

$S = 0.998$   
1307 reflections  
201 parameters  
Only H-atom  $U$ 's refined  
Unit weights applied

Extinction correction: none  
Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV)

Financial support from the University of the Basque Country (Proyect UPV 170.310-EA052/92) and the Basque Government (Proyect PGV 9213) is gratefully acknowledged.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{eq}$
C1	0.4618 (4)	0.1973 (2)	1.5611 (5)	0.054 (1)
C2	0.5099 (4)	0.1279 (2)	1.6449 (5)	0.046 (1)
C3	0.6126 (4)	0.0931 (2)	1.5804 (5)	0.051 (1)
C4	0.6583 (4)	0.0287 (3)	1.6433 (7)	0.063 (1)
C5	0.6019 (5)	-0.0031 (2)	1.7728 (6)	0.065 (1)
C6	0.5010 (5)	0.0307 (2)	1.8405 (6)	0.061 (1)
C7	0.4547 (4)	0.0959 (2)	1.7786 (5)	0.054 (1)
N	0.3541 (3)	0.1840 (2)	1.4526 (4)	0.046 (1)
C8	0.2461 (4)	0.1488 (3)	1.5250 (5)	0.065 (1)
C9	0.3922 (4)	0.1454 (2)	1.3084 (5)	0.048 (1)
C10	0.2937 (4)	0.1461 (2)	1.1809 (5)	0.044 (1)
C11	0.2653 (4)	0.2117 (2)	1.1024 (5)	0.042 (1)
C12	0.1750 (3)	0.2141 (2)	0.9861 (5)	0.040 (1)
C13	0.1099 (3)	0.1496 (2)	0.9447 (4)	0.041 (1)
C14	0.1388 (4)	0.0842 (2)	1.0229 (5)	0.050 (1)
C15	0.2300 (4)	0.0830 (2)	1.1402 (5)	0.048 (1)
C16	0.4322 (6)	0.2603 (2)	1.6706 (7)	0.072 (1)
O17	0.3770 (4)	0.3190 (2)	1.5838 (5)	0.078 (1)
O18	0.0218 (3)	0.1567 (2)	0.8278 (3)	0.055 (1)
C19	-0.0323 (5)	0.0909 (3)	0.7687 (7)	0.070 (1)
O20	0.1422 (3)	0.2757 (2)	0.9015 (4)	0.057 (1)
C21	0.2022 (5)	0.3433 (2)	0.9412 (6)	0.062 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—N	1.488 (6)	C10—C15	1.370 (6)
C1—C16	1.492 (6)	C10—C11	1.385 (5)
C1—C2	1.523 (6)	C11—C12	1.372 (5)
C2—C3	1.377 (6)	C12—O20	1.362 (5)
C2—C7	1.389 (6)	C12—C13	1.398 (5)
C3—C4	1.364 (6)	C13—O18	1.365 (5)
C4—C5	1.365 (7)	C13—C14	1.382 (5)
C5—C6	1.365 (7)	C14—C15	1.385 (6)
C6—C7	1.375 (6)	C16—O17	1.413 (6)
N—C9	1.449 (5)	O18—C19	1.409 (6)
N—C8	1.453 (6)	O20—C21	1.417 (5)
C9—C10	1.500 (6)		
N—C1—C16	109.2 (4)	C15—C10—C11	118.8 (4)
N—C1—C2	114.3 (3)	C15—C10—C9	121.3 (4)
C16—C1—C2	114.5 (4)	C11—C10—C9	119.9 (4)
C3—C2—C7	117.8 (4)	C12—C11—C10	121.1 (4)
C3—C2—C1	117.7 (4)	O20—C12—C11	125.1 (3)
C7—C2—C1	124.5 (4)	O20—C12—C13	114.8 (3)
C4—C3—C2	121.6 (4)	C11—C12—C13	120.1 (4)
C3—C4—C5	120.1 (4)	O18—C13—C14	124.9 (4)
C6—C5—C4	119.5 (4)	O18—C13—C12	116.4 (3)
C5—C6—C7	120.8 (5)	C14—C13—C12	118.6 (4)
C6—C7—C2	120.1 (4)	C13—C14—C15	120.4 (4)
C9—N—C8	111.1 (3)	C10—C15—C14	121.0 (4)
C9—N—C1	111.3 (3)	O17—C16—C1	110.2 (4)
C8—N—C1	115.9 (3)	C13—O18—C19	117.2 (3)
N—C9—C10	112.7 (3)	C12—O20—C21	117.5 (3)

Structure solution: *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Structure refinement: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965). Geometric calculations: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Arriortua, M. I., Urtiaga, M. K., Badía, D., Domínguez, E., González-Cameno, A. M. & Solans, X. (1995). *Acta Cryst.* **C51**, 109–112.
- Cook, R. E., Glick, M. D., Rigau, J. J. & Johnson, C. R. (1971). *J. Am. Chem. Soc.* **24**, 924–928.
- Debaerdemaeker, T., Germain, G., Main, P., Tate, C. & Woolfson, M. M. (1987). *MULTAN87. Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, Louvain, Belgium, and Ulm, Germany.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Reetz, M. T. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1531–1546.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Venkov, A. P. & Vodenicharov, D. M. (1990). *Synthesis*, pp. 253–255.

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## [4,4',6,6'-Tetramethyl-(2,2'-isobutylidene-di-*o*-phenylene)] (2,6,7-Trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl) Phosphite, $C_{25}H_{32}P_2O_6$ †

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## Abstract

The eight-membered ring in the diphosphite exists in a boat-chair conformation in which the electron lone pair on the P atom and the bridged methine have an *anti* relationship. The sterically more demanding isopropyl

† Dedicated to Professor Edward J. Grubbs on the occasion of his 60th birthday.

group is disposed away from the cage phosphite moiety. The endocyclic bond angle at the C atom bearing the isopropyl group is 111.2 (2)°.

### Comment

Because of their ability to decompose peroxides, certain phosphites have a widespread application in protecting polymers during processing and storage (Ivanov & Zheltukhin, 1970). The reactivity of organic phosphites is largely modified when incorporated into a cyclic structure (Pudovik, Ovchinnikov, Cherkasov & Pudovik, 1983). In our efforts to design more effective antioxidants, we have developed a one-pot synthesis of the heterocyclic diphosphite (3).

Addition of the bisphenol (1) to pentaerythritol dichlorodiphosphite (2) resulted in the formation of the diphosphite (3), a molecule of potential mirror symmetry containing two distinctly different phosphite functionalities (see scheme). Dichlorodiphosphite (2) was generated *in situ* by the reaction of phosphorus trichloride and pentaerythritol in refluxing dichloromethane in the presence of a catalytic amount of pyridine. Diphosphite (3) was recrystallized from a heptane–ethyl acetate solution.

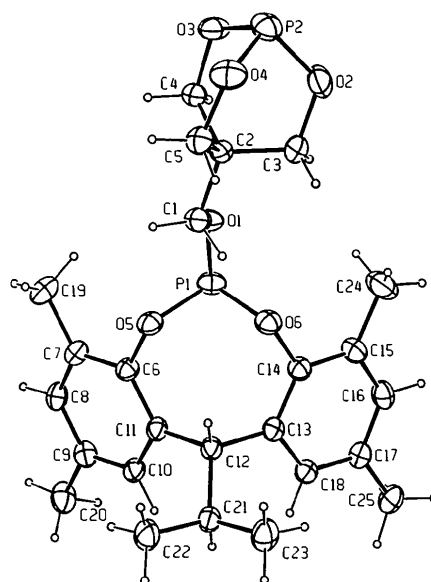
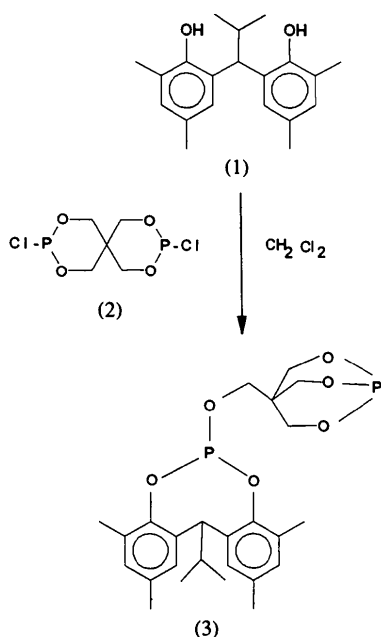


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound, with displacement ellipsoids drawn at the 40% probability level.

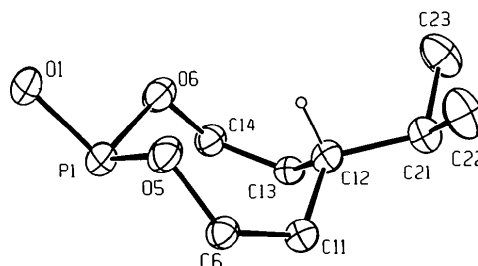


Fig. 2. A view of a portion of the molecule, illustrating the conformation of the eight-membered ring. The phosphite cage, some aryl C atoms and most H atoms are omitted.

The P1—O1 distance, 1.593 (2) Å, is slightly shorter than the cyclic P1—O5, 1.648 (2), and P1—O6, 1.640 (2) Å, distances. In the bicyclic cage, the P—O distances, 1.607 (2)–1.617 (2) Å, are also slightly shorter. The P1—O1—C1—C2 torsion angle is 158.4 (2)°.

The C11—C12—C13 bond angle is 111.2 (2)° and the O5—P1—O6 bond angle is 99.60 (8)°.

The formation of a single diastereomer was demonstrated by the sharp melting point (459–461 K) and <sup>31</sup>P NMR spectroscopy (Grayson & Griffith, 1967), and it was identified by the crystal structure determination. The sterically more demanding isopropyl group and the cage phosphite moiety occupy pseudo-equatorial positions (Figs. 1 and 2) and the heterocyclic eight-membered ring exists in a boat–chair conformation (Arshinova, Danilova & Ovodova, 1986; Quin, 1988; Arshinova, 1988).

### Experimental

#### Crystal data

C<sub>25</sub>H<sub>32</sub>O<sub>6</sub>P<sub>2</sub>  
*M<sub>r</sub>* = 490.5  
 Monoclinic  
 P2<sub>1</sub>/n  
*a* = 11.9111 (10) Å  
*b* = 16.036 (2) Å  
*c* = 13.1202 (9) Å  
 β = 93.761 (6)°

Cu Kα radiation  
 λ = 1.54184 Å  
 Cell parameters from 25 reflections  
 θ = 25–30°  
 μ = 1.89 mm<sup>-1</sup>  
*T* = 296 K  
 Fragment

$V = 2500.7(7) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.303 \text{ Mg m}^{-3}$

**Data collection**

Enraf-Nonius CAD-4  
 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction:  
 empirical

$T_{\min} = 0.869$ ,  $T_{\max} =$   
 0.995

5335 measured reflections

4913 independent reflections

3925 observed reflections

$|I| > 3\sigma(I)$

**Refinement**

Refinement on  $F^2$

$R = 0.046$

$wR = 0.056$

$S = 2.762$

3925 reflections

427 parameters

All H-atom parameters  
 refined

$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$   
 $(\Delta/\sigma)_{\max} = 0.04$

$0.33 \times 0.30 \times 0.25 \text{ mm}$

Colorless

$R_{\text{int}} = 0.012$

$\theta_{\max} = 75^\circ$

$h = 0 \rightarrow 14$

$k = 0 \rightarrow 20$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 167 min

intensity decay:  $< 2\%$

$\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.11 \text{ e \AA}^{-3}$

Extinction correction:  $(I +$   
 $gI_c)^{-1}$  applied to  $F_c$

Extinction coefficient:

$7.1(6) \times 10^{-7}$

Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P1—O1	1.593 (2)	O3—C4	1.447 (3)
P1—O5	1.648 (2)	O4—C5	1.447 (3)
P1—O6	1.640 (2)	O5—C6	1.405 (3)
P2—O2	1.611 (2)	O6—C14	1.418 (3)
P2—O3	1.607 (2)	C1—C2	1.516 (3)
P2—O4	1.617 (2)	C2—C3	1.520 (3)
O1—C1	1.439 (3)	C2—C4	1.524 (3)
O2—C3	1.448 (3)	C2—C5	1.517 (3)
O1—P1—O5	98.70 (9)	P1—O6—C14	115.5 (1)
O1—P1—O6	98.58 (9)	O1—C1—C2	107.8 (2)
O5—P1—O6	99.60 (8)	C1—C2—C3	110.2 (2)
O2—P2—O3	100.3 (1)	C1—C2—C4	111.0 (2)
O2—P2—O4	99.9 (1)	C1—C2—C5	109.6 (2)
O3—P2—O4	100.3 (1)	C3—C2—C4	109.1 (2)
P1—O1—C1	126.3 (1)	C3—C2—C5	108.4 (2)
P2—O2—C3	117.5 (2)	C4—C2—C5	108.5 (2)
P2—O3—C4	117.4 (1)	O2—C3—C2	110.0 (2)
P2—O4—C5	117.4 (1)	O3—C4—C2	110.3 (2)
P1—O5—C6	115.0 (1)	O4—C5—C2	110.1 (2)
O5—P1—O1—C1	47.3 (2)	P1—O6—C14—C13	-81.9 (2)
O6—P1—O5—C6	-99.6 (2)	O5—C6—C11—C12	3.6 (3)
O5—P1—O6—C14	100.1 (2)	C6—C11—C12—C13	-91.8 (3)
P1—O1—C1—C2	158.4 (2)	C11—C12—C13—C14	89.3 (3)
P1—O5—C6—C11	80.2 (2)	C12—C13—C14—O6	-0.9 (3)

H atoms were refined with isotropic displacement parameters. Final C—H distances were 0.87(3)–1.11(3) Å for the methyl groups and 0.93(2)–1.05(3) Å for all other non-H atoms. The mean C—H distance for all H atoms was 0.97 Å.

The structure was solved by direct methods using *MULTAN* (Main *et al.*, 1978) and refined by full-matrix least squares using *MolEN* (Fair, 1990). *ORTEP* (Johnson, 1965) was used for the molecular drawings.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{\text{eq}}$
P1	0.87823 (6)	0.10462 (4)	0.82252 (4)	3.74 (1)
P2	0.95579 (6)	0.11370 (5)	0.34356 (5)	4.58 (1)
O1	0.8661 (2)	0.1070 (1)	0.7009 (1)	4.25 (4)
O2	1.0509 (2)	0.1103 (1)	0.4365 (1)	5.25 (4)
O3	0.8584 (2)	0.0594 (1)	0.3909 (1)	4.49 (4)
O4	0.9076 (2)	0.2067 (1)	0.3593 (1)	5.04 (4)
O5	0.7808 (1)	0.1738 (1)	0.8459 (1)	3.59 (3)
O6	0.9907 (1)	0.1632 (1)	0.8404 (1)	3.66 (3)
C1	0.8606 (2)	0.1805 (1)	0.6380 (2)	3.71 (5)
C2	0.8944 (2)	0.1561 (1)	0.5327 (2)	2.85 (4)
C3	1.0201 (2)	0.1389 (2)	0.5356 (2)	3.91 (5)
C4	0.8310 (2)	0.0786 (2)	0.4941 (2)	3.56 (5)
C5	0.8678 (2)	0.2269 (2)	0.4583 (2)	3.95 (5)
C6	0.7409 (2)	0.1694 (1)	0.9442 (2)	3.16 (4)
C7	0.6385 (2)	0.1292 (1)	0.9547 (2)	3.49 (5)
C8	0.6012 (2)	0.1225 (1)	1.0520 (2)	3.69 (5)
C9	0.6625 (2)	0.1545 (2)	1.1375 (2)	3.58 (5)
C10	0.7620 (2)	0.1958 (2)	1.1227 (2)	3.35 (4)
C11	0.8038 (2)	0.2053 (1)	1.0263 (2)	2.94 (4)
C12	0.9117 (2)	0.2535 (1)	1.0096 (2)	3.00 (4)
C13	1.0145 (2)	0.1966 (1)	1.0202 (2)	2.87 (4)
C14	1.0513 (2)	0.1540 (1)	0.9364 (2)	3.28 (4)
C15	1.1450 (2)	0.1033 (2)	0.9410 (2)	4.01 (5)
C16	1.2041 (2)	0.0945 (2)	1.0354 (2)	4.00 (5)
C17	1.1709 (2)	0.1343 (1)	1.1223 (2)	3.48 (5)
C18	1.0766 (2)	0.1852 (1)	1.1130 (2)	3.19 (4)
C19	0.5711 (2)	0.0954 (2)	0.8633 (2)	4.92 (6)
C20	0.6204 (2)	0.1454 (2)	1.2430 (2)	5.27 (6)
C21	0.9240 (2)	0.3339 (1)	1.0736 (2)	3.49 (5)
C22	0.8226 (2)	0.3907 (2)	1.0555 (3)	5.33 (7)
C23	1.0305 (2)	0.3807 (2)	1.0491 (3)	5.04 (7)
C24	1.1834 (3)	0.0591 (2)	0.8477 (2)	6.81 (8)
C25	1.2347 (2)	0.1222 (2)	1.2244 (2)	4.58 (6)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: BK1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**References**

- Arshinova, R. P. (1988). *Russ. Chem. Rev. (Engl. Trans.)*, **57**, 1142–1161.
- Arshinova, R. P., Danilova, O. I. & Ovodova, O. V. (1986). *Dokl. Akad. Nauk SSSR*, **287**, 1135–1139.
- Fair, C. K. (1990). *MolEN. An Interactive Structure Solution Procedure*. Enraf-Nonius, Delft, The Netherlands.
- Grayson, M. & Griffith, E. J. (1967). Editors. *Topics in Phosphorus Chemistry*, Vol. 5, p. 267. Chichester: John Wiley.
- Ivanov, B. E. & Zhelutkin, V. F. (1970). *Russ. Chem. Rev. (Engl. Trans.)*, **39**, 358–372.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Pudovik, M. A., Ovchinnikov, V. V., Cherkasov, R. A. & Pudovik, A. N. (1983). *Russ. Chem. Rev. (Engl. Trans.)*, **52**, 361–376.
- Quin, L. D. (1988). *Conformational Analysis of Medium-Sized Heterocycles*, edited by R. S. Glass, pp. 181–216. New York: VCH Publishers.