

Akira Onoda, Taka-aki Okamura,  
Hitoshi Yamamoto and Norikazu  
Ueyama\*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence e-mail:  
ueyama@chem.sci.osaka-u.ac.jp

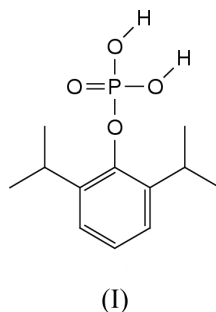
## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
 $R$  factor = 0.035  
 $wR$  factor = 0.106  
Data-to-parameter ratio = 14.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.One-dimensional  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bonds restricted by the bulky molecule 2,6-diisopropylphenyl dihydrogen phosphate

The title compound,  $\text{C}_{12}\text{H}_{19}\text{OP}_4$ , with a bulky group, exhibits one-dimensional hydrogen-bonded chains of bifurcated  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  interactions. This one-dimensional chain structure with double  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bonds is induced by the bulky isopropyl groups.

## Comment

Phosphate groups are attractive molecular building blocks in crystal engineering to form hydrogen-bond networks (Krishnamohan Sharma & Clearfield, 2000). Our attention has been focused on the control of crystal structures through the  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bond using a bulky phosphate compound. The title molecule (Kosolapoff *et al.*, 1968), (I), has a  $\text{P1}-\text{O1}-\text{C1}-\text{C2}$  torsion angle of  $-97.2(2)^\circ$ . Atoms O3 and O4 form  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bonds with O2, which is an acceptor of bifurcated hydrogen bonds formed by the two neighbouring molecules. Thus, the title compound forms a one-dimensional chain.



Most of the reported hydrogen-bond networks in the dihydrogen phosphate or phosphonate state are characterized by single  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bonds (Weakley, 1976; Calvo & Berg, 1984; Tkachev *et al.*, 1986). Only a few double  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen-bond structures have been reported: *o*-hydroxyphenoxymethylphosphonic acid (Choi *et al.*, 1994) and *N*-phenyl-1-methylamido-benzylphosphonic acid (Ignatéva *et al.*, 1989). The bulky isopropyl groups interrupt the formation of inter-column hydrogen bonds. Both of the  $\text{P}-\text{OH}$  atoms interact with intra-column phosphate O atoms. Thus, a one-dimensional chain structure with double  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  hydrogen bonds is induced by the bulky isopropyl groups.

## Experimental

The title compound was synthesized according to literature methods (Kosolapoff *et al.*, 1968). The product was recrystallized from chloroform.

Received 23 July 2001  
Accepted 2 October 2001  
Online 13 October 2001

## Crystal data

$C_{12}H_{19}O_4P$   
 $M_r = 258.24$   
 Monoclinic,  $P2_1$   
 $a = 10.0298$  (15) Å  
 $b = 6.3718$  (15) Å  
 $c = 11.2238$  (14) Å  
 $\beta = 100.685$  (11)°  
 $V = 704.9$  (2) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.217$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 14.7$ – $15.0^\circ$   
 $\mu = 0.20$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 Prismatic, colourless  
 $0.30 \times 0.20 \times 0.20$  mm

## Data collection

Rigaku AFC-5R diffractometer  
 $\omega$ - $2\theta$  scans  
 2329 measured reflections  
 2219 independent reflections  
 1627 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.014$   
 $\theta_{max} = 30.0^\circ$

$h = 0 \rightarrow 14$   
 $k = -8 \rightarrow 0$   
 $l = -15 \rightarrow 15$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 0.7%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.106$   
 $S = 1.02$   
 2219 reflections  
 156 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1189P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.25$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.11 (15)

Table 1

Selected geometric parameters (Å, °).

|          |             |          |             |
|----------|-------------|----------|-------------|
| P1–O3    | 1.4917 (16) | P1–O2    | 1.545 (2)   |
| P1–O4    | 1.543 (2)   | P1–O1    | 1.5668 (18) |
| O3–P1–O4 | 112.98 (12) | O4–P1–O1 | 106.74 (11) |
| O3–P1–O2 | 113.17 (11) | O2–P1–O1 | 102.83 (11) |
| O4–P1–O2 | 106.75 (12) | C1–O1–P1 | 123.23 (16) |
| O3–P1–O1 | 113.60 (10) |          |             |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$                          | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|-------|--------------|--------------|----------------|
| O2–H1 <sup>i</sup> ···O3 <sup>i</sup>   | 0.82  | 1.81         | 2.624 (3)    | 175            |
| O4–H2 <sup>ii</sup> ···O3 <sup>ii</sup> | 0.82  | 1.80         | 2.611 (3)    | 169            |

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

The torsion angles about the PO bonds of the two hydroxyl groups were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Support of this work by JSPS Fellowships [for AO; grant 2306(1999–2002)] and a Grant-in-Aid for Scientific Research on Prior Area (A) (No. 10146231) from the Ministry of

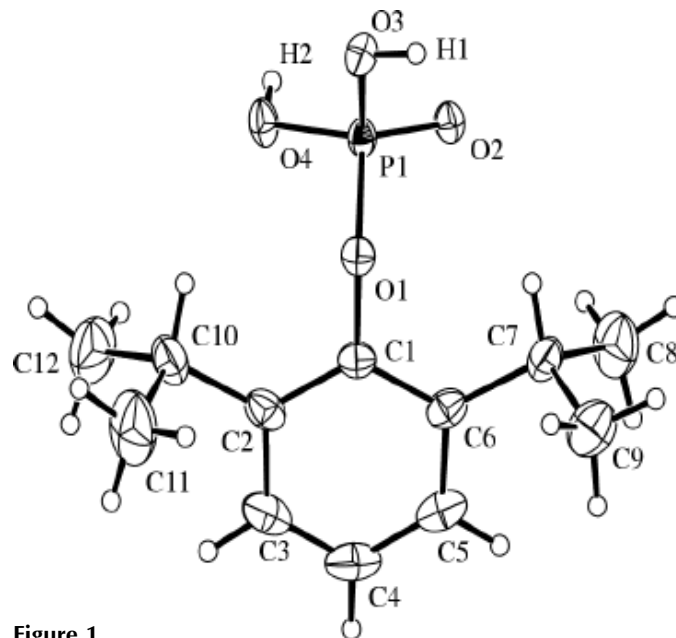


Figure 1

The molecular structure of the title compound, with 25% probability ellipsoids.

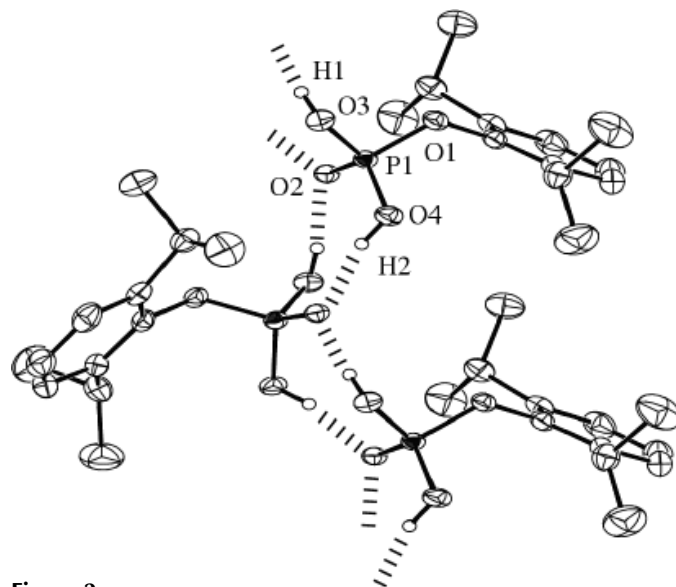


Figure 2

A view of the one-dimensional structure formed by P–OH···O=P hydrogen bonds.

Education, Science, Sports and Culture, Japan, is gratefully acknowledged.

## References

- Calvo, K. C. & Berg, J. M. (1984). *J. Am. Chem. Soc.* **106**, 4202–4204.  
 Choi, N., Failla, S., Finocchiaro, P., MacPartlin, M. & Scowen, I. J. (1994). *J. Chem. Res.* **340**, 1813–1821.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Ignat'eva, T. I., Bovin, A. N., Yarkov, A. V., Chekhlov, A. N., Tsvetkov, E. N. & Raevskii, O. A. (1989). *Koord. Khim.* **15**, 1179.  
 Kosolapoff, G. M., Arpke, C. K., Lamb, R. W. & Reich, H. (1968). *J. Chem. Soc. C*, pp. 815–818.  
 Krishnamohan Sharma, C. V. & Clearfield, A. (2000). *J. Am. Chem. Soc.* **122**, 4394–4402.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Forest Drive, The Woodlands, TX 77381, USA.  
Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
Tkachev, V. V., Atovmyan, L. O., Timokhin, B. V., Bragina, O. A., Ratovskii, G. V. & Sergienko, L. M. (1986). *Zh. Strukt. Khim.* **27**, 121–123.  
Weakley, T. J. R. (1976). *Acta Cryst.* **B32**, 2889–2890.