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Structure of Menthyl Methylphenylphosphinate, an Important Intermediate in Chiral Phosphine Syntheses

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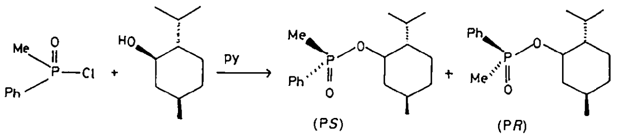
Abstract. (P*S*)-Menthyl methylphenylphosphinate, $C_{17}H_{27}O_2P$, $M_r = 294{\cdot}4$, monoclinic, $P2_1$, $a = 8{\cdot}575\,(1)$, $b = 6{\cdot}069\,(5)$, $c = 16{\cdot}788\,(2)$ Å, $\beta = 93{\cdot}26\,(1)^\circ$, $V = 872{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}12$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}52$ cm^{-1}, $F(000) = 320$, $T = 295$ K, $R = 0{\cdot}030$, $wR = 0{\cdot}039$ for 2003 reflections with $|F^2| > 3\sigma(F^2)$. The geometry at phosphorus is approximately tetrahedral with distortions due to substituent size and polarity. P—O, 1·600 (1), P═O, 1·469 (1), P—CH_3, 1·766 (2), P—Ph, 1·802 (2) Å, O—P—O 114·59 (7), O—P—Ph 105·45 (7), Me—P—Ph 109·3 (1)°.

Experimental. The complex was prepared by the reaction of (−)-menthol (1*R*,2*S*,5*R*) and racemic phenylmethylphosphinyl chloride (1) (Korpiun, Lewis, Chickos & Mislow, 1968). Separation of the diastereoisomers was by fractional crystallization from hexane and well formed crystals of the (P*S*) diastereoisomer (2) ($\alpha_D^{20^\circ C} = -94^\circ$, m.p. 352–353 K) were obtained by crystallization from hexane. Data collected using a crystal *ca* 0·4 × 0·25 × 0·2 mm on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation in the θ–2θ mode, with $\Delta\theta = (0{\cdot}8 + 0{\cdot}35\tan\theta)^\circ$ and a max. scan time of 1 min. 2414 reflections were measured for $2 < \theta < 28^\circ$ and $h\,0 \rightarrow 11$, $k\,0 \rightarrow 8$, $l\,-22 \rightarrow 22$, 2291 unique reflections, $R_{\text{int}} = 0{\cdot}01$ and 2003 observed reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0{\cdot}04I)^2]^{1/2}/\text{Lp}$, were used in the refinement. Unit-cell parameters were obtained by least-squares fit of 25 reflections with $8 < \theta < 12^\circ$, and the space group $P2_1$ from systematic absences of $0k0$ for k odd and successful refinement. Two reference reflections remeasured every hour showed a max. variation of −2·1%, which was corrected for. Lorentz–



(1) (2)

Table 1. *Fractional atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
P	3961·0 (5)	6807·0	3667·9 (2)	38·5 (1)
O1	4095·0 (13)	6939·8 (26)	2722·1 (6)	41 (1)
O2	4858·9 (14)	5009·9 (27)	4059·5 (7)	51 (1)
C1	5383 (2)	1803 (5)	1670·4 (11)	55 (1)
C2	5484 (2)	3830 (4)	2199·4 (11)	48 (1)
C3	3906 (2)	4938 (3)	2244·3 (10)	40 (1)
C4	3197 (2)	5593 (4)	1419·6 (10)	44 (1)
C5	3143 (3)	3545 (5)	883·0 (12)	63 (1)
C6	4728 (3)	2443 (4)	846·8 (12)	63 (1)
C7	6957 (3)	643 (5)	1642·3 (16)	80 (1)
C8	1610 (2)	6762 (5)	1448·9 (11)	57 (1)
C9	289 (3)	5288 (6)	1697·9 (16)	81 (2)
C10	1144 (3)	7860 (5)	652·4 (15)	77 (1)
C11	4570 (3)	9486 (4)	3954·2 (12)	58 (1)
C12	1906 (2)	6513 (4)	3814·6 (9)	47 (1)
C13	1398 (2)	4595 (5)	4170·7 (13)	59 (1)
C14	−193 (3)	4279 (6)	4259·3 (14)	77 (1)
C15	−1252 (3)	5836 (7)	3996·9 (15)	90 (2)
C16	−755 (3)	7754 (7)	3660·2 (15)	90 (2)
C17	838 (3)	8125 (5)	3566·4 (13)	67 (1)

Table 2. *Intramolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P—O1	1·600 (1)	P—O2	1·469 (1)
P—C11	1·766 (2)	P—C12	1·802 (2)
O1—C3	1·460 (2)	C1—C2	1·517 (3)
C1—C6	1·513 (3)	C1—C7	1·526 (4)
C2—C3	1·517 (3)	C3—C4	1·532 (2)
C4—C5	1·534 (3)	C4—C8	1·538 (3)
C5—C6	1·519 (3)	C8—C9	1·521 (4)
C8—C10	1·527 (3)	C12—C13	1·390 (3)
C12—C17	1·388 (3)	C13—C14	1·395 (3)
C14—C15	1·366 (5)	C15—C16	1·372 (5)
C16—C17	1·402 (3)		
O1—P—O2	114·59 (7)	O1—P—C11	100·77 (9)
O1—P—C12	105·45 (7)	O2—P—C11	114·99 (9)
O2—P—C12	110·93 (9)	C11—P—C12	109·3 (1)
P—O1—C3	119·4 (1)	C2—C1—C6	109·4 (2)
C2—C1—C7	111·8 (2)	C6—C1—C7	111·9 (2)
C1—C2—C3	111·5 (2)	O1—C3—C2	108·9 (1)
O1—C3—C4	107·9 (1)	C2—C3—C4	112·3 (1)
C3—C4—C5	108·5 (2)	C3—C4—C8	113·4 (1)
C5—C4—C8	113·3 (2)	C4—C5—C6	112·5 (2)
C1—C6—C5	111·3 (2)	C4—C8—C9	114·3 (2)
C4—C8—C10	111·2 (2)	C9—C8—C10	109·6 (2)
P—C12—C13	118·3 (2)	P—C12—C17	121·5 (2)
C13—C12—C17	120·2 (2)	C12—C13—C14	119·6 (2)
C13—C14—C15	120·5 (3)	C14—C15—C16	120·2 (2)
C15—C16—C17	120·6 (3)	C12—C17—C16	118·9 (3)

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polarization correction was applied, but no absorption or extinction corrections. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) with refinement by full-matrix least squares on F using programs from the *SDP-Plus* (B. A. Frenz & Associates, Inc., 1984) package with non-H atoms refined anisotropically. H atoms which were located from the difference map were refined isotropically. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0{\cdot}030$ and $wR = 0{\cdot}039$ for 2003 observed reflections; $S = 1{\cdot}5$, $(\Delta/\sigma)_{\max} = 0{\cdot}11$, $(\Delta\rho)_{\max,\min} = 0{\cdot}26$, $-0{\cdot}16$ e Å^{-3} in the final difference map. f'' multiplier $\eta = 1{\cdot}001$ (1) from least squares. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Drawings prepared using *PLUTO* (Motherwell, 1976).

Atomic parameters are given in Table 1,* intramolecular bond distances and angles in Table 2. Fig. 1 shows the molecular structure and the numbering scheme.

Related literature. The synthesis (Korpiun, Lewis, Chickos & Mislow, 1968) and characterization of this and its diastereoisomer by spectroscopic means has been reported (Lewis, Korpiun & Mislow, 1968). It has been widely used for the synthesis of chiral phosphine oxides and phosphines (Vineyard, Knowles, Sabacky, Bachman & Weinkauff, 1977). The structures of the related compounds S-methyl (PS)-phenylphosphonothioate and menthyl methyl (PR)-phenylphosphonate have been reported (Donohue & Mandel, 1981)

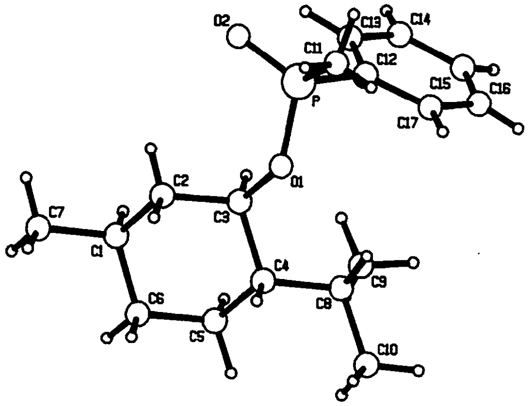

Fig. 1. Molecular structure and numbering scheme for (2).

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters, torsion angles and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54192 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1:2 Product of 2,7-Dimethyl-2*H*-benzothieno[2,3-*c*]pyrrole with Dimethyl Acetylenedicarboxylate

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Abstract. $C_{24}H_{23}NO_8S$, tetramethyl 1,9-dimethyl-3a,10c-dihydro-1*H*-benzothieno[2,3-*g*]indole-2,3,3a,4-tetracarboxylate, $M_r = 485{\cdot}51$, orthorhombic, $Iba2$, $a = 23{\cdot}358$ (8), $b = 24{\cdot}250$ (7), $c = 8{\cdot}360$ (1) Å, $V = 4735$ (2) Å^3, $Z = 8$, $D_x = 1{\cdot}362$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}18$ mm^{-1}, $F(000) = 2032$, $T = 291$ (1) K, final $R = 0{\cdot}043$ for 3486 unique observed [$F \geq 4{\cdot}0\sigma(F)$] diffractometer data. The constitution and configuration of the crystalline 1:2 product has been elucidated from