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(*S*)-(−)-5,5′-Bis(diphenylphosphino)-2,2,2′,2′-tetramethyl-4,4′-bi-1,3-benzodioxole

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.081
Data-to-parameter ratio = 8.5

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

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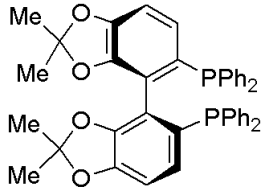
The title molecule, $C_{42}H_{36}O_4P_2$, is a new atropoisomeric bis-phosphine ligand. All bond lengths and angles are normal. In the crystal structure, the molecule possesses a crystallographically imposed C_2 axis. The two benzene rings in the biphenyl moiety make a dihedral angle of 84.23 (6)°.

Comment

Since 1968, when a chiral phosphine was first utilized in asymmetric hydrogenation (Knowles & Sabacky, 1968 Horner *et al.*, 1968), much effort has been devoted to the design and synthesis of chiral phosphine ligands. The atropoisomeric C_2-symmetric bis-phosphine ligands play an important role in asymmetric hydrogenation (Zhang *et al.*, 2000; Saito *et al.*, 2001). We report here the crystal structure of the title compound, (I), a new atropoisomeric C_2-symmetric bis-phosphine ligand.



(I)

In the crystal structure, molecules of (I) possesses a crystallographically imposed C_2 axis (Fig. 1). All bond lengths and angles are normal. The two benzene rings in the biphenyl moiety make a dihedral angle of 84.23 (6)°. All rings are planar.

Experimental

Under argon, a 100 ml three-necked flask was charged with (*S*)-(−)-5,5′-bis(diphenylphosphinoyl)-2,2,2′,2′-tetramethyl-4,4′-bi-1,3-benzodioxole (0.0698 g, 1 mmol), toluene (11 ml), *N,N*-dimethylaniline (1.4 ml, 10 mmol) and trichlorosilane (1.01 ml, 10 mmol). The mixture was refluxed for 10 h. After the mixture had cooled to 273 K, a degassed 50% NaOH solution (50 ml) was added carefully. The product was extracted with toluene (30 ml) twice, The extract was washed successively with 10% HCl, water and brine, then dried with anhydrous Na_2SO_4 and concentrated to give the crude product. Recrystallization from MeOH afforded a white solid. ^{1}H NMR (chloroform-*d*): δ 1.12 (6H, *s*), 1.58 (6H, *s*), 6.56 (2H, *d*, *J* = 7.8 Hz), 6.67 (2H, *d*, *J* = 7.8 Hz), 7.11–7.25 (20H, *m*). ^{13}C NMR (chloroform-*d*): 25.27, 25.93, 108.46, 118.27, 122.77–147.86. ^{31}C NMR (chloroform-*d*): -14.44. MS (ESI): 667 HRMS (ESI). Calculated for $C_{42}H_{36}NaO_4P_2$ $[M + Na]^+$: 689.1891; found: 689.1966.

Crystal data

$C_{42}H_{36}O_4P_2$
M_r = 666.65
Orthorhombic, $P2_12_12$
a = 9.7007 (9) Å
b = 20.774 (2) Å
c = 8.9149 (9) Å
V = 1796.6 (3) Å^3
Z = 2
D_x = 1.232 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2896 reflections
θ = 4.6–22.3°
μ = 0.16 mm^{-1}
T = 298 (2) K
Block, colorless
0.50 × 0.41 × 0.35 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.924, T_{max} = 0.946
9313 measured reflections
1877 independent reflections
1677 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25.2°
$h = -11 \rightarrow 10$
$k = -22 \rightarrow 24$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.081
S = 0.99
1877 reflections
220 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0085 (14)
Absolute structure: Flack (1983), 1357 Friedel pairs
Flack parameter = 0.00 (9)

H atoms were placed in calculates positions (C—H = 0.93–0.96 Å) and refiend as riding, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL*97.

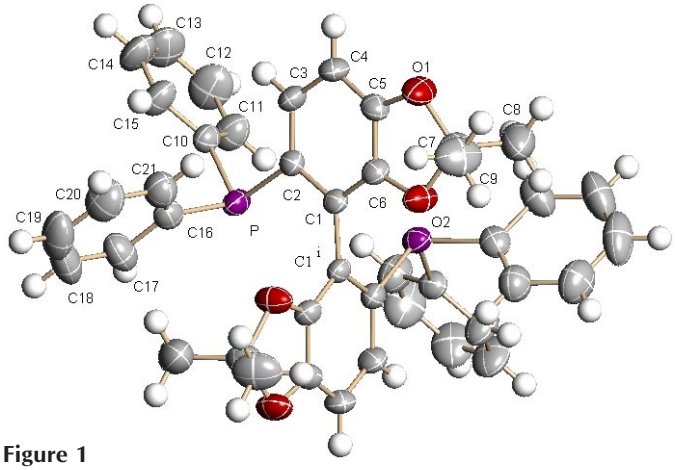


Figure 1
The formula unit of (I), with the atom numbering, showing displacement ellipsoids at the 50% probability level [symmetry code: (i) $-x, 1-y, z$].

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