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Key indicators

Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.032
 wR factor = 0.082
Data-to-parameter ratio = 14.6

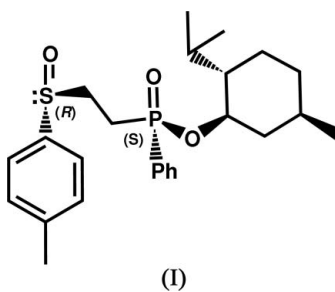
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

(–)-Menthyl (S_P, R_S)-(2-*p*-tolylsulfinylethyl)- phenylphosphinate

The title compound, $\text{C}_{25}\text{H}_{35}\text{O}_3\text{PS}$, is a chiral phosphinate containing five stereogenic centers, one at the P atom, one at the S atom and three in the (–)-menthyl group. The crystal packing reveals that molecules are linked into chains along the a axis by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions.

Comment

The title compound, (I), was easily prepared by the base-promoted coupling of homochiral (*R*)-(*p*-tolyl)vinylsulfoxide (Buese & Hogen-Esch, 1985) with a *P*-epimeric mixture of diastereoisomers of (–)-menthyl phenylphosphinate (Farnham *et al.*, 1970). The resulting diastereomeric mixture was subsequently fractionally crystallized. The best solvent system proved to be diethyl ether/pentane. After recrystallization, the first pure diastereomer, which was not suitable for X-ray determination, was isolated. After recrystallization from diethyl ether of the remaining material (mother liquor), the second diastereomer was isolated as a single stereoisomer. This increased the yield of separation and made both diastereoisomers synthetically available. More importantly, this study enabled the configuration of the P chiral center to be determined as (S_P).



The synthetic utility of (I) was exemplified by the elimination of the sulfoxide substituent, which proceeds readily in refluxing toluene (72% conversion after 5 h). The expected product, (–)-menthyl (*S*)-phenylvinylphosphinate might serve as a *P*-chirogenic olefinic substrate in hydroformylation and related reactions (Eilbracht *et al.*, 1999). The elimination of sulfoxide performed on a pure diastereoisomer resulted in the formation of a single diastereomerically pure product, proving the phosphorus stereogenic center remains unaffected under the applied conditions.

In the crystal structure, molecules are linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions, forming a chain along the a axis. In addition, $\text{C}-\text{H}\cdots\pi$ interactions involving the phenyl ring (centroid C_g) bonded to P are observed (Table 1).

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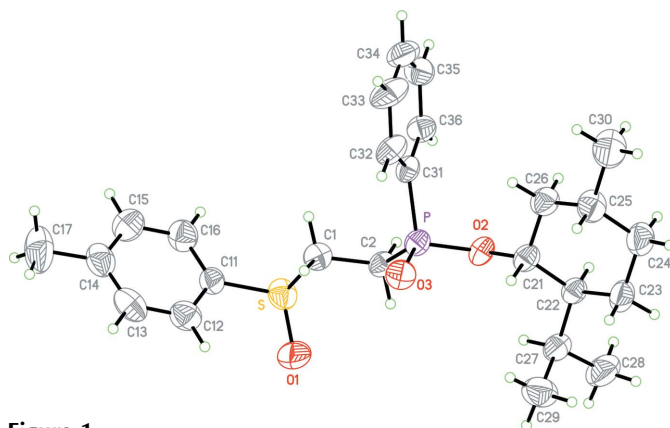


Figure 1
The molecular structure of (I), showing the labelling of all non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

(-)-Menthyl phenylphosphinate (2.80 g, 10 mmol) was dissolved in toluene (100 ml) under an argon atmosphere. DBU (1,8 diazabicyclo[5.4.0]undec-7-ene) (1.52 g, 1 equivalent) and (*R*)-(*p*-tolyl)vinylsulfoxide (1.66 g, 1 equivalent) were added and the reaction mixture was sealed under argon and stirred. After 14 d (when no substrate was visible on TLC), the contents of the flask were washed with 20 ml of 5% HCl, and the organic layer was washed with water, and dried over MgSO_4 . The adduct was purified *via* column chromatography, using trichloromethane and acetone in a 10:1 ratio as eluent, to give 3.22 g (72%) of the product as a mixture of diastereomers (1:1). This material was dissolved in small amount of warm diethyl ether (*ca* 5 ml), a few drops of pentane were added and the solution was left to stand overnight. Cotton-like precipitation was then observed. The precipitate was filtered off and the procedure was repeated to obtain 0.74 g (23%) of a diastereomerically pure compound (m.p. 382.6–383.0 K); $[\alpha]_{\text{D}}^{20} = +71$ (*c* 1.0, CHCl_3).

The remaining material (mother liquor) was evaporated and dissolved in a small amount of warm diethyl ether (*ca* 4 ml) and the solution was left overnight. The crystals that formed were filtered off to obtain 0.68 g (21%) of pure compound (I) (m.p. 385.5–385.8 K); $[\alpha]_{\text{D}}^{20} = +90$ (*c* 1.0, CHCl_3). MS (FAB+ LR): m/z (%) 447.2 ($M + \text{H}^+$), (55); exact mass (FAB+ HR): 447.2147 ($M + \text{H}^+$), (100), (calculated for $\text{C}_{25}\text{H}_{35}\text{O}_3\text{PS}$: 447.2124). Spectroscopic data are available in the deposited CIF.

Crystal data

$\text{C}_{25}\text{H}_{35}\text{O}_3\text{PS}$
 $M_r = 446.56$
Orthorhombic, $P2_12_12_1$
 $a = 5.6199$ (11) Å
 $b = 16.824$ (3) Å
 $c = 26.870$ (5) Å
 $V = 2540.6$ (9) Å³
 $Z = 4$
 $D_x = 1.167$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 10129 reflections
 $\theta = 3.0$ – 29.0°
 $\mu = 0.21$ mm⁻¹
 $T = 291$ (1) K
Block, colourless
 $0.15 \times 0.09 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans
Absorption correction: none
10129 measured reflections
4029 independent reflections

1555 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -6 \rightarrow 6$
 $k = -19 \rightarrow 20$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.082$
 $S = 0.89$
4029 reflections
276 parameters
H-atom parameters constrained
 $w = [\exp[5.20(\sin\theta/\lambda)^2]]/[\sigma^2(F_o^2)]$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.10 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.09 \text{ e } \text{Å}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0020 (4)
Absolute structure: Flack (1983);
1472 Friedel pairs
Flack parameter: 0.00 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C2}-\text{H2A} \cdots \text{O3}^i$	0.97	2.29	3.085 (4)	139
$\text{C29}-\text{H29A} \cdots \text{Cg}^{ii}$	0.96	2.86	3.695 (6)	146

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

H atoms were placed in calculated positions, with $C-H = 0.93$ – 0.98 Å, and were refined as riding, with $U_{\text{iso}} = 1.5U_{\text{eq}}(C)$ for methyl groups and $1.2U_{\text{eq}}(C)$ for others; the methyl groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995), *PLATON* (Spek, 2003).

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