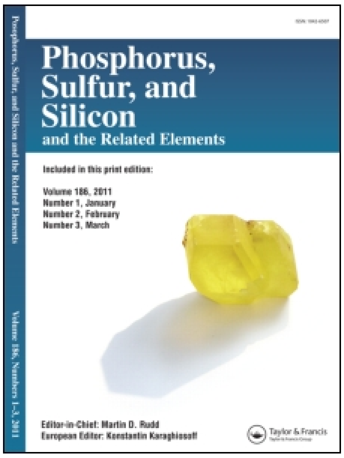

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STERIC STRUCTURE OF PHOSPHORUS CONTAINING HETEROCYCLES XLV. SPECTRAL ^{1}H AND ^{13}C NMR CRITERIA FOR CONFORMATIONAL STUDIES OF 1,3,2-DIOXAPHOSPHOCINES

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STERIC STRUCTURE OF PHOSPHORUS CONTAINING HETEROCYCLES XLV. SPECTRAL ^{1}H AND ^{13}C NMR CRITERIA FOR CONFORMATIONAL STUDIES OF 1,3,2-DIOXAPHOSPHOCINES

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The ^{13}C and dynamic ^{1}H NMR spectroscopy were employed to derive spectral tests for conformational studies of eight-membered phosphorus (P^{III} and P^{IV}) containing heterocycles: 4,5; 7,8-dibenzo-(I) and dinaphto-(II) 1,3,2-dioxaphosphocines. Passing from series (I) to (II) causes a dramatic change in the shift difference of methylene protons at C-6. The geminal ^2J(HH) and long-range ^5J(PH) spin–spin couplings are determined by the ring structure. The latter is also influenced by the phosphorus valence state and the orientation of substituents at phosphorus. Fairly definite stereo-chemical assignments can be made using the $^nJ(^{31}P^{13}C)$ couplings with n of 2 to 5.

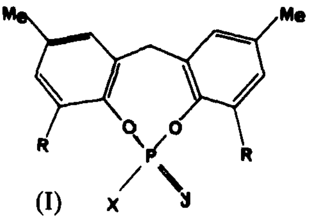
KEYWORDS 8-membered rings with two planar fragments Conformations NMR spectral criteria.

INTRODUCTION

The conformational study of middle-sized, eight-membered in particular, phosphorus containing heterocycles is impeded by the lack of spectral criteria for assigning conformations. These criteria can only be well founded upon clear theoretical concepts about basic canonical conformations. This is, however, also insufficient to solve the problem, for the number of possible eight-membered ring conformations is large, and it increases twice or more if various orientations of exocyclic substituents are included.

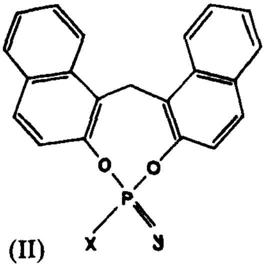
A theoretical analysis of conformational energy characteristics and elucidation of factors stabilising particular forms should be very helpful in the choice of preferred conformations. Information of just this kind has at present been accumulated for 1,4-cyclooctadiene heterocyclic derivatives. A critical comparative analysis of these data provides a basis for conformational studies in solutions, especially ^{1}H and ^{13}C NMR studies. Investigation of a wide range compounds and measuring temperature dependences promotes the determination of spectral criteria for certain conformers. These criteria can further be applied on the purposes of conformational analysis of similar systems. On just these premises, we undertook the search for spectral tests for 1,3,2-dioxaphosphocines with two planar fragments and tri- and tetra-coordinated phosphorus in the ring.

In this article, we describe the results of a conformational analysis of the following 4,5; 7,8-dibenzo- (I) and dinaphto- (II) 1,3,2-dioxaphosphocines containing P^{III} and P^{IV}



(I)

1–11



(II)

12–16

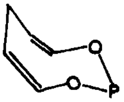
This enabled us to discover new interesting conformational behaviour patterns and determine the effects of the planar fragments and exocyclic substituents at phosphorus on the conformations.

RESULTS AND DISCUSSION

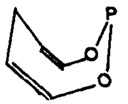
1. Canonical conformations of 1,3,2-dioxaphosphocines

The approach suggested by Cremer and Pople[1] and extended to 8-membered rings by Palyulin and Zefirov[2] is exceedingly helpful in determining basic ring conformations. Applying it to 1,3,2-dioxaphosphocines has for the first time made it possible to describe the set of ring structures that can be realized these species, define them quantitatively, introduce a unified terminology, and through this give a general analysis of conformational data on this type compounds.

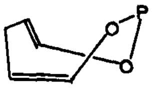
Calculations show that compounds may have four conformations including the boat-chair (BC), boat-boat (BB), boat (B) and twist-boat (TB) ones



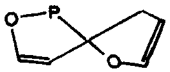
BC



BB



B



TB

The torsion angles about ring bonds and the Cremer–Pople puckering parameters for P^{III} and P^{IV} derivatives are listed in the Table I. Various conformers are characterized by different torsion angles. A comparison of the available X-ray data on heterocyclic 1,4-cyclooctadiene dervatives[2–9] shows these angles to vary only insignificantly over series of like conformers in spite of considerable differences in the geometrical parameters (see Table II). This very circumstance allowed us to establish an unambiguous correlation between disconnected literature data and the suggested terminology.[3] In the last column of Table II, conformational terms used in References[4–10] are given in parentheses. The designation presented in the last but one column is based on a quantitative approach. It follows from Table II that there is no agreement in terminology

TABLE I

Torsion angles and puckering parameters of 1,3,2-dioxaphosphocines

Conformation*	Torsion angles†								Puckering parameters				
	1	2	3	4	5	6	7	8	q_2	φ_2	q_3	φ_3	q_4
BC	95	−95	80	0	−91	91	0	−80	0.46	180	0.86	0	0.23
BB	−93	93	6	0	−89	89	0	−6	1.30	180	0.11	180	−0.38
B	−110	17	51	0	−96	54	0	59	1.38	146	−0.18	282	−0.33
TB	63	54	−111	0	86	39	0	−64	1.33	123	0.36	48	−0.13
BC	91	−91	80	0	−90	90	0	−80	0.51	0	0.80	180	−0.19
BB	−88	88	5	0	−88	88	0	−4	1.27	180	0.06	180	−0.35
B	−112	14	55	0	−92	51	0	63	1.35	−36	0.18	270	0.30
TB	66	55	−112	0	83	38	0	−67	1.30	123	0.36	46	−0.12

* In the upper half of the table there are given the values for P^{III} compounds, in the lower half—for P^{IV} compounds.

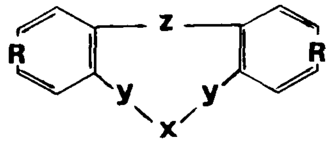
† Torsion angle 1 corresponds to an angle formed by atoms $C_8O_1P_2O_3$, angle 2—$O_1P_2O_3C_4$, etc.

between various authors which causes confusion and seriously impedes treatment of experimental data. It is only through the use of objective quantitative criteria such as torsion angles and Cremer–Pople parameters that a unique designation can be developed. Some remarks concerning the twist-form should be made. For an ideal T-conformation the torsion angles φ_1 and φ_2 are equal to 60°, and deviations from these values by +30° or more result in TB-forms. In a less skewed non-symmetrical boat conformation, the two angles have opposite signs and differ by 60 to 90°. The twist-conformation is found in compound with the carbonyl group at C-6 in an 1,3-dioxasubstituted ring.[4,5] Ring angle widening at C-6 appears to favour twisting. The BC[6,9] and B[6–8,10] conformations are more typical for compounds with methylene groups, as can be seen from Table II.

As concerns preferred conformations certain conclusions can be drawn from *ab initio* conformational energy calculations on compounds A with double bonds in place of dibenzo-fragments. The calculations were made for 2-chloro-, 2-methoxy and 2-hydro-2-oxo-1,3,2-dioxaphosphocines.[11,12] They favoured the BC form with an equatorial substituent X (e-BC). The BB conformation with equatorial and, especially, axial X is the least stable one because of close contacts between a-H at C-6 and P-2. An axial orientation of one of the substituents at P-2 causes a drammatic decrease in stability. The energy difference between the conformers is large enough for BB conformer to be excluded from consideration. A direct experimental evidence of the lack of this conformer is, however, a more weighty argument. The same results have been done for dibenzo-azocines.[13] As to the other forms no far-reaching conclusions can be drawn from energy difference values, the more so that the calculations were made for model compounds without optimizing the geometry and including solvent effects. In real systems planar fragments are as rule arylene or naphthene systems rather than double bonds and therefore, the calculation data can hardly be expected to reproduce real conformational energies accurately.

TABLE II

Torsion angles and ring conformation designation of dibenzo-derivatives 8-membered heterocycles (X-ray data)



X	Y	Z	Torsion angles* 1	2	3	4	5	6	7	8	Con-for-mation	Ref.†
SO	O	CO	71	57	−92	−8.5	39.6	18	−1.7	−96.7	(a)-T	(DBB)[4]
SO_2	O	CO	67.7	59.7	−94.2	−6.2	42.4	11.1	1.2	−93.7	T	(DB)[5]
NMe	CH_2	CH_2	−88.6	88.1	−71.5	1.1	86.9	−88	0.3	71.3	a-BC	(a-BC)[6]
NBu-t	CH_2	CH_2	−115.4	44.1	41.3	−2.8	−91.0	59.4	−3.1	42.3	e-B	(TB)[6]
			−64.5	135.9	−41.3	2.8	−59.4	91.0	3.1	−42.3	e-B*	"-"
P(O, S)Cl	NR	CH_2	−96	6	—	—	—	—	—	—	B	(DC)[7,8]
POPh	O	CH_2	−94.7	95.3	−80.1	−0.1	90.9	−92.5	1.2	−79.2	e-BC	(e-BC)[9]
$PNEt_2$†	O	CH_2	−110.8	20.9	48.9	−0.4	−96.2	54.2	−1.5	56.2	e-B	(e-B)[10]
$P(O)NEt_2$†	O	CH_2	−101.4	1.5	57.5	9.5	−100.7	50.7	−0.9	61.0	e-B	(e-B)[10]

* The torsion angles numeration is the same as in the Table I.

† Dinaphto-derivatives.

‡ D—designes deformed conformation.

2. *Structural investigations in solutions*

Some conformational studies in solutions were also performed for 1,4-cyclooctadiene heterocyclic derivatives.[14–24] Their major drawback was that not all possible flexible conformers [T] (viz. BB, B, TB or ones) were considered. Almost all the compounds were found to be nonhomogeneous conformationnally.[14–20] The BC form was assigned the highest probability. As to the second transformer, various considerations were presented in favour of the T[14–19] and BB[20] ones. In one instance, stabilization of B conformer by an intramolecular hydrogen bond was claimed.[15] Almost in all articles cited, the probability of the presence of some other flexible forms was disregarded. However in principle, general conformational considerations and the quantum mechanical calculations[3,11,12] show that the substituent orientation at phosphorus being the same, equilibria involving flexible forms such as BB $\rightleftharpoons$ B, BB $\rightleftharpoons$ T or B $\rightleftharpoons$ T are hardly realized, for energy barriers separating these forms are small. In the process of pseudorotation a molecule as a rule either adopts a certain preferred flexible form or exists as a mixture of all the possible conformers. The latter leads to averaging of NMR spectral parameters, especially in temperature experiments. According to the available X-ray data the most probable forms are boat[6–8,10] or twist[4,5] ones depending on geometrical ring parameters (determined by the ring closure condition) and the nature of planar fragments. This conformer can be in an equilibrium with the BC form and/or one of flexible forms with an alternative phosphorus substituent orientation. As energy differences between various flexible [T] conformers and energy barriers are small, equilibria involving flexible forms with alternative position X can not be ruled out (e.g. e-B $\rightleftharpoons$ a-TB equilibrium, for example, its probability follows from quantum chemical calculations on chlorophosphite of series A).[11]

The ^2J(HH) geminal two bond coupling constant of the bridging methylene group is believed to be the important criterion in identification of conformers by means of ^{1}H nmr spectroscopy.[14–18] Its absolute value is supposed to be smallest for the BC form (on the order of 12 Hz) and increase to 19 Hz on passing to the T form.[18] The parameter has an averaged value in equilibrium mixtures. For 1,3,2-dioxaphosphocines, one more criterion can be used, namely the long-range (via five bonds) ^5J(PH) spin-spin coupling constant. It was for the first time observed in P^{III} derivatives[20,21] and interpreted as indicative of the BB conformation, for this form very was characterised by a short P . . . H distance. An analysis of atomic distances, however, made the conclusion seem doubtful.[3] Additional structural evidence is required. This prompted us to undertake a detailed examination of ^{1}H and ^{13}C NMR spectra of a large series of 1,3,2-dioxaphosphocines **1–16**. Temperature studies were exceedingly helpful in correctly interpretation of experimental results. For the P^{III} (**1**) and one P^{IV} (**10**) derivatives collapses were observed and therefore, spectra of individual conformers could be obtained below its coalescence temperature. This facilitated our search for conformational criteria applicable to the systems under consideration.

3. *^{1}H NMR spectra*

The methylene protons give AB-signals at 3.24 to 4.52 ppm for compounds of series I and at 4.45 to 5.28 ppm for compounds of series II (see Table II). The

TABLE III

^{1}H NMR spectral parameters (δ, ppm, J, Hz) of methylene and t-butyl protons in 1,3,2-dioxaphosphocines

Compound†	X	Y†	$\delta(H^A)$	$\delta(H^B)$	$\lvert\Delta\delta\rvert$	δ(t-Bu)	^2J(HH)	^5J(PH)
1	Cl	LP	3.68	3.97	0.29	1.38	12.6	2.4
2	NEt_2	LP	3.25	4.31	1.06	1.36	12.1	2.8
3	NPh_2	LP	3.30	4.27	0.97	1.23	12.7	3.1
4	OEt	LP	3.24	4.22	0.98	1.36	12.3	3.2
5	OPh	LP	3.41	4.18	0.77	1.28	12.6	2.9
6	OC_6H_4-t-Bu-p	LP	3.40	4.28	0.88	1.30	12.8	2.8
7	ONf	LP	3.51	4.39	0.88	1.22	12.8	2.7
8	OPh	LP	3.38	4.29	0.91	1.22	12.8	3.0
9	NEt_2	S	3.31	4.12	0.81	1.38	12.6	3.4
10	OEt	S	3.65	4.52	0.87	1.38	14.6	—
11	H	O	3.61	4.39	0.78	1.38	14.0	—
12	NMe_2	LP	5.12	4.56	0.56	—	15.9	3.5
13	NEt_2	LP	5.06	4.54	0.52	—	16.3	3.6
14	OPh	LP	5.06	4.45	0.61	—	16.0	—
15	NEt_2	O	5.28	5.03	0.25	—	15.6	—
16	NEt_2	S	5.22	5.12	0.10	—	16.2	—

* In all compounds R is tert-Bu except compound **8** with R = $C_6H_{10}CH_3$.
† LP—lone pair.

lower-field doublet of many compounds (I) and the higher-field one of many compounds (II) split because of longrange spin–spin couplings with ^{31}P nucleus. Compounds (I) except chlorophosphite **1** show a difference in chemical shifts of their C-6 methylene protons ($\Delta\delta$) in the order of 1 ppm. In dinaphto-derivatives (II) the shift difference is smaller. The two series also differ in geminal constant values. Most dibenzo-derivatives have ^2J(HH) of 12 to 13 Hz and a noticeably large ^5J(PH) value (including P^{IV} compound **9**).

Observed variations in ^{1}H NMR spectra of 1,3,2-dioxaphosphocines are indicative of conformational rearrangements. Temperature studies were performed from +80° to −100°C. Resonance signals of two methylene groups from different conformers are observed below the coalescence temperature in compound **1** at −80°C: δ (H^A) 3.38, δ (H^B) 4.26, δ (H$^{A'}$) 4.16 and δ (H$^{B'}$) 3.31 ppm (Figure 1). They have similar geminal constants of 12.4 and 12.6 Hz and ^5J(PH^B) 3.9 Hz. In contrast ^5J(PH^A) is not observed, as ^5J(PH$^{A'}$) and ^5J(PH$^{B'}$). The process is characterised by $\Delta G^\circ_{195} = 0.4$ and $\Delta G^{\neq}_{235} = 45.5$ kJ/mol. The $\Delta\delta$ magnitude is significant in both forms and only low, of 0.29 ppm, in their mixture. This is indicative of different $\Delta\delta$ signs in individual conformers, i.e. the exchange turns the a, e protons into the e′ a′, ones. In a number of compounds (I) (**2**, **5**, **8**) a considerable broadening of AB signals and a jump-wise increase in $\Delta\delta$ is observed near −40°C. This points to hindering of intramolecular exchange with a barrier of interconversion of 45.5 + 3 kJ/mol. The jump in $\Delta\delta$ after the collapse also shows that the signs of $\Delta\delta$ for the minor and major forms are opposite to each other. The exchange process involves an equilibrium between forms *C* and *D* which is shifted on the side of *C*. The degree of shifting increases along the series **1** ≪ **5** ≪ **6**, **7** < **8** < **3**, **4**. The spectral characteristics of form *C* are: ^2J(HH) ~ 12.5 Hz, ^5J(PH) ~ 3–4 Hz and $\Delta\delta$ ~ 1 ppm. The geminal constant of *D*

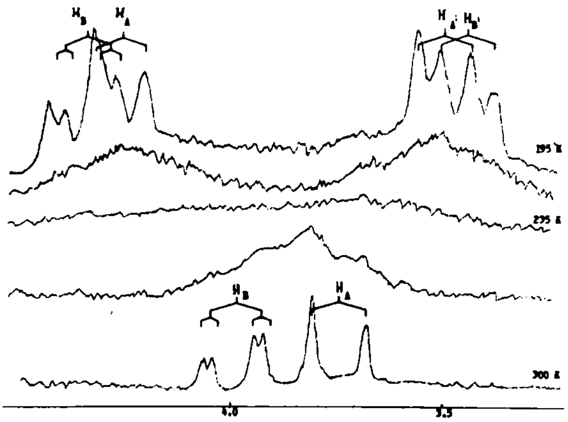


FIGURE 1 Temperature NMR ^{1}H spectra of the methylene protons in chlorophosphite **1**.

form is the same, long-range coupling vanishes and the sign of $\Delta\delta$ changes. Opposite $\Delta\delta$ signs and close ^2J(HH) and δ values show that the two equilibrium forms have the same ring conformation and differ by the orientation of the exocyclic substituent at phosphorus.

The spectral characteristics under consideration vary fairly widely over dibenzo-derivatives (I) containing P^{IV}. Only in compound **9** they are close to those of their P^{III} analogues. In this compound the difference between the methylene proton chemical shifts decreases slowly and continuously with cooling. All the other P^{IV} derivatives of series (I) and (II) are characterized by lower geminal constants, of 14.0 to 15.5 Hz (negative) and the absence of long-range coupling with phosphorus. A rapid increase in $\Delta\delta$ is observed in 2-hydro-2-oxo-1,3,2-dioxaphosphocine **11** at −40 to −60°C. This may be caused by hindering of intramolecular exchange characterized by $\Delta G^{\neq}_{220} = 43.7$ kJ/mol, with one of the forms present in only a small proportion. As follows from behaviour near collapse the $\Delta\delta$ values for the minor and major forms again have opposite signs (cf. P^{III} derivatives). The percentage of minor component does not exceed 10%.

A collapse is observed in thiophosphate **10** at −15°C (Figure 2), and below the

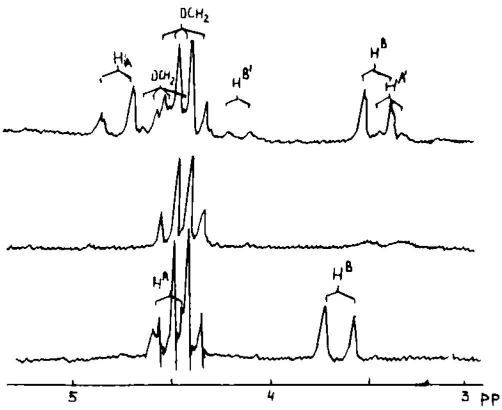


FIGURE 2 Temperature ^{1}H spectra of the methylene protons in thiophosphate **10**.

coalescence temperature at −70°C two AB signals are observed, $\delta(\mathrm{H^A})$ 4.80, $\delta(\mathrm{H^B})$ 3.47, $\delta(\mathrm{H^{A'}})$ 3.39, $\delta(\mathrm{H^{B'}})$ 4.15 ppm. Their intensities are substantially different (86:14), and the coupling constants values are also so ($^2J(\mathrm{H^AH^B}) = 15.5$, $^2J(\mathrm{H^{A'}H^{B'}}) = 12.2$ and $^5J(\mathrm{PH^{B'}}) = 3.5$ Hz). The signs of $\Delta\delta$ for the two conformers are different. The exchange proceeds with $\Delta G^\circ_{203} = 3.1$ and $\Delta G^{\ne}_{258} = 51.3$ kJ/mol. The minor conformer spectral characteristics are close to those of compounds **2** to **9** (see above).

According to temperature measurements taken for dinaphto-derivatives at +90 to −110°C $\Delta\delta$ increases continuously with lowering temperature (Figure 3). On the other hand the geminal coupling constant value is practically independent of temperature. Hence it can be inferred that in compounds of series (II) equilibria take place between the same ring conformations with different phosphorous substituent orientations. Combined ^{1}H NMR evidence indicates that the difference in the spectral parameters of various compounds reflect differences in their three dimensional structure. Attention should be given to the following parameters: 1) methylene proton shift difference $\Delta\delta$, 2) geminal $^2J(\mathrm{HH})$ coupling constant, 3) long-range $^5J(\mathrm{PH})$ coupling.

1) *Shift difference of methylene protons*

The principal spectral feature characterizing dibenzo- and dinaphto-1,3,2-dioxaphosphocines is a noticeably decrease in $\Delta\delta$ on passing from the former to the latter. A proton interaction with phosphorus gives the resonance signal in approximately the same region in the two series, whereas the second proton not involved in coupling appears in spectra of compounds (II) at a ca. 1.5 ppm lower field than in compounds (I). The ordering of the chemical shifts in dinaphto derivatives is therefore inverted compared with compounds (I), i.e. the corresponding $\Delta\delta$ values have opposite signs. To understand the reasons for this difference we undertook calculations of the effects of magnetic anisotropy and electric fields of benzene[25] and naphthene[25,26] fragments and their $\mathrm{C_{sp}}$ 2-H bonds[26] and also the lone pair of $\mathrm{P^{III}}$ on the $\Delta\delta$ magnitude in various conformers. In

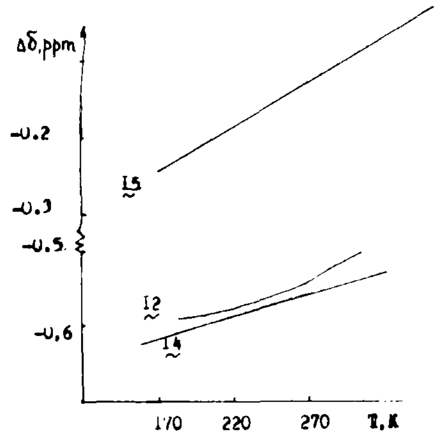


FIGURE 3 Temperature dependences of $\Delta\delta$ of methylene protons for some dinaphto-1,3,2-dioxaphosphocines.

dibenzo derivatives the H^A proton is screened far stronger than the H^B one, whereas in series II screening is ca. 3 ppm weaker. Substitution of naphthyl groups for benzene ones shifts the proton resonance signals to the lower field, by ca. 0.5 ppm for H^B and ca. 3 ppm for H^A. The H^A signal is therefore observed at higher fields than the H^B one in all compounds I and at lower fields in all compounds II. The following estimates for $\Delta\delta$ were obtained:

series (I) BC 0.5; BB 0.8; B 1.97; TB 1.28 ppm;
series (II) BC 2.1; BB 1.8; B 0.7; TB 0.9 ppm.

A change of planar fragment nature thus cause a substantial effect on $\Delta\delta$. The results for BC and B forms are diametrically opposite. A decrease of $\Delta\delta$ in series II compared I may be caused by a change in the ring conformation from BC (compounds I) to boat (compounds II). Small $\Delta\delta$ values are also observed for equilibria involving species with the same ring conformation and different P-substituent orientations, as for chlorophosphite **1**.

2) *Geminal $^2J(HH)$ coupling*

According to numerous experimental data the two bond coupling constant value for methylene protons adjacent to double bonds depends on the orientation of C—H bonds relative to substituent π-orbitals. A stereospecific nature of this interactions was confirmed by the valence bond[29] and MO LCAO[30] calculations which showed the negative $^2J(HH)$ constant shift caused by hyperconjugation to be a maximum with the H—H axis parallel to π-orbitals. Consideration of Newman projections along the C_6—C_7(C_5—C_6) bond for four possible ring conformations shows that the largest hyperconjugation contribution, ΔJ^{π}, is to be expected for the TB conformation. As to the BC and BB forms, no such enhancement should be observed (Figure 4). In fact, the constant for 8-membered rings with two planar fragments that had the largest absolute magnitude, 19 Hz, was associated with the TB conformation.[18] It follows that in compounds **1**–**8**, the smallest $^2J(HH)$ absolute value of 12.5 Hz may correspond to BC and BB forms, and that of ca. 15.5 Hz either to B form or to an equilibrium which must involve TB form.

3) *Long-range $^5J(PH)$ coupling*

Stereospecific nature of this coupling in the H—C—C=C—O—P fragment has not been studied. Coupling in such systems can be transmitted either through

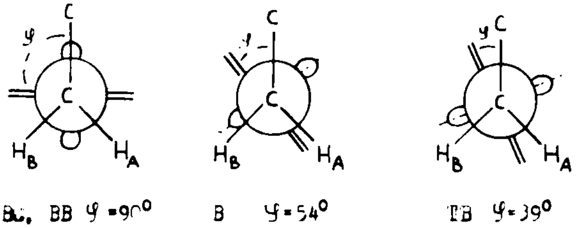


FIGURE 4 Newman's projections along C_5—C_6 (C_6—C_7) bonds for different ring conformations.

space[31] or via bonds by hyperconjugation mechanism.[20,32] Through space transmission were suggested to occur in e-BB form characterized by a small distance between the P and a-H atoms.[19] As mentioned above it is, however, doubtful that such a form can really exist. The P and H atoms are also fairly close to each other in B conformer (2.5 Å) and therefore, if P atom is not screened by an axial substituent (it inevitably is in P^{IV} derivatives) the ^5J(PH) coupling should also be detectable in e-B form. Suggestions concerning the second mechanism can only be made by analogy, e.g. with ^nJ(HH) couplings.[32-34] According to the calculations[35] the ^5J(HH) homoallyl constant in the H-C—C=C—C—H fragment depends on the C—H bonds orientation relative to the double bond and reaches its maximum value when the H—C—C=C dihedral angle is equal to 90°. It follows (that like the mechanism of through space transmissions) that of hyperconjugation via five bonds predicts a substantially stronger coupling of pseudoaxial protons compared with pseudoequatorial ones in dihydrobenzenes and dihydroanthracenes.[36] In dibenzo 1,3,2-dioxaphosphocines, the orientation of P—O and C—H bonds favouring hyperconjugation (two POCC angles of 90°) is found in BC and, in part, TB forms where only one of the HCCC angles is close to 90°. The ^5J(PH) constant also depends on the phosphorus valence state and the orientation of exocyclic substituents on phosphorus.

4) Conformational results

The analysis of spectral characteristics of 1,3,2-dioxaphosphocines given above allows to draw conclusions on the three-dimensional structure of the studied compounds, especially those for which spectra of individual conformers are available. In chlorophosphite **1**, two forms are in equilibrium and, according to dipole moment measurements and calculations, one of them is e-BC.[11] Among other possible conformers (a-BC, TB and B) only the a-BC one is consistent with NMR ^{1}H data, for as mentioned above, C and D conformers have the same ring structure. Otherwise it would be impossible to explain the preservation of the geminal constant and $\Delta\delta$ magnitudes and the reversal of $\Delta\delta$ sigh on passing to the inverted form. It follows that *C* form is e-BC and *D* is a-BC. The percentage of the second conformer, a-BC, in phosphites **2–8** is far smaller; it is a minimum in phosphite **3** and **4** containing diphenylamino- and ethoxy-groups. The crystal structure of phenylphosphite **5** is e-BC,[9] it corresponds to one the major conformer. In this conformation the long-range coupling is observed. The e-BC conformation is also predominant according dipole moments in P^{IV} containing compound **9**,[37] whose spectral parameters are similar to those of phosphites, including ^5J(PH). This is the direct improvement of presence of long-range coupling in e-BC conformation. Substituting the diethylamino-group for ethoxy-group, however, decreases the population of this conformer drastically.[37] The geminal and long-range couplings for the predominant form of the ethoxyl derivative **10** are close to those found in the dinaphto series. According to the dipole moment value this form must be e-B.[37] The existence of BC and BB forms in compounds II is hardly probable because of strong steric interactions between the α-H atoms of neighbouring naphthyl fragments. In the crystal state compounds **14** and its oxide **16** possess B conformation with an equatorial diethylamino group.[10] An equilibrium between e-B and a-B conformers in containing P^{IV} compounds should be characterised by a small $\Delta\delta$ value, ^2J(HH) about 15.5 Hz and ^5J(PH) equal to zero. This predictions agree with the measurement results. In P^{III} derivatives the populations of e-B conformer compared with a-B is higher for $X = NR_2$ and lower for $X = OPh$, which explains the observed differences in ^5J(PH) values.

Applying similar arguments augmented by dipole moment data to 2-hydro-2-oxo-1,3,2-dioxaphosphocines **11** leads to conclude that these systems involve three-component equilibria e-B $\rightleftharpoons$ a-BC $\rightleftharpoons$ e-BC with a 47:43:10 mixture ratio.[12] If B and BC forms are assigned geminal constants of 15.6 and 12.5 Hz, respectively, the effective constant value should be 14 Hz, which agrees with the experiment. A jump in $\Delta\delta$ observed in temperature studies is caused by freezing of e-BC conformer where the sign of nonequivalence is opposite to that for e-B and a-BC.

4. ^{13}C nmr spectra

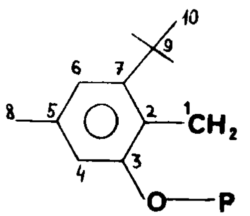
^{13}C NMR spectra of some P^{III} and P^{IV} containing dibenzo-1,3,2-dioxaphosphocines were reported,[21-23] however, without discussing their applications to conformational analysis problems. The most informative parameters are the ^{31}P ^{13}C couplings magnitudes listed in Table IV. In accordance with chemical shifts the pairs of tert-butyl and methyl groups are equivalent. Both ^1H and

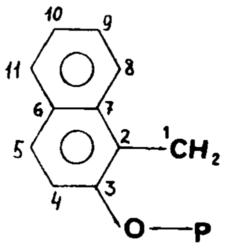
TABLE IV

^{13}C NMR spectral parameters of 1,3,2-dioxaphosphocines ($^nJ(^{31}P^{13}C)$, Hz)

Compound	$^2J(PC_3)$	$^3J(PC_2)$	$^3J(PC_4)$	$^4J(PC_1)$	$^5J(PC_6)$	$^5J(PC_{10})$
1	0	3.7	4.4	3.7	1.5	2.9
2	7.3	3.7	0	0.5	1.5	4.4
3	8.8	4.4	3.7	*	2.2	3.7
4	7.9	2.9	4.4	4.4	0	4.4
5	6.6	3.7	4.4	1.5	0	3.7
6	2.9	3.7	3.7	*	0	0
8	7.4	3.7	3.7	0	*	*
10	9.7	6.6	3.7	0		
11	10.3	5.8	1.5	0	2.9	—
12	2.2	0	3.7	8.1	0	—
13	1.5	0	3.7	10.4	0	—
14	2.9	0	*	0	0	—
16	4.5	0	4.4	0	0	—

* This constant is not determined. Atoms numeration:





^{13}C NMR spectral data require that the ring conformer possess a σ-plane symmetry passing through the P and C-6 (bridging methylene) atoms such as in BC and BB structures. This must be the case in order to explain both the observation of nonequivalent C_6 methylene protons along with observation of two equivalent pairs of tert-butyl and methyl groups. But on the other hand this situation corresponds to twisted nonplanar conformers (B or TB) that rapidly pass through structures possessing the required symmetry plane ($TB \rightleftharpoons TB^*$ or $B \rightleftharpoons B^*$).

The geminal $^2J(PC_3)$ coupling constant in the P—O—$C_{sp}2$ fragment undergoes characteristic changes. In P^{III} derivatives I (**2** to **5**) it amounts to 6.6–8.8 Hz. Higher values of 9.7 to 10.3 Hz are observed for P^{IV} containing molecules. Series II shows a similar behaviour $^2J(PC)$ being of 4.5 Hz in compound **16** and 1.5 to 2.9 Hz in **12–14**. The coupling depends on the phosphorus electronic configuration, the lone pair of P^{III} vs. π-bond orientation. It is a maximum if the latter is cis- (16–20 Hz) and a minimum if it is trans- (2–7 Hz).[38–40] Hyperconjugation contribution to couplings through non-conjugated bond systems are only small.[31] A near cis- C—O bond vs. lone pair orientation in 1,3,2-dioxaphosphocines is found in one fragment of e-B form ($\theta \sim 10°$) and in two fragments of e-BC and e-BB conformations ($\theta \sim 25°$). Thus $^2J(PC)$ should be a maximum in the latter two conformers and smaller somewhat in the former one. $\pi - \sigma^*(P—O)$ Hyperconjugation contributions can only be of significance in BC form, the only one with a near 90° P—O—C═C dihedral angle. The corresponding effects should be different in axial and equatorial conformers. As $^2J(PC)$ is zero in chlorophosphite **1** where the a- to e-conformer ratio is about unity (56:44) they should have opposite signs. A comparison of geminal constants for compounds with the same substituents at P^{III} (**2** vs. **13** and **5** vs. **14**) and equilibria shifted on the side of either e-BC (**2** and **5**) or boat (**13** and **14**) lead us to conclude that BC form was in fact characterized by higher constants (6.6 to 8.8 Hz) than boat (1.5 to 2.2 Hz). Revealing stereospecificity of $^2J(PC)$ in P^{IV} compounds requires further studies.

In the P^{III}—O—C═C fragment the vicinal constants have different magnitudes for the eight-membered ring (C_2) and aromatic substituent carbon atoms (C_4). The $^3J(PC_2)$ value is equal to zero in dinaphto derivatives, varies in the range of 2.9 to 4.4 Hz in their dibenzo analogues, and increases noticeably in P^{IV} compounds. The stereochemical dependences obtained for $^3J(PC_{sp}3)$ reveal variations on the orientations of the lone pair in P^{III} compounds or the P═Y ($Y = O, S$) bond involving P^{IV}.[40–42] The P—O—C═C dihedral angle in 1,3,2-dioxaphosphocines is close to zero in BB conformation (6°), and as follows from the stereochemical nature described above, these conformers should show the largest constant values about 10–15 Hz. Conversely, the constants should decrease to about zero in a-BC form, because the dihedral angle is then close to 90° (~80°). For other conformations we have $^3J(B) > {}^3J(TB) > {}^3J(e\text{-}BC)$. Comparing these predictions with the experiment leads one to conclude that the BB form must be ruled out. This is the first direct predictions of the absence of BB-form. Taking into account that the dihedral angles in the $POCC_2$ fragments are related as $\theta(PC_4) = 180° - \theta(PC_2)$ and that both are close to 90° in BC conformer, the equality of two vicinal constants 3.7 and 4.4 Hz can be used as a spectral criterion for the BC conformation. This equality is observed in dibenzo-1,3,2-dioxaphosphocines **1–8** which have the BC conformation.

As to long-range ^4J(PC) and ^5J(PC) coupling constants, far-reaching conformational conclusions can hardly be drawn from their values, for at present stereospecific nature have not been determined for these parameters. In the studied systems, the $^4J(PC_1)$ constant is detectable if the ^5J(PH) one is nonzero (compounds **1**, **4**, **5**, **12**, **13**). However the reverse is not always true. As is seen from Table IV the $^5J(PC_6)$ constant is characteristic of compounds having the BC conformation.

5. *Conclusions*

A systematic study of a wide range of 1,3,2-dioxaphosphocines characterized by mobile equilibria involving a variety of forms has made it possible to determine spectral criteria for the BC and B conformations which differ not only by their ring structure but also by the orientation of exocyclic bonds at phosphorus. We were also able to give the first description of the effects produced by the nature of planar fragments and phosphorus substituents and the phosphorus electronic configuration on the conformational behaviour of 8-membered rings with two planar fragments. The criteria obtained can be employed in conformational analysis of like systems. The preferred conformation for P^{III} containing 1,3,2-dioxaphosphocines is BC with an equatorial substituent at phosphorus. This form is often in equilibrium with an alternative a-BC conformer whose population is a maximum in chlorophosphite **1**. A relative stabilization of e-B form which is the preferred ethyl phosphate conformer (**10**) is observed in some P^{IV} derivatives. Substituting the ethoxyl group by the diethylamino one stabilizes e-BC form. Conformations of 4.5; 7,8-dinaphto-1,3,2-dioxaphosphocines are less varied. The presence of two bulky naphthyl fragments destabilizes the BC structure and therefore, the compounds typically exist as B conformers. Their exocyclic substituent orientations depend on the substituent nature.

EXPERIMENTAL

The ^{1}H NMR spectra of 1,3,2-dioxaphosphocines were obtained on a Varian-HA 100D spectrometer. Samples were prepared as 5% solutions in chloroform. Temperature measurements were taken using a 50:50 chloroform/carbon disulphide mixture as solvent. Hexamethyl disiloxane was added as internal reference. The ^{13}C NMR spectra were recorded on a Bruker-Physic WH-90 NMR spectrometer. Samples were 15% solutions in chloroform. Completely and partially ^{13}C-{^{1}H} decoupled spectra were obtained to facilitate the interpretation of NMR data. Synthesis and sample characteristics were reported earlier.[11,12,37,43]

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