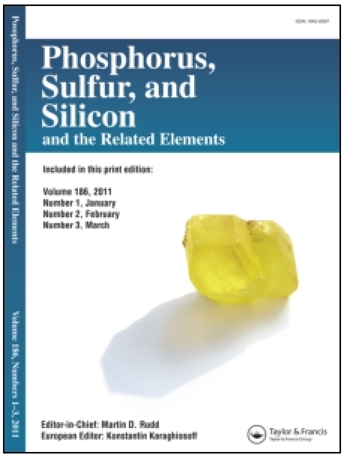


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

OPTICALLY ACTIVE SPIROPHOSPHORANES. ABSOLUTE CONFIGURATION AND SEPARATION OF THE CONTRIBUTIONS OF THE HELIX AND THE LIGANDS TO THE OPTICAL ROTATION

A. Klaebe[a]; J. F. Brazier[a]; B. Garrigues[a]; R. Wolf[a]; Y. Stefanovsky[b]
[a] Equipe de Recherche du CNRS n° 82, Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université P. Sabatier, Toulouse cedex, France [b] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Klaebe, A. , Brazier, J. F. , Garrigues, B. , Wolf, R. and Stefanovsky, Y.(1981) 'OPTICALLY ACTIVE SPIROPHOSPHORANES. ABSOLUTE CONFIGURATION AND SEPARATION OF THE CONTRIBUTIONS OF THE HELIX AND THE LIGANDS TO THE OPTICAL ROTATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 1, 53 — 59

To link to this Article: DOI: 10.1080/03086648108078272

URL: http://dx.doi.org/10.1080/03086648108078272

Phosphorus and Sulfur, 1981, Vol. 10, pp. 53–59
0308-664X/81/1002-0953$06.50/0

OPTICALLY ACTIVE SPIROPHOSPHORANES. ABSOLUTE CONFIGURATION AND SEPARATION OF THE CONTRIBUTIONS OF THE HELIX AND THE LIGANDS TO THE OPTICAL ROTATION

A. KLAEBE, J. F. BRAZIER, B. GARRIGUES and R. WOLF

Equipe de Recherche du CNRS n° 82, Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université P. Sabatier, 31062 Toulouse cedex, France

and

Y. STEFANOVSKY

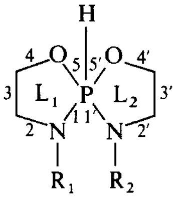
Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

(*Received June 6, 1980*)

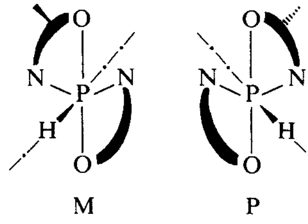
The molecular rotation of optically active spirophosphoranes containing ephedrine and other optically active ligands, is separated into several independent components giving the rotational contributions of the ligands and the helix structure. Using this separation as well as the X-ray data for the structure of the compound with two (-)ephedrine ligands, it is shown that in the case of two ephedrine ligands the M-helix is levorotatory and therefore the M-isomer is more negative. This allows the prediction of the absolute configuration of a large number of compounds including also some new ones. The influence of the structure and the configuration of the ligands on the components of the molecular rotation is discussed. Ephedrine ligands with erythro-configuration have a larger contribution to the rotation than the corresponding threo-isomers. The separation into independent components allows the application of the principle of optical superposition for calculation of the molecular rotation and its components for new representatives of this class of compounds. A very strong ligand effect is observed in the case of one optically inactive *o*-aminophenol ligand, explained at the moment by nonbonded interactions between the substituents in the active ligand and the conjugated *o*-aminophenol system. The observed strong increase of the helix contribution in the same case is due probably to the increased atomic asymmetry of the chiral P-atom.

INTRODUCTION

A large number of optically active spirophosphoranes of the type (Structure 1) have been synthesized recently where at least one of the ligands (L_1 or L_2) is derived from optically active ephedrine (E), norephedrine (NE), pseudoephedrine (ψE), pseudonorephedrine (ψNE) or phenylglycine (PhGl), alaninol (ALOL) and alanine (ALA).[1–5] In all cases, two diastereomers were observed[6] (Structure 2). Usually only one of them was isolated after the synthesis as a result of a second-order asymmetrical transformation.[7] The second one was observed spectroscopically (^{31}P, ^{1}H N.m.r) and its molecular rotation was determined polarimetrically during the study of the barrier of isomerization (see experimental part).

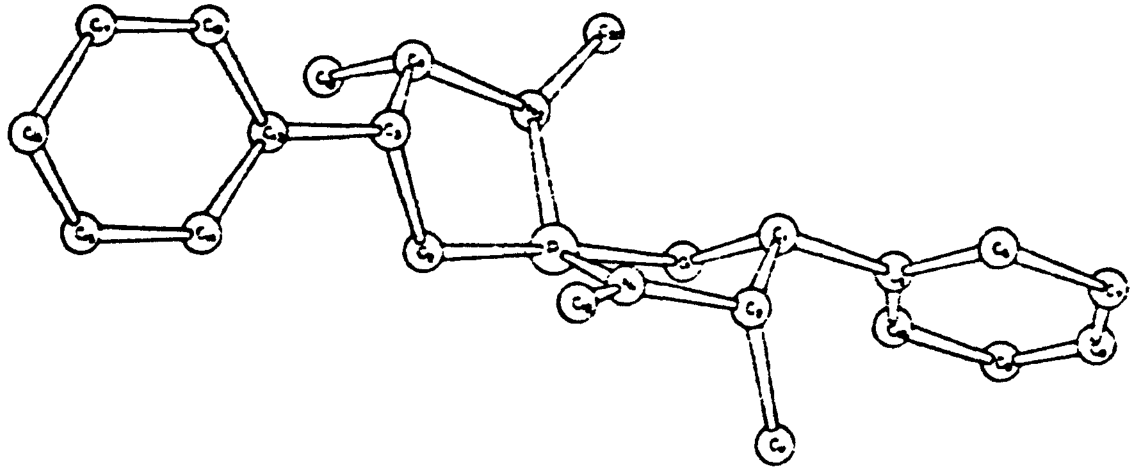


STRUCTURE 1



STRUCTURE 2

The existence of enantiomeric helixes in each diastereomer was proved and an attempt was made to determine their specific rotations.[2] In the case when $L_1 = L_2 =$ (-) E the absolute configuration of the helix in the isolated diastereomer was determined by means of X-ray analysis and found to be a levorotatory M-helix:[8] (Structure 3). The present work attempts to separate the contributions of the ligands and the helix to the molecular rotation and to study the influence of the structure and configuration of the ligands on the rotatory



STRUCTURE 3

power of the compounds. It is also attempted to demonstrate the possibility for predicting the molecular rotations of new compounds or the absolute configurations of the compounds studied here.

RESULTS AND DISCUSSION

All compounds with two ephedrine ligands, described in previous work are listed in Table I numbers (**1**) to (**7**). The molecular rotations: ϕ are reduced to 436 nm.† The molecular rotation of the spirophosphoranes in question could be represented as a sum of the rotation of the helix (ϕ_{Hel}), the contribution of the conformational asymmetry of the ligands (C_L), the atomic asymmetry of the P-atom in the case of two different ligands (A_P) and the atomic asymmetry of the chiral centers of the ligands (A_L):

$$\phi = \phi_{\mathrm{Hel}} + C_L + A_p + A_L \qquad (1)$$

In a first approximation, one can assume that the helix contribution (ϕ_{Hel}) in both diastereomers of this type is equal and independent of the other members (see below). The detailed consideration of the conformational contribution (C_L) leads us to propose its separation into two effects:

1) Conformational effect around bonds 2, 3 and 4 (and resp. 2′, 3′ and 4′) (Structure 1). This effect is constant for every ligand in all compounds, independent of the other ligand and with the same sign in both diastereoisomers. It has been demonstrated using X-ray structure determination and nmr spectroscopy that the envelope conformation of ligands derived from 1-phenyl, 2-methyl ethanolamines, in hydrogenospirophosphoranes, is independent of the helicity of the spiro skeleton. It depends only on the configuration of the carbon bearing the phenyl group.

2) Conformational effect around the bonds 1, 5 and 1′, 5′ (Structure 1). This effect is different when two ephedrines ($R_1 = R_2 = CH_3$), two norephedrines ($R_1 = R_2 = H$) or two different ligands ($R_1 = CH_3, R_2 = H$) are fixed on the molecule and independent of the configuration of the carbon atoms of the ligands. Its sign is opposite in both isomers. The evaluation of the contribution could be done using Brewster's rules for determination of conformational asymmetry.[9] In the case of an M-helix when $L_1 = L_2 = E$ the substituents around the bonds 1 and 5 (P-atom is at the rear) are located as pictured below: (Structure 4). One can be easily convinced that the same location exists around bonds 1′ and 5′ (the molecule bears a C_2 axis) and in the P isomer the situation is enantiomeric. When $R = CH_3$ the contribution of the substituents around bond 1 is zero (+CH—CH + CN—CN interactions) and this around bond 5 is positive determined by the interactions +CN + (:)H—CH—(:)N = 480 + 81 − 270 − 123 = +98°.[10] The total effect C_{CH_3/CH_3} (the contribution of bonds 1, 1′, 5 and 5′) could be valued at +196° at $\lambda = 598$ nm or about +400° at 436 nm. When R = H (NE and ψNE) the contribution of 5 remains the same (+98°) and this of 1 is deter-

---

† See experimental part concerning a possible C.D. study.

TABLE I

Components of the molecular rotation of spirophosphoranes with ephedrine ligands (temp.: 25°C, $\lambda = 436$ nm, solvent: C_6H_6). The isolated diastereoisomers are underlined

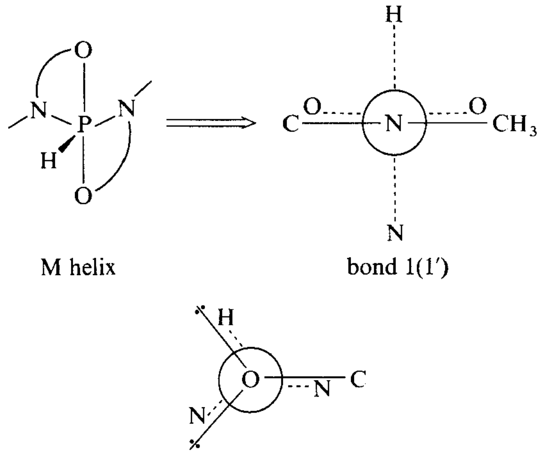
No.	L_1	L_2	ϕ_M	ϕ_P	$\phi_{Hel} + C^b$	C^c	$\pm\phi_{Hel}$	$\phi_{L_1L_2}{}^d$
(1)	$-E$	$-E$	$\underline{-1240}^a$	-1018	-111	400	511	-1129
(2)	$-NE$	$-NE$	$\underline{-1339}$	-693	-353	200	553	-1046
(3)	$+NE$	$+NE$	$+672$	$\underline{+1365}$	-346	200	546	$+1019$
(4)	$+\psi E$	$+\psi E$	$+195$	$\underline{+490}$	-147	400	547	$+342$
(5)	$+\psi NE$	$+\psi NE$	$+290$	$\underline{+950}$	-330	200	530	$+620$
(6)	$-E$	$+NE$	-304	$\underline{+302}$	-303	300	603	-1
(7)	$+E$	$-NE$	$\underline{-290}$	$+296$	-293	300	593	-3

[a] The absolute configuration is determined (X-rays).

[b] From $\phi_M - \phi_P = 2(\phi_{Hel} + C)$.

[c] C is calculated by Brewster.

[d] From $\phi_M + \phi_P = 2\phi_{L_1L_2}$.



M helix

bond 1(1′)

bond 5(5′)

STRUCTURE 4

mined by $+CH—HH + HN—CN$ equal to $-52°$. The total effect $C_{H/H}$ is $+92°$ at $\lambda = 598$ nm or about $+200°$ at 436 nm. In the case of mixed ligands ($R_1 = CH_3, R_2 = H$) the effect is averaged ($C_{CH_3/H} = +300°$).

All these considerations allow one to define the following independent contributions to the molecular rotation of the spirophosphoranes:

1-The Ligand Contribution $\phi_{L_1L_2}$

This includes the conformational effect of the bonds 2, 3 and 4 resp. 2′, 3′ and 4′ (part of C_L) and the atomic asymmetry of the chiral atoms in the ligands (if any: A_L). It has the same sign and absolute value in both isomers.

2-Conformational Effects of the Bond 1, 1′, 5 and 5′: C

As already discussed it is equal in value and opposite in sign in both diastereomers (+ in M and − in P). The calculation of this effect was given above. An independent way for its evaluation will be considered below.

3-Contribution of the Helix Structure ϕ_{Hel}

It is approximately equal in value (for the case of ephedrine ligands) and opposite in sign. For correlating the sign of rotation with the configuration of the helix, one can use compound **(1)** for which the known value $-1240°$ corresponds to the M-helix (X-ray analysis, Structure 3) and apply the following general expression:

$$\phi = \phi_{L_1L_2} + \phi_{Hel} + C \qquad (2)$$

for both isomers:

$$\phi_M = \phi_{L_1L_2} + \phi_{Hel} + C = -1240°$$

$$\phi_P = \phi_{L_1L_2} + \phi_{Hel} - C = -1018°$$

The difference $\phi_M - \phi_P = \phi_{Hel} + C = -111$, knowing that the sign of ϕ_{Hel} is opposite in both isomers leads to the conclusion that this system has only one solution concerning the contribution of the helix structure: -511 for the (**1**) M helix ($C = 400$ has been calculated using Brewster's rules). Therefore the M isomer in the general case must show the smallest algebraic value. This allows one to determine the absolute configuration of all compounds and to predict it for new compounds of the same type.

Analogous calculations for all compounds give an average absolute ϕ_{Hel}-value of 540 (see Table I). For (**6**) and (**7**), we can observe deviation from this value: $\phi_{\text{Hel}} = 603$ and 593. This deviation can be fairly explained by an additional contribution of the asymmetric P-atom ($L_1 \neq L_2 \Rightarrow A_P \neq 0$), equal in sign to that of the helix.

The $C_{H/H}$ and C_{CH_3/CH_3} values were calculated using Brewster's rules, but they can be also evaluated independently from experimental values of Table I. For this purpose, we assume that when $L_1 = L_2$, the contribution of the helixes is constant and take the ratio between the two contributions: $C_{CH_3/CH_3}/C_{H/H} = 2/1$. For the couples (**1**), (**2**) and (**4**), (**5**) respectively one can write:

$$\phi_{\text{Hel}_1} = \phi_{\text{Hel}_2} \text{ and } \phi_{\text{Hel}_4} = \phi_{\text{Hel}_5}$$

Replacing the ϕ_{Hel} from $\phi_{\text{Hel}} + C = -111$ (for (**1**)) and -353 (for (**2**)) we can get the equation:

$$-111 - C_{CH_3/CH_3} = -353 - C_{H/H}$$

knowing that $C_{CH_3/CH_3} = 2 \cdot C_{H/H}$ one can obtain

$$-111 - 2 \cdot C_{H/H} = -353 - C_{H/H}$$

from which $C_{H/H} = 242°$ and $C_{CH_3/CH_3} = 484°$.

Analogously from (**4**) and (**5**) we reach the equation:

$$-147 - 2 \cdot C_{H/H} = -330 - C_{H/H}$$

from where $C_{H/H} = 183°$ and $C_{CH_3/CH_3} = 366°$.

The average values are 213° and 426°. Therefore, the used approximate values (calculated by Brewster's rules) of 200° and 400° are satisfactory.

Taking the sum of the above given expressions for ϕ_M and ϕ_P one can get the $\phi_{L_1L_2}$ values. Comparing these values for (**1**), (**2**), (**4**) and (**5**) (Table I) one can see that the contribution of the "erythro" ephedrines as ligands in (**1**) and (**2**) is higher than the contribution of the "threo" isomers in (**4**) and (**5**). This is in good agreement with the observation for the case of cyclization of ephedrines to the corresponding 2-oxazolidones[11] and for other cyclizations of diastereomeric amino alcohols,[12] where the change of the molecular rotation is larger in the cyclization of the "erythro" isomers.

Compounds (**6**) and (**7**) are of particular interest. Their ligands are similar in structure and opposite in configuration. That leads to the internal compensation of the rotation and their molecular rotation remains to be a sum of ϕ_{Hel} and C. It is a little surprising that the methyl group in one of the ligands does not make any difference in the ligand contribution (as in (**1**) and (**2**)). The zero value for $\phi_{L_1L_2}$ in this case is an evidence that the helix contribution is equal in absolute value in both diastereomers. If this contribution does not coincide—it will be the case for compounds bearing two different ligands—then the difference $\Delta\phi_{\text{Hel}}$ is added to the $\phi_{L_1L_2}$ value: from Eq. 2 it comes:

$$(\phi_M + \phi_P) = 2\phi_{L_1L_2} + \Delta\phi_{\text{Hel}} \tag{3}$$

The above demonstrated separation of the contributions to the molecular rotation allows one to apply the principle of the optical superposition for calculation of the molecular rotation of compounds with two different ligands ($L_1 \neq L_2$) or its components. Using the values for separated ligands (the halves of the values where $L_1 = L_2$) given in the Table II one can easily find that:

$$\phi_{M_{\text{cal.}}} = 1/2\phi_{M'} + 1/2\phi_{M''}$$

The calculated values for 11 products synthetized but not yet studied by polarimetry are given under numbers (**8**) to (**18**) in Table III. Compound (**6**), (Tables I and III) gives a possibility to test our predictions. The calculated values ϕ_M and ϕ_P in Table III are not equal as in Table I for the same product. This is due probably to the already mentioned difference between the ligand contributions of (**1**) and (**2**) (one hydrogen replaced by methyl group). One has to assume that the

TABLE II

Experimental values for calculation of molecular rotation and its components

Ligand	$1/2\phi_M$	$1/2\phi_P$	$1/2(\phi_{\text{Hel}} + C)$	$1/2\phi_{L_1L_2}$
−E	−620	−509	−56	−565
+E	+509	+620	−56	+565
−NE	−700	−347	−177	−523
+NE	+347	+700	−177	+523
−ψE	−245	−98	−74	−171
+ψE	+98	+245	−74	+171
−ψNE	−474	−145	−165	−310
+ψNE	+145	+475	−165	+310

TABLE III

Components of the molecular rotation of spirophosphoranes with ephedrines ligands not yet studied (except (**6**)) (see Table I)

No.	L_1	L_2	ϕ_M	ϕ_P	$\phi_{Hel} + C$	C	$\pm\phi_{Hel}$	$\phi_{L_1L_2}$
(**8**)	−E	−NE	−1320	−856	−233	300	533	−1088
(**9**)	−E	$-\psi$E	−865	−607	−130	400	530	−736
(**10**)	−E	$-\psi$NE	−1094	−654	−221	300	521	−875
(**11**)	−NE	$-\psi$E	−945	−445	−251	300	551	−694
(**12**)	−NE	$-\psi$NE	−1174	−492	−342	200	542	−833
(**13**)	$-\psi$E	$-\psi$NE	−719	−243	−239	300	539	−481
(**6**)	−E	+NE	−273	+191	−233	300	533	−42
(**14**)	−E	$+\psi$E	−522	−264	−130	400	530	−394
(**15**)	−E	$-\psi$NE	−475	−34	−221	300	521	−255
(**16**)	−NE	$+\psi$E	−602	−102	−251	300	551	−352
(**17**)	−NE	$+\psi$NE	−555	+128	−341	200	541	−213
(**18**)	$-\psi$E	$+\psi$NE	−100	+377	−239	300	539	+139

contribution of the methyl group is negligibly small and the observed difference between (**1**) and (**2**) is due to the experimental error. Nevertheless it is worth noting that ΔM_D of E and NE is $\pm 24°$ (which gives 48° at 436 nm). It seems quite possible that the methyl group contribution is balanced by the difference in the contributions of the enantiomeric helixes. If that is the case, the predicted value of 42° for $\phi_{L_1L_2}$ of (**6**) (Table III) is evidence that this difference is really a small one in the case of ephedrine ligands as postulated before.

All compounds from (**8**) through (**18**) contain an asymmetric P-atom which in spite of the very near polarisability of the attached atoms can also contribute to the rotation ($A_P \neq 0$). This effect must be equal in value and opposite in sign in M and P isomers, but its separation from $\phi_{Hel} + C$ at the moment is difficult.

A large group of compounds, containing ephedrine and other optically active and inactive ligands also prepared in our previous work are listed in Table IV. The separation of the components of the molecular rotation, as seen from the table, leads to some unexpected values which should be discussed. For example the optically inactive ligands L_2 as *o*-aminophenol and its N- and 5-methyl derivatives in (**19**), (**20**), (**21**), (**22**), (**24**), (**26**) and (**28**) show a large "ligand effect." This effect could be due to a significant difference in the helix contribution. The benzene ring is attached to the P-atom by P—O and P—N bonds and L_2 is more conjugated than in the case of two ephedrine ligands and therefore more sensitive to the structural changes in L_1 than each ephedrine ligand. For the evaluation of the difference between the two helix contributions in (**19**) one can use the Eq. (3):

$$\phi_M + \phi_P = -111° = 2\phi_{L_1L_2} + \Delta\phi_{Hel}$$

where $\phi_{L_1L_2} = +171°(+342/2$ from Table I, compound (**4**))

$$\Delta\phi_{Hel} = -454°$$

It shows that $\phi_{Hel_M} > \phi_{Hel_P}$. The same evaluation could be done for the other cases too. The calculated $\Delta\phi_{Hel}$ values are given in Table IV. The observed difference in the helix contributions is probably due to the nonbonded interactions between the substituents in L_1 with the conjugated *o*-aminophenol system L_2.

Other optically active ligands have been used for compounds (**23**), (**24**), (**26**), (**27**) and (**28**) in Table IV: phenylglycine, alaninol and alanine. Phenylglycine in (**23**) and (**24**) shows a large rotatory effect. This is in good agreement with the abnormal specific rotation of the phenylglycine itself, due to the cyclic structure because of hydrogen bonding.

(+) Alaninol has a very small contribution in (**26**) and (**27**) probably because of the low conformational asymmetry of the ligand and absence of atomic asymmetry (fast libration of the cycle observable in ^{1}H nmr spectroscopy).

The mentioned group of compounds with *o*-aminophenol ligands are characterized also by a very increased $\phi_{Hel} + C$ values. This could be due either to a very large change of the molecular asymmetry of the compounds, or to a high atomic

TABLE IV

Components of the molecular rotation of spirophosphoranes with mixed ligands

No.	L_1	L_2	ϕ_M	ϕ_P	$\phi_{Hel} + C$[a]	$\phi_{L_1L_2}$[b]	$\Delta\phi_{Hel}$[c]
(19)	$+\psi$E	5Me—oAPh	−1169	+1058	−1113	−56	−454
(20)	$+\psi$E	oAPh	−761	+649	−705	−56	−454
(21)	+E	5Me—oAPh	−925	+1800	−1365	+437	−256
(22)	+E	NMe—oAPh	−926	+1814	−1370	+444	−242
(23)	−E	PhGl	−1644	−1000	−322	−1322	−253
(24)	+PhGl	NMe—oAPh	−376	+2241	−1308	+932	+350
(25)	−E	α-AIBA	−867	−115	−376	−491	
(26)	+ALOL	NMe—oAPh	−551	+872	−716	+161	+194
(27)	+ALOL	+ALOL	−15	+272	−143	+128	
(28)	+ALA	NMe—oAPh	−2310	+3024	−2665	+357	

α-AIBA: α-aminoisobutyric acid

PhGl: phenylglycine

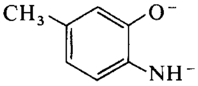
ALOL: alaninol

ALA: alanine

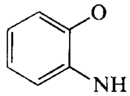
E: ephedrine

ψE: pseudoephedrine

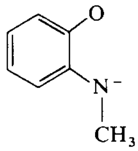
5Me-oAPh:



oAPh:



NMe-oAPh:



[a] $\phi_M - \phi_P = 2(\phi_{Hel} + C) \Rightarrow \phi_{Hel} + C = (\phi_M - \phi_P)/2$ the calculation of C in this group is not possible.

[b] $\phi_M + \phi_P = 2\phi_{L_1L_2} \Rightarrow \phi_{L_1L_2} = (\phi_M + \phi_P)/2$.

[c] From equation 3: $\phi_M + \phi_P = 2\phi_{L_1L_2} + \Delta\phi_{Hel}$.

asymmetry effect of the P-atom equal in sign to that of the helix. The latter could be explained by the resonance stabilization of the ligand leading to a strong change in the polarizability of the O- and N-atoms attached to the phosphorous. It is well known that groups with a high polarizability, attached to an asymmetric atom increase the rotatory power of the molecule. The magnitude of this effect in **(24)** is −1308°, in **(28)** by similar ligands it reaches −2665°. This as well as the differences in values for **(19)** and **(20)** and an unexpected low value for **(26)** are difficult to explain and impossible to be predicted.

EXPERIMENTAL

100 MHz ^{1}H nmr spectra were made with a Varian HA 100 instrument for C_6D_6 solution with tetramethylsilane as internal standard. The integrations were determined in three ways, using the HA 100 device integrator, a Dupont curve resolver 310 and the "cut up and weight" method: accuracy ~2%.

Polarimetric measurements were made with a Perkin–Elmer 141 instrument to within 0.002° in a temperature controlled cell (±0.02°C) using a SECASI APC 150 RA thermostat. The data were collected with 3490 Hewlett Packard Multimeter (±1 μV) and a thermal printer Hewlett Packard 5150 A.

The determinations of the rotation of two diastereoisomers were done using polarimetric kinetic data. α_0 was extraplalted using LSG[14] Program and TEKTRONIX 4051 calculator. The value of α_0, α_∞ and the nmr determination of the equilibrium constant allows the rotation of the two diastereoisomers to be calculated. This kinetic determination of the rotation precludes any C.D. study. (The R.D. spectra of the mixture of the two diastereisomers do not show any anomaly in the field of used wavelength.)

All rotations are given as molecular rotation ϕ, in benzene, at 30°C and at 436 nm: some values have been determined at 589 nm and converted to 436 nm applying an experimental coefficient which is almost constant for all compounds (c.a. 2).

The synthesis of compounds **(1)** to **(7)** are given in Ref. 13. Compounds **(19)**, **(20)**, **(21)** and **(22)** have been described in Ref. 4 and 1c and compounds **(26)**, **(27)**, **(28)** and **(29)** in 1d.

The preparations of compounds **(23)**, **(24)** and **(25)** are described in Ref. 5.

All these molecules bear, at least, two chiral units: the phosphorus atom and one or several asymmetric carbons. The structure of these compounds have been chosen (electronegativity rules for the TBP geometry)[6] so that only two optically pure diastereoisomers are energetically stable. These two stereoisomers are in equilibrium through a pseudorotation process and a slow crystallization of the mixture, in benzene, yields only one crystalline isomer, by a second order asymmetric transformation.[7] Determinations of the specific rotations of two diastereoisomers are indirect and derived from the measure of the apparent rate constants of epimerization of these molecules by the plot of $\mathrm{Ln}(\alpha_t - \alpha_\infty)$ against time, where α_t is the optical rotation at time t and α_∞ at equilibrium; this needs an accurate experimental determination of α_∞. The slope gives $-k_{\mathrm{app}}$ and extrapolation at $t = 0$ gives $\mathrm{Ln}(\alpha_0 - \alpha_\infty)$, that is to say α_0.

The $[\alpha_0]$ value is the specific rotation of the optically pure diastereoisomer given by the second order asymmetric transformation. A careful determination of the equilibrium constant-under the same experimental conditions as the kinetics, by ^1H N.m.r. spectroscopy—and the two extrema rotations allows the specific rotation of the other diastereoisomer to be calculated (the assumption of the stability of the specific rotation related to concentration for each diastereoisomer within our experimental field is implicit).

The ^1H nmr studies of these compounds are well documented[1b,1e] we give here only the most general nmr parameters for this class of compounds: $\delta_{\mathrm{H-P}}$ and $^1J_{\mathrm{H-P}}$ (Hz) in C_6D_6 respectively for each diastereoisomer: the first couple is related to the isolated isomer by second-order asymmetric transformation.

(**1**) 7.54 (758.5), 7.49 (744.5)
(**2**) 7.61 (748.2), 7.37 (728.2)
(**3**) 7.37 (728.2), 7.61 (748.2)
(**4**) 7.54 (758.5), 7.49 (744.5)
(**5**) 7.54 (723.0), 7.63 (745.0)
(**6**) 7.50 (747.5), 7.43 (743.8)
(**7**) 7.43 (743.8), 7.50 (747.5)
(**19**) 8.14 (792.5), 8.40 (792.5)
(**20**) 8.14 (793), 8.24 (798)
(**21**) 8.15 (806.6), 8.25 (777.2)
(**22**) 8.13 (796), 8.15 (820).
(**23**) 7.26 (802), 7.40 (784)
(**25**) 7.27 (800), 7.29 (789)
(**26**) 8.02 (797), 8.02 (797) ($C—CH_3$ = 0.66 and 0.54; ^3J = 6.2 and 5.8)
(**27**) 7.10 (731.4), 7.26 (729.3)
(**28**) 8.17 (842), 8.11 (841)

REFERENCES AND NOTES

1a. R. Contreras, Thèse de Doctorat de Spécialité, n° 1385, Université Paul Sabatier, Toulouse, 1973.
1b. J. F. Brazier, Thèse de Doctorat ès Sciences, n° 562, Université Paul Sabatier, Toulouse, 1973.
1c. A. Carrelhas Cachapuz, Thèse de Doctorat de spécialité, n° 1680, Université Paul Sabatier, Toulouse, 1974.
1d. M. R. Marre, Thèse de Doctorat de spécialité, n° 1794, Université Paul Sabatier, Toulouse, 1975.
1e. A. Klaebe, Th se de Doctorat ès Sciences, n° 737, Université Paul Sabatier, Toulouse, 1976.
2. R. Contreras, J. F. Brazier, A. Klaebe, et R. Wolf, *Phosphorus*, **2**, 67 (1972).
3. J. F. Brazier, A. Carrelhas Cachapuz, A. Klaebe, and R. Wolf, *C.R. Acad. Sc. Paris*, **277** (C) 183 (1973).
4. A. Klaebe, A. Carrelhas Cachapuz, J. F. Brazier, and R. Wolf, *J.C.S. Perkin II*, 1668 (1974).
5. B. Garrigues, A. Munoz, M. Koenig, M. Sanchez, and R. Wolf, *Tetrahedron*, **33**, 635 (1977).
6. Phosphorus atom is a chiral center and in these cases, only two diastereoisomers are stable in the trigonal bipyramid geometry, bearing two oxygen in apical positions.
7. J. D. Morrison and H. S. Mosher, *Asymmetric Organic Reactions*, Prentice-Hall, Englewood Cliffs (1971).
8. M. G. Newton, J. E. Collier, and R. Wolf, *J. Amer. Chem. Soc.*, **96**, 6888 (1974).
9. J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959); J. H. Brewster, *Topics in Stereochemistry*, Interscience Pub., **2** (1967).
10. The basic expression $M_D = 165\, R_X^{1/2} \cdot R_Y^{1/2}$ was used for the calculation of the contribution of the conformational interactions XY. The R_D value for the electron pair (:) was calculated from the expression $k(\mathrm{E—H})\ (\mathrm{C—H}) = -50 = 165\ (R_F^{1/2} - R_H^{1/2})\ (R_C^{1/2} - R_H^{1/2})$ taken from the page 5492 of Ref. 9. The symbol E is replaced by (:).
11. G. Fodor, Y. Stefanovsky, and B. Kurtev, *Monatsh. Chem.*, **98**, 1027 (1967).
12. G. Fodor, Y. Stefanovsky, and B. Kurtev, *Chem. Ber.*, **98**, 705 (1965); Y. Stefanovsky, S. Spassov, B. Kurtev, M. Balla, and L. Ötvös, *Chem. Ber.*, **102**, 717 (1969).
13. R. Contreras, R. Wolf, and M. Sanchez, *Synthesis in Inorg. and Metalorg. Chem.*, **3**, 37 (1973).
14. D. F. Detar, *Computer Programs for Chemistry*, W. A. Benjamin, New York, **1**, 117 (1968).