

Table 4. *Selected geometric parameters (Å, °) for (2)*

N(1)—C(2)	1.330 (5)	C(41)—C(42)	1.379 (7)
N(1)—C(9)	1.376 (5)	C(42)—C(43)	1.371 (8)
C(2)—C(3)	1.431 (6)	C(43)—C(44)	1.376 (8)
C(2)—C(20)	1.485 (6)	C(44)—C(45)	1.383 (7)
C(3)—C(4)	1.377 (6)	C(5)—H(5)	1.02 (4)
C(3)—C(30)	1.514 (6)	C(6)—H(6)	1.04 (5)
C(4)—C(10)	1.437 (6)	C(7)—H(7)	0.90 (5)
C(4)—C(40)	1.487 (6)	C(8)—H(8)	1.04 (5)
C(5)—C(6)	1.377 (7)	C(21)—H(21)	0.94 (6)
C(5)—C(10)	1.403 (6)	C(22)—H(22)	1.08 (7)
C(6)—C(7)	1.393 (8)	C(23)—H(23)	1.08 (6)
C(7)—C(8)	1.362 (7)	C(24)—H(24)	0.92 (5)
C(8)—C(9)	1.418 (6)	C(25)—H(25)	1.03 (5)
C(9)—C(10)	1.402 (6)	C(30)—H(30a)	1.00 (6)
C(20)—C(21)	1.378 (7)	C(30)—H(30b)	1.12 (6)
C(20)—C(25)	1.404 (6)	C(30)—H(30c)	0.89 (8)
C(21)—C(22)	1.378 (7)	C(41)—H(41)	1.07 (5)
C(22)—C(23)	1.398 (8)	C(42)—H(42)	0.92 (5)
C(23)—C(24)	1.366 (8)	C(43)—H(43)	0.99 (4)
C(24)—C(25)	1.367 (7)	C(44)—H(44)	1.08 (6)
C(40)—C(41)	1.391 (6)	C(45)—H(45)	0.94 (5)
C(40)—C(45)	1.387 (6)		
C(20)—C(2)—N(1)	114.3 (4)	C(40)—C(4)—C(10)	120.3 (4)
C(20)—C(2)—C(3)	122.2 (4)	C(30)—C(3)—C(2)	120.7 (4)
C(40)—C(4)—C(3)	120.7 (4)	C(30)—C(3)—C(4)	120.6 (4)

Table 5. *Least-squares planes data*

(a) Angles (°) between planes in (1) and (2); (b) distances (Å) of relevant atoms from the mean quinoline planes of (1) and (2).

	(1)	(2)
(a)		
Mean quinoline plane / 2-phenyl plane	21.1 (2)	52.6 (1)
Mean quinoline plane / 4-phenyl plane	64.9 (1)	88.9 (1)
(b)		
C(20) 2-phenyl <i>ipso</i> C atom	0.034 (3)	−0.081 (4)
C(40) 4-phenyl <i>ipso</i> C atom	0.036 (3)	0.127 (4)
C(30) methyl C atom	—	−0.258 (6)

Table 6. 270 MHz ¹H NMR spectra of compounds (1) and (2)

Assignment	(1) δH (p.p.m.)	Multiplicity	(2) δH (p.p.m.)	Multiplicity
H(3)	7.819	<i>ddd</i>	—	—
H(5)	7.905	<i>ddd</i>	7.386	<i>ddd</i>
H(6)	7.469	<i>ddd</i>	7.351	<i>ddd</i>
H(7)	7.728	<i>ddd</i>	7.619	<i>ddd</i>
H(8)	8.249	<i>ddd</i>	8.175	<i>ddd</i>
2-Phenyl				
o-	8.19	<i>m</i>	7.61	<i>m</i>
m-/p-	7.46–7.53	<i>m</i>	7.42–7.52	<i>m</i>
4-Phenyl				
o-	7.55–7.57	<i>m</i>	7.27–7.31	<i>m</i>
m-/p-	7.55–7.57	<i>m</i>	7.45–7.55	<i>m</i>
CH ₃	—	—	2.143	<i>s</i>

Accurate unit-cell dimensions and the crystal-orientation matrices for (1) and (2) were determined by a least-squares refinement of the setting angles of 25 centred reflections using the automatic indexing routine of the diffractometer. The space group for (1) was determined by systematic absences and from Harker planes in the Patterson function. Inversion symmetry was detected statistically from *E* maps. The usual corrections for Lorentz and polarization factors were made. For structure (2), an empirical absorption correction was made after scanning nine reflections, each at 36 different azimuthal angles (ψ scan). In the case of structure (1), the data were collected using the *FLAT* procedure (Enraf–Nonius, 1990) in which each collection was carried out at an azimuthal angle ψ

calculated to minimize absorption by minimizing the path of the X-rays through the crystal. No further absorption corrections were applied. Both structures were determined by direct methods using *SHELXS86* (Sheldrick, 1985); subsequent full-matrix least-squares refinement and difference Fourier synthesis using *MolEN* (Fair, 1990) located all remaining atoms, including H atoms. All non-H atoms were refined anisotropically, while the H atoms were refined with isotropic displacement parameters. Killean & Lawrence (1969) weights were used in the refinement. All computations were performed on a MicroVAX computer. Diagrams were drawn using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[3,3-Dimethyl-1-(2-pyridylthio)butyl]-methyl(2,4,6-trimethylphenyl)phosphine Oxide

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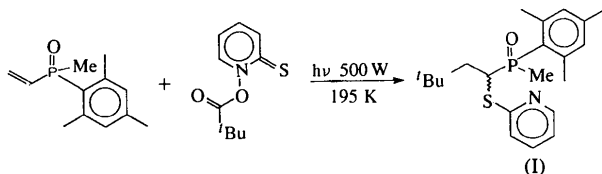
Abstract

In the molecule of [3,3-dimethyl-1-(2-pyridylthio)-butyl]methyl(2,4,6-trimethylphenyl)phosphine oxide, C₂₁H₃₀NOPS, the P=O bond is nearly coplanar with

the mesityl ring and nearly parallel to the pyridyl ring. In the chain connecting the mesityl and pyridyl rings two extended fragments are found, twisted at the C11—S bond; likewise, two extended fragments exist in the chain connecting the methyl atom C10 and the terminal atom C15 of the butyl moiety, twisted at the C11—C12 bond. The structure is stabilized by C11—H111...N intramolecular and C20(py)—H201...O intermolecular hydrogen bonds.

Comment

The availability of enantiomerically pure vinylphosphine oxides is one of the reasons for their broad applications (Pietrusiewicz, Zabłocka & Monkiewicz, 1984; Johnson & Imamoto, 1987; Pietrusiewicz, Zabłocka & Wiśniewski, 1990). Recently, vinylphosphine oxides have been shown to be excellent dipolarophiles in the 1,3-dipolar cycloaddition of nitrones (Brandi, Cicchi, Goti, Pietrusiewicz & Wiśniewski, 1990). Chiral vinylphosphine oxides were able to induce diastereofacial selection in cycloaddition to a cyclic nitrone, with a selectivity as high as 9:1 in the case of mesitylmethylvinylphosphine oxide (Brandi, Cicchi, Goti, Pietrusiewicz, Zabłocka & Wiśniewski, 1991; Brandi, Cicchi, Goti & Pietrusiewicz, 1991). The stereochemistry of this addition was suggested by Brandi, Cicchi, Goti & Pietrusiewicz (1991). The present paper corroborates the suggested approach of *N*-hydroxypyridine-2-thione-*O*-pivaloate to mesitylmethylvinylphosphine oxide, namely on the opposite side of the large 2,4,6-trimethylphenyl substituent.



Inspection of the bond angles reveals that the phosphorus tetrahedron in the title compound (I) is deformed, showing an increased O—P—C1 angle and a decreased C1—O—C11 angle, the corresponding values being 114.8 (1) and 103.9 (1)°, respectively.

In the chain connecting the mesityl and pyridyl rings, two extended fragments, *i.e.* C1—P—C11—S and C11—S—C17—C21, twisted at the C11—S bond, are found. The corresponding torsion angles are C1—P—C11—S = −170.9 (1), P—C11—S—C17 = 101.0 (2) and C11—S—C17—C21 = −170.8 (2)°. The chain connecting atoms C10 and C15 of the methyl groups has a similar conformation [C10—P—C11—C12 = −176.7 (2), P—C11—C12—C13 = −140.3 (2) and C11—C12—C13—C15 = −174.8 (3)°].

The P=O bond is nearly coplanar with the mesityl ring [distances of the P and O atoms from the best

plane are 0.137 (1) and 0.038 (2) Å, respectively] and nearly parallel to the pyridyl ring [distances of the P and O atoms from the best plane are −1.940 (1) and −2.182 (2) Å, respectively].

The structure is stabilized by a C11—H111...N intramolecular hydrogen bond [H111...N 2.37, C11...N 2.915 (4) Å, C11—H111...N 115°] and a C20—H201...O(−1 + *x*, $\frac{1}{2}$ − *y*, $\frac{1}{2}$ + *z*) intermolecular hydrogen bond [H201...O 2.41, C20...O 3.254 (4) Å, C20—H201...O 148°] (Fig. 2).

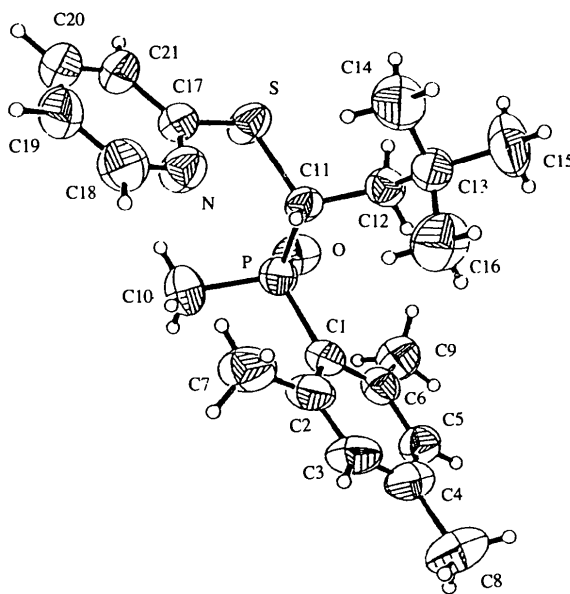


Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids.

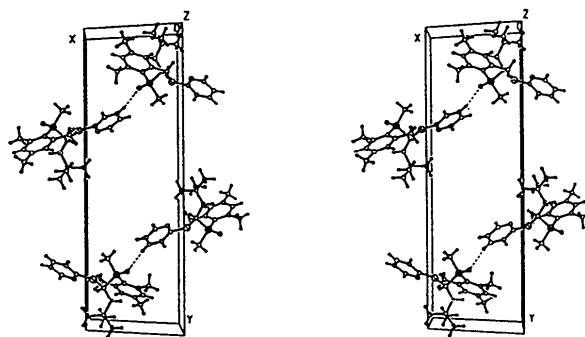


Fig. 2. Packing diagram viewed down the *c* axis.

Experimental

[3,3-Dimethyl-1-(2-pyridylthio)butyl]methyl(2,4,6-trimethylphenyl)phosphine oxide was prepared according to the method of Brandi, Cicchi, Goti & Pietrusiewicz (1991). The crystal density *D_m* was measured by flotation in a CH₃I/C₆H₆ solution.

Crystal data

C₂₁H₃₀NOPS
M_r = 375.51
 Monoclinic
*P*2₁/*c*
a = 9.759 (1) Å
b = 27.561 (1) Å
c = 8.941 (1) Å
 β = 114.87 (1)°
V = 2181.8 (4) Å³
Z = 4
D_x = 1.143 (3) Mg m⁻³
D_m = 1.13 Mg m⁻³

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 ψ scan (North, Phillips
 & Mathews, 1968; Frenz,
 1983)
T_{min} = 0.952, *T_{max}* =
 0.994
 3931 measured reflections
 3707 independent reflections

Refinement

Refinement on *F*
R = 0.049
wR = 0.053
S = 2.03
 3079 reflections
 259 parameters
 Only H-atom *U*'s refined
 (riding, C—H 0.96 Å)

Cu *K*α radiation
 λ = 1.54184 Å
 Cell parameters from 25
 reflections
 θ = 18.0–24.0°
 μ = 2.04 mm⁻¹
T = 293 K
 Plate
 0.56 × 0.16 × 0.12 mm
 Colourless

3079 observed reflections
 $[F > 4\sigma(F)]$
R_{int} = 0.015
 $\theta_{\max}$ = 69.91°
 $h = -11 \rightarrow 10$
 $k = 0 \rightarrow 33$
 $l = 0 \rightarrow 10$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.5%

$w = 1/[\sigma^2(F) + 0.00025F^2]$
 $(\Delta/\sigma)_{\max} = 0.02$
 $\Delta\rho_{\max} = 0.23 \text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e Å}^{-3}$
 Atomic scattering factors
 from *SHELXTL/PC*
 (Sheldrick, 1990)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
P	0.3195 (1)	0.3248 (1)	1.0122 (1)	0.058 (1)
S	0.0691 (1)	0.3346 (1)	0.6794 (1)	0.067 (1)
O	0.4300 (2)	0.3115 (1)	0.9456 (3)	0.073 (1)
N	−0.1257 (3)	0.3388 (1)	0.8182 (3)	0.069 (1)
C1	0.3990 (3)	0.3577 (1)	1.2079 (3)	0.057 (1)
C2	0.3098 (3)	0.3700 (1)	1.2920 (3)	0.068 (1)
C3	0.3718 (4)	0.3982 (1)	1.4341 (4)	0.079 (2)
C4	0.5177 (4)	0.4145 (1)	1.4971 (4)	0.073 (1)
C5	0.6046 (4)	0.4019 (1)	1.4160 (3)	0.066 (1)
C6	0.5507 (3)	0.3737 (1)	1.2733 (3)	0.058 (1)
C7	0.1464 (4)	0.3541 (2)	1.2410 (5)	0.099 (2)
C8	0.5822 (6)	0.4451 (2)	1.6525 (5)	0.105 (2)
C9	0.6623 (4)	0.3629 (1)	1.2012 (4)	0.075 (2)
C10	0.2226 (5)	0.2716 (1)	1.0353 (5)	0.094 (2)
C11	0.1797 (3)	0.3665 (1)	0.8718 (3)	0.049 (1)
C12	0.2567 (3)	0.4113 (1)	0.8396 (3)	0.055 (1)
C13	0.1792 (3)	0.4601 (1)	0.8311 (4)	0.063 (1)
C14	0.0163 (4)	0.4601 (1)	0.7050 (5)	0.097 (2)
C15	0.2658 (5)	0.4986 (1)	0.7812 (7)	0.106 (3)
C16	0.1866 (9)	0.4724 (2)	0.9998 (5)	0.105 (3)
C17	−0.0995 (3)	0.3198 (1)	0.6969 (3)	0.057 (1)
C18	−0.2589 (4)	0.3276 (1)	0.8220 (5)	0.084 (2)
C19	−0.3649 (4)	0.2981 (1)	0.7086 (5)	0.089 (2)
C20	−0.3340 (4)	0.2784 (1)	0.5856 (5)	0.087 (2)
C21	−0.1998 (4)	0.2886 (1)	0.5788 (4)	0.071 (1)

Table 2. Selected geometric parameters (Å, °)

P—O	1.481 (3)	C11—C12	1.536 (4)
P—C1	1.829 (3)	C12—C13	1.527 (4)
P—C10	1.802 (4)	C13—C14	1.514 (4)
P—C11	1.822 (2)	C13—C15	1.535 (6)
S—C11	1.826 (2)	C13—C16	1.518 (6)
S—C17	1.765 (3)	C17—C21	1.394 (4)
N—C17	1.323 (4)	C18—C19	1.370 (5)
N—C18	1.350 (5)	C19—C20	1.369 (7)
C1—P—C10	109.0 (2)	C14—C13—C15	108.5 (3)
O—P—C11	109.8 (1)	C12—C13—C16	109.4 (3)
C1—P—C11	103.9 (1)	C14—C13—C16	109.6 (4)
C10—P—C11	108.4 (2)	C15—C13—C16	109.4 (3)
C11—S—C17	103.4 (1)	S—C17—N	119.4 (2)
C17—N—C18	116.8 (3)	S—C17—C21	117.4 (3)
P—C11—S	108.7 (1)	N—C17—C21	123.3 (3)
P—C11—C12	110.7 (2)	N—C18—C19	123.5 (4)
S—C11—C12	110.6 (2)	C18—C19—C20	118.5 (4)
C11—C12—C13	116.5 (3)	C19—C20—C21	119.5 (3)
C12—C13—C14	112.4 (2)	C17—C21—C20	118.4 (4)
C12—C13—C15	107.5 (3)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*; *SDP* (Frenz, 1989). Structure solution: *SHELXTL/PC* (Sheldrick, 1990). Structure refinement: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC XP*. Preparation of material for publication: *SHELXTL/PC XPUBL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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