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NMR Experiments on Cyclic Sulfites. VII. Lanthanide Induced Chemical Shifts in Trimethylene Sulfites with Respect to the Orientation of the S=O Bond

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Lanthanide induced chemical shifts (LIS) in sulfoxides have been published.[1] The LIS chemical shift increases linearly with the concentration of the shift reagent for a given sulfoxide concentration. Several workers have attempted to correlate the shifts with the internuclear distance between the proton studied and the lanthanide ion on the basis of assumed models. Apparently the lanthanide induced shifts should make it possible to distinguish between an axial and an equatorial functional group in cyclic compounds since the internuclear distance is changed substantially when the coordination site is moved from one position to the other. Accordingly, the shift induced on complexing the substrate will depend on the relative contributions of rotamers or conformers. The trimethylene (TM) sulfites have been shown to exist in a rigid chair conformation preferably with the S=O group in the axial position.[2–7] However, equatorial S=O groups have been observed for some substituted TM sulfites.[4] A study of LIS of TM sulfites with

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either S=O equatorial or axial should give additional information with regard to the stereochemistry of cyclic sulfites.

Results and discussion. The following TM sulfites have been prepared and examined with regard to the lanthanide induced shifts of the 4- and 5-protons and 4- and 5-substituted methyl groups: TM sulfite (I), 5-methyl-TM sulfite (II), 5,5-dimethyl-TM sulfite (III), 4-methyl-TM sulfite (IV), 5-phenyl-TM sulfite (V), 5-*tert*-butyl-TM sulfite (VI), 4,6-dimethyl-TM sulfite (with axial S=O bond VII a, with equatorial S=O VII b, and a twisted form VII c) and *trans*-1,3,2-dioxathiadecalin-2-oxide (with axial S=O VIII a, with eq. S=O VIII b).

The compounds I − VI have been reported to be in a 100 % or close to a 100 % rigid chair conformation with axial S=O bond. VII b and VIII b are found to be in a rigid chair conformation with equatorial S=O bond.[5,15]

When the concentration of the LSR is plotted against the chemical shift for the discrete protons, the "shiftslope" will depend on the position of the proton in the molecule. This is shown by Fig. 1 for TM sulfite and *cis*-4,6-dimethyl-TM sulfite (S=O eq. and twisted) and in Table 1 the corresponding slopes are calculated together with the "shiftslopes", K^s, of the other molecules examined.

From each of the three conformational forms in Table 1 and Fig. 1, it is evident that we are able to differentiate between axial and equatorial groups or protons on the same carbon atom. Likewise, we can differentiate between the two rigid chair forms with axial and equatorial S=O bond and the twisted conformer by comparing the Eu-shift for the 4 (6) axial protons.

Under certain conditions for internal rotation or for axial symmetry in the susceptibility tensor, the pseudocontact contribution to the

Table 1. The "shiftslope" K^s (v/x) for the methyl protons in the rigid chair conformations of the trimethylenesulfites with axial S=O bond, equatorial S=O bond, and the twisted form.

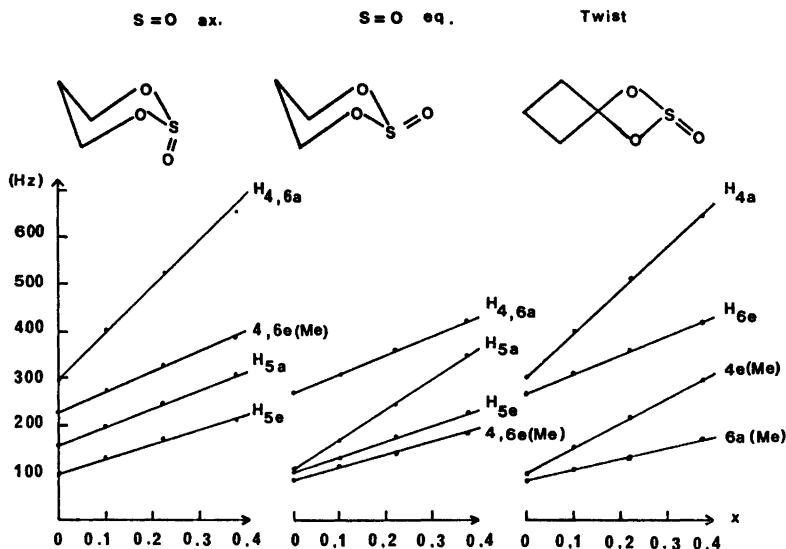| R/K^s (Hz)	S = O ax	S = O eq	Twist
$H_{4,6a}$	8.5 − 11.2	3.7 − 3.8	9.7 (H_{4a})
$H_{4,6e}$	3.5 − 4.4	5.7	4.4 (H_{6e})
H_{5a}	3.8 − 5.6	6.2 − 7.6	−
H_{5e}	3.1 − 3.8	3.2	−
$Me_{4,6e}$	2.1 − 2.6	2.8	5.7 (Me_{4e})
Me_{6a}	−	−	2.2
Me_{6a}	2.4 − 3.7	−	−
Me_{5e}	1.6 − 2.0	−	−

Fig. 1. Lanthanide induced shifts, as a function of the mol fraction, x, for the ring protons (methyl groups) in the rigid chair conformations of trimethylenesulfites with axial $S = O$ bond, equatorial $S = O$ bond, and the twisted form.

^{1}H NMR shift of a proton in a paramagnetic complex can be expressed by eqn. 1. The experimental studies on induced europium shifts can in these cases be analysed in terms of eqn. 1.

$$\varDelta\delta_i = k(3 \cos^2 \theta - 1)/R_i^3 \qquad (1)$$

where $\varDelta\delta_i$ is the induced shift of the i'th proton, R_i is the proton europium distance, k is a constant and θ is the angle between the radius vector from the europium ion to the i'th proton and the symmetry axis of the complex. The experimental paramagnetic shifts have been shown to depend on $1/R_i^3$.[1] Small discrepancies [9–10] from the $1/R_i^3$ dependency have been assumed to be due to the failure to consider the angular dependency portion of the pseudo-contact term.

In this work we have found a good qualitative measure for the distinguishing between a chair form with axial $S = O$ bond, equatorial $S = O$ bond or a twisted form without numerical evaluation of the different terms of eqn. 1.

Application of this method to conformationally mobile sulfites should be made with caution, for it is extremely difficult to predict rotamer populations in the complex with $Eu(FOD)_3$. It has been found for three 5-axial substituted sulfites [11] that on complexing with $Eu(FOD)_3$ the coupling constants are changed towards those of the rigid chair conformation with an axial $S = O$ bond which is assumed [12] to be the most preferable energetically.

Experimental. The synthesis of the unsubstituted and 4- and 5-substituted TM sulfites has been reported previously.[2,7,8,13–15] The compounds I – VI with axial $S = O$ bond were purified by GLC on an Aerograph Autoprep A-700 with a 2.1 m × 6.0 mm column packed with 10 % PDEAS and 10 % Carbowax on Chromosorb W, OMCS A/W, 45/60 Mesh. The compounds VII showed 3 isomers which have been reported to consist of rigid chair forms, with axial $S = O$ (VII a), one with equatorial $S = O$ (VII b) and one twisted (VII c). Compound VIII showed two isomers, also reported [15] consisting of two rigid chair forms, one with axial $S = O$ (VIII a) and one with equatorial $S = O$ (VIII b). The isomer b of these two compounds (with equatorial $S = O$) was purified by dissolving the reaction mixture, prior to distillation, in ethanol, from which white needles of isomer b were crystallized.

The NMR spectra were obtained on a JEOL-JNM-C-60-H instrument. Carbon tetrachloride was used as solvent. The concentration of the various sulfites were 5 mol % and the mol fractions between $Eu(FOD)_3$ and sulfite were 0.1, 0.22, and 0.375, respectively. 2 vol % tetramethylsilane was added as an internal reference. The $Eu(FOD)_3$ reagent was dried in vacuum at 50 °C for several hours prior to use.

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On ^{13}C NMR Spectra of *lel-* and *ob-* Conformations in Tris(diamine)-cobalt(III) Complexes

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The inert tris(diamine)cobalt(III) complexes with their puckered and flexible rings are often used as test-compounds for the study of theoretical and experimental aspects of conformational analysis.

One well-known stereochemical detail in these compounds is the occurrence of *lel-* and *ob-*rings (Fig. 1).[1]

In the present communication we wish to draw attention to a possibility of distinguishing *lel-* and *ob-*conformations of certain five-membered rings on the basis of proton-decoupled ^{13}C NMR spectra.
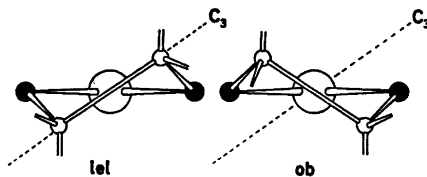
Fig. 1. A chelate ring, $\overline{C-N-M-N-C}$, viewed perpendicular to the C$_3$-axis (or pseudo C$_3$-axis) of a tris-complex.

In the following it is assumed that the reader is familiar with the IUPAC nomenclature for conformations and configurations.[2]

A family of complexes, [Co(en)$_x$(lbn)$_{3-x}$]-Cl$_3$.nH$_2$O ($x=0$, 1, 2), where en is 1,2-ethanediamine and lbn is $(-)_D$-(R,R)-1,2-dimethyl-1,2-ethanediamine, has been separated and resolved by descending paper chromatography.[3]

It is reasonable to assume that the chelated lbn ligand is forced to have the energetically favoured λ-conformation with two equatorially oriented methyl groups.[4] This assumption together with the knowledge of the absolute configuration of lbn makes it possible to deduce if an lbn ligand will adopt a *lel-* or an *ob-*conformation in a tris-complex, where the absolute configuration about the central atom is known.

This possibility of predicting ring conformations makes lbn complexes particularly suited for the present study.

The lbn conformations in complexes I−VI are given in Table 1.

The proton-decoupled 22.63 MHz ^{13}C NMR spectra of the six complexes with known lbn-ring conformations were measured in D$_2$O solution. The characteristics of the lbn patterns are presented in Table 1.

Two spectral features seem to mark a difference between *lel-* and *ob-*rings.

The linewidths of the methyl peaks from *lel-*conformations are broader than from *ob-*conformations. The half linewidths lie in the two separate intervals 14−26 Hz and 6−10 Hz, respectively. Both categories of peaks appear in the graphical representation as bands without structure and have a chemical shift of ca. 18.3.

The chemical shifts of the CH-resonances are different, the position of *lel-*ring peaks being 0.9−1.2 ppm downfield relative to the *ob-*ring peaks. The linewidths are all 2−4 Hz.

These findings are in accordance with a study of 1-propylenediamine complexes by Kojima and Yamasaki.[5] These authors observed that the methyl half linewidths in *fac-Δ*-[Co(lpn)$_3$-*lel*$_3$]$^+$ and *fac-Δ*-[Co(lpn)$_3$*ob*$_3$]$^{3+}$ were ∼27 and ∼7 Hz, respectively,[6] and that the shift difference between the CH carbon atoms was 1.3.