Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diphenyl (3,3-diphenoxycyclohexyl)phosphonate

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Received 11 December 2002
Accepted 23 December 2002
Online 10 January 2003

Key indicators

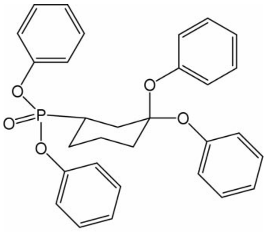
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.010 Å
R factor = 0.069
wR factor = 0.165
Data-to-parameter ratio = 9.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The solid-state structure of the title compound, $C_{30}H_{29}O_5P$, has been determined at 100 K. The generalized puckering coordinates, Q_2 (0.587), φ_2 (286.82°) and θ_2 (178.9°), confirm that the cyclohexane ring is in the chair conformation $^2C_5$. The phosphine ligand is equatorial to the ring, with the P atom in a slightly distorted tetrahedral configuration.

Comment

Over the last few decades, P—C bond-forming reactions have received considerable attention, since the resulting compounds have applications in organic and medicinal chemistry (Jung & McClure, 1991; Mori *et al.*, 1995; Errington *et al.*, 1997). Much of the recent work is complementary to the existing Arbusov and Pudovik processes (Bhattacharya & Thyagarajan, 1981, Pudovik & Konovalova, 1979). However, a limitation of all of this chemistry is the fact that triarylphosphites are generally unreactive. For example, it is well known that trialkylphosphites such as $P(OEt)_3$ are converted into γ-keto phosphonates upon treatment with Michael acceptors, while analogous reactions employing triarylphosphites are rare (Harvey, 1966). In order to probe this reaction further, we have studied the reaction of cyclohexenone with triphenylphosphite.



(I)

Heating a solution of cyclohexenone in phenol with triphenylphosphite afforded a dark solid. Distillation (0.05 mm Hg) of this residue, followed by purification (column chromatography), afforded a colorless solid. Instead of generating the addition product, the title compound, (I), was isolated. While a number of complexes containing this *gem*-aryloxide group have been reported, few contain a cyclohexane ring (Peters *et al.*, 1998 Gawronski *et al.*, 1989; Harada *et al.*, 1994, 1997).

This work presents a noteworthy side reaction available to triarylphosphites, although the precise mechanism is not clear.

The central six-membered ring in (I) is in the chair conformation. Four ring C atoms C1, C3, C4, and C6 are coplanar within 0.01 Å, while C2 is situated 0.69 (1) Å above

DOI: 10.1107/S160053680202370X

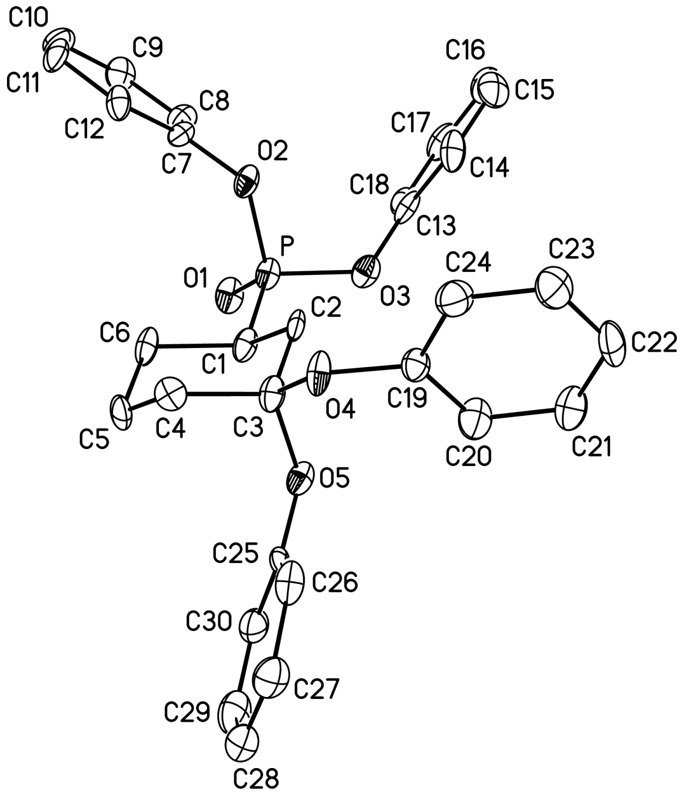


Figure 1

The molecular structure of (I). The displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted.

and C5 −0.68 (1) Å below the plane. The C2 and C5 dihedral flap angles are 51.8 (4) and 51.2 (4)° relative to the four-carbon plane, respectively. This yields an almost undistorted ${}^2C_5$ conformation for the central six-membered ring, which is confirmed by the generalized puckering coordinates, Q_2 (0.587), φ_2 (286.82°) and θ_2 (178.9°) (Nardelli, 1995; Giacovazzo *et al.*, 1998).

A Cambridge Structural Database (Allen, 2002) search found three relevant molecules with the phosphine–cyclohexane skeleton and similar substitution pattern to that of (I). These molecules, 1-hydroxycyclohexanephosphonic acid, (II) (Ohms *et al.* 1996), 8-cyclohexyl-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine-8-oxide, (III) (Naidu *et al.*, 1992), and (−)-diethyl-3-hydroxy-3-(2-trityl-1,2,4-triazol-3-yl)cyclohexylphosphonate, (IV) (Mori *et al.*, 1995), contain equatorial phosphine ligands and low-energy chair conformation cyclohexane rings.

The phosphine ligand is bound to atom C1, the only chiral C atom in the molecule. The absolute configuration about the chiral atom could not be unequivocally established. Bond distances for the phosphine ligand are listed below and are in good agreement with the corresponding averages of (II)–(IV) given in brackets: 1.467 (5) Å for P═O1 [average 1.47 (2) Å], 1.595 (4) Å for P—O [average 1.58 (3) Å], and 1.797 (6) Å for P—C1 [average 1.80 (2)]. The P atom is in a slightly distorted tetrahedral configuration, with angles about it ranging between 101.0 (2) and 116.0 (2)°.

Experimental

Phenol (50.0 ml, dried) was heated to 323 K in a clean dry flask under nitrogen. While stirring, triphenylphosphite (8.7 mmol; Aldrich) and cyclohexenone (10.3 mmol; Aldrich) were added and the temperature was increased to 373 K for 36 h. The product was distilled under vacuum (0.05 mm Hg) and purified by column chromatography (silica gel; hexane/EtOAc 7:3). After collecting fractions, the product crystallized from the solution. The crystals were collected on a filter, washed with hexanes and dried (0.020 g).

Crystal data

$C_{30}H_{29}O_5P$
$M_r = 500.50$
Monoclinic, $P2_1$
$a = 13.612$ (3) Å
$b = 5.8536$ (11) Å
$c = 16.900$ (3) Å
$\beta = 112.63$ (1)°
$V = 1242.9$ (4) Å^3
$Z = 2$

$D_x = 1.337$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 528 reflections
$\theta = 2.4$–24.5°
$\mu = 0.15$ mm^{-1}
$T = 100$ (2) K
Needle, colorless
0.52 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD-1000 area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000–2001)
$T_{\min} = 0.926$, $T_{\max} = 0.985$
5397 measured reflections

3050 independent reflections
2482 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 24.5°$
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 6$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.165$
$S = 1.02$
3050 reflections
325 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0897P)^2 + 0.2739P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Data collection: *SMART* (Bruker, 2000–2001); cell refinement: *SAINT* (Bruker, 2000–2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000–2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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