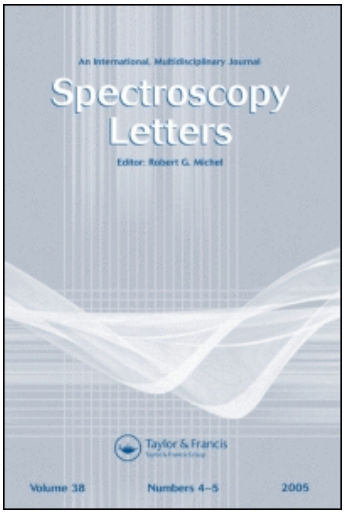

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ON THE TWIST-BOAT CONFORMATION OF THE TETRAHYDROPYRAN CYCLE IN THE TRIOXA-BIS-SPIROKETAL SERIES

Key words : ^{1}H and ^{13}C NMR, X-rays, twist, boat conformation tetrahydropyran.

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INTRODUCTION

In the solid state the trioxa-bis-spiroketal 2 (fig.1) has a twist-boat conformation (tetrahydropyran cycle) and its infrared absorption and nuclear magnetic resonance (^{1}H at 250 MHz, ^{13}C at 15,06 MHz) spectra let forsee the same conformation in solution[1].

So, molecule 2 is a particularly interesting model for establishing structure spectroscopic properties relationships, by comparison with its diastereoisomer 1 which has a chair conformation[2]. Besides, compounds such 1 and 2 which have a bis-spiroketal structure can be considered as synthons for synthesis of new ionophore polyethers. This has led us to study more thoroughly these two molecules by ^{1}H NMR at 500 MHz. If for 1 one could analyse entirely the spectrum, the 8,8' and 10,10' proton signals have been only analysed for 2*.

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* At 500 MHz the 9,9' nuclei signals of the tetrahydropyran cycle and the 3,3' nuclei signal of the tetrahydrofuran cycles still resone at nearly the same frequency.

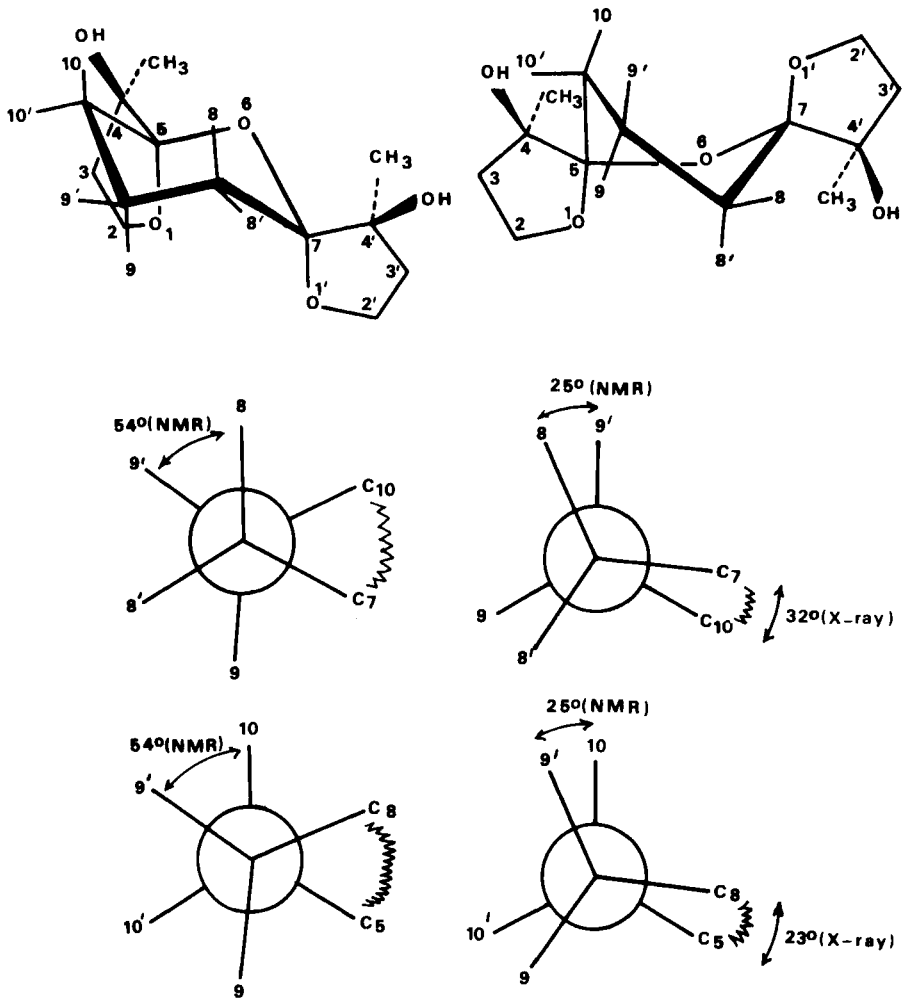

Figure 1- Conformations and dihedral angles of trioxa-bis-spiroketals 1 and 2

RESULTS AND DISCUSSION

The coupling constants observed after a LACOON III type calculation (Table I), very different for 1 and 2, indicate strong structures modifications between these two molecules and are consistent with an important flattening of the dihedral angles ψ (8,9) and

TABLE I- ^{1}H NMR spectra at 500 MHz of trioxa-bis-spiro-ketals 1 and 2. Solvent DMSO (Concentration 10 %). Coupling constants (Hz).

Compounds	H_8H_9	$H_8H_{9'}$	$H_{8'}H_9$	$H_{8'}H_{9'}$	$H_8H_{8'}$	$H_9H_{9'}$	R	ψ
1	13,01	4,52	5,20	3,65	-13,6	-12,9	1,71	54
2	0,86	9,81	10,27	7,62	-13,4	*	0,42	25

Compounds	$H_{10}H_9$	$H_{10}H_{9'}$	$H_{10'}H_9$	$H_{10'}H_{9'}$	$H_{10}H_{10'}$	$H_9H_{9'}$	R	ψ
1	13,01	4,52	5,20	3,65	-13,6	-12,9	1,71	54
2	7,62	9,81	10,27	0,86	-13,4	*	0,42	25

* no determined

TABLE II- ^{13}C NMR spectra at 15,06 MHz of trioxa-bis-spiro-ketals 1 and 2. Solvent DMSO (Concentration 10 %) Chemical shifts / TMS (ppm).

Compounds	$C_2C_{2'}$	$C_3C_{3'}$	$C_4C_{4'}$	CH_3	C_5	C_7	C_8	C_9	C_{10}
1	63,5	38,0	79,3	21,4	106,8	106,8	26,0	15,8	26,0
2	63,2	37,8	78,5	21,5	107,3	107,3	20,5	12,2	20,5
$\delta_C(2)\delta_C(1)$	-0,3	-0,2	-0,8	+0,1	+0,5	+0,5	-5,5	-3,6	-5,5

ψ (9,10) on passing from 1 to 2. These dihedral angles calculated following the R ratio method proposed by G.B. Lambert[2] are in good agreement for 2 with the cristallographic data [ψ (NMR) = 25°, ψ(X-ray)* = 27°5] and so confirm the transferability from solid state to solution of the twist-boat conformation of 2.

* Arithmetic average of the dihedral angle values ψ (8,9)= 32° and ψ (9,10) = 23° obtained for 2 in solid state by X-ray diffraction[1]. It is likely that molecule 2 slightly rearranges from solid state to solution where it admits a C_2 axis of symetry passing by O_6 and C_9 atoms.

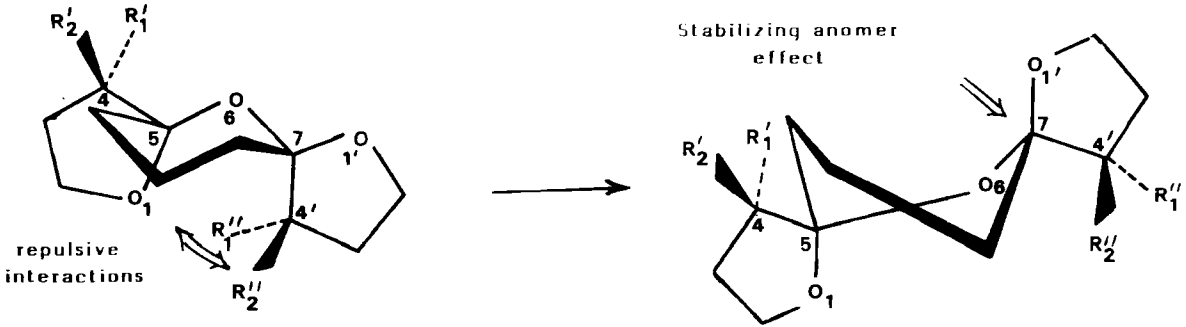

Figure 2- Chair form -> twist form conformation rearrangement for type 2 isomers.
2 : $R'_1 = R''_1 = CH_3$, $R'_2 = R''_2 = OH$; 2' : $R'_2 = R''_2 = CH_3$,
$R'_1 = R''_1 = OH$; 2'' : $R'_1 = R''_2 = OH$, $R'_2 = R''_1 = CH_3$

These results also allow to confirm that the strong shielding effect ($-5,5 \leqslant \Delta\delta\ ^{13}C_{\leqslant}\ -3,6$) observed in ^{13}C NMR (Table II) on the C_8, C_9 and C_{10} nuclei of 1 and 2 is a caracteristic information of a twist boat conformation. Such an observation had already been made by Roberts and al.[3], Booth and al.[4] in cyclohexane series, but, in our knowledge, it is the first time that it is made upon a molecule whose twist-boat conformation is demonstrated in solid state.

In the considered trioxa-bis-spiroketal series, six diastereoisomers among which the compounds 1 and 2 forseeable and have been isolated[1]. Three of them, among which 1, have the chair conformation, the three others, among which 2, adopting the twist-boat conformation. By comparison with an hypothetic chair form (fig. 2) the conformational rearragment of the type 2 isomers into a twist boat conformation favours, on one hand, the lowering of repulsive Van der Waals interactions between the O_1 atom and the CH_3 and OH groups linked to the $C_{4'}$ atom, on the other hand, the stabilizing anomer effect $O_6/C_7O_{1'}$.

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