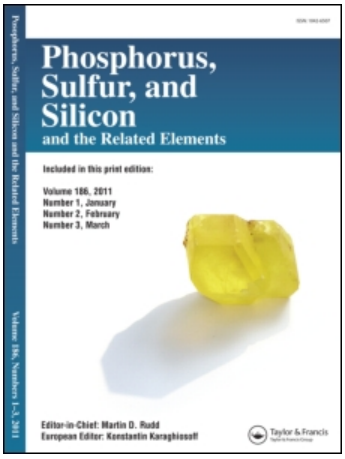

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. XXVII. SOLVENT EFFECTS ON THE ^{31}P NMR CHEMICAL SHIFTS OF SOME CYCLIC PHOSPHONATES

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. XXVII. SOLVENT EFFECTS ON THE ^{31}P NMR CHEMICAL SHIFTS OF SOME CYCLIC PHOSPHONATES

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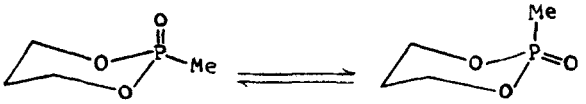
The solvent effect on the ^{31}P NMR chemical shift and the characteristic behaviour of the ^{13}C NMR spectra of substituted 2-alkyl-2-oxo-1,3,2-dioxa-phosphorinanes were investigated. In aprotic solvents no significant change was found for $\delta\ ^{31}P$ which is correlated linearly with dielectric constants of the solvents. In protic solvents $\delta\ ^{31}P$ was shifted to downfield in a considerable extent, depending on the hydrogen donating ability of the solvent.

It was found that 2-methyl-2-oxo-1,3,2-dioxa-phosphorinane existed in an equilibrium of equatorial(e) and axial(a) forms. ^{13}C NMR chemical shifts of 2-axial methyl-2-oxo-1,3,2-dioxaphosphorinane (**3a**) and 2-equatorial methyl-2-oxo-1,3,2-dioxa-phosphorinane (**3e**) showed an unusual behaviour, which is difficult to rationalize either by the conception of steric compression or by the local van der Waals interaction model.

It was reported that no significant solvent effect on the chemical shifts in the NMR spectra of acyclic phosphates and phosponates was observed.[1] The largest ^{31}P chemical shift difference ($\Delta\delta\ ^{31}P$) between nonpolar and protic solvents was of the order of 3–4 ppm. For triethyl phosphate $\Delta\delta\ ^{31}P$ between aqueous and carbon tetrachloride solutions was only 0.6 ppm, and no difference of the ^{31}P chemical shift was found in carbon tetrachloride and chloroform. However, Maciel[2] found that the ^{31}P chemical shift of triphenyl phosphine oxide was downfield in protic solvents, i.e. in sulfuric acid solution was 35 ppm downfield in protic solvents, compared to carbon tetrachloride. Lerner[3] also found a moderate solvent effect on the ^{31}P chemical shift of adenosine-3′,5′-cyclic phosphate, with $\Delta\delta\ ^{31}P$ around 3 ppm. Nevertheless, there was no correlation between $\delta\ ^{31}P$ and the dielectric constant of solvents. It was, however, associated, at least to a certain extent, with the hydrogen donating ability of the solvent.

For 2-methyl 2-oxo-1,3,2-dioxa-phosphorinane, according to ^{31}P chemical shift and dipole moment results,[4] two conformations, equatorial and axial forms, were suggested to exist in equilibrium:

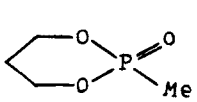


e-form *a*-form

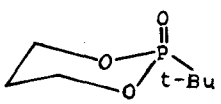
In the dynamic ^{31}P NMR study, however, no such evidence was observed.[5] If the conformational equilibrium existed in solution, the characteristic equilibrium

should be found in various solvents of different dielectric constant. The ^{31}P chemical shift will be, therefore, correlated with the nature of the solvents.

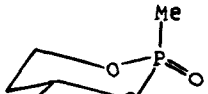
In this paper 2-methyl-2-oxo-1,3,2-dioxa-phosphorinane, **1**,2-*t*-butyl-2-oxo-1,3,2-dioxa-phosphorinane, **2**, 2,4-dimethyl-2-oxo-1,3,2-dioxa-phosphorinane, **3a**—methyl in axial, **3e**—methyl in equatorial position, were selected for the



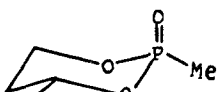
1



2

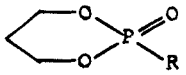


3a



3e

study of the correlation between the nature of the solvent and the ^{31}P chemical shifts. In the meantime, the ^{13}C NMR chemical shifts of compounds **1–3** and **4–6** were also reported.



R = Et **4**, Pr **5**, *i*-Pr **6**

RESULTS AND DISCUSSION

Solvent Effect on the ^{31}P Chemical Shifts

The ^{31}P chemical shifts of **1, 2, 3a** and **3e** in a series of solvents are listed in Table I. The chemical shifts of these cyclic phosphonates in aprotic solvents were found not to differ very much from each other. The largest ^{31}P chemical shift difference was found to be no more than 2 ppm while the dielectric constants of these

TABLE I

^{31}P chemical shifts of some cyclic phosphonates in a series of solvents (in ppm)

Solvent	D	$D-1$* / $2D+1$	^{31}P chemical shift (δ ^{31}P)			
			1	**2**	**3a**	**3e**
$CHCl_3$	4.8	0.359	27.3	35.1	22.6	29.5
CH_3COOH	6.2	0.386	30.6	35.9	26.9	32.5
t-C_4H_9OH	12.5	0.442	27.0	34.0	—	—
CH_3OH	32.7	0.477	28.1	35.4	25.7	31.0
CF_3COOH	39.5	0.418	36.0	41.5	—	—
H_2O	78	0.490	32.5	38.1	—	—
cyc-C_6H_{12}	2.02	0.202	—	33.4	—	—
C_6H_6	2.3	0.232	24.6	33.9	19.4	27.7
1,3,5-$(Me)_3C_6H_3$	2.28	0.230	24.9	33.3	—	—
Dioxane	2.2	0.222	25.0	33.4	20.2	28.2
$(C_2H_5)_2O$	4.3	0.344	24.7	32.9	—	—
Tetrahydrofuran	7.6	0.407	23.1	32.7	—	—
C_5H_5N	12	0.440	23.5	32.8	20.8	27.5
$(CH_3)_2CO$	21	0.465	23.1	31.9	20.4	27.7
$C_6H_5NO_2$	35	0.479	23.7	33.0	—	—
Dimethyl foramide	37	0.480	23.1	31.9	—	—
Dimethyl sulfoxide	47	0.484	24.4	32.4	22.6	27.7

* See Equation (1) in the text.

solvents differ substantially. However, in protic solvents the ^{31}P chemical shifts were changed a lot. The difference of the ^{31}P chemical shifts between protic and aprotic solvents was found to be more than 10 ppm. We can conclude that the stronger proton donating ability of the solvent caused the ^{31}P chemical shifts moving downfield. Some similar results were reported.[2,3]

The solvent effect on the chemical shifts was also influenced by the structure of the compounds studied. For example, **2** showed the smallest, **3a** the largest solvent effect. Furthermore, the $\Delta\delta$ ^{31}P between chloroform and acetic acid for **1, 2, 3a** and **3e** was 3.3, 0.8, 4.3 and 3.0 ppm, respectively and $\Delta\delta$ ^{31}P between dioxane and acetic acid was 5.6, 2.5, 6.7 and 4.1 ppm, respectively. It may be rationalized by the steric hindrance in solvation by a bulky *t*-butyl group in **2**, while in **3a** the phosphoryl group is located in an equatorial position, so that the steric hindrance of solvation was relieved in this case.

Although the solvent effect of aprotic solvents is not significant, the ^{31}P chemical shifts tended to be more upfield with the increase of dielectric constants of the solvents. As far as the solvation energies (E_{solv}) are considered with the dielectric constant of the solvents in the first order of approximation, Equation (1) can be used[6]

$$E_{solv} = \frac{(D-1)\mu^2}{(2D+1)a^3} \tag{1}$$

where D—dielectric constant of the solvent, μ—dipole moment of the solute, a—the radius of the solute as a sphere. Therefore, the strength of the interaction between the solute and solvent will be proportional to the quantity $D - 1/2D + 1$. If this interaction will influence the chemical shifts to a certain extent, δ ^{31}P will also be proportional to $D - 1/2D + 1$. Figure 1a shows the correlation between δ ^{31}P and $D - 1/2D + 1$. The lines for **2** and **1** are nearly parallel, and the stronger the solvation, the more upfield the δ ^{31}P values are. The compound, **3a**, however, showed the opposite tendency, while **3e** did not seem to exhibit an influence of aprotic solvents on its ^{31}P chemical shift.

It is obvious that **2**, **3a** and **3e** exist in a single conformation, due to the substituents which make the ring more rigid. But **1** might exist as axial form (**1a**—methyl group axial) and equatorial form (**1e**—methyl group equatorial). If it does so the ratio of **1a** to **1e** will be changed with the magnitude of $D - 1/2D + 1$. According to Equation (1), the proportion of **1a** will be increased in solvents of high dielectric constant. Suppose the ^{31}P chemical shifts of pure **1a** and **1e** (δ_a and δ_e) were approximately taken as those of **3a** and **3e**, the proportion of **1a** in the equilibrium may be estimated by Equation (2)

$$A = \frac{\delta_e - \delta}{\delta_e - \delta_a} \tag{2}$$

where A—proportion of **1a**, δ—the ^{31}P chemical shift of a mixture of **1a** and **1e** in a given solvent, δ_a, δ_e—the chemical shifts of **3a** and **3e** in the same solvent.

The results obtained from equation (2) are listed in Table II. It was found that A is linearly correlated with $D - 1/2D + 1$ (see Fig. 1b), and two straight lines were obtained for aprotic and protic solvents, respectively. Obviously, **1** exists in the equilibrium of *e*-form and *a*-form in solution, and in solvents of high dielectric

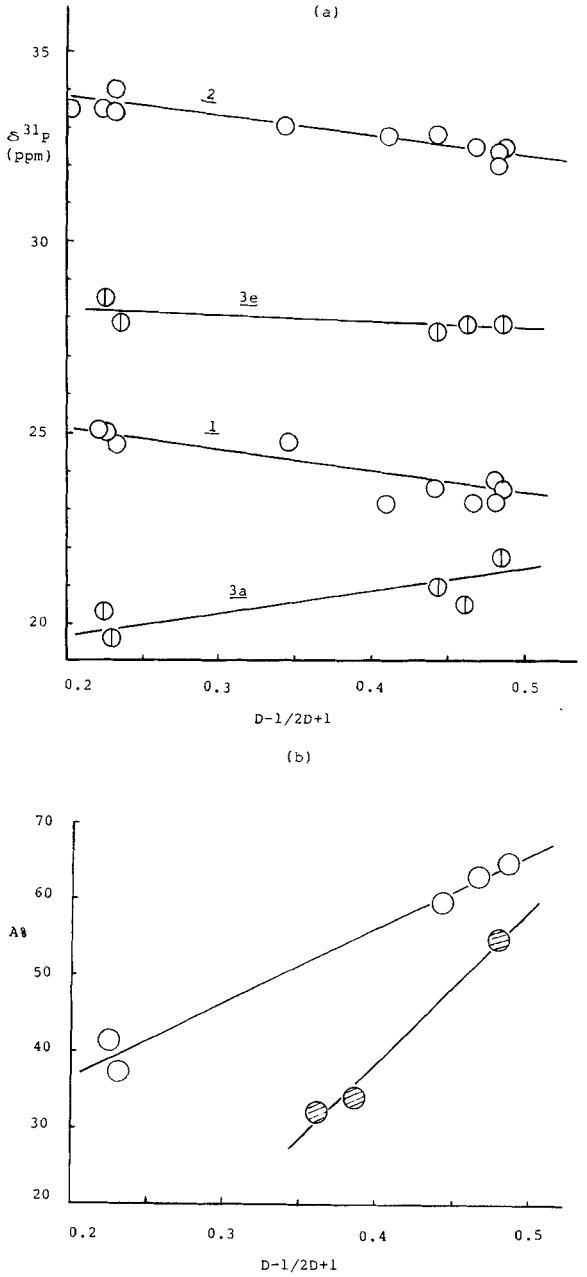


FIGURE 1 Influence of $D - 1/2D + 1$ of the solvent on the δ ^{31}P (a) and percentage of axial form (b). ○—aprotic solvent ●—protonic solvent.

TABLE II

The calculated proportion of the *a*-form of **1** in different solvents

Solvent	$CHCl_3$	CH_3OH	CH_3COOH	C_6H_6	Dioxane	C_6H_5N	$(CH_3)_2CO$	DMSO
a-form%	31.9	54.7	33.9	37.3	41.5	59.7	63.0	64.7
$\frac{D-1}{2D+1}$	0.359	0.477	0.386	0.232	0.222	0.440	0.465	0.484

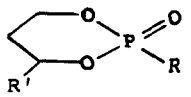
constant such as acetone ($D = 21$) and DMSO ($D = 47$), the **1a** form is predominant, while in solvents of low dielectric constant, e.g. benzene ($D = 2.3$) and chloroform ($D = 4.8$), the proportion of **1e** is greater than **1a**. Since the protic solvents are able to stabilize the *e*-form due to the higher basicity of the phosphoryl oxygen in **1e**, compared to **1a**[4] and favourable in forming hydrogen bonding. Therefore, if the aprotic and protic solvents possess similar dielectric constants, the content of the *a*-form in protic solvents is less than that in aprotic solvents.

^{13}C Chemical Shifts of the Substituted 2-oxo-1,3,2-dioxa-phosphorinanes.

The chemical shifts of compounds **1–6** are recorded in Table III. The change of structure in the 2-alkyl group did not influence the ^{13}C chemical shifts of the ring carbons very much. But there are some special structural effects on the ^{13}C chemical shifts in **3a** and **3e**. Although the ^{13}C chemical shift of the axial 2-methyl carbon in **3a** is more upfield, compared to that of the equatorial 2-methyl carbon in **3e** (δ ^{13}C of *a*-form 8.53 ppm, δ ^{13}C of *e*-form 11.38 ppm) than expected, the δ ^{13}C of the ring carbons is unusual. It is not only in the substituted cyclohexane[7] but also in the phosphorinanes[8] that the δ ^{13}C of both axial methyl carbon and the ring carbons in gauche γ-position to the axial methyl group are shifted upfield, compared to equatorial methyl isomer. However, the ^{13}C chemical shifts of the ring carbons (carbon No. 1, 3 in Table III) in the gauche γ-position to the 2-methyl carbon in **3a** are not shifted upfield, but down-field in comparision with

TABLE III

^{13}C Chemical shifts of compounds of **1–6** in $CDCl_3$ (in ppm)



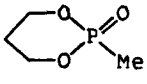
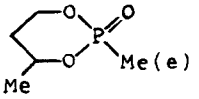
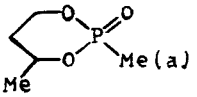
$R = CH_3, \underset{4}{CH_2}CH_3, \underset{4}{CH_2}\underset{5}{CH_2}CH_3, \underset{4}{CH}(CH_3)_2, \underset{4}{C}(CH_3)_3$

		δ ^{13}C in ppm of various carbons						
R'	R*	1	2	3	4	5	P—CH_3	ring-CH_3
H	CH_3	65.75	26.58	65.75			10.06	
H	CH_2—CH_3	65.30	26.70	65.30	17.99		6.13	
H	CH_2—CH_2—CH_3	65.21	26.81	65.21	26.16	15.40	14.59	
H	$CH(CH_3)_2$	65.02	26.81	65.02	25.03		15.61	
H	$C(CH_3)_3$	65.62	26.90	65.62	30.96		24.45	
CH_3	CH_3(e)	71.63	33.58	63.66			11.38	21.80
CH_3	CH_3(a)	74.75	32.97	65.53			8.53	21.94

* The number refers to the location of the carbon as illustrated in the formula on the top of this Table.

TABLE IV

^{13}C and $E_{vdw.c}$ of **1**, **3a** and **3e**

Compound	Carbon No.*	δ ^{13}C (ppm)	$E_{vdw.c}$(K_{cal}/mol)†
	1,3	65.75	0.1723(0.1389)
	2	26.58	1.4490(1.2845)
	Me	10.06	−0.1915(−0.1103)
	1	71.63	0.1559
	2	33.58	1.6072
	3	63.66	0.1326
	P-Me	11.38	−0.2137
	ring-Me	21.80	—
	1	74.75	0.1176
	2	32.97	1.4515
	3	65.53	0.1031
	P-Me	8.53	−0.1365
	ring-Me	21.94	—

* The number of the carbon atoms is as in Table III.
† The values in parentheses are $E_{vdw.c}$ in the *a*-form.

equatorial 2-methyl isomer, **3e**. This can not be rationalized, either by Grant's steric compression model[9] or by the intramolecular Van der Waals interaction model.[10] According to the van der Waals interaction model, δ ^{13}C is determined by the local van der Waals interaction energy of the resonant carbon nuclei ($E_{vdw.c}$) evaluated by molecular mechanics calculations. The lower the $E_{vdw.c}$ (for the same type of carbon), the more upfield the δ ^{13}C. The $E_{vdw.c}$ for **1**, **3e**, and **3a** were estimated by Allinger's force field (MM2 program).[11] The δ ^{13}C and $E_{vdw.c}$ for each atom in **1**, **3e** and **3a** are listed in Table IV. The assignment of resonance for axial or equatorial carbons were determined by the δ ^{31}P NMR spectra. The δ ^{31}P of axial methyl isomer (**3a**) is 6.9 ppm upfield, compared to that of equatorial isomer (**3e**). It can be seen from Table 4 that the $E_{vdw.c}$ of the ring carbons (No. 1, 3) in **3a** are lower than that in **3e**. But the δ ^{13}C of the ring carbons (No. 1, 3) in **3a** are downfield, compared to that in **3e**. Possibly, in this case the main factor which controls the ^{13}C chemical shifts is not the $E_{vdw.c}$ but other effects such as the magnetic susceptibility anisotropy. Perhaps, the difference of the magnetic susceptibility anisotropy between the P—C and the P═O bonds is of much larger influence than the steric interaction.

EXPERIMENTALS

The substituted 2-alkyl-2-oxo-1,3,2-dioxa-phosphorinanes used in this study were prepared by the method given in Reference 5. The ^{31}P and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer, operating at 36.19 MHz and 22.49 MHz, respectively. For the ^{31}P NMR studies the samples were dissolved in a series of solvents at the concentration of 0.1 M, using 85% H_3PO_4 as the external reference. Positive chemical shift values are downfield, negative ones upfield. For the ^{13}C NMR measurements, the samples were dissolved in $CDCl_3$ at the concentration of 0.1 M δ ^{13}C values are relative to TMS. All the NMR spectra were recorded at 25°C.

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