

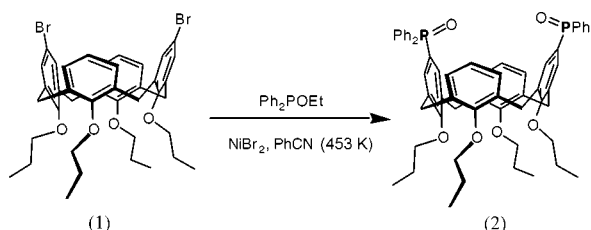
Catherine Jeunesse,^a Dominique
Matt,^a Peter G. Jones^{b*} and
Holger Thönnessen^b^aLaboratoire de Chimie Inorganique
Moléculaire, Université Louis Pasteur, UMR
7513 CNRS, 1 rue Blaise Pascal, 67008
Strasbourg Cedex, France, and ^bInstitut für
Anorganische und Analytische Chemie,
Technische Universität Braunschweig, Postfach
3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

Key indicators

Single-crystal X-ray study
 $T = 173\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.034
 wR factor = 0.085
Data-to-parameter ratio = 19.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.5,17-Bis(diphenylphosphinoyl)-25,26,27,28-
tetrapropoxycalix[4]areneThe title compound, $\text{C}_{64}\text{H}_{66}\text{O}_6\text{P}_2$, possesses crystallographic twofold symmetry and displays the calixarene cone conformation. The two symmetry-independent calixarene rings subtend interplanar angles of $143.06(3)$ and $97.71(4)^\circ$ to the reference plane of the bridging C atoms. The phosphoryl O atom accepts three $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds from the same neighbouring molecule.

Comment

Phosphine oxides constitute an important class of molecules that have been extensively studied in coordination chemistry for three main reasons: (i) they may specifically bind certain metal ions, in particular, lanthanides and actinides; (ii) they constitute valuable precursors for the preparation of tertiary phosphines, suitable in turn for the preparation of transition metal complexes; (iii) when used as additional ligands in transition metal catalysed reactions, *e.g.* carbonylations, they may drastically modify the outcome of the reaction (Clark *et al.*, 2002).As part of our ongoing investigations of the preparation of phosphorus-functionalized calixarenes (Bagatin *et al.*, 1999), we recently reported the synthesis of the upper rim diphenylphosphorylated calix[4]arene (2) (Wieser-Jeunesse *et al.*, 1998). The extraction properties of (2) towards rare-earth metal ions are similar to those of triphenylphosphine oxide (Burgard *et al.*, 2000). Here we present the structure of (2).The molecular structure of (2) is shown in Fig. 1; it displays crystallographic twofold symmetry. Bond lengths and angles (*e.g.* those at phosphorus, Table 1) may be considered normal. The cone conformation of the calixarene core is retained from the precursor (1). The reference plane of the calixarene, defined as the mean plane of the bridging C atoms (here C17, C37 and their equivalents) is exact by symmetry; the rings C11–C16 and C31–C36 subtend angles of $143.06(3)$ and $97.71(4)^\circ$, respectively, to this plane. The distances between centroids are 4.95 \AA for C31–C36 and its symmetry-equivalent ring, and 7.68 \AA for C11–C16 and its equivalent.The phosphoryl O atom is directed away from the ring system in such a way that the angle between the $\text{P}=\text{O}$ vector

Received 27 February 2003

Accepted 3 March 2003

Online 14 March 2003

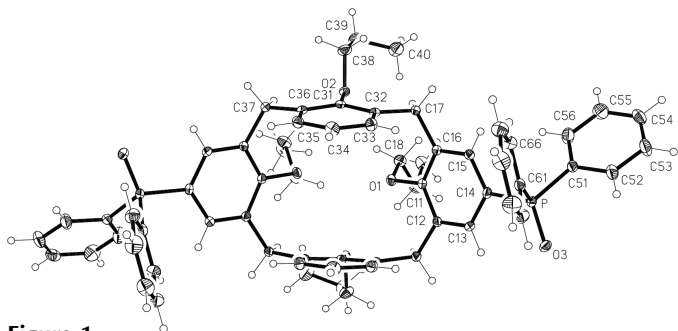


Figure 1
The molecular structure of the title compound in the crystal. Displacement ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

and the normal to the reference plane is 79.8° . This enables O3 to accept three C—H \cdots O hydrogen bonds from a neighbouring molecule (Table 2 and Fig. 2) related by the 2_1 axis parallel to *a*.

Experimental

Compound (2) was conveniently prepared in a one-step procedure starting from the dibromocalixarene (1) (see Scheme), and crystallized from dichloromethane/methanol.

Crystal data

$C_{64}H_{66}O_6P_2$	Mo $K\alpha$ radiation
$M_r = 993.11$	Cell parameters from 65 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 5\text{--}25^\circ$
$a = 12.1097$ (15) Å	$\mu = 0.13$ mm $^{-1}$
$b = 24.311$ (3) Å	$T = 173$ (2) K
$c = 9.2090$ (15) Å	Block, colourless
$V = 2711.1$ (6) Å 3	$0.7 \times 0.6 \times 0.5$ mm
$Z = 2$	
$D_x = 1.217$ Mg m $^{-3}$	

Data collection

Siemens P4 diffractometer	$h = -15 \rightarrow 8$
ω scans	$k = -31 \rightarrow 31$
9442 measured reflections	$l = -11 \rightarrow 0$
6225 independent reflections	3 standard reflections
5469 reflections with $I > 2\sigma(I)$	every 247 reflections
$R_{int} = 0.022$	intensity decay: none
$\theta_{max} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.26$ e Å $^{-3}$
6225 reflections	$\Delta\rho_{min} = -0.21$ e Å $^{-3}$
327 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2713 Friedel pairs
	Flack parameter = -0.01 (7)

Table 1

Selected geometric parameters (Å, °).

P—O3	1.4871 (11)	P—C61	1.8144 (16)
P—C14	1.8006 (15)	P—C51	1.8164 (16)
O3—P—C14	111.90 (7)	O3—P—C51	112.70 (7)
O3—P—C61	110.96 (7)	C14—P—C51	108.90 (7)
C14—P—C61	108.81 (7)	C61—P—C51	103.16 (7)

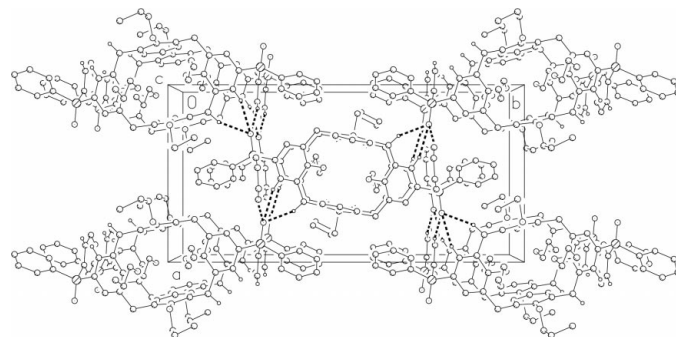


Figure 2
Packing diagram of the title compound, viewed parallel to the *c* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonds have been omitted.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C15—H15 \cdots O3 ⁱ	0.95	2.36	3.2546 (19)	158
C17—H17A \cdots O3 ⁱ	0.99	2.52	3.4410 (18)	155
C66—H66 \cdots O3 ⁱ	0.95	2.59	3.512 (2)	163

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

Methyl H atoms were located in difference syntheses, idealized (C—H = 0.99 Å and H—C—H = 109.5°) and refined on the basis of rigid groups allowed to rotate but not to tip. Other H atoms were included using a riding model, with fixed C—H bond lengths of 0.95 Å (sp^2 C atoms) or 0.98 Å (methylenes). $U_{iso}(H)$ values were fixed at $1.2U_{eq}$ of the parent atom. The absolute configuration was established solely for the measured crystal, because the bulk sample is racemic.

Data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL97.

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr A. Weinkauff for technical assistance.

References

- Bagatin, I. A., Matt, D., Thönnessen, H. & Jones, P. G. (1999). *Inorg. Chem.* **38**, 1585–1591.
- Burgard, M., Ernst, B., Yaftian, M. R., Matt, D., Wieser-Jeunesse, C. & Dielemann, C. (2000). *Solvent Extraction of Rare Earth Nitrates by Phosphorylated Calix[4]arenes*, in *Solvent Extraction for the 21st Century*, ISEC 1999, Vol. 1, edited by M. Cox, M. Hidalgo and M. Valiente, pp. 681–686. London: Society of Chemical Industry.
- Clark, H. J., Wang, R. & Alper, H. (2002). *J. Org. Chem.* **67**, 6224–6225.
- Fait, J. (1991). XSCANS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Siemens (1994). XP. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wieser-Jeunesse, C., Matt, D. & De Cian, A. (1998). *Angew. Chem. Int. Ed.* **20**, 2861–2864.