

NMR Experiments on Cyclic Sulfites. VI. The Orientation Effect of an S=O Group on the Proton Chemical Shifts in Trimethylene Sulfites

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The shielding of protons in trimethylene sulfites has been discussed in terms of the electrical field effect and the anisotropy effect of the S=O dipole.

Studies on the conformational behaviour of six-membered cyclic sulfites give evidence for the preferential occurrence of chair forms with an axial S=O bond.¹⁻³ Two heavily substituted sulfites have, however, been reported^{4,5} to exist in a chair form with an equatorial S=O bond. Ultrasonic experiments⁶ suggest an equilibrium between chair forms with an axial (ca. 99 %) and an equatorial S=O group as regards the trimethylene sulfite. The nature of the data from ultrasonic measurements is, however, such that one cannot use it to prove any structural assignments. The axial S=O bond is quoted to be 14.7 ± 4 kJ mol⁻¹ more stable as compared to the equatorial bond.⁷ It is the purpose of this paper to demonstrate the orientation effects of the S=O bond on the proton chemical shifts.

EXPERIMENTAL

The sulfites were prepared from appropriate diols and thionyl chloride according to the methods previously reported.¹ The isomers of 4,6-dimethyl-TM**-sulfite were purified using a preparative gas chromatograph. The isomers of *trans*-1,3,2-dioxathiadecalin-2-oxide were separated by distillation. The distillate containing

the isomer with axial S=O bond was purified by GLC. The residue from the distillation was dissolved in ethanol and cooled to -10°C and the isomer with equatorial S=O bond crystallized then as white needles, m.p. $50-50.5^\circ\text{C}$.

The NMR spectra were obtained on samples containing 20 % sulfite dissolved in CCl₄, using a Varian Associates HA-100 operating at 98 MHz for proton resonance. The spectra were analysed using the computer programmes LAOCN3⁸ and UEAITR.⁹

The parameters are assumed to be correct to ± 0.2 Hz. The computations are carried out using a UNIVAC 1110 computer.

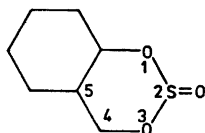
RESULTS AND DISCUSSION

From X-ray data¹⁰ of TM-sulfite it can be calculated that the internuclear distance between the axial sulfinyl oxygen and the axial 4-hydrogen is ca. 2.5 Å, a value within the range of the sum of the van der Waals radii of hydrogen and oxygen. An axial S=O bond is, however, more stable as compared to an equatorial S=O bond.¹ The stability of an axial S=O bond in TM-sulfites has been attributed to an increased rotational barrier about single bonds in system containing adjacent electron pairs and polar bonds.^{1,11} Moreover, it is possible that in addition to this effect similar effects as proposed¹² for cyclic sulfoxides contribute; *i.e.*, that attractive terms outweigh repulsions and create a favourable interaction between the axial sulfinyl oxygen and the axial 4 and 6 hydrogens. The difference between the chemical shifts of protons in a cyclic sulfite has been interpreted¹³ as being due to the electric field effect and

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** Tm = trimethylene.

Table 1. Chemical shifts in ppm from TMS and coupling constants in Hz.



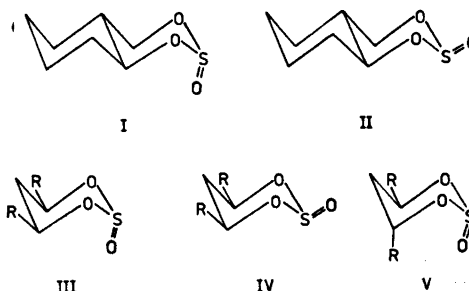
Comp. No.	δ_{4a}	δ_{4e}	δ_{6a}	δ_{6e}	2J_4	${}^2J_{4a5e}$	${}^2J_{4a5a}$	${}^2J_{4e5e}$	${}^2J_{4e5a}$	2J_5	${}^2J_{CH_3}$
I	4.507	3.630	^a	—	-11.43	—	11.22	—	4.14	—	—
II	4.053	4.187	^a	—	-11.81	—	11.27	—	5.54	—	—
III	5.01	1.25 ^b	1.76	1.78	—	2.4	11.6	—	—	-14.1	6.4
IV	4.48	1.40 ^b	1.78	1.72	—	2.2	11.5	—	—	-14.1	6.3
V	5.00	1.35 ^b	2.08	1.97	—	4.0	9.5	5.5	5.4	-14.1	6.3
	1.55 ^b	4.42									

^a Cannot be measured. ^b The methyl group.

magnetic anisotropy effect of the S=O bond. The shielding region of the S=O bond is assumed to be similar to the $-C\equiv C-$ bond,¹ i.e. a positive shielding cone and a negative area transverse to the bond direction.

Assuming a chair form for the TM-sulfite with an axial S=O bond it can be seen that the protons in the positions 4 and 6 lie within the deshielding region. The *syn* axial 4 and 6 protons relative to the axial S=O bond are exposed to the maximum deshielding. This has, however, been used as evidence for an axially situated S=O bond in TM-sulfites.¹ For TM-sulfites with an equatorial S=O bond it is expected that the chemical shift difference between axial and equatorial 4 (or 6) protons should be small. This is because the axial 4 and 6 protons lie within a similar shielding region. This orientation effect of the S=O bond on the chemical shift difference between the geminal 4 (or 6) protons is easily demonstrated by experiments (Table 1). In compound I, with axial S=O bond, the axial 4 proton is 0.9 ppm more deshielding as compared to the geminal equatorial proton. The data of compound II, with equatorial S=O bond, show, however, that the axial 4 proton is *ca.* 0.15 ppm more shielded compared to the geminal equatorial proton.

The orientation effect of the sulfinyl group can easily be demonstrated from the chemical shift difference of the corresponding 4 (or 6)



I: *trans*-1,3,2-Dioxathiadecalin-2a-oxide. II: *trans*-1,3,2-Dioxathiadecalin-2e-oxide. III: 4e,6e-Dimethyl-1,3,2-dioxathiane-2a-oxide. IV: 4e,6e-Dimethyl-1,3,2-dioxathiane-2e-oxide. V: 4e,6a-Dimethyl-1,3,2-dioxathiane-2a-oxide. R = methyl.

protons in the two isomers with the S=O bond either axial or equatorial. The chemical shift difference of the axial 4 proton of the isomers I and II, or III and IV is *ca.* 0.5 ppm (Table 1). This difference is due to the difference in both the electrical field effect and the magnetic anisotropy effect of the S=O bond in the two systems. The contribution to the proton shielding of a C—H bond of the electric field effect, due to an axial or an equatorial neighbouring S=O dipole can be obtained from the formula derived by Buckingham¹⁴ and generalized by Pritchard and Lauterbur.¹⁵ The results from such calculations (Table 2) suggest that the change in the electrical field effect,

Table 2. The effect of the S=O electric field on the chemical shift of ring protons in position 4 and 6.^a

	Axial proton	Equatorial proton
S=O axial	-0.31	-0.17
S=O equatorial	-0.12	-0.06
S=O _{ax} - S=O _{eq}	-0.19	-0.11

^a Calculated from formula derived by Buckingham.¹³ Negative values mean a high frequency shift. The values are in ppm.

caused by changing the S=O dipole from the axial to the equatorial position, is responsible for ca. 0.2 ppm of the shift difference between the axial 4 (or 6) protons in compounds I and II, or III and IV. Similar calculations (Table 2) for the equatorial 4 (or 6) protons as regards the different orientations of the S=O dipole suggest that the difference in the field effect is ca. 0.1 ppm. The chemical shift differences caused by the field effect of the sulfinyl bond accounts for only 20–30 % of the observed shift difference for the axial and the equatorial 4 (or 6) protons. The shielding effect of the axial S=O bond on the *syn* axial 4 and 6 protons in TM-sulfites appears to be large. Studies on substituted thiane-1-oxides¹² show that an axial S=O bond is 5.4 kJ mol⁻¹ more stable as compared to an equatorial S=O bond and this preference was attributed to an attractive interaction between an axial S=O bond and the *syn* axial hydrogens. Such interactions, as regards TM-sulfites, could give rise to an anomalous high frequency shift of the *syn* axial 4 and 6 protons relative to the geminal equatorial protons. CNDO* calculations¹⁶ give, however, no significant difference in the charge density on the two geminal 4 protons. It is apparent that the major contribution to the chemical shift difference of the 4 and 6 protons in cyclic sulfites is due to the anisotropy of the S=O bond. The shift difference of the protons in position 5 is little affected by the change of the S=O dipole from the axial position to the equatorial position.

* CNINDO: CNDO and INDO molecular orbital program including *d* orbitals.¹⁵

The orientation effect of the S=O dipole on the 4 and 6 protons in compound V is in accordance with findings of compounds III and IV. Compound V is assumed to be twisted⁴ with the two "*syn* axial" groups, S=O and axial-4-methyl group, pointing away from each other. Models of a twist conformation of compound V suggest that the "equatorial" 4 proton occupies a similar position relative to the S=O bond as the axial 4 (6) proton in compound IV. The "axial" 6 proton in V has a position similar to the 4 (6) proton in compound III, relative to the S=O bond. This is also in accordance with the observed shift difference, 0.6 ppm, obtained for the 4 and 6 protons of compound V.

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