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REVISED CONFORMATIONAL ASSIGNMENTS IN 1,3-DIMETHYLTRIMETHYLENE SULFITES

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Although the conformation of trimethylene sulfite and related compounds has been the subject of extensive publication (1), further work is required to establish the conformational properties of this interesting system (2).

We have measured the dipole moments of the three 1,3-dimethyl compounds and the results indicate the need for revision of the original conformational assignments (4). Our data and the corresponding numbers for the 2-t-butyl compounds are presented in Table I.

Table I. Dipole moments (20°)[a]

Compound	Solvent	
	CCl_4	C_6H_6
2-t-butyl-trimethylene sulfite (I)	3.61[b]	3.66[b]
" " " (II)	3.76[b]	4.00[b]
1,3-dimethyl-trimethylene sulfite (A) (meso)	3.51	3.60
" " " (B) (meso)	5.31	5.37
" " " (C) (dl)	3.93	3.93

a. Calculated according to ref 5. b. Ref 1a. Our determinations generally agree with ref 1a within 0.1 D.

van Woerden (1a) has made extensive use of dipole moments in his analysis, and in particular, the moments of the 2-t-butyl compounds in benzene and in carbon tetrachloride allowed isomer I to be assigned a chair conformation with S=O axial and t-butyl equatorial. Isomer II was considered to be a mixture of chair forms, with the more polar S=O equatorial form favored in polar solvents. In our opinion, the barrier to ring flipping in these compounds is too high for the chair forms to be in equilibrium and we, therefore, prefer to consider isomer II as a non-chair form. In agreement with this view is the fact that low temperature nmr spectra (to -99° in acetone-d_6) of isomer II are identical with room temperature spectra (6).

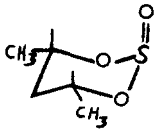
One of the two meso isomers in the 1,3-dimethyl series can take up the preferred (for these compounds) chair conformation in which the S=O group is axial and both methyl groups are equatorial. We assign this conformation to isomer A of this set, since its moments correspond to those of isomer I of the 2-t-butyl pair.

Isomer B has a moment which is unusually large and constant in the solvents used. Its nmr spectrum and behavior on acid treatment (7) leave little doubt that it is the other meso isomer. The size of the moment is consistent with the chair conformation with equatorial S=O (8), and we, therefore, assign this orientation to the S=O group and locate the methyl groups equatorially.

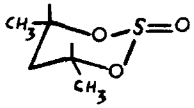
Isomer C (racemic) may be either a distorted chair or a flexible form. Recent nmr and ir evidence from a series of racemic sulfites (9) suggests a mixture of forms including about 30% non-chair for isomer C. This leaves the question as to why the moment does not change with solvent nor the nmr spectrum with temperature. It may be that for some sulfites, unlike cyclohexanes, certain arrangements within the flexible form are strongly preferred. This idea corresponds to our general view that torsional barriers in the sulfites are high (6), so that we are not inclined to admit the presence of any chair form for isomer C until some specific evidence for it is found.

In summary, we believe the correct conformational assignments for the 1,3-dimethyltrimethylene sulfites are as follows:

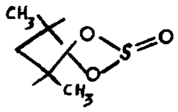
isomer A



isomer B



isomer C



It should be emphasized that isomer B is the first cyclic sulfite to exist in a chair form with S=O equatorial and that in this compound the alternative chair conformation would suffer very serious interactions from the axial 1,3-dimethyls and axial S=O group.

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REFERENCES

1. (a) H. F. van Woerden and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **86**, 341, 353 (1967); (b) references contained therein.
2. Electron diffraction patterns of the three 1,3-dimethyl isomers are now being analyzed by Prof. J. L. Hencher of this department. An X-ray study on trimethylene sulfite has been reported (3).
3. C. Altona, H. J. Giese and C. Romers, *ibid*., **85**, 1197 (1966).
4. P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc*., 5307 (1963). When the S=O assignments in this work are reversed (ref 1a, p 353), our conclusions for isomer A agree. In our opinion, the nmr and ir evidence presented by these authors for the other isomers is far from conclusive.
5. F. Moll and E. Lippert, *Z. Electrochem*., 58, 853 (1954).

6. (a) Other recent work on molecules with vicinal electron pairs indicates high rotational barriers; e.g., M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., Tetrahedron letters, 5055 (1968); A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, J. Am. Chem. Soc., 90, 4185 (1968); (b) See also A. Rauk, S. Wolfe, and I. G. Csizmadia, Can. J. Chem., 47, 113 (1969). Calculations on hydrogen methyl sulfinyl anion and related molecules not only relate high rotational barriers to interaction of vicinal electron pairs, but further suggest that the favored conformation in such molecules (p. 128) corresponds to the S=O axial conformation of cyclic sulfites.
7. Addition of a trace of acid converts this compound cleanly into the corresponding isomer A.
8. Calculations (ref 1a) would suggest a moment of 5.0-5.2 D for this conformation. Private communication from H. F. van Woerden.
9. P. Maroni and L. Cazaux, Abstracts of the 51st Annual Conference of the Chemical Institute of Canada, Vancouver, June, 1968.