^{1}H and ^{31}P NMR study of 3,9-di(alkylphenoxy)-2,4,8,10--tetraoxa-3,9-diphosphaspiro[5, 5]undecanes and their 3,9-dioxo analogues

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The ^{1}H and ^{31}P NMR data concerning the spiro moiety of 3,9-di(alkylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecanes and their 3,9--dioxo analogues were used for the study of conformation. As for the derivatives of tricoordinated phosphorus, the values of spin-spin coupling constants as well as their constancy in the temperature interval 23—72 °C imply the existence solely of the chair conformation with —OR in the axial position. The temperature dependence of the coupling constants J(P—H) and J(H—H) of the derivatives of tetracoordinated phosphorus suggests the presence of a mixture of conformers, but the chair conformation with axial —OR group remains preferred. A dependence of concentration of the chair conformation on steric factors due to alkyl substitution has been observed.

Данные ^{1}H- и ^{31}P-ЯМР спектроскопического изучения спиро части 3,9--ди(алкилфенокси)-2,4,8,10-тетраокса-3,9-дифосфаспиро[5,5]ундеканов и их 3,9-диоксо аналогов были использованы для изучения их конформации. У производных с трехкоординированным фосфором величины констант спин-спинового взаимодействия и их постоянность в интервале температур 23—72 °C свидетельствуют о конформации кресла как о единственно возможной с —OR в аксиальном положении. Температурная зависимость констант спин-спинового взаимодействия J(P—H) и J(H—H) у производных с четырехкоординированным фосфором говорит о наличии смеси конформеров, причем предпочтительной остается кон-

формация кресла с аксиальной группой OR. Наблюдалась зависимость концентрации конформации кресла от стерических факторов, являющихся следствием алкильного замещения.

Towards the end of sixtieth and in the course of seventieth years considerable attention was paid to the NMR study of structure of 1,3,2-dioxaphosphorinanes as well as their 2-oxo derivatives. The ^{1}H, ^{31}P, and ^{13}C NMR parameters were successfully used for determining the conformation of dioxaphosphorinane ring as well as the orientation of substituents on the phosphorus atom [1—7]. The derivatives of 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane (*A*) which are structurally similar to 1,3,2-dioxaphosphorinanes are widely used in the region of polymer chemistry either as antioxidants or as light stabilizers. However, there are only the papers by *White et al.* [8, 9] in the literature that are concerned with these substances. The ^{1}H NMR study of the 3,9-dimethoxy derivative (*A*) performed by these authors has revealed that both cycles possess chair conformation. The subject of our study have been the 3,9-dialkylphenoxy derivatives (*A*) because of the fact that some properties of these compounds are dependent on the type of the phenoxy substituents.

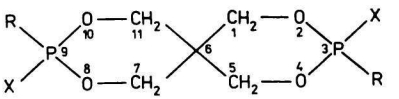
Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Jeol FX-100 instrument. The investigations were carried out with *ca.* 0.1 M solutions of the compounds in $CDCl_3$ or dimethyl sulfoxide DMSO-d_6. The ^{1}H NMR spectra were measured within the range of 1000 Hz by the use of 8 *K* memory. The chemical shifts are referred to internal standard TMS. The ^{31}P NMR spectra were measured within the range of 10 000 Hz by the use of 8 *K* memory. Phosphoric acid (85 %) was used as external standard.

The preparation of the investigated derivatives *I—XXI* was described in preceding communications [10, 11].

Results and discussion

The compounds studied in this paper are represented by the following formula



where X = LP for compounds *I–XIV*

X = O for compounds *XV–XXI*

Compound	R
I, XV	Phenoxy
II	4-Methylphenoxy
III	4-Isopropylphenoxy
IV	4-*tert*-Butylphenoxy
V, XVI	4-(α,α-Dimethylbenzyl)phenoxy
VI, XVII	2-Methylphenoxy
VII, XVIII	2-Isopropylphenoxy
IX, XIX	2-*tert*-Butyl-4-methylphenoxy
VIII	2-Methyl-4-*tert*-butylphenoxy
X	2-*tert*-Butyl-4-isopropylphenoxy
XI, XX	2,4-Di-*tert*-butylphenoxy
XII	2-*tert*-Butyl-4-(α,α-dimethylbenzyl)phenoxy
XIII, XXI	2,6-Dimethylphenoxy
XIV	2,6-Di-isopropylphenoxy

LP — lone pair.

As the study has been focused on the geometry of their spiro moiety, the spectral parameters concerning the exocyclic substituents are not given. The protons and phosphorus atoms of the spiro moiety represent a ten-spin system from the view-point of NMR analysis because the axial protons of axial carbon atoms (with respect to vicinal ring) in chair conformation can acquire a nonzero four-bond coupling constant. *Anderson* [12] and *Lapuka et al.* [13] investigated 2,4,8,10-tetraoxaspiro[5,5]undecanes and observed that the value of this coupling constant was equal to 1.0—1.8 Hz. Because of relatively poor resolution of the ^{1}H NMR spectra (Figs. 1 and 2) as well as outfit with iterative program only for 8 spins, we used a simplified approach to analysis. The spectra were analyzed as a five-spin system ABCDX where X stood for phosphorus. For simulating, we used FASNO-2 program and the error in frequency of the lines of the simulated and experimental spectrum did not exceed 0.3 Hz. The use of successive iteration by means of LAOCOON III program on a computer Varian 76 gave spectral parameters practically identical with input values, which was attributed to poor resolution of the spectra as well as to simplified approach to the analysis. Figs. 1 and 2 show the consistence of the experimental and simulated spectra.

The obtained values of the NMR parameters are summarized in Table 1. This table contains only the ^{1}H NMR parameters of protons in one ring of the spiro moiety because of the C_2 symmetry of the analyzed compounds. Moreover, the chemical shifts of phosphorus are presented in this table.

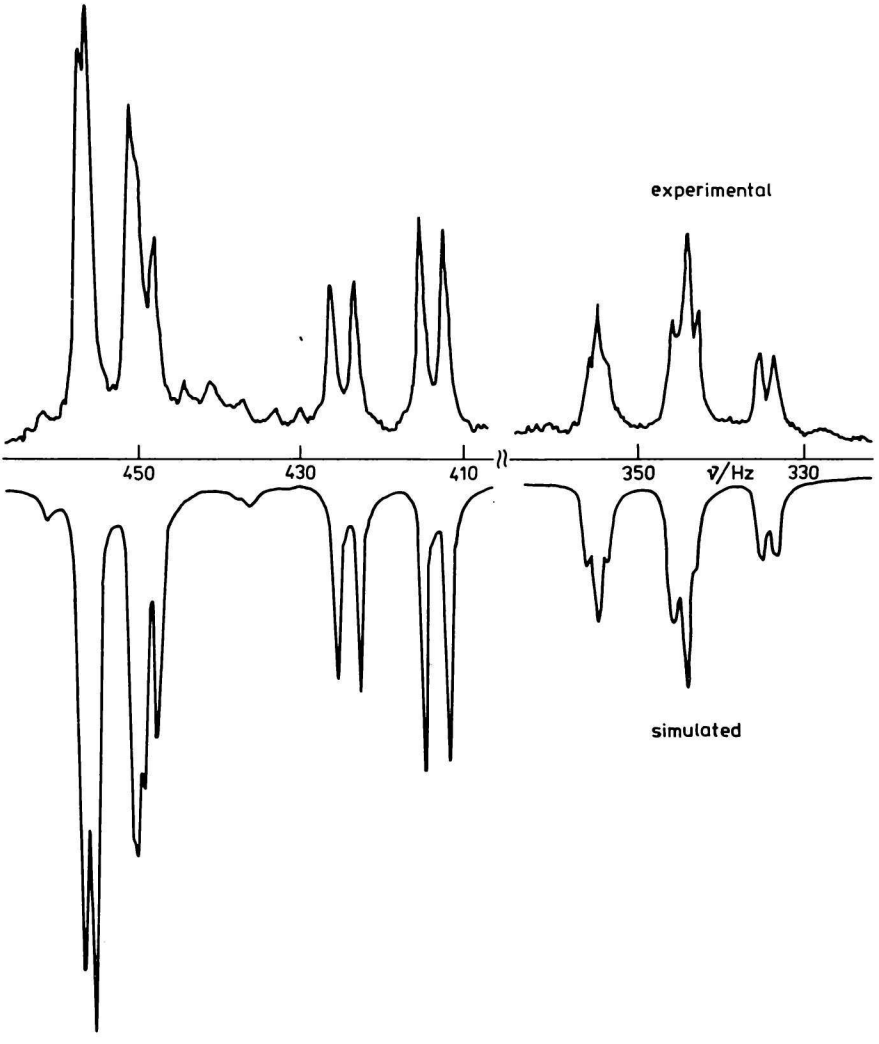


Fig. 1. ^{1}H NMR spectrum of compound *I* — spiro moiety.

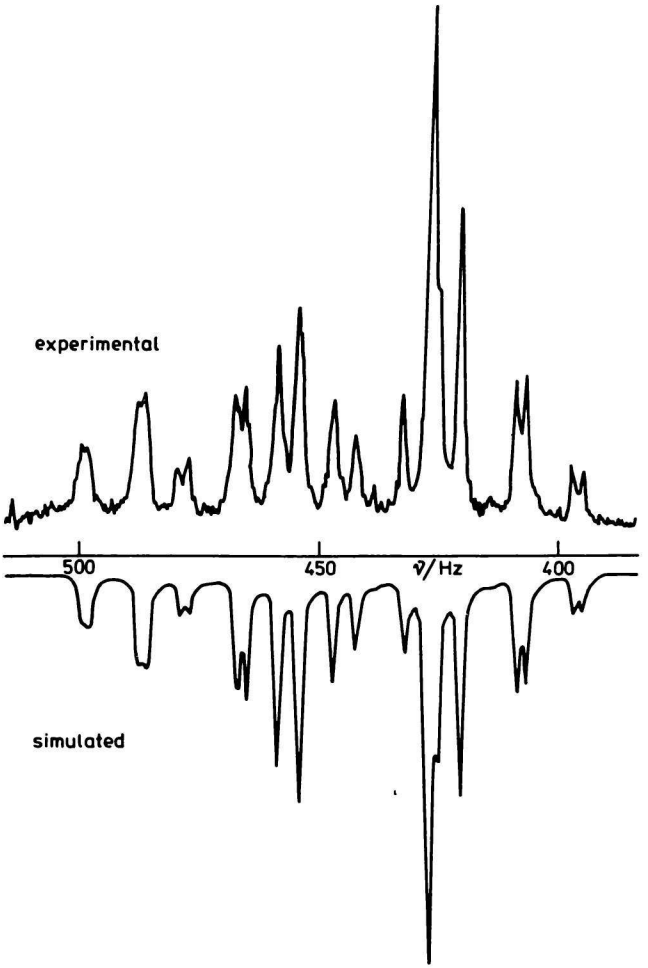


Fig. 2. ^{1}H NMR spectrum of compound *XV*—spiro moiety.

Table 1

^{1}H and ^{31}P NMR data[a] for compounds *I*—*XXI*

Compound	δ/ppm					J/Hz			
	H-1′	H-1″	H-5′	H-5″	P	H-1′—H-1″	H-1′—H-5′	H-1′—H-5″	H-1″—H-5′
I	4.54	4.57	3.47	4.20	117.2	−11.3	2.5	0	−0.3
II	4.53	4.56	3.46	4.20	117.5	−11.3	2.5	−0.4	−0.4
III	4.54	4.57	3.48	4.21	117.3	−11.3	2.5	−0.4	−0.4
IV	4.54	4.57	3.48	4.21	117.1	−11.3	2.5	−0.3	−0.3
V	4.51	4.56	3.45	4.19	117.2	−11.3	2.5	−0.4	−0.4
VI	4.56	4.60	3.47	4.22	117.3	−11.3	2.5	−0.4	−0.4
VII	4.59	4.60	3.50	4.23	117.2	−11.3	2.5	−0.3	−0.3
VIII	4.56	4.59	3.47	4.23	117.2	−11.3	2.5	−0.4	−0.4
IX	4.61	4.57	3.50	4.18	116.4	−11.3	2.5	−0.4	−0.4
X	4.61	4.57	3.49	4.18	116.2	−11.3	2.5	−0.4	−0.4
XI	4.61	4.57	3.49	4.18	116.2	−11.3	2.5	−0.4	−0.4
XII	4.60	4.56	3.48	4.17	116.2	−11.3	2.5	−0.4	−0.4
XIII	4.60	4.72	3.56	4.37	121.6	−11.4	2.5	−0.4	−0.4
XIV	4.64	4.71	3.62	4.37	121.9	−11.3	2.5	−0.3	−0.3
XV	4.84	4.55	4.16	4.30	−13.8	−11.8	2.2	0	0
XVI	4.79	4.49	4.10	4.24	−13.7	−11.8	2.1	0	0
XVII	4.79	4.54	4.21	4.27	−13.7	−11.9	2.1	0	0
XVIII	4.81	4.54	4.22	4.27	−13.7	−11.9	2.0	0	0
XIX	4.87	4.58	4.26	4.33	−13.7	−12.0	2.0	0	0
XX	4.91	4.59	4.25	4.33	−13.7	−12.0	2.0	0	0
XXI	4.78	4.65	4.39	4.44	−12.7	−11.8	1.5	0	0

a) ^{1}H chemical shifts are relative to internal TMS, ^{31}P chemical shifts are relative to external H_3PO_4; solvent — $CDCl_3$.

Table 1 (Continued)

Compound	J/Hz					
	H-1″—H-5″	H-5′—H-5″	H-1′—P	H-1″—P	H-5′—P	H-5″—P
I	0	−11.3	10.8	3.0	10.5	3.0
II	0	−11.3	10.6	2.8	10.6	2.8
III	0	−11.3	10.6	2.8	10.6	2.8
IV	0	−11.3	10.6	2.9	10.6	2.9
V	0	−11.3	10.6	2.7	10.6	2.7
VI	0	−11.3	10.6	2.9	10.6	2.9
VII	0	−11.3	10.6	2.9	10.6	2.9
VIII	0	−11.3	10.6	2.9	10.6	2.9
IX	0	−11.3	10.6	2.8	10.6	2.8
X	0	−11.3	10.6	2.8	10.6	2.8
XI	0	−11.3	10.6	2.8	10.4	2.8
XII	0	−11.3	10.6	2.8	10.6	2.8
XIII	0	−11.4	10.6	2.9	10.6	2.9
XIV	0	−11.3	10.4	3.1	10.4	3.1
XV	0	−11.7	21.2	4.0	21.2	4.4
XVI	0	−11.7	21.2	4.4	21.2	4.4
XVII	0	−11.9	19.7	5.6	19.4	5.6
XVIII	0	−11.9	19.6	5.6	19.6	5.6
XIX	0	−12.0	20.1	5.4	19.7	5.6
XX	0	−12.0	20.3	5.4	19.7	5.6
XXI	0	−11.9	17.9	7.5	17.0	8.0

Compounds of tricoordinated phosphorus

The preceding NMR investigations of the derivatives of 1,3,2-dioxaphosphorinanes have shown that the dependence of the vicinal coupling constant ^3J(POCH) on dihedral angle has the Karplus-like character and this constant has positive value in the whole range of angles [14, 15]. In the case of compounds with tricoordinated phosphorus, the coupling constant ^3J(POCH) of the hydrogen atoms with dihedral angle of about 180° with respect to phosphorus is approximately equal to 10 Hz while its value for the protons with dihedral angle of about 60° varies within the range 2—6 Hz according to the character of substituent [16, 17].

The vicinal couplings of protons of the CH_2 groups with phosphorus are thus convenient parameters for estimating the conformation of the cycle. For determining the conformation of compounds *I—XIV*, we took into consideration four variants (Fig. 3), *i.e.* chair, 1,4-boat, 3,6-boat, and twist boat. On the basis of two coupling constants ^3J(POCH) measured in the range 10.4—10.6 Hz and other two constants with the values in the range 2.7—3.0 Hz we may rule out the 3,6-boat

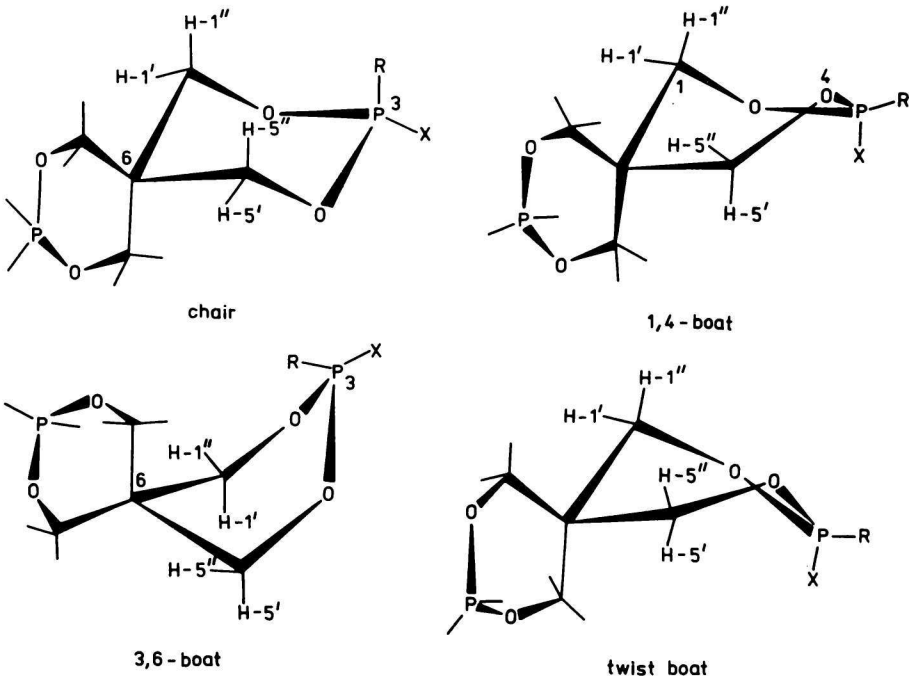


Fig. 3. Alternative conformations of compounds *I—XXI*.

conformation as well as the twist boat conformation. The four-bond coupling (*ca.* 2.5 Hz) of the protons which have ^3J(POCH) in the range 10.4—10.6 Hz and are thus orientated into the *trans* position with respect to phosphorus enables us to arbitrate between the chair conformation and 1,4-boat conformation. In the 1,4-boat conformation the protons which occur in the *trans* orientation with respect to phosphorus do not make up a transfer way proper for the observed value of four-bond coupling ^4J(H—H). The values of three-bond ^3J(POCH) and four-bond ^4J(H-1′—H-5′) interactions thus unambiguously prefer the chair conformation of cycles of the spiro moiety of the analyzed compounds. Equal conformation was ascertained for the alkyl derivatives of 2-methoxy-, 2-chloro-, and 2-phenoxy-1,3,2-dioxaphosphorinane [8, 9, 18] where the simultaneous presence of two isomers made possible to find out that the thermodynamically stabler isomer had the —OR group in the axial position. The energetic preference of axial orientation is attributed to anomeric effect [19].

In contrast to coupling constants, the chemical shifts in protons of the investigated compounds exhibit a certain dissimilarity in comparison with the protons of 1,3,2-dioxaphosphorinanes, which is due to the presence of the second ring. The equatorial proton on the axial carbon atom of the second ring is considerably deshielded by the lone electron pairs of oxygen atoms of the second ring when compared with the corresponding proton on the equatorial carbon atom. This influence manifests itself, but to a smaller extent, in the axial proton. Both these effects may be superimposed by possible 1,3 *syn*-diaxial interactions between protons and lone electron pairs of oxygen atom in the —OR substituent provided this substituent is axially orientated. Therefore we cannot infer the orientation of substituent on phosphorus only from the order of chemical shifts in protons.

Compounds *I*—*XIV* may be compared with the 5,5-disubstituted derivatives of 1,3,2-dioxaphosphorinane containing equal type of substituent, *e.g.* with 2-phenoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane.

In conformity with this compound, we also observed the presence of only one isomer with compounds *I*—*XIV* because the equilibrium of isomers with axial and equatorial orientation of the —OR group is determined merely by energetic difference of these orientations and is not influenced by disubstitution in the 5,5 position.

The temperature measurements of proton spectra in the temperature range 23—72 °C (solvent $CDCl_3$ and C_6D_6) showed merely a change in chemical shifts while the coupling constants did not change. The chair conformation of the analyzed compounds is thus thermodynamically stable and the concentration of other conformers present in the solution (on the assumption of rapid exchange) is either small and constant or is equal to zero. The temperature change in chemical shift may be attributed to a change in influence of the solvent. The thermodynamic stability of the preferred conformation indicates axial orientation of the —OR

substituents. A certain contradiction with this assumption is represented by chemical shifts of ^{31}P according to which the substituted phenoxyl of compounds *XIII* and *XIV* with *ortho* disubstitution of the aromatic ring might occur in equatorial position owing to the difference $\Delta\delta \approx 4.5$ ppm when compared with compounds *I*—*XII*. According to literature data, the difference between the ^{31}P chemical shifts of equatorially and axially substituted phosphorus in the derivatives of 1,3,2-dioxaphosphorinanes varies within the range 2—4 ppm and phosphorus with an axial substituent is always more shielded [20—22]. Thus in spite of constancy of the values of coupling constants observed in the ^{1}H NMR spectra of the whole series of compounds *I*—*XIV*, these substances were also subjected to the ^{13}C NMR analysis which confirmed axial orientation of the —OR substituents for compounds *XIII* and *XIV* as well [23]. The influence of inductive and mesomeric effects of *ortho* substituents does not come into consideration because no more conspicuous change in chemical shift of ^{31}P appears if we pass from nonsubstituted to *ortho*-monosubstituted derivative.

The observed difference in chemical shifts of phosphorus may be explained by a change in the angle between the P—O—C-1_{arom} plane and the plane of the aromatic ring. As for compounds *I*—*XII*, this angle (ω), which is varied in the course of rotation about the O—C-1_{arom} bond, is small on the average and likely near to zero for compounds with *ortho* substitution. But for *ortho*-disubstituted compounds, it approaches 90° due to steric factors. In this case, the conjugation of the π electrons of the aromatic ring and lone electron pairs of oxygen decreases, which manifests itself by a change in chemical shift of phosphorus. Different angles between the P—O—C-1_{arom} and the aromatic ring plane of compounds with one or two alkyl substituents in the *ortho* position may be responsible for the observed change in chemical shifts in protons of the CH_2 groups. In both cases, the aromatic ring must be *gauche* orientated with respect to the lone electron pair of phosphorus owing to steric factors. Provided the plane of the aromatic ring is turned round perpendicularly to the P—O—C-1_{arom} plane, we may expect an increase of chemical shifts of axial protons because of an increased effect of anisotropic circular π-currents, which also was observed. The difference $\Delta\delta$ of 0.15 ppm corresponds to this effect.

Compounds of tetracoordinated phosphorus

A comparison of the ^{1}H NMR data of the compounds with tetracoordinated phosphorus atom with the data concerning the compounds with P(III) (Table 1) shows that the introduction of phosphoryl oxygen into the molecule brings about a considerable change in chemical shifts and coupling constants between protons and the phosphorus nucleus. As for equatorial proton (H-5′) on equatorial carbon, we observed an increase in chemical shift of about 0.7 ppm while an increase of

about 0.3 ppm appeared for equatorial proton on axial carbon (H-1′). A comparison with the change $\Delta\delta$ observed for the derivatives of 1,3,2-dioxophosphorinanes (*ca.* 0.65 ppm) [18, 24] shows that a change in steric interaction between the equatorial proton on axial carbon and lone electron pairs of both oxygen atoms in the second ring arises from the introduction of phosphoryl oxygen. In the series of the derivatives of 2-oxo-1,3,2-dioxaphosphorinanes for which the chair conformation was ascertained different authors observed the values of vicinal coupling constants $^3J(POCH_{eq})$ and $^3J(POCH_{ax})$ to be in the range 20.2—24.4 Hz and 0—3.8 Hz, respectively [25, 26]. It is interesting that the sum $^3J(POCH_{ax})+{}^3J(POCH_{eq})$ was constant within the bounds of 0.5 Hz almost for all investigated compounds. According to *Kainosho* [27], the increase in $^3J(POCH_{trans})$ is caused by the fact that the π electrons of the phosphoryl bond play a certain role in the mechanism of formation of $^3J(POCH_{eq})$. The values of vicinal ^3J(P—H) interactions obtained by us for compounds *XV*—*XXI* indicate the preferential presence of chair conformation because we simultaneously observed a four-bond ^4J(H-1′—H-5′) coupling constant of about 2 Hz.

Owing to lower values of the vicinal coupling between phosphorus and equatorial protons and higher values of $^3J(POCH_{ax})$ when compared with literature data, we had to take into consideration either the presence of further conformer (both conformers should be in rapid mutual exchange) or deformation of the chair conformation. The temperature dependence of coupling constants (Tables 2 and 3) indicates that the first variant is more probable. The presence of a mixture of conformers may be also responsible for the decrease in $^3J(POCH_{eq})$ due to the introduction of a substituent into the *ortho* position of the aromatic ring as well as the additional decrease due to the introduction of the second substituent into the *ortho* position. Provided compound *XXI* is dissolved in $CDCl_3$, a higher concentration of the second conformer may already be expected. It results from these facts that the energetic barrier is lower for P(V) compounds than for P(III) compounds and steric factors of the type of *ortho* substitution significantly affect the equilibrium in the mixture of conformers.

As we are lacking in the vicinal ^3J(H—H) interactions for the investigated compounds, we cannot arbitrate whether an equilibrium of two chair conformations or a chair—twist boat conformation, observed by other authors [28—30] for some 2-oxo-1,3,2-dioxaphosphorinanes, exists in our case. As for the preferred chair conformation, we may assume the axial orientation of the —OR substituent because the measurements in DMSO displayed an increase in $^3J(POCH_{eq})$ when compared with the measurements in $CDCl_3$, which meant that the concentration of this conformer increased. Owing to a higher value of dielectric constant of DMSO when compared with that constant of $CDCl_3$, it appears that DMSO prefers conformations with higher dipole moment. The axial orientation of the —OR substituent was confirmed on the basis of the ^{13}C NMR analysis [23].

Table 2

Temperature dependence of chemical shifts and coupling constants of P(V) derivatives in $CDCl_3$

Compound	θ/°C	δ/ppm				J/Hz			
		H-1′	H-1″	H-5′	H-5″	H-1′—H-1″	H-1′—H-5′	H-1′—H-5″	H-1″—H-5′
XV	22	4.84	4.55	4.16	4.30	−12.2	2.4	0	0
	55	4.79	4.52	4.16	4.27	−11.7	2.0	0	0
XVI	22	4.83	4.52	4.12	4.26	−11.8	2.3	0	0
	55	4.77	4.49	4.13	4.23	−11.8	2.2	−0.5	0
XVII	22	4.80	4.55	4.22	4.28	−11.9	2.1	0	0
	55	4.76	4.53	4.23	4.26	−12.3	2.2	0	0
XIX	22	4.88	4.59	4.27	4.33	−11.8	1.9	−0.4	−0.4
	55	4.81	4.56	4.29	4.31	−12.0	2.2	−0.4	−0.4
XXI	22	4.78	4.65	4.39	4.44	−11.8	1.5	0	0
	55	4.72	4.61	4.40	4.41	−11.9	1.0	0	0

Table 2 (Continued)

Compound	J/Hz					
	H-1″—H-5″	H-5′—H-5″	H-1′—P	H-1″—P	H-5′—P	H-5″—P
XV	0	−11.8	21.2	4.0	21.2	4.4
	0	−12.0	20.0	4.9	19.5	6.6
XVI	0	−11.8	21.2	4.3	21.3	4.2
	0	−11.8	20.1	5.3	19.9	5.4
XVII	0	−11.9	19.7	5.6	19.4	5.6
	0	−12.1	18.8	6.7	17.3	7.2
XIX	0	−11.8	20.1	5.2	19.5	5.6
	0	−12.2	19.2	6.5	18.1	6.8
XXI	0	−11.9	17.9	7.5	17.0	8.0
	0	−11.9	16.0	9.2	16.0	9.2

Table 3

Temperature dependence of chemical shifts and coupling constants of P(V) derivatives in DMSO

Compound	θ/°C	δ/ppm				J/Hz			
		H-1′	H-1″	H-5′	H-5″	H-1′—H-1″	H-1′—H-5′	H-1′—H-5″	H-1″—H-5′
XV	45	4.81	4.70	4.49	4.42	−11.6	2.5	0	0
	69	4.78	4.69	4.48	4.40	−12.0	2.5	0	0
	90	4.77	4.68	4.47	4.39	−11.7	2.6	0	0
	110	4.74	4.67	4.46	4.38	−11.5	2.6	0	0
XVI	50	4.76	4.65	4.45	4.36	−11.8	2.0	0	0
	69	4.74	4.64	4.43	4.34	−11.8	2.4	0	0
	90	4.72	4.64	4.42	4.33	−11.8	2.4	0	0
	110	4.70	4.63	4.41	4.32	−11.8	2.4	0	0
XXI	45	4.89	4.75	4.63	4.51	−11.7	2.0	0	0
	69	4.85	4.74	4.62	4.50	−11.8	2.2	0	0
	90	4.83	4.73	4.60	4.50	−11.8	2.2	0	0
	110	4.80	4.72	4.59	4.50	−11.8	2.0	0	0

Table 3 (Continued)

Compound	J/Hz					
	H-1″—H-5″	H-5′—H-5″	H-1′—P	H-1″—P	H-5′—P	H-5″—P
XV	0	−11.7	3.7	20.5	3.7	20.5
	0	−11.7	4.2	20.2	4.6	19.6
	0	−11.8	5.6	18.8	5.2	18.9
	0	−12.0	6.3	18.2	5.6	18.4
XVI	0	−11.9	4.2	20.6	4.4	19.8
	0	−11.8	5.6	18.3	5.7	18.5
	0	−11.8	6.2	17.7	5.9	18.0
	0	−11.8	6.9	17.4	6.7	17.6
XXI	0	−11.7	4.0	21.0	4.2	21.4
	0	−11.8	5.0	20.3	4.8	20.6
	0	−11.8	6.0	19.4	5.4	20.3
	0	−11.8	7.0	18.2	5.6	19.8

References

1. Gagnaire, D. and Robert, J. B., *Bull. Soc. Chim. Fr. 1968,* 2240.
2. Albrand, J. B., Gagnaire, D., Robert, J. B., and Haemers, M., *Bull. Soc. Chim. Fr. 1969,* 3496.
3. Campbell, J. R. and Hall, L. D., *Chem. Ind.* (London) *1971,* 1138.
4. McPhail, A. T., Luhan, P. A., Featherman, S. I., and Quinn, L. D., *J. Amer. Chem. Soc. 94,* 2126 (1972).
5. Bentrude, W. and Yee, K. C., *J. Chem. Soc.; Chem. Commun. 1972,* 169.
6. Hall, L. D. and Malcolm, R. B., *Can. J. Chem. 50,* 2102 (1972).
7. Bodkin, C. and Simpson, P., *J. Chem. Soc., Perkin Trans. II 1973,* 676.
8. White, D. W., Bertrand, R. D., McEwen, G. K., and Verkade, J. G., *J. Amer. Chem. Soc. 92,* 7125 (1970).
9. White, D. W., McEwen, G. K., Bertrand, R. D., and Verkade, J. G., *J. Magn. Resonance 4,* 123 (1971).
10. Paričiová, M., Holčík, J., and Mašek, J., *Czechoslov.* 205212 (1980).
11. Göghová, M., Durmis, J., Karvaš, M., Mašek, J., and Holčík, J., *Czechoslov. Appl.* 4970 (1982).
12. Anderson, J. E., *J. Chem. Soc. B1967,* 712.
13. Lapuka, L. F., Kantor, E. A., Mustavirov, R. S., and Rakhmankulov, D. L., *Zh. Obshch. Khim. 51,* 934 (1980).
14. Wei-Jen Kung, Marsh, R. E., and Kainosho, M., *J. Amer. Chem. Soc. 99,* 5471 (1977).
15. Samitov, Y. Y., *Zh. Obshch. Khim. 52,* 2211 (1982).
16. White, R. F. M., *J. Mol. Struct. 6,* 75 (1970).
17. Bergesen, K. and Albriktsen, P., *Acta Chim. Scand. 26,* 1680 (1972).
18. Bergesen, K. and Albriktsen, P., *Acta Chim. Scand. 25,* 2257 (1971).
19. Cooper, D. B., Inch, T. D., and Lewis, G. L., *J. Chem. Soc., Perkin Trans. I 1974,* 1043.
20. Chan, S., Goldwhite, H., Keyzer, H., Roeusell, D. G., and Tang, R., *Tetrahedron 25,* 1097 (1969).
21. Haemers, M., Ottinger, R., Zimmermann, D., and Reise, J., *Tetrahedron 29,* 3539 (1973).
22. Mosbo, J. A. and Verkade, J. G., *J. Amer. Chem. Soc. 95,* 4659 (1973).
23. Pätoprstý, V., Malík, Ľ., Goljer, I., Göghová, M., Karvaš, M., and Durmis, J., *Magn. Resonance Chem. 23,* 122 (1985).
24. Hall, L. D. and Malcolm, R. B., *Can. J. Chem. 50,* 2092 (1972).
25. Majoral, J. P., Pujol, R., and Navech, J., *Bull. Soc. Chim. Fr. 1972,* 606.
26. Donaldson, B. and Hall, L. D., *Can. J. Chem. 50,* 2111 (1972).
27. Kainosho, M., *J. Chem. Phys. 74,* 2853 (1970).
28. Brault, J. F., Majoral, J. P., Savignac, P., and Navech, J., *Bull. Soc. Chim. Fr. 1973,* 3149.
29. Sopchik, A. E. and Bentrude, W. G., *Tetrahedron Lett. 21,* 4674 (1980).
30. Bouchu, D., *Phosph. Sulfur 15,* 33 (1983).

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