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NONCHAIR CONFORMATION IN 2,4,7-TRIOXA-3-PHOSPHA-3-THIONO-BICYCLO [4.4.0] DECANE SERIES

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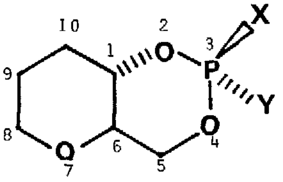
Summary : The NMR analysis of the less stable isomer of the 2,4,7-trioxa-3-chloro-3-phospha-3-thiono-bicyclo(4.4.0)decane 1a shows that this compound exists predominantly in a twist-boat conformation.

It is now well documented[1] that six membered phosphorus heterocycles exist predominantly in chair conformation especially in dioxaphosphorinane series, electronegative substituents on phosphorus adopting an axial orientation. Large values (20 to 30 Hz) of trans $^{3}J_{POCH}$ and low values (1 to 5 Hz) of gauche $^{3}J_{POCH}$ are generally typical of such conformation. Intermediate values have mostly been interpreted by the existence of a chair $\rightleftharpoons$ chair equilibrium[2]. However evidence has been reported[2b,3] of nonchair conformations in dioxaphosphorinanes in which the phosphorus substituent is forced into a thermodynamically disfavored orientation.

In connection with stereochemical studies of nucleophilic substitution at phosphorus, this paper reports results of NMR spectral analysis of one pair of diastereoisomeric dioxaphosphorinanes in the 2,4,7-trioxa-3-phospha-3-thiono-bicyclo [4.4.0] decane series bearing a chlorine atom on phosphorus.



1a X=S Y=Cl

1b X=Cl Y=S

The trans cycle jonction preventing any chair$\rightleftharpoons$chair equilibrium and limiting the number of nonchair conformations (figure 1) , it is interesting to study the prefered conformations when such a strong electronegative substituent is forced into a disfavored position. The normal chair conformation for the dioxaphosphorinane cycle of 1a (figure 1) would place the chlorine atom equatorial and the P=S bond axial.

Configurational assignments have been made on ^{31}P, ^{1}H NMR spectra basis (table I) and by means of mass spectrometry[5]. It can be stated, according to results given in other series[1a], that ^{31}P resonance of compounds with equatorial P=S bond is shifted upfield relative to compounds having axial P=S bond in this series[4] (excepted when the nonchalcogen is $-N(CH_3)_2$[5,6]). But the main criterions retained are the δ, $^{3}J_{HH}$ and $^{3}J_{POCH}$ obtained from the ^{1}H NMR spectral analysis.

Table I

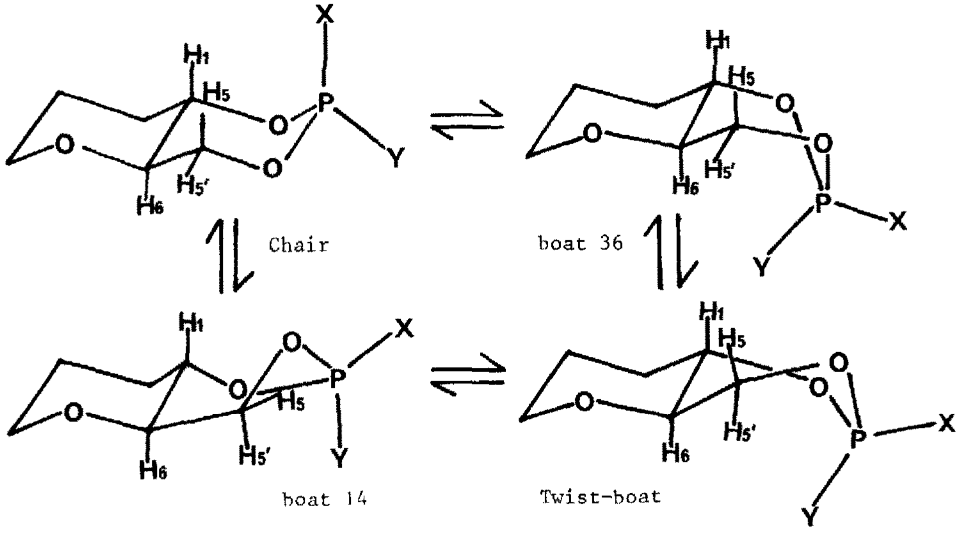
	X	Y	H_1 (a)	H_5	$H_{5'}$	H_6	J_{1-6}	$J_{5-5'}$	J_{5-6}	$J_{5'-6}$	J_{1-P}	J_{5-P}	$J_{5'-P}$	^{31}P (c)
1a	S	Cl	4.40	4.26	4.56	3.87	9.5	10.6	9.1	6.8	1.9	21.2	10.6	63.9
1b	Cl	S	4.29	4.24	4.37	3.58	9.7	10.7	10.7	5.0	(b)	4.6	29.0	59.2

(a) The ^1H NMR spectra were obtained from isomerically pure compounds in $CDCl_3$ solutions on a CAMECA spectrometer at 250 MHz. δ are positive in p.p.m. downfield from internal TMS. NMR parameters are resulting of a first order analysis. Coupling constants (Herz) are absolute values.

(b) The poorly resolved multiplet corresponding to H_1 is obscured by the H_5 signal, so we were unable to measure this coupling constant.

(c) The ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian XL 100 spectrometer. δ are positive in p.p.m. downfield relative to H_3PO_4 (85%) as external standard (*1a* $\delta^{31}P$ = 59 p.p.m. *1b* $\delta^{31}P$ = 55 p.p.m., neat)[5].

Figure 1



The ^1H NMR parameters for *1b* (especially $^3J_{5-6}$ = 10.7 Hz, $^3J_{5'-6}$ = 5.0 Hz, $^3J_{5-P}$ = 4.6 Hz and $^3J_{5'-P}$ = 29.0 Hz) are consistent with a chair form where the chlorine atom is axially oriented. It is noteworthy that $\delta H_{5'}$ is larger than δH_5 due to a greater deshielding effect of the equatorial P=S bond relative to the effect of chlorine.

The coupling constants values for *1a* (especially $^3J_{5-6}$ = 9.1 Hz, $^3J_{5'-6}$= 6.8 Hz, $^3J_{5-P}$ = 21.2 Hz and $^3J_{5'-P}$ = 10.6 Hz) are inconsistent with a single chair form, but could be explained by an equilibrium between chair, boat 36 [7], boat 14, and twist-boat conformations in which the chlorine atom recovers a much favored axial orientation. Low temperature

^{31}P NMR experiment from 261 to 131 °K did not show any evidence supporting this equilibrium. However ^{13}C NMR spectra (Table II) between 293 and 195°K show little modifications, especially for $^{3}J_{C6-P}$, $^{3}J_{C10-P}$ and $^{2}J_{C5-P}$. It is likely that 1a is a rapidly equilibrating mixture of conformations.

Table II

^{13}C NMR spectral parameters [8] of 1a in CD_3COCD_3 at 293 and 195°K

T°K	C 8$^{(a)}$	C 9	C 10	C 1	C 5	C 6	$^{4}J_{C9-P}$$^{(b)}$	$^{3}J_{C10-P}$	$^{3}J_{C6-P}$	$^{2}J_{C1-P}$	$^{2}J_{C5-P}$
293	68.0	25.4	30.3	79.9	71.4	72.7	1.8	8.3	13.1	8.4	10.9
195	67.6	25.2	29.9	79.4	71.4	71.9	2.2	7.3	14.3	8.6	12.2

(a) δ are positive in p.p.m. downfield relative to internal TMS.

(b) J are absolute values in Hz (± 0.3 Hz).

It should be noted that $\delta H_{5'}$ is still greater than δH_5 indicating that H_5 is not deshielded by the P=S bond. On the contrary, $H_{5'}$ is now submitted to the deshielding effect of the chlorine atom. Additionally the great downfield shift of H_6 (0.4 p.p.m. relative to other compounds predominantly existing in a chair form in the same series) eliminates the chair conformation as significant contributor to the overall conformation of 1a.

Boat 36 conformation may be excluded on the basis of the following arguments : the values of $^{3}J_{5-6}$ and $^{3}J_{5'-6}$ relative to those of 1b are indicative of $H_6C_6C_5H_5$ and $H_6C_6C_5H_{5'}$ dihedral angles changes that are unexpected in this boat form ; $\Delta\ \delta H_1$ (a-b) = 0.11 p.p.m. > $\Delta\ \delta H_5$ (a-b) = 0.02 p.p.m. shows some distorsion of the dioxaphosphorinane ring which permits a greater deshielding of H_1 ; furthermore $^{3}J_{1-P}$ should increase [9] from chair to boat 36 conformation ($H_1C_1O_2P$ dihedral angle changes from ≈ 60° to 120°). This result is not surprising because of the expected great syn axial 1,4 steric interaction between H_6 and chlorine atoms in the boat 36 conformation.

The J_{H-H} and J_{H-P} values do not allow us to conclude firmly between the boat 14 and the twist-boat forms. However, the $^{3}J_{1-P}$ value (smaller than those in other 2-chloro-2-thiono-1,3,2-dioxaphosphorinanes [10]) , gives some argument for an increase of the $H_1C_1O_2P$ dihedral angle to ≈ 90°, and is in favor of the twist-boat conformation. Indeed this $H_1C_1O_2P$ dihedral angle is not altered from chair to boat 14 conformation.

Finally compound 1a seems to be preferentially in a twist-boat conformation in which the chlorine atom occupies a pseudo-axial orientation although we cannot rule out some additional small contributions from other conformations.

This result may have some importance in stereochemical studies for the evaluation of stereoelectronic effects [11] in nucleophilic substitution of 3-halogeno-1,3,2-dioxaphosphorinanes in this series.

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[6] - It has been recently emphasized by D.G. Gorenstein and R. Rowell, J.Amer.Chem.Soc., 101, 4925 (1979) that the similarity between the ^{31}P chemical shifts of diastereoisomeric oxazaphosphorinanes could be explained by a similar orientation of the nonchalcogen substituent at phosphorus. In view of our not yet published results (the two diastereoisomeric 2,4,7-trioxa-3-N,N-dimethylamino-3-phospha-3-thionobicyclo[4.4.0]decanes exist predominantly in chair form),the use of ^{31}P chemical shift for configurational and conformational assignements must be regarded with caution.

[7] - The numbers following boat are the ring positions that serve as the bow and stern.

[8] - Details on ^{13}C resonance assignments will appear elsewhere.

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