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The Crystal Structures of a Pentacoordinate Phosphorus Compound: 3,4,8,9-Dibenzo-5,7-dimethyl-1-phenyl-2,6,10,11-tetraoxa-1-phosphatricyclo[5.3.1.0^{1,5}]undecane and its Hydrolysis Product: [1-Hydroxy-1-(2-hydroxyphenyl)ethyl]phenylphosphinic acid

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Abstract

Reaction of PhPCl_2 with $o\text{-HOC}_6\text{H}_4\text{COCH}_3$ gives an unusual tricyclic tetraoxaphosphaundecane. Crystals of this compound are monoclinic, $P2_1/c$, with $a = 13.874$ (7), $b = 7.924$ (4), $c = 16.572$ (8) Å, $\beta = 94.5$ (2)°, $Z = 4$. The geometry around the P atom is distorted trigonal bipyramidal, with the two five-membered rings and one six-membered ring all in apical-equatorial positions. It is postulated that permutational isomerization in solution is unlikely for this compound partly because of its molecular rigidity. Crystals of the disubstituted phosphinic acid formed as its hydrolysis product are monoclinic, $P2_1/n$, with $a = 13.886$ (7), $b = 7.378$ (4), $c = 15.280$ (8) Å, $\beta = 116.9$ (2)°, $Z = 4$. The P atom has the expected tetrahedral environment. $\text{O}\cdots\text{O}$ close contacts < 2.76 Å indicate hydrogen bonding which extends throughout the lattice.

Introduction

The synthesis of $\text{PhP}(\text{OC}_6\text{H}_4\text{COCH}_3)_2$ by the reaction of PhPCl_2 with $o\text{-HOC}_6\text{H}_4\text{COCH}_3$ in the presence of triethylamine was attempted as part of a general study of the influence of transition metals on the photochemistry of organic molecules. The resulting solid (I) is an unusual tricyclic tetraoxaphosphaundecane. On recrystallization from wet acetone, (I) underwent hydrolysis to yield the substituted phosphinic acid (II). The structures of these compounds could not be readily ascertained by spectroscopic techniques and were thus solved by X-ray methods.

Experimental

12.62 g (0.1 mol) $o\text{-HOC}_6\text{H}_4\text{OCH}_3$ in 70 ml benzene was added dropwise at 273 K to a solution of 10.12 g

(0.1 mol) NEt₃ and 8.95 g (0.05 mol) PhPCl₂ in 170 ml benzene. The reaction, carried out under N₂, was stirred at 273 K for a further 3 h and left overnight. After filtration to remove the amine hydrochloride, the filtrate was concentrated under reduced pressure. The crystalline product (I) was purified by recrystallization from hot benzene. (II) resulted from an attempted recrystallization of (I) from acetone which had not been rigorously dried.

¹H NMR spectra were obtained on a Varian XL-100 spectrometer. Freshly made solutions in CDCl₃ were run with Me₄Si as internal reference.

Experimental crystal data appear in Table 1. Intensities and lattice constants for both compounds were obtained on a four-circle diffractometer with graphite-monochromated Mo K α radiation. Crystal stability was monitored by periodically measuring three standard reflections; there was no evidence of crystal deterioration. The data were corrected for Lorentz-polarization effects but not for absorption.

Solution and refinement of the structures

The structure of the tetraoxaphosphaundecane (I) was solved by the automatic centrosymmetric routine of *SHELX* (Sheldrick, 1976), in which an *E* map yielded the positions of all the heavy atoms. Some of the H atoms were located in subsequent difference maps. The

Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of the phospho-undecane (I) and its hydrolysis product (II)*

	(I)	(II)
Crystal data		
Molecular formula	C ₂₂ H ₁₉ O ₄ P	C ₁₄ H ₁₅ O ₄ P
<i>M_r</i>	378.4	278.2
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i>	13.874 (7) Å	13.886 (7) Å
<i>b</i>	7.924 (4)	7.378 (4)
<i>c</i>	16.572 (8)	15.280 (8)
β	94.5 (2)°	116.9 (2)°
<i>D_m</i>	1.36 Mg m ⁻³	1.20 Mg m ⁻³
<i>D_c</i>	1.38 for <i>Z</i> = 4	1.22 for <i>Z</i> = 4
μ (Mo K α)	0.133 mm ⁻¹	0.159 mm ⁻¹
<i>F</i> (000)	792	584
Data collection		
Crystal dimensions	0.38 × 0.50 × 0.88	0.14 × 0.16 × 0.20
	mm	mm
Scan mode	ω -2 θ	ω -2 θ
Scan width	1.0° θ	1.2° θ
Scan speed	0.03° θ s ⁻¹	0.04° θ s ⁻¹
Range scanned (2 θ)	6–50°	6–44°
Stability of standard reflections	3.4%	1.4%
Number of reflections collected	3257	1880
Number of observed reflections	2463	1140
	<i>I</i> _(rel) > 2 σ <i>I</i> _(rel)	<i>I</i> _(rel) > 2 σ <i>I</i> _(rel)
Final refinement		
Number of variables	252	177
<i>R</i> = $\sum F_o - F_c / \sum F_o $	0.049	0.058
<i>R_w</i> = $\sum w^2 F_o - F_c ^2 / \sum w^2 F_o ^2$	0.065	0.050
Weighting scheme <i>w</i>	($\sigma^2 F + 1.34 \times 10^{-2} F^2$) ⁻¹	($\sigma^2 F$) ⁻¹
<i>U</i> (aromatic H)	0.067 Å ²	0.085 Å ²
<i>U</i> (methyl H)	0.050	0.076

Table 2. *Fractional atomic coordinates (× 10⁴) with e.s.d.'s in parentheses for (I)*

	<i>x</i>	<i>y</i>	<i>z</i>
P	2463 (1)	828 (1)	1680 (1)
O(2)	1440 (1)	273 (3)	1059 (1)
O(6)	3764 (1)	-1529 (2)	1913 (1)
O(10)	2933 (1)	1575 (3)	885 (1)
O(11)	3457 (1)	1190 (2)	2318 (1)
C(3)	1562 (2)	-1291 (4)	717 (2)
C(4)	2284 (2)	-2279 (4)	1098 (2)
C(5)	2737 (2)	-1436 (4)	1844 (2)
C(7)	4205 (2)	122 (4)	2112 (2)
C(8)	4588 (2)	864 (3)	1355 (2)
C(9)	3929 (2)	1676 (3)	811 (2)
C(12)	2322 (2)	-2104 (4)	2612 (2)
C(13)	4939 (2)	-96 (4)	2830 (2)
C(1A)	1756 (2)	2254 (4)	2245 (2)
C(2A)	1918 (3)	2388 (5)	3085 (2)
C(3A)	1360 (3)	3458 (6)	3511 (2)
C(4A)	652 (3)	4429 (5)	3111 (2)
C(5A)	497 (2)	4328 (4)	2274 (2)
C(6A)	1031 (2)	3229 (4)	1843 (2)
C(4B)	2465 (2)	-3879 (4)	818 (2)
C(5B)	1905 (3)	-4476 (5)	142 (2)
C(6B)	1175 (3)	-3477 (5)	-228 (2)
C(7B)	998 (2)	-1877 (5)	54 (2)
C(8C)	5562 (2)	895 (4)	1210 (2)
C(9C)	5865 (3)	1738 (5)	541 (2)
C(10C)	5191 (3)	2577 (5)	17 (2)
C(11C)	4222 (3)	2545 (4)	157 (2)

final refinement was carried out with the heavy atoms treated anisotropically, with the methyl H atoms refined as rigid groups and the remaining H atoms constrained at 1.08 Å from their respective C atoms, their positions dictated by the geometry of the molecule. The isotropic temperature factors of the H atoms were treated as two single parameters. Details of the final refinements are reported in Table 1.

The substituted phosphinic acid structure (II) was solved analogously, although hydroxyl H atoms could not be located in difference syntheses and were therefore omitted from the final model.

Final positional parameters appear in Tables 2 and 3.*

Description of the structures and discussion

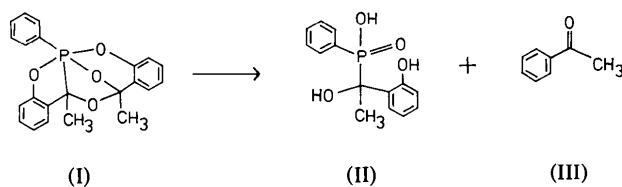
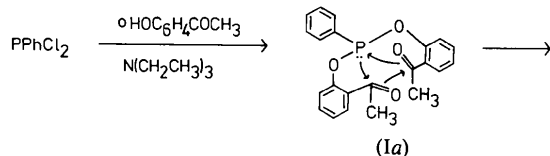
A possible route for the formation of (I) would be initial reaction of two molecules of *o*-HOC₆H₄COCH₃ with PhPCl₂ to form the intermediate phosphonite (Ia). Concerted intramolecular nucleophilic attack would then yield the tricyclic phosphoundecane. This pos-

* Lists of hydrogen positional coordinates, anisotropic temperature factors and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34703 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses for (II)

	x	y	z
P	6521 (1)	584 (2)	2397 (1)
O(1)	7664 (3)	1236 (4)	2735 (3)
O(2)	6194 (3)	-941 (4)	1597 (3)
O(3)	4510 (3)	3254 (6)	3098 (3)
O(4)	5911 (3)	3911 (4)	2491 (3)
C(1)	5542 (4)	2441 (7)	1789 (4)
C(2)	5594 (4)	3020 (7)	856 (4)
C(3)	4414 (4)	1840 (7)	1618 (4)
C(4)	3811 (4)	751 (7)	797 (4)
C(5)	2822 (5)	61 (8)	635 (5)
C(6)	2411 (5)	433 (9)	1288 (5)
C(7)	2985 (5)	1508 (8)	2091 (5)
C(8)	3988 (4)	2208 (8)	2279 (5)
C(11)	6307 (4)	-271 (7)	3393 (4)
C(21)	6919 (5)	436 (8)	4333 (5)
C(31)	6698 (5)	-145 (9)	5090 (5)
C(41)	5914 (5)	-1395 (9)	4925 (5)
C(51)	5322 (5)	-2098 (8)	4004 (5)
C(61)	5523 (4)	-1544 (7)	3235 (5)

tulated mechanism is supported by the report of Evangelidou-Tsolis, Ramirez, Pilot & Smith (1974) that $\text{PhP}(\text{OPh})_2$ reacts with hexafluoroacetone *via* attack at the carbonyl C atom, although in this case the initial P-C-O bond rearranges to give a product containing a P-O-C bond.



The ^1H NMR spectrum of a freshly prepared solution of (I) shows a singlet at 2.00δ due to the protons on C(13) and a doublet at 1.65δ ($J_{\text{HP}} = 20$ Hz) due to the protons on C(12) (Fig. 1). The spectrum run on the same solution after 24 h contains, besides the original set of three lines, an additional set of three lines consisting also of a singlet and a doublet at 2.63δ and 1.39δ ($J_{\text{HP}} = 18$ Hz) respectively. Given that the ^1H NMR spectrum of acetophenone shows a singlet at 2.59δ (Bhacca, Johnson & Shoolery, 1962), and assuming that in this reaction the introduction of the phosphoryl group has a shielding effect, the spectrum of the aged solution of (I) can be interpreted in terms of the formation of the hydrolysis products (II) and (III).

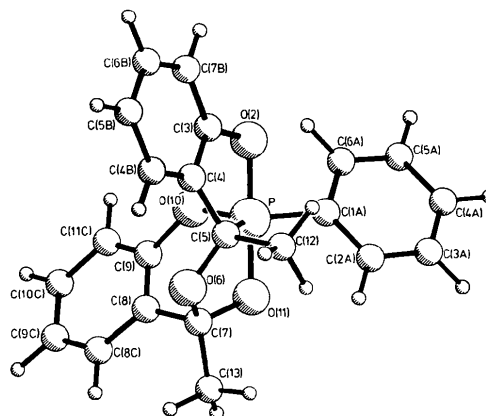


Fig. 1. Perspective view of the phosphorane (I).

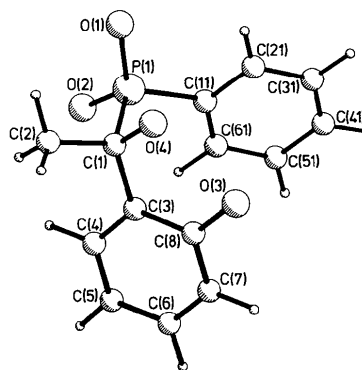


Fig. 2. Perspective view of the substituted phosphinic acid (II).

As a result of the mechanistic versatility of (I), a discussion using available data concerning the reaction pathway and possible intermediates leading to the hydrolysis products would be purely speculative. Presumably the process involves nucleophilic attack at the P atom followed by concerted cyclic proton-transfer mechanisms.

The molecular structures with atomic nomenclature for (I) and (II) appear in Figs. 1 and 2 respectively, with bond lengths and angles for the two structures in Tables 4 and 5. The undecane (I) shows remarkable ability in accommodating the relatively crowded environment around the P atom, probably due to the presence of five- and six-membered rings involving this atom. As discussed by Ramirez & Ugi (1971), this factor plays a significant role in minimizing prohibitive non-bonding interactions within pentacoordinated P-containing molecules. The P atom in (I) lies at the centre of a distorted trigonal bipyramid (Fig. 3), with the two five-membered rings and one six-membered ring all in apical-equatorial planes, and both C atoms equatorial. The apical-equatorial position for five-membered rings and the tendency for the more electro-negative atoms to occupy apical rather than equatorial

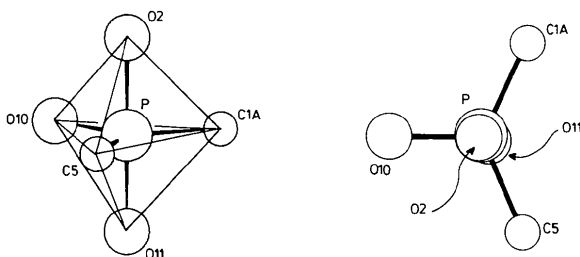


Fig. 3. Coordination about the P atom in (I).

Table 4. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses for (I)

P—O(2)	1.741 (1)	C(6B)—C(7B)	1.380 (2)
P—O(10)	1.626 (1)	C(7B)—C(3)	1.378 (2)
P—O(11)	1.696 (1)	C(4)—C(5)	1.499 (2)
P—C(5)	1.849 (1)	C(5)—C(12)	1.533 (2)
P—C(1A)	1.806 (1)	C(5)—O(6)	1.421 (2)
C(1A)—C(2A)	1.397 (2)	O(6)—C(7)	1.471 (2)
C(2A)—C(3A)	1.379 (2)	C(7)—C(13)	1.512 (2)
C(3A)—C(4A)	1.377 (3)	C(7)—O(11)	1.402 (2)
C(4A)—C(5A)	1.388 (3)	C(7)—C(8)	1.519 (2)
C(5A)—C(6A)	1.379 (2)	C(8)—C(9)	1.391 (2)
C(6A)—C(1A)	1.395 (2)	C(8)—C(8C)	1.392 (2)
O(2)—C(3)	1.379 (2)	C(8C)—C(9C)	1.388 (2)
C(3)—C(4)	1.383 (2)	C(9C)—C(10C)	1.393 (3)
C(4)—C(4B)	1.380 (2)	C(10C)—C(11C)	1.384 (2)
C(4B)—C(5B)	1.395 (2)	C(11C)—C(9)	1.371 (2)
C(5B)—C(6B)	1.390 (2)	C(9)—O(10)	1.399 (2)
O(2)—P—O(10)	88.5 (1)	O(6)—C(7)—C(13)	108.5 (1)
O(2)—P—O(11)	174.9 (0)	O(11)—C(7)—C(13)	110.0 (1)
O(10)—P—O(11)	94.9 (0)	C(8)—C(7)—C(13)	115.8 (1)
O(2)—P—C(5)	89.5 (1)	O(6)—C(7)—C(8)	109.0 (1)
O(10)—P—C(5)	112.4 (1)	O(11)—C(7)—C(8)	106.3 (1)
O(11)—P—C(5)	85.7 (1)	C(7)—C(8)—C(9)	117.4 (1)
O(2)—P—C(1A)	90.8 (1)	C(7)—C(8)—C(8C)	123.9 (1)
O(10)—P—C(1A)	117.4 (1)	C(8C)—C(8)—C(9)	118.5 (1)
O(11)—P—C(1A)	91.1 (1)	O(10)—C(9)—C(8)	121.3 (1)
C(1A)—P—C(5)	130.1 (1)	O(10)—C(9)—C(11C)	117.1 (1)
P—O(2)—C(3)	110.4 (1)	C(8)—C(9)—C(11C)	121.6 (1)
C(5)—O(6)—C(7)	111.6 (1)	P—C(1A)—C(2A)	120.9 (1)
P—O(10)—C(9)	123.7 (1)	P—C(1A)—C(6A)	120.0 (1)
P—O(11)—C(7)	109.1 (1)	C(2A)—C(1A)—C(6A)	119.1 (1)
O(2)—C(3)—C(4)	115.4 (1)	C(1A)—C(2A)—C(3A)	120.3 (2)
O(2)—C(3)—C(7B)	123.4 (1)	C(2A)—C(3A)—C(4A)	120.4 (2)
C(4)—C(3)—C(7B)	121.2 (1)	C(3A)—C(4A)—C(5A)	119.8 (1)
C(3)—C(4)—C(5)	111.4 (1)	C(4A)—C(5A)—C(6A)	120.4 (2)
C(3)—C(4)—C(4B)	120.8 (1)	C(1A)—C(6A)—C(5A)	120.0 (2)
C(4B)—C(4)—C(5)	127.7 (1)	C(4)—C(4B)—C(5B)	118.5 (1)
P—C(5)—O(6)	104.8 (1)	C(4B)—C(5B)—C(6B)	120.1 (1)
P—C(5)—C(4)	104.0 (1)	C(5B)—C(6B)—C(7B)	121.1 (1)
O(6)—C(5)—C(4)	113.3 (1)	C(3)—C(7B)—C(6B)	118.3 (2)
P—C(5)—C(12)	111.7 (1)	C(8)—C(8C)—C(9C)	120.4 (2)
C(4)—C(5)—C(12)	111.7 (1)	C(9C)—C(10C)—C(11C)	120.0 (2)
O(6)—C(7)—O(11)	106.8 (1)	C(9)—C(11C)—C(10C)	119.6 (2)
O(6)—C(5)—C(12)	110.8 (1)	C(8C)—C(9C)—C(10C)	119.8 (1)

positions appears to be a general phenomenon in trigonal bipyramidal P (Ramirez & Ugi, 1971).

In (I), the diapical bond axis is slightly distorted, with the angle $O(2)-P-O(11) = 174.9(0)^\circ$. The apical-equatorial bond angles range from $85.7(1)$ to $94.9(0)^\circ$, the equatorial bond angles being $112.4(1)$, $117.4(1)$, and $130.1(1)^\circ$.

Table 5. Intramolecular bond lengths (Å) and angles (°) with *e.s.d.*'s for (II)

P—O(1)	1.509 (3)	C(6)—C(7)	1.374 (7)
P—O(2)	1.570 (3)	C(7)—C(8)	1.389 (7)
P—C(1)	1.857 (5)	O(3)—C(8)	1.367 (6)
P—C(11)	1.792 (5)	C(8)—C(3)	1.409 (7)
C(1)—C(2)	1.522 (7)	C(11)—C(21)	1.399 (7)
C(1)—O(4)	1.447 (6)	C(21)—C(31)	1.391 (7)
C(1)—C(3)	1.532 (7)	C(31)—C(41)	1.361 (8)
C(3)—C(4)	1.404 (7)	C(41)—C(51)	1.371 (8)
C(4)—C(5)	1.378 (7)	C(51)—C(61)	1.387 (7)
C(5)—C(6)	1.382 (7)	C(61)—C(11)	1.374 (6)
O(1)—P—O(2)	112.6 (2)	C(3)—C(4)—C(5)	121.1 (6)
O(1)—P—C(1)	110.8 (2)	C(4)—C(5)—C(6)	120.0 (6)
O(2)—P—C(1)	104.5 (2)	C(5)—C(6)—C(7)	119.9 (6)
O(1)—P—C(11)	111.9 (2)	C(6)—C(7)—C(8)	121.4 (6)
O(2)—P—C(11)	108.0 (2)	O(3)—C(8)—C(3)	123.0 (5)
C(1)—P—C(11)	108.6 (2)	O(3)—C(8)—C(7)	117.8 (6)
P—C(1)—O(4)	104.4 (3)	C(3)—C(8)—C(7)	119.2 (6)
P—C(1)—C(3)	109.5 (3)	P—C(11)—C(21)	119.0 (4)
O(4)—C(1)—C(3)	109.6 (4)	P—C(11)—C(61)	120.9 (5)
P—C(1)—C(2)	110.0 (4)	C(21)—C(11)—C(61)	120.0 (5)
O(4)—C(1)—C(2)	109.5 (4)	C(11)—C(21)—C(31)	118.7 (6)
C(2)—C(1)—C(3)	113.5 (5)	C(21)—C(31)—C(41)	120.9 (7)
C(1)—C(3)—C(8)	123.4 (5)	C(31)—C(41)—C(51)	120.3 (7)
C(1)—C(3)—C(4)	118.0 (5)	C(41)—C(51)—C(61)	120.1 (6)
C(4)—C(3)—C(8)	118.4 (5)	C(51)—C(61)—C(11)	120.0 (6)

The P atom lies 0.01 \AA from the equatorial plane. The phenyl groups have normal geometry. The two five-membered rings are slightly puckered, the $P-C(5)-O(6)-C(7)-O(11)$ ring containing two tetrahedral C atoms showing the greater deviation from planarity. Torsion angles in the six-membered dioxaphosphorin ring vary between 76° for $P-O(11)-C(7)-C(8)$ and -10° for $C(7)-C(8)-C(9)-O(10)$.

It is well established that many pentacoordinate P compounds are able to change their ligand distributions by bond-deformation processes which may be explained by the Berry (1960) pseudorotation or the turnstile rotation mechanisms (Ramirez & Ugi, 1971). Five-coordinated P having trigonal bipyramidal symmetry, D_{3h} , can exist as 20 isomers, or 10 pairs of enantiomers, when all the ligands are different. Application to the present study shows that when one considers each of the ten enantiomeric pairs only one is plausible. The other nine exhibit serious drawbacks to their possible formation for one or more of the following reasons:

(i) the planes of one or both five-membered rings lie in diequatorial or diapical positions,

(ii) one or both of the apical positions is occupied by a C atom which has lower electronegativity than O,

(iii) serious steric hindrances exist because of the enforced orientation of bulky groups about the central P atom.

The remaining enantiomeric pair is that found in the crystal structure and the molecular rigidity largely precludes any significant positional changes or rotations of

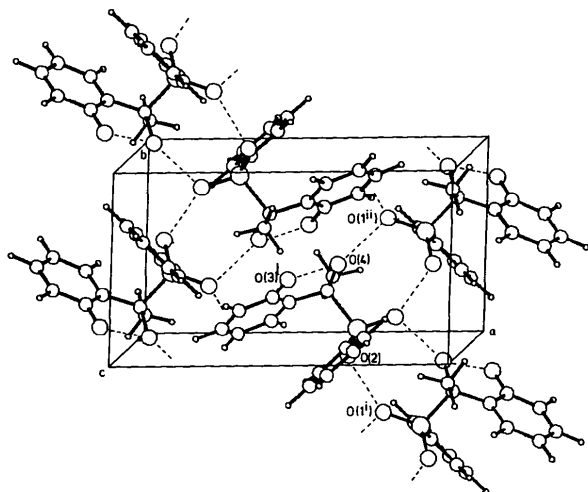


Fig. 4. Unit-cell contents of (II). Probable hydrogen bonds are shown by dotted lines.

a pair of ligands relative to a trio without rupture of bonds. Hence the likelihood of isomerism taking place in solution for this compound by either of the above mechanisms is considered remote.

This conclusion is supported by the examination of the ^1H NMR spectrum, which shows no splitting of the methyl resonance on C(12) throughout the temperature range 213–338 K.

The ligands around the P atom in (II) are in the expected tetrahedral environment. The P–C(11) length of 1.792 (5) Å agrees favourably with the average P–C length of 1.786 (4) Å in diphenylphosphinic acid (Fenske, Mattes, Löns & Tebbe, 1973). The P–C(1) length is somewhat longer, 1.857 (5) Å.

The presence of $\text{O}\cdots\text{O}$ close contacts (< 2.76 Å) are indicative of hydrogen bonding which extends throughout the lattice. Although the hydroxyl H atoms could not be located, the P–O(1) distance of 1.509 (3) Å, typical of a P=O linkage, and the P–O(2) distance of 1.570 (3) Å, typical of a P–OH linkage (Giordano & Ripamonti, 1967), allow a reasonable assessment to be made concerning the donor and acceptor O atoms

Table 6. Intramolecular and intermolecular hydrogen bonding in (II)

E.s.d.'s are in parentheses.

Symmetry code: (i) $1\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

O(2)···O(1 ⁱ)	2.536 (5) Å
O(4)···O(1 ⁱⁱ)	2.756 (6)
O(3)···O(4)	2.551 (7)

involved in the hydrogen-bonding scheme; O(1) acts as H acceptor as regards both the O(2)···O(1) and O(4)···O(1) intermolecular bonds, the H atom in the O(3)···O(4) intramolecular bond being donated by O(3). This is illustrated in Fig. 4 and distances are given in Table 6.

All calculations were carried out on a Univac 1106 computer at the University of Cape Town.

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