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(*R*)-(6,6′-Dihydroxybiphenyl-2,2′-diyl)bis(diphenylphosphine oxide) methanol solvate

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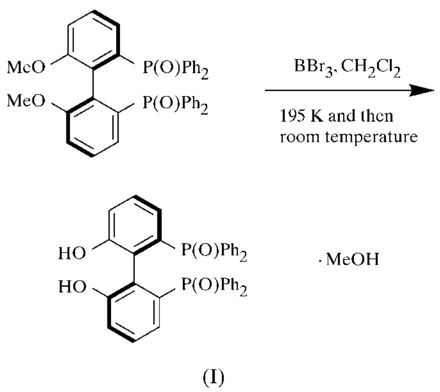
The title compound, $C_{36}H_{28}O_4P_2{\cdot}CH_4O$, was synthesized directly from the methoxy analogue. The crystal structure shows that one OH group interacts with an O atom of a phosphine oxide group in an adjacent molecule, while the other OH group complexes with the methanol solvent molecule *via* intermolecular hydrogen bonds. An O atom of one phosphine oxide group interacts with the hydroxy H atom of methanol *via* a hydrogen bond. There are intra- and intermolecular π–π interactions between the phenyl rings. All these interactions result in the formation of supramolecular chiral parallelogram channels *via* self-assembly.

Comment

Chiral bidentate phosphines are among the most important auxiliaries in enantioselective homogeneous catalysis. The atropisomeric diphosphine ligands, such as Noyori's BINAP (Noyori, 1989; Noyori & Takaya, 1990) and Schmid's BIPHEP classes (Schmid *et al.*, 1988, 1991, 1996) have been widely applied in asymmetric catalysis, especially in hydrogenation, and excellent results have been achieved.

The theories of supramolecular chemistry and crystal engineering inspire the design of microporous layers employing self-assembly of molecular subunits (tectons), driven by non-covalent interactions, as the synthetic tool (Moulton & Zaworotko, 2001). In this paper, the synthesis of the title compound, (I), a derivative of (*R*)-(6,6′-methoxybiphenyl-2,2′-diyl)bis(diphenylphosphine oxide), MeO-BIPHEPO, is described. The compound can be used as a building block for the synthesis of new diphosphine ligands.

In the crystal of (I), there are three kinds of hydrogen bonds (Fig. 1): (i) the O1—H1 group of one molecule of (I) interacts with atom O4 of a phosphine oxide group in an adjacent molecule, with an O1···O4*A* distance of 2.648 (2) Å; (ii) the O2—H2*B* group in (I) complexes with methanol atom O5*B*, with an O2···O5*B* distance of 2.669 Å; (iii) atom O3 of the phosphine oxide group interacts with the methanol H5—O5 group, with an O3···O5 distance of 2.656 Å.



(I)

In addition to these hydrogen bonds, there are intra- and intermolecular π–π interactions between the phenyl rings of (I). The distance between the centroid (*CgA*) of ring C1–C6 and that (*CgB*) of ring C25–C30 is 3.568 Å, and the angle between the two ring planes of this intramolecular π–π stacking interaction is 13.7°. Phenyl rings C7–C12 (centroid *CgC*) and C31–C36 (centroid *CgD*) are also involved in a weak intramolecular π–π stacking interaction, with a *CgC*···*CgD* distance of 4.91 Å and an angle between the two planes of 180°. There are also π–π-stacking interactions

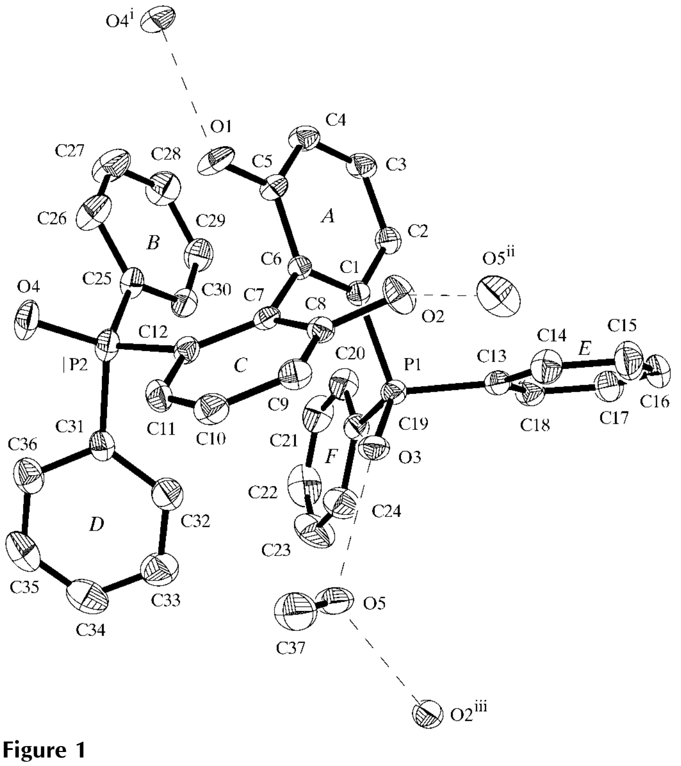


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids shown at the 30% probability level. H atoms are not shown. The symmetry codes are as given in Table 1, plus (iii) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$.

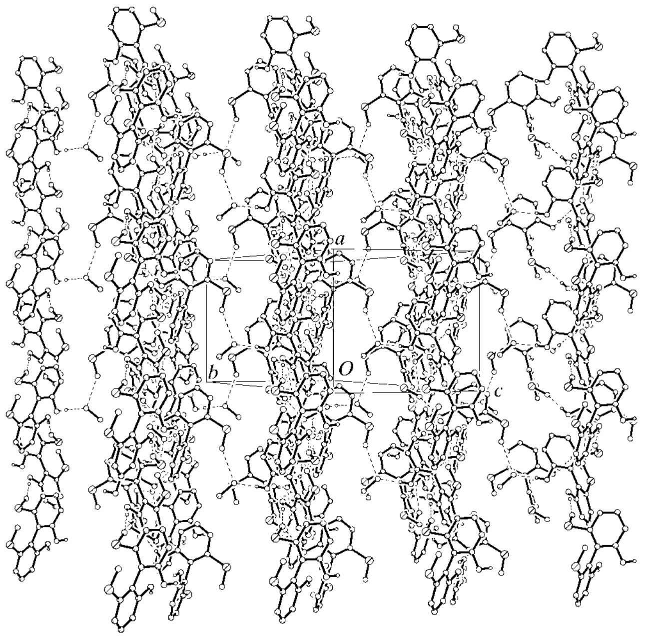


Figure 2
The packing of molecules in the crystal of (I) along the [110] direction. For clarity, phenyl rings connected to P atoms and H atoms not involved in hydrogen bonding have been omitted.

between the phenyl rings of the Ph_2PO groups and the equivalent phenyl rings in an adjacent molecule. The shortest of these interactions has a distance between the two symmetry-related phenyl rings of 4.34 Å and an angle of 162° (Table 1 and Fig. 1).

Through these rich hydrogen-bonding interactions, every molecule of (I) is linked to four adjacent molecules. Furthermore, a three-dimensional supramolecular chiral parallelogram channel (cavity dimensions *ca* 9.2 × 6.7 $Å^2$) along the crystallographic *a* axis, having the formula $C_{36}H_{28}O_4P_2\cdot CH_3OH$, is constructed *via* self-assembly (Figs. 2 and 3). These channels are divided into small compartments by the phenyl groups linked to the P atoms. This result suggests a novel approach to the design of chiral microporous structures containing P atoms.

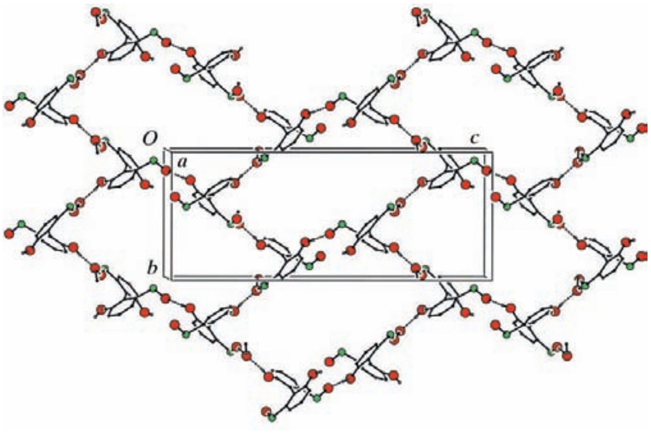


Figure 3
The packing of molecules in the crystal of (I), viewed along the *a* direction. For clarity, phenyl rings connected to P atoms and H atoms not involved in hydrogen bonding have been omitted.

Experimental

For the preparation of (I), a solution of (*R*)-(6,6′-methoxybiphenyl-2,2′-diyl)bis(diphenylphosphine oxide) (1 g, 1.6 mmol) in CH_2Cl_2 (20 ml) was cooled to 195 K. To this solution, BBr_3 (1.6 g, 6.4 mmol) was added *via* a syringe over a period of 30 min. The mixture was stirred at 195 K for 1 h, and then warmed slowly to room temperature and allowed to react overnight. After cooling the mixture to 273 K, water was added slowly and the aqueous layer removed *via* a cannula. The organic layer was mixed with methanol and dichloromethane (1:1). The resulting solution was dried over Na_2SO_4 and evaporated to dryness, giving the raw product, which was purified by silica-gel column chromatography using $CHCl_3$ and CH_3OH (100:7). Spectroscopic analysis, ^1H NMR (DMSO, 500 MHz, δ, p.p.m.): 6.5–6.6 (*dd*, 2H, J = 13.3 and 8.3 Hz,), 6.6–6.8 (*d*, 2H, J = 8 Hz), 7.0–7.1 (*m*, 2H), 7.3–7.7 (*m*, 20H); ^{31}P NMR (DMSO, δ, p.p.m.): 29.2; high-resolution MS: 586.1439; calculated for $C_{36}H_{28}P_2O_4$: 586.1463.

Crystal data

$C_{36}H_{28}O_4P_2\cdot CH_4O$
$M_r = 618.57$
Orthorhombic, $P2_12_12_1$
$a = 9.9351$ (16) Å
$b = 11.1490$ (17) Å
$c = 27.977$ (4) Å
$V = 3098.9$ (8) $Å^3$
$Z = 4$
$D_x = 1.326$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5948 reflections
$\theta = 1.0$–27.5°
$\mu = 0.18$ mm^{-1}
$T = 294$ (2) K
Plate, colourless
0.26 × 0.24 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SAINT*; Siemens, 1995)
$T_{min} = 0.954$, $T_{max} = 0.982$
21 252 measured reflections
7141 independent reflections
3814 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 10$
$l = -35 \rightarrow 36$

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.075$
$S = 0.83$
7141 reflections
400 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e $Å^{-3}$
$\Delta\rho_{min} = -0.24$ e $Å^{-3}$
Absolute structure: Flack (1983)
Flack parameter = −0.06 (8)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.82	1.83	2.648 (2)	177
O2—H2B···O5^{ii}	0.82	1.85	2.669 (3)	172
O5—H5···O3	0.82	1.84	2.656 (3)	177

Symmetry codes: (i) $x - \frac{1}{2}, \frac{5}{2} - y, 2 - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

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The absolute stereochemistry of the title compound was known from the synthetic route and is confirmed by the value [−0.06 (8)] of the Flack (1983) parameter. H atoms were placed in geometrically calculated positions and included in the final refinement in a riding-model approximation, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.98 Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SHELXTL-NT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1193). Services for accessing these data are described at the back of the journal.

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