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Optically Active Phosphine Oxides: 10 [1]; X-ray Structure and Conformation of (S_P)- and (R_P)-*L*-Menthyl α-(Phenylvinylphosphinyl)acetates

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ABSTRACT

The structures and solid-state stereochemistry of the two P-epimeric compounds (**1** *and* **2**) *formed in a reaction of butyl phenylvinylphosphinite with* (−)-L-*menthyl bromoacetate were studied by X-ray crystallography and CP–MAS* ^{13}C *NMR spectroscopy. The two compounds were also analyzed in solution by means of 2D* ^{1}H *NMR,* ^{13}C *NMR, IR, UV, and dipole moment measurement techniques. Compound* **1**, $C_{20}H_{29}O_3P$, *crystallized in the orthorhombic group* $P\ 2_12_12_1$ *with* $Z = 4$, $a = 20.491(2)$, $b = 16.719(1)$, *and* $c = 5.910(1)$. *Compound* **2**, $C_{20}H_{29}O_3P$, *crystallized in the monoclinic space group* $P\ 2_1$ *with* $Z = 2$, $a = 9.266(1)$, $b = 9.852(1)$, $c = 10.954(1)$, *and* $\beta = 95.20(1)°$. *In the crystals both compounds possess their C═C—P═O fragments in an* s-cis *array, and have their P═O and C═O dipoles oriented uniformly in a syn, nearly parallel, fashion. In solution, however, an anti arrangement of these two dipoles is slightly preferred.*

INTRODUCTION

In the course of our project on the synthesis of optically active phosphorus compounds we have found [2] that the Arbuzov reaction of butyl phenylvinylphosphinite with *L*-menthyl bromoacetate affords good yields of the two P-epimeric menthyl phenylvinylphosphinylacetates **1** and **2** (Equation 1). The two epimers were formed in nearly equal amounts but, importantly, only one of them, i.e., **2**, crystallized out of the reaction mixture upon cooling to room temperature, making isolation of the diastereomerically homogeneous material straightforward. The other epimer (**1**) showed very little tendency to crystallization, and its isolation in the pure state from the residual mixture, albeit possible, proved tedious and inefficient. As we [3] and others [4] found later, the high incidence of crystallinity associated with only one configurational pairing of the chiral menthol and phosphinyl residues in this family of compounds is of great practical advantage. It seems to warrant relatively easy access to the diastereomerically homogeneous P-chiral menthyl phosphinylacetates, which, by removal of the auxiliary menthyl residue, can eventually be transformed into antiomerically homogeneous (homochiral) tertiary phosphine oxides [2–5]. In the original case this protocol secured the access to

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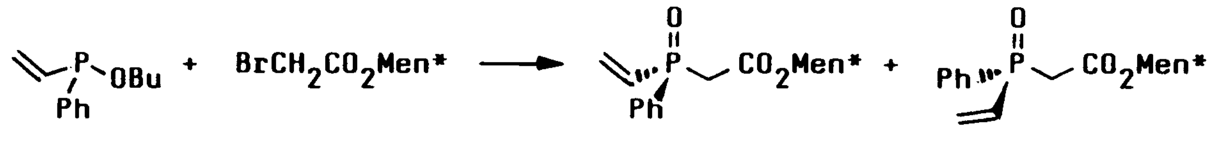

1 2

Men* = L-Menthyl

preparative quantities of homochiral (−)-*S*-methylphenylvinylphosphine oxide [5], a versatile precursor to the large variety of structurally diversified homochiral phosphine oxides of well defined configuration [6]. In this report we wish to present a detailed structural and conformational analysis of the two P-epimeric *L*-menthyl phenylvinylphosphinylacetates **1** and **2** in the solid state and in various solutions. The comparative studies comprised the single-crystal X-ray diffraction, routine and 2D ^{1}H NMR, solid-state and solution ^{13}C NMR, UV, IR, and dipole moments measurements.

RESULTS AND DISCUSSION

X-Ray Structure Analysis of 1 *and* 2

Slow crystallization of **1** from hexane and of **2** from benzene afforded orthorhombic and monoclinic crystals, respectively, which were subsequently subjected to X-ray diffraction measurements. Details of these measurements and parameters of the crystals, as well as the corresponding positional parameters of nonhydrogen atoms, bond lengths, and bond angles for **1** and **2** are all listed in the Experimental section. The three-dimensional views of the studied molecules with the numbering systems are displayed in Figures 1 and 2, which also show the molecules in their absolute configurations. The absolute configuration at phosphorus is found *R* in **1** and *S* in **2**, a finding that is in full agreement with previous assignments [2, 5]. Also, the 1*R*, 2*S*, 5*R* (menthol numbering) configuration of the carbocyclic ester residues found in the two compounds corresponds to the known chirality of *L*-menthol used for the preparation of the bromoacetate reagent.

Several features of the two structures are noteworthy. The $R_3P{=}O$ tetrahedrons exhibit their usual deformation consisting of an increase of the O—P—C and the simultaneous decrease of the C—P—C valency angles. The found values fall in the range of 112.9(1)°–114.2(1)° and 103.5(1)°–107.1(1)°, respectively. More interestingly, however, in the two structures the P=O bonds are found in a nearly coplanar arrangement with the P-phenyl and P-vinyl groups as indicated by the corresponding torsional angles 01–P–C5–C10 = −9.6 and 01–P–C3–C4 = −2.9° in **1**, and 01–P–C5–C10 = −0.6 and 01–P.C3–C4 = 4.6° in **2**, as well as by the resulting nonbonding distances between 01 and H101 and 01 and H41, which were found to be 2.62 and 2.62 Å in **1** and 2.59 and 2.62 Å, in **2**. While this type of alignment in the case of Ph—P=O fragments has occasionally been observed in crystal structures of phenyl bearing phosphine oxides [7], observation of the C=C—P=O coplanar arrangement is, to the best of our knowledge, unprecedented. Of the two possible coplanar arrangements of the C=C—P=O unit, i.e., *s*-cis and *s*-trans, the found *s*-cis one is apparently energetically favored. In the two studied structures the vinyl groups

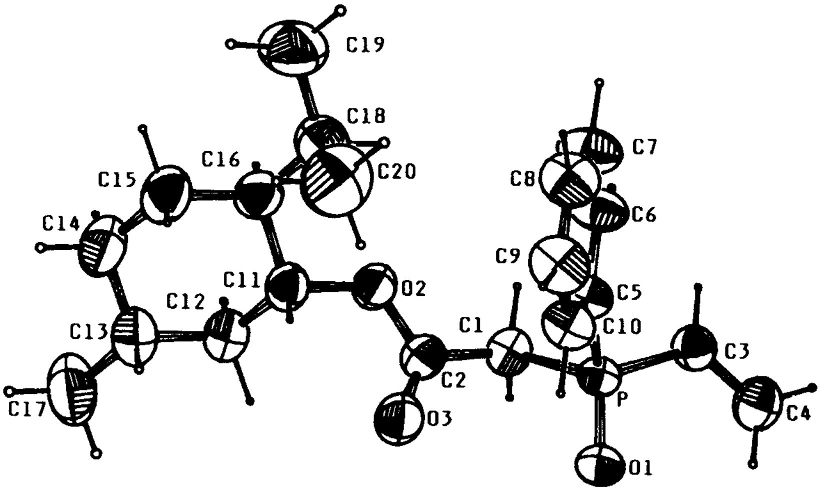

FIGURE 1 ORTEP Stereoview of **1** with Atom Numbering.

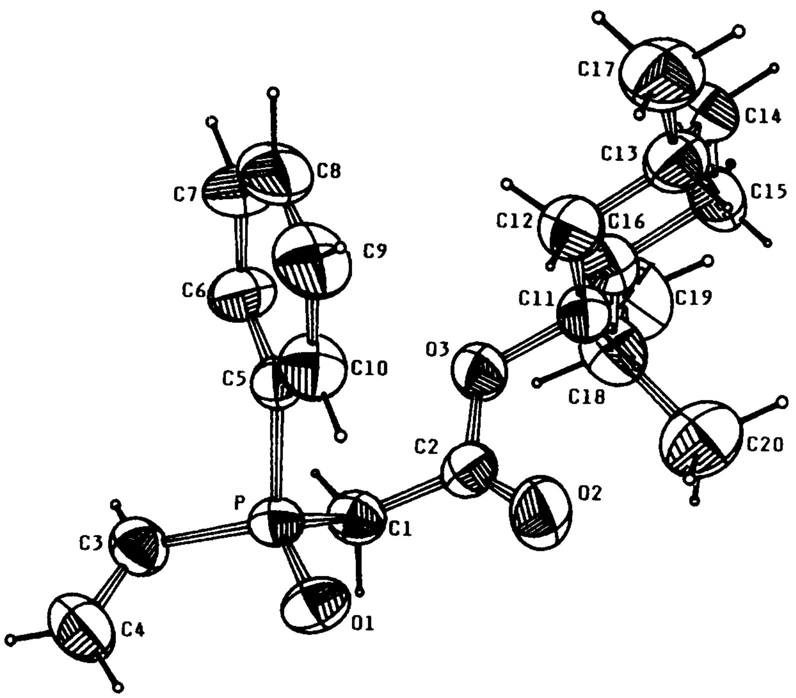

FIGURE 2 ORTEP Stereoview of **2** with Atom Numbering.

occupy decidedly peripheral positions and the possibility that their placement in this particular conformational array has resulted from severe steric constraints of either intra or intermolecular (cf. crystal packing below) nature can probably be excluded. In addition, for closely related α,β-unsaturated sulfoxides [8] as well as for several α,β-unsaturated carbonyl derivatives [9] the considerable preference for the analogous *s*-cis arrangement of the conjugated units in their ground state and/or their reactive conformations has already been well established.

Another interesting feature of the studied molecules is the relative orientation of their P=O and C=O dipoles. As can be seen in Figures 1 and 2, and as indicated by the corresponding 01–P···C2–02 torsion angles of 15.4° and −10.4° for **1** and **2**, respectively, as well as the acute angles between P=O and C=O bonds of 22.7° and 27.8° in **1** and **2**, respectively, the two polar groups are oriented uniformally in a syn, not far from parallel, fashion. This kind of arrangement places the 01 and 02 atoms in a distance of only 3.19 Å in **1**, and 3.36 Å in **2**, the significant density of negative charge on both atoms notwithstanding [10]. This structural observation implies, however, that the complexation of this family of compounds with metal cations should be very facile. Some pertinent examples can already be found in the literature [11].

The carbocyclic ester parts of the two molecules are found in rather typical conformations and therefore require no comments. The expected short contacts involving carboxylic oxygens have been found in both molecules and are listed in Table 1,

TABLE 1 Details of Hydrogen Contacts for **1** and **2**

		Distance (Å)			*Angle (°)*
Compound	*D—H···A*	*D—H*	*D···A*	*H···A*	*D—H···A*
1	C11–H111···02[a]	1.09(4)	2.675(3)	2.38(4)	93(3)
	C3–H31···01[b]	1.04(5)	3.178(4)	2.44(5)	127(4)
	C3–H31···02[b]	1.04(4)	3.355(3)	2.43(4)	148(4)
	C8–H81···01[c]	1.08(5)	3.448(4)	2.41(4)	161(4)
2	C11–H111···02[a]	0.92(4)	2.710(4)	2.32(3)	106(3)
	C18–H181···03[a]	1.01(3)	2.864(3)	2.42(3)	105(2)
	C1–H12···01[d]	0.96(4)	3.276(3)	2.34(3)	163(2)

Symmetry code: [a] x, y, z;
[b] x, y, z − 1;
[c] −x + 0.5, y − 0.5, −z + 1;
[d] −x − 1, y − 0.5, −z

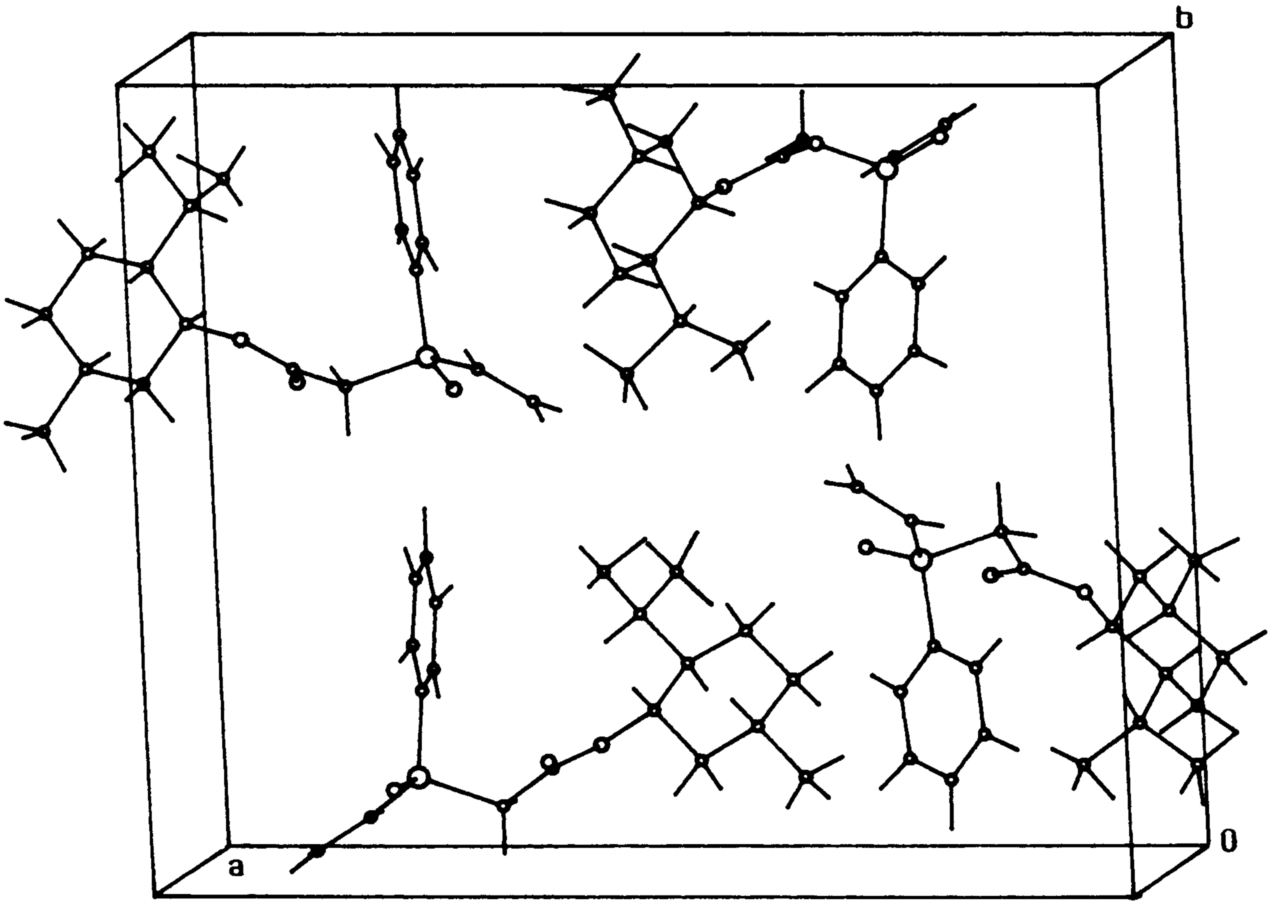

FIGURE 3 Packing of the Unit Cell for **1**.

which also lists the revealed intermolecular contacts. It should also be noted that, as a result of the configurational difference at phosphorus, the *iso*-Pr group in **1** is juxtaposed with P-phenyl, whereas P-phenyl in **2** faces the C12 methylene.

The crystal packing for **1** and **2** is shown in Figures 3 and 4, respectively. While the density of these packings (four molecules in a unit cell of V = 2024.7 Å^3 in **1**, and two molecules in a cell of V = 995.9 Å^3 in **2**) can be judged very similar, the relative orientation of individual molecules in the two crystals is certainly distinct. In **1**, translation of the molecules along both Oa and Ob axes is accompanied by 180° rotation around Ob, whereas in **2** only molecules translated along Ob are similarly rotated by 180° around this axis. These operations in **1** create a situation in which one half of the molecules have their polar heads oriented in the opposite direction from the other half. In **2** all the molecules have their polar heads oriented in one direction, composing in polar terms a more highly ordered overall structure. Considering the very close conformational similarity of individual molecules of **1** and **2**, it is probably this orientationally distinct packing in the crystal that may be held responsible for the observed difference in crystallinity of the two compounds.

^{13}C NMR Analysis of **1** *and* **2**

The issue whether the conformational features seen for **1** and **2** in the crystals are also retained in solution was addressed first by ^{13}C NMR spectroscopy, which allows for the direct comparison of the solid-state and solution data. The corresponding solid-state (CP MAS) and solution ($CDCl_3$) ^{13}C NMR spectra of **1** and **2** as well as of model menthyl acetate are presented in Table 2. Assignment of signals for solution spectra of **1** and **2** followed from DEPT experiments and from comparison with the spectrum of menthyl acetate used as the reference. The shifts in solid-state spectra were assigned by analogy to those recorded in $CDCl_3$.

In $CDCl_3$ the two isomers gave very similar spectra with the differences between shifts of the corresponding carbons not exceeding 0.15 ppm. Their solid-state spectra were analogously very similar, and, importantly, they also matched closely the spectra in solution. Besides making the assignment of the solid-state spectra relatively straightforward,

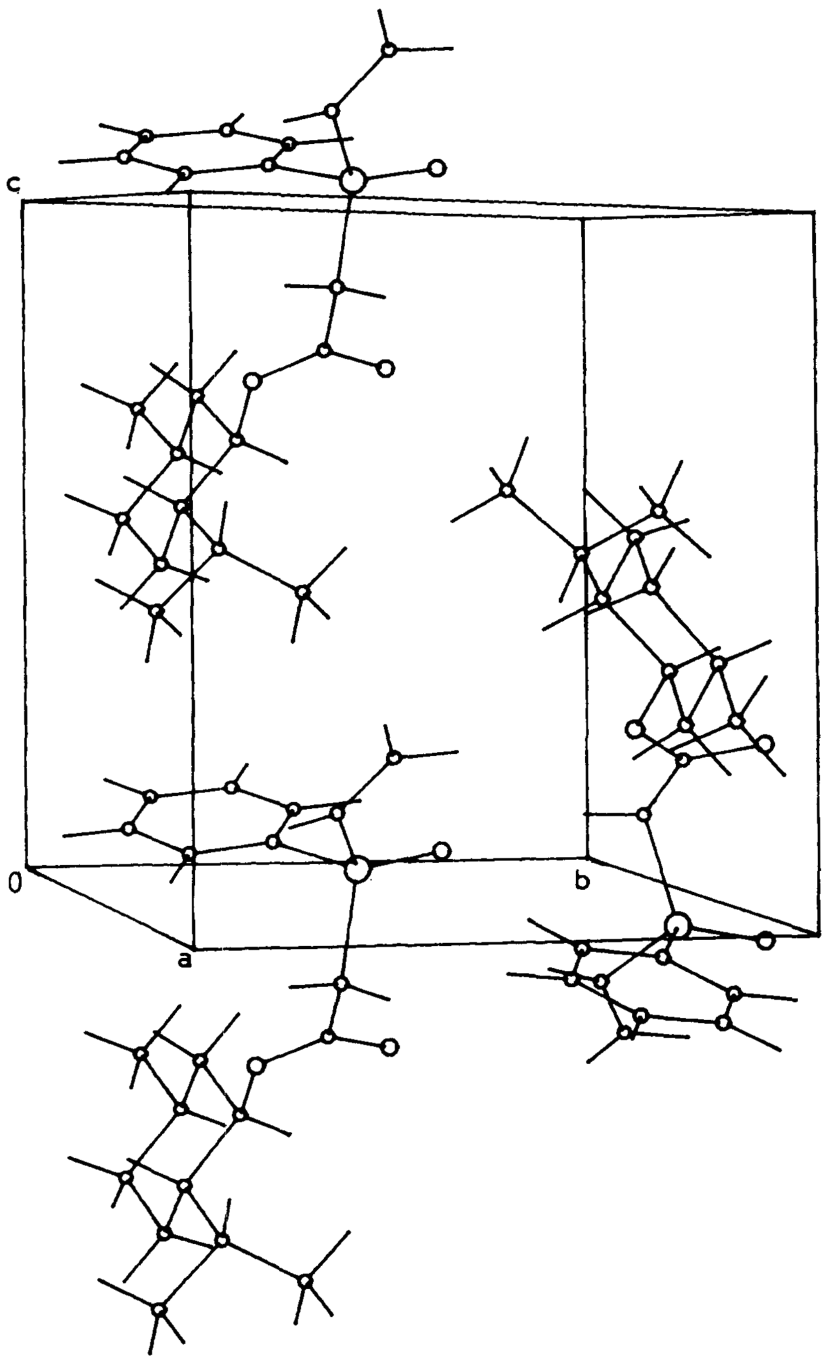

FIGURE 4 Packing of the Unit Cell for **2**.

this finding suggested additionally that either conformations of the two studied compounds are quite similar in solution and in the solid-state, or the technique is not sensitive enough to respond detectably to the possible changes in molecular conformations of **1** and **2** in the two states. The differences of 3–4 ppm discernible for C11 and for peripheral C14 and C16 carbons in the two solid-state spectra should probably be associated with some lattice interactions rather than with any of the subtle conformational differences revealed in the two individual molecules by comparison of Figures 1 and 2.

^1H NMR Analysis of **1** *and* **2**

The spectra of **1** and **2** and model menthyl acetate are listed in Table 3. All individual protons in these compounds have been assigned by means of 2D COSY experiments, which revealed practically all the expected crosspeaks corresponding to geminal, vicinal, and W-path proton–proton couplings. As

TABLE 2 Solid-State and Solution ($CDCl_3$) ^{13}C NMR spectra of **1** and **2** and Menthyl Acetate[a]

	CP–MAS ^{13}C NMR δ [ppm]		*^{13}C NMR ($CDCl_3$) δ [ppm]*		
	1	**2**	**1**	**2**	*menthyl acetate*
C1	39.7	39.4	40.1[b]	40.1[c]	21.1
C2	167.5	166.5	166.3[d]	166.4	170.1
C3	132.4[f]	132.0[f]	130.6[g]	130.9[h]	
C4	136.1	136.7	135.6	135.7	
C5	[i]	[i]	132.1[f,j]	[i]	
C6	134.5	133.0	131.1[k]	131.2[l]	
C7	129.1	129.0	129.1[m]	129.2[m]	
C8	133.5[f]	132.5[f]	132.7	132.8	
C9	129.1[f]	129.0[f]	129.1	129.2	
C10	134.5	133.0	131.1[k]	131.2[l]	
C11	76.3	73.5	76.2	76.4	73.9
C12	40.5	41.0	41.0	41.2	41.0
C13	30.6	32.2	31.8	32.0	31.4
C14	31.8	35.8	34.5	34.7	34.3
C15	23.2	24.4	23.6	23.8	23.6
C16	44.8	48.1	47.2	47.2	47.1
C17	23.2	23.2	23.4	22.5	22.0
C18	25.5	25.5	26.3	26.4	26.3
C19	21.9	20.4	21.2	21.3	20.7
C20	14.9	16.3	16.5	16.6	16.9

[a] Numbering of the carbon atoms in all the compounds including menthyl acetate corresponds to the numbering shown in Figures 1 and 2.
[b] J_{PC} = 62 Hz.
[c] J_{PC} = 62.8 Hz.
[d] J_{PC} = 4.3 Hz.
[e] J_{PC} = 4.5 Hz.
[f] Tentative assignment.
[g] J_{PC} = 97 Hz.
[h] J_{PC} = 97.4 Hz.
[i] Not assigned.
[j] J_{PC} = 100 Hz.
[k] J_{PC} = 9.9 Hz.
[l] J_{PC} = 9.8 Hz.
[m] J_{PC} = 12.3 Hz.

can be seen from the collected data, most of the corresponding protons resonated at practically the same frequencies for **1** and **2**, which also matched the model values of menthyl acetate. Only C12 methylene protons of **1** were found somewhat upfield from those of **2** and menthyl acetate, as were C18, C19 protons in **2** with respect to **1** and menthyl acetate. This was just opposite to what one could expect from the proximity of the P—Ph and *iso*-Pr and the P—Ph and C12 methylene protons, seen in the crystal conformations of **1** and **2**, respectively. It could therefore be suggested that from the point of view of the internal spatial relationship of ester and phosphinyl residues neither **1** nor **2** retains its crystal conformation in solution. A related question that remained open was whether this difference between the solid-state and solution conformations of **1** and **2** also includes different relative orientation of their P=O and C=O dipoles.

In an attempt to address the aforementioned question, a ^{1}H NMR spectrum of **1** in the presence of 1 equivalent of LiBr was run in $CDCl_3$ under exactly the same conditions as the one without added salt. It was assumed that little change in the spectrum of **1** should be observed upon its possible complexation with LiBr, except for the effects connected with a change in charge distribution (especially in the O=P—CH_2—C=O fragment), if only the crystal conformation of **1** also predominates in solution. A comparison of the two spectra (Table 3) reveals that, in line with expectations [11], in the spectrum of **1** + **LiBr** the two C1 methylene protons are shifted downfield by δ 0.16 and 0.36, respectively. At the same time, the appearance of these protons change from a six-line AB part of the ABX system of **1** into a fully resolved eight-line one ($\nu_A - \nu_B$ = 0.16 ppm) of **1** + **LiBr**, again in accord with the expected inclusion of this methylene into

TABLE 3 ^{1}H NMR Spectra of **1**, **2**, **1 + LiBr** and Menthyl Acetate in CDCl$_3$ (non-aromatic region)[a]

	^{1}*H NMR δ [ppm]*			
Proton[b]	**1 + LiBr**	**1**	**2**	*menthyl acetate*
H11	3.52 dd[c]	3.20[d]	3.21 d[e]	1.94 s
H12	3.36 dd[f]	3.20[d]	3.21 d[e]	
H31	6.71 ddd[g]	6.66 ddd[h]	6.67 ddd[i]	
H41	6.41 ddd[j]	6.40 ddd[k]	6.40 ddd[l]	
H42	6.30 ddd[m]	6.29 ddd[n]	6.30 ddd[o]	
H111	4.54 dt[p]	4.58 dt[q]	4.59 dt[q]	4.61 dt[p]
H121(ax)	0.72 m	0.61 m	0.88 m	0.88 m
H122(eq)	1.67 bd[r]	1.66 bd[r]	1.85 bd[s]	1.91 bd[r]
H131	1.32 bm	1.34 bm	1.37 bm	1.41 bm
H141(ax)	0.81 m	0.76 m	0.78 m	0.79 m
H142(eq)	1.60 bm	1.60 bm	1.60 bm	1.60 bm
H151(ax)	0.91 m	0.94 m	0.94 m	0.96 m
H152(eq)	1.60 bm	1.60 bm	1.60 bm	1.60 bm
H161	1.20 btt[t]	1.25 btt[u]	1.26 btt[t]	1.29 btt[v]
H171-3	0.80 d[w]	0.82 d[x]	0.86 d[w]	0.83 d[y]
H181	1.49 dsep[z]	1.75 dsep[z]	1.60 bm[aa]	1.80 dsep[z]
H191-3	0.53 d[bb]	0.65 d[bb]	0.59 d[y]	0.65 d[bb]
H201-3	0.73 d[bb]	0.81 d[bb]	0.78 d[y]	0.82 d[bb]

[a] Aromatic protons in all studied compounds gave typical patterns of multiplets at δ 7.32–7.64 (3H) and δ 7.71–7.83 (2H).

[b] Numbering of protons in **1** and **2** as well as in model menthyl acetate corresponds to crystallographic numbering of atoms as shown in Figures 1 and 2.

[c] J_{HH} = 16.4; J_{PH} = 14.4.

[d] Center of a six-line multiplet of AB part of ABX spin system.

[e] Deceptively simple doublet of AA′ part of AA′X spin system with line separation of 15.7 Hz corresponding to the averaged J_{AX} and $J_{A'X}$.

[f] J_{HH} = 16.4; J_{PH} = 14.8.

[g] J_{HH} = 18.6; 12.5; J_{PH} = 22.4.

[h] J_{HH} = 18.6; 12.5; J_{PH} = 28.0.

[i] J_{HH} = 18.6; 12.4; J_{PH} = 27.9.

[j] J_{HH} = 18.6; 1.5; J_{PH} = 23.2.

[k] J_{HH} = 18.6; 1.7; J_{PH} = 22.7.

[l] J_{HH} = 18.6; 1.8; J_{PH} = 22.7.

[m] J_{HH} = 12.6; 1.5; J_{PH} = 43.2.

[n] J_{HH} = 12.5; 1.7; J_{PH} = 42.0.

[o] J_{HH} = 12.4; 1.8; J_{PH} = 42.0.

[p] J_{HH} = 10.8; 4.3.

[q] J_{HH} = 10.9, 4.4.

[r] Only one arm of this bd is discerned.

[s] J_{HH} = 11.4.

[t] J_{HH} = 11.5, 3.0.

[u] J_{HH} = 12.2, 3.0.

[v] J_{HH} = 11.1, 3.0.

[w] J_{HH} = 6.6.

[x] J_{HH} = 6.8.

[y] J_{HH} = 7.0.

[z] J_{HH} = 6.9, 2.6.

[aa] Signal completely overlapped with H152, H142.

[bb] J_{HH} = 6.9.

a rigid six-membered ring of a bidentate complex.

Of the remaining protons in **1 + LiBr**, only the protons of the *iso*-Pr group were found shifted (upfield) in respect to those in **1**, with the C18 proton having experienced the largest (δ −0.28) shift. This particular observation seems to indicate clearly that the crystal conformation of **1** as shown in Figure 1 does not in fact predominate in solution; however, it can be readily restored to facilitate a bidentate complexation of **1** with LiBr.

IR, UV and Dipole Moments Measurements

IR spectroscopy gave us another possibility to directly compare the solid state (KBr) and solution ($CHCl_3$) spectra of **1** and **2**. These appeared different only in regions that could be associated with the phosphinyl parts of the two molecules. Each of the sharp bands of the KBr spectrum at 1115, 1600, and 1180 cm^{-1} in **1**, and at 1120, 1600, and 1195 cm^{-1} in **2**, which could be considered characteristic of the P—Ph, C=C, and P=O groupings [12], respectively, underwent splitting in solution into two, or even three, closely lying bands at 1110 and 1120, 1600 and 1615, and 1175, 1190 and 1210 cm^{-1}, respectively (same for **1** and **2**). These changes probably reflect the conformational variety of the possible arrangements of the Ph—P=O and C=C—P=O fragments in solution, contrasting sharply with their unique coplanar alignments in the crystal.

The UV spectra of **1** and **2** with their absorption bands at 200 and 220 nm enabled no insight into this conformational problem. Besides being identical for the two compounds, they were also superimposable with a spectrum of model 1-phenyl-2-phospholene oxide, for which the relative orientation of C=C and P=O is likely to differ from those in **1** and **2** for geometrical reasons.

Finally, the dipole moment measurements were carried out on **1** and **2**. Both the P=O and the C=O groups are strong dipoles and their relative spatial disposition in the molecule must affect the overall dipole moment significantly. The dipole moments for **1** and **2** in CCl_4 solutions were nearly identical, and were equal to 4.01 and 4.03 D, respectively. These values are to be compared with the dipole moments of 4.28 D and 2.24 D measured for model methylphenylvinylphosphine oxide and menthyl acetate, respectively. It can thus be concluded that, in contrast to the crystal state, the P=O and C=O groups in **1** and **2** prefer an anti array in solution, albeit to a small extent. An averaged value of ca 4.8 D calculated for **1** and **2** under condition of unrestricted rotation (with the corresponding bond angles taken from the X-ray data) corroborates this conclusion further.

CONCLUSIONS

The R_P absolute configuration for **1** and the S_P absolute configuration for **2** have been confirmed by the single-crystal X-ray diffraction analysis of the two compounds. The structural analysis revealed also that both molecules assume very similar conformations in the solid-state in which the C=C—P=O units exist in an *s*-cis array, and the C=O and P=O polar bonds are oriented uniformly in a syn, nearly parallel, fashion. Different relative orientations of these polar fragments in the crystal lattice cause considerable difference in crystallinity of **1** and **2**. In solution, the two compounds prefer the conformation with an anti arrangement of the

TABLE 4 Crystal Data and Experimental Parameters for **1** and **2**

	1	**2**
Molecular formula	$C_{20}H_{29}O_3P$	$C_{20}H_{29}O_3P$
Molecular weight	348.42	348.42
Space group	$P\ 2_12_12_1$	$P\ 2_1$
a(Å)	20.491(2)	9.266(1)
b(Å)	16.719(1)	9.852(1)
c(Å)	5.910(1)	10.954(1)
β(deg)	—	95.20(1)
V(Å^3)	2024.7(4)	995.9(2)
Z	4	2
D_x(Mg m^{-3})	1.13	1.16
D_m(Mg m^{-3})	1.14	1.15
Absorption coefficient, μ(cm^{-1})	12.95	13.17
F(000)	752	376
Radiation	CuK_α	CuK_α
Crystal size (mm)	0.3 × 0.2 × 0.5	0.3 × 0.25 × 0.4
Maximum and minimum hkl	$0 \leq h \leq 25$	$0 \leq h \leq 11$
	$0 \leq k \leq 20$	$0 \leq k \leq 11$
	$0 \leq l \leq 7$	$-13 \leq l \leq 13$
Unique data measured	2254	2078
2θ range (deg)	2–150	2–150
Reflections observed ($I > 3\sigma\|I\|$), n	2110	2048
R	0.047	0.039
R_w	0.055	0.041
R^-	0.052	0.043
R_w^-	0.063	0.046

TABLE 5 Positional Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for **1**

Atom	x^a	y^a	z^a	$B(Å^2)^{a,b}$
P	0.24726(3)	0.87516(3)	0.35517(9)	3.34(1)
O1	0.2069(1)	0.9027(1)	0.5484(4)	4.35(5)
O2	0.3495(1)	0.8812(2)	0.7565(5)	6.34(8)
O3	0.4249(1)	0.8441(1)	0.4995(3)	4.30(5)
C1	0.3315(1)	0.9107(1)	0.3623(6)	3.98(6)
C2	0.3684(1)	0.8773(2)	0.5606(6)	4.03(6)
C3	0.2176(1)	0.9070(2)	0.0847(5)	3.89(6)
C4	0.1632(1)	0.9476(2)	0.0707(7)	5.06(7)
C5	0.2556(1)	0.7678(1)	0.3436(5)	3.77(5)
C6	0.2831(2)	0.7295(2)	0.1571(6)	4.86(7)
C7	0.2890(2)	0.6470(2)	0.1539(8)	5.98(9)
C8	0.2669(2)	0.6023(2)	0.3370(8)	5.9(1)
C9	0.2399(2)	0.6400(2)	0.5193(7)	5.66(9)
C10	0.2336(1)	0.7230(2)	0.5254(6)	4.56(7)
C11	0.4658(1)	0.8131(2)	0.6844(5)	4.25(6)
C12	0.5041(1)	0.8819(2)	0.7864(6)	5.07(7)
C13	0.5476(2)	0.8513(3)	0.9784(7)	5.75(9)
C14	0.5931(2)	0.7874(3)	0.8895(9)	6.5(1)
C15	0.5561(2)	0.7205(2)	0.7716(9)	6.22(9)
C16	0.5103(2)	0.7486(2)	0.5862(6)	4.87(7)
C17	0.5847(3)	0.9207(3)	1.094(1)	8.2(1)
C18	0.4729(2)	0.6806(2)	0.4693(9)	6.3(1)
C19	0.5202(3)	0.6214(3)	0.359(1)	8.6(2)
C20	0.4253(3)	0.6379(4)	0.622(2)	9.6(2)

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[a] Values in parentheses are estimated standard deviations.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

C=O and P=O groups. However, **1** was shown to restore its crystal conformation in solution in the presence of LiBr in order to act as a bidentate ligand for lithium. A great facility of bidentate complexation of metal cations by phosphylacetates is therefore implied.

TABLE 6 Bond Lengths for **1**

Bond	*Length* (Å)^a	*Bond*	*Length* (Å)^a
O1–P	1.483(2)	C1–P	1.825(2)
C3–P	1.791(3)	C5–P	1.805(2)
C2–O2	1.223(4)	C2–O3	1.333(3)
C11–O3	1.472(3)	C2–C1	1.502(4)
C4–C3	1.308(3)	C6–C5	1.394(4)
C10–C5	1.385(4)	C7–C6	1.385(5)
C8–C7	1.392(6)	C9–C8	1.365(6)
C10–C9	1.394(5)	C12–C11	1.517(5)
C16–C11	1.527(5)	C13–C12	1.531(6)
C14–C13	1.512(7)	C17–C13	1.546(8)
C15–C14	1.521(6)	C16–C15	1.517(6)
C18–C16	1.535(5)	C19–C18	1.532(8)
C20–C18	1.509(9)		

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[a] Values in parentheses are estimated standard deviations.

EXPERIMENTAL

Compounds

Phosphinylacetates (+)-**1** and (−)-**2** were obtained in a reaction of butyl phenylvinylphosphinite with menthyl bromoacetate as described previously [2]. (−)-**2** crystallized out of the reaction mixture and was collected by filtration. Recrystallization from benzene gave an analytical sample of (−)-**2**. A small sample of (+)-**1** was obtained by extraction of the crude reaction mixture with hexane followed by several recrystallizations of the isolated material from this solvent. (+)-**1**: $[\alpha]_D$ = +5° (c, 3.2, $CHCl_3$); mp 74°C; δ_P(benzene) 19.90. (−)-**2**: $[\alpha]_D$ = −93° (c, 4.8, $CHCl_3$); mp 152°C; δ_P(benzene) 19.93.

General

All NMR spectra were obtained on a Bruker MSL-300 spectrometer at 75.47 and 300.13 MHz frequencies for ^{13}C and ^1H, respectively. For ^{13}C CP–MAS (cross-polarization magic-angle spinning) experiments a 7-mm rotor was used and the spinning rates of 4.5–5.0 kHz were applied. The IR spectra were recorded on a UR-10 Carl–Zeiss spectrometer. For recording the UV spectra a Kontron UVIKON 860 instrument was used. The dipole moments were de-

TABLE 7 Bond Angles for **1**

Bonded atoms	*Bond angle (°)*[a]	*Bonded atoms*	*Bond angle (°)*[a]
C1–P–O1	114.1(1)	C3–P–O1	113.9(1)
C3–P–C1	104.2(1)	C5–P–O1	113.0(1)
C5–P–C1	103.6(1)	C5–P–C3	107.1(1)
C11–O3–C2	116.1(2)	C2–C1–P	111.9(2)
O3–C2–O2	123.6(3)	C1–C2–O2	124.0(2)
C1–C2–O3	112.3(2)	C4–C3–P	120.0(1)
C6–C5–P	121.7(2)	C10–C5–P	118.5(2)
C10–C5–C6	119.8(2)	C7–C6–C5	120.2(3)
C8–C7–C6	119.8(3)	C9–C8–C7	119.9(3)
C10–C9–C8	121.2(4)	C9–C10–C5	119.2(3)
C12–C11–O3	108.9(2)	C16–C11–O3	107.8(2)
C16–C11–C12	112.1(3)	C13–C12–C11	110.1(3)
C14–C13–C12	109.7(3)	C17–C13–C12	111.4(4)
C17–C13–C14	112.4(3)	C15–C14–C13	111.8(3)
C16–C15–C14	114.3(3)	C15–C16–C11	108.3(3)
C18–C16–C11	113.4(3)	C18–C16–C15	113.8(3)
C19–C18–C16	110.8(4)	C20–C18–C16	113.8(4)
C20–C18–C19	111.0(4)		

[a] Values in parentheses are estimated standard deviations.

TABLE 8 Positional Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations for **2**

Atom	x^a	y^a	z^a	$B(A^2)^{a,b}$
P	0.57138(4)	0.93890	0.96376(4)	3.25(1)
O1	0.5842(2)	1.0869(2)	0.9407(2)	4.50(4)
O2	0.7046(3)	1.0365(3)	1.2365(2)	6.46(6)
O3	0.7118(2)	0.8098(2)	1.2595(2)	4.16(4)
C1	0.5302(2)	0.8967(3)	1.1184(2)	3.73(5)
C2	0.6563(2)	0.9151(3)	1.2109(2)	3.70(5)
C3	0.4287(2)	0.8589(3)	0.8691(2)	4.15(6)
C4	0.3543(3)	0.9296(5)	0.7834(2)	5.64(7)
C5	0.7348(2)	0.8470(3)	0.9409(2)	3.44(5)
C6	0.7434(3)	0.7071(3)	0.9567(3)	4.77(6)
C7	0.8706(4)	0.6408(5)	0.9329(4)	6.64(9)
C8	0.9863(3)	0.7108(5)	0.8968(3)	6.9(1)
C9	0.9780(3)	0.8495(5)	0.8833(3)	6.8(1)
C10	0.8516(2)	0.9190(4)	0.9044(2)	4.98(7)
C11	0.8361(2)	0.8194(3)	1.3505(2)	3.90(5)
C12	0.9721(3)	0.7910(4)	1.2875(2)	5.00(7)
C13	1.1060(3)	0.7933(4)	1.3796(3)	5.25(7)
C14	1.0846(3)	0.6922(4)	1.4816(3)	5.42(7)
C15	0.9474(3)	0.7203(4)	1.5432(2)	5.21(8)
C16	0.8129(2)	0.7173(3)	1.4504(2)	4.16(5)
C17	1.2426(4)	0.7624(6)	1.3146(5)	7.6(1)
C18	0.6680(3)	0.7380(4)	1.5068(2)	5.25(7)
C19	0.6383(4)	0.6245(6)	1.5959(4)	7.9(1)
C20	0.6568(4)	0.8756(5)	1.5688(4)	7.1(1)

[a] Values in parentheses are estimated standard deviations.

[b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

termined by literature methods [13], employing a Dipolmeter DM 01. A precision of ± 0.02 D is ascribed to the dipole moments reported in this work.

X-Ray Diffraction Measurements

Crystals of **1** and **2** suitable for X-ray investigation were obtained by crystallization from hexane and benzene, respectively. The cell parameters and intensities were measured on an Enraf-Nonius CAD4 diffractometer. Accurate cell parameters were determined from a least-squares refinement of the $(\sin \theta/\lambda)^2$ values for 25 reflections. The intensity data were collected using graphite-monochromated CuKα radiation and the ω-2θ scan technique. The measured intensities were corrected for Lorentz, polarization, absorption, and extinction effects. Crystal data and experimental details for **1** and **2** are listed in Table 4.

Solution and Refinement of the Structure

The structure was solved by direct methods using the SHELXS-86 program [14], and was refined by the full-matrix least-squares method. All nonhydrogen atoms were refined with anisotropic thermal parameters; H atoms were refined in the riding mode. The function $\Sigma w([F_o] - [F_c])^2$ was minimized, and in the final cycles of calculation a weighting based on counting statistics was used with $w = [\sigma^2(F_o) + 0.0073(F_o)^2]^{-1}$ for **1** and $w = [\sigma^2(F_o) + 0.0033(F_o)^2]^{-1}$ for **2**. An empirical isotropic extinction correction was introduced, and the parameter x was refined to the value 0.015(2) and 0.051(5) for **1** and **2**, respectively. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. The final difference Fourier map did not show any peaks higher than 0.24 eÅ^3 for **1** and 0.31 eÅ^3 for **2**. Most of the computations were performed with the SHELX-76 crystal structure determination program [15] on an AMSTRAD 1512 microcomputer. The final positional parameters of nonhydrogen atoms, bond lengths, and bond angles for **1** and **2** are listed in Tables 5, 6 and 7, and Tables 8, 9 and 10, respectively.

TABLE 9 Bond Lengths for 2

Bond	*Length (Å)*[a]	*Bond*	*Length (Å)*[a]
O1–P	1.486(2)	C1–P	1.818(2)
C3–P	1.788(3)	C5–P	1.801(2)
C2–O2	1.209(4)	C2–O3	1.337(3)
C11–O3	1.456(3)	C2–C1	1.502(3)
C4–C3	1.313(4)	C6–C5	1.390(4)
C10–C5	1.383(4)	C7–C6	1.393(5)
C8–C7	1.363(5)	C9–C8	1.376(7)
C10–C9	1.394(4)	C12–C11	1.517(3)
C16–C11	1.516(4)	C13–C12	1.527(4)
C14–C13	1.523(5)	C17–C13	1.536(5)
C15–C14	1.518(4)	C16–C15	1.536(3)
C18–C16	1.541(3)	C19–C18	1.526(6)
C20–C18	1.524(6)		

[a] Values in parentheses are estimated standard deviations.

Absolute Configuration

The absolute configuration was determined by the Hamilton method [16]. The model of the structure with the reversed sign of all the positional atom

TABLE 10 Bond Angles for 2

Bonded atoms	*Bond angle (°)*[a]	*Bonded atoms*	*Bond angle (°)*[a]
C1–P–O1	114.2(1)	C3–P–O1	113.6(1)
C3–P–C1	103.4(1)	C5–P–O1	112.8(1)
C5–P–C1	105.4(1)	C5–P–C3	106.5(1)
C11–O3–C2	118.0(2)	C2–C1–P	111.7(2)
O3–C2–O2	123.9(2)	C1–C2–O2	125.1(2)
C1–C2–O3	110.9(2)	C4–C3–P	119.5(3)
C6–C5–P	118.2(2)	C10–C5–P	121.3(2)
C10–C5–C6	120.4(2)	C7–C6–C5	118.8(3)
C8–C7–C6	121.2(4)	C9–C8–C7	119.7(3)
C10–C9–C8	120.6(4)	C9–C10–C5	119.2(3)
C12–C11–O3	108.4(2)	C16–C11–O3	107.2(2)
C16–C11–C12	112.6(2)	C13–C12–C11	110.8(2)
C14–C13–C12	108.9(3)	C17–C13–C12	110.2(3)
C17–C13–C14	112.5(3)	C15–C14–C13	112.2(3)
C16–C15–C14	111.4(2)	C15–C16–C11	107.8(2)
C18–C16–C11	112.8(2)	C18–C16–C15	114.6(2)
C19–C18–C16	111.9(3)	C20–C18–C16	113.2(3)
C20–C18–C19	110.1(3)		

[a] Values in parentheses are estimated standard deviations.

parameters was refined as described above. The resulting R^- and R_w^- values of 0.052 and 0.063 for **1** showed that the model with inverse configuration has to be rejected at a very high probability level: $R_w(b,N,\alpha) = R_w(1, 1863, \alpha) = 1.145$ gives $\alpha < 10^{-6}$, where $b = 1$ is the dimension of the hypothesis and $N = 1863$ is the number of reflections minus number of refined parameters [17]. Analogously for **2**: $R_w(b,N,\alpha) = R_w(1, 1802, \alpha) = 1.122$ gives $\alpha < 10^{-6}$.

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