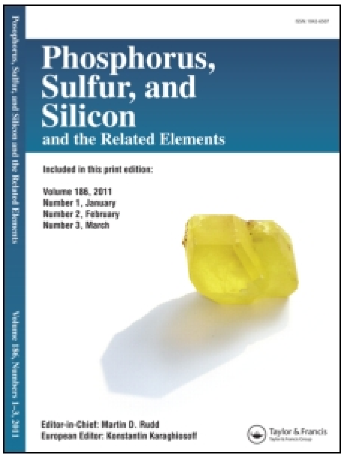

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X-RAY STRUCTURE OF (S_P)-*L*-MENTHYL (2-METHOXYPHENYL)PHENYLPHOSPHINYL-ACETATE AND ASSIGNMENT OF CONFIGURATION IN MENTHYL PHOSPHINYLACETATES[1]

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The structure and absolute configuration of enantiomeric (S_P)-*L*-menthyl (2-methoxyphenyl)phenylphosphinylacetate, the only crystalline of the two *P*-epimers, was analyzed by a single-crystal X-ray diffraction technique. $C_{25}H_{33}O_4P$, space group $P2_12_12_1$, $a = 9.890(1)$Å, $b = 10.011(3)$Å, $c = 24.177(3)$Å, $V = 2393.7(8)$Å^3, $Z = 4$. The structure was solved by direct methods and was refined by full matrix least-squares calculations to $R = 0.045$ using 2697 unique reflections with $I > 3\sigma(I)$. The absolute configuration was determined by the Hamilton method. The P=O and C=O dipoles of the studied molecule were found oriented in a syn fashion and the phenyl and the methoxyphenyl rings were both arranged coplanarly with the P=O bond. Two intermolecular C—H···O short contacts involving methoxyphenyl hydrogens and P=O and C=O oxygens were revealed. A potential possibility of using differentiated crystallinity of *P*-epimeric menthyl phosphinylacetates as a mnemonic for the assignment of their configuration at *P* is discussed.

Key words: Enantiomeric phosphine oxide; X-ray analysis; absolute configuration; C—H···O interactions; menthyl phosphinylacetates.

INTRODUCTION

One of the recently developed convenient procedures for resolution of tertiary phosphine oxides relies on the temporary chiral modification of the P-Me substituent with menthoxycarbonyl auxiliary.[2-4] This auxiliary can be introduced into the phosphine oxide structure in one step together with the latent methyl group by employment of menthyl bromoacetate[2] or menthyl chloroacetate[4] and straightforward Michaelis-Arbusov or Michaelis-Becker chemistry,[5] respectively, and it can also be readily removed from the resolved intermediate menthyl phosphinylacetates by means of a one-step decarbalkoxylative procedure of Krapcho.[2,3,6,7] Of great practical advantage is also the fact that the introduction of menthoxycarbonyl auxiliary into the phosphine oxide structure leads to a pronounced differentiation of the resulting *P*-epimers in crystallinity. This feature was most strikingly mani-

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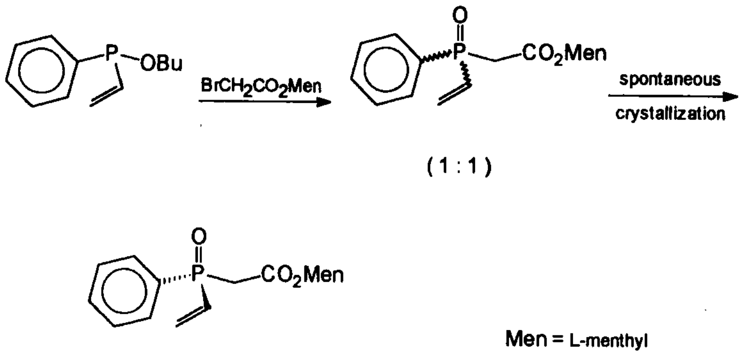
fested in the pioneering study[2] in which a single epimerically pure menthyl phenylvinylphosphinylacetate separated itself by spontaneous crystallization from the crude reaction mixture containing the two *P*-epimers in ca. 1:1 ratio (Equation 1).



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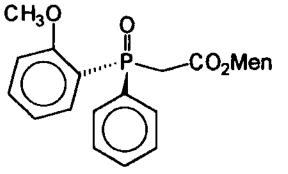
Similarly high propensity for crystallization related to only one configurational pairing in *P*-epimeric menthyl phosphinylacetates recurred recently during the course of our synthesis of (2-methoxyphenyl)methylphenylphosphine oxide, (PAMPO[8]), in which analogously derived menthyl (2-methoxyphenyl)phenylphosphinylacetates **2** and **3** were employed as intermediates.[9] In that case again only one *P*-epimer, i.e., **2**, crystallized out from the reaction mixture upon addition of chilled pentane. Interestingly, also a homogenized by dissolution in chloroform and slow evaporation 1:1 mixture of purified epimers **2** and **3** (2g), when left unattended on a bench for over 2 years separated itself into crystalline **2** (large octahedral crystals), and its noncrystalline epimer **3** (colorless lucid oil), essentially quantitatively. Presented in this paper is an X-ray diffraction study of **2** which reveals its structure and solid state conformation, as well as the absolute configuration. The obtained crystal and physical data are compared with those collected previously for analogous pairs of *P*-epimeric menthyl phosphinylacetates.[4,10]



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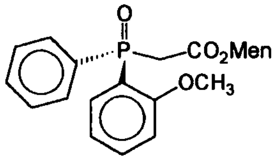

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RESULTS AND DISCUSSION

A perspective view of the studied menthyl (2-methoxyphenyl)phenylphosphinylacetate, **2**, is shown in Figure 1 together with the numbering scheme. The found bond lengths and bond angles are listed in Table I and Table II, respectively.

Inspection of the collected data reveals that the phosphorus tetrahedron is distorted in the way characteristic for $R_3P = X$ compounds showing somewhat in-

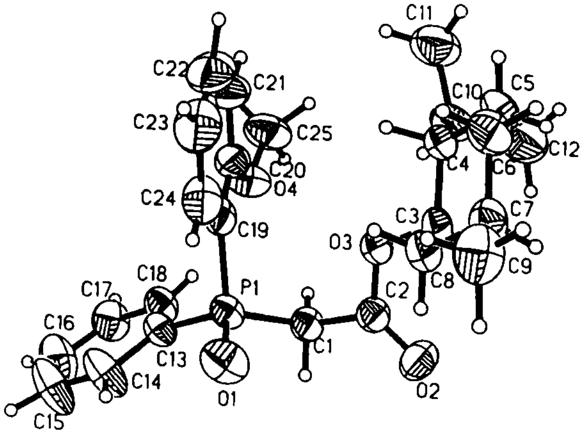

FIGURE 1 ORTEP view of 2 showing 50% probability elipsoids and atom numbering scheme.

TABLE I
Bond lengths (Å) in 2

O1 ---P1	1.482(2)	C1 ---P1	1.824(2)
C13 ---P1	1.806(2)	C19 ---P1	1.806(3)
C2 ---O2	1.199(3)	C2 ---O3	1.326(3)
C3 ---O3	1.463(3)	C20 ---O4	1.377(3)
C25 ---O4	1.428(4)	C2 ---C1	1.500(3)
C4 ---C3	1.528(4)	C8 ---C3	1.510(4)
C5 ---C4	1.537(4)	C10 ---C4	1.537(4)
C6 ---C5	1.518(4)	C7 ---C6	1.527(4)
C8 ---C7	1.532(4)	C9 ---C7	1.522(5)
C11 ---C10	1.529(5)	C12 ---C10	1.526(6)
C14 ---C13	1.390(4)	C18 ---C13	1.383(3)
C15 ---C14	1.380(5)	C16 ---C15	1.377(6)
C17 ---C16	1.369(5)	C18 ---C17	1.391(4)
C20 ---C19	1.393(4)	C24 ---C19	1.401(3)
C21 ---C20	1.385(5)	C22 ---C21	1.385(7)
C23 ---C22	1.361(6)	C24 ---C23	1.383(5)

creased O—P—C angles and decreased C—P—C angles with the corresponding values ranging from 110.7(1) to 112.2(1)°, and from 104.2(1) to 108.9(1)°, respectively. The other bond angles as well as the bond lengths in **2** represent rather typical values and require no comments.

The solid state conformation of the studied molecule has several interesting features. Both the phenyl and the methoxyphenyl rings assume a nearly coplanar arrangement with the P=O bond. The corresponding deviations from coplanarity are 12.1(1)° and 10.0(1)° for the phenyl and the methoxyphenyl ring, respectively.

TABLE II

Bond angles (°) in 2

C 1	-P 1	-O 1	111.8(1)	C 13	-P 1	-O 1	112.2(1)
C 13	-P 1	-C 1	104.2(1)	C 19	-P 1	-O 1	110.7(1)
C 19	-P 1	-C 1	108.9(1)	C 19	-P 1	-C 13	108.8(1)
C 3	-O 3	-C 2	119.1(2)	C 25	-O 4	-C 20	118.9(2)
C 2	-C 1	-P 1	112.0(2)	O 3	-C 2	-O 2	125.1(2)
C 1	-C 2	-O 2	125.2(2)	C 1	-C 2	-O 3	109.7(2)
C 4	-C 3	-O 3	105.5(2)	C 8	-C 3	-O 3	109.2(2)
C 8	-C 3	-C 4	113.0(2)	C 5	-C 4	-C 3	108.8(2)
C 10	-C 4	-C 3	112.7(2)	C 10	-C 4	-C 5	114.3(2)
C 6	-C 5	-C 4	113.4(2)	C 7	-C 6	-C 5	111.7(2)
C 8	-C 7	-C 6	108.5(2)	C 9	-C 7	-C 6	113.3(3)
C 9	-C 7	-C 8	111.4(3)	C 7	-C 8	-C 3	111.4(2)
C 11	-C 10	-C 4	111.5(3)	C 12	-C 10	-C 4	114.1(3)
C 12	-C 10	-C 11	110.4(3)	C 14	-C 13	-P 1	116.0(2)
C 18	-C 13	-P 1	124.4(2)	C 18	-C 13	-C 14	119.6(2)
C 15	-C 14	-C 13	119.7(3)	C 16	-C 15	-C 14	120.4(4)
C 17	-C 16	-C 15	120.4(4)	C 18	-C 17	-C 16	119.8(3)
C 17	-C 18	-C 13	120.1(2)	C 20	-C 19	-P 1	126.0(2)
C 24	-C 19	-P 1	115.7(2)	C 24	-C 19	-C 20	118.2(3)
C 19	-C 20	-O 4	115.5(2)	C 21	-C 20	-O 4	123.6(3)
C 21	-C 20	-C 19	120.9(3)	C 22	-C 21	-C 20	118.8(3)
C 23	-C 22	-C 21	121.7(4)	C 24	-C 23	-C 22	119.4(3)
C 23	-C 24	-C 19	120.8(3)				

The dihedral angle between the planes of the two aryl rings is 64.1(1)°. The methoxy group lies practically in the plane of the aryl ring [C25-O4-C20-C21 = 6.1(4)°], and is in an anti arrangement in respect to the P=O bond. As expected, the cyclohexane ring of the menthyl residue exists in a chair conformation with the non-hydrogen substituents at C3, C4 and C7 occupying the equatorial positions. The asymmetry parameter[11] in this ring is $\Delta C_s(C_4) = 1.6°$, $|\phi|_{av} = 55.7°$.

In the acyclic part of the studied molecule two extended fragments, i.e., C13-P1-C1-C2 and C1-C2-O3-C3, which are twisted at the C1—C2 bond, are found. The corresponding dihedral angles are C13-P1-C1-C2 = −177.5(2)°, C1-C2-O3-C3 = 173.0(2)° and P1-C1-C2-O3 = −62.2(2)°, respectively. Such an arrangement of bonds places the P=O and C=O dipoles in a syn array with the dihedral angle between them equal to 57.0(2)°. Similar relative orientation of the P=O and C=O bonds has been observed previously in two other menthyl phosphinylacetates[10] and it seems to emerge as a common crystal state feature of this class of compounds.

Figure 2 shows a view of the molecular packing in the unit cell. Inspection of the packing reveals the presence of two intermolecular interactions of the C—H···O

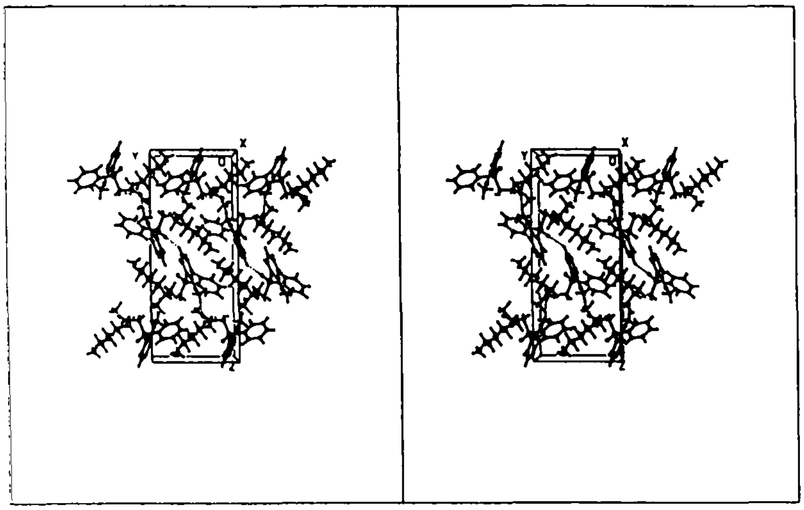

FIGURE 2 Stereoview of cell packing for 2 showing the C—H···O interactions.

type[12]: H253···O2 $(-x, 0.5 + y, 0.5 - z) = 2.50(2)$Å and H231···O1 $(x - 0.5, 0.5 - y, -z) = 2.50(3)$Å. Apparently, the presence of CH_3O-group in the studied molecule dominates its C—H···O interactions as no longer short contacts involving hydrogens adjacent to phosphorus which were seen previously in the closely related menthyl phenylvinylphosphinylacetates[10] have been found.

As can be seen from Figure 1 which shows the studied molecule in its absolute configuration, the configuration of the menthyl moiety corresponds expectedly to the 1*R*, 2*S*, 5*R* configuration of the *L*-menthol used in the synthesis of **2**, and the configuration at *P* is *S*.

The found *S* configuration at phosphorus in the crystalline epimer **2** is worthy of notice. In the two previously described resolved pairs of menthyl phosphinylacetates of known configurations the same S_P epimers were the ones which crystallized first, either in the expeditious fractional crystallization,[4] or spontaneously.[2,3] The melting points of the S_P and R_P epimers also differed correspondingly within each pair, i.e., 152 vs. 74°C for the S_P- and R_P-menthyl phenylvinylphosphinylacetates,[3] and 116.5–117.5 vs. 75–76°C for the S_P- and R_P-menthyl *tert*-butylphenylphosphinylacetate,[4] respectively. In the present study this difference has been found to be even more profound; S_P – **2** melts at 104–105°C whereas R_P – **3** is an oil.[13] It seems quite likely then that these features may provide the basis for a mnemonic which would allow one to tentatively assign the configuration at phosphorus in epimeric menthyl phosphinylacetates solely on the basis of their crystalline properties provided that the epimers are separated. Further examples are however required to test the validity of this presumption.

EXPERIMENTAL

Crystals of **2** suitable for the structure analysis were obtained by crystallization from ethyl acetate solution. Accurate unit cell dimensions were obtained by the least-squares fit to the θ value of 25 reflections measured on an Enraf Nonius CAD 4 diffractometer. The intensity data were collected on the diffractometer using CuKα radiation and graphite monochromator in an $\omega - 2\theta$ scan mode. A reference reflection monitored every hour of exposed X-ray time showed no significant change during the data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption. The 2697 reflections with $I > 2\sigma(I)$ were used in the subsequent analysis. Crystal data and experimental details are listed in Table III.

The structure was solved by direct methods, using the SHELXS-86 program[14] and was refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were located from a difference Fourier map and their positional and individual isotropic thermal parameters were refined. The function $\Sigma\, w(|F_0| - |F_c|)^2$ was minimized, and in the final cycles of calculation a weighing based on counting statistics was used with $w = [\sigma^2(F_0) + 0.0071(F_0)^2]^{-1}$.

An empirical isotropic extinction correction was introduced, and the parameter x was refined to the value of 0.008(1). The final difference Fourier synthesis showed only peaks with electron density <0.4 eÅ^{-3}.

Table IV lists the final positional parameters of **2**. Most of the computations were performed with SHELX-76 crystal structure determination program[15] on an AMSTRAD-1512 minicomputer.

The absolute configuration of the studied molecule was confirmed with the Hamilton R-test.[16] The final $R(R_w)$ factor was 0.045, (0.045), for a refinement of the structure with the S_P configuration and $R^-(R_w^-)$ was 0.052, (0.056), for the opposite configuration. The resulting R^- and R_w^- values showed that the model with inverse configuration had to be rejected with very high probability. The R_{ratio} ($R_{w\,ratio}$) is 1.156, (1.244), for $N = 2296$ independent parameters. According to the Pearson and Hartley tables of R_{ratio} values[17] as the function of the significance level α, and the number of independent parameters, the significance level was $\alpha < -10^{-6}$.[18]

TABLE III

Crystal data and experimental parameters for **2**

Molecular formula	$C_{25}H_{33}O_4P$
M_r	428.507
Space group	$P2_12_12_1$
a(Å)	9.890(1)
b(Å)	10.011(3)
c(Å)	24.177(3)
V(Å^3)	2393.7(8)
Z	4
F(000)	920
D_x(Mgm^{-3})	1.189(3)
D_m(Mgm^{-3})	1.18(2)
μ (CuKα)(cm^{-1})	12.15
Radiation	CuKα
Scan mode	ω–2θ
2θ range(°)	1–75
Reflections with $I>2\sigma(I)$	2697
R	0.045
R_w	0.045
R^-	0.052
R_w^-	0.056

TABLE IV

Positional parameters $(\times 10^4)$ for the nonhydrogen atoms of 2 with equivalent thermal parameters $(\text{Å}^2 \times 10^4)$

	x	y	z	U_{eq}
P1	1101(1)	4149(1)	1224(0)	414(1)
O1	2104(2)	3308(2)	931(1)	653(6)
O2	783(2)	1137(2)	2098(1)	616(5)
O3	-911(2)	2004(2)	1598(1)	502(4)
O4	-1648(2)	5288(2)	1551(1)	614(5)
C1	708(3)	3490(3)	1909(1)	450(5)
C2	228(3)	2070(2)	1885(1)	443(5)
C3	-1486(3)	694(2)	1469(1)	471(5)
C4	-2970(3)	954(3)	1330(1)	511(6)
C5	-3606(3)	-344(3)	1115(1)	615(8)
C6	-2814(3)	-980(3)	646(1)	680(8)
C7	-1346(3)	-1240(3)	809(1)	579(7)
C8	-711(3)	81(3)	994(1)	537(7)
C9	-522(5)	-1894(4)	351(2)	776(11)
C10	-3746(3)	1604(3)	1811(1)	656(8)
C11	-5087(4)	2203(5)	1617(2)	875(13)
C12	-3975(5)	681(6)	2305(2)	850(13)
C13	1732(2)	5812(3)	1358(1)	448(5)
C14	2892(3)	6177(3)	1071(1)	706(9)
C15	3424(4)	7441(4)	1140(2)	906(12)
C16	2827(4)	8329(4)	1500(2)	784(10)
C17	1695(3)	7973(3)	1790(1)	617(7)
C18	1143(3)	6706(2)	1721(1)	505(6)
C19	-444(3)	4276(2)	830(1)	470(5)
C20	-1665(3)	4798(3)	1020(1)	527(6)
C21	-2807(4)	4789(4)	688(2)	728(10)
C22	-2714(5)	4259(4)	160(2)	867(12)
C23	-1540(5)	3734(4)	-36(1)	853(12)
C24	-397(3)	3754(3)	293(1)	630(8)
C25	-2891(3)	5699(4)	1799(2)	764(10)

TABLE IV (*Continued*)
Positional parameters (× 10³) and U_{iso} (× 10³) for the hydrogen atoms of 3

	x	y	z	U
H11	2(3)	402(3)	205(1)	54(8)
H12	158(3)	353(3)	213(1)	50(8)
H31	-128(3)	12(2)	178(1)	43(7)
H41	-287(3)	166(3)	99(1)	70(9)
H51	-367(3)	-99(3)	143(1)	65(9)
H52	-445(3)	-21(3)	100(1)	64(9)
H61	-278(4)	-33(4)	30(2)	93(12)
H62	-326(4)	-177(4)	56(2)	103(13)
H71	-136(4)	-183(4)	115(1)	75(10)
H81	-68(3)	72(3)	66(1)	59(8)
H82	21(3)	-4(3)	108(1)	48(8)
H91	-56(4)	-131(4)	8(2)	98(14)
H92	-99(4)	-276(4)	22(2)	103(12)
H93	45(4)	-211(5)	52(2)	110(14)
H101	-311(4)	230(4)	194(2)	80(11)
H111	-568(5)	157(5)	149(2)	108(15)
H112	-492(5)	286(5)	128(2)	118(16)
H113	-554(5)	278(5)	194(2)	115(16)
H121	-305(5)	38(5)	243(2)	112(15)
H122	-474(5)	-2(4)	220(2)	102(13)
H123	-440(5)	134(5)	260(2)	126(17)
H141	334(5)	540(5)	82(2)	123(15)
H151	428(4)	774(4)	91(2)	90(11)
H161	307(5)	916(5)	154(2)	98(15)
H171	117(4)	858(3)	206(1)	73(10)
H181	31(3)	646(3)	191(1)	60(9)
H211	-356(5)	508(4)	85(2)	99(14)
H221	-357(5)	416(4)	-4(2)	111(14)
H231	-154(5)	333(5)	-41(2)	123(16)
H241	46(5)	346(4)	18(2)	60(14)
H251	-338(5)	647(4)	155(2)	147(15)
H252	-366(4)	493(4)	180(2)	78(14)
H253	-262(5)	586(4)	222(2)	94(14)

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