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CONFORMATIONAL ANALYSIS OF 2-THIONO-1,3,2-DIOXAPHOSPHORINANES

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In contrast to the numerous studies available concerning the conformation and the conformational mobility of the 2-oxo-2R-1,3,2-dioxaphosphorinanes [1], relatively little attention has been devoted to the corresponding 2-thiono derivatives [2]. From an I.R. study [3], it was shown that for the 2-methyl-2-thiono-1,3,2-dioxaphosphorinane, a dynamic equilibrium of two conformers exists with the amounts of the two species depending on the dielectric permeability of the medium. In the case of the corresponding 2-chloro derivative, there exists essentially one conformational form.

We wish to report here nmr data (^1H, ^{13}C, ^{31}P) which give additional information concerning the conformation and conformational mobility of 2-thiono-2R-1,3,2-dioxaphosphorinanes (**1** R = CH_3 ; **2** R = C_6H_5 ; **3** R = $O-C_6H_5$; **4** R = Cl).

The nmr spectra (^1H, ^{13}C, ^{31}P) have been recorded in two solvents of highly different dielectric permeability values (CCl_4, $\varepsilon = 2.23$; CD_3CN, $\varepsilon = 37.5$) [4]. The results of the nmr spectral analysis are reported in Table I and Table II.

Table I

^1H nmr spectral parameters of 2-thiono-2R-5,5-dimethyl-1,3,2-dioxaphosphorinanes. ^1H chemical shifts are in ppm relative to internal TMS, the spin-spin coupling constants are in Hz.
A) refers to a 0.5 M solution in CCl_4 ; B) refers to a 0.5 M solution in CD_3CN.

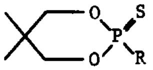
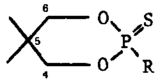
R			$\delta(CH_{3eq})$	$\delta(CH_{3ax})$	$\delta(CH_{eq})$	$\delta(CH_{ax})$	$^3J(POCH_{eq})$	$^3J(POCH_{ax})$
	**1** CH_3	A	0.89	1.23	3.59	4.39	23.2	5.3
		B	0.94	1.11	3.82	4.24	17.5	9.8
	2 C_6H_5	A	0.93	1.31	3.70	4.52	22.0	5.2
		B	1.02	1.16	3.88	4.37	17.1	10.4
	3 OC_6H_5	A	0.93	1.28	3.97	4.18	19.8	6.8
		B	0.87	1.26	4.01	4.39	22.9	3.3
	4 Cl	A	0.94	1.36	3.94	4.27	28.8	4.0
		B	0.89	1.27	4.06	4.36	29.1	3.8

Table II

^{13}C and ^{31}P nmr spectral parameters of 2-thiono-2R-5,5-dimethyl-1,3,2-dioxaphosphorinanes. ^{13}C chemical shifts are in ppm relative to internal TMS, ^{31}P chemical shifts in ppm relative to an external 85 % H_3PO_4 solution.

	R		$\delta^{31}P$	$\delta^{13}C_4,C_6$	$\delta^{13}C_5$	$\delta^{13}CH_3$	$\delta^{13}CH_3$
	1 CH_3	A	-95.3	72.3	33.2	22.9	21.3
		B	-94.8	73.9	32.9	21.0	20.5
	2 C_6H_5	A	-86.0	73.4	33.1	22.9	21.4
		B	-83.8	75.1	33.0	21.3	20.7
	3 OC_6H_5	A	-53.7	76.8	32.1	21.9	21.1
		B	-54.3	78.0	32.1	21.0	19.6
	4 Cl	A	-55.2	78.0	32.0	22.2	20.6
		B	-58.7	79.2	32.2	21.0	19.3

Several types of evidence establish that compound 1 exists predominantly in one conformation in CCl_4 : the large chemical shift difference between the signals corresponding to the methyl groups attached to the C_5 carbon atom ($\Delta\delta$ = 0.34 ppm) ; the existence of a long range spin-spin coupling between one of the methyl groups CH_{3ax}, and one of the methylene protons (CH_{ax}) [5] ; the large difference observed in the $^3J(POCH)$ values (ΔJ = 17.9 Hz). This statement is supported by the following observation ; the nmr spectral parameters of 1 in CS_2 (ε = 2.64) [4] ($\delta CH3_{ax}$= 0.85 ppm ; $\delta CH3_{eq}$ = 1.20 ppm ; $\delta P\text{-}CH_3$ = 1.80 ppm ; δCH_{eq} = 3.54 ppm ; δCH_{ax} = 4.36 ppm ; $^3J(POCH_{eq})$ = 24.2 Hz ; $^3J(POCH_{ax})$ = 5.0 Hz) which are close to the one observed in CCl_4 show only slight changes by lowering the temperature down to -50°C. The X-ray structure of 1 (chair form, P=S bond axial) [6] which shows no significant interatomic interactions allows us to state that in a medium of low electric permeability such as CCl_4, 1 exists predominant in a chair conformation with the P=S bond in the axial orientation.

The decrease observed in the following quantities $\delta CH3_{ax}$ - $\delta CH3_{eq}$; δCH_{ax}-δCH_{eq} ; $J(POCH_{eq})$ - $J(POCH_{ax})$; $\delta^{13}CH_{3ax}$ - $\delta^{13}CH_{3eq}$, in going from a CCl_4 solution of 1 to a CD_3CN solution (Table I and II) indicates that 1 exists in CD_3CN in an equilibrium between two conformations. These two conformations will differ by the bond orientation around the phosphorus (P=S axial or equatorial). The bond dipole moment of these two conformers may be calculated by using standard values for the individual bond dipole moment [7]. The molecular geometry used for the P=S axial conformer is the one reported in the X-ray structure analysis [6]. For the P=S equatorial conformer, we assumed the same ring geometry as for the P=S axial conformer, and just exchanged the P=S and $P\text{-}CH_3$ bond orientation. The calculated values of the dipole moments of the two conformers ($\mu_{P=S\ axial}$ = 3.1 D ; $\mu_{P=S\ eq}$ = 4.0 D) show that the conformer with the higher dipole moment becomes more favored as the dielectric constant of the solvent increases.

In compounds 1 and 2, the nmr spectral parameters have nearly the same values and show the same trend in going from a CCl_4 solution to a CD_3CN solution. Thus one can conclude that 2 also exists in a chair conformation with a P=S axial bond in CCl_4 and is in dynamic equilibrium in CD_3CN.

No significant changes are observed in the nmr parameters of 4 as measured in CCl_4, CD_3CN or a mixture of both solvents. The value of $\delta CH_{3ax} - \delta CH_{3eq}$, $\delta CH_{ax} - \delta CH_{eq}$, $^3J(POCH_{eq}) - {}^3J(POCH_{ax})$, and the difference in the half-width of the two CH_3 signals, show that there is one highly preferred chair conformation for molecule 4 in CCl_4 and CD_3CN.

For compound 3 , in comparison with 1 and 2 , an opposite trend is observed in the nmr parameters in going from CCl_4 to CD_3CN. An axial orientation of the P=S bond is expected to give similar chemical shift differences between the axial and equatorial methylene protons. This is indeed the case for the CCl_4 solutions of compounds 1 and 2. In compounds 3 and 4, the chemical shift difference $CH_{ax} - CH_{eq}$ is considerably smaller. This strongly suggests that in compounds 3 and 4 the chair conformation with a P=S equatorial bond is highly preferred. By assuming that the $^3J(POCH)$ values are independent of the bond orientation around the phosphorus, and by use of the $J(POCH_{ax})$ and $J(POCH_{eq})$ values measured at low temperature in the solvent in which there is one preponderent conformer at room temperature, one can calculate the approximate percentage X (± 5 %) of the P=S axial bond conformer at room temperature (20°C) by using equations (1) and (2) :

$$J(POCH_1) = X\ J(POCH_{ax}) + (1 - X)\ J(POCH_{eq}) \qquad (1)$$

$$J(POCH_2) = (1 - X)\ J(POCH_{ax}) + X\ J(POCH_{eq}) \qquad (2)$$

The calculated X values which are summarized below are in agreement with the I.R. study presented by O.A. Raevskii et al [3].

R	X (CCl_4)	X (CD_3CN)
CH_3	95	70
C_6H_5	100	70
OC_6H_5	10	15
Cl	0	0

X = percentage of the P=S axial conformer

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References

(1) R.S. Edmundson and E.W. Mitchell, J. Chem. Soc.(C), 3033 (1968) ; M. Kainosho, T. Morofushi and A. Nakamura, Bull. Chem. Soc. Jap., 42, 845 (1969) ; A.R. Katritzky, M.R. Nesbit, J. Michalski, Z. Tulimowski and A. Zwierzak, J. Chem. Soc (B), 140 (1970) ; J.P. Majoral, R. Pujoc and J. Navech, C.R. Acad. Sci., 272, C, 1913 (1971) ; W.G. Bentrude, H.W. Tan and K.C. Yee, J. Amer. Chem. Soc., 94, 3264 (1962); J.A. Mosbo and J.G. Verkade, ibid., 95, 4659 (1973).

(2) J.P. Majoral, Thesis, Toulouse University, 1972.

(3) O.A. Raevskii, A.N. Vereshchagin, F.G. Khalitov, Yu.A. Donskaya, R.A. Cherkasov and V. Ouchinnikov, Izvest. Akad. Nauk. SSSR, 1704 (1972).

(4) D.C. Reichardt, Angew. Chem., Int. ED., 4, 29 (1965).

(5) D. Gagnaire and J.B. Robert, Bull. Soc. Chim. Fr., 2240 (1967).

(6) J.P. Dutasta, A. Grand and J.B. Robert, previous communication.

(7) O.A. Raevski, F.G. Khalitov, Yu. A. Donskaya, I.M. Shermergorn, Izvest. Akad. Nauk. SSSR, 4, 795 (1973).