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Applications of New Methods of Structure Determination

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APPLICATIONS OF NEW METHODS OF

STRUCTURE DETERMINATION

BY

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APPLICATIONS OF NEW METHODS OF

STRUCTURE DETERMINATION

This dissertation is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable as meeting the dissertation requirements for the degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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Abstract

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Under the supervision of Dr. William Jensen

The structures of: 1) 2-piperidino-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan; 2) 2-phenoxy-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan; 3) 2-p-bromophenoxy-5-chloromethyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan have been resolved by x-ray single crystal studies. A Picker 4 circle diffractometer employing molybdenum x-rays and a zirconium filter was used to obtain accurate data. The space group of the first two compounds is $P2_1/c$ while that of the third is $Pca2_1$. The lattice constants of the compounds are: 1) $a = 10.035(8)Å$, $b = 6.503(4)$, $c = 20.19(1)$, $\beta = 96.8(3)°$; 2) $a = 6.237(3)Å$, $b = 11.437(5)$, $c = 19.419(9)$, $\beta = 109.95(3)$; and 3) $a = 12.67(2)Å$, $b = 9.13(1)$, $c = 11.89(1)$. Density measurements indicated 4 molecules per unit cell for all the compounds.

The structures of the first two compounds were solved by the direct method of symbolic addition as the initial sign determining process. The bromine atom of the third compound was located from a Patterson map and the remaining atoms located by Fourier and least squares techniques. All nonhydrogen atoms were anisotropically

refined. The final weighted R factors are: 0.033, 0.036, and 0.054.
The unweighted R factors are: 0.054, 0.063, and 0.12.

The amide derivative prefers the lone oxygen in the axial position
while the phenoxy and p-bromo-phenoxy derivatives prefer it in the
equatorial position.

Substituted 5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan compounds provide an interesting means of studying the reactions of the phosphorus atom. With the chloromethyl group and methyl group placed on carbon atom 5, the determination of inversion or retention of configuration about the phosphorus atom is possible.

Two piperidine substituted compounds have been reported.[1] The two are formed under widely differing reaction pathways, and each reaction seems to produce only one isomer. The two isomers have widely different melting points.

Two phenoxide derivatives are also formed. Reactions forming them seem to produce mixtures of the two isomers.[2] The ratios of the two products varies with reaction conditions. Again, widely differing melting points are observed.

Mixtures of any two isomers of the same derivative do not equilibrate upon heating to near the decomposition point. Indeed, mixtures have been subjected to sustained heating of 200°C for hours with insignificant changes observed in their ratios.[3] This could only be true if they were geometric isomers.

The two geometric isomers differ in axial-equatorial conformation of the methyl and chloromethyl groups on carbon atom 5. The hydrogen atoms on an axial positioned chloromethyl group have an nmr signal shifted up field from those of an equatorial positioned chloromethyl

group. The same is true for the methyl group hydrogens. Whether a
peak is due to the chloromethyl or methyl group can be verified from
the integrated peak intensity of the signal. The hydrogen atoms on
these two groups are observed as two single peaks.

Although one can determine the conformation on carbon atom 5
by using nmr spectra, he cannot unambiguously predict the conformation
of the phosphorus atom. To confirm inversion (or retention) of con-
figuration it is necessary to establish the conformation about the
phosphorus atom because changes observed in the conformation of carbon
atom 5 are not necessarily accompanied by changes in conformation
about the phosphorus atom.

X-ray single crystal studies were made on three substituted
phosphorinans to determine the conformation about the phosphorus atom.
The results of these investigations leave little doubt as to the
reaction pathway of substitution reactions involving phosphorinans
in these three types of compounds.

HISTORICAL

Basic Theory

While the x-ray spectrum produced by a Coolidge tube consists of a continuous background radiation usually referred to as "white radiation," it also has two sharp x-ray peaks designated as K_α and K_β.[4] These monochromatic peaks are intense and their wavelengths are a function of the type of metal used as the anode of the Coolidge tube.

X-rays can be produced by the bombardment of a metal target with high energy electrons. The effect of this beam is to dislodge electrons belonging to atoms in the target material. Electrons from higher energy levels replace the vacated orbitals, with a subsequent loss of potential energy.

The decrease in potential energy appears as radiation. The most intense radiation is caused by an electron going from an L shell to a K shell. It is a close doublet because of the closeness in energy of the two types of electrons in the L shell. The two radiations are given the symbols $K_\alpha 1$ and $K_\alpha 2$ and together are called $K_\bar{\alpha}$. X-ray single crystal studies use primarily this monochromatic x-radiation.

The x-ray tube is thus a source of radiation that is nearly monochromatic. Two types of x-rays were used for this investigation. They were molybdenum radiation whose characteristic wavelength is 0.7069 $\overset{o}{A}$ and copper radiation whose characteristic wavelength is 1.5418 $\overset{o}{A}$.

X-rays are reflected by a crystal according to the Bragg Equation which is:[5]

$$2d \sin\theta = n\lambda \tag{1}$$

The term, λ is the wavelength of the x-ray beam, d is the spacing between planes of atoms in the crystal, and θ is the angle of incidence.

The data obtained from the x-ray diffraction pattern of a crystal are a list of detected x-rays characterized by an angle of incidence relative to the orientation of the crystal and a specified intensity of the reflected beam.

The angle of incidence is determined by planes of atoms in the crystal (the distance between parallel planes as well as their orientation). It is a function of the crystal's lattice parameters.

Miller indices are used to catalogue reflected x-rays. In general h, k, and l describe the planes of atoms that are present in the crystal. The letters h, k, and l are the symbols used for Miller indices and correspond to whole number ratios of the lattice constants a, b, and c, which are needed to intercept sets of parallel planes in the crystal lattice.

The distance between given planes (d) can be found in any monoclinic crystal using the following equation:[6]

$$1/d^2 = (h^2/a^2 + l^2/c^2 - 2hl\cos\beta/ac)\sin^2\beta + k^2/b^2 \tag{2}$$

In this equation a, b, and c are lattice constants and the angle β is the unique angle between the a and c axis.

Equation 2 will also hold true for all crystals of orthorhombic or cubic symmetry. For example, in the orthorhombic case β is 90° and the equation is greatly simplified. The sine term is equal to one and the cosine term is equal to zero. It is simplified even more for the cubic case. Additional terms have to be added, however, for the triclinic case.

Mathematical Relationships

From the intensity of the reflected x-ray, a term (F) known as the structure factor may be calculated according to equation 3.

$$|F| = \sqrt{\frac{KI}{Lp}} \qquad (3)$$

I is the intensity of the x-ray beam, and K is a proportionality constant. It is common practice to give this structure factor the symbol (Fo) and call it the observed structure factor because it is derived from observed intensity data. The L and p terms are the Lorentz and polarization factors, respectively, and are basically a simple function of the Bragg angle 2θ. For a detailed discussion of L and p, consult Nuffield.[7]

In addition to having a numerical value, the structure factor must have a sign corresponding to its phase. The term F, as defined in equation 3, can have two values, one positive in sign and the

other numerically equal but negative in sign. Only one of them is correct. Determining which one is correct might be called the fundamental problem of crystal structure solutions.

The correct atom positions in the unit cell can be used to calculate the magnitude of the structure factor as well as its correct sign, which indicates its phase. This structure factor is given the symbol Fc and represents the calculated structure factor derived from atom positions.

Fc is calculated from the proposed atom positions according to equation 4.[8]

$$Fc = \sum A\sin(xh+yk+zl)2\pi + A\cos(xh+yk+zl)2\pi \tag{4}$$

The letters x, y, and z represent atom coordinates in terms of unit cell parameters. The summation is over all atom positions in the unit cell. The term A is the atomic scattering factor for each individual atom and is basically a function of the angle of reflection and the atomic number of the atom involved. It will be discussed in detail later. If all atoms or most of the atoms contribute to the structure factor in the same phase, the structure factor will have a relatively high value.

From the general structure factor terms (and mathematical relationships), the electron density at position x, y, and z expressed in unit cell fractions is equal to:[9]

$$\rho(x,y,z) = \frac{1}{V}\sum_h \sum_k \sum_l F_{hkl}\exp(-2\pi i(hx+ky+lz)) \tag{7}$$

Using this relationship it is possible to calculate an electron density map if one knows the signs of the structure factors. The term 1/V is the unit cell column and it normalizes the density in terms of electrons per cubic A. The term ρ is the electron density at position x, y, z.

After several atoms have been placed in the structure, it is often useful to calculate an electron density map of the unit cell using the structure factors. The remaining atoms of a molecule can usually be located if the signs of the calculated structure factors and the magnitudes of the observed structure factors are used to make an electron density map. This type of map is called a Fourier synthesis and is often used to locate atoms for the model structure.

The correct atom coordinates will give (using equation 4) a value of Fc which will match in magnitude the value of Fo. Since experimental errors are involved, no match of Fc to Fo will be perfect. A measure of how well the two agree is calculated by the following equation:

$$R = \frac{\Sigma||Fo|-|Fc||}{\Sigma|Fo|} \tag{5}$$

The R value is commonly called the reliability factor and is an arbitrary measure of the correctness of a structure.

There are many reflections which are only slightly above background. The accuracy of these reflections is obviously questionable.

The very intense reflections are also not as reliable as those of intermediate intensity. A structure refined and based heavily on these two types of reflections would not be a true representation of the molecule.

To compensate for the inherent errors of these two types of reflections, a weighting scheme is usually developed whereby the two extreme cases of reflections are not counted as heavily in the calculation of the R factor. A number known as the weight and given the symbol w is calculated for each reflection. It is a function of the estimated standard deviation of the intensity and must be calculated for every reflection. The R factor is then calculated according to the following equation:

$$R = \frac{\Sigma||wFo|-|wFc||}{\Sigma|wFo|} \tag{6}$$

A more valid structure model is obtained when this R factor is the one minimized. Once the R factor is sufficiently low the structure is declared solved. The atom coordinates may be used to calculate bond lengths, bond angles, etc. Diagrams of the molecule may also be made.

Methods of Solving Structures

The essential steps in a structure solution may be classified in two areas. First the trial structure is obtained. Many variations are known to accomplish this. The other and final step is the

refinement of the structure. Once the atom parameters are known approximately, a computer program is used to vary the positional parameters in such a way as to minimize the R factor. This step does not vary significantly regardless of what method is used to obtain the trial structure.

One direct method known as the symbolic addition process can be used to obtain a trial structure. This method is one of determining the signs of an arbitrary number of structure factors using mathematical relationships which will be described later in this thesis. These structure factors with their determined signs are then used to construct an electron density map. Regions of high electron density on the map are chosen for atom positions. These atom positions are used for a least-squares calculation of structure factors. The signs of the calculated structure factors and the magnitude of the observed structure factor are then used to construct a new electron density map. More atoms are then located and eventually all the structure is determined.

The symbolic addition process depends to a large extent on probability. Reflections that are high in intensity have statisticaly a large number of electrons within the crystal contributing in the same phase to the structure factor. If enough signs of structure factors with high intensity can be determined correctly, a Fourier synthesis will reveal sufficient atom positions to obtain a trial structure.

Intensity alone cannot be used as the criterion for the selection
of reflections for sign determination by symbolic addition. Because
atoms are not point charges, the x-ray beam when reflected behaves as
if it is not being reflected by all of the electrons in an atom. The
exact amount is always less than the number of electrons in the atom.
The amount of the electronic charge that the x-ray beam appears to be
reflected by, is known as the atomic scattering factor and is a
function of the angle of reflection. This scattering factor falls
off sharply with increasing angle of incidence (approximating half of
a Gaussian curve).

Thus, the intensity of reflected x-rays depends to a large extent
on the angle of reflection. An "E" value is calculated for each
reflection by the following equation to remove the angular dependency:

$$E = \sqrt{F_o^2 / \epsilon \sum_i^n A_i^2} \tag{8}$$

The term ϵ is a multiplicity factor and the summation is over all atoms
in the unit cell. A is the atomic scattering factor for atom i at that
angle. A high E value, thus, is the result of most of the atoms in the
unit cell diffracting the x-ray beam in the same phase angle.

Besides being useful in determining trial structures, E values can
reveal information about the crystal symmetry. E values are distribu-
ted statistically in such a way that they indicate whether a crystal
belongs to a centric or a non-centric space group. A centric space

group is one which has a similar atom positioned at -z, -y, -z for every atom positioned at x, y, z. Table 1 shows the expected values for the two classes of crystals.[10]

The number of reflections for which signs are to be determined is arbitrary and requires a decision by the crystallographer. A minimum of 5 reflections per atom is recommended.[11] If the standards for assigning are too high, an insufficient number of signs will be determined. Too many signs determined prevents one from finding a suitable trial structure.

If one uses 5 reflections per atom as a standard, a crystal with 16 atoms per unit cell would need the signs of 80 reflections determined. These reflections have 80^2 possible sign combinations. This is too many combinations to try even with today's high speed computers.

A system is needed to reduce the number of sign combinations to a reasonable number so that all possible sign combinations can be tried by Fourier synthesis.

Sayre is generally credited with the first basic method of relating the signs of reflections to each other when certain conditions of the Miller indexes are met.[12] His general equation is:

$$S(F_{hkl}) = S(F_{h'k'l'}) \cdot S(F_{h'-h\ k'-k\ l'-l})$$ (9)

The equation is not concerned with the magnitude of the product so much as with its sign. The equation states that the sign of the

Table 1

Statistics of E Values

Quantity	Centric	Acentric
Average value of E	0.798	0.886
Average value of E^2	1.000	1.000
Average value of $\left|E^2-1\right|$	0.968	0.736
Percentage greater than one	32.0	37.0
Percentage greater than two	5.0	1.8
Percentage greater than three	0.3	0.01

reflection on the left in equation 9 will be the same as the sign of the product of the two reflections on the right if the Miller indexes of the two reflections on the right yield the Miller indexes of the reflections on the left.

If E values are used with this relationship and the sign determination is treated statistically, the following formula is obtained:[13]

$$P = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{\sigma_1}{\sigma_2}\Sigma E_{hkl} \cdot E_{h'k'l'} \cdot E_{h-h'k-k'l-l'}\right) \qquad (10)$$

The term σ_1/σ_2 can be approximated by $1/n$ where n is the number of atoms present in the unit cell.[14] The procedure of determining signs was not generally applicable until Karle and Karle introduced the method of using letters to represent the sign of the reflection. The reflections with high E values are given letter symbols for their signs, and the letter symbol is used for sign determination.[15]

The letter represents its true sign and may at the beginning be equally probable of being plus or minus. Utilizing equation 10, the signs of other reflections may be determined. If 8-letter symbols are used (as was the case in this investigation), the possible sign combinations is reduced to 8^2. This is a drastic reduction from the possible combinations required for the 16 atom example, but still quite high.

Due to the trigonometrical dependance of the structure factor (equation 4), the sign of any one reflection is arbitrary and has the

effect of fixing at least one origin coordinate of the unit cell. In the primitive monoclinic system, three symbols may be assigned arbitrary values of signs (for simplicity +) to fix the origin of the unit cell. Each selected symbol has to assign only one origin coordinate, and therefore the three reflections must be selected by "parity arithmetic".[16] The possible sign combinations for a primitive monoclinic system using 8-letter symbols for signs may thus be reduced from 8^2 to 5^2.

With the aid of a contradiction table which numerically counts the number of times each sign combination is in conflict, the statistically favorable sign combinations can usually be reduced to 4 or less. All combinations can then be tried as the number of sign combinations is usually reduced to 4 or less.

An easier method than the symbolic addition process exists in solving a structure if an atom with a relatively high atomic number is present in the structure. This is an indirect method of structure solution and is known as the heavy atom method. The heavy atom contributes significantly to most of the structure factors. Thus by finding its position, the signs of most of the structure factors are calculated correctly.

A. L. Patterson developed the method that consists of constructing a map of the unit cell which indicates inter-atomic distances. The distances from peaks to the origin correspond to the distances between

atoms. The formula used is:[17]

$$P(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l /F_{hkl}/^2 \cos(2\pi(hx+ky+lz)) \qquad (11)$$

The terms on the right are the same as in equation (7). P is the height of the peak at coordinants x,y,z. Since all distances between all atoms are calculated, there are many peaks shown on this type of map. The peaks associated with the heavy atom are dominating, however. Fourier syntheses will frequently reveal the remaining portion of the molecule.

Peaks associated with distances between symmetry equivalent atoms are also shown. These peaks are known as Harker peaks.[18] By finding these peaks, the coordinates of the heavy atom can usually be obtained.

Obviously, if the position of the heavy atom is known, most of the structure factor signs will be calculated correctly when the heavy atom is placed in the structure.

After the trial structure is obtained, final refinement of the structure begins. This is usually a routine step handled primarily by the computer program. Most of the computer time used is required during this procedure. A computer program minimizes the R factor, calculates bond angles and distances, and determines standard deviations for all parameters. For this work a full matrix least squares procedure was used. Diagrams and models can then be prepared to picture the structure.

SAMPLE PREPARATION

The compounds used in the structure determinations were synthe-
sized by Dr. William Wadsworth and Samuel Larsen.[19,20] The compound
cis-2-chloro-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan was
often used as an intermediate. For simplicity this compound will
hereafter be designated compound A.

Compound A was prepared by treating methyl bicyclic phosphite
with either chlorine gas or sulfuryl chloride. The latter reaction is
shown in Reaction 1.

$$CH_3C-CH_2O \xrightarrow{} P \qquad \xrightarrow{SO_2Cl_2} \qquad$$

Bicyclic phosphite   Compound A
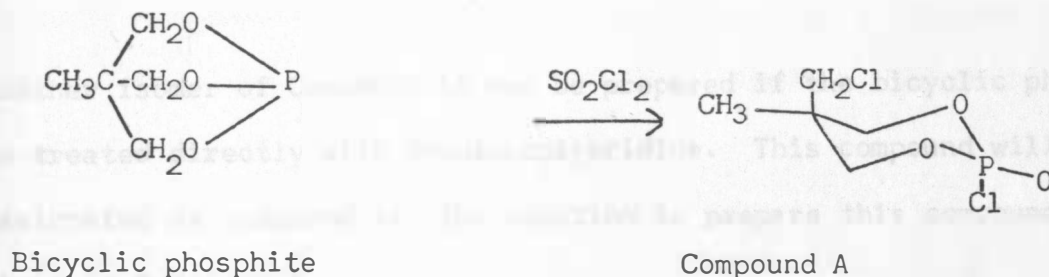
Reaction 1

The product, compound A, is recrystallized from CCl_4. Although its
structure has not been resolved by x-ray single crystal techniques,
compound A's similarity to its bromine analog in method of preparation
and nmr spectrum, leaves little doubt as to its structure. The bromo
analog has previously been solved by single crystal x-ray methods.[21]

The reaction of compound A with piperidine gives only one product
namely, 2-piperidine-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphos-
phorinan. The reaction is shown in Reaction 2. The lone oxygen has

been shown by this x-ray single crystal analysis to be in the axial

position and trans to the chloromethyl group. This compound will be

designated Compound 1A. Its melting point was found to be 182°C.[22]
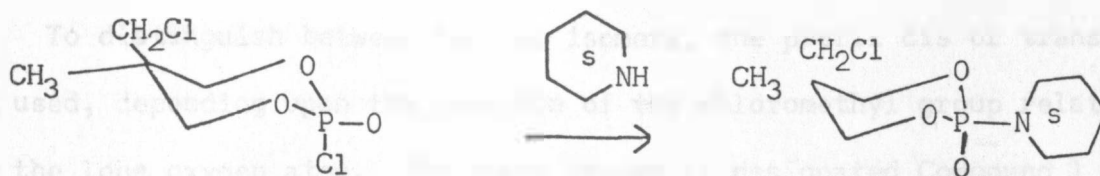
Compound A   Compound 1A

Reaction 2

Another isomer of Compound 1A can be prepared if the bicyclic phosphite

is treated directly with N-chloropiperidine. This compound will be

designated as Compound 1. The reaction to prepare this compound is

shown in Reaction 3.
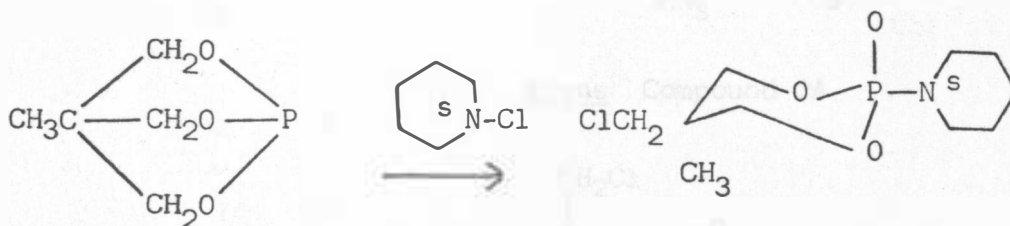
Bicyclic phosphite   Compound 1A

Reaction 3

Compound 1 has a melting point of 153°C.

The products of Reactions 2 and 3, and Compounds 1 and 1A, are geometric isomers since the molecular weights of the two are the same as are several other properties. Sustained heating of mixtures of the two have not produced isomeric equilibrium.[23]

To distinguish between the two isomers, the prefix cis or trans is used, depending upon the position of the chloromethyl group relative to the lone oxygen atom. The trans isomer is designated Compound 1 while the cis is Compound 1A. The cis isomer has been studied by nmr, but no x-ray structure determination has been attempted.

Unlike the amide derivative which gave only one product, two products are found when phenoxide ion is reacted with Compound A. The ratio of the two products varies with the strength of the nucleophiles. Reaction 4 describes their preparation.
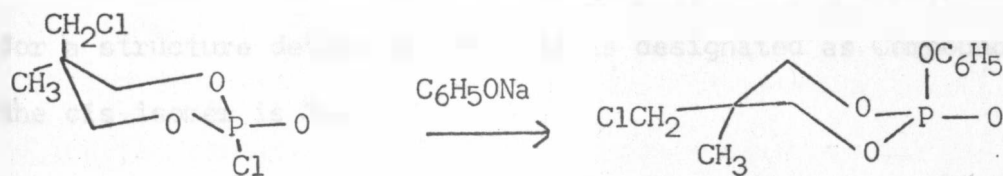
trans Compound 2A
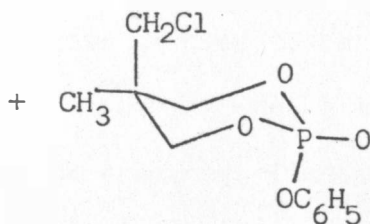
cis Compound 2

Reaction 4

The two products are the trans and cis forms of 2-phenoxy-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan and will be designated Compound 2A and Compound 2, respectively. From x-ray single crystal analysis the oxygen atom in this case prefers the equatorial position.

The trans isomer of Reaction 4, Compound 2A, did not lend itself to a single crystal structure determination. It belonged to a non-centric space group which, together with its lack of a relatively heavy atom, made its structure determination appear to be time consuming if not impossible.

The trans isomer of the p-bromophenoxide derivative, while similarly belonging to a non-centric space group, had a heavy atom present. Its production was carried out in a similar manner as Reaction 4. Since a heavy atom was present, the trans isomer was prepared and used for a structure determination. It is designated as Compound 3 while the cis isomer is 3A.

EXPERIMENTAL

Weissenberg Film Data

The film data was collected at South Dakota State University using a Nonuis, Weissenberg camera Manufactured in Delft, Holland. A copper anode x-ray tube was used together with a nickel filter. The diffractometer data collected at Lawrence Livermore Laboratory was obtained using a molybdenum x-ray tube with a zirconium filter.

Using a Weissenberg film camera, suitable single crystals were aligned along one of the direct crystal axis. A correctly aligned crystal has an oscillation photograph characterized by vertical rows of x-ray reflections.[24] Oscillation photographs were exposed by rotating the crystal 20° to either side of a central axis. The center row of reflections, (that is the line of reflections passing through the unreflected x-ray beam) is composed of all reflections that have a Miller index of 0 relative to the axis of rotation. For example, if b axis rotation is used all k Miller indexes are 0. The first row on either side of the center row contains the reflections which have Miller indexes equal to 1 and -1. The second row 2 and -2, etc.

The oscillation photograph can be used to reveal information about the crystal. The lattice constant corresponding to the axis of rotation can be determined, as well as the symmetry of that axis. A mirror plane present in the oscillation photograph indicates the crystal belongs to the monoclinic class or one with higher symmetry. The absence

of a mirror plane on a correctly aligned crystal means the crystal belongs to the monoclinic class or lower.

The numerical value of the axis of rotation may be calculated from the oscillation photograph by measuring the distances between vertical rows of reflections. The distances are then used for y_n in equation 12.[25]

$$d = \frac{n\lambda}{\sin[(\tan^{-1}(y_n/R)]} \qquad (12)$$

R is the camera radius and n is the number corresponding to the number of the row from the center of the film. The value of the axis of rotation, d, can be calculated as many times as there are pairs of vertical rows. The various measured values can then be averaged together for a more accurate value.

To compensate for film shrinkage, some films were doubly exposed, first by the sample crystal and second by a sodium chloride standard crystal. Knowing the lattice constants of NaCl accurately, equation 12 was employed to determine the factor for film shrinkage. The sodium chloride double exposure technique was used with crystals of Compounds 1 and 2.

The values of lattice constants shown in Table 2 were obtained from Weissenberg oscillation photographs. If a sodium chloride standard was employed, it is indicated in the table. The more accurate diffractometer data (the method of obtaining this data will be described later) is shown for comparison.

Table 2

Lattice Constants Obtained from Weissenberg Oscillation Photographs

Compound	NaCl Standard	Film Value	Diffractometer Value	Mirror Plane
1	yes	6.52A	6.503A	yes
2	yes	11.16	11.43	yes
2A	no	6.51	not taken	yes
3	no	9.15	9.13	yes

On either side of the center row of reflected x-ray spots, the rows were identical. Mirror planes were present in the oscillation photographs. Thus, all compounds were known to be of monoclinic or higher symmetry. Compounds 1 and 2 were found to be monoclinic, while Compounds 2A and 3 were found to be orthorhombic.

The preliminary oscillation photographs serve one other purpose. Crystals must be exactly aligned before a Weissenberg moving film technique exposure can be made. The oscillation photograph provides the means to do this.

The Weissenberg moving film technique spreads a vertical line of reflections, observed on an oscillation photograph, over the entire film. This is accomplished by the film moving simultaneously as the crystal is being rotated. Each exposure of this type represents a layer line, in which one Miller index is common to all reflections. Because the center row is the zero layer line, the remaining layer lines are numbered outward consecutively. While a convenient exposure time varied on an oscillation photograph from 20 to 60 minutes, the moving film Weissenberg exposure took considerably longer. The exact time varied with the size of the crystal and whether all possible reflections or just the more intense reflections were desired.

The method of identifying and labeling reflected x-ray spots on Weissenberg films (using Miller indexes) was carried out as described by Stout and Jensen.[26] On the O layer line films, with a "b" axis rotation, all reflections with a k Miller index equal to O would be

observed; on the first layer line, all reflections indexed with a k

value of 1 would be observed; further layer lines contain reflections

with higher k values.

Using the zero and first layer lines, the systematic absences

shown in Table 3 were determined. Compounds 1, 2, and 2A required

two crystal settings in order to obtain all systematic absences. No

other setting was necessary for Compound 3, as the (0, k, 0) systematic

absences were not needed to determine the unique space group.

The two remaining unknown lattice constants, those not the axis

of rotation, can be calculated using equation 13. The data is sup-

plied by the 0 layer Weissenberg moving film exposure.[27]

$$d = 2\sin(2y_n/4R \times 57.3) \tag{13}$$

The symbol d is the lattice constant being determined. The symbol y

is the distance from the base line on the film to be reflected x-ray

spot. The term n is the Miller index of the reflected spot. The

other two Miller indexes are 0. If the Weissenberg camera has a diam-

eter of 57.3 mm, the perpendicular distance y_n in mm is the value of

the sine angle function, $2y_n/4R \times 57.3$.

A NaCl standard can be doubly exposed with the sample in the same

manner as the oscillation exposure was. Corrections for film shrinkage

can thus be made.

Table 3

Conditions Limiting Possible Reflections

Compound	Conditions Necessary to Observe Reflection						
	(hkl)	(0kl)	(h0l)	(hk0)	(h00)	(0k0)	(00l)
1	*	*	$l=2n$	*	*	$k=2n$	*
2	*	*	$l=2n$	*	*	$k=2n$	*
3	*	$l=2n$	$h=2n$	*	$h=2n$	*	$l=2n$
2A	*	$k+l=2n$	$h=2n$	*	$h=2n$	$k=2n$	$l=2n$

*No conditions

Table 4 shows the lattice constants obtained by the Weissenberg film method. The more accurate diffractometer data which were obtained later are also shown for comparison.

Using the zero layer Weissenberg exposure, the angle between lattice axes can be obtained. The camera is precisely made so that a crystal rotation of 180° corresponds to a film-camera motion of 90 mm. The distance between the points where the base line intercepts the two axes can be readily measured. This distance in mm multiplied by 2 is the degrees of the angle between lattice axes. Table 5 shows the non-90° angles determined in this manner. Diffractometer values are shown for comparison.

Using systematic absences shown in Table 3, the space groups for each compound were determined.[28] The results are shown in Table 6.

The systematic absences for Compounds 3 and 2A allow two possible choices for space group assignments. In each case one of the choices is a centric space group, while the other is a non-centric space group. To belong to the centric space group, the choice must meet the special condition that a mirror plane be present in the molecule. Due to the proposed structure of the molecules, this requirement seems very unlikely.

In solving the structure for Compound 3, the non-centric case was assumed, and this assumption is verified by the successful solution of the structure. It would seem logical that Compound 2A would be similar. However, until the structure of Compound 2A is solved, its space group remains to be determined uniquely.

Table 4

Lattice Constants Obtained from Weissenberg Moving Film Photographs

Compound	NaCl Standard	Axis a		Axis c	
		Film Value	Diffractometer Value	Film Value	Diffractometer Value
1	yes	9.89A	10.035(8)A	20.0A	20.19(1)A
2	yes	6.16	6.237(3)	18.93	19.42(1)
2A	no	10.0	*	18.41	*
3	no	12.6	12.67(2)	11.8	11.89(1)

*Data not taken

Table 5

Non 90° Angles in the Monoclinic Crystals

Compound	Angle	
	Film Value	Diffractometer Value
1	97.0°	96.8(3)°
2	109.9	109.95(3)

Table 6

Space Groups of the Compounds

Compound	Space Group	Space Group Number
1	$P2_1/c$	14B
2	$P2_1/c$	14B
3	$Pca2_1$	29
	(not Pbcm)	57
2A	$Pna2_1$	33
	Pnma	62

Weissenberg photographs were used also for intensity measurements for Compounds 1 and 2. These intensity measurements were used for preliminary structure determinations for the two compounds but were not used for final refinement as more accurate diffractometer data became available.

To measure the intensity, a standard consisting of an x-ray film divided into 1/4 inch strips was prepared. Each strip on the film was exposed independently at the same crystal setting and to the same x-ray spot.

The strips on the standard were numbered consecutively higher with increasing exposure time. Exposure time increased by $\sqrt{2}$ with each strip. The standard was placed on top of the film that was to have the intensity of the reflected x-ray spots measured. For each reflection on the sample film, the reflected spot on the standard was found that matched it in darkness. The number of the strip on the standard film was then recorded for that reflection.

Since x-radiation follows Beer's Law, the number for this reflection was converted into intensity by the following formula:

$$I = K \exp (c) \tag{14}$$

I is the calculated intensity while c is the concentration of the x-ray spot (its darkness) and K is an arbitrary constant. The term c was the number of the standard spot assigned to the reflection multiplied by the square root of 2.

To obtain reflections of very low intensity on film it is necessary to use long exposure times. This presents a problem with very strong reflections, as long exposure times causes them to become too intense to measure. To overcome this problem, three sheets of film were placed in the camera and exposed simultaneously. A factor of about 4 was usually found, for intensity losses between successive films. Thus, the intensities of the more intense reflections were read from the bottom film while the very weak reflections were measured from the top film. Moderate intensity reflections were used to determine the film factors.

As a result of its extremely large size, the first crystal of Compound 1 revealed approximately 2,700 reflections which were recorded in six layer lines. The exposure time was 24 hours for each layer line. The x-ray tube settings were 35 KV and 17 ma. Some reflections with 2θ angles as much as 170° were shown.

Film intensity data were collected for Compound 2 in much the same manner as with Compound 1, except the a axis was used for the axis of rotation.

When using the Weissenberg film technique for the collection of intensity data, it is expedient to have as much data present on each film as possible. Fewer films are required. To accomplish this, the shortest axis is used for the axis of rotation. The total number of films required is less because fewer layer lines are required to collect the data. Also, fewer film factors are necessary to correlate the independently exposed layer line films.

Although the x-ray tube conditions are maintained the same throughout the data collection, the x-ray beam varies, due to uncontrolled variables such as line voltage. This makes duplications of exactly the same conditions for each layer line set of films impossible. Hence, a film factor to correlate layer lines is needed.

Since the b axis is the shortest axis for Compound 1, it was the axis of choice for rotation. The angle was observed on the zero line film. The -a and +a axis as well as the -c and +c axis were easily identified and no major problem arose in indexing.

The a axis of Compound 2 was the shortest axis and, therefore, was desired axis rotation for intensity data collection. In addition to being the shortest axis, the a axis of Compound 2 was also the needle axis and easily found. By mounting the crystal along the a axis the crystal approximated a cylinder which made the absorption of x-rays during the data collection easy to calculate.

Although the a axis is the desired axis of rotation indexing and measuring the β angle presented problems. This was due to the right angle relation between the b and c axes. The b and c axes were the two axes shown on the zero layer Weissenberg film. Although the angle can be measured from film data utilizing upper layer line photographs, the process is quite difficult because the geometry is complex.[29]

The problems were resolved by mounting another crystal which used the b axis for the axis of rotation. The zero and first layer lines were photographed. Comparing reflections of the b rotation films,

which were easily indexed, to the a rotation films made it possible to index the a rotation films. As an example the b rotation zero layer line film contained the (0, 0, 1) reflections and so did the zero layer a rotation.

By indexing the b rotation (0, 0, 1) row of reflections, the a rotation (0, 0, 1) row could be indexed. Once the pattern of indexing was established, the remainder of the reflections could be indexed.

Diffractometer Data

A crystal of Compound 1 was taken to Lawrence Livermore Laboratory to be used to collect a more accurate set of data using a computer controlled Picker 4 circle diffractometer. The crystal was determined to be too large; therefore, the process of obtaining a smaller crystal was undertaken. Since the search to find another single crystal was unsuccessful, the original crystal was placed in a solvent and allowed to be dissolved until it was of convenient size (0.2 x 0.2 x 0.3 mm). It was then remounted, aligned, indexed and sent to Lawrence Livermore Laboratory for intensity data collection. When collected, the data were sent to South Dakota State University.

An unexpected characteristic of Compound 2 was apparent after examining the diffractometer data. Except for the (0, k, 1) data (the 0 layer line), the intensities of the diffractometer data and the film data did not seem to be in agreement. The discovery was made

that there were two ways of indexing the crystal, both having approximately the same lattice constants. Both indexing systems used the same b axis but not the other axes. The angle β, though numerically about equal, did not describe the same quantity.

To convert the atom positions used on the film data to new positions which were equivalent for the diffractometer data, the following transformation equations were used:

$$x_{film} = x_d - 2z_d \tag{15}$$

$$y_{film} = y_d \tag{16}$$

$$z_{film} = z_d \tag{17}$$

The transformation proved successful and at this point the diffractometer data and film data were in agreement.

Unlike Compound 1, Compound 2 was not destined to be solved from film data. While still attempting a solution, the diffractometer data arrived and the new data were used for the remaining solution of the structure.

During the diffractometer data collection, all reflections within a maximum 2θ angle of 40° were recorded. For all reflections having a corrected intensity equal to zero or more than zero, a computer card was supplied having h, k, l, Fo, sinθ, and the intensity value punched on it. The standard deviation of the intensity (σ_I) was supplied in a computer printout. The way in which σ_I is calculated is described elsewhere.[30]

Accurate lattice constants and their estimated standard deviations were determined by the diffractometer and computer. This was accomplished by centering 12 reflections of moderately high angle of incidence through a narrow slit in the detector and measuring the angle of reflection. The lattice constants were then obtained by the method of least squares refinement by means of a PDP-8 computer. The results provided the lattice constants and their estimated standard deviations.

Data Reduction

To use the computer program adapted for a least squares calculation at South Dakota State University, each reflection must have a card and each card must have in addition to h, k, l, and Fo values, a term equal to $1/4d^2$. The atomic scattering factor which is a function of the angle of reflection, must appear on the card for each atom type present. It is also eventually necessary to have a 2-digit number which allows the least squares program to weigh each reflection. This number will be referred to hereafter as the weight number. It was decided that for accuracy and to save time, a program was necessary to punch cards from the data cards from Lawrence Livermore Laboratory. The format in which the data cards were to be punched for the least squares program as well as FAMEB is described in the appendix.

The term $1/4d^2$ was obtained using the Bragg Equation which is:

$$\lambda n = 2d\sin\theta \qquad (18)$$

It follows that:

$$1/4d^2 = \sin\theta/_{n\lambda^2} \tag{19}$$

Lambda was 0.70169 A since molybdenum radiation was used with the dif-
fractometer. The film data used copper radiation in which case λ
= 1.5418 A.

Scattering factors used initially with Compound 1 were obtained
from the "International Tables for X-ray Crystallography".[31] Since
the tables give scattering factor values for atoms every 0.05 value
of $\sin\theta/\lambda$, a graph was prepared for each atom type to obtain values
halfway between the given values (every 0.025 value). A computer
program was developed to interpolate values between the 0.025 values.

The process of obtaining scattering factors for nonhydrogen
atoms changed when new data cards were required. The scattering
factors were then calculated using the formula submitted by Cromer
et al. which is:[32]

$$f(\sin\theta/\lambda) = \sum_{i=1}^{4} a \exp(-b\sin^2\theta/\lambda^2) + c \tag{20}$$

Except for hydrogen atoms, this method was used to obtain scattering
factors for data cards used on all subsequent compounds. The con-
stants used, a_i, b_i(i = 1 to 4), and c were supplied by Cromer.[32]
Hydrogen atom scattering factors were obtained in the original manner
as no constants were supplied by Cromer for this atom.

Two spaces are reserved on the data card for the weight number. A weight number of zero can exclude a reflection from least squares calculation. The least squares program will calculate the proper weight for a reflection (based on the standard deviation of Fo) if the following value is calculated for the weight number:

$$w = (\sigma_I / I) \times 100 \tag{21}$$

Each reflection will have a weight equal to:

$$w = 1/\sigma^2_{Fo} \tag{22}$$

W is the weight of the reflection and not the weight number. The term σ_{Fo} is calculated by the computer using the following equation:[33]

$$\sigma_{Fo} = \frac{1}{2} \frac{k}{\sqrt{Lp}} \frac{\sigma_I}{\sqrt{I}} \tag{23}$$

The term σ_I is the standard deviation of the intensity. The other terms have the same meaning as in equation 3.

For the excluded reflections which were the ones that had corrected intensity values less than zero, a card was added for that reflection. This card contained the h, k, l values along with an Fo value of zero. The weight number was set at zero.

The Compound 2 diffractometer data cards had the σ values for each reflection added to them at South Dakota State University. This

enabled the weight number to be calculated and subsequently punched on the new data cards. No further punching of data cards was thus required for Compound 2.

This was not the case with Compound 1. The weight number was added after being calculated independently when the weighting scheme was desired. The excluded zero weight cards for Compound 1 were added when a calculation using all data points was desired.

Although the limit of the weight number is 99, it never goes above 33 when all reflections having an intensity less than 3 standard deviations are given zero weight. Care must be used for reflections having a calculated weight number less than 1. These are very accurate reflections, but if the weight number is rounded off to zero, the reflection will be excluded from calculations. The weight of this type of reflection should be 1.

The equation used to calculate the weight number from diffractometer data is:

$$w = \frac{(\sigma_i^2 + KI^2)^{\frac{1}{2}}}{I} \times 100 \tag{23}$$

K is an arbitrary constant usually equal to 0.01 or 0.02 depending upon the diffractometer used. The term σ_i is the counting standard deviation. The expression in equation 23, $(\sigma_I^2 + kI^2)^{\frac{1}{2}}$ is actually σ_I. A value of 0.01 was used for Compound 2.

For Compound 1, the weight number was calculated using this
formula:

$$w = \frac{\sigma_i}{I} \times 100 \qquad (24)$$

The effect was to give the more intense reflections more weight
than they deserve. Presumably, no major difference will be noticed.

SYMBOLIC ADDITION

The direct method of sign determining, symbolic addition, was used to initialize the sign determination in the solution of the structures of Compounds 1 and 2.

After a number of attempts at writing and using a symbolic addition program of our own, the programs MAGIC, LINK, and FAMEB as described in the appendix were obtained from Dr. Norman Baenziger (University of Iowa). The programs were adapted for use with the IBM 360/40 computer.

The program FAMEB is first used to generate E values from structure factor input data. It is possible to operate the program MAGIC with a pre-written tape made as one of the options of the program FAMEB. While there are, no doubt, many cases where the structure solving process can be left to the computer, for Compounds 1 and 2 this was not the case. Before using MAGIC, the output of routine FAMEB should be examined to see if the assigned symbols are the logical choices.

Because of the possible large printing output, the mode of operating MAGIC is important. If some of the printing is not suppressed (one of the options), it is possible to get a computer print-out stack approximately 3 inches thick containing information of marginal interest. Three runs were made using the program until it was learned how to suppress the unnecessary printing. With all excess printing stopped, the time of operation was about 20 minutes on the IBM 360/40 system.

The third time symbolic addition was run using Compound 1 was perhaps the first completely successful attempt. A total of 162 reflections were assigned letter symbols for their signs during the first iteration. A total of 280 signs were determined after the second iteration. The minimum probability value, 0.99, set at the start and controlled by the computer program did not change. The new atom positions found on the E map which followed allowed the R factor to go below 0.40 for Compound 1.

The overall process is an iterative one following the sign determinations of MAGIC. The most probable sign combinations of letter symbols are chosen by the program LINK. These signs are then used to make a Fourier-E map plot. From the map the best atom positions are chosen. These positions, shown by the E map, are then used as data for a least squares cycle for R factor determination.

The output of the least squares program is examined using the following criterion. If the observed structure factor is large and if the calculated structure factor is between 90 and 120 percent of the observed structure factor, the sign of the reflection is judged to have been determined correctly. While other atom positions added later might decrease the calculated structure factor, they could not decrease the structure factor enough to change its sign. The structure factors that obey this criterion are considered correct in sign. They are used as knowns for a succeeding run of symbolic addition. With each iteration of this nature the structure becomes more complete and more accurate.

By this method and least squares adjustment of atom parameters, Compound 1 was resolved and refined to an R factor value of 0.20 using film data. It may have been possible to carry the solution further; however diffractometer data became available at this point and were used for the remainder of the solution of the structure of Compound 1.

The symbolic addition process when attempted on Compound 2 using film data proved unsuccessful. Diffractometer data became available before a second try could be made and so was used for the next attempt. The first attempt with the new data did not at first lead to the solution of the structure either. The R factor was reduced to 0.30 but attempts to lower it further proved useless and the atom positions thought to be reasonable did not conform to any possible structure. The structure at this point was close to being classified as unsolvable.

A selective run of symbolic addition was initialed as follows upon the advice of Dr. Johnson.[34] All E values with one or more Miller index equal to zero were excluded from the known and unknown lists of input to the program MAGIC. Of the remaining unknowns, the signs of 48 unknowns were determined in two iterations of MAGIC. This brought the total knowns to 58. The reflections initially excluded were then included and the 58 determined signs were used as knowns for another calculation of symbolic addition. Some 184 reflections had their signs determined in two iterations with a minimum calculated probability of 0.9994. There had to be three contributers to each sign determined and no more than two inconsistencies were tolerated.

A careful study of the resulting E map revealed all of the non-hydrogen atom positions for Compound 2. However, proceeding cautiously, adding four or five atoms at a time, the nonhydrogen atoms were slowly but eventually all added. The least squares run in which all of the 17 nonhydrogen atoms were introduced, gave an R factor of slightly below 0.20.

COMPOUND 1

Preliminary

To obtain a suitable crystal for an x-ray single crystal structure analysis, crystals of Compound 1 were grown, making use of the compound's increasing solubility with temperature. The compound is soluble in many solvents and a 50 percent benzene-cyclohexane mixture was used as a recrystallizing solvent.

The crystal growing solution was carefully adjusted by boiling away or adding solvent so the saturation point was below 40°C but above 30°C. It was then placed in a vial in the growing apparatus described below where the temperature was adjusted to 45°C, before it was allowed to cool.

The crystal growing apparatus consisted of a wide mouth one liter vacuum Dewar flask with a 4-inch diameter opening at the top, placed inside a polystyrene five gallon acid bottle package.

The flask was filled with hot water and the sample vial was immersed in the water. The cooling rate was about 4°C per hour. After a few unsuccessful attempts, suitable crystals of Compound 1 were obtained.

From these crystals a hexagonal shaped plate with dimensions of 0.40 x 0.8 x 0.9 mm was mounted for the Weissenberg camera. The systematic absences found are shown in Table 3. These confirm that this crystal belongs to the $P2_1/c$ space group.

Density and unit cell volume measurements indicated a unit cell containing four molecules. The symmetry equivalent positions in the unit cell are[35] 1) x, y, z; 2) -x, -y, -z; 3) x, 0.5-y, 0.5+z; and 4) -x, 0.5+y, 0.5-z. The calculated density is 1.36 g/cm^3 and the observed density is 1.37 g/cm^3 (determined by the flotation method utilizing a potassium iodide solution).[36]

The diffractometer yielded 1,252 reflections, of which 944 were above three estimated standard deviations of their intensity. These 944 reflections were used for the final structure refinement.

The lattice constants for Compound 1 are: a = 10.035(8)Å; b = 6.503(4)Å; c = 20.19(1)Å; and β = 96.8(3)°. The numbers in parenthesis are the estimated standard deviations.

The agreement of the diffractometer data with the film data was indicated by the first least squares computer calculation when the new data was adapted. After the substitution of -x for all x values of the atom positions, necessitated by the left handed axis coordinates of the film data crystal, the R factor was 0.15.

Refinement of Structure

Inspecting the new diffractometer data revealed that three reflections, namely the (0, 2, 0); (2, 0, 0); and the (1, 1, 0) reflections were so intense that they were truncate to lower values. The program used at Lawrence Livermore Laboratory for data reduction could not handle intensity values greater than 10,000,000. The first

digit of the intensity value was removed from these three reflections.
As an example, 1,000,051 would be rounded off to 51. After correcting
these three reflections the R factor dropped about 1 percent.

The introduction of anisotropic temperature parameters, followed
by three cycles of least squares refinement, dropped the R factor to
0.09. A difference Fourier map was calculated to attempt to locate
the hydrogen atom positions. All hydrogen atoms were located and a
least squares cycle without varying any parameters diminished the R
factor by about 1 percent.

Due to the large number of parameters and limited computer stor-
age, all 190 parameters of the nonhydrogen atoms and the positional
parameters of the hydrogen atoms could not be minimized in one least
squares refinement cycle. By partitioning the parameters in groups
of about 70 for succeeding runs of the least squares program, the
final refinement of the structure was accomplished.

The R factor before the final refinement was started was 0.0945.
The position and temperature parameters of five atoms were allowed to
vary in two cycles with the result that the R factor dropped to 0.084.
All positional and temperature parameters of seven more nonhydrogen
atoms were varied and the R factor dropped to 0.035. Part of this
decline was due to the introduction of a weighting scheme at this
point.

The positional parameters of the hydrogen atoms were next varied
for two cycles of refinement and the R factor decreased to 0.033.

While the R factor of the weighted R factor was declining, so was the unweighted R factor. The unweighted R factor at this point was 0.054 using the 944 data points.

Results

When the weighted and unweighted R factor for 944 data points were 0.033 and 0.054, respectively, a final calculation with all 1,252 data points being assigned unit weights was made. This R factor was found to be 0.074.

Final positional parameters of the nonhydrogen atoms are shown in Table 7. The positional parameters of the hydrogen atoms are shown in Table 8. Bond distances as calculated by the program ORTEP are shown in Table 9. The standard deviations were calculated utilizing the program DINT at Lawrence Livermore Laboratory. Table 10 shows the angles between atoms with their estimated standard deviations found with the aid of the program DINT.

Figure 1 shows a drawing of the molecule. The drawings of the compound's structure were made using the program ORTEP and utilizing a Calcomp plotter. Figure 2 shows a stereo view of the molecule.

Table 11 shows the Fo and Fc values for the structure. Table 13 is E value statistics for the compound as calculated by the program FAMEB.

Table 12 contains the anisotropic temperature parameters for the nonhydrogen atoms. The hydrogen atoms were all assigned an arbitrary

Table 7

Positional Parameters of the Nonhydrogen Atoms
(x 10^4) for Compound 1

Cl	7088(2)	7043(3)	4370(1)
P	7651(2)	1725(3)	2587(1)
N	8356(5)	2707(7)	1983(2)
O(1)	6204(4)	2741(6)	2522(2)
O(2)	8342(4)	2775(6)	3257(2)
O(3)	7639(4)	-516(6)	2609(2)
C(1)	8000(7)	5350(10)	1130(4)
C(2)	5477(6)	2893(10)	4315(3)
C(3)	6250(6)	3449(10)	3732(3)
C(4)	5464(6)	2518(9)	3102(3)
C(5)	7636(6)	2506(9)	3841(3)
C(6)	8391(6)	4940(10)	1853(3)
C(7)	8882(6)	4166(10)	712(3)
C(8)	9266(6)	1500(10)	1608(3)
C(9)	8863(7)	1850(10)	869(3)
C(10)	6291(6)	5800(10)	3629(3)

Table 8

Position Parameters of the Hydrogen Atoms
(x 10^4) for Compound 1

Atom	x	y	z
H(1)	910(5)	-9(8)	170(2)
H(2)	967(5)	112(8)	62(2)
H(3)	452(5)	325(8)	296(2)
H(4)	597(5)	244(9)	476(2)
H(5)	540(5)	150(8)	435(2)
H(6)	453(5)	361(8)	427(2)
H(7)	533(5)	632(8)	359(2)
H(8)	680(5)	618(8)	329(2)
H(9)	762(5)	93(8)	394(2)
H(10)	821(5)	321(8)	420(2)
H(11)	522(5)	101(9)	313(2)
H(12)	793(5)	563(9)	217(2)
H(13)	934(5)	549(8)	199(2)
H(14)	806(5)	680(9)	100(2)
H(15)	700(5)	492(9)	99(2)
H(16)	986(5)	426(8)	80(2)
H(17)	854(5)	460(8)	25(2)
H(18)	785(5)	217(8)	177(2)
H(19)	1017(5)	217(8)	177(2)

Table 9

Interatomic Distances (Å) for Compound 1

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cl	C(10)	1.802(7)Å	C(4)	H(10)	1.02(6)Å
P	O(3)	1.458(4)	C(4)	H(18)	1.07(5)
P	O(1)	1.586(4)	C(4)	O(1)	1.467(8)
P	O(2)	1.598(5)	C(5)	H(11)	0.99(5)
P	N	1.613(6)	C(5)	H(12)	1.04(5)
N	C(6)	1.474(8)	C(5)	O(2)	1.457(7)
N	C(8)	1.480(8)	C(6)	H(9)	0.95(5)
C(1)	H(7)	0.98(6)	C(6)	H(8)	1.03(5)
C(1)	H(6)	1.05(5)	C(7)	H(5)	0.98(5)
C(1)	C(6)	1.490(9)	C(7)	H(4)	1.01(5)
C(1)	C(7)	1.50(1)	C(7)	C(9)	1.54(1)
C(2)	H(16)	0.91(5)	C(8)	H(2)	1.03(5)
C(2)	H(17)	1.04(5)	C(8)	H(1)	1.07(6)
C(2)	H(15)	1.05(5)	C(8)	C(9)	1.515(8)
C(2)	C(3)	1.528(9)	C(9)	H(3)	1.09(5)
C(3)	C(5)	1.513(9)	C(9)	H(19)	1.10(5)
C(3)	C(4)	1.539(9)	C(10)	H(13)	0.93(5)
C(3)	C(10)	1.546(9)	C(10)	H(14)	1.02(5)

Table 10

Interatomic Angles for Compound 1

O(3)	P	O(1)	114.1(2)°	H(11)	C(5)	O(2)	104(3)°
O(3)	P	O(2)	113.9(2)	H(11)	C(5)	C(3)	111(3)
O(3)	P	N	115.1(3)	H(12)	C(5)	O(2)	106(3)
O(1)	P	O(2)	101.2(3)	H(12)	C(5)	C(3)	113(3)
O(1)	P	N	104.6(3)	O(2)	C(5)	C(3)	111.1(5)
O(2)	P	N	106.6(2)	H(9)	C(6)	H(8)	99(4)
C(6)	N	C(8)	113.7(5)	H(9)	C(6)	N	109(3)
C(6)	N	P	123.1(4)	H(9)	C(6)	C(1)	119(3)
C(8)	N	P	122.0(4)	H(8)	C(6)	N	110(3)
C(4)	O(1)	P	115.9(4)	N	C(6)	C(1)	110.1(5)
C(5)	O(2)	P	115.5(4)	H(5)	C(7)	H(4)	112(4)
C(7)	C(1)	H(6)	106(4)	H(5)	C(7)	C(1)	121(3)
H(7)	C(1)	C(6)	110(3)	H(5)	C(7)	C(9)	93(3)
H(7)	C(1)	C(7)	106(3)	H(4)	C(7)	C(1)	103(3)
H(6)	C(1)	C(6)	110(3)	H(4)	C(6)	C(9)	117(3)
H(6)	C(1)	C(7)	109(3)	C(1)	C(7)	C(9)	111.3(6)
C(6)	C(1)	C(7)	110.6(6)	H(2)	C(8)	H(1)	120(4)
H(16)	C(2)	H(17)	108(4)	H(2)	C(8)	N	101(3)
H(16)	C(2)	H(15)	111(4)	H(2)	C(8)	C(9)	112(3)
H(16)	C(2)	C(3)	110(3)	H(1)	C(8)	N	108(3)
H(17)	C(2)	H(15)	105(4)	H(1)	C(8)	C(9)	107(3)
H(17)	C(2)	C(3)	111(3)	N	C(8)	C(9)	108.4(5)
H(15)	C(2)	C(3)	112(3)	H(3)	C(9)	H(19)	116(4)
C(5)	C(3)	C(2)	109.5(5)	H(3)	C(9)	C(8)	108(2)
C(5)	C(3)	C(4)	109.4(5)	H(3)	C(9)	C(7)	110(3)
C(5)	C(3)	C(10)	112.5(5)	H(19)	C(9)	C(8)	105(3)
C(2)	C(3)	C(4)	106.7(5)	H(19)	C(9)	C(7)	107(3)
C(2)	C(3)	C(10)	111.3(5)	C(8)	C(9)	C(7)	110.1(6)
C(4)	C(3)	C(10)	107.2(5)	H(13)	C(10)	H(14)	117(4)
H(10)	C(4)	H(18)	104(4)	H(13)	C(10)	C(3)	113(3)
H(10)	C(4)	O(1)	107(3)	H(13)	C(10)	Cl	105(3)
H(10)	C(4)	O(3)	116(3)	H(14)	C(10)	C(3)	107(3)
H(18)	C(4)	O(1)	105(2)	H(14)	C(10)	Cl	104(3)
H(18)	C(4)	C(3)	113(3)	C(3)	C(10)	Cl	110.3(4)
O(1)	C(4)	C(3)	111.3(5)	H(8)	C(6)	Cl	109(3)
H(11)	C(5)	H(12)	110(4)				
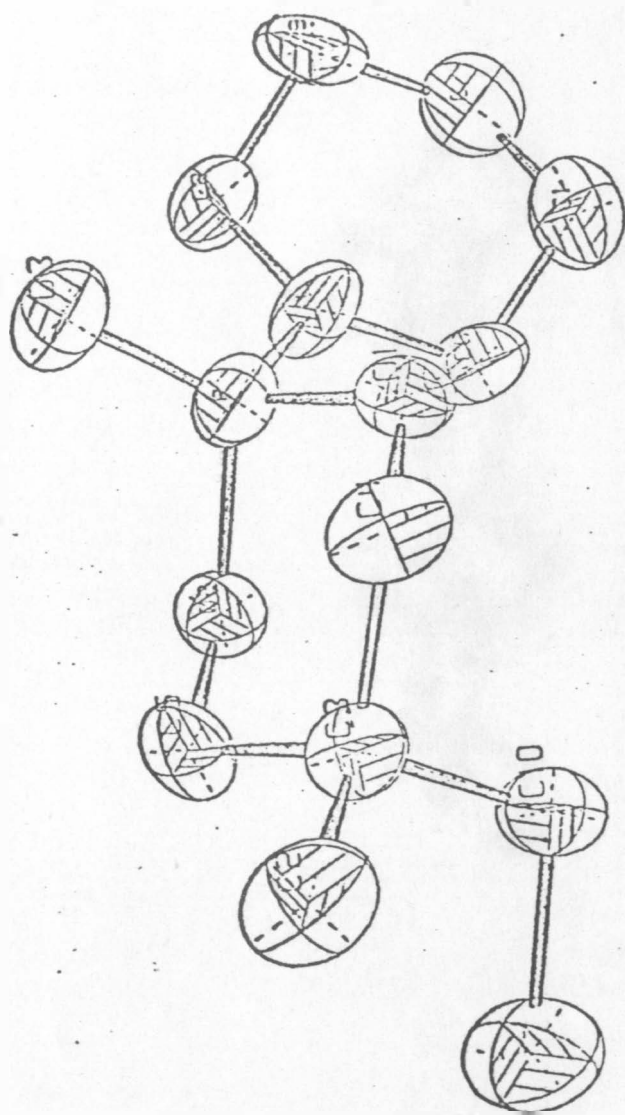
Figure 1. View 1 of Compound 1.
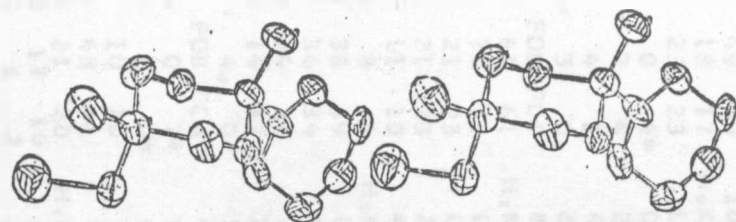
Figure 2. Stereo View of Compound 2.

Table 11

Fo-Fc Values for Compound 1

Column 1

H,K= -9, 0		
L	FOB	FCA
2	8	9
4	0	1*
6	22	22
8	6	4

H,K= -8, 0		
L	FOB	FCA
0	15	18
2	15	16
4	25	23
6	29	31
8	46	46
10	27	26
12	4	3

H,K= -7, 0		
L	FOB	FCA
0	12	15
2	22	24
4	4	3
6	21	22
8	33	34
10	18	17
12	3	0
14	9	11

H,K= -6, 0		
L	FOB	FCA
0	22	23
2	13	15
4	35	34
6	24	23
8	46	46
10	54	55
12	18	19
14	17	17
16	6	6

H,K= -5, 0		
L	FOB	FCA
0	29	29
2	40	40
4	21	23
6	34	34
8	15	14
10	3	2*
12	7	6*
14	27	28
16	1	6*

H,K= -4, 0		
L	FOB	FCA
0	0	7*
2	22	21
4	66	69
6	45	44
8	6	8
10	11	13*

Column 2

12	9	10
14	35	35
16	18	19
18	4	5*

H,K= -3, 0		
L	FOB	FCA
0	61	61
2	15	14
4	25	25
6	56	56
8	64	60
10	35	36
12	21	19
14	5	3*
16	19	18
18	10	7

H,K= -2, 0		
L	FOB	FCA
0	130	132
2	80	84
4	67	65
6	63	64
8	31	29
10	42	44
12	0	0*
14	43	45
16	46	48
18	11	10

H,K= -1, 0		
L	FOB	FCA
2	43	43
4	7	9
6	39	40
8	23	22
10	44	45
12	36	37
14	2	3*
16	44	44
18	36	37

H,K= 0, 0		
L	FOB	FCA
2	119	108
4	17	16
6	105	104
8	20	20
10	45	46
12	43	43
14	20	20
16	54	52
18	9	12

H,K= 1, 0		
L	FOB	FCA
2	58	60
4	38	39
6	12	10

Column 3

8	31	30
10	3	3*
12	63	64
14	11	11
16	9	8
18	24	22

H,K= 2, 0		
L	FOB	FCA
0	133	132
2	182	177
4	12	11
6	86	82
8	49	49
10	18	17
12	23	23
14	0	4*
16	7	4
18	4	2*

H,K= 3, 0		
L	FOB	FCA
0	61	61
2	73	75
4	21	23
4	21	23
6	11	10
8	8	6
10	38	39
12	36	34
14	34	37
16	14	12

H,K= 4, 0		
L	FOB	FCA
0	0	7*
2	2	0*
4	10	10
6	43	41
8	21	20
10	17	16
12	6	2
14	8	9
16	3	2*

H,K= 5, 0		
L	FOB	FCA
0	30	29
2	64	64
4	9	9
6	31	31
8	69	72
10	9	12
12	6	4
14	20	22

H,K= 6, 0		
L	FOB	FCA
0	23	23
2	13	14

Column 4

4	9	12
6	49	49
8	22	21
10	2	0*
12	6	5

H,K= 7, 0		
L	FOB	FCA
0	12	15
2	20	22
4	11	13
6	6	6
8	43	41
10	34	36

H,K= 8, 0		
L	FOB	FCA
0	15	18
2	18	18
4	3	6*
6	19	19
8	18	19

H,K= 9, 0		
L	FOB	FCA
0	0	4*
2	12	12
4	12	12

H,K= -9, 1		
L	FOB	FCA
0	15	16
1	6	6
2	12	11
3	7	8
4	5	6*
5	8	8
6	20	19
7	0	6*
8	12	11

H,K= -8, 1		
L	FOB	FCA
0	13	13
1	14	13
2	4	3*
3	11	11
4	4	2*
5	3	1*
6	22	20
7	8	6
8	0	2*
9	6	6
10	3	5
11	6	5

H,K= -7, 1		
L	FCB	FCA
0	14	15
1	14	14
2	11	11

Column 5

3	7	7
4	0	2*
5	8	8
6	33	32
7	16	16
8	43	45
9	8	8
10	26	25
11	8	9
12	15	12
13	14	14
14	1	3*

H,K= -6, 1		
L	FOB	FCA
0	23	22
1	7	6
2	12	13
3	13	14
4	15	17
5	20	20
6	15	16
7	10	10
9	12	12
10	5	5
11	4	3*
12	5	3*
13	6	6
14	13	16
15	4	4*
16	10	10

H,K= -5, 1		
L	FOB	FCA
0	4	7
1	46	46
2	38	39
3	28	28
4	17	18
5	9	10
6	20	18
7	20	20
8	21	21
9	18	21
10	0	3*
11	9	9
12	20	19
13	12	11
14	8	8
15	19	18
16	12	12
17	13	14

H,K= -4, 1		
L	FOB	FCA
0	73	71
1	12	12
2	3	3*

Table 11 (Continued)

Column 1:

3	14	14
4	7	6
5	31	30
6	10	12
7	23	24
8	62	60
9	16	16
10	5	6÷
11	8	8
12	7	6
13	13	13
14	6	5
15	12	13
16	23	24
18	4	1*

H,K= -3, 1

L	FOB	FCA
0	56	56
1	66	67
2	72	75
3	63	63
4	2	2*
5	35	35
6	9	8
7	32	32
8	37	37
9	31	31
10	35	34
11	20	22
12	6	6
13	0	1*
14	19	20
15	3	1*
16	8	7
17	22	22
18	16	13

H,K= -2, 1

L	FOB	FCA
0	56	58
1	3	1*
2	5	5
3	36	36
4	72	73
5	20	19
6	36	37
7	16	17
8	55	53
9	5	5
10	43	42
11	2	2*
12	20	19
13	11	12
14	37	37
15	17	19
16	25	27

Column 2:

17	8	8
18	9	6
19	3	3*

H,K= -1, 1

L	FOB	FCA
0	114	107
1	25	24
2	52	54
3	93	92
4	17	16
5	33	32
6	16	16
7	41	41
8	25	26
9	34	33
10	0	5*
11	27	28
12	28	28
13	14	18
14	38	38
15	12	15
16	16	18
17	0	0*
18	15	13
19	13	13

H,K= 0, 1

L	FOB	FCA
1	11	11
2	3	2*
3	4	4
4	60	62
5	26	26
6	30	30
7	38	37
8	6	6
9	33	32
10	36	36
12	23	22
14	9	10
16	25	28
18	14	17

H,K= 1, 1

L	FOB	FCA
0	113	107
1	42	43
2	151	153
3	68	68
4	21	22
5	51	49
6	26	25
7	26	25
8	55	57
9	19	20
10	13	14
11	11	10

Column 3:

12	20	21
13	22	22
14	33	33
15	8	9
16	3	1*
17	3	7*
18	15	12

H,K= 2, 1

L	FOB	FCA
0	57	58
1	22	22
2	24	24
3	25	24
4	8	10
5	3	3*
6	63	61
7	21	21
8	50	49
9	52	51
10	25	23
11	17	17
12	0	0*
13	0	1*
14	14	12
15	12	9
16	16	12
17	7	8
18	3	1*

H,K= 3, 1

L	FOB	FCA
0	57	56
1	9	7
2	13	11
3	11	13
4	19	19
5	27	27
6	21	23
7	28	27
8	55	55
9	20	21
10	18	18
11	5	5*
12	13	15
13	8	7
14	15	13
15	9	10
16	14	13
17	5	6*

H,K= 4, 1

L	FOB	FCA
0	72	71
1	3	1*
2	24	22
3	28	28
4	17	16

Column 4:

5	19	20
6	10	9
7	4	1*
8	9	7
9	24	25
10	15	15
11	22	22
12	1	5*
13	0	2*
14	10	12
15	7	6
16	19	15

H,K= 5, 1

L	FOB	FCA
0	5	7
1	36	35
2	31	30
3	16	16
4	21	21
5	4	3*
6	9	7
7	5	3*
8	13	9
9	10	11
10	13	12
11	9	9
12	9	9
13	5	5*
14	4	2*
15	3	0*

H,K= 6, 1

L	FOB	FCA
0	24	22
1	4	1*
2	10	10
3	7	8
4	14	13
5	19	18
6	23	23
7	0	1*
8	30	31
9	4	4*
10	35	35
11	17	16
12	9	9
13	9	8

H,K= 7, 1

L	FOB	FCA
2	4	3*
0	14	15
1	14	14
3	17	16
4	21	21
5	8	8
6	22	25

Column 5:

7	3	3*
8	16	14
9	4	3*
10	5	3*
11	3	2*

H,K= 8, 1

L	FOB	FCA
2	4	1*
0	10	13
1	9	8
3	6	6
4	3	4*
5	10	11
6	11	11
7	6	7
8	5	5*

H,K= 9, 1

L	FOB	FCA
0	13	16*
1	0	0*
2	4	5*
3	5	2*
4	7	5*

H,K= -9, 2

L	FOB	FCA
0	0	0*
1	8	8
2	3	4*
3	4	4*
4	4	5*
5	3	0*

H,K= -8, 2

L	FOB	FCA
0	0	3*
1	4	0*
2	3	6*
3	10	7
4	7	6
5	11	10
6	9	10
7	3	3*
8	27	25
9	8	6
10	12	10

H,K= -7, 2

L	FOB	FCA
0	8	5
1	10	8
2	17	17
3	11	8
4	8	8
5	5	5
6	10	11
7	2	4
8	14	14

Table 11 (Continued)

```
 9   6    7        11  12  11        6   39  39        1   36  37        0    5    1*
10  12   11        12  22  21        7   13  14        2   12  11        1    5    2
11   2    2*       13   6   4        8   10   8        3    9   9        2   35   33
12   3    2        14   4   2*       9   17  17        4   26  26        3   10   10
13   2    1        15  24  23       10   11  10        5   40  40        4    5    4
H,K= -6,  2        16  19  17       11   16  16        6   34  34        5    3    1*
  L FOB FCA        17   6   5       12    9   8        7   15  14        6    2    0*
 0   6    5       H,K= -3,  2       13    5   3        8   11  11        7   15   13
 1   9    8          L FOB FCA      14    8   6        9    4   3*       8   26   26
 2  11   10        0   5   1        16   29  33       10   13  13        9    9   10
 3  11   10        1  23  23        18   22  22       11   11  11       10    9   11
 4   7    5        2   0   1*      H,K=  0,  2        12   14  14       11    5    1*
 5  10    8        3   8   8          L FOB FCA       13    6   3       12    9    9
 6   0    3*       4  12  13        0  118 124        14    6   4       13    5    2*
 7   0    1*       5   0   0*       1   31  32        15   14  14       14    5    6*
 8  22   21        6  12  13        2   18  18        16    0   0*     H,K=  6,  2
 9  12   11        7  21  20        3   12  10        17    6   5*       L FOB FCA
10  23   23        8  18  18        4   15  16       H,K=  3,  2        2    7    7
11   9    9        9  20  19        5    9   9          L FOB FCA       0    6    5
12   5    6*      10  25  25        6   34  34        0    5   1        1   28   26
13  15   14       11  17  16        7    9   9        1   14  13        3   11   10
14  13   11       12   8   8        8   31  32        2   38  36        4    6    2
15  12   10       13   0   0*       9   14  16        3   17  16        5    0    2*
H,K= -5,  2       14   4   2*      10   19  20        4   29  30        6   26   24
  L FOB FCA       15   6   4       11   22  21        5    3   2*       7    6    3
 0   3    1       16  12  11       12   20  20        6   38  38        8    8    6
 1   9    8       17  11  10       13    3   3*       7   31  32        9    2    1*
 2  16   16      H,K= -2,  2       14    8   6        8    5   6       10    8    9
 3  12   11         L FOB FCA      15    0   2*       9   10   9       11    9    8
 4  25   25        0  21  22       16   24  23       10    9   9       12    6    4
 5   6    6        1   6   8       17    0   2*      11    3   1*     H,K=  7,  2
 6  10   10        2  12  14       18    3   2*      12    8   6        L FOB FCA
 7   4    4        3  28  28      H,K=  1,  2        13   17  17       0    7    5
 8   4    1        4  29  29         L FOB FCA       14    2   2*       1   10   11
 9   3    3        5  47  47        0   40  40       15    9   9        2    0    0*
10   6    4        6   5   4        1   25  26      H,K=  4,  2        3    9   10
11   7    7        7  27  27        2   70  71         L FOB FCA       4    3    5*
12   0    3*       8  24  24        3   16  15        0    4   4*       5    2    2*
13   4    0        9  21  20        4   44  44        1   40  39        6    4    0*
14  21   24       10  15  16        5    4   4*       2   35  35        7    7    5
15   7    7       11  22  21        6   17  17        3    0   2*       8   19   18
16   5    9*      12  10  12        7   36  37        4   35  35        9    6    5
H,K= -4,  2       13   8  10        8    7   6        5   14  14       10   14   15
  L FOB FCA       14   5   6*       9    4   3*       6    0   7*     H,K=  8,  2
 0   3    4*      15   1   4*      10   25  25        7   19  18        L FOB FCA
 1  14   13       16  21  21       11   16  17        8    2   3*       2    8    7
 2   3    2*      17  12  13       12    4   2*       9    4   5*       0    2    3*
 3  20   19      H,K= -1,  2       13   18  19       10    4   3*       1    7    6
 4  12   11         L FOB FCA      14    7   9       11   12  11        3    5    5*
 5  38   38        0  40  40       15    2   5*      12    7   6        4    4    5*
 6  11   11        1   5   2       16    2   3*      13    4   0*       5    5    3*
 7   0    1*       2  69  69       17    8   6       14    9   9        6   13   13
 8  14   15        3  17  17      H,K=  2,  2        15    5   7*     H,K=  9,  2
 9  19   18        4   7   9         L FOB FCA      H,K=  5,  2        L FOB FCA
10   0    1*       5   7   8        0   21  22         L FOB FCA       0    2    0*
```

Table 11 (Continued)

```
   1    9    8*
H,K= -8,  3
   L  FOB  FCA
   0    5    5*
   1   10    9
   2    7    5
   3    2    2*
   4    3    3*
   5    5    3*
   6   11   11
H,K= -7,  3
   L  FOB  FCA
   0    0    1*
   1   13   11
   2    5    4*
   3    3    1*
   4    4    4*
   5   14   13
   6   13   14
   7   17   15
   8   19   20
  10   14   15
  11   12   11
H,K= -6,  3
   L  FOB  FCA
   0   18   18
   1    7    6
   2    2    1*
   3    7    6
   4    5    5
   5    7    7
   6   11   11
   7    4    5*
   8    3    5*
   9    6    5
  10    4    6*
  11   10   10
  12    4    2*
  13    3    3*
H,K= -5,  3
   L  FOB  FCA
   0    0    2*
   1   29   29
   2    5    3
   3   16   15
   4    5    5
   5    3    2*
   6   17   17
   7   30   29
   8    7    5
   9   12   12
  10    6    3
  11   12   10
  12    6    8
  13   23   21

  14    2    3*
H,K= -4,  3
   L  FOB  FCA
   0   48   48
   1    5    3
   2   13   13
   3   16   16
   4    5    5
   5   13   13
   6    5    3
   7   14   15
   8   34   34
   9    9    9
  10   10   10
  11    0    1*
  12   10   11
  13    8    7
  14    0    4*
  15    1    1*
H,K= -3,  3
   L  FOB  FCA
   0    4    5*
   1   21   19
   3   22   22
   4   12   13
   5    7    7
   6   12   14
   7   35   35
   8   14   15
   9   25   26
  10   24   24
  11   17   16
  12    4    2*
  13   17   14
  14    9   11
  15    6    5
  16    5    3*
H,K= -2,  3
   L  FOB  FCA
   0    2    1*
   1   48   46
   2    9    9
   3   24   24
   4   23   24
   5    3    1*
   6    9    8
   7   18   17
   8   16   17
   9   11    9
  10   32   33
  11    5    4*
  12    3    1*
  13   11   10
  14   10   10
  15    8    5

  16   12   12
H,K= -1,  3
   L  FOB  FCA
   0   48   48
   1   13   13
   2   58   56
   3   21   21
   4    6    7
   5   10   10
   6    7    7
   7   33   33
   8   25   26
   9   18   18
  10   12   10
  11   11   11
  12    4    5*
  13   24   23
  14   26   26
  15    7    9
  16    8   12
  17    2    4*
H,K=  0,  3
   L  FOB  FCA
   1   64   65
   2   23   22
   3   20   18
   4   25   26
   5   23   23
   6    9    9
   7   10    9
   8    9    7
   9   30   29
  10    4    4*
  11   12   13
  12    0    1*
  13    5    5*
  14    9   10
  15   15   12
  16   10   10
H,K=  1,  3
   L  FOB  FCA
   0   49   48
   1    9    8
   2   64   63
   3   45   46
   4   23   22
   5    3    5*
   6    6    5
   7   20   19
   8   36   35
   9   10    8
  10    3    6*
  11   13   14
  12    3    0*
  13   25   24

  14   15   14
  15   11   11
H,K=  2,  3
   L  FOB  FCA
   0    5    1
   1   15   13
   2   13   16
   3    9    8
   4   11   10
   5   22   22
   6   25   26
   7    8    8
   8   19   18
   9   23   21
  10    1    3*
  11   17   16
  12   10    9
  13   12   12
  14   11   10
  15   18   14
H,K=  3,  3
   L  FOB  FCA
   0    3    5*
   1   15   14
   2    7    8
   3   40   41
   4    8    6
   5   15   16
   6   12   13
   7   24   26
   8   20   19
   9   24   24
  10   13   13
  11   12   14
  12    6    5
  13    7    6
  14    6    6*
  15   15   16
H,K=  4,  3
   L  FOB  FCA
   0   46   48
   1    6    5
   2    3    2*
   3   12   12
   4    2    1*
   5   20   20
   6    5    4
   7    2    2*
   8    7    6
   9   14   14
  10   10   10
  11    7    4
  12    4    2*
  13    2    2*
H,K=  5,  3

   L  FOB  FCA
   0    1    2*
   1   15   15
   2   11   11
   3   28   26
   4    9    9
   5    5    4*
   6    6    6
   7    3    1*
   8    6    2
   9   23   22
  10    2    1*
  11    4    5*
  12   10   10
H,K=  6,  3
   L  FOB  FCA
   0   18   18
   1    8    6
   2    7    8
   3    5    6*
   4    2    1*
   5   19   18
   6   14   15
   7    2    1*
   8   16   17
   9    4    4*
  10   17   16
H,K=  7,  3
   L  FOB  FCA
   2    2    0*
   0    0    1*
   1    5    6*
   3   11   11
   4   11   10
   5    6    6
   6   12   14
   7    5    6*
H,K=  8,  3
   L  FOB  FCA
   0    2    5*
   1   14   12
   2    0    1*
   3    8    6
H,K= -7,  4
   L  FOB  FCA
   0   11    9
   1    7    7
   2    1    1*
   3   15   13
   4    3    2*
   5    4    2*
   6    7    9
H,K= -6,  4
   L  FOB  FCA
   0   13   13
```

Table 11 (Continued)

1	17	19
2	19	20
3	13	13
4	2	2*
5	16	14
6	4	5*
7	16	16
8	8	7
9	18	16

H,K= -5, 4

L	FCB	FCA
0	6	6
1	13	13
2	4	2*
3	17	16
4	6	5
5	0	1*
6	5	4
7	0	3*
8	5	0*
9	4	0*
10	2	2*
11	12	13
12	9	11

H,K= -4, 4

L	FOB	FCA
0	4	4*
1	30	28
2	22	22
3	33	33
4	18	20
5	26	26
6	8	7
7	10	12
8	0	1*
9	44	43
10	6	5
11	21	20
12	14	14
13	5	4*

H,K= -3, 4

L	FCB	FCA
0	16	17
1	26	27
2	13	13
3	9	10
4	7	4
5	5	7
6	14	13
7	2	3*
8	8	9
9	18	19
10	19	20
11	17	17
12	4	6*

13	9	11
14	16	15

H,K= -2, 4

L	FCB	FCA
0	17	15
1	25	24
2	3	5*
3	24	24
4	16	16
5	54	53
6	23	25
7	8	8
8	20	19
9	33	34
10	5	1*
11	41	40
12	0	1*
13	2	6*
14	5	6*

H,K= -1, 4

L	FCB	FCA
0	4	4*
1	7	5
2	0	4*
3	5	5
4	6	5
5	4	3*
6	14	14
7	19	18
8	7	7
9	2	2*
10	6	4
11	13	11
12	14	14
13	9	9
14	3	2*

H,K= 0, 4

L	FOB	FCA
0	38	38
1	19	20
2	14	13
3	10	9
4	2	3*
5	55	55
6	4	1*
7	15	15
8	23	24
9	7	7
10	14	13
11	33	32
12	3	2*
13	5	6*
14	7	9

H,K= 1, 4

L FOB FCA

0	2	4*
1	23	24
2	7	7
3	14	13
4	26	25
5	9	11
6	13	13
7	40	40
8	3	2*
9	11	12
10	21	20
11	25	25
12	5	4*
13	12	10

H,K= 2, 4

L	FOB	FCA
0	16	15
1	39	39
2	9	9
3	7	8
4	17	17
5	47	48
6	13	15
7	30	31
8	5	6*
9	4	2*
10	9	9
11	16	13
12	5	5*
13	7	6

H,K= 3, 4

L	FOB	FCA
0	16	17
1	28	28
2	15	13
3	21	22
4	20	20
5	5	3*
6	31	32
7	36	36
8	8	9
9	17	17
10	9	8
11	14	14
12	9	7

H,K= 4, 4

L	FOB	FCA
0	4	4*
1	44	44
2	13	13
3	16	15
4	25	25
5	17	17
6	2	2*
7	24	24

8	5	3*
9	8	10
10	5	6*
11	12	12

H,K= 5, 4

L	FOB	FCA
0	5	6*
1	5	1*
2	19	19
3	29	28
4	4	6*
5	5	5*
6	7	5
7	9	9
8	0	2*
9	11	10

H,K= 6, 4

L	FOB	FCA
0	14	13
1	28	27
3	14	13
4	5	5*
5	9	6
6	6	6
7	4	1*

H,K= 7, 4

L	FOB	FCA
0	12	9
1	0	3*
2	6	6
3	16	16

H,K= -5, 5

L	FOB	FCA
0	11	11
1	24	24
2	21	22
3	17	16
4	27	27
5	0	3*
6	8	8
7	13	13

H,K= -4, 5

L	FOB	FCA
0	9	8
1	2	2*
2	7	7
3	4	1*
5	13	13
6	3	1*
7	7	7
8	10	10
9	4	0*

H,K= -3, 5

L FOB FCA

0	16	18

1	13	13
2	11	11
3	24	24
4	34	33
5	8	9
6	31	31
7	20	21
8	11	11
9	11	12
10	13	12

H,K= -2, 5

L	FOB	FCA
0	2	3*
1	6	6*
2	4	5*
3	16	15
4	5	1*
5	17	18
6	8	7
7	13	14
8	4	0*
9	12	9
10	5	4*
11	14	13

H,K= -1, 5

L	FOB	FCA
0	18	17
1	5	4*
2	5	6*
3	19	17
4	15	13
5	4	1*
6	32	33
7	28	29
8	27	29
9	17	17
10	14	14
11	1	0*

H,K= 0, 5

L	FOB	FCA
1	20	19
2	5	2*
3	14	14
4	3	1*
5	14	15
6	8	9
7	16	15
8	11	12
9	22	21
10	12	12

H,K= 1, 5

L	FOB	FCA
0	17	17
1	10	10
2	20	19

Table 11 (Continued)

L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA
3	23	22	7	7	9	0	7	8	1	5	4*	4	10	9
4	9	9	8	13	14	1	9	8	2	7	8	5	8	6
5	1	4*	9	14	16	2	7	8	3	12	13	H,K= 1, 6		
6	10	8	10	1	7*	3	4	3*	4	14	13	L FOB FCA		
7	11	11	H,K= 3, 5			4	10	11	H,K= -1, 6			0	7	6
8	15	15	L FOB FCA			5	13	12	L FOB FCA			1	7	5
9	19	19	0	15	18	6	18	19	0	7	6	2	0	2*
10	16	17	1	4	3*	7	4	5*	1	10	10	3	3	3*
11	2	1*	2	32	33	H,K= 5, 5			2	11	10	4	2	1*
H,K= 2, 5			3	27	27	L FOB FCA			3	8	6	H,K= 2, 6		
L FOB FCA			4	24	24	0	11	11	4	4	5*	L FOB FCA		
0	5	3*	5	6	5*	1	3	3*	5	8	7	0	10	12
1	8	8	6	11	11	2	17	19	H,K= 0, 6			1	10	8
2	7	8	7	4	3*	3	20	18	L FOB FCA			2	13	12
3	3	1*	8	2	3*	4	13	13	0	5	6*	3	12	13
4	20	22	9	14	12	H,K= -2, 6			1	4	8*			
5	29	29	H,K= 4, 5			L FOB FCA			2	5	6*			
6	22	22	L FOB FCA			0	12	12	3	19	19			

*Indicates zero weight reflection.

Table 12

Temperature Parameters of the Nonhydrogen Atoms

($\times 10^4$) for Compound 1

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	288(1)	260(7)	36(7)	112(9)	30(3)	31(4)
P	103(2)	173(5)	26(1)	14(7)	13(2)	-10(4)
N	198(2)	171(32)	25(3)	32(44)	81(13)	0(15)
O(1)	85(1)	231(31)	20(2)	-10(31)	-10(9)	-30(15)
O(2)	107(11)	209(28)	21(2)	-50(32)	0(89)	0(11)
O(3)	147(9)	185(17)	32(2)	-10(24)	34(7)	5(11)
C(1)	190(17)	304(36)	33(4)	58(45)	13(13)	56(21)
C(2)	152(10)	273(23)	32(2)	-60(28)	68(9)	-10(13)
C(3)	99(9)	175(21)	22(2)	-50(23)	22(7)	0(11)
C(4)	91(18)	248(48)	29(4)	-80(51)	30(16)	-30(26)
C(5)	99(11)	276(30)	18(2)	20(31)	27(9)	35(15)
C(6)	194(15)	204(31)	25(3)	-70(38)	34(12)	-30(17)
C(7)	245(19)	393(39)	28(3)	55(46)	21(13)	27(20)
C(8)	133(13)	268(32)	29(3)	115(36)	34(11)	-30(18)
C(9)	153(21)	509(66)	18(4)	113(70)	-10(10)	-90(32)
C(10)	152(14)	233(32)	18(3)	-4(33)	15(9)	10(14)

Factor expression is:

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

Table 13

E Value Statistics for Compound 1

Average value of E	0.801
Average value of E^2	1.032
Average value of $|E^2 - 1|$	1.017
Percentage greater than one	31.25
Percentage greater than two	5.46
Percentage greater than three	0.30

isotropic value of 4.0. The B_{11} temperature parameter of the chlorine

atom is quite large. This is presumably due to the ability of the

chloromethyl group to move from its proposed position in a circular

path. In Figure 1, one can note that the chloromethyl group is free

to rotate.

COMPOUND 2

Preliminary

A different crystal growing apparatus was developed for Compound
2 than had been used for Compound 1. A constant temperature bath ap-
paratus with a circulating motor and electric heater housed in a large
glass jar, was fitted snugly into a large polystyrene acid bottle
packing case which had sides approximately two inches thick. The top,
made of the same material, enclosed the entire apparatus. When filled
with water at 30° to 40°C, it provided an apparatus for growing
crystals with a very slow rate of cooling (2°C per hour or less).

Using benzene as a solvent, a solution was prepared in a vial that
was saturated at 35°C. The temperature of the water bath was adjusted
to about 40°C and the vial was suspended by a wire into the water.
When temperature equilibrium was considered complete, the electrical
system (circulating and heating) was disconnected and the slow cooling
process was allowed to begin. Although the cooling rate was at first
about 2°C per hour, it soon slowed as the water temperature approached
room temperature. When only a few degrees above room temperature, the
cooling rate was observed to be only a few degrees per day.

Compound 2 grew in long needles with a cross section approximating
a rectangle with rounded edges. A few crystals were used for density
measurements which was accomplished in the same manner as for Compound
1. The observed density was 1.410 g/cm^3 as compared to the calculated
density (using 4 molecules per unit cell) of 1.411 g/cm^3. The space

group and equivalent symmetry positions for Compound 2 is the same as for Compound 1, $P2_1/c$.

To obtain a single crystal suitable for a structure determination, a needle crystal was broken and the shattered ends dissolved in solvent. The resulting crystal approximated a rectangular box with rounded edges and corners. The needle grains were clearly visible under moderate magnification. This made finding the needle axis a simple task.

The lattice constants were found to be: $a = 6.237(3)\overset{\circ}{A}$; $b = 11.437(5)\overset{\circ}{A}$; $c = 19.419(9)\overset{\circ}{A}$; and $\beta = 109.95(3)^\circ$.

Solving the Structure

When all 17 nonhydrogen atoms were placed in the structure utilizing the symbolic addition process, the R factor was 0.23. The temperature parameters were isotropic at this stage, and after three least squares cycles in which all positional, temperature, and scale factors were allowed to vary, the R factor had reduced to 0.12. The temperature parameters were then converted to anisotropic terms, and after two cycles of varying only the temperature parameters varying the R factor was 0.07. At this point a difference Fourier map was plotted, and all of the hydrogen atoms showed up as peaks with few if any other significant electron densities. The 14 hydrogen atoms were added after obtaining their coordinates from the difference map and a least squares computer run dropped the R factor to 0.06.

Refinement from this point on was conducted at the computer facilities at Lawrence Livermore Laboratory. Running the least squares program for three cycles with all data points above three standard deviations (914 data points) reduced the weighted R factor to 0.036. A final R factor calculation using all data points (1,337) at unit weights gave an unweighted R factor of 0.063.

The weighting scheme used for the refinement at Lawrence Livermore Laboratory was one built into the computer program. For Fo's above an arbitrary constant, FB, the weight of the reflection was calculated as:

$$w = Fo^{-1} \tag{26}$$

For Fo's below the arbitrary constant, FP, the weight was:

$$w = Fo^{\frac{1}{4}} \tag{27}$$

All reflections with intensity values below three times their estimated standard deviation were excluded.

The arbitrary number FB used in the weighting scheme was the value of Fo which had the highest weight. This number could be fed into the program. The computer program print-out for Compound 2 from South Dakota State University which used the other weighting scheme was examined to determine which value of Fo had the highest unit weight. The Fo's with a value of about 30 were found to have the highest unit weight. This value was then used in the program at Lawrence Livermore Laboratory for FB.

Summary

Table 17 shows the thermal parameters for the nonhydrogen atoms. Table 15 gives the final nonhydrogen atom positional parameters, and the final hydrogen parameters are shown in Table 16. The temperature parameters for the hydrogen atoms are also included in Table 16. Four hydrogen atom temperature parameters did not give realistic values upon refinement. An arbitrary value of 4.0 was substituted for these atom thermal parameters, and in subsequent refinements these values were not allowed to vary.

Bond lengths and angles are shown in Tables 18 and 19, respectively. The values were obtained using the program DINT which also calculated the estimated standard deviations. The program CRTEP and the Calcomp plotter were used to make the molecular diagrams shown in Figures 3 and 4. The Fo-Fc Table is shown in Table 20. E value statistics are shown in Table 14.

Table 14

E Value Statistics for Compound 2

Average value of E	0.793
Average value of E^2	0.989
Average value of $\left|E^2 - 1\right|$	0.946
Percentage greater than one	32.09
Percentage greater than two	5.46
Percentage greater than three	0.30

Table 15

Positional Parameters of the Nonhydrogen Atoms
(x 10^4) for Compound 2

Atom	x	y	z
Cl	1655(3)	4775(2)	957(1)
P	6583(2)	5194(1)	3462(1)
O(1)	5950(5)	5192(3)	4179(2)
O(2)	6396(6)	3877(3)	3258(2)
O(3)	4587(5)	5809(3)	2859(2)
O(4)	8759(6)	5722(4)	3529(2)
C(1)	2370(10)	5248(6)	2619(4)
C(2)	2477(8)	4007(5)	2366(3)
C(3)	4127(12)	3341(5)	2999(4)
C(4)	3338(11)	3935(6)	1725(3)
C(5)	94(14)	3447(9)	2180(6)
C(6)	4097(10)	6808(6)	4523(3)
C(7)	6053(10)	6225(5)	4583(3)
C(8)	6304(16)	8202(7)	5398(4)
C(9)	4236(14)	7802(7)	4929(4)
C(10)	8260(13)	7592(7)	5454(4)
C(11)	8143(11)	6601(6)	5052(3)

Table 16

Parameters of the Hydrogen Atoms on Compound 2

(Positional Parameters are x 10^4)

Atom	x	y	z	B
H(1)	3536(74)	3358(39)	3399(27)	2(1)
H(2)	4407(86)	2636(51)	2880(29)	4*
H(3)	1810(58)	5260(31)	3005(21)	4*
H(4)	1528(80)	5750(40)	2244(27)	2(1)
H(5)	3152(73)	3199(43)	1520(25)	2(1)
H(6)	4891(93)	4225(44)	1875(28)	4*
H(7)	169(83)	2604(50)	2018(29)	4*
H(8)	-195(94)	3369(51)	2625(35)	5(2)
H(9)	-808(124)	3875(70)	1746(42)	7(3)
H(10)	2642(90)	6506(44)	4238(29)	4*
H(11)	2922(99)	8184(50)	4889(31)	3(2)
H(12)	6456(86)	8808(50)	5667(29)	3(2)
H(13)	9693(96)	7804(47)	5833(30)	4(2)
H(14)	9437(82)	6189(42)	5022(26)	2(1)

Table 17

Temperature Parameters of the Nonhydrogen Atoms

$(\times 10^4)$ for Compound 2

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	103(1)	88(1)	54(1)	22(1)	17(1)	8(1)
P	39(1)	55(1)	50(1)	1(1)	17(1)	2(1)
O(1)	59(2)	49(2)	46(2)	2(1)	22(1)	-1(2)
O(2)	49(2)	52(2)	59(2)	-13(2)	14(2)	2(2)
O(3)	45(2)	39(2)	49(2)	-4(1)	15(1)	2(1)
O(4)	44(2)	108(3)	75(2)	22(2)	30(2)	22(2)
C(1)	51(3)	60(4)	49(3)	10(3)	21(3)	-3(3)
C(2)	37(3)	43(3)	53(3)	-1(2)	18(2)	-5(2)
C(3)	91(5)	40(3)	61(4)	0(3)	40(4)	-1(3)
C(4)	57(3)	53(3)	49(3)	7(3)	19(3)	-5(3)
C(5)	67(4)	97(6)	83(6)	-31(4)	39(4)	-28(5)
C(6)	46(3)	61(3)	51(3)	3(3)	17(3)	-2(3)
C(7)	43(3)	53(3)	37(3)	5(3)	14(2)	-5(2)
C(8)	94(6)	56(4)	55(4)	-10(4)	32(4)	-9(3)
C(9)	69(5)	69(5)	64(4)	17(4)	31(4)	6(4)
C(10)	57(4)	73(4)	59(4)	-12(4)	13(4)	-6(4)
C(11)	52(4)	62(4)	50(3)	6(3)	18(3)	-1(3)

Factor expression used is:

$$\exp\left\{ -\tfrac{1}{4}\left[\frac{B_{11}h^2}{a^2} + \frac{B_{22}k^2}{b^2} + \frac{B_{33}l^2}{c^2} + \frac{2B_{12}hk}{ab} + \frac{2B_{13}hl}{ac} + \frac{2B_{23}kl}{bc} \right]\right\}$$

Table 18

Interatomic Distances (Å) for Compound 2

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cl	C(4)	1.784(6)Å	C(8)	C(10)	1.378(12)Å
P	O(1)	1.572(4)	C(10)	C(11)	1.364(10)
P	O(2)	1.552(4)	H(1)	C(3)	0.97(5)
P	O(3)	1.556(4)	H(2)	C(3)	0.87(6)
P	O(4)	1.450(4)	H(3)	C(1)	0.93(4)
O(1)	C(7)	1.408(7)	H(4)	C(1)	0.94(5)
O(2)	C(3)	1.465(8)	H(5)	C(4)	0.92(5)
O(3)	C(1)	1.450(7)	H(6)	C(4)	0.97(5)
C(1)	C(2)	1.511(9)	H(7)	C(5)	1.02(6)
C(2)	C(3)	1.512(9)	H(8)	C(5)	0.95(6)
C(2)	C(4)	1.517(8)	H(9)	C(5)	0.97(8)
C(2)	C(5)	1.544(10)	H(10)	C(6)	0.95(5)
C(6)	C(7)	1.360(8)	H(11)	C(9)	0.91(6)
C(6)	C(9)	1.369(10)	H(12)	C(8)	0.85(6)
C(7)	C(11)	1.380(9)	H(13)	C(10)	0.97(6)
C(8)	C(9)	1.379(12)	H(14)	C(11)	0.95(5)

Table 19

Interatomic Angles for Compound 2

O(1)	P	O(2)	101.9(2)°	C(2)	C(1)	H(4)	114(3)°
O(1)	P	O(3)	106.8(2)	H(3)	C(1)	H(4)	111(4)
O(1)	P	O(4)	115.6(2)	O(2)	C(3)	H(1)	108(3)
O(2)	P	O(3)	106.0(2)	C(2)	C(3)	H(1)	108(3)
O(3)	P	O(4)	111.3(2)	C(2)	C(3)	H(2)	113(4)
P	O(1)	C(7)	121.0(3)	H(1)	C(3)	H(2)	113(4)
P	O(2)	C(3)	118.3(3)	Cl	C(4)	H(5)	100(3)
P	O(3)	C(1)	118.2(4)	Cl	C(4)	H(6)	108(3)
O(3)	C(1)	C(2)	112.2(4)	C(2)	C(4)	H(5)	112(3)
C(1)	C(2)	C(3)	107.6(5)	C(2)	C(4)	H(6)	109(3)
C(1)	C(2)	C(4)	112.7(5)	H(5)	C(4)	H(6)	114(4)
C(1)	C(2)	C(5)	108.7(5)	C(2)	C(5)	H(7)	109(3)
C(3)	C(2)	C(4)	107.8(5)	C(2)	C(5)	H(8)	107(4)
C(3)	C(2)	C(5)	108.4(6)	C(2)	C(5)	H(9)	103(4)
C(4)	C(2)	C(5)	111.6(6)	H(7)	C(5)	H(8)	104(5)
O(2)	C(3)	C(2)	112.2(5)	H(7)	C(5)	H(9)	106(6)
Cl	C(4)	C(2)	112.6(4)	H(8)	C(5)	H(9)	127(6)
C(7)	C(6)	C(9)	118.6(6)	C(7)	C(6)	H(10)	121(3)
O(1)	C(7)	C(6)	119.7(5)	C(9)	C(6)	H(10)	120(3)
O(1)	C(7)	C(11)	118.9(5)	C(9)	C(8)	H(12)	124(4)
C(6)	C(7)	C(11)	121.4(6)	C(10)	C(8)	H(12)	117(4)
C(9)	C(8)	C(10)	119.1(7)	C(6)	C(9)	H(11)	118(4)
C(6)	C(9)	C(8)	121.1(7)	C(8)	C(9)	H(11)	121(4)
C(8)	C(10)	C(11)	120.2(7)	C(8)	C(10)	H(13)	120(3)
C(7)	C(11)	C(10)	119.4(6)	C(11)	C(10)	H(13)	120(3)
O(3)	C(1)	H(3)	108(2)	C(7)	C(11)	H(14)	116(3)
O(3)	C(1)	H(4)	101(3)	C(10)	C(11)	H(14)	124(3)
C(2)	C(1)	H(3)	110(2)				
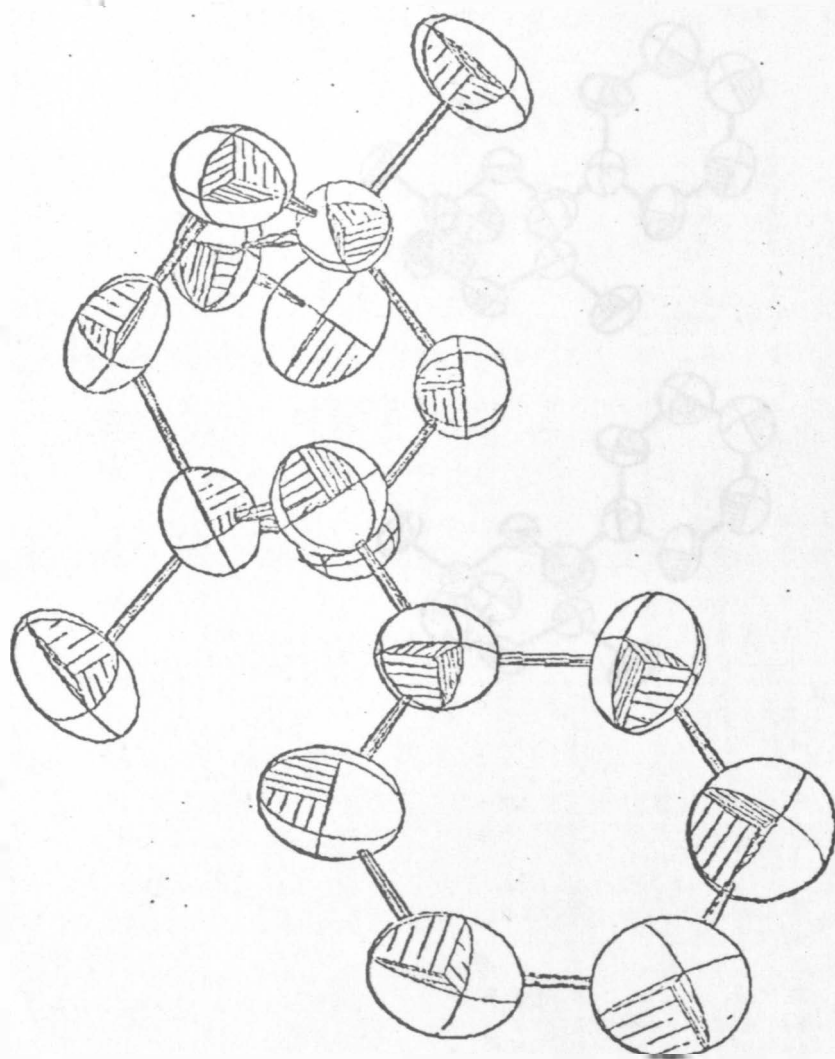
Figure 3. View 1 of Compound 2.
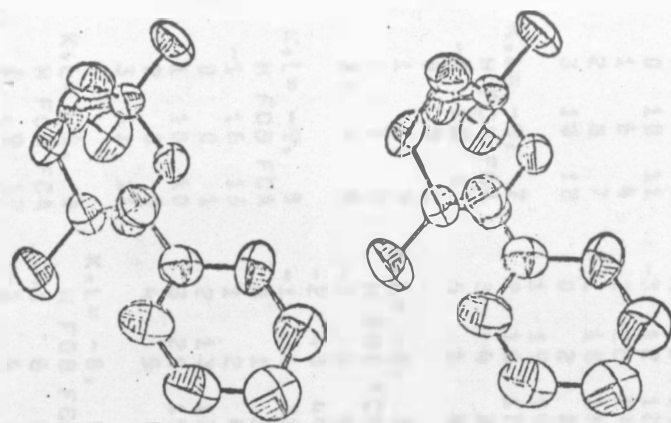
Figure 4.   Stereo View of Compound 2.

Table 20

Fo-Fc Values for Compound 2

```
K,L=-11,  0        K,L=-10,  7       -2   6   6        H FOB FCA      -2  10  10
   H FCB FCA                          -1   8   8      -3  16  15      -1   8   8
   0   3   0          H FCB FCA        0   6   5      -2  31  30       0   0   3
                      0   2   2        1   4   2      -1   3   3       1   2   4
K,L=-10,  0           1   0   3        2   3   2       0  10   9       2  11  11
   H FCB FCA                           3   7   8       1  17  15       3  24  24
  -2   7   6       K,L= -9,  0                         2   2   4       4   9   9
  -1   9  11          H FCB FCA     K,L= -9,  6        3  17  18
   0  11  12         -3  12  12        H FOB FCA                    K,L= -8,  7
   1   9  11         -2  11  11       -2   8   7     K,L= -8,  2       H FOB FCA
   2   5   6         -1  17  16       -1   7   8        H FOB FCA     -2   0   3
                      0   4   0        0  10  11      -3  12  12      -1   7   7
K,L=-10,  1           1  16  16        1   6   4      -2  26  27       0   8   9
   H FCB FCA          2  11  11        2   8   7      -1  18  18       1  10  10
  -2  22  21          3  12  12        3  10  12       0   2   0       2   4   4
  -1   0   0                                           1  19  19       3  13  15
   0   3   3       K,L= -9,  1     K,L= -9,  7         2  16  17       4  19  19
   1   6   6          H FCB FCA        H FOB FCA        3   4   3
   2  13  12         -3   2   0       -1  12  13        4   1   0    K,L= -8,  8
                     -2  12  13        0   3   2                       H FOB FCA
                     -1   8   9        1   6   5     K,L= -8,  3      -2  10  11
K,L=-10,  2           0   2   2        2   7   7        H FOB FCA     -1   6   5
   H FCB FCA          1   0   1        3   4   5      -3   0   0       0   3   3
  -2  11  12          2   9   9                       -2  43  44       1   3   4
  -1  10   9          3  17  17     K,L= -9,  8       -1  31  31       2  15  15
   0   4   6                           H FOB FCA       0   1   1       3   2   2
   1   8   9       K,L= -9,  2        -1  16  15       1   2   4
   2   0   0          H FCB FCA        0   0   1       2  13  13    K,L= -8,  9
                     -2   1   0        1  10  10       3  20  19       H FOB FCA
K,L=-10,  3          -1   5   5        2   0   0       4   5   4      -1  10  10
   H FOB FCA          0  17  17        3  11  11                      0  15  15
  -1   9   9          1  10  11                     K,L= -8,  4       1   7   7
   0   3   0          2  14  14     K,L= -9,  9        H FOB FCA       2  12  11
   1   9   9          3  10  11        H FOB FCA      -3   6   5       3   0   2
   2   5   6                           0   9  10      -2   4   3
                  K,L= -9,  3          1   6   5      -1  12  12    K,L= -8, 10
K,L=-10,  4          H FCB FCA         2   0   3       0  14  14       H FOB FCA
   H FCB FCA         -2   6   7                        1   9  10      -1   9   9
  -1   5   5         -1   2   2     K,L= -9, 10        2   5   5       0   4   3
   0   4   4          0   4   5        H FOB FCA       3   2   2       1   4   2
   1   4   5          1   4   6        0   6   7       4   0   3       2   3   3
   2   9   9          2   0   1        1   0   2                       3   4   4
                      3   1   3        2  11  10    K,L= -8,  5
K,L=-10,  5                                            H FOB FCA    K,L= -8, 11
   H FOB FCA      K,L= -9,  4     K,L= -8,  0         -3   8   9       H FOB FCA
  -1   7   7         H FCB FCA        H FOB FCA       -2   5   4       0  19  19
   0   4   4         -2   6   7       -3  11  11      -1  18  18       1  12  11
   1   6   5         -1  15  16       -2  15  15       0  10  10       2   9  10
   2   5   4          0   8   8       -1   3   3       1  10  10       3   9   8
                      1   7   7        0  19  19       2   4   5
K,L=-10,  6          2   3   3        1   4   3       3  12  11    K,L= -8, 12
   H FCB FCA         3  13  13        2  14  15       4  10  11       H FOB FCA
   0   0   1                          3  10  11                       0  11  10
   1   4   1       K,L= -9,  5                     K,L= -8,  6       1   7   7
   2   4   3          H FCB FCA · K,L= -8,  1          H FOB FCA      2   5   6
```

Table 20 (Continued)

```
K,L= -7,  0        K,L= -7, 10       -2  30  30        5  10   9
  H FOB FCA          H FOB FCA       -1  20  19
-4   1   4  K,L= -7,  5   -2   9   8    0  44  42  K,L= -6,  6
-3  19  19    H FOB FCA   -1  17  17    1  18  17    H FCB FCA
-2  15  15  -3   9   9     0  13  13    2  13  14  -3   4   3
-1  20  21  -2  17  18     1   3   1    3  17  17  -2  15  15
 1  21  21  -1  10  10     2   9  10    4  13  11  -1  10  10
 2  15  15   0  11  10     3   5   6                0   7   8
 3  19  19   1   0   1     4  23  24  K,L= -6,  2    1  26  26
 4   3   4   2   6   7                  H FOB FCA    2  13  12
             3   2   2  K,L= -7, 11  -4   2   2      3  10  10
K,L= -7,  1  4  11  11     H FOB FCA  -3   9   9     4   2   1
  H FOB FCA               -1   5   4  -2   2   3     5   1   1
-4   8   7  K,L= -7,  6    0   1   1  -1  29  29
-3   3   2    H FOB FCA    1  12  13   0  27  26  K,L= -6,  7
-2  21  21  -3   9   8     2  20  21   1   5   4     H FCB FCA
-1  21  21  -2  13  14     3   2   4   2   5   5   -3   7   8
 0  19  18  -1  19  19     4   4   4   3  11  12   -2   8   8
 1  13  13   0  17  18                 4   1   0   -1  17  17
 2  21  21   1   3   2  K,L= -7, 12                  0  17  15
 3  17  17   2  17  17     H FOB FCA  K,L= -6,  3    1  18  18
 4   5   3   3   4   1  -1  12  13      H FOB FCA    2   2   0
             4   0   2   0   6   5  -4  10  11       3   0   1
K,L= -7,  2              1   0   2  -3   1   1       4  16  17
  H FOB FCA  K,L= -7,  7  2   2   2  -2  33  33
-4  12  11    H FOB FCA  3  17  17  -1  39  38  K,L= -6,  8
-3   9   9  -3   0   2                0  17  17     H FCB FCA
-2   7   6  -2   4   4  K,L= -7, 13   1  16  15   -3   3   6
-1   4   4  -1  15  15    H FOE FCA   2  15  15   -2   2   1
 0  32  32   0  15  14   0   8   8    3  17  16   -1  11  11
 1   8   7   1   0   2   1   8   8    4   7   6    0   5   4
 2  21  22   2   0   1   2   9   8                 1   0   2
 3  20  20   3   4   4   3   8   7  K,L= -6,  4    2  13  13
 4   8   9   4   3   2                 H FOB FCA   3  17  17
                        K,L= -7, 14  -4   7   5    4  15  15
                          H FOB FCA  -3   3   2
K,L= -7,  3  K,L= -7,  8  1  11  11  -2   9   9  K,L= -6,  9
  H FOB FCA    H FOE FCA  2   5   6  -1   2   3     H FCB FCA
-3  17  18  -2   3   3                0  18  17   -2   8   8
-2  19  19  -1  12  12  K,L= -6,  0   1  34  32   -1   4   3
-1  11  12   0   0   1    H FOB FCA   2  20  21    0  12  11
 0   9   8   1   9   8  -4   8   8    3   7   6    1  25  25
 1   3   3   2   6   7  -3  15  15    4   6   6    2  16  16
 2   7   7   3   9   9  -2  10  11    5   3   0    3   7   7
 3  14  13   4   0   1  -1   8   7                 4  10  10
 4   9   9               0  32  32  K,L= -6,  5
            K,L= -7,  9  1   7   7     H FCB FCA  K,L= -6, 10
K,L= -7,  4    H FOE FCA  2  10  11  -3  10  11     H FCB FCA
  H FOB FCA  -2   0   2  3  15  15  -2   0   2    -2   4   5
-3  15  14  -1   0   3  4   9   8  -1  21  21    -1  20  20
-2   7   8   0  12  12              0  16  17     0   4   3
-1  18  18   1  13  12  K,L= -6,  1  1   2   4    1  13  13
 0  11  11   2   7   8    H FOB FCA  2   1   1    2   9  10
 1  29  29   3  10  10  -4   3   5  3  18  19    3  16  16
 2   2   1   4   7   7  -3  21  22  4  17  17    4   6   4
 3  21  21
```

Table 20 (Continued)

```
K,L= -6, 11        -4    8    8      -1   33   33       5    3    4      2   18   18
   H FOB FCA       -3   17   17       0    0    1                         3    3    6
 -2   10   10      -2   30   30       1   28   27    K,L= -5,  10
 -1   10   10      -1   17   17       2   11   11       H FOB FCA       K,L= -5,  16
  0   19   19       0   16   16       3   10   10     -2    6    5         H FOB FCA
  1    7    8       1   12   11       4    9    8     -1    6    6        1    6    6
  2   30   31       2   29   28       5    7    8      0    7    7        2    6    6
  3   17   18       3   16   16                        1    8    9        3    3    3
  4    9   11       4    8    6    K,L= -5,   6        2   12   12
                    5    3    2       H FCB FCA        3    1    1      K,L= -4,   0
K,L= -6,  12                        -4   14   15       4    7    7        H FOB FCA
   H FCB FCA       K,L= -5,   2     -3    2    4       5   10   10      -5    0    1
 -1    3    1        H FOB FCA      -2    8    7                        -4   10    8
  0    8    9      -4   18   18     -1   22   22    K,L= -5,  11        -3   11   10
  1    0    0      -3    0    1      0   15   13       H FOB FCA        -2   22   22
  2   13   14      -2    6    5      1   13   14     -2    0    3       -1   14   14
  3   16   16      -1    6    6      2   18   19     -1    5    6        0   13   14
  4    8    6       0   55   54      3    4    2      0    9    9        1   14   14
                    1   18   18      4    7    7      1   20   20        2   22   22
K,L= -6,  13        2   10   10      5    3    2      2   25   25        3   11   10
   H FCB FCA        3    3    2                        3    4    3        4    8    8
 -1    0    2       4   10   10    K,L= -5,   7        4   12   12        5    0    1
  0    4    1       5    8    9       H FCB FCA
  1   20   20                       -3   13   11    K,L= -5,  12     K,L= -4,   1
  2   13   13     K,L= -5,   3      -2   12   12       H FOB FCA        H FOB FCA
  3    0    0        H FOB FCA      -1   12   12     -2    6    6      -5    0    4
  4    4    0      -4    6    5      0    6    7     -1   10   10      -4    5    5
                   -3   23   24      1    8    8      0    3    1      -3   10   10
K,L= -6,  14       -2   24   24      2    9    9      1    2    3      -2    2    1
   H FCB FCA       -1   28   28      3    3    3      2   17   18      -1   12   12
  0    3    1       0   21   21      4    2    2      3   20   21       0   47   46
  1    6    6       1    7    7      5   11   12      4    4    0       1   18   18
  2   18   18       2    8    9                                         2   45   44
  3   21   22       3   21   21    K,L= -5,   8    K,L= -5,  13        3   11   10
K,L= -6,  15        4   15   15       H FOB FCA       H FOB FCA        4    9    9
   H FCB FCA        5    6    2     -3   16   16     -1    4    2       5    3    1
  1    5    6                       -2    2    3      0   17   17
  2    0    3     K,L= -5,   4      -1    5    6      1   16   15    K,L= -4,   2
  3    1    2        H FOB FCA       0   10   10      2   22   23       H FOB FCA
                   -4    7    7      1   15   14      3   17   17      -5    8    6
K,L= -5,   0       -3   13   13      2    3    0      4    4    1      -4    3    1
   H FOB FCA       -2    3    2      3   20   20                       -3   12   12
 -5   13   13      -1   18   18      4   11   10    K,L= -5,  14       -2   15   14
 -4    8    7       0   23   22      5    2    3       H FOB FCA       -1   32   32
 -3    8    8       1   70   69                      -1    2    1       0   41   41
 -2   14   14       2    3    4    K,L= -5,   9       0   17   18       1   24   24
 -1   19   19       3   10   10       H FOB FCA       1    3    3       2    1    3
  1   19   19       4    3    2     -3    0    3      2    2    0       3    2    1
  2   13   14       5    7    5     -2    3    4      3    3    1       4    0    1
  3    8    8                       -1    3    4      4   14   15       5    6    4
  4    8    7     K,L= -5,   5      0   17   17
  5   13   13        H FCB FCA      1   28   27    K,L= -5,  15     K,L= -4,   3
                   -4    7    9      2    8    9       H FOB FCA        H FOB FCA
K,L= -5,   1       -3    5    5      3   12   12      0    5    3      -4    6    7
   H FOB FCA       -2   34   35      4   12   12      1   12   12      -3   12   11
```

Table 20 (Continued)

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```
-2  31  30        1   0   1        -2  13  13      -1  41  41        0   5   4
-1   0   0        2  11  12        -1  11  13       1  40  41        1  39  39
 0  47  46        3  16  15         0  18  18       2   3   1        2  10  10
 1   3   4        4   4   4         1  12  12       3   7   8        3  14  14
 2  13  13        5   3   0         2  39  39       4   5   5        4  10  11
 3   7   7                         3   6   6       5   8   8        5   0   0
 4   6   6      K,L= -4,  8         4  22  21
 5  11  12       H FOB FCA         5  17  17    K,L= -3,  1      K,L= -3,  5
                -3  18  18                        H FOB FCA        H FCB FCA
K,L= -4,  4     -2  10  10       K,L= -4, 13      -5   3   1      -4  16  16
 H FOB FCA      -1   0   2        H FOB FCA       -4  17  16      -3   9   9
-4  11   8       0  18  18       -2   4   4       -3  17  17      -2  27  27
-3   3   2       1  39  38       -1   4   3       -2  57  56      -1  65  65
-2   0   0       2   6   7        0  12  14       -1  42  43       0  18  17
-1  17  16       3   3   4        1   0   0        0   6   6       1   5   5
 0  54  54       4  16  16        2   0   1        1  24  24       2   0   3
 1  25  25       5   0   2        3   0   1        2  37  37       3   3   4
 2  11  12                        4   7   6        3  53  52       4   7   8
 3  11  11     K,L= -4,  9                         4  14  13       5  10  11
 4   0   1       H FOB FCA       K,L= -4, 14       5  14  14
 5   4   2      -3   7   6        H FOB FCA                      K,L= -3,  6
                -2   3   3       -1  23  23      K,L= -3,  2       H FOB FCA
                -1   7   7        0   7   7        H FOB FCA      -4  10  10
K,L= -4,  5      0   8   8        1   5   7       -5   3   2      -3   4   2
 H FOB FCA       1  55  56        2   2   2       -4  19  19      -2   3   2
-4   4  15       2  23  23        3  27  27       -3  14  12      -1  17  17
-3   8   9       3   8   8        4  13  13       -2  27  27       0  21  20
-2  31  31       4  20  20                        -1  15  14       1  28  28
-1  12  11       5   8   7       K,L= -4, 15       0  86  86       2   9  10
 0  28  27                        H FOB FCA        1   1   0       3  15  15
 1  18  17     K,L= -4, 10       -1   8   7        2  26  26       4   9  10
 2  18  18       H FOB FCA        0  16  17        3  45  43       5   8   8
 3   4   5      -3  11  10        1  13  13        4   0   1
 4   5   5      -2   4   3        2   4   5        5   9  10     K,L= -3,  7
 5   9  10      -1  11  12        3  13  12                       H FCB FCA
                 0   3   1        4  10  10      K,L= -3,  3      -4  10   9
                 1   3   3                        H FOB FCA      -3  13  14
K,L= -4,  6      2   0   1       K,L= -4, 16      -5   3   0      -2  18  19
 H FOB FCA       3  16  15        H FOB FCA       -4   2   1      -1  38  38
-4   4   4       4   5   6        0  14  13       -3  20  21       0  20  21
-3  14  13       5   0   2        1  15  15       -2  40  40       1   5   6
-2   3   4                        2   3   2        -1   2   3       2  10   9
-1  25  23     K,L= -4, 11        3   0   0        0  34  36       3   3   3
 0  39  39       H FOB FCA                         1  24  23       4  21  21
 1  47  46      -2   4   3       K,L= -4, 17       2  16  17       5  15  15
 2  11  11      -1  20  21        H FOB FCA        3  17  16
 3  26  26       0   0   2        1   2   6        4  10  10     K,L= -3,  8
 4   4   4       1  15  15        2   7   6        5   7   6       H FCB FCA
 5   3   0       2  12  13                                        -3   9   9
                 3   6   7       K,L= -3,  0     K,L= -3,  4      -2   4   4
                 4   8   9        H FOB FCA        H FOE FCA      -1  23  22
K,L= -4,  7      5   8   8       -5   7   8       -4   6   7       0  13  11
 H FOB FCA                       -4   4   5       -3   8   9       1   3   1
-4   3   1      K,L= -4, 12      -3   8   8       -2  25  24       2  20  20
-3   4   4       H FOB FCA       -2   0   1       -1   7   6       3   9   8
-2   2   2                                                        
-1  26  25                                                        
 0   2   1                                                        
```

Table 20 (Continued)

```
  4  13  14        1  36  37       -3  23  22       -1  54  54        3   7   6
  5   1   5        2   6   6       -2  29  28        0  38  37        4  24  24
                   3  15  15       -1  12  12        1  73  72        5  10  10
K,L= -3,  9        4   4   4        0  37  38        2  21  22
  H FCB FCA        5   0   4        1  11  11        3  21  20    K,L= -2, 10
 -3   0   3                         2   5   4        4   4   5      H FOB FCA
 -2   3   4    K,L= -3, 14          3  33  32        5  12  12     -3  16  16
 -1  17  17      H FCB FCA          4   0   1                      -2   3   4
  0  20  20     -1   4   4          5   5   4    K,L= -2,  6        -1  24  24
  1   8   8      0   9  10                         H FOB FCA        0   0   0
  2  48  47      1   0   2      K,L= -2,  2       -4   1   2        1   0   2
  3   9   9      2  10  10        H FOB FCA       -3  28  28        2  17  17
  4  25  25      3   2   1       -5  18  17       -2  12  12        3  39  39
  5   9   8      4   0   4       -4   0   0       -1  10   8        4   6   5
                               -3  20  20         0  38  38        5  10   8
K,L= -3, 10   K,L= -3, 15       -2  36  33        1  11  12
  H FCB FCA      H FOB FCA      -1  77  77        2  11  11    K,L= -2, 11
 -3   5   5     -1   6   5        0  76  79        3  46  46      H FOB FCA
 -2  12  12      0   0   0        1 137 154       4  21  20     -3   2   3
 -1   9   9      1  19  19        2   4   5        5  11  11     -2   0   1
  0  10  10      2  15  14        3  31  29                      -1  11  11
  1   2   4      3   4   4        4   2   2    K,L= -2,  7        0   3   2
  2  12  13      4   5   4        5  23  22       H FOB FCA       1  11  10
  3   5   4                                      -4   5   5       2   2   0
  4  12  13   K,L= -3, 16    K,L= -2,  3         -3   0   4       3   6   7
  5   3   1      H FOB FCA       H FOB FCA       -2  12  11       4  16  17
                 0   2   3      -5   8   8       -1  35  35       5  17  18
                 1   6   5      -4   7   7        0   8   8
K,L= -3, 11      2  11  10      -3  19  19        1  28  28    K,L= -2, 12
  H FCB FCA      3   3   1      -2  20  20        2  18  18      H FOB FCA
 -3   9   8      4   0   1      -1  12  11        3  15  15     -2  21  21
 -2   2   2                      0  60  60        4   8   7     -1   6   5
 -1   4   2   K,L= -3, 17        1  44  44        5   3   3      0  36  37
  0  28  28      H FOB FCA       2  26  25                       1   6   6
  1  45  43      1  11  11       4   3   2    K,L= -2,  8        2   5   4
  2  42  41      2   5   5       5   6   5       H FOB FCA       3   3   5
  3   3   1      3   9   9                       -4  10   9       4  31  31
  4  11  11                   K,L= -2,  4        -3   4   6       5  18  18
  5  13  14   K,L= -2,  0        H FOB FCA       -2  17  17
                 H FOB FCA      -4  43  43       -1   2   2    K,L= -2, 13
K,L= -3, 12     -5   8   8      -3  13  12        0  11  11      H FOB FCA
  H FCB FCA     -4  16  15      -2  14  14        1  33  32     -2   3   3
 -2   3   4     -3   0   1      -1  23  23        2  52  52     -1  11  12
 -1  17  18     -2  41  40       0 105 108       3   3   3      0  25  25
  0  16  17     -1   7   5       1  42  42        4  22  22      1   6   7
  1  10   9      0  99 102       2  27  29        5  13  13      2   0   2
  2   3   2      1   8   6       3   5   4                       2   0   2
  3   7   8      2  39  40       4   4   3    K,L= -2,  9        3   5   3
  4   9   8      3   3   1       5   8   5       H FOB FCA       4   8   9
  5   0   1      4  16  15                       -3   3   4      5  11  12
                 5   7   8    K,L= -2,  5        -2   9   8
K,L= -3, 13                     H FOB FCA       -1   1   2    K,L= -2, 14
  H FOB FCA   K,L= -2,  1       -4  11  11        0  30  30      H FOB FCA
 -2   5   5      H FOB FCA      -3   9   9        1  15  14     -2   5   6
 -1   5   5     -5   4   5      -2  31  31        2  21  20     -1  24  24
  0  27  28     -4   8   8
```

Table 20 (Continued)

```
 0   3   6      -3   1   1      -3  22  23       2  30  28       0  10  10
 1   8   8      -2  51  52      -2  12  13       3   1   2       1   2   2
 2   1   1      -1  42  43      -1  63  64       4  28  29       2  12  12
 3  15  16       0  55  52       0  61  62       5  23  22       3   4   1
 4   6   6       1  79  82       1  62  64                       4   4   3
 5  16  16       2  24  24       2  28  26    K,L= -1, 10        5   4   2
                 3  53  54       3  28  28      H FCB FCA
K,L= -2, 15      4   8   8       4  18  18      -3   2   1    K,L= -1, 15
  H FOB FCA      5  21  21       5  14  13      -2  10  10      H FCB FCA
 -1   5   6                                     -1  14  14      -1   4   1
  0   3   3   K,L= -1,  2    K,L= -1,  6         0  10  10       0  12  11
  1  19  20     H FOB FCA      H FOB FCA        1   7   5       1  21  21
  2   3   1     -5   7   7      -4   4   6       2   4   4       2  19  19
  3   0   1     -4   6   6      -3   0   3       3   7   7       3  14  13
  4   0   0     -3   5   3      -2  23  23       4   8   7       4  12  11
                -2  24  24      -1   8   7       5   0   0
K,L= -2, 16     -1  21  20       0   0   1                   K,L= -1, 16
  H FOB FCA      0  30  29       1  15  15    K,L= -1, 11      H FCB FCA
  0  24  24      1   9   9       2  13  14      H FCB FCA      -1   0   1
  1   8   8      2  17  17       3  15  15      -3  16  15       0   0   1
  2   2   0      3   0   0       4  12  12      -2   6   6       1   6   7
  3   5   4      4   5   5       5   9   9      -1  18  17       2   4   4
  4  13  12      5   5   5                       0  29  30       3   0   4
                             K,L= -1,  7         1  35  34       4   4   1
K,L= -2, 17   K,L= -1,  3       H FOB FCA        2  26  26
  H FOB FCA     H FOB FCA      -4  10   9        3  10   9    K,L= -1, 17
  0   7   8     -5   0   0      -3  12  12        4   6   7      H FCB FCA
  1  16  17     -4  16  15      -2  30  30        5  22  23      0   7   6
  2  12  12     -3  29  30      -1  14  14                      1  13  13
  3   3   3     -2  54  54       0  32  33    K,L= -1, 12       2   6   6
                -1  14  14       1 116 121      H FCB FCA       3   8   9
K,L= -2, 18      0  62  62       2  27  26      -2   5   4       4   4   1
  H FOB FCA      1  82  86       3   4   5      -1   1   2
  1  18  17      2  63  64       4  19  19       0  12  12    K,L= -1, 18
  2   0   0      3   8   8       5  18  18       1   5   6      H FCB FCA
  2   0   0      4  22  23                       2  11  11      1   2   1
  3   0   3      5  19  20    K,L= -1,  8        3   5   6      2   9   9
                                H FCB FCA       4   0   1      3   5   7
K,L= -1,  0   K,L= -1,  4      -4   3   5        5   4   3
  H FOB FCA     H FOB FCA      -3   0   2                    K,L=  0,  0
 -5   8   9     -5   5   4      -2   9   8    K,L= -1, 13      H FCB FCA
 -4   0   1     -4   9   9      -1  10   9      H FOB FCA      -5  15  15
 -3   6   5     -3   5   5       0  12  12      -2   9  10     -4  40  40
 -2  28  27     -2  14  14       1  14  14      -1   7   7     -3  12  12
 -1  69  70     -1  31  31       2  13  13       0  25  24     -2  25  26
  1  70  70      0  12  12       3  15  14       1  27  27     -1  92  95
  2  27  27      1  57  56       4  15  14       2  35  36      1  91  95
  3   5   5      2   2   2       5   4   2       3  24  24      2  25  26
  4   0   1      3  22  21                       4  13  14      3  11  12
  5  10   9      4  12  12    K,L= -1,  9        5   0   2      4  39  40
                 5   7   7      H FCB FCA
K,L= -1,  1                    -3  17  17                    K,L=  0,  2
  H FOB FCA   K,L= -1,  5      -2   5   5    K,L= -1, 14      H FOB FCA
 -5  24  23     H FOB FCA      -1  26  26      H FCB FCA      -5  35  35
 -4  39  40     -4   5   4       0  41  40      -2   0   1     -4  32  32
                                1  24  24      -1   2   1
```

Table 20 (Continued)

H	FOB	FCA
-3	39	39
-2	9	9
-1	104	113
0	20	19
1	107	113
2	16	16
3	4	6
4	4	5
5	16	15

K,L= 0, 4
H	FOB	FCA
-5	0	5
-4	48	49
-3	19	19
-2	8	8
-1	19	18
0	18	19
1	70	68
2	54	56
3	8	9
4	5	5
5	38	39

K,L= 0, 6
H	FCB	FCA
-4	26	26
-3	45	46
-2	4	2
-1	25	24
0	19	18
1	119	123
2	5	5
3	19	20
4	16	17
5	4	5
6	22	23

K,L= 0, 8
H	FOB	FCA
-4	2	6
-3	17	18
-2	24	24
-1	31	31
0	19	20
1	52	51
2	83	83
3	11	11
4	49	48
5	20	21

K,L= 0, 10
H	FOB	FCA
-3	14	14
-2	6	6

H	FOB	FCA
-1	43	44
0	9	9
1	25	25
2	67	65
3	62	61
4	27	28
5	18	17

K,L= 0, 12
H	FOB	FCA
-3	5	6
-2	28	28
-1	5	5
0	26	26
1	2	1
2	18	18
3	2	2
4	24	25
5	6	5

K,L= 0, 14
H	FOB	FCA
-2	12	13
-1	28	29
0	3	2
1	32	32
2	4	3
3	12	13
4	4	3
5	19	19

K,L= 0, 16
H	FOB	FCA
-1	6	5
0	27	27
1	0	2
2	7	6
3	3	5
4	13	14

K,L= 0, 18
H	FOB	FCA
1	15	14
2	6	6
3	6	4

K,L= 2, 0
H	FOB	FCA
0	98	102

COMPOUND 3

Preliminary

Crystals were grown in the same manner as with Compound 2. The compound crystallized in rectangular crystals, and a suitable one was easily found.

For the solution of the structure the $Pca2_1$ space group was assumed where the equivalent positions are: 1) x, y, z; -x, -y, 0.5+z, y, 0.5+z; and 0.5+x, -y, z.[35] The lattice parameters were determined by diffractometer data to be: a = 12.67(a)Å; b = 9.13(1)Å; and c = 11.89(1)Å.

The unique data were limited to 916 reflections, of which 616 were greater than two standard deviations of their intensity and were used to refine the structure. Over 250 parameters were present. This placed the data point to parameter ratio well below the five to one minimum recommended for meaningful refinement.[37]

Solving the Structure

A Patterson map, made with all 916 collected reflections, showed four equivalent y coordinates for the bromine atom namely, 0.2, -0.2, 0.3, and -0.3. The z coordinate, not being critical for the first atom placed, was given an arbitrary value of zero. This is charac-teristic of many non-centric space groups.[38] The x coordinate for the bromine atom was observed to be zero.

When the bromine atom was placed at each of the four possible positions, the least squares calculations gave equivalent R factors. It was determined later that the difference between the four was a choice of origins. Any one of the four choices for the bromine atom position would have led to the solution of the structure. The only difference would have been the atom positions moving 0.5 units of the unit cell or changing to negative in signs.

All calculations were performed at Lawrence Livermore Laboratory. In performing Fourier calculations, the data were examined visually and all reflections having an Fc less than 50 percent or more than 200 percent of their respective Fo were eliminated from the Fourier calculations. This was not necessary for the other structure solutions as the computer program used at South Dakota State University automatically rejected these reflections.

Three hundred of the more intense reflections were selected as a partial data deck for obtaining the trial structure. Computer time would thus be conserved.

Arbitrarily, the bromine atom was placed at (0.0, 0.2, 0.0). The first Fourier map of one molecular unit revealed two mirror planes. After the first atom was placed, the second atom could be placed in any one of four equivalent positions revealed by the Fourier map. The second atom placed destroyed a pseudosymmetry plane, and the subsequent Fourier map showed only the one remaining mirror plane. The third atom could be arbitrarily placed in one of two equivalent positions

destroying the remaining mirror plane. All subsequent atoms had to be placed in only one position relative to the first three atoms.

The first attempt at solving the structure proved unsuccessful as the conditions relating to destroying mirror planes were violated. The effect of the second atom placed, the phosphorus atom, was difficult to observe. Its z coordinate of 0.225 placed it very close to 0.25 which is a "centrosymmetric" location. This, plus its relatively low atomic number, prevented the effective destruction of the pseudosymmetric plane. The subsequent erroneous positioning of the third atom, the chlorine atom, did not lead to the solution of the structure.

Fortunately, the phenoxy derivative, Compound 2, had been solved and while the structure was different, the bromine-phosphorus distance could be calculated with reasonable accuracy. The results of the structure solution of Compound 2 plus the expected bromine-carbon distance gave an expected bromine-phosphorus distance of 6.5Å. A relatively intense peak at this distance from the bromine atom, was determined to be caused by the phosphorus atom.

The position of the chlorine atom was not determined next (a mistake made the first time). The carbon atoms of the benzene ring were located with the aid of a difference Fourier map. After they had been placed, the chlorine atom position was located and placed in the structure with the aid of a difference Fourier map.

The other atoms were then located by calculating difference maps, inspecting the maps for new atom positions and calculating a least squares cycle with the new positions to obtain the R factor. When all the atoms were in place, the R factor was reduced to 0.11 after three cycles of least squares calculations.

Anisotropical temperature parameter refinement was next carried out on all nonhydrogen atoms with all data points greater than two standard deviations above background. This was 616 reflections of the 912 total. A weighting scheme was introduced at this point similar to the one used for the final refinement of Compound 2.

From a difference map made at this time, the hydrogen atom positions could not be unambiguously found. However, all but three of the hydrogen atom positions were fixed by the nonhydrogen atoms. The positions of the 10 hydrogen atoms that were fixed were calculated and placed in the structure. Refinement on these hydrogen atom positions failed to reduce the R factor, so the positions were left unrefined.

The estimated standard deviation values made it evident at this point that Compound 3 was not to be solved as elegantly as the first two structures. With those structures the Fo's above five were above the three standard deviation cutoff point. With the third compound the reflections with Fo's of 20 were below the two standard deviation cutoff point.

Summary

The final atom positions of the nonhydrogen atoms are shown in
Table 21. The hydrogen atom positions are shown in Table 22. Tables
23 and 24 list bond distances and angles, respectively. Thermal para-
meters of the nonhydrogen atoms are shown in Table 25. The isotropic
hydrogen thermal parameters are arbitrarily set at 5.0.

Using all 912 data points at unit weight gave an R factor of
0.12. The weighted R factor using 616 data points was 0.054.

The structure could be better resolved using copper radiation.
Although the data could be improved and thereby the estimated standard
deviations lowered, there is little doubt of the correctness of the
structure. The Table of Fo and Fc's upon which the structure is based
are shown in Table 26. Molecular diagrams were made using the computer
program ORTEP and are shown in Figures 5, 6. 7, and 8.

Table 21

Positional Parameters of the Nonhydrogen Atoms
(x 10^4) for Compound 3

Atom	x	y	z
Br	4939(2)	12022(2)	5000*
Cl	964(7)	2357(9)	5531(7)
P	2619(4)	6063(6)	2248(5)
O(1)	3048(12)	5079(20)	3230(13)
O(2)	1549(14)	5323(21)	1854(12)
O(3)	3390(11)	6245(17)	1372(12)
O(4)	2215(13)	7505(18)	2815(15)
C(1)	3454(18)	9704(25)	4966(22)
C(2)	2888(16)	8523(26)	3327(21)
C(3)	2862(16)	8650(22)	4473(20)
C(4)	3545(17)	9332(25)	2693(20)
C(5)	2223(17)	4541(23)	4094(16)
C(6)	525(21)	3509(26)	4469(21)
C(7)	4104(17)	10574(25)	4340(19)
C(8)	4188(18)	10365(30)	3231(23)
C(9)	1647(22)	2370(29)	2947(23)
C(10)	806(19)	4839(30)	2695(24)
C(11)	1345(17)	3805(25)	3557(18)

*Parameter not refined

Table 22

Positional Parameters of the Hydrogen Atoms

$(x\ 10^4)$ for Compound 3

(No parameters were refined)

Atom	x	y	z
H(1)	3390	9800	5700
H(2)	3610	9210	1980
H(3)	4620	910	2840
H(4)	2410	8110	4900
H(5)	2100	5290	4450
H(6)	500	5500	3000
H(7)	330	4480	2410
H(8)	2530	4030	4500
H(9)	290	4369	4748
H(10)	-70	3175	4139

Table 23

Interatomic Distances (Å) for Compound 3

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Br	C(7)	1.87(2)Å	C(6)	C(11)	1.53(3)Å
Cl	C(6)	1.74(3)	C(7)	C(8)	1.34(4)
P	O(3)	1.44(2)	C(9)	C(11)	1.55(4)
P	O(1)	1.55(2)	C(10)	C(11)	1.55(4)
P	O(2)	1.57(2)	H(1)	C(1)	0.88
P	O(4)	1.59(2)	H(2)	C(4)	0.86
O(1)	C(5)	1.55(3)	H(3)	C(8)	0.87
O(2)	C(10)	1.44(3)	H(4)	C(3)	0.91
O(4)	C(2)	1.40(3)	H(5)	C(5)	0.82
C(1)	C(3)	1.35(3)	H(6)	C(10)	0.80
C(1)	C(7)	1.36(3)	H(7)	C(10)	0.76
C(2)	C(4)	1.34(3)	H(8)	C(5)	0.78
C(2)	C(3)	1.37(4)	H(9)	C(6)	0.90
C(4)	C(8)	1.40(3)	H(10)	C(6)	0.90
C(5)	C(11)	1.45(3)			

Table 24

Interatomic Angles for Compound 3

O(1)	P	O(2)	107(1)°	C(11)	C(5)	H(5)	118°
O(1)	P	O(3)	112(1)	C(11)	C(5)	H(8)	112
O(1)	P	O(4)	106(1)	C(1)	C(6)	C(11)	114(2)
O(2)	P	O(3)	115(1)	C(1)	C(6)	H(9)	111
O(2)	P	O(4)	101(1)	C(1)	C(6)	H(10)	112
O(3)	P	O(4)	114(1)	C(11)	C(6)	H(9)	109
P	O(1)	C(5)	116(1)	C(11)	C(6)	H(10)	109
P	O(2)	C(10)	119(1)	Br	C(7)	C(1)	122(2)
P	O(4)	C(2)	123(1)	Br	C(7)	C(8)	118(2)
C(3)	C(1)	C(7)	121(2)	C(1)	C(7)	C(8)	120(2)
C(3)	C(1)	H(1)	117	C(4)	C(8)	C(7)	120(2)
C(7)	C(1)	H(1)	123	C(4)	C(8)	H(3)	120
O(4)	C(2)	C(3)	118(2)	C(7)	C(8)	H(3)	120
O(4)	C(2)	C(4)	120(2)	O(2)	C(10)	C(11)	111(2)
C(3)	C(2)	C(4)	122(2)	O(2)	C(10)	H(6)	113
C(1)	C(3)	C(2)	119(2)	O(2)	C(10)	H(7)	110
C(1)	C(3)	H(4)	119	C(11)	C(10)	H(6)	112
C(2)	C(3)	H(4)	122	C(11)	C(10)	H(7)	112
C(2)	C(4)	C(8)	118(2)	C(5)	C(11)	C(6)	107(2)
C(2)	C(4)	H(2)	123	C(5)	C(11)	C(9)	114(2)
C(8)	C(4)	H(2)	119	C(5)	C(11)	C(10)	110(2)
O(1)	C(5)	C(11)	112(2)	C(6)	C(11)	C(9)	111(2)
O(1)	C(5)	H(5)	102	C(6)	C(11)	C(10)	106(2)
O(1)	C(5)	H(8)	105	C(9)	C(11)	C(10)	108(2)

Table 25

Temperature Parameters of the Nonhydrogen Atoms
$(\times 10^4)$ for Compound 3

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	43(1)	42(1)	41(1)	12(1)	4(1)	-8(1)
Cl	80(5)	59(4)	45(4)	18(4)	2(4)	18(3)
P	25(3)	28(2)	23(2)	-3(2)	9(3)	2(2)
O(1)	22(7)	38(8)	29(7)	-4(6)	-2(6)	5(7)
O(2)	50(9)	46(9)	19(7)	-16(8)	1(6)	11(6)
O(3)	29(7)	42(8)	22(7)	-2(6)	5(6)	-11(6)
O(4)	36(9)	48(9)	41(8)	-11(6)	-8(6)	-9(7)
C(1)	56(12)	44(10)	20(9)	12(10)	-4(12)	0(12)
C(2)	18(9)	41(11)	33(11)	3(8)	-1(9)	0(9)
C(3)	17(9)	31(10)	34(10)	-3(7)	7(8)	-8(9)
C(4)	24(10)	38(11)	29(9)	-17(9)	-4(8)	-11(9)
C(5)	32(10)	29(10)	17(9)	-6(8)	-5(8)	-5(8)
C(6)	38(11)	32(12)	35(11)	-29(10)	-2(10)	12(9)
C(7)	32(10)	32(10)	26(11)	0(9)	4(8)	0(8)
C(8)	24(11)	51(13)	41(13)	-4(10)	14(9)	1(12)
C(9)	42(13)	36(12)	44(13)	2(10)	7(11)	-4(10)
C(10)	37(13)	37(12)	50(13)	3(10)	-7(11)	-13(12)
C(11)	38(12)	25(10)	21(11)	7(8)	-10(8)	0(9)

Factor expression used is:

$$\exp\left\{-\tfrac{1}{4}\left[\frac{B_{11}h^2}{a^2} + \frac{B_{22}k^2}{b^2} + \frac{B_{33}l^2}{c^2} + \frac{2B_{12}hk}{ab} + \frac{2B_{13}hl}{ac} + \frac{2B_{23}kl}{bc}\right]\right\}$$

Table 26

Fo-Fc Values· for Compound 3

```
H,K=  0,  0      2   34   35     0   10   11     L FOB FCA      11   14   12     10   16   18
  L FCB FCA      4   39   33     1   60   62     0   15   14                    11   32   33
  2   86   80    6   32   28     2   25   28     1   33   33   H,K=  2,  5      12   10   10
  4  164  163    8   24   23     3   84   82     2  209  212     L FOB FCA    H,K=  3,  2
  6   68   69                    4   23   23     4   82   82     0   51   48     L FCB FCA
  8   22   19   H,K=  0,  8      5   54   54     5   48   50     1   19   18     0   10    5
 10   33   34     L FOB FCA      6    0    9     6   67   70     2   89   90     1   95   93
 12   21   21    0    9    9     7   49   51     8   55   52     4   42   43     3   53   56
                 2   34   35     8   27   29     9    9   12     5    8    9
H,K=  0,  1      4   19   21     9   43   43    10   28   31     6   65   66   H,K=  3,  3
  L FOB FCA      6   17   15    10    0   11    12   33   29     7    9    3     L FCB FCA
  2  128  129                  11   17   21                    8   26   26     0    0    7
  4   70   69   H,K=  0,  9                   H,K=  2,  1      9   10   12     1   62   65
  6   34   35     L FOB FCA    H,K=  1,  5      L FOB FCA     10   24   26     3   58   58
  8   25   22    0    0    5     L FOB FCA      0   99   98                    4   51   48
 10    4   14    2   34   33     0   20   23     2   19   18   H,K=  2,  6      5   30   31
 12   20   20                    2   25   24     3   11    9     L FCB FCA      6   10    3
                H,K=  1,  1      5    4   15     4   23   21     0   24   25     7   30   33
H,K=  0,  2      L FOB FCA      6   14   11     5   28   27     1   20   17     9   27   26
  L FCB FCA      0   36   44     9    9   10     6   36   36     2   15   16    10   27   26
  0   48   39    1   60   59     9    0    4     7   18   14     3   16   15
  2  151  158    3   85   81    10   13   16     8   13   14     4   34   32   H,K=  3,  4
  4  103  107    4   42   41                    9   15   15     5   24   25     L FOB FCA
  6   34   34    5   86   82   H,K=  1,  6     10   33   34     6   13   13     0   18   18
  8   43   41    6   25   22     L FOB FCA     11   18   16     7    8    4     1   85   85
 10    8   17    7   82   82    0    6    2    12   18   16     8   11   16     2   26   26
 12    0    3    8   25   23    1   54   53                    9    7   11     3   49   51
                 9   64   62    2   24   24   H,K=  2,  2                      4   37   37
H,K=  0,  3     10   16   12    3   31   33     L FOB FCA    H,K=  2,  7      5   55   52
  L FCB FCA     11   37   38    4   16   19     0  113  116     L FCB FCA      6   22   21
  0  105  101   12    4    5    5   43   43     2  123  122     0   49   50     7   42   38
  2   58   56                   6   22   20     3   48   43     1    0    9     8   19   17
  4   75   73   H,K=  1,  2     7   30   30     4   60   60     2   44   46     9   21   19
  6   63   64     L FOB FCA     8   21   24     6   71   69     3   11    6    10   10    5
  8   26   23    0   16   13     9   23   25     7   29   28     5    0    5    11   31   28
 10   30   30    1   86   84    10    0   10     8   33   33     6   19   20
 12   23   23    2   95   95                    9   20   23     7    5    2   H,K=  3,  5
                 3   66   61   H,K=  1,  7     10   32   32     8   13   16     L FCB FCA
H,K=  0,  4      4   26   27     L FOB FCA     11    6    4                    0   22   19
  L FCB FCA      5   41   42    1   30   29    12   23   25   H,K=  2,  8      2   16   16
  2   34   35    6   22   25    2   22   22                    L FOB FCA      3    6    5
  6   27   27    7   24   26    3   27   27   H,K=  2,  3      0   43   42     5   21   18
  8   38   38    8    8   13    4   20   22     L FOB FCA     1   16   13     6   11    3
                 9   16   15    5   21   24     0   40   41     2    6   10     7   11    3
H,K=  0,  5     10   21   24    6    0   20     1   23   27     3   11   12     8   12   13
  L FCB FCA     11   21   23    7   14   10     2   80   81     4   26   26     9    9    8
  0  101  102   12   24   23    9   13    7     4   88   85     5    0    1    10   12    5
  2   73   75                                  5    0    3     6   21   20
  4   75   76   H,K=  1,  3   H,K=  1,  8       6   42   41     7    4    7   H,K=  3,  6
  6   54   56     L FOB FCA     L FOB FCA      7   19   19                    L FOB FCA
  8   54   55    0   81   79    0   25   27     8   65   64   H,K=  2,  9      0   38   38
 10   28   28    1   40   37    1   15   14     9   16   12     L FCB FCA      1   52   45
                 2   67   64    2    0    2    10   25   26     0   19   25     2    0    3
H,K=  0,  6      3   55   50    3   24   25    11    8    4     1   10   10     3   62   64
  L FOB FCA      4   34   35    4   20   19    12    0   10     2    2    6     4   12   14
  0   13   15    5   60   61    7   29   25                    3   13    5     5   43   46
  2   33   30    6   25   28                  H,K=  2,  4      4    9   18     6   23   23
  4   10   11    7   52   49   H,K=  1,  9     L FOE FCA                      7   35   37
  6   40   39    8   21   19     L FOB FCA     0   49   52   H,K=  3,  1      8    7    3
  8    3    8    9   41   44    0    0    0     1   25   22     L FOR FCA      9   27   28
 10    7    9   10   18   16    1   31   33     2   36   36     1  131  126
                11   27   24    2    0    6     4   35   37     2   17   16   H,K=  3,  7
H,K=  0,  7     12   21   18    3   24   24     5   14   15     5   93   93     L FCB FCA
  L FOB FCA                    4    0    4     6   25   24     6   25   25     0   30   31
  0   64   65   H,K=  1,  4    5   22   21     8   30   33     7   54   52     1   31   32
                 L FOB FCA                    9    0    5     8   16   17     2   15   16
               H,K=  2,  0    10   13   16     9   31   31     3   13   14
```

Table 26 (Continued)

```
  4   19   16      H,K=  4,  3       L FOB FCA        5   54   54       9   26   24       4   24   29
  5   23   25       L FOB FCA       0   18   17       6   17   14      10   39   42       5    7    1
  6   27   27      0   81   80      1    9   12       7   28   30      11   11   10       6   43   43
  7   19   17      1   20   19      2   32   32       8   14   15                         7   22   23
  8   15    9      2   88   82      3   10    7       9   29   28    H,K=  6,  1          8   38   35
                   4   35   35      4    3   15      10    7   10     L FCB FCA           9    4    2
H,K=  3,  8        5   19   18      5   11    5                      0   22   22
 L FOB FCA         6   56   55      6   24   23    H,K=  5,  5       1   27   28       H,K=  6,  6
0    8    7        6   64   55                      L FOB FCA        2   11   10        L FOB FCA
1   20   23        7   18   14    H,K=  4,  9      1    0   10       3   31   31       0   35   32
2   24   25        8   36   38     L FOB FCA       2    1    8       4   63   64       1    7   10
3   14   12        9   18   17    0    5    2      3   18   23       5    0    3       2   11   13
4    9   12       10   14   22    1   12   10      4   16   12       6   23   23       3   20   20
5   15   22       11    0    5    2   23   20      5   17   10       7   19   16       4   16   15
6   10   10                       3    6    9      6   18   19       9    0    5       5   14   11
                 H,K=  4,  4                       7    9    7      10   16   15       6   20   23
H,K=  3,  9        L FOB FCA     H,K=  5,  1        8    6    5      11    0    3       7   13   12
 L FOB FCA        0   15   16     L FOB FCA        9    0   12                         8    0    3
0   12   10       2   30   29    0    4    4                      H,K=  6,  2
1    9   17       4   10   15    1  108  109     H,K=  5,  6        L FCB FCA        H,K=  6,  7
2    0    7       5   18   19    2   58   60       L FOB FCA       0   41   39        L FOB FCA
3   27   25       6   42   42    3   94   95      0   12    2      1   42   42       0   30   33
4   11   11       7   13    9    4   16   13      1   55   58      2   52   42       1   11   13
                  8   34   31    5   74   71      2   28   31      3   35   33       2   12   14
H,K=  4,  0      10   20   18    6   16   19      3   40   39      4   45   45       3   12    7
 L FOB FCA       11    0    7    7   41   40      4    8    8      5    9    5       4   21   15
0   76   77                      8   39   35      5   37   36      6   32   32       5    5   19
1   28   29     H,K=  4,  5     10   12    3      6   25   26      7   17   18       6   26   24
2   81   70       L FOB FCA     11    0   10      7   25   29      8   38   38       7    8   10
3   26   24       0   66   68                     8   12   13      9    0    8
4  117  112       1   17   17   H,K=  5,  2                      10   33   31       H,K=  6,  8
5   16   16       2   27   29    L FOB FCA      H,K=  5,  7      11    0    4        L FOB FCA
6   37   38       3   26   25    0   13   13       L FOB FCA                         0   22   22
7   11   14       4   79   78    1   24   27      1    0    4    H,K=  6,  3         1    7   12
9   37   42       5   22   20    2   38   37      2   24   26      L FCB FCA         2   12   17
10   56   54      6   28   26    3   69   68      3   25   26     0   55   58        3    0    7
11    0    2      7    9    8    4   40   40      4   18   17     1   29   29        4   30   32
12   14   24      8   35   38    5   28   29      5   18   16     2   30   31
                  9    4    7    6   30   34      6   16   14     3    7   10        L FOB FCA
H,K=  4,  1      10   31   29    7   43   41      7   22   21     4   45   45       0    0   14
 L FOB FCA                       8   21   25                     5   23   22       1   77   81
2   37   39     H,K=  4,  6      9   25   22    H,K=  5,  8      6   44   42       2   17   19
4   22   21       L FOB FCA     10   12   11      L FOB FCA      7   10   16       3   74   72
5   24   25      0   10    9    11   22   22      0   27   26     8   13   12       4   36   39
6   48   48      1   24   23                     1   26   26     9    6   11       5   26   29
7   11   11      2   29   32    H,K=  5,  3       2    8    7    10   25   25       6   11    7
8   16   15      3   17   19     L FOB FCA        3   28   25                       7   48   45
9   20   19      4   21   22    0   16   14       4   21   18    H,K=  6,  4        8   19   17
10   18   18      5   22   24    1   87   88       5   20   17     L FCB FCA        9   13    3
11   14   13      6   16   12    2   11   15                     0   20   20       10   17   17
12   16   17      7   14   14    3   57   58    H,K=  5,  9      1   22   21
                  8   13   15    4   14   17      L FOB FCA      2   14    9       H,K=  7,  2
H,K=  4,  2      9    7    4    5   29   30      0    5    9    -3   20   18        L FOB FCA
 L FOB FCA                       6   36   41      1   22   21    4   45   47       0    8   17
0   89   85     H,K=  4,  7      7   15   13      2    5    6    5   19   20       1   39   35
1   40   36       L FOB FCA      8   29   32                     6   19   19       2   17   16
2   45   43      0   12    7    9    8    4    H,K=  6,  0       7    5    6       3   31   32
3   42   41      1    6    9   10   18   19      L FCB FCA       8   25   25       4   30   29
4   77   74      2   33   35   11   11   17     0   40   42      9   11    8       5   48   43
5   59   58      3    0    8                    1   33   32     10   21   22       6   21   22
6   70   70      4   29   26   H,K=  5,  4      2   72   72                        7   20   23
7   16   13      5    0    2    L FOB FCA       3   15   20    H,K=  6,  5         8   11   22
8   45   46      6   28   28   0   18   19      4   32   32      L FCB FCA         9   14   14
9   25   24      7   14   11   1   71   69      5   36   36     0   54   34        10    3   11
10   34   34      8   21   21   2   15   18      6  104  103    1   13   13       H,K=  7,  3
11    0   12                    3   65   61      7   36   38    2   66   65        L FOB FCA
               H,K=  4,  8      4   15   12      8   54   50    3   20   21       0    5    5
```
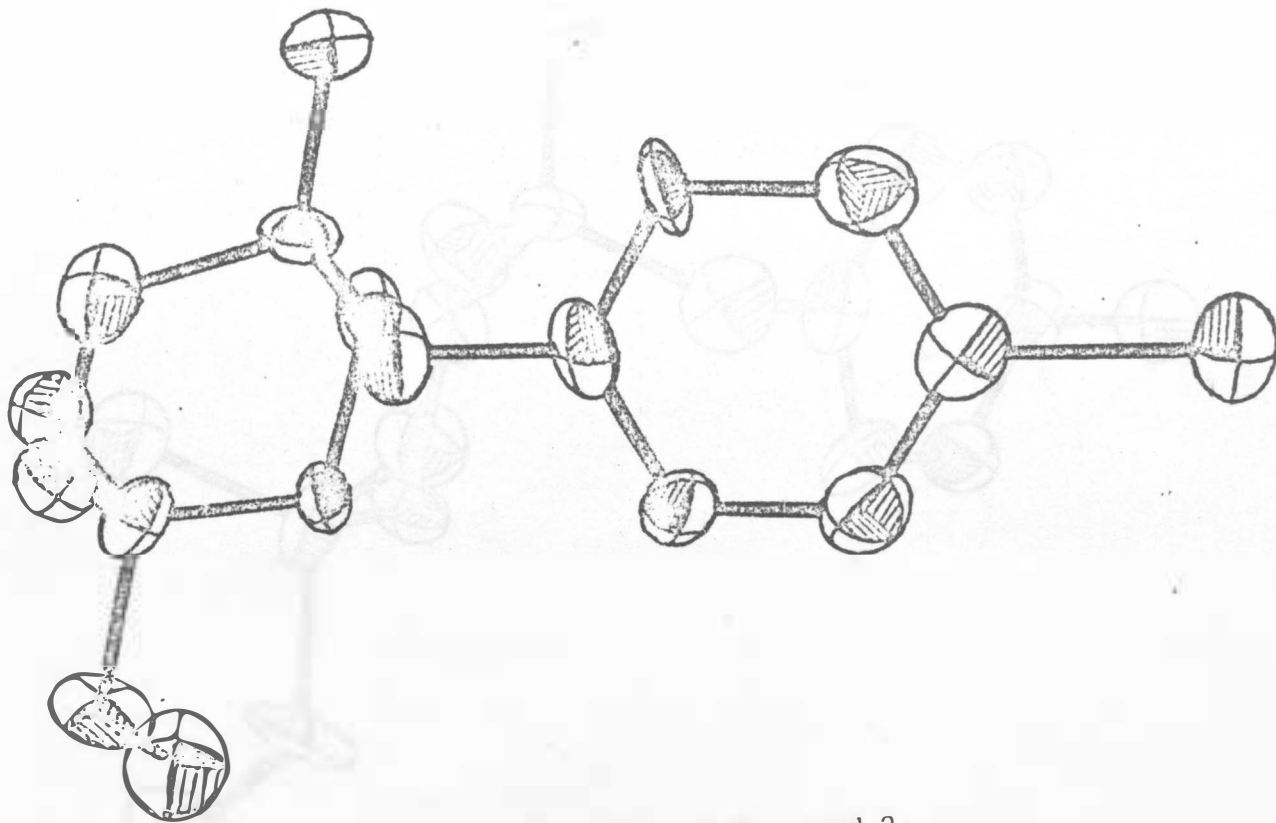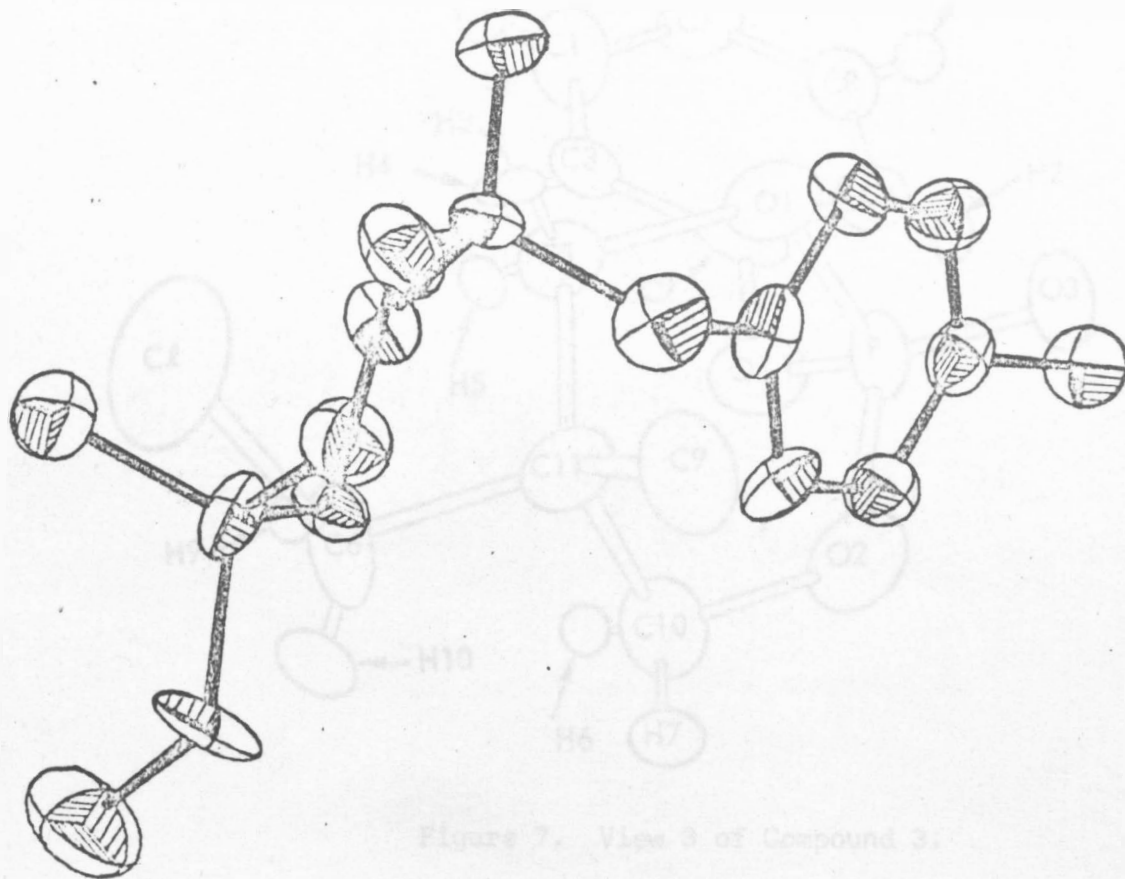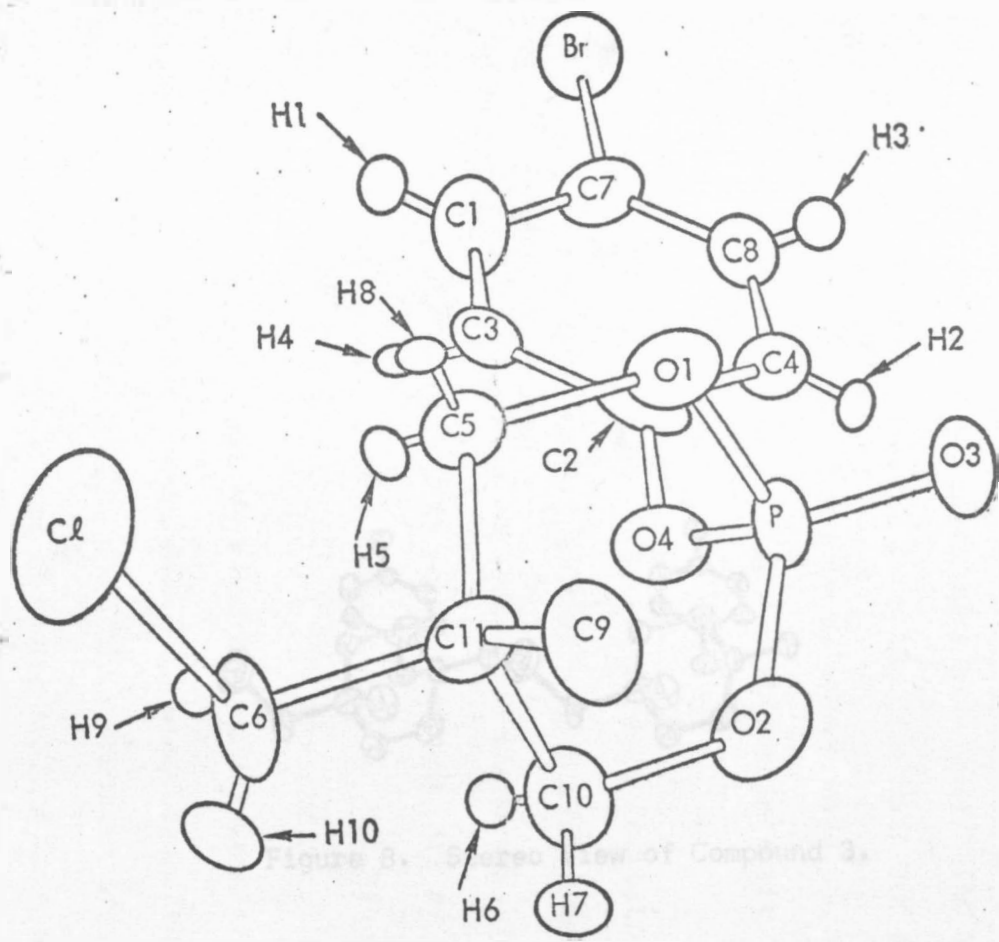
Table 26 (Continued)

```
 1  47  47      1  33  33      2  23  23      1  28  29      7   9   7      4   6  11
 2  22  23      2  46  49      3  23  23      2  21  20      8  19  19      5  19  19
 3  36  36      3  34  34      4  42  40      3  27  25                     6   7  12
 4   7   9      4  63  67      5  22  23      4  15  12   H,K= 10,  3
 5  39  42      5  36  35      6  29  29      5  36  35    L FOB FCA    H,K= 11,  4
 6  38  37      6  40  42      7  11   3      6  16  13    0  52  57     L FOB FCA
 7  11  16      7  40  39      8  19  21      7  23  22    1  12  13     0   6  12
 8  18  21      8  45  47                     8   0   7    2  27  25     1  17  20
 9  10  18      9  33  33   H,K=  8,  6                    3   3   3     2  12  12
10  15  13     10  24  23    L FOB FCA     H,K=  9,  5     4  28  30     3  26  23
                            0   0  16      L FCB FCA      5  18  16     4  13  10
H,K= 7,  4   H,K=  8,  1    1  16  13      0  15  16      6  21  22     5   8  12
 L FOB FCA    L FOB FCA     2  22  24      1  15   9      7   0   5
 0   7  16    0   6  11     3   0   2      2   0   7                  H,K= 11,  5
 1  68  62    1   0   7     4   8   8      3  12  14   H,K= 10,  4     L FOB FCA
 2   6   2    2  24  24     5   7  15      4   0   6    L FCB FCA     0   4  10
 3  46  46    4  22  22     6   7  10      5  14  17    1  16  14     1   0   6
 4  14  16    5   7   3                    6   8   6    2   9   4     2   7  13
 5  35  35    6  26  25   H,K=  8,  7      7   0   7    3  16  14     3  13   8
 6   0   4    7  26  26    L FOB FCA                    4  13  10
 7  32  32    8  16  18    0  18  16    H,K=  9,  6     5  19  18   H,K= 12,  0
 8  12  11    9   7   4    1   9  10      L FCB FCA     6   6   5     L FOB FCA
 9  20  21   10   3   8    2  26  24      0   9   3                  1  14  16
                           3  14  17      1  32  30   H,K= 10,  5     2  26  25
H,K= 7,  5   H,K=  8,  2    4  18  19      2  10  15    L FOB FCA    3  10  13
 L FOR FCA    L FOB FCA                    3  31  29    0  13   8     4  32  31
 0  12   8    0  53  52   H,K=  9,  1      4  11   5    1   0   5     5   6  17
 1  15  16    1  26  24    L FCB FCA      5  21  23    2  40  38     6  20  16
 2   7   4    2  41  38    0   0   3                    3  13  14
 3  12  12    3  28  30    1  34  33    H,K=  9,  7     4  24  23   H,K= 12,  1
 4   0   3    4  37  38    2  27  26      L FOB FCA     5   9   4     L FOB FCA
 5  18  23    5  23  20    3  35  36      0   0   1                  0   7   3
 6  18  16    6  36  39    4   3   6      1  18  17   H,K= 10,  6     1   6  10
 7   9   7    7   6   6    5  51  52      2  18  15    L FCB FCA     2  27  23
 8  16  17    8  13  18    6  24  24      3  20  20    0  18  18     3  17  14
              9   0  12    7  13  14                    1   7   3     4   6  10
H,K= 7,  6   10  17  14    8  15  11    H,K= 10,  0    2  20  11     5   0   9
 L FOR FCA                 9  34  35      L FCB FCA     3   9  11
 0  17  14   H,K=  8,  3                  0  28  30                 H,K= 12,  2
 1  28  31    L FOB FCA   H,K=  9,  2     1  15  12   H,K= 11,  1     L FOB FCA
 2   0   4    0  23  24    L FCB FCA      2  58  62    L FOB FCA    0   5  12
 3  36  37    1  18  17    0  10  16      3  35  35    0  17  16     1   6   7
 4  20  21    2  63  61    1  23  21      4  36  39    1  32  32
 5  23  25    3  10   7    2  17  21      5   0  14    2  10  22
 6   0  10    4  29  29    3  28  30      6  28  30    3  28  28
 7  32  31    5   7   9    4  20  19      7  14  20    4  16  14
              6  24  23    5   2  13      8   3   9    5  20  18
H,K= 7,  7    7  21  18    6   0  12                    6  19  16
 L FOB FCA    8  15  22    7  33  35    H,K= 10,  1    7  25  28
 0  21  21   ·9   0   6    8  13   9      L FOB FCA
 1  19  14                 9  18  16      1  11  10   H,K= 11,  2
 2  15  18   H,K=  8,  4                  2  10  13    L FOB FCA
 3  16   8    L FOB FCA   H,K=  9,  3     3  21  19    0  19  19
 4  22  21    0  15  13    L FOB FCA      4  25  22    1  20  21
 5  11  18    1  41  42    0  28  30      5  17  13    2  19  17
 6   4   3    2  40  41    1  35  34      6   0  12    3  17  14
              3  21  21    2  13  15      7   6   7    4   7  14
H,K= 7,  8    4  10   7    3  18  17      8   0   9    5  27  26
 L FOR FCA    5  13  15    4  28  31                    6   0   2
 0   0   2    6  19  17    5  23  22    H,K= 10,  2    7   0   6
 1  23  20    7  18  16    6   0   5      L FCB FCA
 2  17  18    8   7  12    7  21  23      1  27  29   H,K= 11,  3
 3  15  17                 8  12  11      2  37  38    L FOB FCA
             H,K=  8,  5                  3  13  14    0   0   5
H,K= 8,  0    L FOB FCA   H,K=  9,  4     4  33  34    1  19  25
 L FOB FCA    0  63  65    L FOB FCA      5  21  17    2  23  27
 0  63  59    1  18  19    0  19  18      6  23  25    3  19  18
```

Figure 5.   View 1 of Compound 3.

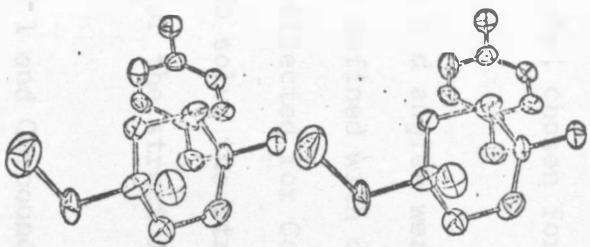Figure 6. View 2 of Compound 3.

Figure 7. View 3 of Compound 3.

Figure 8. Stereo View of Compound 3.

SUMMARY

Single crystals of Compounds 1, 2, and 3 were grown and used to obtain sets of x-ray intensity data. Before diffractometer data was taken a crystal of the compound being studied was aligned and zero and first layer Weissenberg photographs were made. The systematically absent reflections were revealed from the film data and were used to determine the space group. The film data were used to determine the degree of perfection of the crystal chosen for intensity data collection.

The unit cell translations and angles were initially obtained from film data and subsequently refined with diffractometer data. Intensity data from film were collected for Compounds 1 and 2 and the data for Compound 1 were used to solve the structure of that compound. Diffractometer data were used for the structure solutions of Compounds 2 and 3.

The structures of Compound 1 and Compound 2 were solved by the direct method of symbolic addition. This was accomplished using the computer programs FAMEB, MAGIC, and LINK. The atom positions were found from electron density maps and were refined by a full matrix least squares fitting process.

Compound 3 was solved by the heavy atom method and was completed at the Lawrence Livermore Laboratory. First the bromine atom was positioned with the aid of a Patterson map. Difference Fourier maps followed by least squares adjustment of atom parameters located the remaining atoms.

From the final atom positions for each structure a molecular diagram was made using the computer program ORTEP. Bond lengths and bond angles were calculated also using ORTEP. All atom positions had estimated standard deviation values calculated from the full matrix refinement. These standard deviation values were subsequently used to calculate standard deviations in bond lengths and bond angles.

The structures of three different substituted 5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinans have thus been elucidated.

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APPENDIX

A brief description of the computer programs used is presented here. While some programs were only slightly modified, others were drastically altered to permit use in the IBM 360/40 computer or to conform to other policies. They were also modified to permit inter-change of data cards.

FAMEB

This is a FORTRAN program which automatically manufactures E values. It was originally written by Dewar (University of Chicago) and substantially modified by Baenziger (University of Iowa). It is applicable to all centric space groups of orthorhombic or lower symmetry systems. It will convert Fo's (or Fo^2's) to normalized structure factors (E's) suitable for use with the Karle-Hauptman probability relationship.[38] The program will prepare an input tape for the program MAGIC if so desired.

Data Card 1

This card can normally be left blank except for positions 11 and 12. This is the place where the systems number of a linkage tape necessary to connect the two parts of the program must be added. Other spaces are to initiate various printing modes. Consult program for exact options.

Data Card 2 (615)

The fields on this data card are: 1) number of atom types;
2) number of data groups; 3) if 1, use all data for a Wilson plot; if
2, skip first group; 4) same as (3) except for last group; 5) for Fo
input, 1; for Fo^2 input, 2; 6) crystal class, triclinic put in 1,
monoclinic (b unique) put in 2, monoclinic (c unique) put in 3 and
orthorhombic put in 4.

Data Card 3 (14F5.2)

The first seven fields are for epsilon values (E calculations) and
the last seven values are multiplicity factors (for a Wilson plot).
Epsilon and multiplicity values are shown in Tables 27 and 28, respec-
tively.

In case of centering, the epsilon values must be changed if the
systematically absent reflections are omitted. For the Wilson plot
the multiplicity values should be modified if absent reflections are
neglected.

Data Card 4 (215)

There must be one card for every different type of atom (Data
Card 2 Field 1). Each card contains the following: 1) number of
atoms of a specified type in the unit cell; and 2) the atomic number
of the specified atom. The order of the cards must be the same as
the order of the scattering factors on data card 5.

Table 27

Epsilon Values for E Calculation

Miller Index	Field	I	m2	m	2/m	mm2	mmm	222
h 0 0	1	1	1	2	2	2	4	2
0 k 0	2	1	2	1	2	2	4	2
h k 0	3	1	1	1	1	1	2	1
0 0 l	4	1	1	2	2	4	4	2
h 0 l	5	1	1	2	2	2	2	1
0 k l	6	1	1	1	1	2	2	1
h k l	7	1	1	1	1	1	1	1

Table 28

Multiplicity Factors for Wilson Plots

Miller Index	Field	Triclinic	Monoclinic	Orthorhombic
h 0 0	8	2	2	2
0 k 0	9	2	2	2
h k 0	10	2	4	4
0 0 l	11	2	2	2
h 0 l	12	2	2	4
0 k l	13	2	4	4
h k l	14	2	4	8

Data Card 5 (313, I5, I2, Fb.5, 7F6.4)

The fields are: h, k, l, Fo, W, $1/4d^2$, and atomic scattering factors. One card is required for each reflection. This is the same data card used for the least squares program. A -2 in columns 15 and 16 (W) signals the end of a data group. A Wilson plot will be made for each data group. Field 2 in data card 2 specifies the number of data groups.

Data Card 6 (18A4)

This is the title card.

Data Card 7 (2I2)

The two fields are: 1) systems number of linkage tape; and 2) if cards are desired for MAGIC, put in 2.

Data Card 8 (I2, I1, I2, F10.5, I1)

The fields in the data card are as follows:

1. The upper third of the E values are arranged in order according to their magnitude. Beginning with the highest, all reflections that have Miller indexes which add to the Miller indexes of the reflection with the highest E value will be found and printed. The second highest E value will be taken next, etc. This will continue until the number of E value determinations has exceeded the number in this field.

2. Letter symbols (up to 9) will be assigned to high E values conforming to odd-even characteristics of the reflections. The field specifies the number of symbols to assign.

3. This is the systems number of the magnetic tape prepared for MAGIC. If left blank, no tape is prepared.

4. This is usually 1; it is a factor for a weighting index on the symbolic interactions.

5. If 0 interactions will be printed; if 1 only totals will be printed.

MAGIC

This is the symbolic addition program. It will find the reflections that conform to the Karle-Haupman equation, determine a contradiction table, and prepare an output tape for the program LINK.

Data Card 1 (A4, I4, F10.0, 4I2)

The fields on this card are as follows:

1. space group designation,

2. space group number (see subroutine SGSET),

3. sigma (may be left blank if operating from a tape prepared by FAMEB),

4. systems number of input tape (0 if input is from cards),

5. systems number of output tape,

6. not used,

7. not used.

Data Card 2(3I1)

The fields on this card suppress or permit printing output as follows:

1. If 0, the program prints and symbol interaction; if 1, print results; and if 2, no printing.

2. If 0, symmetry related reflections are printed; if 1, no printing.

3. The program prints symbol equivalents if equal to 0.

Data Card 3(2F10.5, 2I2, F10.0)

The fields are:

1. the starting probability for sign determination,

2. the ratio of contributors to inconsistencies,

3. minimum number of contributors necessary for a sign determination (only for iteration 1),

4. number of inconsistencies tolerated for a sign determination (only for iteration 1),

5. the minimum probability tolerated for a recording of a symbol equivalent.

Data Card 4(18A4)

This is the title card.

Data Card 5 (3I3, F11.4, 10X, 10A1)

This card (cards) may be omitted if input is from a magnetic tape prepared by FAMEB. Otherwise, this is the card for reading in the

knowns--one card for each known. Cards prepared by FAMEB or LINK may be used. The fields are: h, k. l, E, and the letter symbols for sign. Letter symbols may be put in any order. A completely blank space for the sign-symbols will signify a plus sign. A completely blank card signals the end of the knowns.

Data Card 6 (3I3, F11.4)

This card (cards) may be omitted if input is from the tape prepared by FAMEB. Otherwise, this card is for the unknowns. See data card 5 for format and Fields.

Data Card 7 (I3, I1, F10.5)

The fields are:

1. number of knowns desired,

2. printing mode after first iteration (see field 1 in data card 2),

3. increment of decrease in probability with each iteration.

LINK

Besides generating sign-symbols, MAGIC also manufactures a table of contradictions which basically is a list of the number of times a particular sign combination is violated. LINK will take these contradictions and calculate the total number of contradictions for each set of possible sign combinations. It will then arrange the sets in increasing order of number of contradictions and print out every sign

combination with the number of contradictions. It then prepares a tape for the electron density program using the best (up to 9) sign combinations.

It also does the following calculations in the process. If a symbol is used for less than 3 percent of the reflections, all reflections having that symbol will be rejected. Symbols fixing the origin will be assigned if appropriate control cards are used. The program will automatically pick the proper reflections for the assignment of + for these symbols as well as determine the proper number of symbols it may assign.

Data Card 1 (18A4)

This is the title card.

Data Card 2 (I2, I1, 2I2, 3I1, 3A4, F10.3, I2, 2I1)

The fields are:

1. This is the systems number of input tape,

2. this specifies the crystal class as 0 for primitive; 1 for A centering; 2 for B centering; 3 for C centering, 4 for F centering; and 5 for I centering,

3. this is the systems number of output tape,

4. this is the number of sign combinations wanted for the electron density program (up to 9),

5. if 1; the all plus sign combination will be skipped,

6. if this is 0; origins will be assigned,

7.   this is not used,

8.   this is the name of problem,

9.   if a contradiction table is wanted, this should be 0; for a weighting index put in 0.00001,

10. this is not used,

11. this is not used,

12. if 0, print output to electron density program on printer,

13. if 1, punch E cards for future runs of MAGIC.

LEAST SQUARES PROGRAM

The least squares program used at South Dakota State University was written by Dr. Norman Baenziger (University of Iowa). It will perform a full matrix least squares calculation to minimize the R factor by finding the best values of up to 140 parameters. Although the maximum number of parameters has been reduced, the program is substantially as it was received. The main change has been a division into several subroutines.

Data Card 1 (18A4)

This is the title card.

Data Card 2 (6F10.5)

The fields are the lattice parameters: a, b, c in Angstroms and α, β, and γ in degrees.

Data Card 3 (14I1, I2, 4X, F10.5, F10.3, 32X, I3, I2)

The fields are:

1. If 1, the program changes atom parameters.

2. If 1, the program includes extinction corrections.

3. If 0, the program uses averaged experimental weights; if 1, it uses a weighting scheme for film data; if 2, it assigns unit weights.

4. Allows output of 0 weighted reflections to the electron density program.

5. If 1, creates a file for the electron density program.

6. If 1, reflection input is from disk or tape.

7. If 1, number of cycles for least squares calculations.

8. If 0, the program refines on all interlayer scale factors; if 1, it refines on overall scale factors; if 2, it refines on individual scale factors; if 3, no refinement of scale factors is carried out.

9. The program minimizes ΔF, otherwise ΔF^2.

10. If 1, a variance-covariance matrix is printed; if 2, in addition to the variance-covariance matrix, the ESD (Estimated Standard Deviation) correction matrix and ESD terms are printed; if 3, the program writes a variance-covariance matrix and ESD terms only; if 4, it writes an ESD correction matrix only; if 5, it only writes ESD terms. Normally 5 should be used.

11. The program rejects absent reflections.

12. Not used.

13. Not used.

14. If 1, the program does not write h, k, l, Fo, etc.

15. If 1, least squares cards are punched; if 2, least squares and ORTEP cards are punched; if 3, ORTEP cards are punched.

16. This is the overall scale factor.

17. This is the weighting number.

18. This is the number of the first cycle.

19. This is the n number.

Data Card 3 (2I5, 2F5.2, 4F10.5)

The fields are:

1. The number of data cards for least squares calculation.

2. The layer line on which calculations are terminated.

3. The weight assigned to zero weight reflections (usually 1).

4. The amount of parameter shift (usually 1).

Data Cards 4, 5, and 6 (10F7.5)

These are the scale factors for the layer lines. Three cards must be present.

Data Card 7 (3F6.5, F7.6, 5F6.5, F3.1, 15L1, 2I1, A4)

This card is for the atom parameters (one card for every atom). The fields are as follows: in this order x, y, z, B_{11}, B_{22}, B_{12}, B_{13}, B_{23} are inputed. Then an occupancy factor term followed by 15 logical fields. If the logical field is "T", the following conditions apply:

1. The atom parameters may be varied.

2. The distance parameters may be varied.

3. The temperature parameters may be varied.

4. The x coordinate is varied.

5. The y coordinate is varied.

6. The z coordinate is varied.

7. Anisotropic parameters are in effect.

8. The B_{22} term is varied.

9. The B_{33} term is varied.

10. The B_{12} term is varied.

11. The B_{13} term is varied.

12. The B_{23} term is varied.

13. Dispersion correction terms will be added.

14. The crystal is centric with dispersion or non-centric.

15. The crystal is non-centric with dispersion. The remaining
three fields are: atom type number corresponding to scattering factor
on data card 9, a non-zero number if input of atom coordinates is in
64ths, and the symbol of the atom. A/* card signals the end of the
atom parameter cards.

Data Card 8 (3I3, I5, I2, F6.5, 7F6.4, I4, 2I3, I2, I3)

This is the reflection data input card. One card is required for
each reflection. The fields are: h, k, l, Fo, W, $1/4d^2$, 7 atomic
scattering factors, 3 dispersion terms, layer line number, and

reflection number. A -2 for W signals the end of reflection data.
A /* card signals the end of the program data.

ELECTRON DENSITY MAPPING PROGRAM

The mapping program adapted at South Dakota State University was
written by Dr. Norman Baenziger (University of Iowa). It is capable
of plotting electron densities in the following ways: 1) Patterson
maps, 2) Fourier maps, 3) difference Fourier maps, and 4) E maps.

The coordinate axes of the unit cell are divided into 64ths. The
density of each cubic 64th is printed using two alphanumeric char-
acters. All or part of a unit cell may be plotted. One unit cell
coordinate is plotted across the page, one is plotted down the page,
while one is plotted in successive layers of pages. All cell edges
are taken to be 90°.

The input, with the exception of one control card, is by a pre-
viously prepared magnetic tape. The tape can be prepared by the least
squares program or by the program LINK. It is, however, possible to
print an E map from cards previously prepared by the programs FAMEB
or LINK.

Data Card 1 (2F10.5, I2, I3, 2I2, 11I1, 2I2, A4)

The fields are:

1. This is the Scale factor for the Fo's.

2. This is the volume of one unit cell in $Å^3$.

3. If input is from tape, this is the systems number of the input drive unit.

4. This is three digit which assigns the crystal axes across the page, down the page, and through the page, respectively. The digit "1", designates the x axis; "2", the y; and "3", the z. For example if the number is 132, x would be plotted across the page, down the page, and y is in layers of pages.

5. This is the beginning layer of the map in 64ths.

6. This is the final layer of the map in 64ths.

7. This is the units of 64ths between layers of pages.

8. This number sets the limit of plotting the unit cell down the page. If 1, the program goes to $\frac{1}{4}$ of a unit cell; if 2, it goes to $\frac{1}{2}$, and if 3 it goes one complete unit cell.

9. This is the same as 8 except this is the limit going across the page.

10. If 1, the program prints a Patterson map; if 2, it prints a Fourier map; if 3, it prints a difference map without zero weight reflections; if 4, it prints a difference map with zero weight reflections; and if 5, it prints an E map.

11. For crystals belonging to a centric space group, put in a 1: otherwise 2.

12. For a tape input from the least squares program, put in 0; for input from LINK, put in 1; for an E map from cards, put in 4.

13. An 0 will rewind the input tape after every map.

14. This is the number of the run from LINK to begin printing maps.

15. If this is 1; h, k, l, Fo, etc. are printed.

16. This initiates writing modes for testing the program. Consult program for exact option.

17. If this number is not zero, the down page limit will be changed to this value.

18. The fields 19 and 20 are normally not used.

ORTEP

This program was used to prepare a magnetic tape for the Calcomp plotter for subsequent diagrams of the molecules. Its method of operation is described in a pamphlet written by the author of the program.[39]