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NMR Experiments on Cyclic Sulfites

III.* Analysis of the High Resolution NMR Spectra of Substituted Ethylene Sulfites

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The high resolution proton magnetic resonance spectra of the isomers of 4-methyl- and 4,5-dimethyl-ethylene sulfite have been fully analysed. The *syn* and *anti* 4,5-dimethyl sulfites have been analysed as $X_3AA'X_3'$ spin systems. The sulfites exist in twist-envelope conformation with the sulfur atom above the ring plane. The S=O bond is found to prefer a pseudo axial orientation. The torsional angle of the O–C–C–O moiety is estimated to about 40° to 60°.

Substituted ethylene sulfites are suitable for conformational investigation on five-membered ring compounds. The NMR spectra are simplified because of the large chemical shift difference of the ring-protons caused by the S=O group. The dipole moment [2] obtained for ethylene sulfite has been explained by an envelope conformation with the sulfur atom above the ring plane. Haake *et al.*[3] investigated ethylene sulfite by NMR and assumed a twist-envelope conformation with the S=O bond pseudo-axial. The dihedral angle between the two C–O bonds was estimated to about 33°.[3] The interest in the compounds studied in this work was aroused by the property of the S=O group in trimethylene sulfite to prefer an axial orientation.[1,4] The strain in the five-membered sulfites might force the S=O group to partly occupy a pseudo-equatorial position in the substituted ethylene sulfites. The methyl–S=O interaction in methylated sulfite is expected to vary with the number of 1,3 transannular interactions. In order to obtain useful information about five-membered ring sulfites, their NMR spectra have been analysed in detail with respect to both coupling constants and chemical shifts.

EXPERIMENTAL

The sulfites were prepared from appropriate diols and thionyl chloride according to the method described previously.[4]

4-Methyl-ethylene sulfite was obtained as a mixture of two isomers. The isomers,

*Part II: Ref. 1.

detected by NMR, could not be separated by gas chromatography. The isomer mixture, b.p. 55°/1 mmHg, contained less than 1 % of other compounds, detected by GC.

The 2,3-dimethyl-ethylene sulfite obtained from *racemic* 2,3-butanediol contained three isomers. The isomers obtained from *erythro* and *meso* diol were separated by GC. The purity of the two fractions was better than 99 % by GC. The sulfite from the *meso*-butanediol is shown by NMR to exist as two isomers, a *syn* and an *anti* isomer.

The isomers were separated and analysed on an Aerograph Autoprep gas chromatograph fitted with a 1.7 m × 0.6 cm column filled with a mixture of 20 % Carbowax 20M and 10 % PDEAS on 50 – 60 mesh Chromosorb acid washed.

The material, neat liquid, was introduced into 5 mm O.D. NMR sample tubes, small amounts of TMS were added to serve as reference and locking substance. The tubes were degassed and sealed under vacuum. The spectra were obtained using a JEOL JNM-C-60-H NMR instrument operating at 60 MHz. The spectra were recorded in internal lock mode with frequency sweep at approximately 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. The counter is accurate to 0.1 Hz. The line positions were taken as an average of several spectra, and are assumed to be correct to about 0.05 Hz. The computation was carried out using an IBM 360/50 computer and graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The NMR spectra of methylated ethylene sulfites consist of two main regions, a high field region due to the methyl groups and a region at low field due to the ring protons. The separation between the two regions is large compared to the coupling constants involved and the spectra can be explained by $X_3AA'X_3'$, X_3ABY_3 or $ABCX_3$ spin systems.

The NMR spectrum of 4-methyl-ethylene sulfite indicated the presence of two isomers in the ratio 2 : 5, which complicated the analysis to some extent. However, the major isomer (A) was easily recognized, as it appeared to be a weakly coupled $ABCX_3$ spin system which could be analysed as an $AMXY_3$ spin system. The resonance due to the H_4 and the *cis* proton relative to the S=O group at carbon 5 was essentially outside the overlapping range between

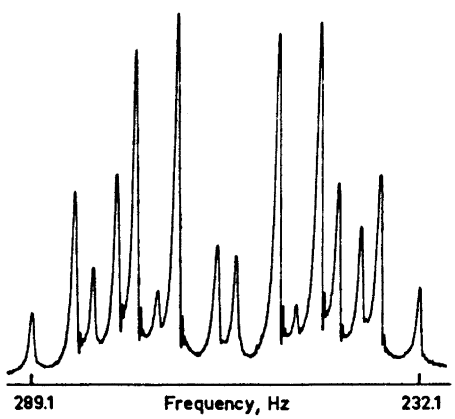


Fig. 1. 60 MHz NMR spectrum of *trans* 4,5-dimethyl-ethylene sulfite; ring protons only are shown.

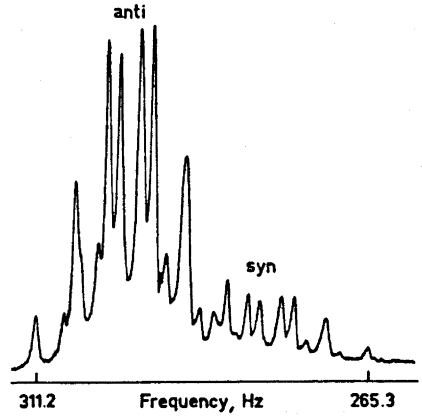


Fig. 2. 60 MHz NMR spectrum of ring protons in the *syn* and *anti* isomers of *cis* 4,5-dimethyl-ethylene sulfite.

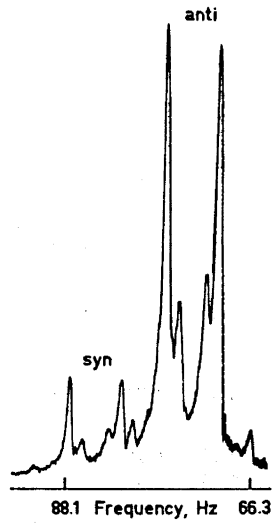


Fig. 3. The methyl groups of the *syn* and *anti* isomers of *cis* 4,5-dimethyl-ethylene sulfite at 60 MHz.

the two isomers, with H_4 at low and H_5 at high field, respectively. The coupling constants involved were all obtained by inspection of the signals from the *syn* protons at C_4 and C_5 and the methyl signal.

The NMR spectrum of *trans* 4,5-dimethyl-ethylene sulfite is easily analysed as an X_3ABY_3 spin system (Fig. 1) with $J_{AX} \simeq J_{BY} \simeq 6.1$ Hz and J_{BX} and J_{AY} negligible. J_{AB} can be obtained from subspectral analysis, from the *ab* subspectra.

The sample of *cis* 4,5-dimethyl sulfite is shown by NMR to consist of two isomers, one *syn* and one *anti* form. The signals at low field due to the ring protons (Fig. 2) appear to be overlapping AA′ parts of two $X_3AA'X_3'$ spin systems.[5] The X part of the spectrum shows a characteristic pattern due to overlap of two individual X_3X_3' ($X_3AA'X_3'$) spectra (Fig. 3). The ratio, *ca.* 1 : 5 between the two isomers, integrated from the NMR spectrum, makes it easy to assign the two individual $X_3AA'X_3'$ spectra. The low field part of the A region is connected to the high field part in the X region. The $X_3AA'X_3'$ spectra obtained for the two isomers resemble characteristic spectra obtained for molecules containing a symmetrical $CH_3-CH-CH-CH_3$ group with negligible $J_{XX'}$.[5]

The separation N is easily recognised in the AA′ and X_3X_3' parts for both isomers. The individual $\varkappa=1$ *xy* sub-spectra[5] can be measured from the overlapping $X_3X_3'(X_3AA'X_3')$ spectra and $J_{AA'}$ can be calculated directly for both isomers.

The fully computer analysed 60 MHz spectra resulted in a good correlation between calculated and experimental spectra. The final RMS value obtained was 0.1 or better when all parameters were allowed to vary. The probable errors in parameters were less than 0.02 Hz when 250 transitions were

Table 1. Chemical shift and coupling constants for ethylene sulfites.[a]

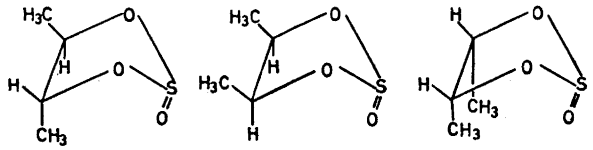
	^3J_c	^3J_t	$^3J_{H,Me}$	J_{gem}	ν_{H_c}	ν_{H_t}	$\nu_{CH_{3c}}$	$\nu_{CH_{3t}}$	RMS	
		8.67	6.11(4c)		274.04	246.13	87.33	82.76	0.08	Neat
	5.85		6.15(5t) 6.36		297.83			73.41	0.10	Neat
	6.06		6.50		301.66	278.69	85.07		0.07	Neat
	5.98	6.73	6.19	−8.39	277.64	231.99		80.67	0.09	Neat
	6.93 6.84	6.66 6.67		−8.59 −8.40	275.63 247.34	258.60 217.39				Neat[b] Benzene[b]

[a] Chemical shift in Hz from TMS and coupling constants in Hz.
[b] Ref. 3.

fitted. The iterative computations were performed using the computer program LAOCN3 [6] with some modifications [1] to accommodate eight coupled nuclei. The spectral parameters obtained are listed in Table 1.

RESULTS AND DISCUSSION

The isomer of 4,5-dimethyl-ethylene sulfite obtained in highest yield is compound I.

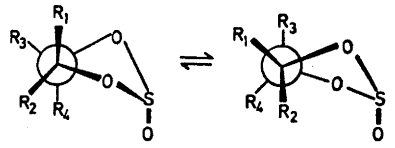


I trans II anti III syn

The yield of compound I compared to the yield of compounds II and III is dependent on the ratio between the diol isomers. The ratio between isomers II and III is dependent on the stability of the two isomers as they are obtained from the *meso*-2,3-butanediol. Compound II is obtained in the higher yield and the chemical shift of ring protons in isomer II to low field compared to the signals due to isomer III. The sequence of chemical shifts for the methyl groups in compounds II and III is the reverse of that for the

corresponding ring protons. This observation agrees with the findings of Haake *et al.*[3] for ethylene sulfite with a pseudo-axial situated S=O group. The protons *syn* relative to the S=O group in ethylene sulfite exhibit a similar shielding as the *axial* protons in the 4 and 6 positions in trimethylene sulfites [1,4] which are always to low field compared to the equatorial protons. A theoretical investigation into the origin of the "gauche effect" of adjacent electron pairs and polar bonds [7] and the preference of the S=O group to occupy the axial position in trimethylene sulfites,[1,4] suggest that the S=O group in ethylene sulfite prefers the pseudo-axial position.

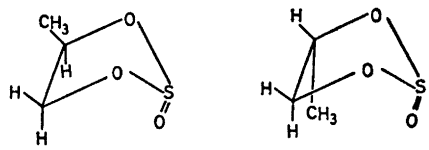
The NMR spectra of compounds II and III, which appear to be $X_3AA'X_3'$ spin systems, suggest that a rapid pseudo rotation occurs between the two twist-envelopes.



II $R_1=R_3=CH_3$, $R_2=R_4=H$
III $R_1=R_3=H$, $R_2=R_4=CH_3$

The barrier to rotation about the C–C bond is assumed to be low, because the vicinal *cis* methyl-methyl interaction is shown to be small in 1,3-dioxolane.[8]

The synthesis of 4-methyl ethylene sulfite gave to isomers, IV and V.



IV V

Compound IV is expected to be in the higher yield, which agrees with the NMR observation that the methyl group to higher field gives the most intense doublet.

The vicinal coupling constants for ethylene sulfites are in the range $J_{cis}=5.5-7.0$ Hz and $J_{trans}=6.5-8.7$ Hz (Table 1). The typical range for vicinal coupling constants in 1,3-dioxolanes [9,10] are: $J_{cis}=5.4-7.5$ Hz and $J_{trans}=5.9-8.5$ Hz, which is assumed to correspond to dihedral angles of $35-50°$ and $125-140°$, respectively. ^3J_c is larger for the unsubstituted ethylene sulfite as compared to the value for methylated sulfites. The variation in magnitude of ^3J_c indicates minor changes in dihedral angles upon methyl substitution. The *cis* vicinal coupling constant decreases and the *trans* coupling constant increases compared to the respective values obtained for the unsubstituted sulfite. This variation in ^3J indicates a greater torsional angle

in the substituted sulfites as compared to ethylene sulfite. Haake *et al.*[3] estimated the dihedral angles in ethylene sulfite to about 33° from the $\cos^2\theta$ relation.[11] The uncertainty in dihedral angle calculations by this method is the determination of the constants involved in the Karplus equation. The R value introduced by Lambert[12] and made to an analytical tool by Buys[13] gives an expression for dihedral angles in which the Karplus factor A is no longer present.

By the relation[13] $\cos\theta = [3/(2+4R)]^{1/2}$ a quantitative determination of the dihedral angle θ within the $-CH_2-CH_2-$ fragment may be made. The previously estimated torsional angle[3] of about 33° for ethylene sulfite is apparently too low compared to values obtained for 1,3-dioxolanes[14,15] and 1,3-dithiolanes.[16] The R value for ethylene sulfite assumes a torsional angle of about 42°, contrary to the value given previously. The R value calculation assumes that the sulfite ring is not distorted in some unusual manner, *i.e.*, the tetrahedral angles are still close to 110° such that the relation can be used in assessing the dihedral angles. It has been pointed out[17,18] that the calculation of dihedral angles from coupling constants in five-membered ring compounds is probably not reliable. The classical method of averaging two or more conformations to account for the observed coupling constants in five-membered ring compounds can give quite bad results. This may arise from the large number of minimum energy conformations which may be possible for many five-membered ring compounds. This objection may not be so important for the sulfites, since these compounds appear to have few conformations with the S=O group pseudo-axial.

The *cis* coupling constants in compounds II and III are $^3J_c = 5.85$ Hz and $^3J_c = 6.06$ Hz, respectively. The variation in this coupling constant may be assigned to different torsional angles in the two isomers. Gagnaire and Roberts[19] report equal, $^3J_c = 5.8$ Hz, coupling in the two corresponding isomers of 2-phenyl-4,5-dimethyl-1,3-dioxolane. The isomers of 2,4,5-tri-*t*-butyl-1,3-dioxolane[8] are, however, found to have different vicinal *cis* coupling constants, $^3J_c = 7.9$ Hz and $^3J_c = 5.2$ Hz for the *syn* and *anti* isomers, respectively. This variation is assumed[8] to be due to torsional angles of about 40° for the *syn* and about 60° for the *anti* isomer. The difference in ^3J_c in compounds II and III may be attributed to the effect of the pseudo-axial S=O group. A similar effect of polar substituents on vicinal *cis* coupling constants are found in 2,5-dimethoxy-tetrahydrofurane[20] where $^3J_{34}$ is 8.42 Hz and 9.71 Hz. The larger coupling constant is between protons *syn* to the methoxy groups. This effect is not observed in dioxolanes[10] upon alkyl substitution on carbon 2. The change in ^3J_c upon substitution (Table 1) indicates only minor changes in dihedral angles in compounds II and III as compared to the unsubstituted sulfite. The $^3J_t = 8.67$ Hz in the *trans* disubstituted ethylene sulfite (I) is about 2 Hz larger as compared to $^3J_t = 6.66$ Hz in the unsubstituted sulfite. A variation in J_{vic} of that magnitude may be explained by an increase of about 10° in the torsional angle. This indicates substantial transannular methyl−S=O interaction in the five-membered sulfites. An increase in the torsional angle O−C−C−O forces the *syn* proton (compound II) closer to the S=O group and the shift difference between *syn* and *anti* protons is expected to be larger as compared to an undistorted ring. The shift difference (Table 1) in isomer

I compared to the shift difference of compounds II and III between the *syn* and *anti* ring protons to the S=O group is *ca.* 28 Hz and 19 Hz, respectively. The shift difference between the methyl groups in compound I and between II and III is 4.5 Hz and 12.5 Hz, respectively. The vicinal coupling constant in compound IV is in the range found for compounds II, III, and the unsubstituted sulfite, indicating similar distortion of dihedral angles as proposed for compounds II and III.

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