Conformational Analysis of Trimethylene Sulfites. The Importance of Vicinal Unshared Electron Pairs[1]

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Dipole moments are reported for trimethylene sulfite and 11 alkyl derivatives in a variety of solvents (C_6H_{12}, CCl_4, C_6H_6, dioxan). The variation of dipole moment with solvent for one of the 5-*t*-butyltrimethylene sulfite isomers is confirmed, but this behavior is not shown by the other compounds. This latter fact is used to rule out rapid chair–chair interconversion for these compounds. Recent ultrasonic absorption experiments are reinterpreted in the context of vicinal electron pair interactions and their effect on conformational analysis of sulfites and similar six-membered compounds. The result is a general scheme which is consistent with available information and which we believe is preferable to analysis of these compounds by analogy with cyclohexane.

On a mesuré, dans quelques solvants (C_6H_{12}, CCl_4, C_6H_6, dioxane), les moments polaires du sulfite de triméthylène et de 11 dérivés alkylés. Nous avons confirmé que le moment polaire de l'un des *tert*-butyl-5 sulfite de triméthylène varie avec le solvant; cette variation n'est pas observée avec les autres composés. Ce dernier fait est utilisé pour exclure la possibilité d'une interconversion chaise–chaise rapide entre ces composés. Des résultats récents d'absorption ultrasonique sont réinterprétés dans le contexte d'interactions entre des paires d'électrons vicinaux et de leurs effets sur l'analyse conformationnelle des sulfites et des composés cycliques à six chaînons de nature similaire. Le résultat est un schéma général qui est consistant avec les informations disponibles et qui, nous le croyons, est préférable à une analyse de ces composés par analogie avec le cyclohexane.

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Introduction

Much data has been reported on the conformations of substituted trimethylene sulfites since the initial attempt by Arbouzov (1) to assign a conformation to the parent ring system, but no clear picture of the shapes of these compounds has emerged. Although trimethylene sulfites are usually assumed to undergo rapid chair–chair interconversion at room temperature, all our attempts to find a coalescence of signals in n.m.r. spectra have been unsuccessful. While this result by itself could indicate the presence of only one chair form in measurable amounts (anancomeric system), dipole moment data will be presented here which rules out that possibility for at least some of the sulfites. The lack of coalescence temperature between −100 and +30 °C for the molecules[3] is sufficient to show that the barrier to ring inversion must lie either substantially above or substantially below the usual cyclohexane barrier of 10.3 kcal/mol.[4] We shall attempt to show that only the former is consistent with all the facts. Recently ultrasonic relaxation studies have been interpreted in terms of chair–chair equilibria for several trimethylene sulfites (2). We suggest that the analysis of the data obtained in these experiments errs by neglecting the effect of vicinal electron pairs.

Our aim is to present, point by point, the evidence which leads us to conclude that the presently held concepts about the conformation of trimethylene sulfites and some related molecules need revision and to develop a new model consistent with all the facts known at this time.

Results and Discussion

Dipole Moments and Solvent Dependence

The dipole moments were calculated by the method of Guggenheim (3) and are presented in Table 1. The values in parentheses were obtained by van Woerden and Havinga (4) and the agreement is satisfactory, considering the different methods of calculation. In keeping with a previous observation (4*b*), these dipole moments permit important conclusions on conformation to be made. In particular, the influence of a polar solvent on an equilibrium between two forms of different dipole moment is such that the form of higher moment is favored. This shift in equilibrium results in a higher (average) dipole moment.

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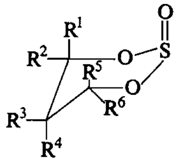
[2] Recipient of NRCC Scholarships, 1966–1970.

[3] Results of our n.m.r. experiments will be reported later.

[4] For a signal separation of 0.5 p.p.m., a coalescence temperature below −100 °C corresponds to a barrier < 8.5 kcal/mol; a temperature above +30 °C to a barrier > 15 kcal/mol. Differences in signal separation have only a small effect on these values.

TABLE 1. Dipole moments for the compounds of the general structure:



		Dipole Moment (D)					
Compounds	Substituents*	C_6H_{12}	CCl_4	C_6H_6	Dioxane	$\Delta_{C_6H_6-CCl_4}$†	$\Delta_{C_6H_6-C_6H_{12}}$‡
1§		Insoluble	3.34				
2§	$R^2 = CH_3$		3.35	3.41		.06	
3	$R^1 = CH_3$		4.66	4.75		.09	
4§	$R^2 = R^6 = CH_3$	3.44	3.51	3.60		.09	.16
5	$R^2 = R^5 = CH_3$	3.97	3.93	3.93		.00	−.04
6	$R^1 = R^5 = CH_3$	Insoluble	5.31	5.37		.06	
7‖	$R^1 = R^2 = R^6 = CH_3$	3.91		3.86			−.05
8	$R^1 = R^2 = R^5 = CH_3$	4.53		4.71			.18
9‖	$R^1 = R^2 = R^5 = R^6 = CH_3$	4.22		4.30			.08
10§	$R^3 = R^4 = CH_3$	3.38					
11	$R^3 = (CH_3)_3C$	3.50	3.54(3.61)¶	3.60(3.66)¶	3.66	.06	.10
12	$R^4 = (CH_3)_3C$	3.54	3.63(3.76)¶	3.90(4.00)¶	4.15	.27	.36

*All R's not specified = H.
†$\mu_{C_6H_6} - \mu_{CCl_4}$.
‡$\mu_{C_6H_6} - \mu_{C_6H_{12}}$.
§Ultrasonic relaxation found.
‖No ultrasonic relaxation found.
¶From ref. 4*a*.

Several of these compounds have dipole moments corresponding at least approximately to a chair form with axial S═O[5] (compounds **1**, **2**, **4**, **10**, **11**). The only molecule with a moment which clearly corresponds to a chair with equatorial S═O is compound **6**.[6] This molecule has been assigned this conformation (5, 6) and recent n.m.r. evidence supports this assignment.[7] Compounds **3** and **8** must also have large amounts of this form or a non-chair form with similar geometry at the sulfite end of the molecule. Our analysis requires that the latter be the case.

The variation of dipole moment with solvent for compound **12** (4*a*) has been confirmed by measurement in two additional solvents. The difference in dipole moment between dioxane and cyclohexane solutions is 0.61 D which is well outside the experimental error and much larger than the corresponding change (0.16 D) for the other (rigid ?) isomer, compound **11**. The behavior exhibited by compound **12** is expected for a molecule existing as interconverting conformations with substantially different dipole moments (4*a* and references therein). In this situation the conformation of higher moment is favored in the more polar solvent. *None of the other compounds studied show enough variation of dipole moment with solvent to implicate a conformational equilibrium with certainty*, although some of them are borderline, *e.g.*, compound **8**.

Compound **9** has a dipole moment of intermediate value which is constant and it therefore seems likely that this compound exists in a non-chair form almost exclusively. Compounds **5** and **7** have moments near 3.9 D which implies either a distortion of the S═O axial chair or a non-chair form. Since both of these molecules have the same axial methyl – axial S═O interaction in the chair form, it is not surprising that they have similar moments, but it is not possible on this basis to decide between the chair and non-chair alternatives.[8]

The general constancy of the dipole moments in various solvents (except for compound **12**) even for compounds whose moments deviate considerably from the values expected for chair forms makes it highly unlikely that any of these

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[5] Calculations give 3.4 D for trimethylene sulfite, see ref. 4*b*.

[6] The dipole moment for this form has been estimated as 5.0–5.2 D by H. F. van Woerden, private communication.

[7] Private communication from Professor R. E. Lack, University of Sydney, Sydney, Australia.

[8] Compound **5** has been assigned as existing as 70% chair and 30% non-chair (7). This result fits very well the general scheme to be developed later in this paper.

compounds exist as equilibrium mixtures of conformations with large differences in dipole moment. *In particular, with the possible exception of compound* ***12***,[9] *none of these compounds exist as equilibrium mixtures of two chair conformations.* Where equilibria do exist, they probably involve chair and non-chair forms with similar moments.

In the remainder of this discussion an attempt will be made to reconcile the conclusions from the dipole moment study with other information available from conformation studies of cyclic sulfites and related molecules.

Ultrasonic Absorption and Conformational Equilibria

Sulfite barriers of 5–7 kcal/mol ($\Delta H^{\ddagger}$, more stable to less stable) are typical of the ultrasonic data. The assignment of these barriers to the chair–chair interconversion process depends on an interpretation of other data (8), chiefly spectral (2), which is less than compelling. In fact, all such interpretations to date implicitly use cyclohexane as the model for six-membered ring behavior.

The most relevant experimental evidence on the nature of the barrier being measured in the ultrasonic work arises from a comparison of the latter with low temperature n.m.r. results on related systems. For example, we have recently determined the ring inversion barrier for 5,5-dimethyltrimethylene sulfate (9). The n.m.r. result is 8.1–8.4 kcal/mol in contrast to the ultrasonic value of 4.6–6.2 kcal/mol for the related 4-methyltrimethylene sulfate. We prefer to handle this anomaly in the way that a similar one was handled for a 1,3-dioxane, namely by assigning the lower barrier observed in the ultrasonic work to a chair – non-chair interconversion (10).

A different kind of difficulty has arisen with compounds having two identical chair forms. Chair–chair interconversion cannot cause ultrasonic absorption for such a system (10), and yet relaxation has been observed. Once again, the assumption of a chair – non-chair equilibrium has been made.

Finally, ultrasonic absorption measurements on 4-phenyl-1,3-dioxan gave results unexpected for a chair–chair equilibrium (11). The most serious discrepancy was the large negative entropy associated with conversion of the less stable to the more stable form. That fact, coupled with the large $-\Delta G^{\circ}$ value expected for 4-axial substituents on this ring (12) can readily be accommodated by assignment of the less stable form to a non-chair conformation.

In conclusion, we suggest that the trimethylene sulfites which have been shown by ultrasonic measurements to exist as a conformational equilibrium (as little as 1% of minor conformer can be detected (8)) have a non-chair conformation of energy comparable to the preferred chair form. According to this notion, compounds which fail to give a relaxation result are limited to a single chair or non-chair conformation. Compound **9** and possibly **7** are examples of the latter and 5-nitro-5-methyltrimethylene sulfite (2) is presumably an example of the former. Compounds in our dipole moment study that have been studied by ultrasonics are noted in Table 1 along with the result.

The nature of the data from the ultrasonic experiment is such that one cannot use it to prove *any* structural assignments. Our claim is simply that considerable evidence can be brought forward from a re-evaluation of this data to support our interpretation of conformational behavior in these systems. The next section will show that there exists a large body of information on the influence of vicinal electron pairs on rotational barriers and conformation which is also consistent with our interpretation.

Vicinal Unshared Electron Pairs and Barriers to Rotation

The transition state for ring inversion in cyclohexane is considered to be the half-chair (13). In other six-membered ring compounds the minimum energy path for ring inversion may involve a twist or other form, but regardless of the form of the transition state, rotation about single bonds of the ring must accompany the process. Indeed, the barrier to ring inversion represents, in large part, the torsional energy required for rotation about these bonds (13, 14). Thus, the barrier of 10.3 kcal/mol in cyclohexane (15) should be related in part to the 3.4 kcal/mol about the C—C bond in propane (16),[10] and a ring containing single bonds with higher barriers to rotation would be expected to have a higher barrier to inversion.[11]

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[9] Since compound **12** shows a constant n.m.r. spectrum from −100 to +180 °C, it is probable that it also fits the scheme proposed later, in spite of its dipole moment behavior.

[10] The choice of propane over ethane or butane for a model is an arbitrary one.

[11] There seems to be no dispute with this principle, see ref. 2, p. 314 and ref. 17. Our disagreement with ref. 2 involves only the choice of suitable acyclic models.

Rotational barriers about single bonds between atoms carrying unshared electron pairs have been measured (16, 18–21) and calculated (22–26) for a large variety of compounds. These barriers are generally of the order of 10 kcal/mol, a value seldom reached by the most hindered ethane derivatives lacking vicinal electron pairs. Although these high barriers may not be wholly resultant from vicinal electron pair interactions (18*b*, 19, 21, 25), all results thus far indicate these interactions make a most important contribution. A comprehensive paper by Wolfe and co-workers reduces the wealth of data and calculations now available on this point to two simple rules (26).

There is also abundant evidence that one or more bonds of this sort in a six-membered ring increase the barrier to ring inversion, in spite of the reduction in rotation barrier for neighboring bonds where only one atom has unshared electron pairs (27).

Thus, it seems to us that for trimethylene sulfites (with unshared electron pairs on three adjacent atoms) the choice between a high (>15 kcal/mol) and a low (<8.5 kcal/mol) barrier to ring inversion can be made with some confidence. The only conclusion compatible with these arguments is that the barrier to ring inversion is high and, further, that interactions of vicinal electron pairs are a major cause of this barrier as well as other conformational properties. The strong preference of the exocyclic S=O bond for the axial position is probably best understood in these terms.[12] Equatorial disposition of S=O would give rise to an arrangement which corresponds to an energy maximum for molecules of this sort ($\theta = 120°$, see Fig. 1 and ref. 28).

Two-fold Rotational Barriers and Minimum Energy Conformations

Attention is drawn by Wolfe *et al.* (26) to an important feature of their calculation of barriers for bonds with vicinal unshared electron pairs; *viz*, the total energy curves for 360° rotation about these bonds show only two maxima and two minima. Perhaps the clearest example of this can be seen by comparison of the calculated barriers for hydrogen methyl sulfoxide and its carbanion (28*c*).[13] Figure 1 shows a sketch combining these results with the corresponding curve for ethane. Note that CH_3SHO has an ethane-like barrier with the three maxima and three minima shifted about 20° to the right. The carbanion has had two of these maxima and the minimum between them ($\theta = 80$–$200°$) replaced by a single maximum ($\theta = 130°$), as well as other smaller shifts. When one considers that the conformational preference for the chair over non-chair forms in cyclohexane is equated with the preference of the staggered over the eclipsed conformation in ethane, it becomes clear that arbitrary assignment of the chair as preferred conformation in six-membered rings containing one or more bonds with vicinal unshared electron pairs is unjustified. The curve for $^-CH_2SHO$ shows energies of 4.4, 12.8, and 0 kcal/mol for the conformations corresponding to staggered ethane. Thus, in six-membered rings with vicinal electron pairs the staggered conformation characteristic of a perfect chair *may* correspond to an energy minimum, *but it also may correspond to the highest energy on the rotation curve or any intermediate value.*

Because of the increased height and, therefore, importance of these two-fold barriers we conclude that the preference for chair forms should decrease with the introduction of one or more bonds of this type. In fact, there is already experimental evidence for twist form preference in some of these molecules. One well-documented case involves 3,3,6,6-tetramethyl-1,2,4,5-tetrathian (29) where the twist form is preferred by 0.5–1 kcal/mol in the various activation parameters. The small entropy difference between the chair and twist forms of this molecule probably reflects the reduced flexibility of non-chair form in these systems. Several recent communications on phosphorus analogues of sulfites also implicate twist forms and high ring inversion barriers for these compounds (30–33).

The current view that trimethylene sulfite prefers the chair form, based mainly on X-ray data (34) may well be correct. However, the possibility of relatively low energy non-chair forms in solution seems to us to be strong. The n.m.r. work of Maroni and Cazaux referred to earlier (7), dipole moment data presented here, and our interpretation of the ultrasonic absorption data of Wyn-Jones may be cited in support

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[12] No direct measure of this preference exists. Acid equilibration of compounds **4** and **6** gives values of 2.6 kcal/mol in CCl_4 and 1.7 kcal/mol in CH_3CN. However, persistent association of these sulfites (5) in dilute solution may influence these results.

[13] For comment on recent experimental work on related molecules, see ref. 26.

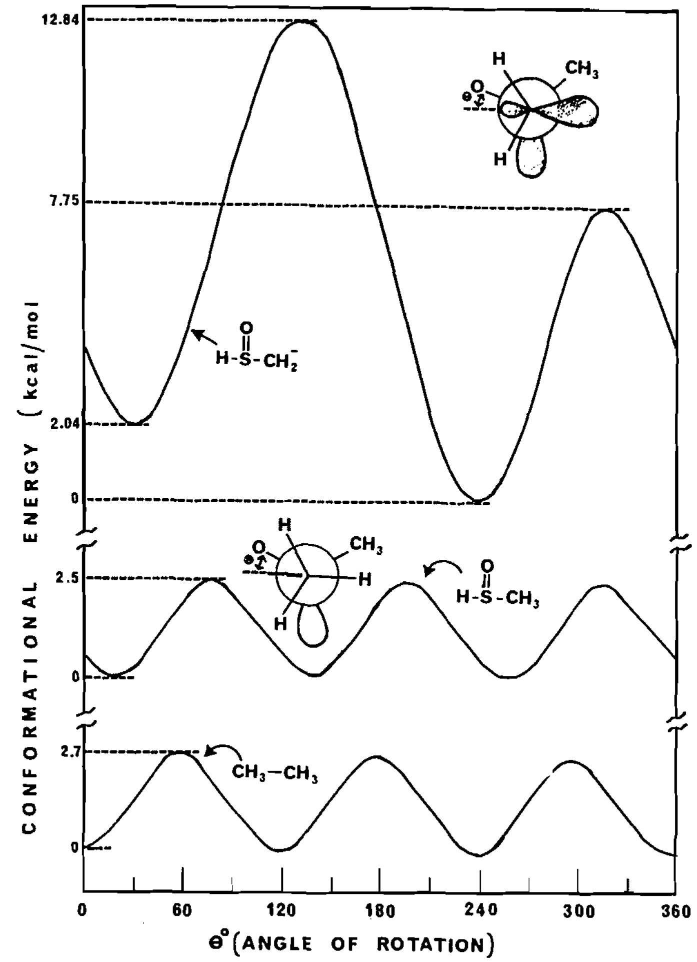

FIG. 1. Variation of the total energy of ethane, hydrogen methyl sulfoxide, and its carbanion as a function of rotation about the C—C or C—S bond (θ).

of this position. Further, it seems likely that steric interactions are capable of changing relative energy levels of sulfite conformations drastically. For example, it seems likely that compound **9** is predominantly non-chair.

Summary and Conclusions

The application of existing notions on trimethylene sulfite conformations to ultrasonic absorption data has led to an interpretation that contradicts a number of conformational studies documenting the importance of unshared electron pairs on adjacent atoms.

In this paper an attempt has been made, using the above results and new data on the sulfites, to define normal behavior for trimethylene sulfites with emphasis on the influence of electron pairs on sulfur and oxygen. This analysis leads to a coherent picture in which trimethylene sulfites have high barriers to chair–chair interconversion, low energy non-chair forms, and a strong preference for axial S=O. No conflict with previously reported facts has been uncovered, and the ultrasonic absorption experiments emerge as an important probe for chair to non-chair equilibria in these systems.

While we feel our conclusions are consistent with the data available at this time, we do not wish to imply that we have proven our contentions beyond any doubt. We offer our model as a possible solution to the difficulties encountered in viewing certain six-membered rings as close relatives of cyclohexane in the hope that it will inspire more definitive experiments. Current work in this laboratory is directed toward that end.

Experimental

The n.m.r. spectra were obtained on a JEOL JNM-C60S or C60HL using TMS as internal standard.

Synthesis of Sulfites

The best synthetic method for the preparation of these sulfites was found to be the thionyl chloride – pyridine method. This gave not only a good yield of sulfites, but also the highest yield of the less stable isomers. The following procedure for 4-methyl-trimethylene sulfite is typical.

To 45 g (0.50 mol) 1,3-butanediol, dissolved in 300 ml dry benzene and 150 ml dry pyridine, was added dropwise with stirring and external cooling 44 ml thionyl chloride (0.60 mol) in 100 ml benzene over a period of 3 h. After filtering off the salt formed and neutralizing with bicarbonate, the organic layer was separated and washed with 0.1 *N* HCl, water, and dried over $MgSO_4$. After filtration and concentration on a rotary evaporator, the sulfites were collected by g.l.c. using either an 8 ft × 0.50 in. 10% DEGS (LAC 728) on 60–80 Diatoport W with an F and M 720, or a 14–19 ft × 3/8 in. 20% DEGS on 40–60 Chromosorb W with a Varian 712 Autoprep. All new compounds gave satisfactory elemental analyses and isomeric purity was in all cases greater than 99% by g.l.c.

Dipole Moments

Dipole moments were calculated by the method of Guggenheim (3) from dielectric constants determined on a Wissenschaftlich-Technische Werkstatten (Germany) Dipolemeter DMO1 at 20 °C. Solvents were spectrograde and dried over Linde molecular sieve type 4A. The determination equation is:

$$\mu^2 = 27kT/4\pi N_L \cdot 1/d_1(\varepsilon_1 + 2)^2 \cdot (a_\varepsilon + a_n) \cdot M_2$$

where

k = Boltzmann constant
N_L = Lohschmidt's number
d_1 = solvent density
ε_1 = solvent dielectric constant
M_2 = solute molecular weight
a_ε = slope of line $(\varepsilon_{12} - \varepsilon_1)$ *vs.* w_2
a_n = slope of line $(n^2_{12} - n_1^2)$ *vs.* w_2
ε_{12} = solution dielectric constant
n_{12} = solution refractive index
n_1 = solvent refractive index
w_2 = solute weight fraction $(m_2/m_1 + m_2)$

At 20 °C the first term is 1.433×10^{-37}

Slopes were determined from a least squares plot on an IBM 1620 Mk II and μ reproducibility was generally better than 0.1 D.

Sulfite Equilibrations

Solutions (1 *M* in sulfite with 100 1 BF_3–etherate per 3 ml solution) initially on each side of equilibrium were stirred at room temperature in sealed vials for 2–10 weeks, neutralized with K_2CO_3 and gas chromatographed on a 6 ft × 0.25 in. Carbowax 20M on 60–80 Porapak S. Area ratios were measured by planimeter and corrected for response ratios determined with a standard mixture under identical conditions. Calculations were done according to Eliel and Reese (35) taking *T* as 298 °K.

NOTE ADDED IN PROOF: Similar conclusions to some of those drawn here are contained in a recent paper by Wucherpfennig (36).

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