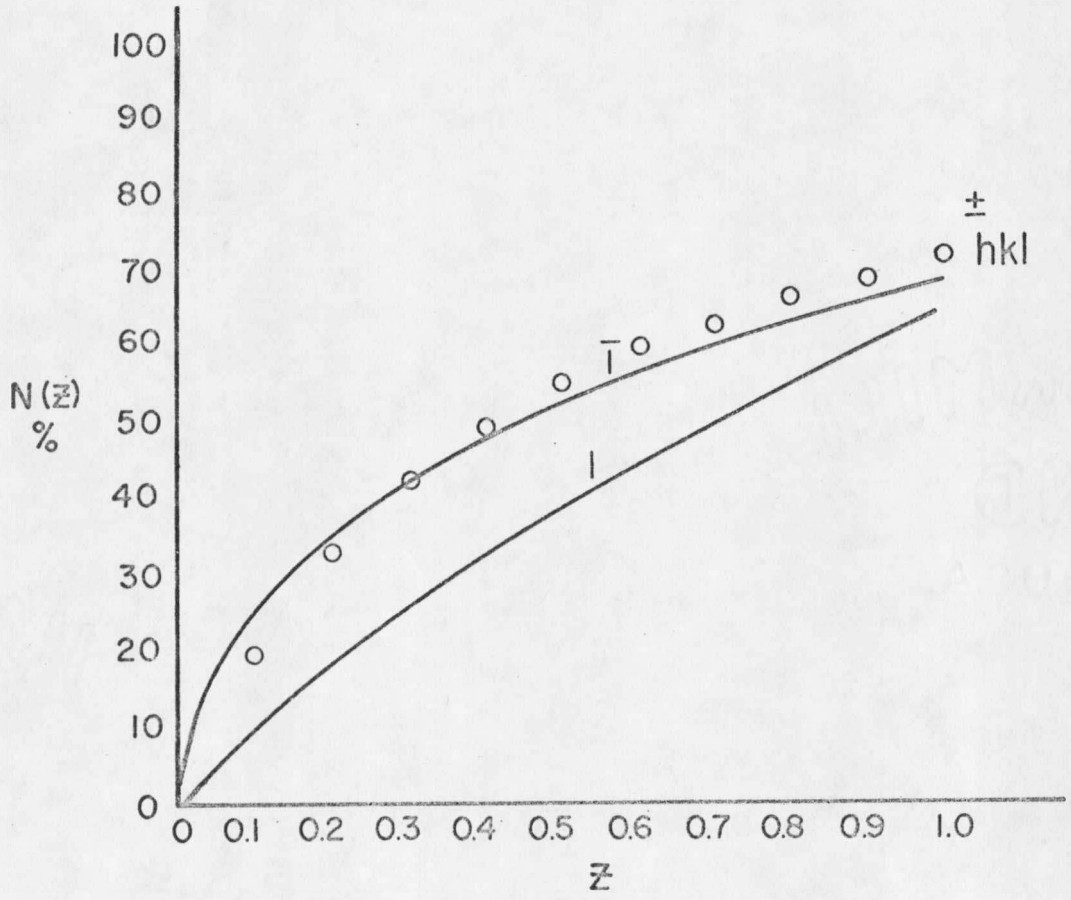



FIGURE 7. Intensity Distribution for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

TABLE XIX

Summary of Crystal Data for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

a = 13.251(4)A

b = 6.511(3)A

c = 26.387(4)A

$\beta$ = 101.455(70)°

| | |
|---|---|
| Space Group | C2/c |
| Molecules per unit cell | 8 |
| Calculated density | = 1.152 g/cm$^3$ |
| Measured density | = 1.156 g/cm$^3$ |

symmetry C2/c, the following equivalent positions exist

$$x, \quad y, \quad z;$$

$$-x, \quad -y, \quad -z;$$

$$x, \quad -y, \quad \frac{1}{2}+z;$$

$$-x, \quad y, \quad \frac{1}{2}-z;$$

$$0, \quad 0, \quad 0;$$

$$\frac{1}{2}, \quad \frac{1}{2}, \quad 0.$$

The Harker section is $u=2x$, $v=0$, $w=\frac{1}{2}+2z$ and the Harker line is at $u=0$, $v=2y$, $w=\frac{1}{2}$.

There are several large peaks ranging from 76 to 86 on the Harker section, several of which "fall off" in the y-direction at a rate indicative of a "true" Harker peak for a P-P vector. There are three major peaks on the Harker line. Several of these Harker peaks give centrosymmetrically related peaks which fit the Patterson map. Three peaks were chosen as possible P-P vectors and structure factors and Fourier maps were calculated for each of the phosphorus positions. The R-index ranged from 46-52% for the positions used and the Fourier maps of all three appeared to make little chemical sense. At this stage, the method of "symbolic sign" determination was tried. The structure factors were normalized and $\sum_2$ relations were calculated for those reflections with E's greater than 1.80. A total of 221 reflections were used in the $\sum_2$ calculation. The initial choice of signs are shown in Table XX. More than 4500 sign relationships were calculated (some reflections having as many as 100 relations contributing to their signs). Subsequently, 210

TABLE XX

Initial Choice of Signs for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| h | k | l | SIGN | E |
|---|---|---|---|---|
| 3 | 3 | 2 | + | 3.77 |
| 1 | 1 | 1 | + | 3.56 |
| -2 | 2 | 4 | a | 4.37 |
| 4 | 2 | 9 | b | 2.52 |
| 7 | 1 | 13 | c | 4.61 |

signs were assigned with only one arbitrary choice remaining. According to the sign development, there was a very strong indication that the symbolic sign should be negative. Using this set of signs thus developed, a three-dimensional E-map was calculated. It was obvious from the map that the signs determined were incorrect since most of the scattering matter was placed on the two-fold special position. It was decided, however, to try the phosphorus position from the E-map (0.0000, 0.1625, 0.7500) since we had no assurance as to the correctness of the molecular structure. Structure factors were calculated using this position and an R-index of 38% was obtained. This is remarkably good and it was decided to continue with this position and assume that we had a product other than that which we believed it to be. Many attempts to obtain a solution from this phosphorus position were made, but in the end all failed to give an acceptable structure. After several discussions with Drs. V. Schomaker and L. Jensen of the University of Washington, it was decided that there was one outstanding peak on the Harker section which should be investigated. At the same time it was decided to calculate an E-map using the other sign set, that is, the symbolic sign was given a positive value. The E-map calculated from this sign set gave a phosphorus position which agreed with the most outstanding peak on the Patterson map and with most of the other major Patterson peaks. Structure factors were calculated using this phosphorus position (0.8938, 0.1606, 0.8422) and an R-index of 46% was obtained. Again, the Fourier map had many extraneous peaks around the phosphorus, many of which made no chemical sense. Peaks that appeared to make chemical sense were used to calculate another set of structure

factors and another Fourier map. In this manner, all of the remaining atoms were found.

It appears that in C2/c, enough phases can be satisfied, for this structure, by placing the phosphorus at the two-fold special position to give a reasonably good R-index. This may be partly due to the fact that the molecules are closely oriented around the two-fold position.

Refinement of the Structure

Refinement started with the atomic positions which gave an R-index of 24%. The block diagonal least squares of G.A. Mair (19) was used. Several cycles, varing positional as well as individual isotropic thermal parameters, dropped the R-index to 14.3%. In using the block diagonal least squares program, a parameter shift damping factor of 0.25 was used initially, but increased to 0.60 as the refinement progressed. The final cycles of refinement were carried out using the block diagonal least squares program of F.R. Ahmed (34) refining positional and anisotropic thermal parameters. A parameter shift damping factor of 0.50 was used. A total of 763 reflections were included in the least square refinement. The final R-index is 7.75%. Unit weights were used during the Mair portion of the refinement and the weighting scheme suggested by Stout and Jensen (35) was used during the final cycles.

Final positional parameters are listed in Table XXI. Table XXII lists the anisotropic temperature factors and Table XXIII lists the anisotropic thermal parameters in terms of the mean-square amplitude of vibration along the principal axes of the thermal ellipsoids. For

calculation of these an orthogonal coordinate system was used in which the x-axis coincided with a and the y-axis coincided with b. Table XXIV shows the equations for the best least squares planes calculated for the ring and, also, for the carbon skeleton, excluding the apex carbon and its methyl group. The least squares planes are calculated according to the methods described by V. Schomaker et al. (23). Table XXVII contains the observed and calculated structure factors.

Discussion of the Structure

The results obtained from the crystallographic analysis are shown in Figures 8 and 9. The bond distances are listed in Tables XXV and the bond angles in Table XXVI.

The four-membered ring is slightly bent as shown by the least squares plane. C(2) and C(3) are 0.12A above the best least squares plane and P and C(3) are 0.10 and 0.14A, respectively, below the least squares plane thus forming a very shallow V. The ring angles deviate from the tetrahedral angle ($109.5^{\circ}$) markedly at three positions; C(2)-P-C(4) $82.5^{\circ}$, P-C(2)-C(3) $85.8^{\circ}$, and P-C(4)-C(3) $85.8^{\circ}$, but less at the apical carbon, C(2)-C(3)-C(4) $101.0^{\circ}$. Due to this, there appears to be a great deal of strain at three of the ring atoms and the molecule is very distorted from the rectangular shape. The exterior angles around phosphorus are also distorted from the tetrahedral angle and range from 106.0 to $120.8^{\circ}$. The exterior angles around the carbon atoms range from 112.0 to $116.9^{\circ}$. It thus appears that if the carbon atoms are truly $sp^3$ hybrides, then the orbital overlap is weakened due to the constrained orientations of the

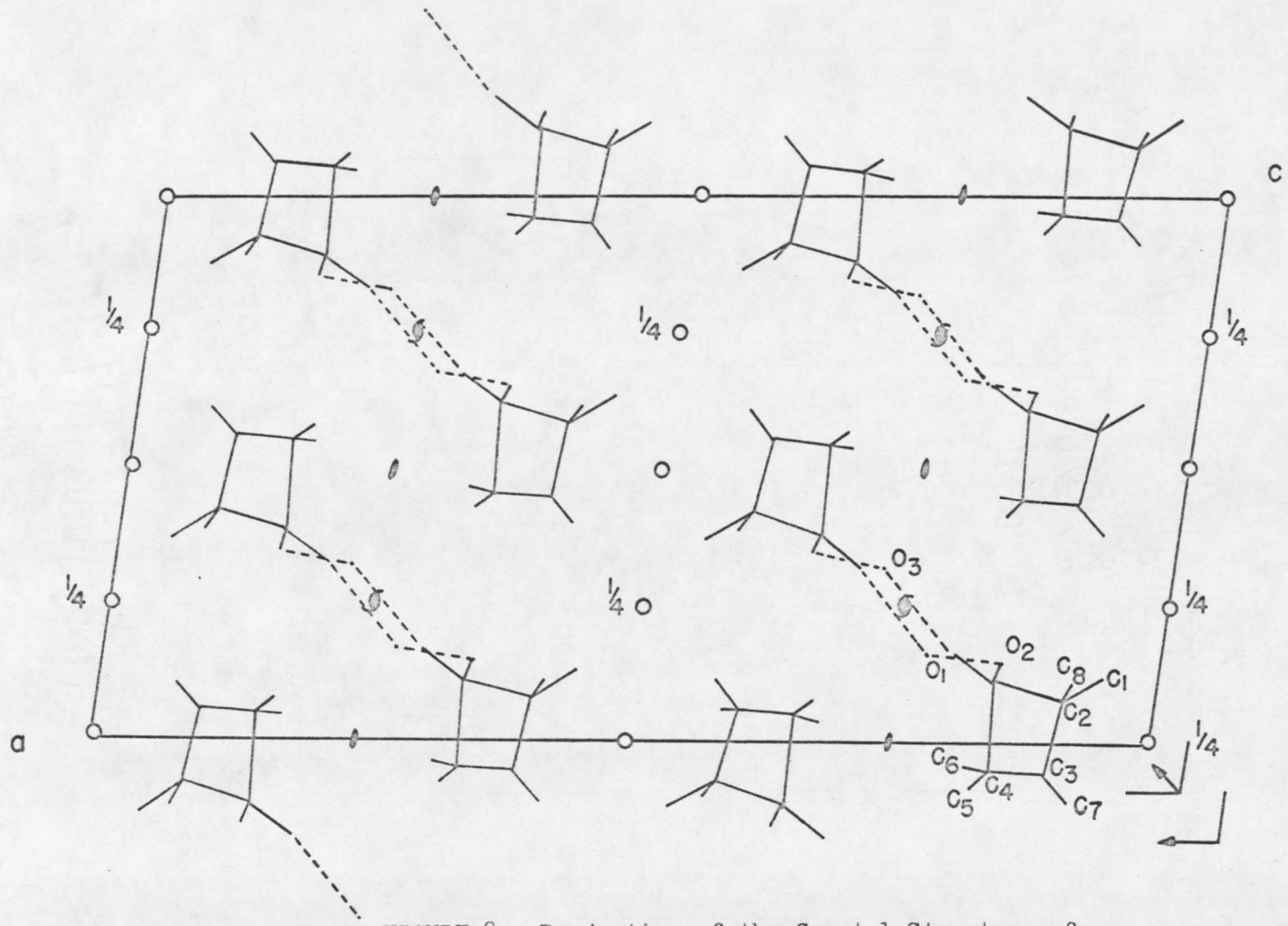



FIGURE 8. Projection of the Crystal Structure of 2,3,4-Trimethylpentane-2,4-Phosphinic Acid Monohydrate onto the ac Plane.

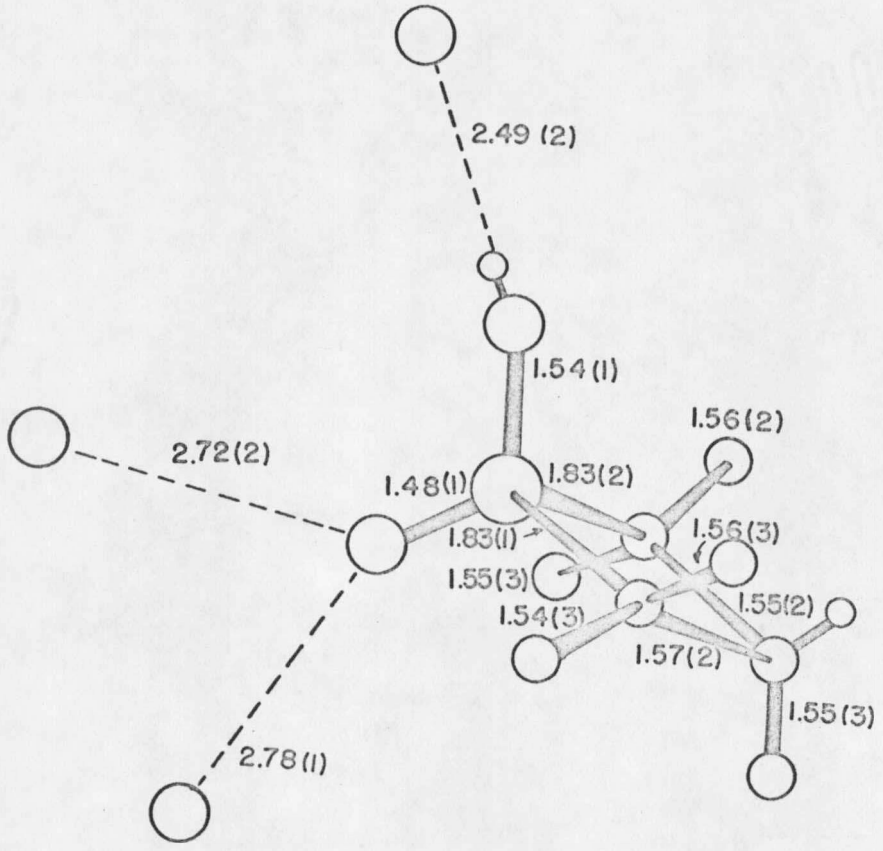



FIGURE 9. Molecular Structure of 2,3,4-Trimethylpentane-2,4-Phosphinic Acid Monohydrate.

TABLE XXI

Final Atomic Coordinates for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOM | x | y | z |
|---|---|---|---|
| P | -0.1017(2)[a] | 0.1620(4) | 0.8432(1) |
| O(1) | -0.1639(6) | 0.2871(11) | 0.8016(3) |
| O(2) | -0.1430(6) | -0.0580(11) | 0.8464(3) |
| O(3) | -0.3324(6) | 0.1971(11) | 0.7275(3) |
| C(1) | -0.1214(10) | 0.1547(29) | 0.9511(5) |
| C(2) | -0.0698(7) | 0.2568(15) | 0.9097(4) |
| C(3) | 0.0412(7) | 0.1802(21) | 0.9097(4) |
| C(4) | 0.0382(7) | 0.1598(19) | 0.8502(4) |
| C(5) | 0.0782(10) | 0.3451(27) | 0.8241(6) |
| C(6) | 0.0850(11) | -0.0464(27) | 0.8353(6) |
| C(7) | 0.1313(10) | 0.3052(25) | 0.9416(6) |
| C(8) | -0.0821(11) | 0.4949(18) | 0.9133(6) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XXII

Thermal Parameters for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOM | $\beta_{11}$ [a,b] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| P | 0438(14)[c] | 1165(44) | 0121(4) | -121(71) | -033(11) | 0028(40) |
| O(1) | 0537(47) | 2049(207) | 0161(13) | -063(162) | -173(38) | 0013(84) |
| O(2) | 0706(59) | 1436(156) | 0201(15) | -457(161) | -089(47) | 0195(95) |
| O(3) | 0717(53) | 1547(189) | 0209(15) | -016(173) | -128(43) | 0085(92) |
| C(1) | 0958(104) | 4964(479) | 0144(20) | 0681(459) | 0242(69) | 0205(228) |
| C(2) | 0486(68) | 1893(242) | 0093(17) | -070(221) | 0105(50) | 0292(108) |
| C(3) | 0450(71) | 2952(330) | 0154(19) | -104(291) | 0003(54) | 0157(168) |
| C(4) | 0403(67) | 2218(267) | 0217(22) | 0020(283) | 0116(57) | 0138(177) |
| C(5) | 0778(99) | 4078(435) | 0279(29) | -1654(404) | 0348(81) | -428(232) |
| C(6) | 0768(112) | 5178(540) | 0222(29) | 1519(408) | 0031(81) | -490(223) |
| C(7) | 0589(81) | 4443(503) | 0263(29) | -473(363) | -209(74) | -697(224) |
| C(8) | 1082(126) | 1885(313) | 0266(29) | 0389(308) | -040(84) | -512(147) |

[a] The $\beta_{ij}$'s have been multiplied by $10^5$.

[b] The form of the anisotropic thermal ellipsoids is

$$T = \exp\left[-\left\{\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl\right\}\right].$$

[c] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XXIII

Principal Axes of the Thermal Ellipsoids for
$PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOM | Mean Square Displacement in $A^2$ | | |
|---|---|---|---|
| | MAX | MED | MIN |
| P | 0.05 | 0.03 | 0.02 |
| O(1) | 0.10 | 0.05 | 0.03 |
| O(2) | 0.08 | 0.04 | 0.03 |
| O(3) | 0.09 | 0.05 | 0.03 |
| C(1) | 0.12 | 0.08 | 0.04 |
| C(2) | 0.05 | 0.04 | 0.02 |
| C(3) | 0.08 | 0.05 | 0.03 |
| C(4) | 0.13 | 0.09 | 0.03 |
| C(5) | 0.07 | 0.05 | 0.04 |
| C(6) | 0.12 | 0.08 | 0.03 |
| C(7) | 0.12 | 0.08 | 0.04 |
| C(8) | 0.14 | 0.07 | 0.05 |

TABLE XXIV

Equations of Least Squares Planes Referred to Orthogonal Axes for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$[a]

| ATOMS | a | b | c | D(A) | S($A^2$) |
|---|---|---|---|---|---|
| PC(2)C(3)C(4) | 0.1499 | 0.9473 | -0.2832 | -4.62 | $5.6 \times 10^{-2}$ |
| C(1)C(2)C(3)C(5) C(6)C(8) | 0.8302 | 0.1108 | 0.5462 | 16.30 | $1.4 \times 10^{-2}$ |
| PO(1)O(2)C(3)C(7) | -0.5978 | 0.2542 | 0.7602 | 15.02 | $3.6 \times 10^{-4}$ |

[a] $X = x + z\cos\beta$ ; $Y = y$; $Z = z\sin\beta$,

$D = a\bar{X} + b\bar{Y} + c\bar{Z}$,

S = sum of squares of deviations of atoms from plane,

D = origin to plane distance in angstroms,

All atoms are given equal weights.

TABLE XXV

Bond Distances for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOMS | DISTANCE |
|---|---|
| P-O(1) | 1.48(1)[a] |
| P-O(2) | 1.54(1) |
| P-C(2) | 1.83(2) |
| P-C(4) | 1.83(1) |
| P-C(3) | 2.32(2) |
| O(1)-O(2) | 2.53(2) |
| O(1)-O(3) | 2.72(2) |
| O(2')-O(3) | 2.49(2) |
| O(1)-O(3') | 2.77(1) |
| C(1)-C(2) | 1.55(3) |
| C(1)-C(8) | 2.53(3) |
| C(2)-C(8) | 1.56(2) |
| C(2)-C(3) | 1.56(2) |
| C(3)-C(7) | 1.55(3) |
| C(3)-C(4) | 1.56(2) |
| C(4)-C(5) | 1.53(3) |
| C(4)-C(6) | 1.56(3) |
| C(5)-C(6) | 2.56(3) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

TABLE XXVI

Bond Angles for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOMS | DEGREES |
|---|---|
| O(1)-P-O(2) | 113.7(4)[a] |
| O(1)-P-C(2) | 120.8(3) |
| O(1)-P-C(4) | 119.1(5) |
| O(1)-P-C(3) | 141.9(3) |
| O(2)-P-C(2) | 106.1(4) |
| O(2)-P-C(4) | 110.5(6) |
| O(2)-P-C(3) | 104.4(4) |
| C(2)-P-C(4) | 82.5(5) |
| P-C(2)-C(1) | 118.6(6) |
| P-C(2)-C(3) | 85.8(6) |
| P-C(2)-C(8) | 112.6(8) |
| P-C(4)-C(5) | 112.2(9) |
| P-C(4)-C(6) | 115.2(8) |
| P-C(4)-C(3) | 85.8(6) |
| C(1)-C(2)-C(3) | 114.2(8) |
| C(1)-C(2)-C(8) | 108.9(8) |
| C(2)-C(3)-C(4) | 101.0(9) |
| C(2)-C(3)-C(7) | 116.9(8) |
| C(4)-C(3)-C(7) | 116.9(10) |
| C(3)-C(4)-C(5) | 116.2(10) |
| C(3)-C(4)-C(6) | 113.2(9) |
| C(5)-C(4)-C(6) | 111.9(10) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| K= | 0 L= | 0 | -10 | 43 | 43 | 4 | 14 | 13 | -13 | 17 | 23 |
| 2 | 141 | 127 | 12 | 28 | 29 | -4 | 52 | 51 | K= | 1 L= | 2 |
| 4 | 254 | 233 | K= | 0 L= | 10 | 6 | 50 | 49 | 1 | 47 | 65 |
| K= | 0 L= | 2 | 0 | 95 | 94 | -6 | 35 | 32 | 3 | 10 | 14 |
| 0 | 109 | 108 | 2 | 33 | 27 | -8 | 59 | 56 | 5 | 99 | 96 |
| 2 | 96 | 106 | -2 | 15 | 5 | -10 | 25 | 25 | -5 | 32 | 32 |
| -2 | 199 | 195 | 4 | 98 | 102 | K= | 0 L= | 20 | 7 | 47 | 45 |
| 4 | 94 | 89 | -4 | 72 | 70 | 0 | 51 | 54 | -7 | 35 | 34 |
| 6 | 53 | 50 | -6 | 44 | 45 | 4 | 38 | 37 | 9 | 22 | 21 |
| -6 | 133 | 132 | 8 | 77 | 77 | -4 | 24 | 26 | 11 | 16 | 12 |
| 8 | 54 | 55 | -8 | 34 | 33 | -4 | 24 | 26 | K= | 1 L= | 3 |
| -8 | 13 | 15 | 10 | 23 | 26 | -10 | 16 | 16 | 1 | 112 | 91 |
| -10 | 15 | 20 | -10 | 37 | 37 | K= | 0 L= | 22 | -1 | 175 | 170 |
| 12 | 41 | 39 | 12 | 21 | 19 | 2 | 20 | 16 | 3 | 56 | 44 |
| -14 | 19 | 25 | K= | 0 L= | 12 | -2 | 28 | 27 | -5 | 54 | 60 |
| K= | 0 L= | 4 | 0 | 101 | 105 | 4 | 29 | 28 | 7 | 41 | 40 |
| 0 | 168 | 184 | 2 | 123 | 124 | -4 | 23 | 19 | -7 | 56 | 52 |
| 2 | 75 | 50 | -2 | 24 | 21 | 6 | 19 | 18 | 9 | 17 | 18 |
| -2 | 201 | 206 | 4 | 29 | 27 | -8 | 29 | 25 | -9 | 28 | 31 |
| 4 | 85 | 76 | -4 | 24 | 25 | -10 | 25 | 22 | 11 | 23 | 19 |
| -4 | 175 | 165 | 6 | 98 | 96 | K= | 0 L= | 24 | 13 | 27 | 27 |
| 6 | 21 | 27 | -6 | 35 | 41 | -2 | 19 | 18 | K= | 1 L= | 4 |
| -6 | 141 | 145 | 8 | 26 | 26 | K= | 0 L= | 26 | 1 | 56 | 56 |
| 8 | 30 | 30 | -10 | 16 | 17 | -2 | 21 | 19 | -1 | 74 | 91 |
| -8 | 40 | 42 | K= | 0 L= | 14 | 4 | 27 | 25 | 3 | 73 | 76 |
| -10 | 33 | 30 | 0 | 53 | 40 | K= | 0 L= | 28 | 5 | 30 | 25 |
| 12 | 21 | 22 | 2 | 61 | 65 | 0 | 39 | 38 | 7 | 27 | 33 |
| K= | 0 L= | 6 | -2 | 52 | 55 | 2 | 32 | 28 | K= | 1 L= | 5 |
| -2 | 46 | 35 | 4 | 39 | 36 | -4 | 27 | 24 | 1 | 24 | 30 |
| -4 | 142 | 129 | 6 | 57 | 54 | K= | 1 L= | 0 | -1 | 47 | 62 |
| 6 | 66 | 66 | -6 | 26 | 22 | 1 | 79 | 83 | 3 | 12 | 2 |
| 8 | 17 | 16 | 8 | 47 | 45 | 3 | 11 | 14 | -5 | 27 | 34 |
| -8 | 77 | 78 | -8 | 30 | 29 | 5 | 45 | 44 | 7 | 33 | 33 |
| 10 | 47 | 48 | K= | 0 L= | 16 | 9 | 25 | 24 | -9 | 31 | 30 |
| -10 | 23 | 27 | 0 | 100 | 105 | K= | 1 L= | 1 | 11 | 19 | 21 |
| K= | 0 L= | 8 | 2 | 56 | 55 | 1 | 187 | 173 | -11 | 39 | 41 |
| 0 | 121 | 116 | -2 | 33 | 27 | -1 | 148 | 128 | K= | 1 L= | 6 |
| -2 | 24 | 15 | 4 | 35 | 33 | 3 | 40 | 40 | 1 | 104 | 121 |
| 4 | 39 | 46 | -4 | 42 | 47 | -3 | 16 | 18 | -1 | 85 | 86 |
| -4 | 66 | 64 | 6 | 41 | 41 | 5 | 78 | 75 | 3 | 65 | 59 |
| 6 | 68 | 72 | -6 | 35 | 38 | -5 | 61 | 56 | -3 | 40 | 39 |
| -6 | 56 | 55 | -10 | 35 | 32 | 7 | 71 | 65 | 5 | 79 | 85 |
| 8 | 30 | 27 | K= | 0 L= | 18 | -7 | 17 | 18 | -5 | 30 | 28 |
| -8 | 22 | 30 | 2 | 59 | 56 | 9 | 18 | 17 | -9 | 18 | 18 |
| 10 | 38 | 36 | -2 | 71 | 73 | -9 | 51 | 49 | -11 | 19 | 16 |

TABLE XXVII

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| K= | 1 L= | 7 | -13 | 16 | 17 | -7 | 16 | 13 | -10 | 22 | 25 |
| 1 | 92 | 82 | K= | 1 L= | 12 | K= | 1 L= | 19 | -12 | 18 | 20 |
| -1 | 41 | 38 | 1 | 50 | 59 | 3 | 34 | 39 | K= | 2 L= | 2 |
| 3 | 54 | 53 | 3 | 12 | 12 | -3 | 24 | 22 | 0 | 47 | 37 |
| -3 | 119 | 111 | -3 | 39 | 44 | 7 | 20 | 19 | -2 | 31 | 48 |
| 5 | 35 | 36 | 5 | 30 | 33 | -7 | 30 | 29 | -4 | 12 | 12 |
| -5 | 20 | 18 | -5 | 24 | 17 | -9 | 31 | 29 | 6 | 12 | 16 |
| 7 | 17 | 16 | 7 | 19 | 15 | K= | 1 L= | 20 | -6 | 35 | 35 |
| -7 | 57 | 58 | -7 | 33 | 30 | -1 | 25 | 41 | 8 | 42 | 42 |
| -9 | 33 | 31 | K= | 1 L= | 13 | 3 | 27 | 28 | -8 | 17 | 14 |
| 11 | 34 | 37 | -1 | 49 | 44 | -5 | 18 | 18 | -10 | 19 | 24 |
| -13 | 16 | 18 | 3 | 56 | 58 | K= | 1 L= | 21 | 12 | 27 | 26 |
| K= | 1 L= | 8 | 5 | 18 | 21 | 1 | 23 | 26 | K= | 2 L= | 3 |
| 1 | 64 | 65 | -5 | 50 | 44 | 3 | 34 | 31 | 0 | 28 | 26 |
| -1 | 93 | 95 | 7 | 91 | 86 | -3 | 29 | 27 | -2 | 80 | 73 |
| 3 | 62 | 63 | -7 | 33 | 28 | 5 | 19 | 20 | 4 | 40 | 42 |
| -3 | 65 | 65 | -9 | 27 | 27 | -7 | 15 | 13 | -4 | 69 | 65 |
| 5 | 30 | 33 | K= | 1 L= | 14 | -9 | 20 | 17 | -6 | 32 | 36 |
| 7 | 19 | 21 | -1 | 22 | 19 | K= | 1 L= | 22 | 8 | 59 | 64 |
| -7 | 22 | 24 | 7 | 15 | 17 | -3 | 16 | 20 | -8 | 65 | 69 |
| K= | 1 L= | 9 | -7 | 14 | 14 | 5 | 24 | 22 | 10 | 19 | 19 |
| 1 | 67 | 68 | K= | 1 L= | 15 | K= | 1 L= | 23 | -10 | 15 | 17 |
| -3 | 48 | 51 | 1 | 44 | 40 | -3 | 23 | 21 | 12 | 31 | 29 |
| -5 | 44 | 44 | -3 | 61 | 62 | -9 | 18 | 13 | K= | 2 L= | 4 |
| 7 | 18 | 15 | 5 | 42 | 41 | K= | 1 L= | 25 | 0 | 50 | 29 |
| -7 | 22 | 26 | 7 | 16 | 16 | 1 | 24 | 27 | 2 | 17 | 25 |
| 9 | 58 | 60 | -7 | 69 | 66 | 3 | 24 | 19 | -2 | 139 | 122 |
| -9 | 25 | 26 | -11 | 19 | 18 | -3 | 25 | 22 | 4 | 50 | 44 |
| -11 | 23 | 22 | K= | 1 L= | 16 | K= | 1 L= | 27 | -4 | 25 | 21 |
| K= | 1 L= | 10 | 1 | 31 | 34 | -1 | 23 | 25 | 6 | 29 | 28 |
| 1 | 57 | 67 | 3 | 21 | 24 | -5 | 17 | 16 | -6 | 54 | 55 |
| -1 | 97 | 99 | 5 | 28 | 28 | K= | 2 L= | 0 | 10 | 18 | 19 |
| 3 | 40 | 37 | K= | 1 L= | 17 | 0 | 140 | 135 | 12 | 21 | 20 |
| -3 | 45 | 47 | 1 | 52 | 56 | 4 | 30 | 33 | K= | 2 L= | 5 |
| 5 | 19 | 21 | 3 | 38 | 35 | 6 | 16 | 20 | -2 | 70 | 68 |
| -5 | 69 | 72 | 5 | 61 | 57 | K= | 2 L= | 1 | 4 | 40 | 40 |
| -9 | 15 | 15 | -5 | 24 | 25 | 0 | 35 | 45 | -4 | 49 | 41 |
| K= | 1 L= | 11 | 7 | 32 | 28 | 2 | 91 | 80 | 6 | 53 | 53 |
| -1 | 85 | 82 | -9 | 52 | 51 | -2 | 41 | 26 | -6 | 25 | 25 |
| 3 | 17 | 20 | -11 | 17 | 16 | 4 | 20 | 10 | 8 | 24 | 25 |
| 5 | 25 | 28 | K= | 1 L= | 18 | -4 | 12 | 19 | 10 | 34 | 34 |
| -5 | 78 | 80 | 1 | 64 | 36 | 6 | 63 | 64 | -10 | 26 | 26 |
| 7 | 39 | 40 | -3 | 18 | 20 | -6 | 26 | 29 | K= | 2 L= | 6 |
| -9 | 38 | 34 | 5 | 35 | 37 | -8 | 48 | 52 | 0 | 27 | 30 |
| 11 | 24 | 25 | 7 | 22 | 23 | 10 | 25 | 22 | -2 | 39 | 48 |

TABLE XXVII (Continued)

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 43 | 44 | K= | 2 | L= 10 | K= | 2 | L= 16 | K= | 3 | L= 1 |
| -4 | 49 | 42 | 2 | 22 | 29 | 2 | 15 | 10 | 1 | 58 | 43 |
| 6 | 33 | 32 | 4 | 25 | 25 | -2 | 21 | 26 | -1 | 23 | 19 |
| -6 | 17 | 19 | -4 | 22 | 15 | 6 | 16 | 19 | 3 | 20 | 18 |
| 8 | 24 | 25 | 6 | 25 | 27 | -6 | 18 | 18 | -3 | 37 | 29 |
| -8 | 46 | 46 | -6 | 29 | 28 | K= | 2 | L= 17 | 5 | 15 | 12 |
| 10 | 35 | 36 | 8 | 36 | 36 | 0 | 43 | 48 | 7 | 23 | 19 |
| -10 | 19 | 18 | 10 | 21 | 23 | 2 | 14 | 9 | K= | 3 | L= 2 |
| K= | 2 | L= 7 | -10 | 26 | 22 | -2 | 23 | 28 | -1 | 53 | 58 |
| 0 | 23 | 21 | K= | 2 | L= 11 | 4 | 27 | 22 | 3 | 112 | 105 |
| 2 | 17 | 15 | 0 | 35 | 39 | -4 | 26 | 28 | -3 | 33 | 36 |
| 4 | 34 | 29 | 2 | 52 | 45 | 8 | 17 | 19 | 5 | 23 | 22 |
| -4 | 51 | 54 | -2 | 15 | 15 | -8 | 32 | 31 | -5 | 17 | 18 |
| 6 | 34 | 33 | 4 | 26 | 30 | -10 | 19 | 16 | 7 | 88 | 92 |
| -6 | 18 | 16 | 6 | 31 | 30 | K= | 2 | L= 18 | -9 | 65 | 69 |
| 8 | 24 | 22 | 10 | 25 | 25 | -4 | 24 | 24 | 11 | 19 | 19 |
| -8 | 67 | 70 | -10 | 22 | 18 | -8 | 33 | 31 | -11 | 17 | 19 |
| 10 | 17 | 15 | K= | 2 | L= 12 | K= | 2 | L= 19 | K= | 3 | L= 3 |
| -10 | 38 | 37 | 2 | 20 | 19 | -2 | 45 | 51 | -1 | 67 | 62 |
| 12 | 16 | 16 | -2 | 24 | 28 | -4 | 25 | 24 | 3 | 13 | 11 |
| -12 | 22 | 24 | 4 | 30 | 27 | -6 | 37 | 38 | 5 | 29 | 24 |
| K= | 2 | L= 8 | 6 | 24 | 22 | -8 | 28 | 28 | -5 | 33 | 35 |
| 2 | 32 | 28 | -6 | 24 | 23 | K= | 2 | L= 20 | 9 | 26 | 27 |
| 4 | 32 | 33 | 8 | 18 | 21 | 4 | 19 | 21 | K= | 3 | L= 4 |
| -4 | 79 | 79 | -8 | 17 | 13 | K= | 2 | L= 21 | 1 | 93 | 89 |
| -6 | 25 | 24 | -12 | 18 | 17 | -2 | 26 | 25 | -1 | 48 | 45 |
| 8 | 39 | 36 | K= | 2 | L= 13 | 4 | 21 | 19 | 3 | 42 | 41 |
| -8 | 50 | 49 | 2 | 36 | 35 | 6 | 32 | 31 | -3 | 26 | 23 |
| -10 | 17 | 19 | -2 | 34 | 34 | -6 | 25 | 21 | 5 | 59 | 61 |
| 12 | 18 | 20 | 6 | 24 | 21 | -10 | 16 | 15 | -5 | 22 | 27 |
| -12 | 20 | 20 | -6 | 31 | 30 | K= | 2 | L= 23 | 7 | 32 | 30 |
| K= | 2 | L= 9 | -8 | 38 | 37 | -4 | 18 | 18 | -7 | 50 | 51 |
| 0 | 52 | 56 | -12 | 21 | 22 | -8 | 20 | 18 | -9 | 21 | 24 |
| 2 | 44 | 48 | K= | 2 | L= 14 | K= | 2 | L= 24 | -11 | 23 | 25 |
| -2 | 63 | 69 | 4 | 17 | 16 | 2 | 16 | 13 | K= | 3 | L= 5 |
| 4 | 74 | 79 | -4 | 22 | 19 | K= | 2 | L= 25 | 1 | 15 | 10 |
| -4 | 26 | 25 | 8 | 22 | 23 | 4 | 17 | 16 | -1 | 25 | 23 |
| 6 | 15 | 15 | -8 | 28 | 30 | -6 | 19 | 15 | 3 | 22 | 22 |
| -6 | 48 | 49 | K= | 2 | L= 15 | K= | 3 | L= 0 | -3 | 52 | 46 |
| 8 | 44 | 45 | 0 | 37 | 40 | 1 | 56 | 51 | 5 | 18 | 18 |
| -8 | 47 | 48 | -2 | 52 | 60 | 3 | 71 | 63 | -5 | 24 | 20 |
| -10 | 17 | 16 | -6 | 28 | 30 | 5 | 59 | 57 | -7 | 22 | 24 |
| -12 | 20 | 23 | -8 | 22 | 26 | 7 | 30 | 33 | K= | 3 | L= 6 |
| | | | | | | 9 | 42 | 41 | 1 | 33 | 33 |

TABLE XXVII (Continued)

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 20 | 25 | -7 | 27 | 29 | K= | 4 L= | 0 | K= | 4 L= | 6 |
| 5 | 43 | 42 | K= | 3 L= | 13 | 2 | 18 | 18 | 0 | 61 | 56 |
| -9 | 46 | 46 | 7 | 19 | 20 | 6 | 21 | 22 | 2 | 38 | 38 |
| K= | 3 L= | 7 | K= | 3 L= | 14 | 8 | 19 | 16 | -2 | 22 | 21 |
| 1 | 16 | 17 | -1 | 20 | 29 | K= | 4 L= | 1 | 4 | 32 | 29 |
| 3 | 40 | 40 | 3 | 14 | 16 | 2 | 55 | 55 | 6 | 42 | 40 |
| -3 | 39 | 35 | -3 | 45 | 46 | -2 | 24 | 24 | -6 | 28 | 31 |
| -5 | 30 | 31 | 5 | 16 | 17 | 4 | 40 | 41 | K= | 4 L= | 7 |
| 7 | 23 | 23 | -5 | 17 | 15 | -4 | 31 | 29 | 2 | 45 | 44 |
| -7 | 19 | 21 | 7 | 22 | 24 | 6 | 53 | 51 | -2 | 20 | 22 |
| -9 | 18 | 21 | -7 | 59 | 59 | -6 | 25 | 31 | -4 | 26 | 29 |
| -9 | 18 | 21 | 9 | 36 | 36 | -8 | 27 | 27 | 6 | 45 | 45 |
| K= | 3 L= | 8 | -9 | 23 | 23 | 10 | 17 | 15 | -8 | 27 | 29 |
| 1 | 43 | 45 | K= | 3 L= | 15 | K= | 4 L= | 2 | K= | 4 L= | 8 |
| -1 | 69 | 69 | 1 | 18 | 22 | 2 | 22 | 18 | 2 | 53 | 54 |
| 3 | 53 | 56 | K= | 3 L= | 16 | -2 | 23 | 25 | 4 | 23 | 23 |
| -3 | 53 | 55 | 1 | 32 | 34 | 6 | 57 | 57 | -4 | 19 | 24 |
| 5 | 13 | 13 | -1 | 57 | 61 | 8 | 27 | 26 | 6 | 22 | 23 |
| -5 | 24 | 19 | -3 | 21 | 22 | -8 | 21 | 21 | -6 | 14 | 14 |
| 7 | 31 | 32 | 5 | 38 | 37 | 10 | 18 | 19 | 8 | 20 | 22 |
| -7 | 40 | 39 | -5 | 33 | 33 | K= | 4 L= | 3 | -8 | 29 | 29 |
| -9 | 27 | 27 | -7 | 16 | 16 | 0 | 19 | 14 | K= | 4 L= | 9 |
| -11 | 16 | 15 | -9 | 20 | 19 | 2 | 21 | 25 | 0 | 56 | 57 |
| K= | 3 L= | 9 | K= | 3 L= | 17 | -2 | 59 | 64 | 2 | 47 | 47 |
| 1 | 22 | 21 | 1 | 20 | 25 | 6 | 26 | 26 | -2 | 34 | 37 |
| -5 | 23 | 23 | 5 | 20 | 20 | -6 | 42 | 47 | 4 | 55 | 56 |
| -7 | 23 | 23 | K= | 3 L= | 18 | 8 | 29 | 29 | -4 | 20 | 18 |
| -9 | 23 | 25 | -3 | 28 | 30 | -8 | 24 | 25 | 6 | 36 | 36 |
| K= | 3 L= | 10 | 5 | 15 | 15 | K= | 4 L= | 4 | -6 | 28 | 31 |
| -1 | 76 | 76 | 7 | 27 | 28 | 0 | 21 | 19 | 8 | 25 | 25 |
| 3 | 46 | 52 | -7 | 39 | 37 | 2 | 14 | 11 | -10 | 15 | 16 |
| -3 | 25 | 22 | -9 | 29 | 26 | -2 | 17 | 15 | K= | 4 L= | 10 |
| 5 | 17 | 18 | K= | 3 L= | 20 | 4 | 44 | 42 | 0 | 40 | 53 |
| -5 | 39 | 41 | -1 | 47 | 47 | -4 | 26 | 23 | 2 | 16 | 15 |
| -7 | 26 | 25 | 3 | 23 | 24 | 8 | 37 | 36 | -2 | 24 | 19 |
| K= | 3 L= | 11 | -3 | 24 | 22 | -8 | 20 | 24 | 4 | 18 | 14 |
| 1 | 17 | 16 | 5 | 16 | 17 | K= | 4 L= | 5 | -4 | 33 | 35 |
| -1 | 18 | 23 | -5 | 23 | 21 | 0 | 56 | 57 | -6 | 34 | 35 |
| K= | 3 L= | 12 | -7 | 20 | 21 | -2 | 35 | 35 | -10 | 15 | 17 |
| 1 | 45 | 47 | K= | 3 L= | 21 | 4 | 55 | 54 | K= | 4 L= | 11 |
| 3 | 15 | 17 | -3 | 19 | 24 | -4 | 23 | 24 | 0 | 50 | 66 |
| -3 | 26 | 28 | K= | 3 L= | 22 | 6 | 31 | 30 | 2 | 42 | 44 |
| 5 | 25 | 23 | 5 | 22 | 18 | -6 | 22 | 21 | -2 | 27 | 28 |
| 7 | 37 | 39 | K= | 3 L= | 24 | 8 | 24 | 24 | 4 | 50 | 48 |
| | | | -3 | 21 | 22 | -8 | 16 | 17 | -4 | 27 | 27 |

TABLE XXVII (Continued)

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

| | | |
|---|---|---|
| 6 | 15 | 15 |
| 8 | 18 | 18 |
| K= | 4 L= | 12 |
| 2 | 22 | 21 |
| -2 | 28 | 29 |
| -4 | 20 | 23 |
| -6 | 14 | 14 |
| -8 | 24 | 23 |
| K= | 4 L= | 13 |
| 2 | 57 | 56 |
| -2 | 47 | 47 |
| 4 | 17 | 21 |
| 6 | 31 | 31 |
| -6 | 28 | 29 |
| K= | 4 L= | 14 |
| -6 | 21 | 21 |
| K= | 4 L= | 15 |
| 0 | 40 | 53 |
| -2 | 39 | 39 |
| -4 | 37 | 34 |
| -6 | 22 | 20 |
| K= | 4 L= | 16 |
| -2 | 18 | 17 |
| K= | 4 L= | 17 |
| 0 | 31 | 47 |
| 4 | 24 | 24 |
| -4 | 30 | 31 |
| 6 | 16 | 17 |
| -8 | 21 | 21 |
| K= | 4 L= | 19 |
| 0 | 14 | 4 |
| -2 | 32 | 38 |
| -6 | 29 | 26 |
| K= | 4 L= | 20 |
| 2 | 21 | 17 |
| -2 | 25 | 30 |
| 4 | 20 | 18 |
| K= | 4 L= | 21 |
| -2 | 17 | 15 |
| 4 | 18 | 18 |
| K= | 4 L= | 22 |
| 0 | 14 | 20 |
| K= | 4 L= | 23 |
| 2 | 17 | 18 |
| -4 | 16 | 18 |
| K= | 5 L= | 0 |
| 3 | 35 | 33 |
| 9 | 18 | 17 |
| K= | 5 L= | 1 |
| 1 | 65 | 59 |
| -1 | 34 | 33 |
| -3 | 21 | 18 |
| 5 | 61 | 58 |
| 7 | 26 | 26 |
| -7 | 21 | 19 |
| 9 | 19 | 17 |
| -9 | 16 | 18 |
| K= | 5 L= | 2 |
| 1 | 15 | 12 |
| 3 | 21 | 19 |
| -3 | 23 | 21 |
| 5 | 24 | 23 |
| -5 | 15 | 15 |
| 7 | 31 | 32 |
| -7 | 18 | 10 |
| -9 | 18 | 19 |
| K= | 5 L= | 3 |
| -1 | 34 | 33 |
| 3 | 35 | 35 |
| -3 | 17 | 15 |
| 5 | 20 | 19 |
| -5 | 22 | 21 |
| 7 | 44 | 44 |
| -7 | 18 | 23 |
| K= | 5 L= | 4 |
| 1 | 30 | 27 |
| 3 | 28 | 30 |
| 5 | 23 | 22 |
| -5 | 28 | 29 |
| 7 | 21 | 22 |
| K= | 5 L= | 5 |
| 1 | 53 | 50 |
| -1 | 61 | 59 |
| 3 | 34 | 32 |
| 5 | 49 | 46 |
| -5 | 28 | 28 |
| K= | 5 L= | 6 |
| 1 | 35 | 37 |
| 5 | 31 | 30 |
| K= | 5 L= | 7 |
| 1 | 68 | 68 |
| 3 | 24 | 25 |
| -3 | 43 | 44 |
| 5 | 45 | 45 |
| -5 | 20 | 17 |
| 7 | 32 | 31 |
| -9 | 18 | 19 |
| K= | 5 L= | 8 |
| 1 | 25 | 21 |
| -1 | 33 | 37 |
| 3 | 29 | 30 |
| -3 | 17 | 17 |
| K= | 5 L= | 9 |
| -1 | 61 | 59 |
| 3 | 42 | 42 |
| -3 | 15 | 12 |
| -5 | 34 | 35 |
| 7 | 18 | 20 |
| -7 | 22 | 23 |
| K= | 5 L= | 10 |
| -1 | 23 | 20 |
| -3 | 17 | 14 |
| -5 | 23 | 22 |
| K= | 5 L= | 11 |
| 1 | 60 | 59 |
| -1 | 26 | 28 |
| -3 | 42 | 43 |
| 5 | 30 | 29 |
| -9 | 20 | 19 |
| K= | 5 L= | 12 |
| 1 | 18 | 10 |
| -3 | 18 | 17 |
| K= | 5 L= | 13 |
| 1 | 22 | 26 |
| -1 | 18 | 15 |
| 3 | 17 | 17 |
| -3 | 20 | 21 |
| 5 | 19 | 20 |
| -7 | 18 | 20 |
| K= | 5 L= | 15 |
| -1 | 30 | 32 |
| 3 | 18 | 20 |
| -5 | 21 | 23 |
| K= | 5 L= | 17 |
| 1 | 34 | 32 |
| -1 | 21 | 19 |
| 5 | 34 | 31 |
| K= | 5 L= | 19 |
| 1 | 17 | 18 |
| -1 | 22 | 20 |
| 3 | 26 | 24 |
| -3 | 26 | 25 |
| K= | 5 L= | 21 |
| 1 | 24 | 20 |
| K= | 6 L= | 0 |
| 0 | 54 | 49 |
| 4 | 25 | 24 |
| 6 | 22 | 23 |
| K= | 6 L= | 2 |
| 2 | 24 | 22 |
| -2 | 15 | 15 |
| 6 | 31 | 29 |
| K= | 6 L= | 3 |
| 2 | 17 | 18 |
| K= | 6 L= | 4 |
| 0 | 22 | 23 |
| -2 | 31 | 31 |
| 4 | 20 | 22 |
| -6 | 22 | 24 |
| K= | 6 L= | 5 |
| 0 | 24 | 20 |
| -4 | 15 | 14 |
| K= | 6 L= | 6 |
| 0 | 25 | 23 |
| 2 | 17 | 18 |
| -4 | 24 | 20 |
| 6 | 32 | 33 |
| -6 | 18 | 16 |
| K= | 6 L= | 7 |
| 0 | 23 | 22 |
| 4 | 17 | 19 |
| K= | 6 L= | 8 |
| 2 | 23 | 24 |
| -2 | 21 | 21 |
| 4 | 16 | 15 |
| -4 | 27 | 24 |
| K= | 6 L= | 9 |
| -2 | 18 | 18 |

TABLE XXVII (Continued)

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

| | | |
|---|---|---|
| K= | 6 | L= 10 |
| 0 | 27 | 29 |
| 4 | 23 | 25 |
| -6 | 24 | 24 |
| K= | 6 | L= 12 |
| 0 | 25 | 21 |
| 2 | 28 | 28 |
| -4 | 22 | 21 |
| K= | 6 | L= 14 |
| -2 | 20 | 22 |
| K= | 6 | L= 16 |
| 0 | 24 | 23 |
| K= | 7 | L= 0 |
| 1 | 19 | 16 |
| K= | 7 | L= 1 |
| 1 | 17 | 13 |
| K= | 7 | L= 2 |
| 1 | 18 | 18 |
| K= | 7 | L= 3 |
| 3 | 19 | 18 |
| K= | 7 | L= 7 |
| 1 | 23 | 22 |

TABLE XXVII (Continued)

Observed and Calculated Structure Factors for $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$.

TABLE XXVIII

Phosphorus-Carbon Bond Lengths in Various Compounds

| COMPOUND | | |
|---|---|---|
| Dimethyl Phosphinic Acid | x-ray[a] | 1.78A (52) |
| 2-Aminoethyl Phosphonic Acid | x-ray | 1.81A (53) |
| 9,10-Dihydro-9-Hydroxy-9-Phosphaphenanthrene-9-Oxide | x-ray | 1.80, 1.79A (54) |
| 1,2-Dimethyl-1,2-Diphenyl Diphosphine Disulfide | x-ray | 1.82A methyl<br>1.88A phenyl (55) |
| Trimethyl Phosphine | e.d.[b] | 1.87A (56) |

[a] x-ray = x-ray diffraction

[b] e.d. = electron diffraction

bonding orbitals. The P-C bonds of 2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate are both 1.83A in length which is slightly shorter than the sum of the covalent radii, 1.87A (51). Table XXVIII lists several P-C bond lengths for comparison.

The hydroxyl group forms an angle of 104.4° with the ring and the phosphoryl oxygen an angle of 141.9° with the ring. The molecule is oriented around the two-fold screw axis in the y-direction and the phosphoryl oxygen of the molecule is hydrogen bonded O(1)-O(3) (2.72A) to a water molecule across this two-fold screw axis. This forms the backbone of a continuous chain made up of phosphinic acid molecules and water molecules. The two-fold screw rotates the water molecule, which is hydrogen bonded to the phosphoryl oxygen, 180° and then translates it 1/2 the unit cell (3.26A) in the y-direction, thus placing an equivalent water O(3') near enough to the hydroxyl group O(2) to form a hydrogen bond with it O(3')-O(2) (2.49A). This is a very short hydrogen bond. The screw related water is also hydrogen bonded to the phosphoryl oxygen O(3')-O(1) (2.77A) of the phosphinic acid molecule. This is illustrated in Figure 10. The hydrogen bonded oxygen angles are given in Table XXIX. The methyl hydrogen densities appear as a toroid of electron densities on the difference map. The hydrogen bound hydrogens do not appear as discrete densities on the difference map. It is likely that the hydrogens have a great deal of thermal motion, as expected, since the melting point of the compound is 75-76° C. The effect of the hydrogen bonding is to produce an infinite zig-zag chain of molecules in the y-direction. This chain is, apparently, built up by hydrogen bonding the oxydimers to one

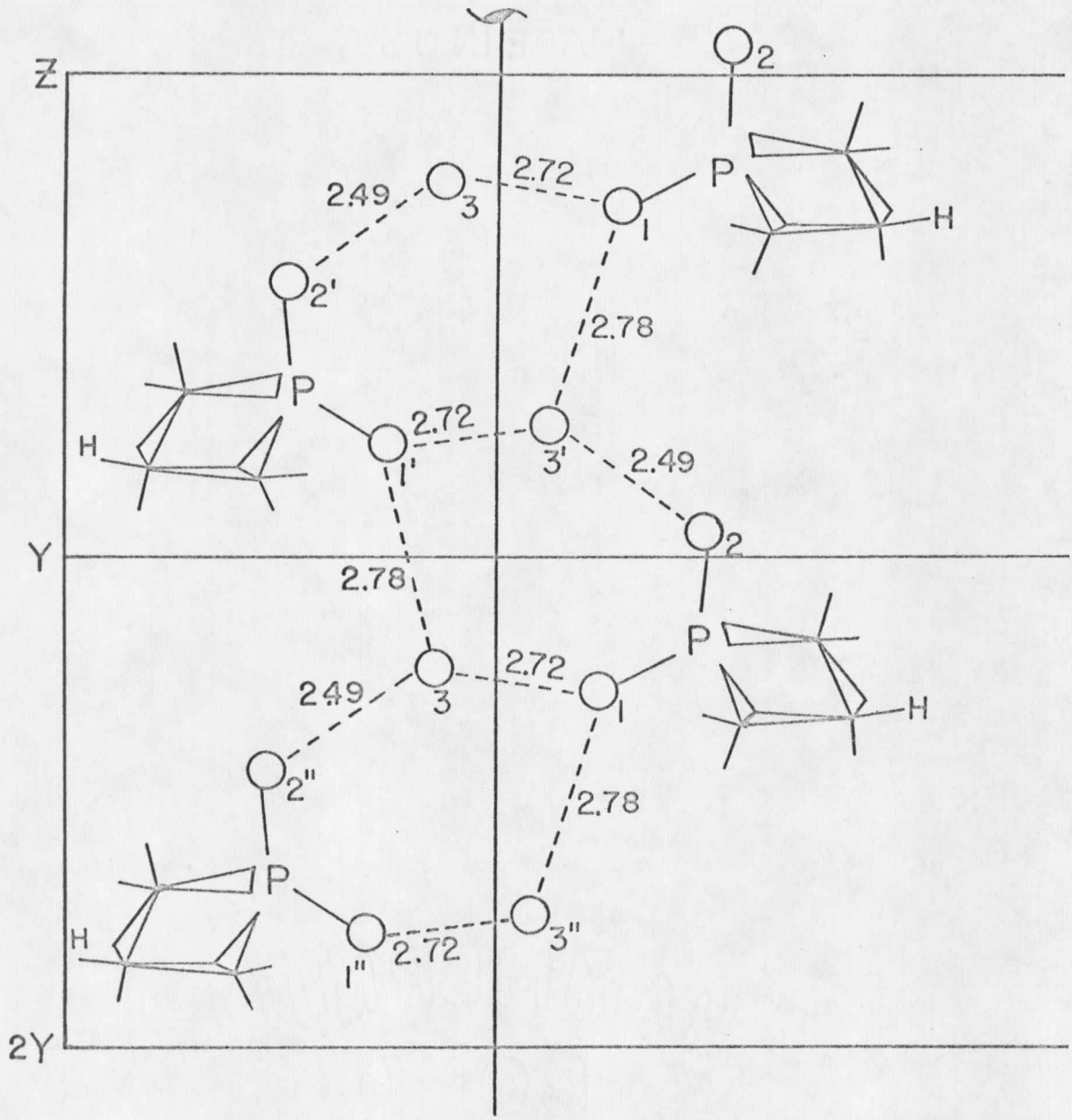



FIGURE 10. Hydrogen Bonding in 2,3,4-Trimethylpentane-2,4-Phosphinic Acid Monohydrate.

TABLE XXIX

Hydrogen Bonding Angles in $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$

| ATOMS | DEGREES |
|---|---|
| O(3')-O(1)-O(3) | 92.4(3)[a] |
| O(1)-O(3)-O(2') | 112.6(3) |
| O(3)-O(2')-O(1') | 102.5(4) |
| P-O(1')-O(3') | 132.0(4) |
| O(1')-O(3')-O(1) | 112.0(3) |
| O(1)-O(3')-O(2) | 113.9(3) |
| O(1')-O(3')-O(2) | 112.6(4) |

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

another through the water molecules. The molecules are reported to be partially associated in solution with n=1.7 (39). The phosphoryl oxygen distance (1.48A) is longer than a normal non-hydrogen bound oxygen (1.43A) indicating that some of the electron density is being distributed over both oxygen centers.

Phosphinic acids and related phosphorus containing acids have a common tendency towards formation, in the solid state, of long chains of molecules held together by strong hydrogen bonds. Not only does it occur in the compound studied, but also in phosphoric acid [O-O, 2.53, 2.84A (57)], dimethyl phosphinic acid [O-O, 2.48A (52)], 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene-9-oxide [O-O, 2.53A (54)], and 2-aminoethyl phosphonic acid [O-O, 2.53A (53)]. Each of these compounds also shows an increase in the P-OH bond which is hydrogen bound. Thus, indicating that the electron density is spread over two oxygen centers.

## SUMMARY AND CONCLUSIONS

The structures reported in this dissertation have provided a considerable number of facts which have led to a better understanding of the chemistry of organic cyclic compounds of phosphorus. The following results are most significant.

The rate of hydrolysis of five-membered cyclic phosphates is much greater than that for non-cyclic and larger or smaller cyclic phosphates. This rate has been attributed to a number of factors including ring strain, bonding, and ease of formation of the transition state.

With the discovery that in the hydrolysis of ethylene phosphate, in acid solution enriched with $O^{18}$, the phosphoryl group had undergone acid catalyzed exchange of oxygen with the water of the solvent prior to hydrolysis and that the rate of exchange was of the same order as the hydrolysis, the argument that the enhanced rate of hydrolysis was due entirely to the relief of strain by ring opening had to be abandoned. It must be concluded that the strain must be relieved in the transition state for both hydrolysis and exchange, although the final product of the hydrolysis no longer contains the strain while in the "final product" of the exchange, recoverable ethylene phosphate, the strain is still present. Two possible intermediates satisfy these requirements; a trigonal bipyramid and a square planar complex. Since all reported instances of nucleophilic attack at phosphorus lead to inversion of configuration and only via the trigonal bipyramid leads to inversion, it is the preferred geometry.

The ease with which the five-membered cyclic phosphate can form the

five coordinated trigonal bipyramid probably accounts for part of the low activation energy required for hydrolysis. This ease is due mainly to the low O-P-O ring angle of 97.3°. A small change will bring this close to the required angle of 90° in the pentavalent intermediate. The actual ring angle found in $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ was 87.3°. Since the transition state for nucleophilic attack at phosphorus in the cyclic compounds must be closer in geometry to the ground state than that of the acyclic compounds, the suggestion is strong that the geometry of the normal nucleophilic attack at phosphorus involves rehybridization of phosphorus so that the substituents are located similarly to those of the ground state of the five-membered ring compounds. If one or more of the empty d-orbitals of the phosphorus are low enough in energy, they could participate in this rehybridization to form the necessary $sp^3d$ orbitals. At the same time, they would also participate in the bonding of the cyclic phosphate in the ground state. Evidence in acetionenediol cyclophosphate suggests that the $d_{xy}$ and $d_{yz}$ orbitals on the phosphorus atom overlap with the $p_y$ lone pair electrons on the methoxy oxygen creating d-p $\pi$ bonding, thus decreasing the external P-O bonds to 1.40 and 1.54A. Also, the fact that the methoxy groups of the three five-membered cyclic phosphates whose structures have been determined are either directly over the ring or 180° from this position clearly indicates the importance of $d_{xy}$ and $d_{yz}$ overlap with the $p_y$ lone pair electrons in these $P-OCH_3$ bonds. The transition state with the lowest energy then is one in which the five-membered ring occupies the axial-equatorial position since this incorporates the O-P-O angle best and, if applicable, places the most

electronegative atoms axial, thus stabilizing the molecule to a greater degree. The structure of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ and both forms of $PO_5(CH(CH_3)_2)_3C_{14}H_8$ contain the five-membered ring in the axial-equatorial position, thus supporting the hypothesis that this is the geometry of the transition state. In the case of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$, the favored geometry has both oxygens axial giving support to the arguments about placement of the most electronegative atoms, in trigonal bipyramids, in the axial positions. Thus, the high rates of hydrolysis of five-membered cyclic phosphates appears to be explained by the above arguments.

The structure of $PO_3(C_6H_5)_4(C_6H_4Br)C_5H_2$ has yielded further insight into the nature of carbon-carbon conjugation. The 1,4-diphenyl butadiene portion of the molecule has a considerable amount of conjugation, even though the phenyl groups are twisted with respect to the plane containing the butadiene group by $136^{\circ}32'$ and $13^{\circ}40'$. The distances are 1.47 and 1.48A to the phenyl groups. The bond order for these bonds is 1.10 while the bond orders in the butadiene group range from 1.25 to 1.80. Thus, $\pi$ p-p overlap can be decreased considerably by twisting and, yet, retain $\pi$ character.

The structure of $PO(OH)C_5H_7(CH_3)_3 \cdot H_2O$ has yielded more insight into the nature of hydrogen bonding and its effect on P-O bond lengths. A chain of molecules about the screw axis is held together by hydrogen bonds from the acid molecules to the water molecules in a fashion similar to other phosphinic and phosphonic acids which contain no water of hydration. The phosphoryl oxygen bond has been lengthened, 1.48 versus 1.43A for a normal P-O bond, due to the hydrogen bonding to the water molecule. This

increase occurs in all hydrogen bound phosphates and indicates distribution of the electron density over both oxygen centers. Even though the molecules are extensively hydrogen bound in the y-direction, these bonds are not strong enough to prevent the crystal from losing water of hydration when exposed to the atmosphere.

It will be noted that the isomer with the methyl group trans to the hydroxyl group was the structure determined even though both isomers existed in solution. Thus, the trans form is the least soluble of the two isomers.

One final point that should be brought out in regards to the use of direct methods for the solution of crystal structures. It has been the authors experience and, also, that of many others that the correct set of signs leading to the correct structure is not necessarily that set which has the highest probability of being correct.

## LITERATURE CITED


1. H.G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest", John Wiley and Sons, Inc., New York, N.Y., (1961).

2. T.A. Steitz and W.N. Lipscomb, J. Am. Chem. Soc., 87, 2488 (1965).

3. M.G. Newton, J.R. Cox, Jr., and J.A. Bertrand, J. Am. Chem. Soc., 88, 1503 (1966).

4. P.C. Haake and F.H. Westheimer, J. Am. Chem. Soc., 83, 1102 (1961).

5. E.A. Dennis and F.H. Westheimer, J. Am. Chem. Soc., 88, 3431 (1966).

6. W.C. Hamilton, S.J. LaPlaca and F. Ramirez, J. Am. Chem. Soc., 87, 127 (1965).

7. W.C. Hamilton, S.J. LaPlaca, F. Ramirez and C.P. Smith, J. Am. Chem. Soc., 89, 2268 (1967).

8. R.D. Spratley, W.C. Hamilton and J. Ladell, J. Am. Chem. Soc., 89, 2272 (1967).

9. A.L. Patterson, Phy. Rev., 46, 372 (1934).

10. M.J. Buerger, "Vector Space and its application in crystal-structure investigation", John Wiley and Sons, Inc., New York, N.Y., (1959).

11. D. Harker and J.S. Kasper, J. Chem. Phys., 15, 882 (1947).

12. Okaya and I. Nitta, Acta. Cryst., 5, 564 (1952).

13. J. Karle and H. Hauptman, Acta. Cryst., 3, 181 (1950).

14. H. Hauptman and J. Karle, Phys. Rev., 80, 244 (1950).

15. H. Hauptman and J. Karle, "The Solution of the Phase Problem I. The Centrosymmetric Crystal", Amer. Cryst. Assoc., Monograph No. 3, Edwards Brothers, Ann Arbor, Michigan, (1953).

16. I.L. Karle and J. Karle, Acta. Cryst., 16, 969 (1963).

17. W.H. Zachariasen, Acta. Cryst., 5, 68 (1952).

18. I.A. Ibers, "International Tables for Crystallography", Kynoch Press, Birmingham, England, Vol. III, pp 202-209 (1962).

19. G.A. Mair, Pure Chemistry Division, National Research Council, Ottawa, Canada (1963).

20. W.R. Busing, K.O. Martin and H.A. Levy, ORFLS-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1962).

21. J.M. Steward, "Crystal Structure Calculations System, X-ray 63", Technical Report TR-64-6, University of Maryland, College Park, Md. (1964).

22. R.D. Willett, C. Dwiggens, Jr., R. Kruh and R.E. Rundle, J. Chem. Phys., 38, 2429 (1963).

23. V. Schomaker, S. Waser, R.E. Marsh and G. Bergman, Acta. Cryst., 12, 600 (1959).

24. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, N.Y. (1954).

25. F. Ramirez, B. Hansen and N.B. Desai, J. Am. Chem. Soc., 84, 4588 (1962).

26. F. Ramirez, O.P. Madan, N.B. Desai, S. Meyerson and E.M. Banas, J. Am. Chem. Soc., 85, 2681 (1963).

27. G. Aksnes and K. Bergesen, Acta. Chem. Scand., 19, 931 (1965).

28. G. Aksnes and K. Bergesen, Acta. Chem. Scand., 20, 2508 (1966).

29. R.L. Collin, J. Am. Chem. Soc., 88, 3281 (1966).

30. D.A. Usher, E.A. Dennis and F.H. Westheimer, J. Am. Chem. Soc., 87, 2320 (1965).

31. "Steric Effects in Organic Chemistry", M.S. Newman, Ed., John Wiley and Sons, Inc., New York, N.Y., Table I, p 529 (1956).

32. R.D. Witters, "Single Crystal Orienter Setting", Harvey Mudd College, Claremont, Calif. (1965).

33. C.N. Caughlan, C.T. Li, G.W. Svetich, K.D. Watenpaugh, R.D. Witters, D.D. Swank, E. Enwall and G.D. Smith, Montana State University Crystallographic Library.

34. F.R. Ahmed, Division of Pure Physics, National Research Council, Ottawa, Canada (1966).

35. G.H. Stout and L.H. Jensen, "X-ray Structure Determination, a Practical Guide", Macmillan Co., New York, N.Y., pp 454-458 (1968).

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

37. D.W.J. Cruickshank, J. Chem. Soc., 5486 (1961).

38. The compound is named according to a system used by P. Haake, Wesleyan University, Conn.

39. J.J. McBride, Jr., E. Jungerman, J.V. Killhefer and R.J. Clutter, J. Org. Chem., 27, 1833 (1962).

40. E. Enwall, "Single Crystal Setting, DSET", Montana State University, Bozeman, Montana (1968).

41. E.R. Howells, D.C. Phillips and D. Rogers, Acta. Cryst., 3, 210 (1950).

42. J. Kumamoto, J.R. Cox, Jr. and F.H. Westheimer, J. Am. Chem. Soc., 78, 4858 (1956).

43. H.G. Khorana, G.M. Tener, R.S. Wright and J.G. Moffatt, J. Am. Chem. Soc., 79, 430 (1957).

44. A. Eberhard and F.H. Westheimer, J. Am. Chem. Soc., 87, 253 (1965).

45. E.A. Dennis and F.H. Westheimer, J. Am. Chem. Soc., 88, 3432 (1966).

46. D. Harker and J.S. Kasper, Acta. Cryst., 1, 70 (1948).

47. M.J. Buerger, "Crystal-Structure Analysis", John Wiley and Sons, Inc., New York, N.Y. (1960).

48. E.W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941).

49. E.B. Wilson, Jr., "An Introduction to Scientific Research", McGraw-Hill, New York, N.Y., pp 191-195 (1952).

50. F. Ramirez, O.P. Madan and C.P. Smith, J. Am. Chem. Soc., 87, 670 (1965).

51. L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, New York (1960).

52. F. Giordano and A. Ripamonti, Acta. Cryst., 22, 678 (1967).

53. Y. Okaya, Acta. Cryst., 20, 712 (1966).

54. P.J. Wheatly, J. Chem. Soc., 3733 (1962).

55. P.J. Wheatly, J. Chem. Soc., 523 (1960).

56. H.D. Springall and L.O. Brockway, J. Am. Chem. Soc., 60, 996 (1938).

57. S. Furberg, Acta. Chem. Scand., 9, 1557 (1955).

58. J.R. Cox, Jr., R.E. Wall and F.H. Westheimer, Chem, Ind., (London), 929 (1959).

Swank, Duane Douglas
Structural studies of cyclic organic phosphorus compounds