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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.063
wR factor = 0.163
Data-to-parameter ratio = 16.9

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

Racemic benzylphenylphosphine oxide

All interatomic distances in the title compound, $\text{C}_{13}\text{H}_{13}\text{OP}$, can be considered normal. The crystal was twinned with a 71:29 participation of the two polar components. The phosphorus tetrahedron exhibits its usual deformation. The mid-part containing $\text{C}_{(\text{phenyl})}-\text{P}-\text{C}_{(\text{phenyl})}$ is almost planar. The $\text{P}=\text{O}$ bond makes angles of $22.2(3)$ and $18.2(2)^\circ$ with the phenyl rings; the phenyl rings are inclined to each other at $4.9(2)^\circ$. Two weak $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds are found in the structure. In this way, a two-dimensional hydrogen-bond net parallel to the bc plane is created. The possibility of π -electron stacking was rejected because the neighbouring benzene rings in the crystal lattice are inclined to each other at $52.4(2)$ and $61.2(2)^\circ$. The geometrical parameters are compared to those reported in the literature for the solid-state structures of phosphine-substituted benzylphenylphosphine oxides.

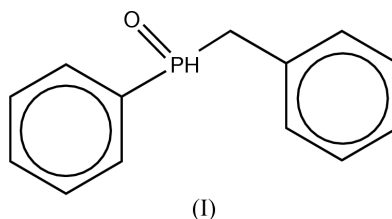
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Comment

Secondary phosphine oxides are important synthetic intermediates in organophosphorus chemistry and their high reactivity is typically connected with the presence of a relatively acidic H atom in their structure (Engel, 1988). They exist in two tautomeric forms: $\text{R}_2\text{P}(=\text{O})\text{H}$ and R_2POH , the former being predominant in the equilibrium (Bailey & Fox, 1963, 1964). There are, however, cases, as in transition-metal complexes, where the latter form is seen exclusively (Parkins, 1996; Han *et al.*, 1996). It was, therefore, deemed interesting to study the crystal structure of some model secondary phosphine oxides in order to reveal their tautomeric preferences in the solid state, and to study the character of the expected hydrogen bonding implied by their acidic functionality. The selected models include one alkylarylphosphine oxide, benzylphenylphosphine oxide, the title compound, (I), and one diarylphosphine oxide, (2-methoxyphenyl)phenylphosphine oxide (Wieczorek *et al.*, 2002).



There are 11 different phosphine-substituted benzylphenylphosphine oxide structures described in the literature, but the three-dimensional coordinates have been determined for only 10 of them: 1-[benzyl(phenyl)phosphinoyl]-1-

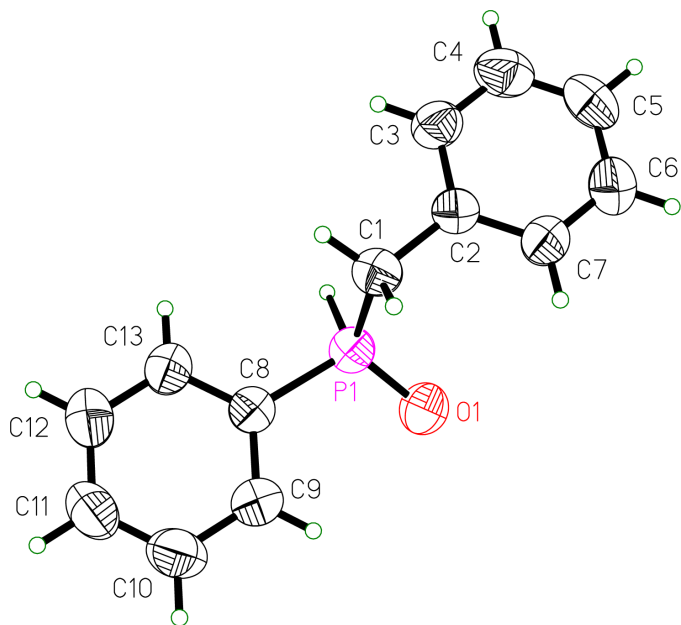


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

phenylethanol [Główka & Gałdecki, 1981*b*; (II) hereafter], *rac*-3-[benzyl(phenyl)phosphinyl]-2-butenoic acid [Główka, 1978; (III) hereafter], (+)-(*S*)-3-benzylphenylphosphinoylbut-2-enoic acid [Główka, 1981; (IV) hereafter], (*R*)-benzylphenyl-2-[2-(*S*)-diphenylphosphinomethylpyrrolidin-1-yl]-phosphine [Faure *et al.*, 1989; (V) hereafter], phenylbenzyl-1-(2,2,3-trimethylcyclopropyl)phosphine oxide [Mazhar-Ul-Haque *et al.*, 1989; (VI) hereafter], methyl 2-methyl-3-[benzyl(phenyl)phosphinyl]butyrate [Gałdecki *et al.*, 1979; (VII) hereafter], methyl-2-(benzylphenylphosphinyl)-1,2,3,4-tetrahydro-1-phenanthrene carboxylate [Główka & Gałdecki, 1981*a*; (VIII) hereafter], 3-aza-2-oxa-3-(benzylphenylphosphinoyl)bicyclo[2.2.1]hept-5-ene and 3-aza-2-oxa-3-(benzylphenylphosphinoyl)bicyclo[2.2.2]oct-5-ene [Ware & King, 1999; (IX) and (X), respectively, hereafter] and (*E*)-benzyl(phenyl)(3-oxo-3-methoxypropenyl)phosphine oxide [Zadło & Bartzak, 1996; (XI) hereafter]

A perspective view of (I), together with the atom-numbering scheme, is shown in Fig. 1. All interatomic distances can be considered normal and the phenyl rings are planar within experimental error. The torsion angles describing the molecular geometry are listed in Table 1. The crystal is twinned with a 71:29 participation of the polar components. The mid-part, namely C8—P1—C1—C2, is almost planar [the maximum deviation of 0.050 (2) Å occurs for atom C1], with a torsion angle of -173.5 (2)°, belonging to the one of two preferred conformations of phosphine-substituted benzylphenylphosphine oxides. This angle lies in the range 173–179° for compounds (III)–(VI) and in the range 56–74° for (VII)–(XI). Only compound (II) exhibits a different angle of 149.4 (8)°. The phosphorus tetrahedron exhibits its

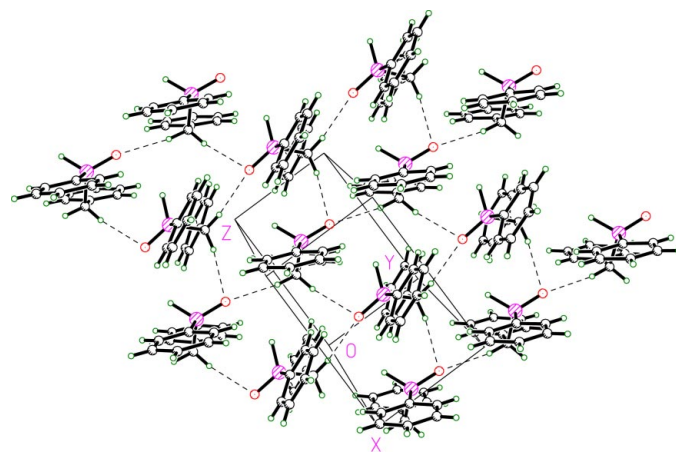


Figure 2
Part of the molecular packing of the title compound, showing the intermolecular hydrogen bonds creating a net structure parallel to the *bc* plane. Hydrogen bonds are indicated by dashed lines.

usual deformation, with C—P—C and C—P—H angles smaller than tetrahedral and O—P—C and O—P—H angles greater than tetrahedral (Table 1). The P=O bond makes angles of 22.2 (3) and 18.2 (2)° with the phenyl rings involving atoms C2 and C8, respectively. Analogous angles are in the range 68–76° for compounds (III) and (V)–(XI), and in the range 46–51° for (II) and (IV) for the former angle; the range of the latter angle is 56–86° for all compounds. The phenyl rings are inclined to each other at 4.9 (2)°, and make angles of 75.88 (13) and 71.14 (14)° (rings indicated by atoms C2 and C8, respectively) with the mid-part containing C8—P1—C1—C2. This is similar only to compound (VI), where the dihedral angle between the phenyl rings is 3.7°. For the rest of the compounds, this value varies significantly, from 46 up to 75°.

Two C—H···O short intermolecular interactions (Table 2) are found in the structure; these can be considered as weak intermolecular hydrogen bonds (Taylor & Kennard, 1982; Desiraju & Steiner, 1999). In this way, a two-dimensional hydrogen-bond net parallel to the *bc* plane is created (Fig. 2). The possibility of π -electron stacking was rejected because the benzene rings are inclined to each other at 52.4 (2) and 61.2 (2)°. There are no unusual intermolecular short contacts, except for the hydrogen bond described in Table 2.

Experimental

The title compound was synthesized from phenylphosphonic dichloride, (–)-menthol and benzylmagnesium chloride. The resulting (–)-menthyl benzylphenylphosphinate was recrystallized from hexane, and then reduced with excess lithium aluminium hydride, and hydrolysed with aqueous ammonium chloride (Emmick & Letsinger, 1968). The resulting benzylphenylphosphine oxide had $[\alpha]_D^{26} = -0.61^\circ$; the remaining physical and spectral properties were in full agreement with the literature data (Maffei & Buono, 1988; Emmick & Letsinger, 1968). Crystals were obtained by crystallization from an equivolume mixture of benzene and *n*-heptane.

Crystal data

C₁₃H₁₃OP
M_r = 216.20
 Monoclinic, *Pc*
a = 12.817 (2) Å
b = 5.713 (1) Å
c = 8.074 (3) Å
 β = 106.15 (3)°
V = 567.9 (2) Å³
Z = 2

D_x = 1.264 Mg m⁻³
 Cu Kα radiation
 Cell parameters from 25 reflections
 θ = 20.4–28.8°
 μ = 1.89 mm⁻¹
T = 293 (1) K
 Prism, colourless
 0.76 × 0.56 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω–2θ scans
 Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
T_{min} = 0.314, *T_{max}* = 0.629
 2329 measured reflections
 2329 independent reflections

2304 reflections with *I* > 2σ(*I*)
 θ_{max} = 74.9°
h = –16 → 16
k = 0 → 7
l = –10 → 10
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.063
wR(*F*²) = 0.163
S = 1.03
 2329 reflections
 138 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.1386*P*)² + 0.0859*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.22 e Å⁻³
 Δρ_{min} = –0.39 e Å⁻³
 Absolute structure: Flack (1983);
 1157 Friedel pairs
 Flack parameter = 0.29 (3)

Table 1

Selected geometric parameters (Å, °).

P1–O1	1.481 (2)	P1–C1	1.798 (3)
P1–C8	1.796 (3)	P1–H1P	1.362
O1–P1–C8	112.62 (15)	C8–P1–H1P	107.0
O1–P1–C1	115.66 (16)	C1–P1–H1P	107.0
C8–P1–C1	107.02 (14)		
O1–P1–H1P	107.0		
C9–C8–P1–O1	17.8 (3)	C8–P1–C1–C2	–173.6 (2)
C13–C8–P1–O1	–159.9 (3)	P1–C1–C2–C3	101.8 (3)
C9–C8–P1–C1	–110.3 (3)	P1–C1–C2–C7	–76.9 (3)
C13–C8–P1–C1	71.9 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C1–H1A...O1 ⁱ	0.97	2.44	3.397 (4)	170
C1–H1B...O1 ⁱⁱ	0.97	2.45	3.405 (5)	170

Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) *x*, 1 – *y*, *z* – ½.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL/PC* (Sheldrick, 1990b) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PLATON* (Spek, 1990).

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