Crystal and molecular structure of calcium 1-naphthyl phosphate trihydrate
by Chi-Tang Li

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

Abstract:
The crystal and molecular structure of calcium 1-naphthyl, phosphate has been solved by x-ray diffraction methods. This crystal has the following lattice parameter: a=7.244±0.002Å α=84°19'±3' Z=2 b=8.994±0.003Å β=78°32'±2' D0=1.503 g/ml c=18.725±0.004Å γ=88°52'±4' Dc=1.508 g/ml Diffraction intensities were measured visually, corrected by the size factor, Lorentz and polarization factors, and the absorption factor. Intensity statistics showed that the crystal had the. symmetry of Pl.

The structure was solved with a three dimensional Patterson function, minimum function, and three dimensional Fourier synthesis. Least-squares refinements, which included first individual isotropic then anisotropic temperature factors were carried out. The final residue factor (R-factor) is 10.3% for 1724 observed reflections. The phosphate groups are distorted tetrahedrons. The four phosphate oxygens are bonded in the following manner. One oxygen is bonded to the naphthyl group, another oxygen is bonded to a hydrogen, the other two oxygens are coordinated to two calcium atoms which are related to each other by an inversion center. The neighboring phosphate groups are joined, together by hydrogen bonding between two oxygens, one of which has a.hydrogen on it. Each calcium is coordinated to seven oxygens, four of which are contributed by four nearby phosphate groups, the other three from three surrounding water molecules. The calcium and the seven coordination oxygens are arranged in a distorted pentagonal bipyramid.

The pentagonal angles of O-Ca-O have the range of 67.4° to 78.6°, with the average of 72.4° (the theoretical pentagonal angle being 72°). Naphthyl groups are distorted planes. In the naphthyl groups, that side which is closest to the two nearby naphthyl groups has the shortest c-c distance of I.30 and 1.31Å. The bond distances and angles are as below: P-0: 1.47 to 1.59 with the average of 1.53Å O-P-O angle: 103 to 117 with the average of 109 degrees C-C: 1.30 to 1.48 with the average of I.38Å C-C-C angle: 116 to 125 with the average of 120 degrees The molecules are held together by strong hydrogen bonding and van der Waals forces. The successful solution of the structure has confirmed a new indexing method developed by the author. New derivations are included for each of the following formulas of equations: 1. Wolf-Bragg equation 2. Equi-inclination Weissenberg index-checking formula 3. Sin^2 θ equation for triclinic symmetry or higher 4. Triclinci interplanar spacing equation 5. Clarified forms of the x-ray Fourier synthesis equations

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March, 1964

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to:

Dr. Charles N. Caughlan for his helpful guidance for directing this research.

National Institute of Health for the financial support.

Montana State College Computing Center for providing time on IBM 1620 electronic data processing machine.

Dr. Graeme S. Baker and Mrs. Rose L. Baker for assisting with the chemical analysis.

Mrs. Kay Roberts for reading over the dissertation and making corrections in English.

Mrs. Chi-Tang Li for immeasurable moral support and for doing the typing.

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ABSTRACT

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$a=7.244\pm0.002$Å	$b=8.994\pm0.003$Å	$C=18.725\pm0.004$Å
$\alpha=84°19'\pm3'$	$\beta=78°32'\pm2'$	$\gamma=88°52'\pm4'$
$Z=2$	$D_o=1.503$ g/ml	$D_c=1.508$ g/ml

Diffraction intensities were measured visually, corrected by the size factor, Lorentz and polarization factors, and the absorption factor. Intensity statistics showed that the crystal had the symmetry of $P\bar{1}$. The structure was solved with a three dimensional Patterson function, minimum function, and three dimensional Fourier synthesis. Least-squares refinements, which included first individual isotropic then anisotropic temperature factors were carried out. The final residue factor (R-factor) is 10.3% for 1724 observed reflections.

The phosphate groups are distorted tetrahedrons. The four phosphate oxygens are bonded in the following manner. One oxygen is bonded to the naphthyl group, another oxygen is bonded to a hydrogen, the other two oxygens are coordinated to two calcium atoms which are related to each other by an inversion center. The neighboring phosphate groups are joined together by hydrogen bonding between two oxygens, one of which has a hydrogen on it. Each calcium is coordinated to seven oxygens, four of which are contributed by four nearby phosphate groups, the other three from three surrounding water molecules. The calcium and the seven coordination oxygens are arranged in a distorted pentagonal bipyramid. The pentagonal angles of O-Ca-O have the range of 67.4° to 78.6°, with the average of 72.4° (the theoretical pentagonal angle being 72°). Naphthyl groups are distorted planes. In the naphthyl groups, that side which is closest to the two nearby naphthyl groups has the shortest c-c distance of 1.30 and 1.31Å. The bond distances and angles are as below:

P-O: 1.47 to 1.59 with the average of 1.53Å
O-P-O angle: 103 to 117 with the average of 109 degrees
C-C: 1.30 to 1.48 with the average of 1.38Å
C-C-C angle: 116 to 125 with the average of 120 degrees

The molecules are held together by strong hydrogen bonding and van der Waals forces.

The successful solution of the structure has confirmed a new indexing method developed by the author. New derivations are included for each of the following formulas or equations:

1. Wolf-Bragg equation
2. Equi-inclination Weissenberg index-checking formula
3. $\sin^2\theta$ equation for triclinic symmetry or higher
4. Triclinci interplanar spacing equation
5. Clarified forms of the x-ray Fourier synthesis equations

SECTION I

INTRODUCTION

Organic phosphates play a very important role in biological processes. The variety of the manifestations and functions of organic phosphate esters in living systems is indeed amazing. "There is hardly anything that goes on in the (living) cell in which esters of phosphoric acid, in one form or another, are not involved at some stage." (23) Two examples are cited below to illustrate the importance of organic phosphates in biological systems. (a) Deoxyribonucleic acid (DNA) which contains many organic phosphate groups, plays a key role in the storage and transport of genetic information. Crick and Watson (11) proposed an ingenious double-helix model for DNA which fits remarkably well all the facts known at the present time, and for this work, they were awarded a Nobel prize in 1962. (b) Adenosine 3',5' cyclic phosphate is a factor stimulating the conversion of inactive glycogen phosphorylase to the active form in tissue preparations. An understanding of the complicated functions of these and other organic phosphates requires basic and precise structural knowledge. The complexity of many of the substances present in living systems makes them, at least for the present, unsuitable for x-ray diffraction studies. However, a variety of simpler organic phosphates are known, and few of their structures have been determined. Although these substances may not actually be present in living systems, the basic structures should not be very much different from those in more complex molecules. Thus, solution of simpler structures will assist in present understanding as well as making solution of structures for more complex substances

easier in the future.

Calcium 1-naphthyl phosphate was chosen for this structural study, because (a) it is very easy to obtain a good single crystal for x-ray work; (b) calcium and phosphorus atoms are fairly large suggesting use of the heavy atom method to solve the crystal structure; (c) this crystal is triclinic. Since I have worked out a method for indexing triclinic crystals as well as an index-checking method, I wanted to gain experience in using this method, even though triclinic crystals present problems not usually present in crystals of higher symmetry.

Despite the importance of knowledge of the detailed structure of organic phosphates for understanding their varied functions, relatively few structures have been accurately determined.

These few organic phosphates whose structures have been determined precisely are described briefly as below.

1. Dibenzyl phosphoric acid, $(C_6H_5CH_2)_2PO_4H$, was studied by Dunitz and Rollett (15). This crystal had the following lattice parameters:

   Monoclinic with $a=20.287\pm0.040$Å $b=5.709\pm0.010$Å

   $c=12.648\pm0.020$Å $\beta=103°13'\pm0°10'$

   $Z=4$, space group of $P2_1/a$

   The final R was 11.0% for 2471 general observed reflections.

   Bond distances and angles are summarized below:

   For phosphate groups:

   P-O (in Å)

   Range 1.469 to 1.566

Average 1.531

P-OR 1.566 & 1.545

P-OH 1.545

O-P-O (in degree)

Range 103.8 to 117.2

Average 109.3

Angle between longest & shortest P-O 103.8 (min.)

Angle between 2 very short P-O 117.2 (max.)

P-O-C (oxygen on ester bond) 122.3 & 118.8

For benzene ring:

C-C (in Å)

Range 1.340 to 1.407

Average 1.378

C-C-C angle (in degree)

Range 118.5 to 121.9

Average 120.0

For close approaches between pairs of atoms indirectly covalently linked:

O-O from 2.444 to 2.573Å

O-C from 3.030 to 3.393Å

2. Calcium Thymidylate, $C_{10}H_{13}O_8N_2CaP^{\circ}6H_2O$, was studied by Trueblood, Horn & Luzzati (34). This crystal had the following lattice parameters:

Monoclinic with $a=14.40\pm0.02$Å $b=6.87\pm0.01$Å

$c=9.181\pm0.01$Å $\beta=90°58'\pm3'$

Z=2, space group of $P2_1$

The final R was 11.6% for 1575 general observed reflections.

The entire structure is held together by the Ca-O bonds and a complex network of hydrogen bonds.

For phosphate group:

P-O (in Å)

Range	1.474 to 1.587
Average	1.515
P-OR	1.587
P-O. . .Ca	1.486 & 1.514

O-P-O (in degree)

Range	102.1 to 118.4
Average	109.3
Angle between longest & shortest P-O	102.1 (min.)
Angle between two very short P-O	118.4 (max.)

P-O-C (ester oxygen) 118.8°

C-O (PO_4) 1.472A

For calcium coordination:

The environment of Ca ion is a distorted pentagonal bipyramid. Calcium coordination number is seven with four phosphate oxygens (from three different molecules) and one water molecule lying approximately in a plane and two waters on a line through the calcium nearly perpendicular to this plane.

O-O (in Å)

Range	2.29 to 2.65
Average	2.42

O-Ca-O angle (in degree)

Range	57 to 80
Average	72

3. 2-Amino-Ethanol Phosphate, $NH_3^+-CH_2-CH_2-O-PO_3H^-$, was studied by Kraut (24). This crystal had the following lattice parameters:

Monoclinic with $a=9.04\pm0.02$Å $b=7.75\pm0.02$Å

$c=8.86\pm0.02$Å $\beta=102^\circ 27' \pm 8'$

$Z=4$, space group of $P2_1/c$

The final R was 6.5% for 1000 observed general reflections. Bond distances and angles for phosphate group are summarized below:

P-O (in Å)

Range	1.493 to 1.591
Average	1.536
P-OR	1.591
P-OH	1.557

Two of the oxygens on the phosphate group were reported to be attached by double bonds (1.493 & 1.503Å)

O-P-O (in degree)

Range	103.9 to 117.4
Average	109.4
Angle between longest & shortest P-O	103.9 (min.)
Angle between two very short P-O	117.4 (max.)

P-O-C (oxygen on ester bond) 118.7°

C-O (PO_4) 1.429Å

4. Adenosine-5'-phosphate, $C_{10}H_{14}O_7N_5P$, was studied by Kraut & Jensen (25). This crystal had the following lattice parameters:

Monoclinic with a=12.77±0.92Å b=11.82±0.02Å

c=4.882±0.01Å β=92°24'±5'

Z=2, space group of $P2_1$

The final R was 6.8% for 1197 general observed reflections. Bond distances and angles for phosphate groups are summarized below:

P-O (in Å)

Range	1.514 to 1.610
Average	1.546
P-OR	1.610
P-OH	1.566

O-P-O (in degree)

Range	105.7 to 118.2
Average	109.4
Angle between longest & shortest P-O	105.7°(min.)
Angle between two very short P-O	118.2°(max.)
P-O-C (oxygen on ester bond)	114.7°
C-O (PO_4)	1.475Å

The following organic phosphates have been solved with either limited data or by projections. No descriptions of these structures is made here. They are mentioned only by title.

1. "Crystal and Molecular Structure of Cytidylic Acid" by Alver &

Furberg (2)

2. "The Crystal Structure of Ba-Ribose-5-Phosphate" by Furberg & Mostad (16)

3. "The Crystal Structure of Triphenyl Phosphate" by Davies & Stanley (13)

4. "The Crystal Structure of Ba-Phenyl Phosphate" by Svetich & Caughlan (33)

SECTION II

EXPERIMENTAL WORK

Preparation and identification of calcium 1-naphthyl phosphate

Calcium 1-naphthyl phosphate was purchased from Aldrich Chemical Company, Inc. in the form of a crystalline powder. It was purchased as Ca $C_{10}H_7PO_4 \cdot H_2O$, however chemical analysis and solution of the crystal structure have shown it to be $Ca(C_{10}H_7HPO_4)_2 \cdot 3H_2O$. To confirm the structure analysis, this compound was analyzed for calcium and phosphorus. In addition, infrared spectra were taken of the original powder and the crystals used for the structure analysis, in order to confirm that the two were identical compounds. These are shown in Fig. 1 and 2.

Calcium was determined with a Beckman Flame Quartz Spectrophotometer (Model DU) by comparing with a standard calcium solution. Phosphorus was determined by colorimetric analysis on a Beckman model B spectrophotometer by comparing with a standard phosphorus compound. Details of the analysis are included in Appendix A.

The results of the analysis, together with the comparison with the two possible structural formulas are listed in the following table. An examination of the table clearly indicates that the compound is $Ca(C_{10}H_7HPO_4)_2 \cdot 3H_2O$.