STRUCTURE OF <u>meso</u>-1,3-DIMETHYLTRIMETHYLENE SULFITE: MONOMER OR DIMER?

PERSISTENT ASSOCIATION IN TRIMETHYLENE SULFITES
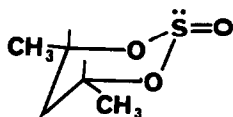
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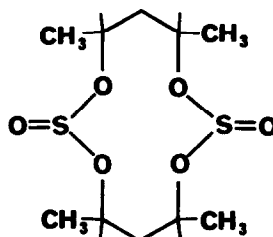
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Recently, we assigned (1) to the second <u>meso</u> isomer of 1,3-dimethyltri-methylene sulfite (originally (2) called isomer B), a chair conformation in which the S=O bond was equatorial (structure 1). A recent publication (3) contains the novel suggestion that this isomer has the structure 2.



The major piece of evidence cited by these authors was a cryoscopic molecular weight determination of $312 \pm 12$. However, no peak at m/e = 300 could be found in the mass spectrum (4). We, therefore, undertook a survey of the apparent molecular weight ($M^x$) of a number of trimethylene sulfites by vapor phase osmometry (5).

While we found no evidence for structure 2, we did discover that the

compound in question and several other trimethylene sulfites are appreciably associated in solution. Although most of our data so far is limited to the determination of $M^{x}$ at one concentration, certain trends are readily apparent. Association is greatest for trimethylene sulfite ($TMSO_3$) in cyclohexane and decreases with increasing sulfite substitution and increasing solvent polarity. The values of $M^{x}/M$, presented in the Table, illustrate these points.

Table. Ratio of Apparent Molecular Weight to Formula Weight $(M^{x}/M)$[a]

| Compound | Solvent | | |
|---|---|---|---|
| | $C_6H_{12}$ | $CCl_4$ | $CH_3CN$ |
| trimethylene sulfite ($TMSO_3$) | 5.35 | 2.36[b] | 1.21 |
| 1,3-dimethyl-$TMSO_3$ (A) (meso) | 1.99 | 1.44 | 1.00 |
| 1,3-dimethyl-$TMSO_3$ (B) (meso) | 1.42 | 1.25 | 1.00 |
| 1,3-dimethyl-$TMSO_3$ (C) (dl) | 1.85 | 1.43 | 1.10 |
| 2-t-butyl-$TMSO_3$ (I) | 1.10 | 1.13 | 1.05 |
| 2-t-butyl-$TMSO_3$ (II) | 1.08 | 1.13 | 1.08 |

a. All determinations were made at ca 1% by weight of solute.
b. Average of three determinations.

For solutions of $TMSO_3$ in $CCl_4$, $M^{x}$ was determined at various concentrations and a plot was made of $M^{x}/M$ vs. concentration (Figure). This plot indicates dimer formation which persists to remarkably low concentrations. Further work will be necessary for more concentrated solutions. The dashed line at 5 mM represents the concentration where intermolecular association is usually assumed to be negligible in i.r. studies (6).
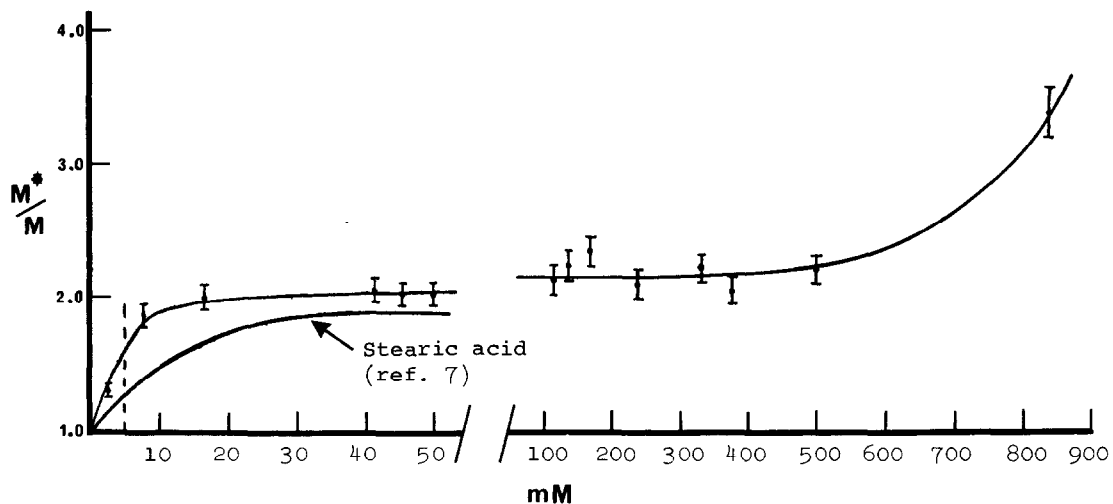
Figure.   Plot of the ratio $(M^*/M)$ of the apparent $(M^*)$ to true (M) molecular weight against molar concentration for solutions in $CCl_4$.   Error limits are $\pm$ 4%.

Some examples of unusually persistent association in H-bonded systems have recently been reported by Kovac and Eglinton (7).   Several points for one of their most strongly associated molecules, stearic acid, are included in the Figure for comparison with the present results.

The behavior of the sulfites in this study is made even more noteworthy by the absence of any likely structure for H-bonding.   It has been suggested pre-viously that intermolecular association in cyclic molecules with large dipole moments may be caused by dipole-dipole interactions (8), but to our knowledge, no such interaction has been demonstrated at the concentrations involved here.

Considerable constraint is placed on possible structures for the complex by the fact that the measured dipole moments of most of these sulfites are essentially constant in a variety of solvents and agree very well with the calculated values (9).   Possible geometries of association are being examined

along with the effects of association on the various spectra. For example,
the changes in i.r. absorption near 1200 cm$^{-1}$ with solvent, which have been
attributed to conformational changes (9a), may instead reflect a change in
the degree of association.

The present work demonstrates that structure 2 and the rather unusual
reaction, which its adoption would require for the known interconversion of
the two meso-1,3-dimethyltrimethylene sulfites (3), are unnecessary.
Structure 1 remains the one which, in our opinion, best accommodates all the
data for this compound and its relatives.

## REFERENCES

1. G. Wood and M.H. Miskow, Tetrahedron Letters, 1109 (1969).
2. P.C. Lauterbur, J.G. Pritchard, and R.L. Vollmer, J. Chem. Soc., 5307, (1963).
3. R.E. Lack and L. Tarasoff, Jr., ibid., 1095 (1969). We thank Professor
   Lack for a preprint of this publication.
4. This result would be surprising if 2 were indeed the structure, since cyclic
   sulfites ordinarily yield molecular ions of significant intensity (ca 1% of
   base peak). The alleged rapid thermal conversion of isomer B to isomer A
   (2,3) cannot explain the lack of an ion at m/e = 300, since we have found
   that sulfites carefully purified to remove all traces of acid do not, in
   fact, isomerize thermally. Further, the mass spectra of the two isomers
   are significantly different, a result incompatible with a fast thermal
   conversion of isomer B to isomer A in the spectrometer.
5. Measurements were made by Schwarzkopf Microanalytical Laboratory, Inc.,
   Woodside, N.Y., 11377.
6. K. Nakanishi, Infrared Absorption Spectroscopy, Holden-Day, San Francisco,
   1962, p. 32.
7. G. Eglinton and S. Kovac, Tetrahedron, 25, 3611 (1969) and earlier papers.
8. A.W. Baker, J. Phys. Chem., 60, 1660 (1956).
9. (a) H.F. van Woerden and E. Havinga, Rec. Trav. Chim. Pays-Bas, 86, 341
   (1967);
   (b) ibid., 353 (1967). Since all work reported to date has assumed
   sulfites are unassociated, it is possible that some incorrect inferences
   have been made.