Acta Cryst. (1970). B**26**, 1528

The Crystal and Molecular Structure of Tri-(*p*-nitrophenyl) Phosphate, $(C_6H_4NO_2)_3PO_4$

BY MAZHAR-UL-HAQUE AND CHARLES N. CAUGHLAN
Department of Chemistry, Montana State University, Bozeman, Montana 59715, *U.S.A.*

(*Received* 30 *July* 1969 *and in revised form* 8 *December* 1969)

The structure of tri-(*p*-nitrophenyl) phosphate, $(C_6H_4NO_2)_3PO_4$, has been determined by X-ray diffraction techniques. The crystals are monoclinic in space group $P2_1/c$. The lattice parameters are: $a=17{\cdot}358$ (14), $b=8{\cdot}493$ (7), $c=12{\cdot}967$ (10) Å and $\beta=91{\cdot}35°$ (20); 2150 independent reflections were measured with a diffractometer using Mo $K\alpha$ radiation. The structure was solved from a Patterson function and several Fourier syntheses. The final R is 0·052 for 1345 observed reflections, refining positional and anisotropic thermal parameters for non-hydrogen atoms and including hydrogen positions in the final structure factor calculation. The O–P–O angles range from 101·1 to 117·1°. The P–O bond distances are 1·58, 1·56, 1·57 and the P=O distance is 1·44 Å; the C–O distances are 1·42, 1·41, and 1·41 Å and the N–O distances average 1·22 Å. The dihedral angles between the nitro groups and the phenyl groups are 5·8, 6·3 and 17·1°, averaging 9·7°.

Introduction

Accurate structural data are important in understanding hydrolysis rates of organic phosphates. The structures of a number of monosubstituted and several disubstituted organic phosphates have been determined (Kraut & Jensen, 1961, 1963; Sundaralingam & Jensen, 1965; Dunitz & Rollett, 1956; Abramson & Pascher, 1966). Both the structure and kinctics of triphenyl phosphate (Svetich & Caughlan, 1965) and several cyclic triesters of phosphoric acid (Steitz & Lipscomb, 1965; Newton, Cox & Bertrand, 1966; Swank, Caughlan, Ramirez, Madan & Smith, 1967*) have been studied in detail (Barnard, Bunton, Kellerman, Mhala, Silver, Vernon & Welch, 1966; Bunton, Kellerman, Oldham & Vernon, 1966).

The effect of electron-attracting substituents such as NO and CH_3CO^- on the structure of phenyl phosphates is also interest in considering the kinetics and the mechanism of hydrolysis. Bunton *et al.* (1966) have shown that the hydrolysis of monoaryl phosphates shows acid catalysis only if an electron-attracting substituent is present on the aryl group. The present study was undertaken to provide accurate structure data for comparison with triphenyl phosphate and the various cyclic triesters of phosphoric acid and to study the effect of the nitrate substituent on the structure.

Experimental

Tri-(*p*-nitrophenyl) phosphate, obtained from Aldrich Chemical Company, was recrystallized from acetone at room temperature. A needle-shaped crystal of about 0·15–0·20 mm in diameter and 1·2 mm in length was used for data collection. Preliminary photographs showed systematic absences for the $0k0$ reflections when $k\neq 2n$ and for the $h0l$ reflections when $l\neq 2n$, uniquely determining space group $P2_1/c$. The lattice parameters, determined on a General Electric XRD-5 diffractometer using six independent 2θ measurements, are: $a=17{\cdot}358$ (14), $b=8{\cdot}493$ (7), $c=12{\cdot}967$ (10) Å, $\beta=91{\cdot}35$ (20), $V=1911$ Å^3. The measured density was 1·594 g.cm^{-3}, by flotation in carbon tetrachloride; the calculated density based on 4 molecules per unit cell is 1·602 g.cm^{-3}. The linear absorption coefficient for Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation is $=2{\cdot}2$ cm^{-1}; $F(000)$ is 944. Intensities were measured by the θ–2θ scan technique on a General Electric XRD–5 diffractometer. 100-second scans were taken across each reflection; the background on each side was counted for 50 seconds. The scan rate was 2° min^{-1} in 2θ; the take-off angle was 4°. Zirconium-filtered molybdeum radiation was used. 1345 of 2150 reflections scanned were considered observed by the criterion $F_o\geq 2\sigma(F_o)$. Standard reflections, measured every 2 hours, showed significant change throughout the data collections. Intensities were reduced to F values without application of absorption or extinction corrections. Form factors were used from *International Tables for X-ray Crystallography* (1962). Anomalous terms of the form factors were not used.

Structure determination, refinement and results

The phosphorus atomic positions were easily located from the Patterson map. Several successive Fourier syntheses showed the complete structure. Refinement proceeded normally using the full-matrix least-squares method (Busing, Martin & Levy, 1962). The final structure factor calculation included all hydrogen atoms in their calculated positions with isotropic temperature factors, B, 0·5 Å^2 greater than those of the atoms to which they are bonded. Anisotropic temperature factors and positional parameters for all non-hydrogen atoms were refined in the final refinement cycles. The final weighting scheme was that outlined by Stout & Jensen (1968) for counter data. The refinement converged at $R=0{\cdot}052$ ($R=\sum||F_o|-|F_c||/\sum|F_o|$), weighted $R=0{\cdot}055$, minimizing $\sum w(|F_o|-|F_c|)^2$. A final difference map showed no significant features.

---

* The bond distances in this work are slightly in error due to a computer mistake. The correct value for the P=O distance is 1·40, rather than 1·38 Å as published.

Atomic positions and thermal parameters are given in Tables 1 and 2. Table 3 gives the mean-square displacements calculated from the thermal parameters. Bond distances and angles are given in Fig. 1 and Table 4, and final observed and calculated structure factors in Table 5. Fig. 2 shows the [001] projection of the structure. Table 6 lists the equations for various least-squares planes. A number of dihedral angles of tri-(*p*-nitrophenyl) phosphate are compared with similar dihedral angles of triphenyl phosphate in Table 7. Fig. 3 shows a stereoscopic view of the molecule (Johnson, 1965).

All programs except the least-squares were by Svetich, Caughlan, Li & Watenpaugh (1965).

Table 1. *Atomic coordinates and their standard deviations (in parenthesis)*

	x	y	z
P(1)	0·2266 (1)	0·1441 (2)	0·3659 (1)
O(2)	0·2882 (3)	0·0446 (5)	0·3065 (3)
O(3)	0·1611 (2)	0·1796 (5)	0·2845 (3)
O(4)	0·1897 (2)	0·0137 (5)	0·4355 (3)
O(5)	0·2530 (3)	0·2855 (5)	0·4166 (3)
C(6)	0·3460 (4)	0·1125 (8)	0·2450 (5)
C(7)	0·3532 (4)	0·0480 (8)	0·1472 (5)
C(8)	0·4083 (4)	0·1107 (7)	0·0847 (5)
C(9)	0·4546 (4)	0·2299 (7)	0·1222 (5)
C(10)	0·4483 (4)	0·2887 (9)	0·2197 (5)
C(11)	0·3925 (4)	0·2259 (8)	0·2826 (5)
N(12)	0·5124 (4)	0·3017 (8)	0·0552 (5)
O(13)	0·5211 (3)	0·2411 (6)	−0·0295 (4)
O(14)	0·5476 (3)	0·4154 (7)	0·0862 (4)
C(15)	0·1283 (4)	0·0699 (8)	0·2144 (5)
C(16)	0·0722 (4)	−0·0290 (8)	0·2455 (5)
C(17)	0·0380 (4)	−0·1305 (9)	0·1771 (5)
C(18)	0·0641 (4)	−0·1211 (8)	0·0751 (5)
C(19)	0·1203 (4)	−0·0184 (8)	0·0414 (5)
C(20)	0·1552 (4)	0·0813 (8)	0·1133 (5)
N(21)	0·0258 (4)	−0·2270 (9)	−0·0010 (6)
O(22)	0·0418 (3)	−0·2098 (7)	−0·0913 (4)
O(23)	−0·0207 (4)	−0·3254 (7)	0·0295 (5)
C(24)	0·2184 (4)	−0·0211 (7)	0·5353 (4)
C(25)	0·2947 (4)	−0·0571 (8)	0·5505 (5)
C(26)	0·3220 (4)	−0·0906 (8)	0·6509 (5)
C(27)	0·2672 (5)	−0·0900 (8)	0·7273 (5)
C(28)	0·1904 (4)	−0·0578 (8)	0·7115 (5)
C(29)	0·1641 (4)	−0·0202 (7)	0·6115 (5)
N(30)	0·2954 (5)	−0·1252 (7)	0·8330 (5)
O(31)	0·2472 (5)	−0·1560 (7)	0·8971 (4)
O(32)	0·3674 (4)	−0·1179 (8)	0·8513 (4)

Calculated hydrogen atom coordinates

H(1)—C(7)	0·3167	−0·0384	0·1211
H(2)—C(8)	0·4145	0·0668	0·0114
H(3)—C(10)	0·4841	0·3753	0·2453
H(4)—C(11)	0·3864	0·2702	0·3548
H(5)—C(16)	0·0547	−0·0316	0·3188
H(6)—C(17)	−0·0023	−0·2065	0·1985
H(7)—C(19)	0·1358	−0·0208	−0·0295
H(8)—C(20)	0·1952	0·1562	0·0906
H(9)—C(25)	0·3312	−0·0604	0·4938
H(10)-C(26)	0·3772	−0·1186	0·6655
H(11)-C(28)	0·1535	−0·0567	0·7699
H(12)-C(29)	0·1092	0·0052	0·5980

Table 2. *Thermal parameters and standard deviations*

	$\beta(1,1)$*	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
P(1)	0·0036 (1)†	0·0123 (3)	0·0044 (1)	−0·0009 (2)	0·0005 (1)	−0·0006 (2)
O(2)	0·0037 (2)	0·0119 (8)	0·0054 (3)	−0·0004 (4)	0·0009 (2)	0·0002 (4)
O(3)	0·0043 (2)	0·0119 (8)	0·0043 (3)	−0·0001 (3)	−0·0005 (2)	−0·0001 (4)
O(4)	0·0041 (2)	0·0137 (8)	0·0041 (3)	−0·0024 (3)	−0·0003 (2)	0·0009 (4)
O(5)	0·0049 (2)	0·0126 (8)	0·0058 (3)	−0·0020 (4)	0·0006 (2)	−0·0023 (4)
C(6)	0·0032 (3)	0·0137 (14)	0·0046 (5)	−0·0005 (5)	0·0004 (3)	0·0006 (7)
C(7)	0·0036 (3)	0·0130 (13)	0·0054 (5)	−0·0004 (5)	0·0010 (3)	−0·0007 (7)
C(8)	0·0034 (3)	0·0154 (14)	0·0051 (5)	0·0007 (6)	0·0002 (4)	−0·0003 (7)
C(9)	0·0028 (3)	0·0126 (12)	0·0054 (5)	0·0001 (5)	0·0007 (3)	0·0002 (7)
C(10)	0·0034 (3)	0·0181 (14)	0·0067 (6)	−0·0015 (6)	0·0001 (4)	−0·0027 (8)
C(11)	0·0036 (3)	0·0188 (15)	0·0046 (5)	−0·0024 (6)	0·0001 (3)	−0·0017 (7)
N(12)	0·0032 (3)	0·0183 (13)	0·0060 (5)	0·0004 (5)	0·0006 (3)	0·0014 (7)
O(13)	0·0041 (2)	0·0259 (12)	0·0068 (4)	−0·0002 (4)	0·0012 (3)	0·0016 (6)
O(14)	0·0045 (3)	0·0189 (11)	0·0124 (6)	−0·0030 (5)	0·0015 (3)	−0·0005 (6)
C(15)	0·0037 (3)	0·0105 (12)	0·0044 (5)	0·0010 (5)	−0·0005 (3)	0·0001 (6)
C(16)	0·0045 (4)	0·0138 (13)	0·0035 (5)	−0·0008 (6)	0·0005 (3)	0·0016 (7)
C(17)	0·0052 (4)	0·0151 (14)	0·0049 (6)	0·0018 (6)	−0·0007 (4)	−0·0011 (8)
C(18)	0·0042 (4)	0·0136 (14)	0·0053 (6)	0·0032 (6)	−0·0029 (4)	−0·0041 (8)
C(19)	0·0031 (3)	0·0135 (14)	0·0081 (6)	0·0001 (5)	0·0034 (4)	0·0004 (7)
C(20)	0·0041 (3)	0·0159 (14)	0·0045 (5)	0·0020 (5)	−0·0004 (3)	−0·0004 (7)
N(21)	0·0054 (4)	0·0154 (14)	0·0091 (6)	0·0029 (6)	−0·0013 (4)	−0·0013 (9)
O(22)	0·0072 (3)	0·0296 (14)	0·0069 (4)	0·0029 (5)	−0·0010 (3)	−0·0058 (7)
O(23)	0·0088 (4)	0·0185 (12)	0·0122 (6)	−0·0018 (6)	−0·0034 (4)	−0·0007 (7)
C(24)	0·0027 (3)	0·0094 (11)	0·0039 (5)	−0·0006 (5)	−0·0003 (3)	−0·0002 (6)
C(25)	0·0035 (4)	0·0170 (14)	0·0063 (6)	0·0001 (6)	0·0001 (3)	−0·0019 (7)
C(26)	0·0040 (3)	0·0161 (14)	0·0045 (5)	0·0006 (5)	0·0005 (4)	0·0001 (7)
C(27)	0·0044 (4)	0·0118 (13)	0·0032 (5)	0·0007 (5)	−0·0010 (4)	0·0024 (6)
C(28)	0·0042 (4)	0·0124 (13)	0·0056 (6)	0·0008 (6)	0·0003 (4)	0·0014 (7)
C(29)	0·0041 (3)	0·0116 (12)	0·0037 (5)	−0·0001 (5)	0·0005 (4)	0·0007 (6)
N(30)	0·0056 (4)	0·0142 (12)	0·0067 (6)	0·0020 (6)	0·0001 (4)	0·0016 (7)
O(31)	0·0072 (3)	0·0216 (12)	0·0069 (4)	0·0029 (5)	0·0008 (3)	0·0041 (6)
O(32)	0·0055 (3)	0·0404 (17)	0·0072 (5)	0·0041 (6)	−0·0015 (3)	0·0014 (7)

* The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

† The number in parentheses is the standard deviation and refers to the least significant digits.

Table 3. *Mean-square displacements of vibration*

	Minimum	Intermediate	Maximum
P(1)	0·0355 Å^2	0·0418 Å^2	0·0601 Å^2
O(2)	0·0392	0·0447	0·0621
O(3)	0·0356	0·0436	0·0679
O(4)	0·0334	0·0377	0·0764
O(5)	0·0330	0·0531	0·0843
C(6)	0·0365	0·0485	0·0535
C(7)	0·0388	0·0462	0·0629
C(8)	0·0431	0·0488	0·0597
C(9)	0·0378	0·0458	0·0515
C(10)	0·0400	0·0549	0·0801
C(11)	0·0339	0·0459	0·0822
N(12)	0·0436	0·0523	0·0711
O(13)	0·0462	0·0714	0·0967
O(14)	0·0446	0·0839	0·0113
C(15)	0·0335	0·0383	0·0627
C(16)	0·0254	0·0532	0·0702
C(17)	0·0394	0·0495	0·0885
C(18)	0·0190	0·0319	0·1098
C(19)	0·0464	0·0492	0·0692
C(20)	0·0375	0·0459	0·0768
N(21)	0·0440	0·0663	0·1071
O(22)	0·0425	0·0905	0·1444
O(23)	0·0591	0·0829	0·1646
C(24)	0·0300	0·0352	0·0444
C(25)	0·0466	0·0533	0·0693
C(26)	0·0376	0·0551	0·0650
C(27)	0·0168	0·0507	0·0716
C(28)	0·0384	0·0523	0·0666
C(29)	0·0297	0·0436	0·0637
N(30)	0·0414	0·0615	0·0909
O(31)	0·0435	0·0788	0·1258
O(32)	0·0459	0·0880	0·1601

Discussion

A number of structural features of organic phosphates, including distortion of the phosphate tetrahedron and the effects of π bonding, have been discussed in relation to hydrolysis of these compounds (Newton *et al.*, 1966; Swank *et al.*, 1967; Collin, 1966). All the structural features suggested by Newton *et al.* (1966) as being common to triesters of phosphoric acid are found in tri-(p-nitrophenyl) phosphate. The three esterified P–O bond lengths are equal and apparently normal. The phosphoryl P=O bond length of 1·44 Å is also essentially the same as that in all triesters of phosphoric acid except for acetoinenediol cyclic phosphate (Swank *et al.*, 1967), in which it is significantly shorter, *i.e.* 1·40 Å. The O–P–O angles are more nearly tetrahedral than in any of the other phosphotriesters, the smallest O–P–O angle being 101·1°, compared with 96·6° in triphenyl phosphate (Svetich & Caughlan, 1965), and about 98·5° in the five-membered cyclic phosphotriesters (Steitz & Lipscomb, 1965), (Newton *et al.*, 1966). Least-squares plane calculations show atoms O(5)–P–O(3)–C(15) to be nearly coplanar, with a maximum deviation from the least-squares plane of less than 0·05 Å, whereas the maximum deviation of the atoms from the least-squares planes of O(5)–P–O(2)–C(6) and O(5)–P–O(4)–C(24) is about 0·2 Å.

In order to see if a simple consideration of d-p π bonding could account for the orientations of the oxygen atom π orbitals, we considered the bonding to occur as suggested by Newton *et al.* (1966). The phosphoryl oxygen π bond involves the mutually perpendicular d_{xz} and d_{yz} orbitals of phosphorus, leaving the $d_{x^2-y^2}$ and d_{z^2} orbitals for π bonding to the remaining oxygen atoms. The three equivalent oxygen atoms are considered to be essentially sp^2 hybridized (120° angles at these oxygen atoms) and one oxygen atom is aligned with its sp^2 plane coicident with the O(5)–P–O(3)–C(15) plane.

Table 4. *Bond angles*

	Angle		Angle
O(2)—P(1)—O(3)	105·4 (2)°*	C(16)-C(15)-C(20)	125·3 (6)°
O(2)—P(1)—O(4)	101·1 (2)	C(15)-C(16)-C(17)	120·2 (7)
O(2)—P(1)—O(5)	117·2 (3)	C(16)-C(17)-C(18)	115·5 (6)
O(3)—P(1)—O(4)	102·9 (2)	C(17)-C(18)-C(19)	125·1 (7)
O(3)—P(1)—O(5)	111·5 (3)	C(17)-C(18)-N(21)	116·2 (6)
O(4)—P(1)—O(5)	117·1 (3)	C(19)-C(18)-N(21)	118·7 (6)
P(1)—O(2)—C(6)	123·6 (4)	C(18)-C(19)-C(20)	118·2 (6)
P(1)—O(3)—C(15)	125·7 (4)	C(19)-C(20)-C(15)	115·8 (6)
P(1)—O(4)—C(24)	122·3 (4)	C(18)-N(21)-O(22)	117·3 (7)
O(2)—C(6)—C(7)	115·1 (6)	C(18)-N(21)-O(23)	119·0 (7)
O(2)—C(6)—C(11)	121·0 (6)	O(22)-N(21)-O(23)	123·7 (7)
C(7)—C(6)—C(11)	123·3 (6)	O(4)—C(24)-C(25)	120·0 (6)
C(6)—C(7)—C(8)	117·6 (6)	O(4)—C(24)-C(29)	115·1 (5)
C(7)—C(8)—C(9)	119·1 (6)	C(25)-C(24)-C(29)	124·9 (6)
C(8)—C(9)—C(10)	122·5 (6)	C(24)-C(25)-C(26)	118·9 (6)
C(8)—C(9)—N(12)	119·8 (6)	C(25)-C(26)-C(27)	116·0 (6)
C(10)-C(9)—N(12)	117·7 (6)	C(26)-C(27)-C(28)	125·0 (6)
C(9)—C(10)-C(11)	118·5 (6)	C(26)-C(27)-N(30)	116·4 (6)
C(10)-C(11)-C(6)	119·0 (6)	C(28)-C(27)-N(30)	118·5 (6)
C(9)—N(12)-O(13)	117·1 (6)	C(27)-C(28)-C(29)	118·6 (6)
C(9)—N(12)-O(14)	118·7 (6)	C(24)-C(29)-C(28)	116·6 (6)
O(13)-N(12)-O(14)	124·2 (7)	C(27)-N(30)-O(31)	117·3 (6)
O(3)—C(15)-C(16)	119·9 (6)	C(27)-N(30)-O(32)	118·3 (6)
O(3)—C(15)-C(20)	114·7 (6)	O(31)-N(30)-O(32)	124·4 (7)

* The number in parentheses is the standard deviation and refers to the least significant digits.

The orientation of the π-bonding orbitals of oxygen can be calculated from the least-squares planes for the P–O–C atoms. To calculate these angles, consider a plane through the phosphorus atom parallel to atoms O(2), O(3) and O(4). This plane will contain the $d_{x^2-y^2}$ and the d_{xy} orbitals of the phosphorus atom, with the d_z orbital perpendicular to the plane. The p orbital of the oxygen atom will be perpendicular to the P–O–C planes, the unused sp^2 orbital being in the P–O–C plane. Angles between the p orbitals and the plane containing the phosphorus $d_{x^2-y^2}$ and the d_{xy} orbitals were calculated for both tri-(*p*-nitrophenyl) phosphate and triphenyl phosphate. For tri-(*p*-nitrophenyl) phosphate the angles are: p(03), 6° 31′; p(02), 39° 8′; p(04), 32° 13′; for triphenyl phosphate the angles are: p(02), 8° 22′; p(03), 59° 21′; p(04), 29° 21′. Comparing these two compounds, two of the angles are nearly the same, *i.e.* the one perpendicular to the most planar C–O–P–O′ plane, which is nearly zero, and the one at O(4). The other angles differ by about 20°. It does not seem that the p orbital or the unused sp^2 orbital of the oxygen atoms are oriented in a manner to provide maximum overlap with the d orbitals of phosphorus, since the angles should be either close to 0° for overlap with the $d_{x^2-y^2}$ or the d_{xy} orbitals, or 90° for overlap with the d_z orbital. One must conclude that this simple consideration does not account for the orientation and that packing seems to dominate the manner in which these planes are oriented.

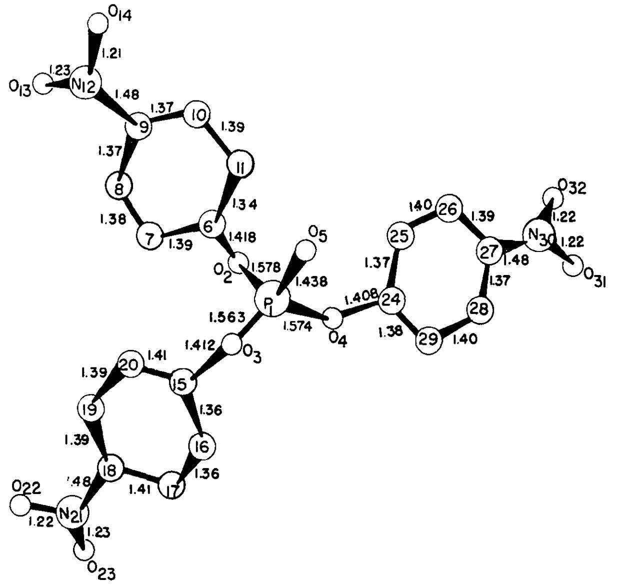


Fig. 1. Interatomic distances of tri-(*p*-nitrophenyl) phosphate. The standard deviations for P–O, C–O and the rest of the bond distances are 0·005, 0·008 and 0·01 Å respectively.

Another significant feature of the structure is the angle between the planes of the $-NO_2$ groups and the phenyl groups to which they are attached. *p*-Dinitrobenzenes have been shown to be nonplanar, the dihedral angles between the aromatic ring and the nitro group being about 9·5° (Abrahams, 1950). In tri-(*p*-nitrophenyl) phosphate the dihedral angles between the nitro groups and the phenyl rings are 5·8° for $N(12)O_2$, 6·3° for $N(21)O_2$, and 17·1° for $N(30)O_2$, averaging 9·7°. One would except these to be identical except for packing effects, which probably account for the difference.

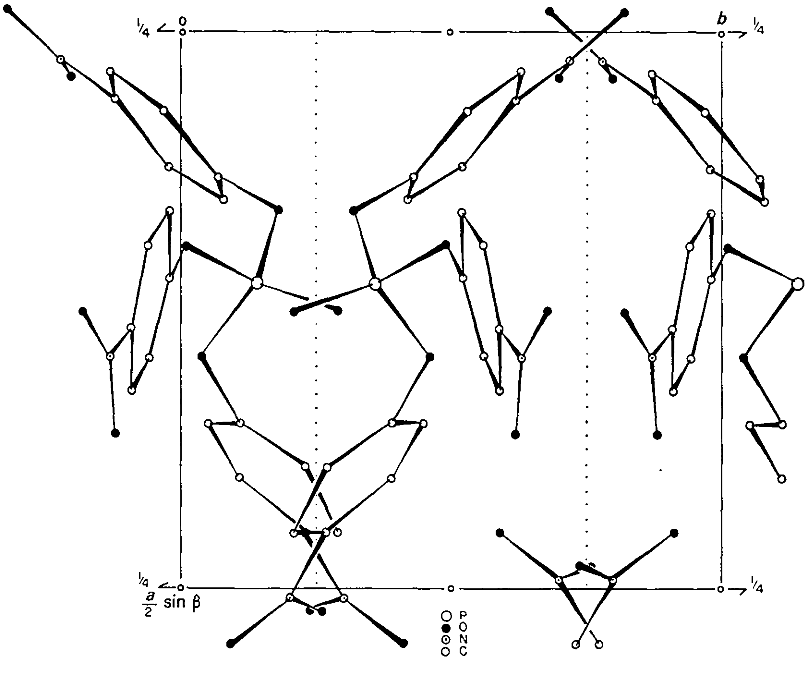
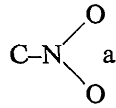


Fig. 2. [001] projection of the structure of tri-(*p*-nitrophenyl) phosphate.

However, it should be noted that the  $\text{C–N}\begin{matrix}\diagup\text{O}\\ \diagdown\text{O}\end{matrix}$ atoms are essentially coplanar, indicating that the nonplanarity of the NO_2 group and the phenyl ring is a twisting around the C–N bond rather than actual bending of this bond.

Several conclusions can be made from these comparisons. First, it appears that if there is a difference in the amount of P–O π bonding in the noncyclic and the five-membered cyclic phosphotriesters, as suggested by Newton *et al.* (1966), this is not evident in the P–O bond lengths. Collin (1966) has indicated as a result of more sophisticated molecular-orbital calculations that P–O bond lengths are insensitive to π bonding in organic

Table 5. *Observed and calculated structure factors*

l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
K=	0 H=	0
2	8	7
4	36	34
6	57	54
10	9	7
12	16	16
K=	0 H=	1
2	91	90
-2	34	34
4	15	15
4	15	15
-4	55	55
6	38	37
-6	25	21
8	7	6
-8	7	8
-10	33	35
K=	0 H=	2
0	68	62
2	79	75
-2	111	118
4	106	110
-4	58	59
6	10	7
-6	8	6
-8	13	15
10	12	11
-10	8	7
-12	32	33
K=	0 H=	3
2	154	159
-2	69	75
4	6	4
6	100	98
-6	29	30
8	9	9
-8	5	5
10	7	5
-10	12	14
-12	37	37
K=	0 H=	4
0	100	103
2	104	104
-2	116	114
4	20	24
6	4	1
10	11	10
12	30	30
-12	36	38
K=	0 H=	5
2	116	109
-2	81	80
4	22	22
-4	77	81
6	63	62
-6	60	58
-8	36	34
-10	14	14
K=	0 H=	6
0	30	36
2	61	60
-2	41	39
4	57	64
6	22	19
-6	55	55
-8	10	11
10	31	30
-10	45	46
K=	0 H=	7
2	62	59
-2	29	25
4	66	65
-4	16	12
6	47	46
-6	50	47
8	24	24
-8	19	18
10	20	23
-10	60	62
K=	0 H=	8
2	7	8
-2	36	34
-4	30	30
6	70	69
-6	44	42
-8	13	11
-10	6	6
K=	0 H=	9
2	44	46
-2	10	7
4	18	18
-4	60	60
6	10	11
-6	33	34
8	24	22
-8	48	47
10	19	21
-10	11	13
K=	0 H=	10
0	36	37
2	22	22
-2	20	19
4	46	47
-4	22	22
6	9	9
-6	60	59
8	28	28
-8	34	34
-10	29	28
K=	0 H=	11
2	8	9
-2	32	32
-4	34	33
6	20	20
K=	0 H=	12
0	24	24
4	35	36
-4	35	34
6	12	12
-6	29	32
8	16	17
K=	0 H=	13
2	10	10
-4	40	39
6	28	27
-6	12	13
-8	31	29
K=	0 H=	14
-2	27	27
4	13	13
-4	17	18
6	11	10
-6	6	6
K=	0 H=	15
-2	6	4
-4	44	42
K=	0 H=	16
0	10	12
2	8	9
-2	12	13
K=	0 H=	17
0	11	13
K=	0 H=	18
-2	7	7
K=	0 H=	19
0	9	10
K=	1 H=	0
1	39	37
4	26	29
5	30	28
6	54	54
7	28	26
8	15	18
10	21	20
11	21	22
12	6	9
K=	1 H=	1
0	45	42
1	20	15
-1	58	55
2	103	102
-2	31	30
-3	3	3
-5	11	14
6	30	30
-6	13	13
7	17	17
-7	32	32
8	12	10
-8	15	14
11	7	8
-12	21	22
K=	1 H=	2
0	7	8
1	16	18
-1	104	100
2	84	81
-2	69	66
3	33	30
-3	24	23
4	8	8
-4	30	33
5	22	25
-5	40	38
6	14	12
-6	46	46
7	33	31
-7	5	7
8	31	30
-8	30	30
9	13	11
-9	9	11
-10	17	18
11	7	7
-11	29	29
12	28	28
-12	10	10
K=	1 H=	3
1	20	19
-1	120	120
2	64	69
-2	62	59
3	53	59
-3	19	22
4	22	22
-4	56	57
5	97	96
-5	41	38
6	16	18
-7	6	7
8	7	7
-9	7	6
10	14	14
-11	8	10
12	8	9
K=	1 H=	4
0	119	123
1	86	87
-1	73	74
2	4	5
-2	71	68
3	90	92
-3	69	69
4	32	33
-4	43	43
5	30	30
-5	6	7
6	10	10
-6	6	7
7	6	6
-7	7	3
8	36	36
-8	15	13
10	13	12
-10	6	4
11	17	17
-11	38	36
K=	1 H=	5
1	36	36
-1	22	19
2	26	27
-2	13	14
3	38	37
-3	14	13
4	11	11
-4	73	74
5	35	33
-5	36	36
6	17	17
-6	27	27
-7	5	4
-8	13	13
10	27	27
11	19	21
-11	13	10
K=	1 H=	6
1	37	37
-1	26	25
2	36	36
-2	7	7
3	28	33
-3	15	16
4	11	11
5	20	18
-5	6	3
6	10	11
-6	23	23
7	36	35
-7	20	19
9	8	6
-9	19	19
10	25	24
-10	21	19
11	11	10
-11	35	33
K=	1 H=	7
0	59	59
-1	12	14
2	19	18
-2	60	58
-3	34	35
4	14	13
-4	13	12
-5	6	10
6	23	24
-6	18	19
7	8	11
-7	9	8
8	11	12
-8	7	6
9	10	8
-9	11	12
-10	8	9
-11	16	14
K=	1 H=	8
1	52	50
-1	32	30
2	4	4
-2	29	30
-3	27	26
4	23	22
-4	34	34
6	7	7
-6	12	13
7	35	35
8	17	15
-8	28	30
9	15	14
-9	24	25
-10	16	15
K=	1 H=	9
1	26	25
2	27	28
-2	27	25
3	8	10
4	23	20
-4	7	8
5	35	34
-5	12	14
6	24	24
-6	37	37
7	31	36
-7	10	10
8	23	23
-8	30	30
9	7	5
-9	13	16
-10	7	9
K=	1 H=	10
0	23	25
1	38	36
-1	13	12
-2	25	24
3	5	6
-3	13	9
-4	12	13
5	13	13
-5	20	21
6	7	6
-6	5	5
8	9	7
-9	13	13
K=	1 H=	11
0	27	28
-1	13	13
2	13	12
-2	34	34
3	16	15
4	28	26
-4	6	4
-5	5	6
6	23	23
-6	19	20
7	29	29
-7	42	42
8	14	15
-8	8	9
-9	17	18
K=	1 H=	12
1	19	19
-2	27	27
-3	15	13
4	17	17
-4	9	9
5	14	15
6	7	8
-6	6	6
7	22	23
-8	21	19
K=	1 H=	13
-1	28	27
2	13	13
-2	9	9
3	5	2
-3	10	10
5	8	7
-5	13	13
6	6	8
-6	13	12
7	22	21
K=	1 H=	14
0	21	22
-3	16	14
4	8	8
5	7	7
-5	19	18
6	8	7
K=	1 H=	15
1	6	5
-1	22	21
-2	12	11
-3	8	7
4	14	14
-4	7	7
-5	18	16
K=	1 H=	16
2	6	6
K=	1 H=	17
0	18	20
-2	8	7
K=	1 H=	18
0	11	12
1	17	19
2	7	7
K=	2 H=	0
0	12	16
1	170	182
2	39	39
3	12	13
4	4	3
5	46	46
7	18	18
8	13	15
9	33	34
10	18	19
11	14	15
K=	2 H=	1
0	55	50
1	38	37
-1	10	6
2	110	108
-2	61	59
3	69	71
4	10	11
-4	37	37
5	34	35
-5	32	35
6	22	21
-6	21	23
7	38	37
-7	23	21
8	8	11
-8	11	10
10	37	37
-10	13	12
11	25	25
-11	13	14
12	11	10
-12	21	19
K=	2 H=	2
0	148	152
1	195	208
-1	103	103
2	94	93
3	36	36
-3	4	3
4	40	46
-4	49	50
5	41	39
-5	5	1
6	28	27
-6	8	9
7	13	13
-7	7	7
8	28	28
9	8	7
-9	18	17
10	18	18
-10	19	19
11	6	5
-12	25	26
K=	2 H=	3
0	17	17
1	39	39
2	33	33
-2	67	65
3	19	19
-3	63	63
4	16	15
-4	19	19
5	27	28
-5	50	48
-6	43	42
7	46	45
-7	7	7
8	7	7
9	21	20
10	6	6
-10	24	25
11	20	22
-11	18	18
K=	2 H=	4
0	115	117
1	78	79
-1	27	26
2	99	100
-2	47	46
3	19	20
-3	18	20
4	30	32
-4	77	75
5	5	5
-6	6	4
7	16	15
-7	19	20
8	21	21
-8	9	8
9	23	23
-9	11	10
10	11	10
11	17	18
-11	36	37
K=	2 H=	5
0	30	34
1	25	23
-1	55	57
2	65	63
-2	24	23
3	83	81
-3	7	9
4	66	64
-4	34	33
5	25	27
-5	7	6
6	9	9
-6	13	12
7	37	36
-7	10	8
-8	6	7
-9	18	19
10	10	10
-10	23	25
K=	2 H=	6
0	8	11
1	36	36
-1	87	85
2	47	46
-3	36	34
4	38	38
-4	83	81
5	44	42
-5	21	20
6	12	14
-6	14	14
-7	14	14
9	5	6
-10	21	22
11	7	6
-11	18	16
K=	2 H=	7
1	16	14
2	39	41
-2	12	11
3	23	24
-3	7	6
-4	36	36
-5	66	67
6	14	14
-6	15	14
7	38	37
-7	7	8
8	13	11
-8	6	4
9	23	24
-9	28	29
10	7	8
-11	12	14
K=	2 H=	8
0	48	49
1	20	19
-1	21	21
2	40	37
-3	4	6
4	21	20
-4	15	16
5	39	38
-5	28	27
-6	16	16
-7	35	33
8	30	31
-8	10	9
9	15	15
-10	8	11
K=	2 H=	9
1	18	19
-1	15	15
-2	45	45
3	14	13
-3	12	11
-4	28	27
5	15	15
-5	23	23
7	14	13
-7	6	8
-8	23	22
9	23	22
-9	26	27
-10	18	16
K=	2 H=	10
0	27	27
1	13	14
-1	10	10
2	12	13
-2	23	23
3	9	10
4	15	15
-4	12	13
5	14	14
-5	6	7
6	16	16
-7	34	33
8	27	27
9	21	23
-9	14	11
K=	2 H=	11
0	12	15
1	12	12
2	15	14
-2	12	13
3	11	11
-3	30	31
4	9	9
5	6	5
-5	14	13
6	21	20
-7	26	26
8	10	10
-9	8	8
K=	2 H=	12
-2	22	22
3	18	17
-3	17	18
4	7	7
-4	15	14
-5	10	9
7	7	9
-7	15	16
-8	27	28
K=	2 H=	13
1	13	14
-2	24	23
-3	29	27
-4	10	10
5	28	28
-6	7	6
K=	2 H=	14
0	17	20
-1	19	19
3	16	16
-3	14	16
-4	13	13
5	19	19
K=	2 H=	15
1	6	8
2	11	10
-2	6	5
-3	24	23
-4	11	11
K=	2 H=	16
-1	20	20
2	7	7
-2	10	9
K=	2 H=	17
0	9	10
1	10	10
K=	3 H=	0
1	47	51
4	11	12
5	40	41
6	10	9
7	24	23
9	10	10
11	38	38
K=	3 H=	1
0	50	53
1	13	11
-1	8	9
2	41	38
-2	42	41
-3	27	26
4	33	38
-4	22	22
5	13	14
-5	20	19
-6	15	14
-7	20	22
8	11	11
-8	14	13
9	29	28
-9	25	24
10	17	16
-10	6	6
-11	21	23
K=	3 H=	2
0	32	33
1	81	81
-1	9	6
-2	7	6
3	28	29
-3	47	45
4	42	42
-4	23	22
5	34	34
-5	53	52
6	27	26
-6	14	12
7	28	28
-7	47	45
8	20	19
9	9	9
-9	14	13
10	21	21
-10	16	16
11	15	16
K=	3 H=	3
-1	9	9
2	27	27
-2	36	36
3	60	59
-3	19	18
4	7	7
-4	32	32
5	12	11
-5	36	38
6	26	26
7	6	7
-7	5	3
-8	15	15
9	40	40
-9	38	38
10	10	9
K=	3 H=	4
0	6	5
1	76	75
-1	42	41
2	57	70
3	8	7
4	57	56
-4	26	25
5	11	9
-5	43	43
6	10	12
-6	8	9
7	41	40
-7	17	16
8	15	15
-8	7	7
9	15	16
-9	10	10
-10	38	38
11	25	25
K=	3 H=	5
0	40	37
1	27	29
-1	5	3
2	32	33
-2	11	10
3	6	5
-3	75	71
5	8	9
-5	39	39
6	45	45
-6	32	32
7	51	51
-7	11	10
-8	6	7
9	30	30
-9	14	15
K=	3 H=	6
0	18	23
1	46	46
-1	17	17
2	22	24
-2	28	28
-3	26	26
4	42	42
-4	6	8
5	8	9
-5	11	9
6	17	17
-6	15	15
-7	33	33
9	9	6
-9	10	9
10	10	10
-10	30	28
K=	3 H=	7
1	17	16
-1	10	11
2	38	39
-2	9	9
3	33	33
-3	27	27
4	44	40
-4	13	12
6	13	14
7	20	21
-7	24	24
8	10	9
-8	10	8
-9	7	7
K=	3 H=	8
1	32	33
-1	36	34
2	51	49
-2	17	15
3	9	8
-3	15	17
4	18	17
5	16	16
-5	12	12
-6	17	18
8	12	12
9	21	21
-10	13	13
K=	3 H=	9
0	20	20
1	33	32
-1	25	23
-2	5	8
3	33	32
-3	12	11
4	22	22
-4	10	8
5	8	8
-5	18	19
6	25	25
7	24	23
-8	18	19
K=	3 H=	10
0	24	24
1	23	22
-1	10	11
2	27	26
3	10	11
4	11	11
-4	7	5
5	32	32
6	17	17
-6	9	8
7	9	10
-7	7	5
8	8	7
-8	11	12
-9	9	8
K=	3 H=	11
1	16	16
-1	9	10
2	23	22
3	24	22
-3	7	6
4	16	16
5	12	11
-5	5	5
6	22	23
-6	10	12
7	7	7
-7	8	7
8	15	13
-8	21	22
K=	3 H=	12
1	14	15
-1	21	21
-2	12	12
3	22	22
-3	18	17
4	13	13
5	19	18
-5	13	12
7	7	6
K=	3 H=	13
1	17	16
2	16	17
-2	22	23
3	27	27
6	10	7
K=	3 H=	14
1	14	15
-3	18	17
4	11	12
-4	6	5
K=	3 H=	15
0	29	30
-1	12	13
-2	7	7
-3	10	10
K=	3 H=	16
0	21	20
K=	3 H=	17
1	12	12
-1	11	12
K=	4 H=	0
1	32	32
2	47	53
3	8	9
4	58	59
5	11	12
6	11	12
7	20	19
8	11	13
9	9	9
K=	4 H=	1
1	16	17
-1	64	61
2	19	20
-2	37	37
3	41	40
-3	27	25
4	12	12
-4	8	8
5	11	11
-5	26	25
6	20	21
-6	46	48
7	10	9
-7	13	15
8	22	21
-8	30	30
9	10	11
-9	32	33
10	23	25
-10	19	19
K=	4 H=	2
0	42	41
1	27	28
-1	35	34
2	9	11
-2	29	29
3	35	34
-3	6	7
-4	9	13
5	14	15
-5	32	31
6	12	13
-6	21	20
7	6	8
8	45	45
-8	34	33
9	28	26
-9	9	11
10	20	21
K=	4 H=	3
0	51	49
1	25	25
2	13	12
-2	38	37
3	17	16
-3	9	9
4	6	8
5	18	20
-5	34	33
6	15	16
-6	18	18
7	22	20
-7	20	22
8	12	13
9	10	10
10	16	14
-10	11	11
K=	4 H=	4
-1	6	6
2	49	51
3	7	7
-3	55	53
4	15	18
-4	30	31
5	20	19
-5	51	49
6	10	11
7	33	33
8	9	13
-8	8	9
9	29	30
10	17	14
-10	8	11
K=	4 H=	5
1	9	8
-1	37	36
2	12	13
3	23	22
-3	27	26
4	7	11
-4	12	14
5	9	9
-5	8	8
6	9	9
-6	17	17
-7	16	16
9	7	5
10	16	19
-10	24	22
K=	4 H=	6
0	24	23
1	38	39
2	44	45
-2	19	18
3	14	13
-3	28	26
-4	44	42
5	8	10
-5	16	16
6	17	15
-6	21	20
7	8	9
-7	20	19
-8	11	11
9	11	9
-9	12	12
-10	20	19
K=	4 H=	7
1	41	43
-1	5	6
-2	19	19
-3	7	7
4	18	17
-4	23	24
-5	10	9
-6	13	14
7	14	15
8	27	27
K=	4 H=	8
1	14	13
-1	6	3
2	54	54
-2	24	23
3	19	18
-3	11	10
5	9	9
-5	6	6
-6	8	9
7	24	25
8	8	11
-8	16	16
-9	9	12
K=	4 H=	9
0	13	12
-1	16	15
2	11	11
-2	26	27
3	36	37
-3	24	21
-4	24	25
5	10	10
6	7	6
8	16	17
-8	9	9
K=	4 H=	10
0	16	17
1	25	26
-1	12	12
2	10	13
-2	13	12
3	6	5
-3	12	13
-4	17	18
5	6	6
-5	6	7
7	14	14
K=	4 H=	11
0	22	21
1	9	11
-1	10	10
-2	5	5
3	10	9
-3	22	22
4	31	31
-4	15	15
6	7	5
-6	7	7
K=	4 H=	12
1	7	9
3	29	27
-3	17	19
-4	10	10
-5	13	13
-6	7	8
K=	4 H=	13
1	20	21
-1	10	11
-2	25	26
-3	10	10
4	12	13
-4	16	15
-5	8	9
K=	4 H=	14
0	11	10
-1	8	7
2	24	24
-2	20	20
K=	4 H=	15
1	10	9
2	9	9
K=	4 H=	16
-2	12	12
K=	5 H=	0
1	13	12
3	7	6
4	14	14
5	20	19
6	36	36
7	18	20
K=	5 H=	1
0	7	10
1	11	14
2	7	7
-2	20	20
3	31	32
-3	19	18
4	9	11
5	5	6
6	15	17
-6	14	14
7	20	21
-7	17	18
8	19	20
-8	20	22
K=	5 H=	2
0	32	33
1	9	7
-1	5	4
2	44	44
3	22	20
-3	8	8
4	11	12
-4	8	8
5	31	31
-5	28	28
6	16	15
-6	39	38
7	7	8
8	21	21
-8	5	4
K=	5 H=	3
0	10	10
1	26	27
2	25	24
4	5	7
-4	43	42
-5	7	7
6	19	18
7	16	16
-7	8	9
8	24	24
-8	7	8
9	6	7
-9	22	22
K=	5 H=	4
0	28	28
1	8	4
-1	24	22
2	11	12
-2	18	19
3	30	28
-3	22	20
4	18	19
-4	20	20
-5	24	25
-6	37	36
7	6	7
-7	10	12
-8	12	14
9	13	13
-9	32	33
K=	5 H=	5
0	11	12
-1	31	30
2	11	11
-2	33	32
3	20	18
-3	31	30
-4	7	8
6	15	15
7	12	14
-8	31	30
9	11	13
-9	14	12
K=	5 H=	6
0	25	24
1	12	12
-1	26	24
2	14	12
-2	21	20
3	17	15
-4	7	7
5	6	7
-5	10	12
-6	18	17
7	10	11
K=	5 H=	7
0	12	14
-1	12	13
2	27	25
-2	19	18
-3	33	33
4	12	13
-4	26	25
-5	7	4
6	22	23
-6	6	7
7	7	11
-8	14	13
K=	5 H=	8
0	24	23
-1	16	17
-2	14	13
3	24	23
-3	20	20
4	20	21
5	12	13
-5	9	9
6	8	9
7	12	14
-8	9	2
K=	5 H=	9
1	33	33
2	12	13
-2	38	39
3	10	12
-3	12	12
4	18	18
5	16	15
-5	7	9
6	16	15
-7	6	7
K=	5 H=	10
0	21	21
-1	35	34
2	30	31
-2	12	10
3	11	12
4	24	24
-4	11	10
5	18	19
6	19	18
K=	5 H=	11
0	7	6
1	9	10
-1	13	13
2	42	42
-2	10	13
3	16	18
-3	20	20
4	9	12
-5	6	7
K=	5 H=	12
0	13	16
-1	7	7
-2	8	8
3	18	19
-4	11	9
K=	5 H=	13
0	8	9
2	16	17
-2	8	6
K=	5 H=	14
0	9	9
1	10	9
-1	11	12
-2	7	7
K=	5 H=	15
0	11	12
2	7	8
K=	5 H=	19
0	10	8
K=	6 H=	0
4	10	10
7	14	14
K=	6 H=	1
0	39	38
1	39	39
-1	9	10
2	36	37
-2	25	25
-3	27	26
4	12	13
-4	8	8
5	7	8
-5	31	31
6	8	9
7	22	20
-7	13	13
-8	12	13
K=	6 H=	2
0	24	23
1	9	6
-1	11	11
2	7	7
-2	25	24
3	10	11
-3	30	31
4	8	8
-4	27	26
5	22	23
-5	27	26
7	25	26
8	18	19
K=	6 H=	3
0	21	20
1	27	29
-1	21	20
2	12	14
-2	19	17
3	11	11
-3	15	15
5	6	6
-5	11	12
6	10	11
-6	7	7
7	8	9
-7	12	10
K=	6 H=	4
0	13	13
1	16	15
-1	11	11
2	12	12
3	10	11
-3	13	14
4	14	13
-4	21	20
5	9	8
-5	7	7
-7	17	18
K=	6 H=	5
0	26	26
1	16	17
-1	9	9
2	11	9
3	6	5
-4	9	11
-5	26	27
6	9	10
-6	14	14
K=	6 H=	6
1	20	20
-1	14	13
2	7	7
-2	6	8
-3	27	26
4	19	20
-5	13	13
6	17	19
-7	15	15
K=	6 H=	7
0	22	21
-1	21	22
3	7	8
4	11	13
-4	10	9
6	16	18
-6	8	6
K=	6 H=	8
1	29	29
-2	15	16
3	17	18
-3	32	33
-4	15	16
5	7	6
-5	7	6
-6	10	9
K=	6 H=	9
0	7	7
1	9	9
-1	27	26
2	7	7
3	13	13
-3	13	14
4	7	8
5	9	10
-5	13	14
K=	6 H=	10
2	14	11
3	22	22
K=	6 H=	11
0	12	13
-1	12	11
K=	6 H=	12
1	18	19
2	12	16
K=	6 H=	13
1	8	12
2	6	7
-2	10	10
K=	6 H=	14
-1	8	8
K=	6 H=	15
0	11	10
K=	7 H=	0
1	16	16
2	13	15
5	19	20
6	9	9
K=	7 H=	1
1	23	23
2	9	12
-2	13	12
3	11	10
-3	10	10
-6	21	21
K=	7 H=	2
1	8	7
-1	21	20
2	8	9
-2	7	7
3	17	15
4	5	6
-4	10	10
5	12	13
-5	17	18
-6	22	22
K=	7 H=	3
1	23	24
2	25	25
-3	26	26
5	12	11
-6	7	8
K=	7 H=	4
0	11	12
1	8	9
-1	10	11
2	7	5
3	10	11
-3	6	4
4	7	7
-4	15	17
-5	16	15
K=	7 H=	5
1	41	40
-2	9	11
-4	19	19
5	14	13
K=	7 H=	6
1	17	17
-1	22	22
2	8	9
-2	17	19
3	17	16
-3	8	7
-4	12	11
K=	7 H=	7
0	14	13
1	8	8
-1	10	11
-2	20	22
-3	21	21
K=	7 H=	8
0	11	11
-1	15	14
-2	17	18
K=	7 H=	9
-1	14	11
K=	7 H=	10
-1	13	13
K=	7 H=	12
0	7	6
K=	8 H=	0
0	6	6
2	8	10
3	18	19
K=	8 H=	1
1	15	15
-1	13	14
2	14	15
3	17	18
-3	13	13
K=	8 H=	2
1	13	13
-1	12	14
2	8	8
3	9	11
-3	18	15
K=	8 H=	3
-1	17	17
2	27	28
K=	8 H=	4
0	8	6
1	22	20
2	7	6
K=	8 H=	5
0	8	8
-1	16	14
-2	11	10
K=	8 H=	6
0	9	10
-1	8	8
K=	8 H=	7
0	13	12
-1	9	8
-2	11	10
K=	8 H=	8
2	8	7
K=	9 H=	0
1	9	11
2	16	15
K=	9 H=	1
1	10	9
2	8	10
K=	9 H=	2
0	12	13
1	7	6
K=	9 H=	3
0	14	12
-1	11	11
K=	9 H=	5
0	7	6
K=	9 H=	8
0	10	10
K=	11 H=	1
3	19	1

Table 6. *Equations of least-squares planes referred to orthogonal axes*

Group tri(*p*-nitrophenyl) phosphate	*A*	*B*	*C*	*D*	*S*
O(5)—P——O(2)—C(6)	0·5485	−0·4105	0·7284	5·3406 Å	78·6 × 10^{-3} Å^{2}
O(5)—P——O(3)—C(15)	0·6994	0·1509	−0·6986	−0·2744	59·7 × 10^{-4}
O(5)—P——O(4)—C(24)	0·8745	−0·4089	−0·2607	1·6391	67·8 × 10^{-3}
O(13)-N(12)-O(14)	0·6984	−0·6155	0·3653	4·9132	0
O(22)-N(21)-O(23)	0·7044	−0·7056	0·0780	1·6681	0
O(31)-N(30)-O(32)	−0·1007	0·9728	0·2085	0·6648	0
C(6)—C(7)—C(8)—C(9)—C(10)-C(11)	0·6456	−0·6912	0·3248	4·2990	33·7 × 10^{-5}
C(15)-C(16)-C(17)-C(18)-C(19)-C(20)	0·6991	−0·6908	0·1844	1·6926	19·0 × 10^{-5}
C(24)-C(25)-C(26)-C(27)-C(28)-C(29)	0·1921	0·9686	0·1576	1·6667	60·3 × 10^{-5}
C(9)—N(12)-O(13)-O(14)	0·7008	−0·6142	0·3628	4·9380	0·424 × 10^{-5}
C(18)-N(21)-O(22)-O(23)	0·7422	−0·6650	0·0835	1·6130	2·907 × 10^{-5}
C(27)-N(30)-O(31)-O(30)	−0·0918	0·9674	0·2359	1·0260	2·149 × 10^{-4}
Group triphenyl phosphate					
O(5)-P-O(2)-C(6)	−0·1235	0·4659	0·8762	3·638	13·04 × 10^{-4}
O(5)-P-O(3)-C(12)	0·6232	0·5657	−0·5292	3·664	13·71 × 10^{-2}
O(5)-P-O(4)-C(18)	0·6745	0·6585	−0·3339	5·063	4·41 × 10^{-2}

$\bar{X}=a_0x+c_0z\cos\beta$; $\bar{Y}=b_0y$; $\bar{Z}=c_0z\sin\beta$. $A\bar{X}+B\bar{Y}+C\bar{Z}=D$; S = sum of squares of deviation of atoms from plane; D = origin-to-plane distance in Ångströms. All atoms given equal weight.

Table 7. *Dihedral angles*

	Plane
P(1), O(2), C(6)	1
P(1), O(3), C(15)	2
P(1), O(4), C(24)	3
O(5), P(1), O(3), C(15)	4
C(6), C(7), C(8), C(9), C(10), C(11)	5
C(15), C(16), C(17), C(18), C(19), C(20)	6
C(24), C(25), C(26), C(27), C(28), C(29)	7

	Planes	Triphenyl phosphate	Tri-(*p*-nitrophenyl) phosphate
Dihedral angles between P-O-C planes	1 and 2	26·43°	95·91°
	1 and 3	78·22	90·93
	2 and 3	84·02	55·58
Dihedral angles between most planar O′-P-O-C and other P-O-C planes	1 and 4	80·16	83·58
	3 and 4	77·54	52·57
Dihedral angles between P-O-C planes and the phenyl ring to which they are attached	1 and 5	69·08	53·19
	2 and 6	94·87	77·75
	3 and 7	50·69	51·79

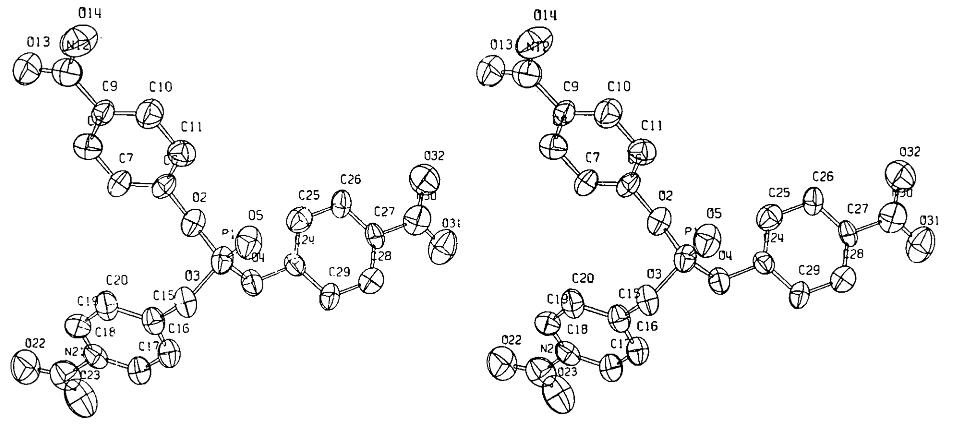


Fig. 3. Stereoscopic diagram of the structure of tri-(*p*-nitrophenyl) phosphate down the *b* axis.

phosphates. Second, it seems unlikely that the small bond angle at phosphorus is necessarily the most important factor for the increased hydrolysis rates in the five-membered cyclic phosphates, inasmuch as the small angle in triphenyl phosphate does not enhance this hydrolysis rate appreciably.

Our simple consideration of the π bonding does not seem to account for the orientation of the P–O–C planes to provide maximum *d–p* overlap between the oxygen and phosphorus orbitals. A more complete analysis, such as that of Collins (1966), may be able to extend this treatment.

We wish to thank the National Institutes of Health for Grant GM–08395–07. We further wish to thank Montana State University for grants which have made possible some of the computing required for this study.

References

ABRAHAMS, S. C. (1950). *Acta Cryst.* **3**, 194.

ABRAMSON, J. D. & PASCHER, I. (1966). *Acta Cryst.* **21**, 79.

BARNARD, P. W. C., BUNTON, C. A., KELLERMAN, D., MHALA, M. M., SILVER, B., VERNON, C. A. & WELCH, V. A. (1966). *J. Chem. Soc.* B, p. 227.

BUNTON, C. A., KELLERMAN, D., OLDHAM, K. G. & VERNON, C. A. (1966). *J. Chem. Soc.* B, p. 292.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *Full Matrix Least-Squares Refinement Program ORFLS.* ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

COLLIN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 3281.

DUNITZ, J. D. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 327.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations.* ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KRAUT, J. & JENSEN, L. H. (1961). *Acta Cryst.* **14**, 1146.

KRAUT, J. & JENSEN, L. H. (1963). *Acta Cryst.* **16**, 79.

NEWTON, M. G., COX, J. R. JR & BERTRAND, J. A. (1966). *J. Amer. Chem. Soc.* **88**, 1503.

STEITZ, T. A. & LIPSCOMB, W. N. (1965). *J. Amer. Soc.* **87**, 2488.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. New York: Macmillan.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *J. Mol. Biol.* **13**, 914.

SVETICH, G. W. & CAUGHLAN, C. N. (1965). *Acta Cryst.* **19**, 645.

SVETICH, G. W., CAUGHLAN, C. N., LI, C. T. & WATENPAUGH, K. D. (1965). *Programs for the IBM* 1620. Montana State University Library.

SWANK, D., CAUGHLAN, C. N., RAMIREZ, F., MADAN, O. P. & SMITH, C. P. (1967). *J. Amer. Chem. Soc.* **89**, 6503.

Acta Cryst. (1970). B**26**, 1534

The Crystal Structure of La_2Sb

BY W. N. STASSEN*, M. SATO† AND L. D. CALVERT‡

Division of Chemistry, National Research Council of Canada, Ottawa, Canada

(*Received* 18 *October* 1968 *and in revised form* 18 *November* 1969)

Crystals of La_2Sb are tetragonal, $a=4{\cdot}626$ (3), $c=18{\cdot}06$ (2) Å, $c/a=3{\cdot}904$; space group $I4/mmm$ (D_{4h}^{17}), $Z=4$; 4 La(1) in 4(*c*), $0\frac{1}{2}0$; 4 La(2) in 4(*e*), $00z$ with $z=0{\cdot}3204$ (2); 4 Sb in 4(*e*), $00z$ with $z=0{\cdot}1377$ (2). The structure of La_2Sb corresponds to two *C*38 structure units joined together by reflexion across a mirror plane perpendicular to the *c* axis. Intensities for 298 *h*0*l* and *h*1*l* reflexions were obtained from multiple-film Weissenberg exposures by visual comparison with a film density scale. The parameters were refined using a structure-factor least-squares program.

Introduction

The lanthanum–antimony system was first studied by Vogel & Klose (1954) who reported the phases La_2Sb, La_3Sb_2, LaSb and $LaSb_2$. The rock-salt structure of LaSb had already been established by Iandelli & Botti (1937). Wang & Steinfink (1967) have determined the structure of $LaSb_2$, Gambino (1967) has assigned the Gd_4Bi_3 (anti-Th_3P_4) structure to La_4Sb_3, and Rieger & Parthé (1968) have recently assigned the Mn_5Si_3 structure to La_5Sb_3. The structure determination of La_2Sb was undertaken as part of a reinvestigation of the La–Sb system which is still underway (Mansey, Sato, Taylor & Calvert, to be published).

Experimental

La_2Sb was prepared as described by Sato, Taylor & Calvert (1967) (La > 99·8, Sb > 99·99 %; total impurities in the alloy were found to be in the range 0·05–0·5 % by semi-quantitative spectroscopic analysis). The single

---

* N.R.C. Postdoctoral Fellow,

† Present address: Applied Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma, Japan.

‡ N.R.C. No. 11,551.