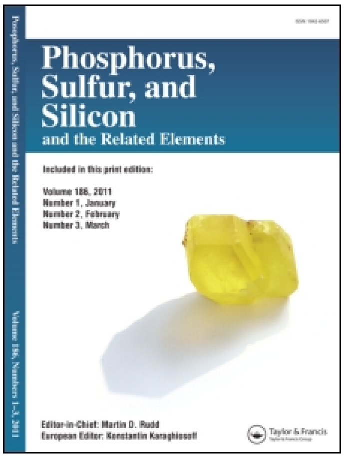

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DETERMINATION OF THE ABSOLUTE CONFIGURATIONS OF 1,2-DIPHOSPHINYLETHANES AND 1,2-DIPHOSPHINYLETHENES POSSESSING TWO NONEQUIVALENT ASYMMETRIC PHOSPHORUS CENTRES. CRYSTAL STRUCTURE OF (*R*,*S*)-1-(*tert*-BUTYLPHENYLPHOSPHINYL)-2-(METHYL-PHENYLPHOSPHINYL)ETHANE.[1]

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DETERMINATION OF THE ABSOLUTE CONFIGURATIONS OF 1,2-DIPHOSPHINYLETHANES AND 1,2-DIPHOSPHINYLETHENES POSSESSING TWO NONEQUIVALENT ASYMMETRIC PHOSPHORUS CENTRES. CRYSTAL STRUCTURE OF (*R*,*S*)-1-(*tert*-BUTYLPHENYLPHOSPHINYL)-2-(METHYLPHENYLPHOSPHINYL)ETHANE.[1]

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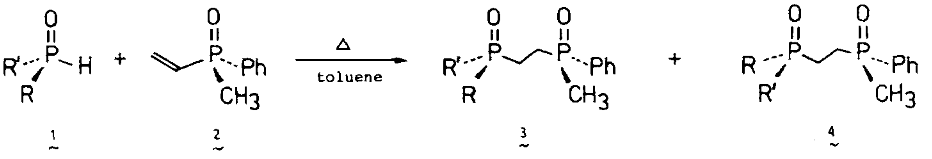
Using single-crystal X-ray diffraction technique the *R*, *S* configuration has been assigned to a homochiral (−)-1-*tert*-butylphenylphosphinyl-2-methylphenylphosphinylethane. This has allowed the assignment of absolute configuration also to its P1-epimer as well as, through chemical correlation, to the two epimeric *trans*-1-*tert*-butylphenylphosphinyl-2-methylphenylphosphinylethenes. Attempted correlation of absolute configurations of the assigned compounds with their spectral and physical features holds some promise as a diagnostic tool for future distinction of epimeric P-chiral 1,2-diphosphinylethanes and 1,2-diphosphinylethenes possessing similar aryl alkyl substitution pattern at phosphorus.

Key words: 1,2-Diphosphinylethanes; 1,2-diphosphinylethenes; enantiomeric; configuration; X-ray; hydrogenation.

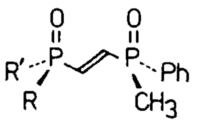
INTRODUCTION

Optically active P-chiral 1,2-diphosphinoethanes constitute an important class of chiral bidentate ligands of great practical utility in the field of asymmetric catalysis.[2] The corresponding P-chiral dioxides, which are the most direct precursors to such ligands,[3] have recently been shown easily accessible through a simple conjugate addition of secondary phosphine oxides **1** to a homochiral (−)-(*S*)-methylphenylphosphine oxide **2**[4] (Equation 1). In the additions involving nonsymmetrical secondary phosphine oxides **1** (R ≠ R′), mixtures of nearly equal amounts of two epimeric 1,2-diphosphinylethanes **3** and **4** differing in configuration of the newly resolved P-centre were typically obtained.[4] Due to their diastereomeric nature the epimers could be readily separated by crystallization or by chromatography on silicagel. However, in only one case, i.e., when R = CH_3, R′ = Ph, a configurational distinction between the two homochiral species appeared straightforward. Simple optical rotation measurements assigned promptly the *S*, *S* configuration to the levorotatory **4a** (R = CH_3, R′ = Ph) and,



(1)

by default, the *R*, *S* configuration to the optically inactive (meso) **3a** (R = CH_3, R′ = Ph). Likewise, for similarly prepared pairs of homochiral *trans*-1,2-diphosphinylethenes **5**, **6**[5] assignment of configuration was again possible only for the analogous symmetrically substituted compounds **5a** and **6a** when R = CH_3 and R′ = Ph. For all the other synthesized[4,5] pairs of compounds of type **3**, **4** and **5**, **6** (R ≠ R′) the sense of chirality of the epimeric centres in individual isomers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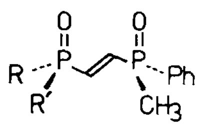
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remain obscured. As these compounds are the unique examples of the homochiral 1,2-diphosphinylethanes and 1,2-diphosphinylethenes possessing two non-equivalent asymmetric phosphorus centres and, are of potential utility as precursors to a yet untested type[2] of chiral ligands, we considered it important to establish their absolute configurations unequivocally and to attempt to correlate their configurational differentiation with the pertinent spectral and/or physical data. In this paper we wish to report on the assignment of absolute configurations to the first two non-symmetrical 1,2-diphosphinylethanes of this type, i.e., **3b** and **4b** (R = Bu^t, R′ = Ph), as well as to their two dehydro counterparts **5b** and **6b** (R = Bu^t, R′ = Ph). The assignment follows from a single-crystal X-ray diffraction study of **4b** and from a subsequent chemical correlation of **6b** to **4b**.

RESULTS AND DISCUSSION

Crystal Structure of Diphosphinylethane 4b

The molecular structure of **4b** is displayed in Figure 1 which shows also its absolute configuration. According to Cahn–Ingold–Prelog rules[6] the configuration at P1 is *R* and at P2 is *S*. The molecule assumes in the solid state a staggered, almost fully stretched conformation[7] as indicated by the following torsional angles: C3–P1–C1–C2, −178.3 (5); P1–C1–C2–P2, −168.0 (4) and C1–C2–P2–C14, −167.3 (6)°. The largest substituents of each phosphorus atom are placed in the most distanct zig-zag positions and P1–O1 and P2–O2 dipoles are oriented in the opposite directions. Typical for compounds of type R_3PO deformations of the

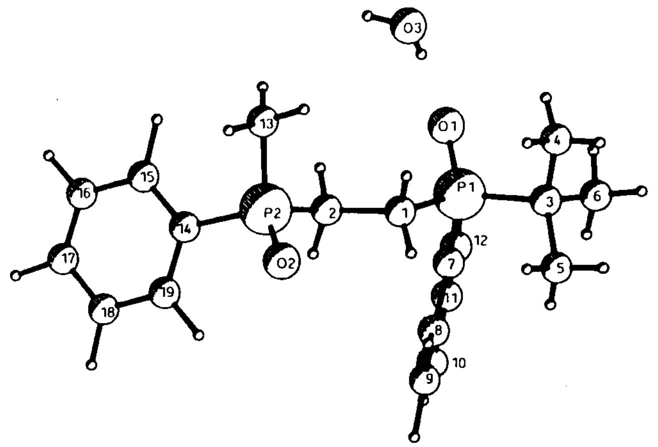


FIGURE 1 Projection of the molecule viewed along *a*, including molecule of hydrating water, with atom labelling.

P coordinating tetrahedrons comprising of an increase of the O–P–C and the simultaneous decrease of the C–P–C valency angles are detected. The found values fall in the range of 110.3(3)–112.3(3)° and 104.7(3)–107.3(5)° for P1 and, 110.5(4)–115.1(5)° and 104.7(3)–107.3(5)° for P2, respectively. Other structural parameters are similar to those commonly observed and therefore do not need to be discussed in detail.

As earlier alluded by its ^{1}H NMR spectra, the studied compound shows a considerable tendency to crystallize as a hydrate. In the analyzed crystal the presence of four molecules of water in the unit cell is in fact evidenced (Figure 2). The water molecules link the molecules of **4b** into chains by means of intermolecular hydrogen bonds connecting the O1 of one molecule with the O2 of the neighbouring one translated along the *x* axis. The details of this bonding are listed in Table I. Other intermolecular and intramolecular distances between nonbonded atoms are close to or greater than the pertinent sums of van der Waals radii.

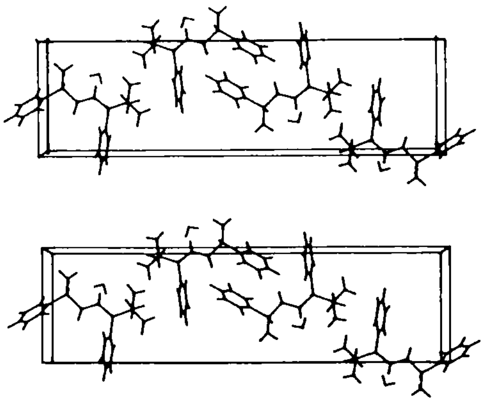


FIGURE 2 The packing in the unit cell. *c* and *b* are parallel to the bottom and side of the page, respectively, and the view is down *a*.

TABLE I

Details of hydrogen bonding involving **4b** and crystallization water

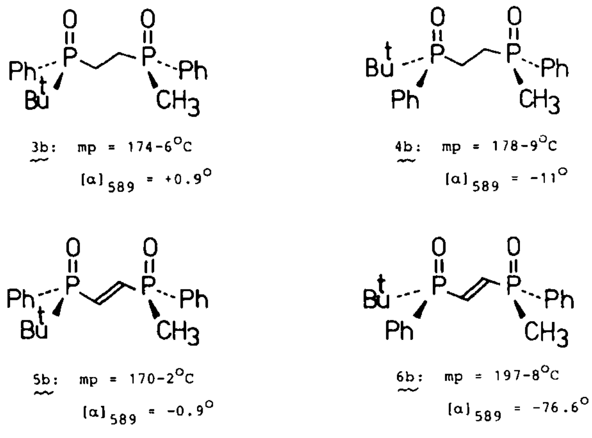
	Distance (A)			Angle (°)
D—H···A	D—H	D···A	H···A	D—H···A
O3-H32···O1	0.86(9)	2.903(7)	2.05(9)	176(7)
O3-H31···O2[a]	0.88(8)	2.833(9)	1.96(8)	171(8)

Symmetry code: none x, y, z.

[a] $x - 1, y, z$.

Assignment of Absolute Configurations

The four studied compounds **3b**, **4b** and **5b**, **6b** are depicted in their absolute configurations in Chart 1. By virtue of their synthesis (starting from the homochiral (*S*)-**2**), all these compounds possess the *S* configuration at the methylphenylphosphinyl phosphorus (P2) and differ only, within each pair, in the configuration at the respective *tert*-butylphenylphosphinyl centres (P1). Therefore, the above presented assignment of the (*R*)-P1, (*S*)-P2 configuration to **4b** enabled us to assign promptly the corresponding (*S*)-P1, (*S*)-P2 configuration to **3b**. A subsequent straightforward chemical transformation of **6b** into **4b** (Equation 2) interlocked configurations of these two compounds



3b: mp = 174-6°C $[\alpha]_{589}$ = +0.9°

4b: mp = 178-9°C $[\alpha]_{589}$ = -11°

5b: mp = 170-2°C $[\alpha]_{589}$ = -0.9°

6b: mp = 197-8°C $[\alpha]_{589}$ = -76.6°

CHART 1 Assignment of absolute configurations to **3b**, **4b** and **5b**, **6b**.

$$\mathbf{6b} \xrightarrow[\text{Pd/C, CH}_3\text{OH}]{[\text{H}_2]} \mathbf{4b} \tag{2}$$

and, ultimately, assigned the (*S*)-P1, (*S*)-P2 configuration to the remaining **5b**.

The spectral comparison of the identified homochiral compounds by means of ^{1}H, ^{13}C and ^{31}P NMR techniques revealed only subtle differences among the pairs of epimers. However, in ^{1}H NMR spectra those differences, albeit small, exhibit

TABLE II

Selected ^{1}H NMR and TLC data for diphosphinylethanes **3**, **4**, and diphosphinylethenes **5**, **6**

	3a	**4a**	**5a**	**6a**	**3b**	**4b**	**5b**	**6b**
$\delta_H{}^a$CH$_3$	1.63	1.71	1.71	1.78	1.58	1.73	1.73	1.79
$\delta_H{}^a$Bu^t	—	—	—	—	0.96	1.09	1.04	1.09
R$_F$ (TLC^b)	0.35	0.32	0.48	0.42	0.47	0.39	0.62	0.54

[a] From spectra recorded in CDCl$_3$ on a Brucker MSL-300 (300 MHz) spectrometer.
[b] For CHCl$_3$–MeOH 12:1 as eluent.

considerable regularity which might have some potential of becoming diagnostic of configuration at phosphorus in other P-chiral (aryl, alkyl substituted) 1,2-diphosphinylethanes and 1,2-diphosphinylethenes.

As appears from ^{1}H NMR data collected for the four pairs of compounds of this type assigned heretofore (Table II) protons of the terminal P-alkyl substituents in the meso or meso-type isomers (by a generalized aryl vs. alkyl distinction of substituents) resonated uniformly at somewhat higher field than in their epimeric counterparts. This trend holds nicely in the two symmetrical pairs **3a**, **4a** and **5a**, **6a** even though these compounds lend only one such signal for comparison.

Interestingly, similar discriminating pattern has also been revealed in routine TLC analysis in which, in every studied pair of epimeric compounds, the meso or meso-type isomer was identified, again uniformly, to be the one which moved on silicagel faster. (The pertinent R$_F$ values are listed in Table II).

It is therefore tempting to suggest that by the combined use of ^{1}H NMR and TLC techniques a preliminary configurational recognition in the pairs of epimeric 1,2-diphosphinylethanes and 1,2-diphosphinylethenes possessing nonequivalent aryl alkyl substitution pattern at P may appear possible.

An analysis of this kind performed with still another pair of 1,2-diphosphinylethanes, i.e., **3c**, **4c**^{4} (separated but individually not fully assigned yet), gives further credit to this premise. As follows from the data displayed in Chart 2, again, the "faster" epimer had the pertinent proton resonances at higher field than the "slower" one. This, by the suggested token, infers the assignment of the meso-type configuration to **3c**, as depicted.^{8} The proposed assignment remains however, to be unequivocally confirmed.

3c: mp = 218-9°C
δ_H CH$_3$ 1.57
δ_H PhCH$_2$ 3.19
R$_F$ = 0.44

4c: mp = 173-5°C
δ_H CH$_3$ 1.59
δ_H PhCH$_2$ 3.27
R$_F$ = 0.37

CHART 2 Identification of epimers **3c** and **4c**.

EXPERIMENTAL SECTION

Preparation of compounds described in this study is reported elsewhere.[4,5] Reported melting points are uncorrected. A crystal of **4b** suitable for X-ray diffraction analysis was obtained by slow crystallization from benzene.

Crystal Structure Determination

Crystal data: $C_{19}H_{26}O_2P_2{\cdot}H_2O$, $M = 366.4$. Orthorhombic. $a = 6.119(2)$, $b = 9.547(1)$, $c = 34.132(4)$ Å. Space group $P2_12_12_1$, $V = 1993.9(7)$ A.^{3} $d_c = 1.220\ \mathrm{gcm}^{-3}$, $Z = 4$, $\mu = 2.25\ \mathrm{cm}^{-1}$, $F(000) = 784$. Approximate crystal dimensions $0.3 \times 0.2 \times 0.2$ mm. Crystallographic measurements were made at room temperature using Enraf Nonius CAD-4 diffractometer operating in the $\omega - 2\theta$ scan mode. The intensity data were collected within a θ range 1–25° using graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ A). Intensities of 1651 unique reflections were measured of which 1344 satisfied the criterion $I \geq 2.5\sigma$ (I) and were used in the structure solution by direct methods employing SHELX 86.[9] Corrections were applied for L_P but not for absorption or extinction. Positional and thermal parameters were refined by full-matrix least squares minimizing the function $\sum w(F_0 - F_c)^2$ with $w = 1/\sigma^2(F)$ for the observed reflections and, $w = 0$ for unobserved reflections. All the hydrogen atoms were revealed in difference Fourier maps and their positional and isotropic thermal parameters were included in the refinements except for hydrogens of one phenyl ring, i.e., H151, H161, H171, H181 and H191 (large temperature parameters of the corresponding carbons indicated sizeable disorder). Convergence was obtained at $R = 0.0457$ and $R_w = 0.0368$. The final difference map showed only peaks $\leq 0.2\ \mathrm{e\AA}^{-3}$.

The absolute configuration was determined by Hamilton method.[10] The model of the structure was refined as described above with the reversed signs of all the f''_- values. The resulting R^- and R_w^- values of 0.0459 and 0.0371 indicated that, with the high probability, the model with inverse configuration has to be rejected. The R_w-ratio = 1.0082, the significance level $\alpha \leq 5 \times 10^{-5}$.[11]

The calculations were performed using program SHELX 76.[12] Table III gives the atomic coordinates and Table IV the bond lengths and angles. Figure 1 shows the structure and atom numbering and Figure 2 the unit cell viewed along the a axis. Tables listing anisotropic thermal parameters and hydrogen atoms parameters have been deposited with the Cambridge Crystallographic Data Centre, U.K.

TABLE III

Positional parameters ($\times 10^4$) for the nonhydrogen atoms

	x/a	y/b	z/c
P1	7377(3)	5913(2)	1694(0)
P2	9628(3)	4052(2)	579(1)
O1	4969(6)	5803(4)	1616(1)
O2	11901(9)	3648(7)	671(2)
O3	3881(11)	2950(6)	1395(2)
C	8942(13)	4882(8)	1353(2)
C2	8523(17)	5295(9)	927(2)
C3	8103(9)	5339(6)	2190(2)
C4	10564(14)	5340(11)	2253(3)
C5	7199(17)	3854(8)	2248(3)
C6	6980(17)	6356(10)	2476(2)
C7	8282(10)	7710(6)	1634(2)
C8	10446(12)	8082(7)	1547(2)
C9	10967(13)	9481(7)	1499(2)
C10	9416(14)	10500(7)	1540(2)
C11	7297(13)	10147(7)	1623(2)
C12	6733(11)	8771(7)	1676(2)
C13	7705(24)	2624(10)	561(3)
C14	9499(14)	4943(7)	113(2)
C15	7706(19)	4875(12)	−126(2)
C16	7724(23)	5559(15)	−481(3)
C17	9401(25)	6375(11)	−589(2)
C18	11144(22)	6472(11)	−349(3)
C19	11192(16)	5746(10)	0(3)

TABLE IV

Bond lengths (Å) and Bond angles (°)

O1-P1	1.501(4)	C-P1	1.800(7)
C3-P1	1.836(6)	C7-P1	1.814(6)
O2-P2	1.477(6)	C2-P2	1.809(8)
C13-P2	1.802(11)	C14-P2	1.806(7)
C2-C1	1.527(10)	C4-C3	1.521(10)
C5-C3	1.535(10)	C6-C3	1.537(10)
C8-C7	1.403(9)	C12-C7	1.395(8)
C9-C8	1.382(9)	C10-C9	1.367(10)
C11-C10	1.369(10)	C12-C11	1.370(9)
C15-C14	1.371(11)	C19-C14	1.346(10)
C16-C15	1.375(12)	C17-C16	1.341(15)
C18-C17	1.349(15)	C18-C19	1.379(13)

C1-P1-O1	111.7(3)	C3-P1-O1	112.3(3)
C3-P1-C1	107.8(3)	C7-P1-O1	110.3(3)
C7-P1-C1	106.4(3)	C7-P1-C3	108.2(3)
C2-P2-O2	112.6(4)	C13-P2-O2	115.1(5)
C13-P2-C2	106.0(5)	C14-P2-O2	110.5(4)
C14-P2-C2	104.7(3)	C14-P2-C13	107.3(5)
C2-C-P1	112.6(5)	C-C2-P2	113.1(5)
C4-C3-P1	111.6(5)	C5-C3-P1	107.9(5)
C5-C3-C4	109.9(7)	C6-C3-P1	106.8(5)
C6-C3-C4	110.7(7)	C6-C3-C5	110.0(7)
C8-C7-P1	123.5(5)	C12-C7-P1	117.9(5)
C12-C7-C8	118.6(6)	C9-C8-C7	119.2(7)
C10-C9-C8	121.1(7)	C11-C10-C9	120.2(6)
C12-C11-C10	120.2(7)	C11-C12-C7	120.7(7)
C15-C14-P2	122.6(7)	C19-C14-P2	119.3(7)
C19-C14-C15	118.1(7)	C16-C15-C14	119.8(10)
C17-C16-C15	121.7(11)	C18-C17-C16	118.5(9)
C18-C19-C14	121.3(9)	C19-C18-C17	120.6(10)

Hydrogenation of **6b**. Low pressure hydrogenation of **6b** (0.1 g, 0.29 mmol) in methanol (3 ml) with 10% Pd/C as a catalyst (10 mol %) was carried out at room temperature until complete reduction of the sample was apparent from TLC monitoring (20 h). Removal of methanol and the catalyst gave crystalline product which, after recrystallization from benzene gave 76 mg (76%) of pure **4b**: $mp = 156 - 8 \cdot 5$°C; $[\alpha]_{589} = -9.7°$ (c, 1.3, $CHCl_3$), which compared favorably with the sample furnished by conjugate addition.[4] (The differences observed are probably due to the lack of crystallization water (^1H NMR) in the crystals of **4b** obtained from hydrogenation reaction.)

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