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THE CONFORMATION OF TRIMETHYLENE SULPHITE

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Benzene as an NMR solvent has been shown to exert a fairly specific influence on the chemical shifts observed for protons located near a carbonyl group in six-membered ring compounds.[1,2,3] In general the observed results are consistent with the formation of a complex between the benzene and the positive centre of the polar group.[1,4] The axial groups generally lie within the region of shielding while the equatorial groups are less shielded or even deshielded.

We now wish to report that the proton spectrum of trimethylene sulphite (I) is shifted by benzene in a manner not expected from the conformational assignment made for this compound. Hellier[5] adduced some evidence that (I) exists in a single conformation and chose the chair form with S-O axial (Ia). However, the measured dipole moment for this molecule (3.5-3.6 D) does not agree with that calculated for form (Ia) (1.8 D). Further, the NMR spectrum was not assigned in detail and was anomolous in that the assignments made placed the equatorial protons at higher field than the axial.[6]

Spectra were measured at 60Mcs on a JEOL JNM-C-60 spectrometer with the results shown in the Table.

Table

Solvent Effects on the NMR Spectrum of Trimethylene Sulphite

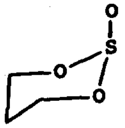
proton assignment[a]	C_2(eq)	C_2(ax)	C_1,C_3(eq)	C_1,C_3(ax)
$CDCl_3$ (10% w/v)[b]	8.38[c]	7.47	6.13	5.05
benzene (infinite dilution)[d]	9.6	8.5	7.0	5.6
Δ(benzene-$CDCl_3$)	1.2	1.0	0.9	0.6
Δ(20% benzene-CCl_4)	1.1	0.8	0.6	0.4
Δ(20% benzene-CCl_4) for (II)[e]	(0.95)[f]		0.6[g]	0.4[h]

a. As proposed in ref. 5.
b. These chemical shifts do not differ appreciably from those found in CCl_4 or in the neat liquid.
c. Chemical shifts are quoted in tau units from tetramethylsilane for the mid-point of each multiplet.
d. Extrapolated from points at 30, 20, 10, and 5% w/v.
e. *meso*-Pentane-2,4-diol cyclic sulphite (isomer B, ref.10).
f. One multiplet reported for protons at C_2.
g. Value for CH group.
h. Value for CH_3 group.

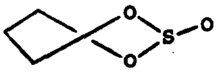
It can be seen that the protons are shielded by benzene to a considerable extent and those protons labelled equatorial[5] are shielded more than those labelled axial. At least for the protons at C_1 and C_3 this result is opposite to that expected. The shielding at C_2 could depend in part on which side of the molecule the benzene approaches. This appears to be the case with the 1,3-dioxans studied by Anderson.[7] He found that the C_4 and C_6

axial protons were shifted 0.3 ppm upfield while the corresponding equatorial protons were shifted only 0.2 ppm by benzene. The equatorial proton at C_5 was shifted substantially more than the axial one (0.6 *vs* 0.3 ppm); this result is consistent with the approach of the benzene molecule from the side opposite to this axial proton.

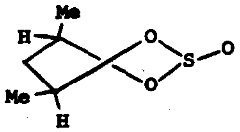
When this anomolous effect of the benzene solvent is added to the considerable difficulties in interpretation of dipole moment, NMR, and (in our hands) IR data[8] for (I) it would seem to cast serious doubt on the assignment of conformation (Ia). Considering all the data presented up to now, the most likely conformation for trimethylene sulphite appears to be the flexible form (Ib). However, more evidence is needed before the earlier suggestion[9] of a chair-chair equilibrium can be completely ruled out.



(Ia)



(Ib)



(II)

It is interesting to note that one of the *meso*-pentane-2,4-diol cyclic sulphites (II)[10] which has been assigned the flexible form shows, in benzene, behavior strikingly similar to that observed for (I). The last two lines of the Table show Δ values for these molecules under comparable conditions. The close agreement is probably fortuitous and depends, among other things, on arbitrary correlation of the two multiplets representing protons at C_1 and C_3. However, the other two isomeric pentane-2,4-diol cyclic sulphites whose spectral properties are in good agreement with those anticipated for a chair conformation show benzene solvent shifts two to five times smaller than (I).[11]

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REFERENCES

1. N.S. Bhacca and D.H. Williams, Applications of NMR Spectroscopy in Organic Chemistry, Chapter 7, Holden-Day, San Francisco, 1964.
2. N.S. Bhacca and D.H. Williams, Tetrahedron Letters, 3127, (1964).
3. D.H. Williams, ibid., 2305, (1965).
4. J.D. Connolly and R. McCrindle, Chem. and Ind., 379, (1965).
5. D.G. Hellier, J.G. Tillett, H.F. VanWoerden, and R.F.M. White, ibid., 1956, (1963).
6. For an attempt to interpret the NMR spectrum see Yu. Yu. Samitov, Doklady Akademii Nauk SSSR, **164**, 347, (1965).
7. J.E. Anderson, Tetrahedron Letters, 4713, (1965).
8. We have found that the IR spectrum of (I) in the region 1300-1150 cm^{-1} is sensitive to solvent changes. For example, substitution of chloroform for carbon tetrachloride increases the intensity of the 1230 cm^{-1} band from about 12% (relative to the main band at 1190) to about 35%. Acetonitrile has a similar effect.
9. B.A. Arbouzov, Bull. soc. chem. France, **27**, 1311, (1960).
10. P.C. Lauterbur, J.G. Pritchard, and R.L. Vollmer, J. Chem. Soc., 5307, (1963). See also C.G. Overberger, T. Kurtz, and S. Yarostavsky, J. Org. Chem., **30**, 4363, (1965).
11. These measurements on (I) were made in 50% benzene solutions for comparison with the data of ref. 10.