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(±)-8-Phenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxaphosphepine

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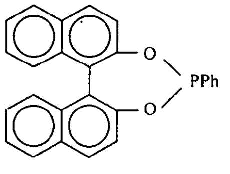
Abstract

Optically active and racemic dioxaphosphepine derivatives containing a binaphthyl moiety, for example, the title compound, $C_{26}H_{17}O_2P$, are prepared from 1,1′-bi-2-naphthol and dichlorophenylphosphine. The racemic compound has a twisted seven-membered ring with a rigid (*S*)(*M*)/(*R*)(*P*)-helical conformation.

Comment

For efficient asymmetric catalysis development of new effective chiral ligands is essential (Nugent, RajanBabu & Burk, 1993). Although various kinds of chiral-P ligands have been prepared, chiral phosphonites are rare (Richter, 1983; Kagan, 1985). Such an electron-deficient P ligand could be expected to be effective for use in asymmetric catalysis, such as hydrocyanation (Baker & Pringle, 1991) or hydroformylation (Kwok & Wink, 1993). As a chiral phosphonite derivative, (*S*)-(+)-8-phenyldinaphtho-[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine, (*S*)-(I), was prepared as a powdery colourless solid from the reaction of (*S*)-(+)-dilithio-1,1′-bi-2-naphtholate and dichlorophenylphosphine [80%, $[\alpha]^{23}_D + 215°$ (*c* 0.481, thf)]. Unlike the structurally related compound (*P*)-7-phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole, which has a five-membered phosphole ring and easily racemizes at room temperature (Tani, Yamagata & Tashiro, 1994), the title chiral dioxaphosphepine, (I), is optically stable even at 473 K. Thus the crystal structure of the dioxaphosphepine (I) is of interest.



(I)

Although the optically active dioxaphosphepine (*S*)-(+)-(I) did not give single crystals suitable for X-ray analysis, crystals of racemic (±)-(I), m.p. 520–522 K, were obtained from acetone or toluene. The (±)-dioxaphosphepine was obtained starting from (±)-1,1′-bis-2-naphthol. Single crystals of (±)-(I) were sealed in thin-walled glass capillary tubes under Ar. The molecular structure and the frame of the seven-membered ring of the dioxaphosphepine moiety are shown in Figs. 1 and 2, respectively.

The seven-membered ring was found to have a twist-helical structure with an (*S*)(*M*)/(*R*)(*P*)-helical conformation. Similar twisted seven-membered rings are found in cationic Rh-binap [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] complexes (Tani *et al.*, 1985; Miyashita *et al.*, 1980). The phenyl ring [C(21)–C(26)] is nearly perpendicular [90.4 (3)°] to the least-squares plane of the seven-membered ring [P, O(1), C(1), C(10), C(11), C(20), O(2)]. The P atom has a slightly distorted *sp*^{3} configuration. The angle O(2)—P—C(21) [104.8 (3)°] is greater than O(1)—P—C(21) [95.1 (3)°]. Very close non-bonding distances between the phenyl [C(21)–C(26)] and naphthyl [C(11)–C(20)] rings are present: C(20)···C(21) 3.22 (1) and C(20)···C(26) 3.36 (1) Å.

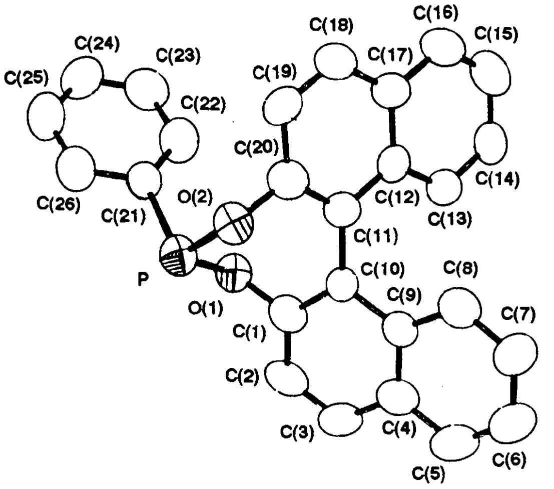


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the molecular structure of the title compound.

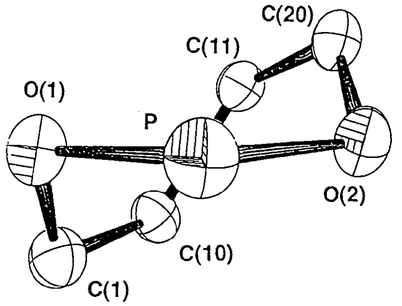


Fig. 2. Framework of dioxaphosphepine moiety, viewed along the plane formed by atoms P, O(1) and O(2).

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Significant repulsion should be present between these rings. Both naphthyl groups are essentially planar and the dihedral angles between the fused benzene rings are 5.8 (4) and 3.7 (3)°, respectively. The dihedral angle between the least-squares planes of the naphthalene rings is 58.2 (1)°. The value is smaller than the corresponding values found for [Rh{(*R*)-(+)-binap}$_2$]ClO$_4$ [72.9 (3) and 71.0 (9)° (Tani *et al.*, 1985)] and (±)-1,1′-bi-2-naphthol [89.39 (7)° (Gridunova *et al.*, 1982; positional parameters taken from the Cambridge Structural Database)]. Incorporation of sp^3 O atoms between 2,2′-C atoms of the 1,1′-binaphthyl moiety and the P atom in the phosphole, (*P*)-7-phenyldinaptho[2,1-*b*:1′,2′-*d*]-phosphole, releases the strain in the five-membered ring and the naphthalene rings, producing the rigid conformation, with high thermal stability, of the dioxaphosphepine.

Experimental

Crystal data

$C_{26}H_{17}O_2P$
$M_r = 392.39$
Monoclinic
$C2/c$
$a = 36.804\ (5)$ Å
$b = 8.6204\ (7)$ Å
$c = 12.914\ (1)$ Å
$\beta = 108.304\ (5)°$
$V = 3889.7\ (7)$ Å^3
$Z = 8$
$D_x = 1.340$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.54178$ Å
Cell parameters from 50 reflections
$\theta = 20.22–26.30°$
$\mu = 1.390$ mm^{-1}
$T = 293\ (1)$ K
Prism
0.50 × 0.20 × 0.17 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω scans < 70° (2θ) < θ–2θ scans
Absorption correction: empirical
$T_{\min} = 0.829$, $T_{\max} = 1.000$
3281 measured reflections
2900 independent reflections
1525 observed reflections
[$F_o > 4\sigma(F_o)$]

$R_{\rm int} = 0.035$
$\theta_{\max} = 60.0°$
$h = -41 \rightarrow 41$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 200 reflections
intensity variation: none

Refinement

Refinement on *F*
$R = 0.074$
$wR = 0.055$
$S = 1.975$
1525 reflections
262 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.04255 (6)	0.1229 (3)	0.2005 (2)	0.060 (1)
O(1)	0.0741 (1)	0.1139 (6)	0.3262 (3)	0.054 (3)
O(2)	0.0717 (1)	0.1839 (5)	0.1332 (3)	0.053 (3)
C(1)	0.0953 (2)	0.2503 (10)	0.3639 (6)	0.058 (5)
C(2)	0.0859 (2)	0.3375 (10)	0.4421 (6)	0.062 (5)
C(3)	0.1070 (2)	0.4660 (10)	0.4850 (6)	0.068 (5)
C(4)	0.1372 (2)	0.5118 (10)	0.4457 (6)	0.061 (5)
C(5)	0.1573 (3)	0.6526 (10)	0.4814 (7)	0.076 (6)
C(6)	0.1846 (2)	0.7022 (10)	0.4384 (8)	0.081 (6)
C(7)	0.1931 (2)	0.6166 (10)	0.3570 (7)	0.075 (6)
C(8)	0.1748 (2)	0.4793 (10)	0.3212 (6)	0.064 (5)
C(9)	0.1466 (2)	0.4220 (9)	0.3655 (6)	0.050 (4)
C(10)	0.1257 (2)	0.2793 (8)	0.3279 (5)	0.045 (4)
C(11)	0.1361 (2)	0.1713 (8)	0.2523 (6)	0.049 (4)
C(12)	0.1735 (2)	0.1060 (9)	0.2737 (6)	0.048 (4)
C(13)	0.2028 (2)	0.1332 (9)	0.3735 (6)	0.056 (4)
C(14)	0.2388 (2)	0.0674 (10)	0.3933 (7)	0.067 (5)
C(15)	0.2465 (2)	−0.0263 (11)	0.3137 (8)	0.078 (6)
C(16)	0.2188 (2)	−0.0555 (9)	0.2184 (7)	0.070 (5)
C(17)	0.1813 (2)	0.0052 (10)	0.1967 (6)	0.057 (5)
C(18)	0.1519 (2)	−0.0324 (9)	0.0998 (6)	0.064 (5)
C(19)	0.1157 (2)	0.0249 (9)	0.0812 (6)	0.057 (5)
C(20)	0.1089 (2)	0.1244 (9)	0.1586 (6)	0.053 (4)
C(21)	0.0394 (2)	−0.0875 (8)	0.1796 (6)	0.050 (4)
C(22)	0.0036 (2)	−0.1389 (10)	0.1143 (6)	0.064 (5)
C(23)	−0.0025 (2)	−0.2964 (11)	0.0973 (7)	0.074 (6)
C(24)	0.0258 (2)	−0.4014 (10)	0.1418 (7)	0.076 (6)
C(25)	0.0613 (2)	−0.3498 (11)	0.2044 (7)	0.074 (6)
C(26)	0.0685 (2)	−0.1930 (11)	0.2260 (7)	0.068 (5)

Table 2. *Selected geometric parameters* (Å, °)

P—O(1)	1.675 (6)	C(10)—C(11)	1.48 (1)
P—C(21)	1.833 (8)	C(11)—C(20)	1.37 (1)
O(2)—C(20)	1.402 (9)	P—O(2)	1.664 (5)
C(1)—C(10)	1.36 (1)	O(1)—C(1)	1.41 (1)
O(1)—P—O(2)	99.0 (3)	P—O(1)—C(1)	115.8 (5)
O(2)—P—C(21)	104.8 (3)	P—C(21)—C(22)	114.0 (4)
P—O(2)—C(20)	120.3 (4)	O(1)—C(1)—C(2)	117.7 (5)
P—C(21)—C(26)	125.5 (4)	O(2)—C(20)—C(11)	119.3 (4)
O(1)—C(1)—C(10)	117.3 (7)	C(2)—C(1)—C(10)	124.7 (6)
O(2)—C(20)—C(19)	116.0 (8)	C(1)—C(10)—C(11)	121.2 (6)
C(1)—C(10)—C(9)	116.4 (8)	C(10)—C(11)—C(12)	123.4 (7)
C(9)—C(10)—C(11)	122.4 (7)	C(12)—C(11)—C(20)	116.5 (8)
C(10)—C(11)—C(20)	120.1 (5)	C(11)—C(20)—C(19)	124.7 (6)
O(1)—P—C(21)	95.1 (3)		

Table 3. *Dihedral angles* (°) *between least-squares planes*

Plane 1: P, O(1), O(2), C(1), C(10), C(11), C(20). Plane 2: C(1)–C(4), C(9), C(10). Plane 3: C(4)–C(9). Plane 4: C(11), C(12), C(17)–C(20). Plane 5: C(12)–C(17). Plane 6: C(21)–C(26). Napl 1: C(1)–C(10). Napl 2: C(11)–C(20).

Napl 1–Plane 2	58.2 (1)	Plane 1–Plane 6	90.4 (3)
Plane 1–Plane 1	46.9 (2)	Plane 1–Napl 2	45.3 (2)
Plane 2–Plane 3	5.8 (3)	Plane 4–Plane 5	3.7 (3)
Plane 2–Plane 4	53.6 (3)	Plane 3–Plane 5	62.3 (3)

The positional parameters for the non-H atoms were determined by direct methods (Sheldrick, 1985). The refinement of the non-H atoms was carried out anisotropically by full-matrix least-squares techniques (Imoto, 1990). All H atoms were located in a difference Fourier map. These atoms were included as fixed contributions in idealized positions with C—H = 0.95 Å (sp^2-hybridized geometry) and $B_{\rm iso} = 5.93$ Å^2.

The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included in the calculation for the P atom (Cromer, 1974). Molecular graphics were produced using *ORTEP*II (Johnson, 1976). All calculations were carried out on an NEC ACOS 930S computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, Japan.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: OH1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(2,6-dimethoxyphenyl)phosphine Sulfide Monohydrate

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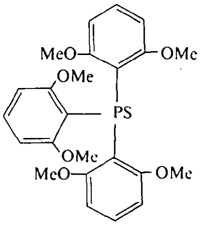
Abstract

The title compound $C_{24}H_{27}O_6PS.H_2O$, or $\Phi_3PS.H_2O$ [$\Phi = 2,6\text{-}(CH_3O)_2C_6H_3$], has an average P—C bond length of 1.840 Å, a P═S length of 1.971 (2) Å and an average C—P—C angle of 107.1°, which are considerably longer and wider than those of triphenylphosphine sulfide, with values of 1.817, 1.950 Å and 105.7°, respectively. Intramolecular distances between the six methoxy O atoms and the P atom are all shorter than the sum of van der Waals radii of O and P atoms, implying the presence of direct electron donation from the methoxy O atoms to the P atom.

Comment

Φ_3PS [$\Phi = 2,6\text{-}(CH_3O)_2C_6H_3$] has been reported to have very high nucleophilicity (Wada, Kanzaki, Fujiwara, Kajihara & Erabi, 1991) and to form unusual 1:1 complexes with dimethyltin dihalides (Wada *et al.*, 1993). While the structure of tris(2,6-dimethoxyphenyl)phosphine (Φ_3P) has been determined (Livant, Sun & Webb, 1991), that of Φ_3PS was unknown; we report here the crystal structure of this compound in order to clarify the origin of these unusual properties.



Φ_3PS

The water molecule of crystallization was detected by IR bands at 3400 and 1630 cm^{-1}, and the amount was estimated from weight reduction at 373 K. The calculated density (D_x) was also consistent with the

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