Tetrahedron Letters No.22, pp. 1649-1652, 1965. Pergamon Press Ltd.
Pergamon Press Ltd.

STRUCTURE OF THE CYCLIC SULPHITE AND SULPHATE FROM 2,2-DIMETHYLPROPANE-1,3-DIOL

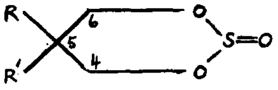
R. S. Edmundson

Department of Chemical Technology, Bradford Institute of Technology,
Bradford 7.

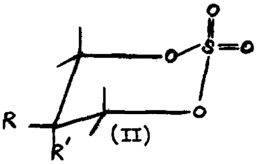
(Received 2 April 1965)

A great deal of interest has recently centred around the stereochemistry of the S=O group as found in cyclic sulphoxides [1,2,3], sultones [4], cyclic sulphates [5] and sulphites [5,6].

De la Mare et al. [6] examined the infrared spectra of two conformers of the cyclic sulphite (I) (R = H , R' = Cl) and concluded that in each, the S=O bond ($\nu_{max.}$ = ca. 1190 cm.$^{-1}$) was equatorially situated, isomerisation being due to axial and equatorial positioning of chlorine.



(I)



(II)

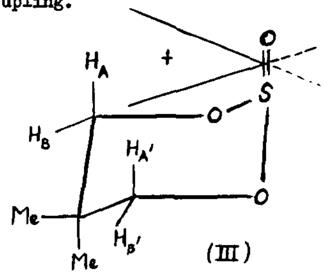
A comparison of the p. m. r. spectra of the sulphite (I) (R = R' = H) and the sulphate (II) (R = R' = H) with those of the separated conformers of the sulphite (I) (R = Me, R' = NO_2) and (I) (R = t-Bu, R' = H) lead Mellier et al. [5] to conclude that the unsubstituted trimethylene sulphite exists in one conformation only, for which the S=O bond is in the axial position.

Further evidence, based on a comparison of the p. m. r. spectra[7] of 5,5-dimethyl-1,3-dioxathiane-2-oxide (I) (R = R' = Me) and the corresponding 2,2-dioxide (II) (R = R' = Me)[8], is now presented for a rigid cyclic sulphite structure possessing axial S=O bond. The absence of a central methylene group at C_5 leads to simpler spectra than those encountered by Hellier <u>et al</u>. In addition, the number of possible structures for the sulphate is restricted.

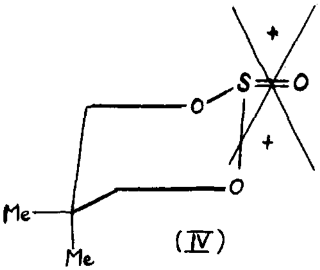
The p. m. r. spectrum of the present sulphate consists of two sharp lines only, at τ= 8.73 and 5.74, of relative intensities 3:2. They are assigned to equivalent Me groups, and to equivalent ring methylene groups in each of which the protons are identically situated. Molecular models indicate that structure (II) is the only reasonable one for this compound, even skew structures being improbable on steric grounds. Inversion of the ring produces an identical structure. It is therefore concluded, either, that the structure is rigid, or that it inverts rapidly.

For the corresponding sulphite, two peaks of equal intensity (3:3) at τ= 9.12 and 8.69 indicate non-equivalent Me groups. The methylene protons are indicated by four sharp peaks of equal intensity (1:1:1:1), as two pairs, centred at τ= 6.67 and 5.43. The general situation of these peaks is as expected for an adjacent, highly electronegative system. Whether we regard the S=O group as being either equatorial or axial in the two structures (III) and (IV) (inversion leading to an identical pair), each methylene group may be considered as an AB system of non-equivalent protons, leading to spin-spin coupling with $J_{AB} = J_{A'B'}$ = 10 c.p.s., and the appearance of four peaks. In addition, the peaks at τ= 6.67 are further split into triplets (J = ca. 2 c.p.s.) while those at τ= 5.43

consisted of doublets with J = ca. 1 c.p.s., possibly due to long range coupling.[9]



(III)



(IV)

In suitable systems, differences in resonance positions of equatorial and axial protons are normally 0.1 to 0.7 p. p. m.[10], the latter occurring at higher field.[11] The present value of 1.3 p. p. m. can only be due to preferential long range shielding by the S=O group. Only in the case of axial S=O would a pronounced shielding of any of the methylene protons (here the axial ones) occur, as opposed to any possible weak shielding in the case of equatorial S=O, and in the sulphate, to strong shielding of axial protons by axial S=O partially nullified by the effect of the equatorial S=O group.

We conclude therefore that the sulphite possesses a rigid structure with axial S=O. The previously determined infrared spectrum[8] of the sulphite therefore indicates that axial S=O absorbs at 1190 cm.$^{-1}$ Hellier *et al*. report the same value for trimethylene sulphite.

Acknowledgements:

Dr. D. W. Jones and Mr. J. E. Pearson are thanked for the spectra, and Dr. H. Heaney for his interest.

References:

1. C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.* **86** 2935 (1964).

2. J. C. Martin and J. J. Uebel, *J. Amer. Chem. Soc.* **86** 2936 (1964).
3. P. B. D. de la Mare, D. J. Millen, J. G. Tillett and D. Watson, *J. Chem. Soc.* 1619 (1963).
4. R. W. Ohline, A. L. Allred and F. G. Bordwell, *J. Amer. Chem. Soc.* **86** 4641 (1964).
5. D. G. Hellier, J. G. Tillett, H. F. Van Woerden and R. F. M. White, *Chem. and Ind.* 1956 (1963).
6. P. B. D. de la Mare, W. Klyne, D. J. Millen, J.G. Pritchard and D. Watson, *J. Chem. Soc.* 1813 (1956).
7. The p. m. r. spectra were determined with a Varian A-60 (60 Mc.) spectrometer. CCl_4 was employed as the solvent.
8. R. S. Edmundson, *Tetrahedron,* **20** 2781 (1964).
9. S. Sternhell, *Rev. Pure and Applied Chem.* **14** 15 (1964).
10. L. M. Jackman, *Applications of N.M.R. Spectroscopy in Organic Chemistry*, Ch. 7. Pergamon (1959).
11. J. C. D. Brand and G. Eglinton, *Applications of Spectroscopy to Organic Chemistry*, Ch. 3. Oldbourne, (1965).