

## NMR Experiments on Cyclic Sulfites

### V\* High Resolution $^{13}\text{C}$ Spectra of Trimethylene Sulfites by Fourier Transform NMR

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The high resolution  $^{13}\text{C}$  NMR spectra of trimethylene sulfite, 5-methyl-, 5-*tert*-butyl-, 5-phenyl-, 5,5-dimethyl-, and 4-methyl trimethylene sulfite obtained without proton noise decoupling, have been analysed. The spectra are consistent with a rigid or anancomeric ring system. The  $^1J_{\text{CH}}$  is found to be larger when the proton has a *cis* lone-electron pair vicinal or remote as compared to the geminal equatorial proton. The  $^2J_{\text{CH}}$  and  $^3J_{\text{CH}}$  are shown to have different values for couplings to an axial as compared to an equatorial proton. The vicinal carbon-proton coupling constant,  $^3J_{\text{CH}}$ , is found to be dependent on the dihedral angle of the  $^{13}\text{C}-\text{C}-\text{C}-\text{H}$  moiety.

The cyclic trimethylene sulfites (TM-sulfites) have been studied in detail by proton NMR.<sup>1-4</sup> It is well known that the TM-sulfites exist mainly in a chair conformation with the S=O group preferentially in the axial position. It has been an increasing interest in the measurement of coupling constants between carbon atoms and protons to which they may or may not be directly bonded. Apart from the inherent interest in such coupling constants, they are expected to give valuable information about molecular structures and conformations.

The recent developed method of pulsed-Fourier transform NMR spectroscopy<sup>5</sup> is shown to be particularly suited for  $^{13}\text{C}$  NMR studies of organic compounds containing natural abundance of  $^{13}\text{C}$ . This work was undertaken in an attempt to obtain experimental data for an angular dependence of the vicinal coupling,  $J^{13}\text{CCH}$ . One problem of high resolution  $^{13}\text{C}$  NMR arises from the fact that the carbon-hydrogen couplings over more than two bonds, are not always attenuated by interposition of an additional bond.<sup>6</sup> The complexity of the spectrum is increased by the number of coupled protons. One simplification is, however, obtained due to the large chemical shift between carbon and proton. The  $^{13}\text{C}$  spectra can be analysed according to first order rules and hence the signs are not easily obtained.

\* Part IV is Ref. 4.

## EXPERIMENTAL

The compounds studied were synthesized as reported previously.<sup>1,3</sup> The spectra were obtained of samples containing the TM-sulfites diluted to ca. 30 % v/v in CDCl<sub>3</sub>. The spectra were obtained at ambient temperature on either a JEOL PFT-100 or a Varian associates XL-100-15 spectrometer, both equipped for continuous wave, CW, and Fourier transform, FT, operation.

The spectrometers were only operated in FT mode at 25.2 MHz. The XL-100-15 spectrometer was connected to a Varian 620i Computer with 4K memory available for data accumulation. The JEOL PFT-100 spectrometer was connected to a JEC-6 computer with 8K available data storage capacity. The spectra were obtained using 12 mm (Varian) or 8 mm (JEOL) O.D. sample tubes with internal <sup>2</sup>H lock to CDCl<sub>3</sub>. All undecoupled spectra which were used in the detailed analyses were obtained using 8K data points. In the FT mode 8 to 9 μsec pulses were applied to either a 2 kHz region or separately to two 1 kHz regions.

The resolution was limited by the computer and is ca. 0.5 Hz for a 2 kHz and ca. 0.25 Hz for a 1 kHz spectral window, corresponding to 4096 output datapoints in the absorption spectrum. The proton undecoupled <sup>13</sup>C spectra were recorded after performing 10 000 to 20 000 spectral accumulations, and no line broadening was observed. The spectral windows were carefully chosen to avoid any folding to obscure the spectral regions of interest.

## SPECTRAL ANALYSIS

The <sup>13</sup>C spectra were analysed using the iterative programs <sup>7</sup> LAOCN3, LACX, and UEAITR. The TM-sulfite were analysed as an AA'BB'CDX (X = <sup>13</sup>C) spin system with the observed spectrum consisting of two separate seven-spin systems (Fig. 1). Iterativ calculations were performed only for the spectral part involving the carbon in position 5.

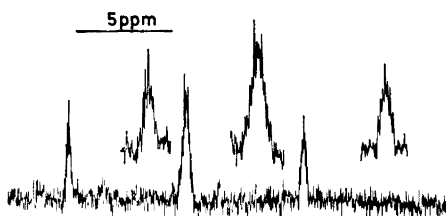


Fig. 1. The <sup>13</sup>C spectrum of carbon 5 of TM-sulfite at 25.2 MHz. The inserts are expanded twice. The spectrum is obtained using 4K data points on a 500 Hz spectral window.

The 5-*tert*-butyl- (Fig. 2) and 5-phenyl-TM sulfite were analysed as an AA'BB'CX spin system with respect to the nuclei in the TM-sulfite ring. Iterative computations were, however, carried out only for the cases with <sup>13</sup>C in positions 4 or 6. The <sup>13</sup>C signals due to C<sub>5</sub> were in both cases broadened by long range couplings to protons of the substituent. These couplings resulted in non-resolvable fine structure of the signals due to <sup>13</sup>C<sub>5</sub>.

The 5-*e*-methyl-TM-sulfite (Fig. 3) was analysed as an AA'BB'CD<sub>3</sub>X spin system only for the <sup>13</sup>C in positions 4 and 6. Treating the <sup>13</sup>C spectrum of C<sub>4(6)</sub> as an AA'BB'CX spin-system gave the same results as the complete AA'BB'CD<sub>3</sub>X spin-system. The spectrum due to <sup>13</sup>C in position 5 was not analysed because the long range C-H couplings (a doublet) have no resolvable fine structure.

Trial <sup>13</sup>C parameters for all compounds studied were obtained by inspection of the undecoupled <sup>13</sup>C spectra. The proton-proton couplings and proton

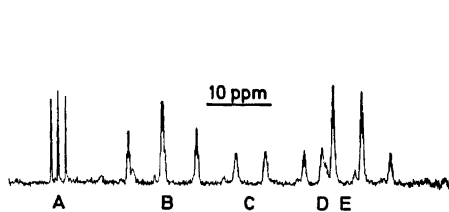


Fig. 2. The total  $^{13}\text{C}$  NMR spectrum of 5-*e*-*tert*-butyl-TM sulfite at 25.2 MHz; A,  $\text{CDCl}_3$  solvent signals; B, the carbons 4 and 6; C, the carbon 5; D, the tertiary carbon of the *tert*-butyl group. (The signal is saturated due to experimental conditions); E, the carbons of the methyl groups. The spectral window is 2 kHz and the spectrum is recorded with 8K data points.

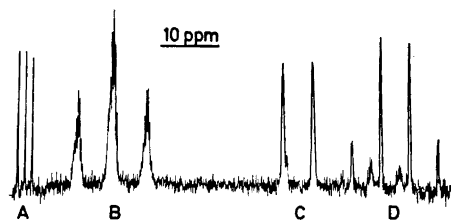


Fig. 3. The  $^{13}\text{C}$  NMR spectrum at 25.2 MHz of the 5-*e*-methyl-TM sulfite; A, signals due to the solvent,  $\text{CDCl}_3$ ; B, the carbons 4 and 6; C, the carbon 5; D, the carbon of the methyl group. The spectrum is recorded with 8K data points on a 2 kHz spectral window.

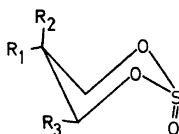
chemical shifts are published previously.<sup>1,3,4</sup> Only  $^{13}\text{C}$  spectral parameters were allowed to vary during the iterative calculations. The RMS values were better than 0.3 Hz for all cases when fitting all theoretical transitions to observed lines. Visual comparisons of observed spectra with theoretical Lorentz-shape spectra indicated that the computed intensities were satisfactory in each case. The calculations were performed using an IBM 360/50 computer and the theoretical spectra were plotted using a Calcomp Plotter.

#### DISCUSSION

The  $^{13}\text{C}$  NMR data (Tables 1 and 2) are consistent with earlier observations that the unsubstituted and 5-substituted TM-sulfites are in a rigid chair conformation. The direct carbon proton coupling,  $^1J_{\text{CH}}$ , is different for the two geminal protons in the 4 (or 6) position as well as in the 5 position in the ring (Table 1). Laszlo<sup>8</sup> postulated that the direct  $^{13}\text{C}-\text{H}$  coupling in a methylene group is dependent on two terms, one inversely proportional to the angle defined by the bonds between  $^{13}\text{C}$  and the substituents and secondly, effects of an ionic perturbation caused by a hetero atom attached to the methylene carbon. The angular dependence of  $^{13}\text{C}$  couplings cannot account for a difference in the direct coupling between  $^{13}\text{C}$  and  $\text{H}_a$  as compared to the coupling to  $\text{H}_e$ . The ionic perturbations are not assumed to perturb the couplings differently.

The  $^1J_{\text{CH}}$  couplings to the carbon atoms in positions 4 and 6 in the sulfite ring are about 147 Hz and 155 Hz for the spin-spin interaction involving the axial and equatorial protons, respectively. The larger coupling is assigned to the direct  $J_{\text{CH}}$  to the equatorial proton situated *cis* to the equatorial lone pair electrons on the oxygen, based on the observations for the 4-*e*-methyl TM-sulfite (see Table 1).

Rattet *et al.*<sup>9</sup> reported different direct C-H couplings, 141.0 Hz and 139.6 Hz, to the two non-equivalent methylene protons in acetaldehyde

Table 1.  $^{13}\text{C}$ -H coupling constants in Hz.

$\text{R}_1, \text{R}_2, \text{R}_3$	$^{13}\text{C}_4(6)$			$^{13}\text{C}_5$		$-\text{CH}_3$
	$^1J_{\text{CH}}$	$^2J_{\text{CH}}$	$^3J_{\text{CH}}$	$^1J_{\text{CH}}$	$^2J_{\text{CH}}$	
I H,H,H	153.9 147.8	7.5 1.3	7.5 3.2	127.5 131.9	2.6 1.4	
II $\text{CH}_3, \text{H}, \text{H}$	153.3 146.9	7.3	7.3 2.9	132.0	$a$	$^1J_{\text{CH}} = 127.4$ $^2J_{\text{CH}} = 3.9$
III t-Bu,H,H	153.6 146.6	6.2	6.3 2.4	132.1	$a$	$^1J_{\text{CH}} = 125.4$ $^2J_{\text{CH}} = 3.0$
IV Ph,H,H	156.5 148.4	5.7	5.9 2.3	132.6	$a$	
V H,H, $\text{CH}_3$	147.5 <sup>b</sup> 155.0 <sup>b</sup> 148.9 <sup>c</sup>	5.6 <sup>b</sup> 1.3 <sup>b</sup> 5.9 <sup>c</sup>	$a$ $a$	127.0 131.0	$a$ $a$	$^1J_{\text{CH}} = 127.0$ $^2J_{\text{CH}} = 2.9$

<sup>a</sup> Not calculated, because bands did not show any resolved fine structure. <sup>b</sup> Coupling to carbon 6. <sup>c</sup> Coupling to carbon 4.

Table 2. Chemical shift in ppm from TMS.

	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$	$\text{CH}_3$	
I	56.92	25.23	56.92	—	
II	60.30	28.01	60.30	10.63	
<sup>a</sup>	61.05	27.62	61.05	12.88	
III	58.64	44.33	58.64	26.46	$^{13}\text{C}_{\text{tert}} 30,22$
IV	60.01	40.41	60.01	—	
<sup>b</sup>	65.79	30.84	65.79	21.71	
V	63.61	32.63	56.85	20.52	

<sup>a</sup> 5-*a*-Methyl TM-sulfito. <sup>b</sup> 5,5-Dimethyl TM-sulfito.

diethylacetal. The direct  $^{13}\text{C}$ -H coupling value, apparently, reflect decisively a non-equivalence of methylene protons. The occurrence of two distinct  $^{13}\text{C}$ -H couplings in methylene protons means that non-equivalence can be localized in the two corresponding C-H bonds. The presence of an S=O group in the proximity of a C-H bond could create field effects which would lower the average triplet excitation energy. Such lowering might produce

changes in  ${}^1J_{\text{CH}}$  without rehybridization occurring at the carbon atom. The effect of the S=O group is expected to be small because polar substituents at remote positions affect the direct C-H coupling to a minor extent (*vide infra*). The lone pair electrons on a nitrogen or an oxygen atom affects the geminal proton-proton coupling in an adjacent CH<sub>2</sub> group.<sup>10,11</sup> The directly bonded <sup>13</sup>C-H coupling constant is shown to depend upon the orientation of a nitrogen lone pair electrons,<sup>12,13</sup> with the direct coupling of a C-H group *cis* to lone pair electrons larger as compared to  ${}^1J_{\text{CH}}$  of the *trans* C-H group. The difference between  ${}^1J_{\text{CH}}(\textit{cis})$  and  ${}^1J_{\text{CH}}(\textit{trans})$  is *ca.* 10 Hz for *N*-methyl aziridine<sup>12</sup> and *ca.* 14 Hz for the methyl proton of acetaldoxime.<sup>12</sup> The difference in  ${}^1J_{\text{CH}}$  of the sulfites, involving C<sub>4</sub> or C<sub>6</sub>, of *ca.* 8 Hz between values for axial and equatorial oriented CH groups is mainly due to the effect of the equatorial lone pair electrons on the oxygens. The smaller difference as compared to for example aziridine<sup>12</sup> may be attributed to the field effect of a *syn* axial S=O group which would oppose the effect of the equatorial lone pair electrons of the ring oxygen. The observed difference between the two direct couplings for the sulfite is substantial with a magnitude of about 50 % of the total effect produced by an oxygen atom substituted into methane.<sup>14</sup> It has, however, in some cases been reported that <sup>13</sup>C-H couplings are affected by the medium.<sup>15,16</sup>

Moreover, the difference in  ${}^1J_{\text{CH}}$  of carbon 5, about 4 Hz, is significant and is paralleled by the observation that the axial proton at carbon 5 in TM-sulfites resonates at higher frequency as compared to the equatorial proton.<sup>1</sup> This is the reversed sequence with respect to cyclohexane. It has been pointed out that the reason for this, as regards dioxanes,<sup>19</sup> might be an interaction between H<sub>5e</sub> and the *p*-orbitals of the ring oxygens. Such an effect could account for the observed difference in  ${}^1J_{\text{CH}}$  between the axial and equatorial C<sub>5</sub>-H groups of the TM-sulfites. The observed direct couplings to carbon 5 are of the magnitude 127.5 Hz and 132.5 Hz for TM-sulfite and *ca.* 127 Hz and 131 Hz for 4-*e*-methyl TM-sulfite. The larger value is the coupling to the axial proton which has two remote *syn* axial lone pair electrons. This assignment is consistent with values obtained for C-H<sub>5a</sub> (*ca.* 132 Hz) in 5-*e*-methyl, 5-*e*-phenyl and 5-*e*-*tert*-butyl TM-sulfite (see Table 1).

The magnitude of two and three bond coupling constants involving carbon atoms in positions 4 and 6 of 5-equatorial substituted TM-sulfites are in the range 7.5 Hz to 1.3 Hz. The values of the pertinent coupling constants to carbon 6 obtained for 4-*e*-methyl TM-sulfite are 5.6 and 1.3 Hz. The observed values in TM-sulfite involving carbons 4 or 6 are 7.5 Hz, 7.5 Hz, 3.2 Hz, and 1.3 Hz. The observed values 7.5–6.0 Hz and 2.0–1.3 Hz may be assigned to the  ${}^2J_{\text{CH}}$  involving the carbons 4 or 6. The larger value is assigned to the coupling to H<sub>5a</sub>, which is consistent with the values obtained for 5-*e*-substituted TM-sulfites. Accordingly, the other pair of values, 7.5–5.9 Hz and 3.2–2.3 Hz, may be assigned to  ${}^3J_{\text{CH}}$ . The larger value is attributed to the spin-spin interaction involving C<sub>6</sub> and H<sub>4e</sub>. This is consistent with the observation of only one large vicinal coupling, 5.6 Hz, to carbon 6 in the 4-*e*-methyl TM-sulfite. Moreover, it is apparent that both the  ${}^2J_{\text{CH}}$  and  ${}^3J_{\text{CH}}$  (Table 1) have pairs of different coupling values, *ca.* 6.0 Hz and 2.0 Hz, indicating conformational dependence of these two coupling constants.

The two bond C–H couplings involving carbon 5 in TM-sulfite, also, have two distinct values, 2.6 Hz and 1.4 Hz. The difference in values obtained for  ${}^2J_{\text{CH}}$  involving carbon 5 as compared to carbons 4 (or 6) indicates substantial effects due to electronegativity of the substituent attached to the carbon. Moreover, the difference between the two  ${}^2J_{\text{CH}}$  indicates that this coupling is dependent on the orientation of the coupling path relative to the substituent on the coupled carbon atom. The observed two bond  ${}^{15}\text{N}$ –H coupling in aliphatic nitrogen compounds is found to be stereospecific and dependent on orientation of the nitrogen lone-pair.<sup>18</sup> Similar observations have been made for  ${}^2J_{\text{PH}}$  in trivalent phosphorus. Theoretical INDO MO calculations<sup>19</sup> verify the effect of the nitrogen lone-pair for aliphatic amines. As regards the sulfites, the observed values of  ${}^2J_{\text{CH}}$  are different whether an *axial* or an *equatorial* proton is involved in the spin-spin interaction. It is apparent that there exists a correlation of the sign and magnitude of  ${}^2J_{\text{CH}}$  with molecular structure.<sup>29</sup> The  ${}^2J_{\text{CH}}$  has been reported to hold either signs,<sup>20–23</sup> but INDO MO calculations<sup>29</sup> suggest that the sign of this coupling constant is negative as regards propane and butane.

The proton-carbon coupling constants through three bonds,  ${}^3J_{\text{CCCH}}$ , are in the range 2.3 Hz to 7.5 Hz for the TM-sulfites (Table 1). Karabatsos and Orzech<sup>24</sup> reported coupling constants in the range 3.59 Hz to 5.99 Hz for  $sp^3$  hybridized  ${}^{13}\text{C}$ . The variation of  ${}^3J_{\text{CH}}$  indicates that in addition to the *s*-character of the  ${}^{13}\text{C}$  hybrid atomic orbital, other factors must affect this coupling. Long range coupling between protons is generally believed to be dominated by the Fermi contact interaction. These terms may also give rise to the most significant contribution to the coupling between other nuclei such as carbon and proton. Substituents bonded to  ${}^{13}\text{C}$  should affect the  ${}^3J_{\text{CH}}$  due to its electronegativity.

Increasing electronegativity of the substituent should increase  ${}^3J_{\text{CH}}$  by virtue of increasing the *s*-character<sup>25</sup> of the  ${}^{13}\text{C}$  atomic orbital used in the carbon-carbon bond. It is reasonable to assume that a relationship similar to the Karplus<sup>25</sup> relation also relating the  ${}^3J_{\text{CH}}$  with the dihedral angle in a  ${}^{13}\text{C}$ –C–C–H fragment. Wasylishen and Schaefer<sup>27</sup> recently proposed an angle dependence of the vicinal  ${}^{13}\text{C}$ –H coupling constant in propane from INDO MO calculations. Their calculations predicted a dihedral angle dependence similar to that observed for  ${}^3J_{\text{CH}}$  in the TM-sulfites. The observation that the vicinal C–H coupling in TM-sulfites to the equatorial and the axial proton is different, 7.5 Hz and 3.2 Hz, respectively, supports the theoretical calculations of Schaefer *et al.*<sup>27</sup> and adds evidence to the assumption that the TM-sulfite exists in a rigid or anancomeric system.

One of the problems in the interpretation of chemical shifts in  ${}^{13}\text{C}$  magnetic resonance is adequate to take into account effects produced by the anisotropy of neighbouring atoms or groups. It has been assumed that in contrast to the  ${}^{13}\text{C}$  coupling constants the  ${}^{13}\text{C}$  chemical shifts should be sensitive to anisotropy, medium effects and factors which do not complicate the interpretation of the coupling constants. Moreover, it appears that  ${}^{13}\text{C}$ –H coupling constants provide a direct and reasonably reliable measure of the *s*-character in the carbon bonding orbital. It might be expected that in the absence of medium effects *etc.* a close relation should exist between  ${}^{13}\text{C}$  shifts and  ${}^1J_{\text{CH}}$ . Such a correlation

is not easily obtained from the available data on TM-sulfites, so it might be relevant to compare shift data for TM-sulfites with those for cyclohexanes<sup>22,23</sup> (Fig. 4) and 1,3-dioxanes<sup>28</sup> (Fig. 5). Plotting the chemical shifts of carbons 4 (or 6) and carbon 5 in 5-substituted TM-sulfites *versus* the pertinent shift values for either 5-substituted 1,3-dioxanes<sup>28</sup> or monosubstituted cyclohexanes<sup>22,23</sup> indicates a linear relationship (Figs. 4 and 5). It is apparent that an alkyl substituent affects the chemical shift of the  $\alpha$ - or  $\beta$ -carbon in TM-

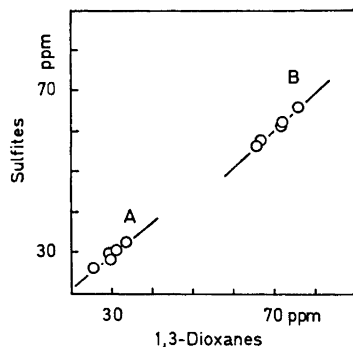


Fig. 4. The plot of  $^{13}\text{C}$  shifts of the TM-sulfites *versus* the pertinent carbon shifts of 1,3-dioxanes;<sup>28</sup> A, the carbon holding the substituent; B, the  $\beta$ -carbon relative to the substituent. The shifts is measured relative to the TMS  $^{13}\text{C}$  signal.

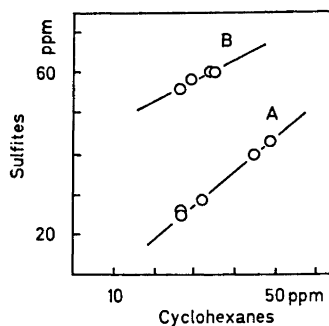


Fig. 5. The plot of  $^{13}\text{C}$  shifts (ppm from TMS  $^{13}\text{C}$ ) of the 5-substituted-TM sulfites *versus* the pertinent  $^{13}\text{C}$  shift of the related mono-substituted cyclohexanes;<sup>22,23</sup> A,  $\alpha$ -carbon *i.e.* the carbon holding the substituent; B,  $\beta$ -carbon relative to the substituent.

sulfites (Table 3) to the same extent as in cyclohexane.<sup>22,23</sup> The shift of carbon 5 is hardly affected by the S=O group. Comparison of the geminal (H,H) coupling constants for sulfites and dioxanes suggests that electronegativity differences between the O-C-O and O-S(O)-O moieties are responsible for the difference in carbon chemical shifts in the two types of compounds. Any substituent into a ring appears to have little effect on the chemical shift of a remote ring-carbon. The effect on the chemical shifts (Table 3) of introducing a phenyl group into the TM-sulfite ring gives rise to similar effects as

Table 3. Substituent effects on  $^{13}\text{C}$  chemical shifts (ppm) in TM-sulfites.

Substituent	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
5- <i>e</i> -Me	+ 3.4	+ 2.8	+ 3.4
5- <i>a</i> -Me	+ 4.1	+ 2.4	+ 4.1
5,5-Me <sub>2</sub>	+ 8.9	+ 5.5	+ 8.9
5- <i>e</i> - <i>t</i> -Bu	+ 1.7	+ 19.1	+ 1.7
5- <i>e</i> -Ph	+ 3.1	+ 15.2	+ 3.1
4- <i>e</i> -Me	+ 6.7	+ 7.4	- 0.1

observed for cyclohexanes.<sup>22,23</sup> The introduction of geminal methyl groups does not change the carbon chemical shift an amount equal to the sum of the changes on introducing the equatorial and axial methyl groups separately.

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