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(2*R*,3*R*)-2,3-Dibenzyloxy-1,4-bis(diphenylphosphino)butane

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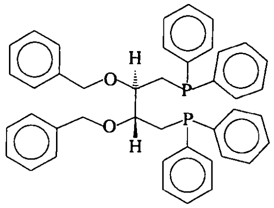
Abstract

The crystal structure of the title compound, $C_{42}H_{40}O_2P_2$, an open-chain diphosphine, is reported. The absolute structure determined by the Flack method [Flack (1983). *Acta Cryst.* **A39**, 876–881] confirms that the stereochemistry at the chiral centers is (2*R*,3*R*). The dihedral angles between the two rings bonded to each phosphine group are 70.94 (10) and 70.20 (10)°, and the angle between the rings of the benzyloxy groups is 59.31 (13)°.

Comment

Catalytic enantioselective synthesis is an area of great interest, where much study has been devoted to the development of new and efficient catalysts (Ojima, 1993; Blystone, 1989; Noyori, 1989; Ojima *et al.*, 1989). The synthesis of chiral diphosphines is an important area of study, due to their vast application as bidentate ligands in homogeneous enantioselective catalysis. Ligands such as DIOP [(2*R*,3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] (Kagan & Dang, 1972), along with others containing a backbone with two chiral C atoms, have demonstrated very efficient chiral induction in catalytic processes by creating a chiral environment around the metal center which allows for the discrimination of the enantiotopic faces of prochiral substrates during the catalytic cycle. Our interest in the development of new enantioselective catalysts led us to synthesize diphosphino DIOP-bz [(2*R*,3*R*)-2,3-dibenzyloxy-1,4-bis(diphenylphosphino)butane], (I), a chiral open-chain analog of DIOP.



(I)

The Rh^I complexes of DIOP-bz will be used to study the enantioselective reduction of prochiral functionalized olefins by hydrogenation with molecular hydrogen as well as transfer hydrogenation. A detailed structural knowledge of these types of ligands is required in order to rationalize the efficiency of their transition metal complexes in inducing chirality on the reaction products.

The average P—C_{aryl} and P—C_{alkyl} distances of 1.834 (2) and 1.846 (2) Å, respectively, are not significantly different from values observed in DIOP and other related ligands (Ball *et al.*, 1981; Ball & Trotter, 1981). The mean C_{sp3}—C_{sp3} and C—O bond lengths are 1.524 (3) and 1.425 (5) Å, respectively; the internal angles of the molecule are unexceptional.

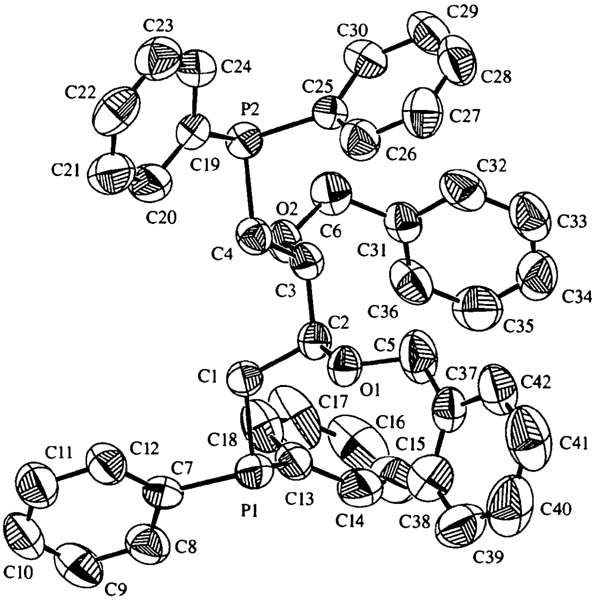


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The phenyl rings show no significant distortion from planarity, with a mean C—C bond length of 1.375 (2) Å and C—C—C angle of 119.9 (2)°. The dihedral angles between the two rings bonded to each phosphine group are 70.94 (10) (P1) and 70.20 (10)° (P2), and the angle between the rings of the benzyloxy groups is 59.31 (13)°. The absolute structure was determined by the Flack method (Flack, 1983) and the chirality of the molecule expected from the synthesis route was confirmed. The stereochemistry at both chiral centers, C2 and C3, is *R*. This enantiomer has a negative specific rotation in CH_2Cl_2 solution ($[\alpha]_D^{20}$ = −15°). There are no close intermolecular contacts and the molecular packing appears to be stabilized only by van der Waals interactions. There is a short intramolecular contact between atoms C1 and O2 [C1—O2 2.956 (3) Å and C1—H1···O2 105°].

Experimental

A solution of (2*S*,3*S*)-2,3-benzyloxy-1,4-ditosyloxybutane (Nemoto *et al.*, 1991; Cunningham & Kündig, 1988) (1.64 mmol) in dry THF (10 ml) was added dropwise to 3.6 mmol of potassium diphenylphosphide in THF (0.5 *M*), under N_2 at 273 K, stirring continuously. The resulting solution was slowly brought to room temperature and stirred for an additional 2 h, the reaction being monitored with thin-layer chromatography until complete. After filtering with celite and concentrating the filtrate, a white solid was obtained which was recrystallized from 2-propanol–dichloromethane to give the pure diphosphine. M.p. 388 (2) K, $[\alpha]_D^{20}$ = −15° (c = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ (p.p.m.): 2.32 (*m*, 2H), 2.54 (*m*, 2H), 3.65 (*m*, 2H), 4.24 (*d*, 2H, J = 11.4 Hz, *AB* system), 4.36 (*d*, 2H, J = 11.4 Hz, *AB* system), 7.10–7.42 (*m*, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (p.p.m.): 29.2 (*d*, J_{CP} = 13.8 Hz, P—CH_2), 72.3 (Ph—CH_2), 76.6 (*m*, CH—CH_2), 127.5–128.7 [*m*, P—Ph($C_{m,p}$), OCH_2Ph($C_{o,m,p}$)], 133.3 [*d*, J_{CP} = 16.7 Hz, P—Ph(C_o)], 132.5 [*d*, J_{CP} = 18.6 Hz, P—Ph(C_o)], 138.0 [OCH_2Ph(C_i)], 138.3 [*d*, J_{CP} = 13.1 Hz, P—Ph(C_i)], 139.1 [*d*, J_{CP} = 12.9 Hz, P—Ph(C_i)]. ^{31}P NMR (121.6 MHz, $CDCl_3$) δ (p.p.m.): −23. IR (KBr), ν_{max} (cm^{-1}): 3066, 3053, 3027, 2884, 1480, 1455, 1431, 1360, 1204, 1105, 1086, 1076, 1067, 1026. MS: *m/z* 639 (M^+, 1%), 561 (14), 453 (15), 347 (47), 239 (26), 185 (56), 121 (21), 108 (41), 91 (100). Analysis calculated for $C_{42}H_{40}O_2P_2$: C 78.98, H 6.31%; found: C 78.86, H 6.03%.

Crystal data

$C_{42}H_{40}O_2P_2$
M_r = 638.68
Orthorhombic
$P2_12_12_1$
a = 9.545 (2) Å
b = 16.271 (4) Å
c = 22.797 (3) Å
V = 3540.5 (12) Å^3
Z = 4
D_x = 1.198 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.11–16.18°
μ = 0.157 mm^{-1}
T = 293 (2) K
Truncated pyramid
0.56 × 0.44 × 0.22 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
9702 measured reflections
6312 independent reflections
3793 reflections with $I > 2\sigma(I)$

R_{int} = 0.024
θ_{max} = 27.41°
h = −12 → 12
k = −15 → 21
l = −27 → 27
3 standard reflections
frequency: 360 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 1.016
6312 reflections
415 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.6727P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.144 e Å^{-3}
$\Delta\rho_{min}$ = −0.168 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.16 (9)

Table 1. *Selected geometric parameters (Å, °)*

P1—C7	1.830 (3)	O1—C2	1.423 (3)
P1—C13	1.835 (3)	O2—C3	1.428 (3)
P1—C1	1.847 (3)	O2—C6	1.436 (3)
P2—C25	1.831 (3)	C1—C2	1.522 (3)
P2—C19	1.839 (3)	C2—C3	1.531 (4)
P2—C4	1.844 (3)	C3—C4	1.521 (4)
O1—C5	1.413 (3)		
O1—C2—C3—O2	172.96 (19)		

The title structure was solved by direct methods using *SHELXS*97 (Sheldrick, 1990). The H atoms of the organic moiety were placed at calculated positions and refined as riding using the *SHELXL*97 defaults. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1325). Services for accessing these data are described at the back of the journal.

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2,7-Dichlorothianthrene

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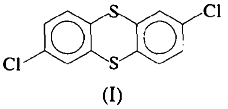
Abstract

The crystal structure of the title compound, $C_{12}H_6Cl_2S_2$, has been determined. The dihedral angle for 2,7-dichlorothianthrene is 132.55 (4)°. This value is similar to that found in other 2,7-substituted thianthrenes and also the parent thianthrene.

Comment

This structural investigation was performed as a result of our interest in the effect that substitutions in or on the aromatic rings of thianthrene have on the dihedral angle of the two planes in the title compound, (I), which are defined by one aromatic ring and the two S atoms (Larson *et al.*, 1984).



(I)

On comparison of the dihedral angles of 2,7-dichlorothianthrene, 2,7-dimethylthianthrene (Weakley, 1982), perfluorothianthrene (Rainville *et al.*, 1980) and thianthrene itself (Larson *et al.*, 1984), it is evident that the differences are small. The observed dihedral angle is 132.55 (4)° for 2,7-dichlorothianthrene, 131.1 (1)° for 2,7-dimethylthianthrene, 132.0 (1)° for perfluorothianthrene and 127.14 (3)° for thianthrene. These differences could be the result of the 2,7-disubstitution, the inductive effects of halogens or packing considerations. Despite the small magnitude of these differences, some trends can be observed when comparing these compounds. The S···S distance increases to 3.226 (1) Å in 2,7-dichlorothianthrene compared with 3.193 (1) Å in thianthrene. The C—S—C angles in the central ring increase from 101.31 (8) and 101.05 (8)° in 2,7-disubstitution to 100.4 (1) and 99.8 (1)° in thianthrene. These effects seem to be geometrically related to the flattening (increasing dihedral angle) of the thianthrene molecule when 2,7-disubstituted.

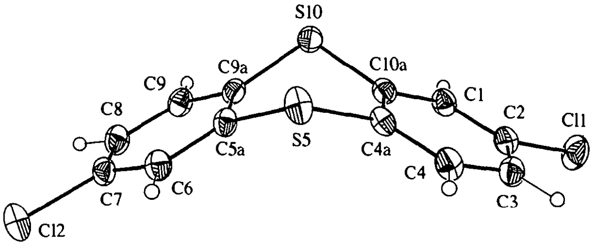


Fig. 1. View of the title compound showing the atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. H atoms are drawn to an arbitrary scale.

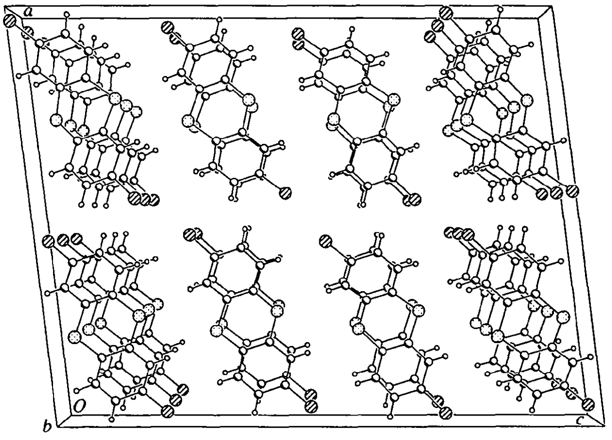


Fig. 2. Packing diagram of the title compound.

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† Deceased, 29 July 1996.