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(*N*,*N*-Diethylamino)(2-hydroxyphenyl)phenylphosphine oxide

Henriëtte de Bod, D. Bradley G. Williams,* Andreas Roodt* and Alfred Muller

Department of Chemistry and Biochemistry, Rand Afrikaans University, PO Box 524, Auckland Park, Johannesburg 2006, South Africa

Correspondence e-mail: aroo@rau.ac.za

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.057
wR factor = 0.145
Data-to-parameter ratio = 19.4

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

The title compound, $C_{16}H_{20}NO_2P$ [O═P(C_6H_5)(C_6H_4OH)(Et_2N) or P(Ph)(PhOH)(Et_2N)], crystallizes as a 21:79 racemic mixture of the *R* and *S* isomers in the asymmetric unit and is stabilized by strong intramolecular hydrogen bonds with H···O = 1.97 (4) and 1.84 (5) Å. The Tolman cone angle is calculated to be 199°.

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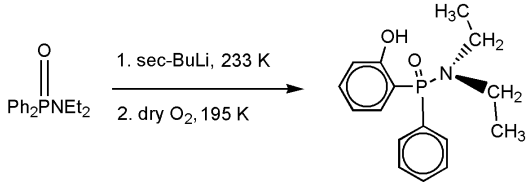
Comment

The synthesis and use of phosphine ligands in homogeneous catalysed reactions is a field of research that is gaining more interest (van Leeuwen *et al.*, 2000). There is currently a special focus (Tang & Zhang, 2003) on the synthesis of unsymmetrical ligands, for various reasons, including asymmetric catalytic transformations (Jeulin *et al.*, 2004). The stereoelectronic nature of the ligand plays a significant role in the outcome of the reaction (Tang & Zhang, 2003) and, as a result, we have investigated a potentially new route to *ortho*-substituted arylphosphine ligands. The subject of the present paper is a product of our research effort, which investigates the use of directed *ortho*-metallation chemistry as a route to new ligands.



(I)

The title compound, (I), crystallizes as a 21:79 racemic mixture of the *R* and *S* isomers in the asymmetric unit of the monoclinic space group $P2_1/c$, with the molecule disordered on a general position (Fig. 1). Symmetry generates a 50:50 *R*:*S* mixture in the unit cell. This is, to our knowledge, the second example of this type of phenol–phosphine oxide where intramolecular hydrogen bonding occurs (Cambridge Structural Database, Version 5.25 of 2004; Allen, 2002), the other example being that of *anti*-(2-hydroxy-3-phenyl)(phenyl){2-([(*o*-phenylene)amino)methyl]pyrrolidinyl}phosphine oxide (Legrand *et al.*, 1999). The hydrogen bonding leads to the formation of channels along the *a* axis (Fig. 2). Important bond distances and angles are also comparable to other amidophosphine oxides (Table 3).

The most widely used method for determining ligand steric behavior at a metal center is by calculating the Tolman cone angle (Tolman, 1977), using an *M*—P bond distance of 2.28 Å, C—H bond distances of 0.97 Å and 1.2 Å as the van der Waals radius of hydrogen. For the title compound, a dummy atom

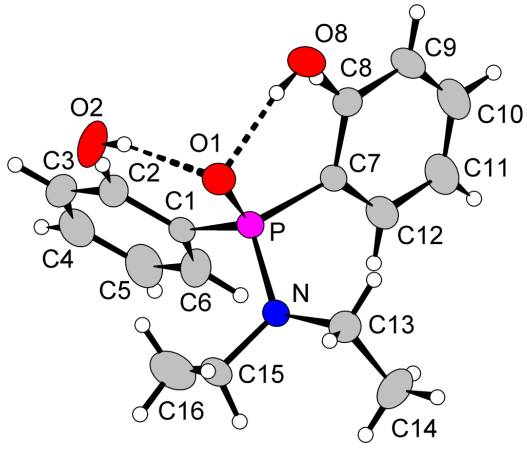


Figure 1
View of (I), with 30% probability displacement ellipsoids. Both components of the OH/H disorder are shown.

was created along the P═O bond at a distance of 2.28 Å from the P atom and was used for the determination of the Tolman cone angle. The value of 199° obtained for the Tolman cone angle is probably not a reliable indication of the steric effect of the phosphine due to the intramolecular hydrogen bond between the hydroxyl H and O1 (see Table 2). A calculation was also performed on the same molecule refined without hydroxyls and a value of 184° was obtained, which may be a better indication of the true steric properties of the title compound. The Tolman cone angle is also compared to those in other similar phosphine oxides in Table 3, showing a slightly larger cone angle for the title compound than in other similar compounds.

It is also of interest to note that the C14—C13···C15—C16 pseudo-torsion angle of the ethyl substituents on the N atom, which have a distorted *anti* conformation, is 128.5 (6)°. This effect is also observed in similar compounds containing the *N*,*N*-diethylamide moiety (Table 3).

Experimental

The substrate *N*,*N*-diethyldiphenylphosphinic amide (0.37 mmol) was dissolved in THF (4 ml) and cooled to 213 K. *sec*-BuLi (0.37 ml, 0.37 mmol, 1 *M* solution) was added and the reaction mixture was allowed to stir at 233 K for 3 h. The solution was cooled to 195 K and the solution was exposed to dry O_2 for 2 h. The reaction mixture was allowed to warm to room temperature over a period of 2 h, then was extracted with EtOAc and brine. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The products were isolated by flash chromatography using 5% Et_3N in acetone as eluant [yield: 71% (white crystals); m.p. 383–384 K]. TLC: R_F 0.74 (EtOAc); IRν_{max} ($CHCl_3$)/cm^{-1}: 2981, 1604, 1129; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.63 (*s*, 1H, OH), 7.87 (app. *dq*, 2H, aromatic, J = 7.8, and 1.2 Hz), 7.50–7.30 (*m*, 5H, aromatic), 6.90–6.80 (*m*, 2H, aromatic), 3.08 (*dq*, 4H, CH_2CH_3, J = 11.4 and 7.1 Hz), 1.11 (*t*, 6H, CH_2CH_3, J = 7.1 Hz); ^{13}C NMR (75 MHz, CDCl3): δ 163.6 (*d*, 1C, J = 5.2 Hz), 134.2 (*d*, 1C, J = 2.0 Hz), 132.1 (*d*, 2C, J = 9.2 Hz), 132.0 (*d*, 1C, J = 2.7 Hz), 131.6 (*d*, 1C, J = 7.2 Hz), 131.1 (*d*, 1C, J = 131.0 Hz), 128.6 (*d*, 2C, J = 12.7 Hz), 118.9 (*d*, 1C, J = 11.6 Hz), 118.2 (*d*, 1C, J = 9.3 Hz), 111.5 (*d*, 1C, J = 128.5 Hz), 39.4 (*d*, 2C, J = 3.8 Hz), 14.1 (*d*, 2C, J = 4.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ 39.8 (*s*, 1P); EIMS: *m*/*z* 289 ([*M*]$^+$), 217 ([*M* − NEt_2]$^+$), 199 ([*M* − NEt_2–OH]$^+$); FAB–HRMS, calculated for $C_{16}H_{20}NO_2P$: 289.12317; found: 289.12314.

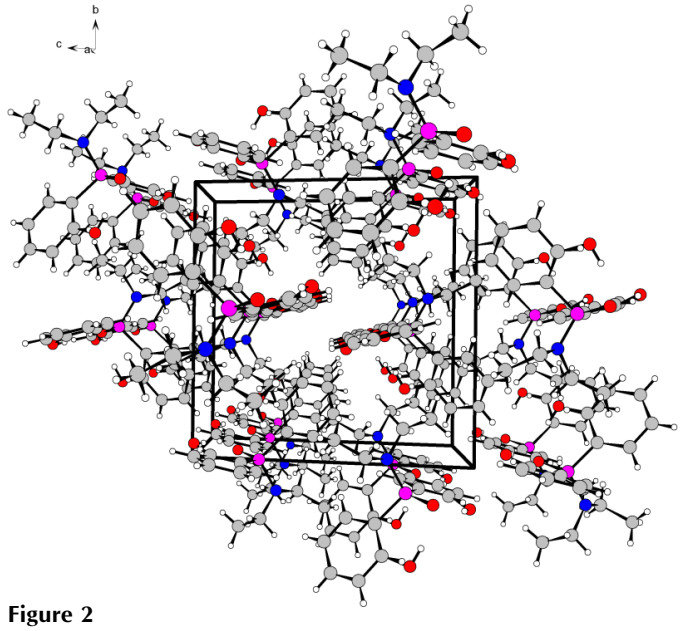


Figure 2
Packing diagram showing channels along the *a*axis.

Crystal data

$C_{16}H_{20}NO_2P$	D_x = 1.232 Mg m^{-3}
M_r = 289.3	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 789 reflections
a = 8.4348 (15) Å	θ = 2.9–22.9°
b = 13.635 (2) Å	μ = 0.18 mm^{-1}
c = 13.842 (2) Å	T = 294 (2) K
β = 101.606 (3)°	Plate, colorless
V = 1559.4 (5) Å^3	0.44 × 0.15 × 0.08 mm
Z = 4	

Data collection

Bruker SMART 1K CCD diffractometer	2053 reflections with $I > 2\sigma(I)$
	R_{int} = 0.060
ω scans	θ_{max} = 28.3°
Absorption correction: none	$h = -9 \rightarrow 11$
10440 measured reflections	$k = -18 \rightarrow 16$
3854 independent reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.1233P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.057	
$wR(F^2)$ = 0.145	
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
3854 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
199 parameters	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

P—O1	1.4896 (17)	P—C7	1.800 (2)
P—N	1.646 (2)	P—C1	1.801 (2)
O1—P—N	118.53 (10)	O1—P—C1	110.00 (10)
O1—P—C7	109.16 (11)		
C14—C13···C15—C16	128.2 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O1	0.84 (2)	1.97 (4)	2.735 (9)	152 (7)
O8—H8B···O1	0.85 (5)	1.84 (5)	2.637 (3)	157 (5)
C2—H2A···O1	0.93	2.58	2.989 (3)	107
C8—H8A···O1	0.93	2.61	3.006 (3)	106

Table 3
Comparative geometrical data (Å, °) for O═P(Ph)(X){N(Y)(Z) compounds.

(X)(Y)(Z)	O═P	N—P	O═P—N	C—N—C	Θ_T	Ref.
(C_6H_4OH)(Et)(Et)	1.491 (4)	1.646 (4)	118.6 (2)	114.4 (4)	199	*a*
(Ph)(Me)(Me)	1.481	1.681	117.5	115.1		*b*
(Ph)(C_2H_4)	1.479	1.672	117.6	59.8	177	*c*
(Ph)(Me)(C_6H_4Et)	1.489 (1)	1.646 (2)	117.9 (1)	114.0 (1)	179	*d*
(C_6H_4OMe)(Et)(Et)	1.473	1.654	118.3	114.3	177	*e*

Notes: (*a*) This work; (*b*) Ul-Haque & Caughlan (1976) (methyl H atoms not included in structure from CSD); (*c*) Davidowitz *et al.* (1985); (*d*) Cameron & Duncanson (1981); (*e*) Utenova *et al.* (1998). CSD data extracted from Cambridge Structural Database for *b*, *c*, *d* and *e*; no s.u. values available. Θ_T = Tolman cone angle.

The aromatic, methylene and methyl H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic and methylene H and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl H. The disordered hydroxyls and aromatic H atom site occupancies were refined to 0.787:0.213 (6). The hydroxyl H atoms were located in a Fourier difference map and were refined with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SIR*2002 (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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