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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1295). Services for accessing these data are described at the back of the journal.

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An Unusual Calix[4]arene Derivative Containing Phosphorus with Coordination Numbers 4, 5 and 6

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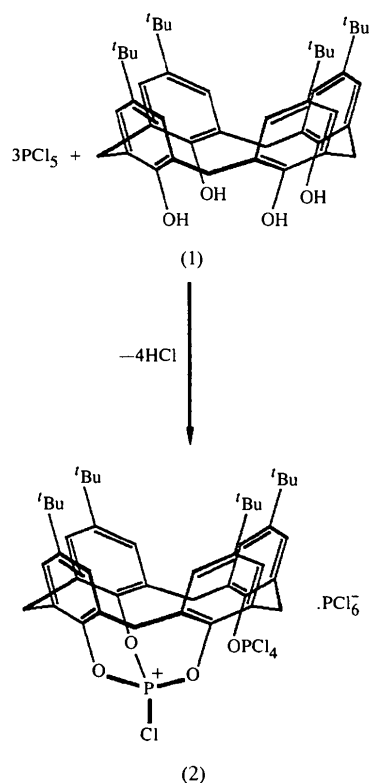
(Received 11 March 1997; accepted 25 March 1997)

Abstract

The title compound, chloro[5,11,17,23-tetra-*tert*-butyl]-28-(tetrachlorophosphoranyloxy)calix[4]arene-25,26,27-trioxy]phosphonium hexachlorophosphate dichloromethane solvate, C₄₄H₅₂Cl₅O₄P₂⁺.PCl₆⁻.CH₂Cl₂, contains pentavalent phosphorus with three different coordination numbers, 4, 5 and 6. The calixarene adopts a non-standard conformation between the partial cone and 1,2-alternate conformations.

Comment

The introduction of phosphorus-containing substituents into calix[4]arene systems *via* oxygen linkages has been achieved during the past few years in a number of ways, some of which we have described (Neda *et al.*, 1995; Gloede, Keitel, Costisella, Kunath & Schneider, 1996, and references therein). The reaction of *p*-*tert*-butylcalix[4]arene, (1), with phosphorus pentachloride was reported (Gloede, Costisella, Ramm & Bienert, 1993; Gloede & Keitel, 1995) to proceed as shown in the scheme, forming an unusual phosphorus-containing derivative, (2), that involves P atoms with coordination numbers 4, 5 and 6; the conformation of the calix[4]arene was, however, not established. (In the scheme the common cone conformation is presented for clarity.)



The proposed structure of (2) was originally based on the ³¹P NMR spectrum in solution, with three δ values of equal intensity at 8.1, –66.0 and –296 p.p.m. These values agree well with the presence of P with coordination numbers 4, 5 and 6 (Gloede *et al.*, 1993; Mark, Dungan, Crutchfield & van Wazer, 1967; Brazier, Lamandé & Wolf, 1991).

Compound (2) was originally reported as being highly deliquescent. This was not confirmed during the studies reported here. After crystallization from CH₂Cl₂/hexane under absolutely anaerobic conditions, (2) proved to be remarkably stable towards atmospheric moisture. We report here the crystal structure of its dichloro-

methane solvate, confirming the constitution of (2) and determining its conformation.

The results (Fig. 1) are in complete agreement with the structural conclusions derived from the ^{31}P NMR study of (2); one P atom with coordination number 4 (P1) is present as a (positively charged) trioxychlorophosphonium centre and another pentacoordinate P atom (P2) as part of an oxytetrachlorophosphorane group. Both these P atoms are bonded to the calix[4]arene framework *via* oxygen. The third P atom (P3) is part of the counterion, PCl_6^- , which is readily recognized by its $\delta(^{31}\text{P})$ value at exceptionally high field.

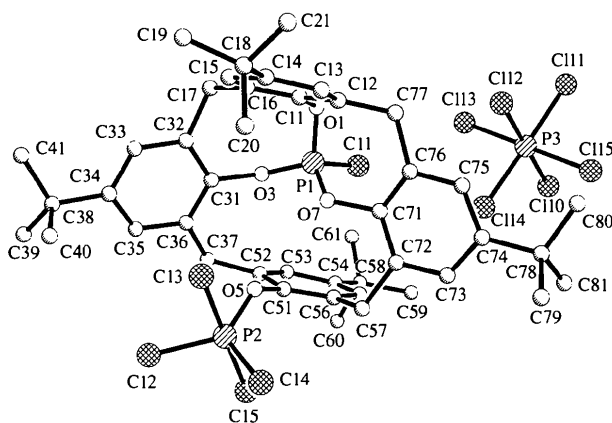


Fig. 1. The molecule of compound (2) in the crystal. Radii are arbitrary. H atoms and the solvent molecule have been omitted for clarity. Only one position of the disordered butyl group, C39–C41, is shown.

The positively charged P1 atom displays a somewhat distorted tetrahedral coordination geometry, with the largest deviations from ideal angles for O1–P1–C11 [$104.79(11)^\circ$] and O7–P1–C11 [$112.85(11)^\circ$]. The P1–O bonds [1.528(3)–1.544(3) Å] are, as expected, shorter than P2–O [1.591(3) Å]. The coordination geometry at P2 is nearly ideal trigonal bipyramidal. C13 and C15 are axial [C13–P2–C15 $178.59(8)^\circ$], whereas C12, C14 and O5 occupy the equatorial positions. As expected, the axial P–Cl bonds, P2–C13 2.116(2) and P2–C15 2.130(2) Å, are longer than the equatorial bonds, P2–C14 2.011(2) and P2–C12 2.024(2) Å. As far as we are aware, this is the first structure determination of a compound containing an $-\text{OPCl}_4$ moiety; a search of the Cambridge Database (Allen & Kennard, 1993) found no other examples. The coordination geometry of the PCl_6^- anion is octahedral, with insignificant deviations from ideal angles.

The calix[4]arene framework does not in fact adopt the cone conformation implied by the scheme. The dihedral angles from the plane of the methylene bridge C atoms (main plane) [deviations 0.300, -0.299 , 0.295 and $-0.297(2)$ Å to C17, C37, C57 and C77, respectively] to the aromatic rings are $64.4(1)$ (plane 1, C11–

C16), $48.6(1)$ (plane 2, C31–C36), $74.0(1)$ (plane 3, C51–C56) and $5.3(1)^\circ$ (plane 4, C71–C76). Thus, plane 4 is nearly coplanar with the main plane, whereas plane 3 and planes 1 and 2 lie on alternate sides of it; the conformation of compound (2) thus lies between the partial cone and the 1,2-alternate conformation (for a summary of common calixarene conformations, see Gutsche, 1992; Böhmer, 1995).

Experimental

The compound was prepared as described by Gloede *et al.* (1993) and Gloede & Keitel (1995) and recrystallized from dichloromethane/hexane.

Crystal data

$\text{C}_{44}\text{H}_{52}\text{Cl}_5\text{O}_4\text{P}_3 \cdot \text{PCl}_6^- \cdot$
 CH_2Cl_2

$M_r = 1212.64$

Triclinic

$P\bar{1}$

$a = 10.5549(10)$ Å

$b = 14.3979(14)$ Å

$c = 18.1350(2)$ Å

$\alpha = 96.474(8)^\circ$

$\beta = 90.053(6)^\circ$

$\gamma = 96.379(8)^\circ$

$V = 2721.1(5)$ Å³

$Z = 2$

$D_x = 1.480$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 63

reflections

$\theta = 3.5$ – 12.5°

$\mu = 0.788$ mm⁻¹

$T = 173(2)$ K

Prism

$0.50 \times 0.35 \times 0.20$ mm

Colourless

Data collection

Siemens P4 diffractometer

ω scans

Absorption correction: none

12 178 measured reflections

9533 independent reflections

6662 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.017$

$\theta_{max} = 25^\circ$

$h = -12 \rightarrow 12$

$k = -17 \rightarrow 3$

$l = -21 \rightarrow 21$

3 standard reflections

every 247 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.182$

$S = 1.049$

9512 reflections

624 parameters

Methyl H atoms rigid, other

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.1087P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.499$ e Å⁻³

$\Delta\rho_{min} = -0.977$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

P1–O3	1.528(3)	P3–Cl13	2.122(2)
P1–O7	1.534(3)	P3–Cl10	2.136(2)
P1–O1	1.544(3)	P3–Cl15	2.139(2)
P1–C11	1.9285(14)	P3–Cl14	2.140(2)
P2–O5	1.591(3)	P3–Cl12	2.146(2)
P2–C14	2.011(2)	O1–C11	1.442(5)
P2–C12	2.024(2)	O3–C31	1.435(4)

P2—C13	2.116 (2)	O5—C51	1.417 (4)
P2—C15	2.130 (2)	O7—C71	1.471 (4)
P3—C111	2.101 (2)		
O3—P1—O7	111.15 (14)	C113—P3—C110	90.64 (8)
O3—P1—O1	111.05 (15)	C111—P3—C115	89.14 (8)
O7—P1—O1	110.10 (14)	C113—P3—C115	179.26 (8)
O3—P1—C11	106.70 (11)	C110—P3—C115	89.22 (7)
O7—P1—C11	112.85 (11)	C111—P3—C114	91.48 (9)
O1—P1—C11	104.79 (11)	C113—P3—C114	90.25 (7)
O5—P2—C14	121.66 (12)	C110—P3—C114	176.06 (10)
O5—P2—C12	124.12 (12)	C115—P3—C114	89.83 (6)
C14—P2—C12	114.08 (7)	C111—P3—C112	178.84 (9)
O5—P2—C13	85.61 (11)	C113—P3—C112	89.12 (7)
C14—P2—C13	91.01 (7)	C110—P3—C112	88.57 (9)
C12—P2—C13	90.07 (7)	C115—P3—C112	90.14 (7)
O5—P2—C15	93.48 (10)	C114—P3—C112	87.60 (7)
C14—P2—C15	90.39 (7)	C11—O1—P1	114.4 (2)
C12—P2—C15	89.55 (7)	C31—O3—P1	137.3 (2)
C13—P2—C15	178.59 (8)	C51—O5—P2	131.0 (2)
C111—P3—C113	91.60 (8)	C71—O7—P1	126.3 (2)
C111—P3—C110	92.34 (11)		

One butyl group, C39—C41, is disordered over two positions. The maximum difference peak of 1.5 e Å⁻³ lies near C114 (in the PCl₆ anion) and may indicate a minor disorder component (or atomic displacements not well approximated by ellipsoids).

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994). Software used to prepare material for publication: SHELXL93.

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Absolute Configuration of an Intermediate in the Asymmetric Synthesis of Natural β -Hydroxy and β -Amino Acids

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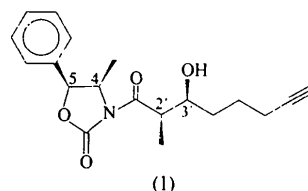
(Received 9 September 1996; accepted 18 April 1997)

Abstract

The single-crystal X-ray structure determination of enantiomerically pure (4*R*,5*S*)-3-[(2*R*,3*S*)-3-hydroxy-2-methyl-7-octynoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one, C₁₉H₂₃NO₄, at 223 K is reported. The absolute configuration of this molecule has been determined.

Comment

(4*R*,5*S*)-3-[(2*R*,3*S*)-3-Hydroxy-2-methyl-7-octynoyl]-4-methyl-5-phenyl-1,3-oxazolidin-2-one, (1), was prepared as an important intermediate in the asymmetric synthesis of the β -amino acid and β -hydroxy acid derivatives of onchidins (Rodríguez *et al.*, 1994; Fernández *et al.*, 1996), dimeric depsipeptides from the mollusc *Onchidium sp.* Compound (1) has been synthesized from enantiomerically pure commercially available (1*S*,2*R*)-norephedrine (Fernández *et al.*, 1996), thus fixing the absolute configurations of C atoms 4 and 5 in the title compound. This allows determination of the absolute configuration at C atoms 2' and 3', which is important in the context of the synthetic strategy to control the stereochemistry of the final β -hydroxy and β -amino acids.



A view of (1) showing the displacement ellipsoids, atomic numbering and the correct absolute configuration is given in Fig. 1. The absolute configuration of the molecule was also determined by refinement of the structure according to the method of Flack (1983).