Acta Chemica Scandinavica A 34 (1980) 223–227

# A Theoretical Study of the Molecular Structure of Trimethylene Sulfoxide with Emphasis on the Local Symmetry of the Methylene Groups

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The geometry of the equatorial form of trimethylene sulfoxide has been optimized completely using the gradient technique of Pulay. The calculations are based on an *ab initio* SCF wave function constructed from a 4–21 basis for carbon and oxygen and a 3-3-21 basis for sulfur. The calculations have demonstrated that the $CH_2$-groups in the molecule are distorted, and a quantitative estimate of the distortions is given in comparison with results obtained from microwave spectroscopy.

Our results support one of the two alternative sets of distortion parameters given in the experimental work. Localized orbitals obtained by a transformation of the canonical SCF functions show that the carbon–carbon bonding orbitals have their charge centers in the CCC plane whereas the carbon–sulfur bonding orbitals have their charge centers outside the CSC plane. This is discussed with reference to the principle of minimum bond tortuosity.

In a recent paper one of us (J.W.B.) and coworkers have undertaken a detailed study of the molecular structure of trimethylene sulfoxide (TMSO) by microwave spectroscopy.[1] Of particular interest in that investigation was the local symmetry of the $CH_2$-groups described in terms of bends, tilts and twists. This molecule was considered to be suitable for an experimental study of this kind since the equatorial conformer exists in a deep potential minimum, and is significantly lower in energy than the axial conformer the existence of which has not been unequivocally established.

The spectroscopic investigation is a very extensive one including determination of rotational constants for eight different singly substituted isotopic species in addition to the common one. This has led to a completely determined $r_s$-structure.

The availability of a precisely determined structure of a four-membered organic ring system containing two heteroatoms does give a good opportunity for testing theoretically founded models for chemical binding and intramolecular interactions.

Two of us (P.N.S. and J.E.B) have recently studied closely related systems by SCF calculations[2] coupled to a gradient method developed by Pulay.[3] By means of these studies a complete geometry optimization within the Hartree-Fock limit has been carried out giving information both on ring puckering and $CH_2$-group deformations. For most of the four-membered rings included in those calculations the experimental information is scarce.

The purpose of the present study is two-fold. Firstly we want to scrutinize the geometry of TMSO in order to look at possible disagreements between theoretical and experimental values for structural parameters. Previously it has been demonstrated that theoretical calculations of the kind applied here, have led to very accurate and reliable relative values of related structural parameters.[4–6] In TMSO there are four structurally inequivalent C–H bonds. The uncertainties in the experimentally obtained[1] $r_s$-values for these bond lengths are too large (up to $\pm 0.01$ Å) to decide

0302-4377/80/030223-05$02.50

conclusively whether these bond lengths are equal or not. As will be discussed below, this uncertainty prevents an unambiguous discussion of the local symmetry of the $CH_2$-groups.

Secondly we include a discussion of the bonding in the ring system in terms of localized orbitals. Hopefully such a discussion will give additional information about the electronic structure that cannot be obtained from microwave spectroscopy.

## METHOD

The calculations were performed using the program TEXAS written by Pulay.[3] The essential feature of this program system is that, beyond the usual SCF procedure, it calculates the gradient of the energy in exact analytic form. Complete geometry optimization is carried out by the force relaxation method.[7]

For the first-row atoms we applied a 4−21 Gaussian basis set[8] which is similar to the 4−31G basis of Pople *et al.*[9] In the former set the valence shell contains three functions instead of four, split into two-one. Especially for gradient calculations this basis is considerably more economic than the 4−31G basis, and it gives very similar energy surfaces.

For the S-atom we used a 3−3−21 basis set[2] which is related to the Hehre-Lathan[10] basis 4−4−31G in a way that is consistent with the relation between the 4−21 and 4−31G sets mentioned above. The sulfur basis was augmented by a set of 5 *d*-functions having an orbital exponent of 0.8. These functions were constructed from *p*-functions displaced 0.1 a.u. from the nucleus.[11] To these functions were added two primitive *s*-functions contracted to a single one representing the sum of the diagonal *d*-functions.[11]

In previous calculations aiming at geometry predictions the importance of *d*-functions on sulfur has been demonstrated. See, *e.g.*, Refs. 2 and 12.

In the optimization of the structural parameters the end points were defined by changes in bond distances less than 0.002 Å, and by changes in angles less than 0.35°.

The final canonical molecular orbitals were transformed to localized ones using the criterion of Boys.[13]

## RESULTS AND DISCUSSION

The calculated structural parameters except those describing $CH_2$-group orientations are presented in Table 1. which also contains the corresponding experimental values. The labelling of atoms is given in Fig. 1. The orientation and deformation of the $CH_2$-groups are described in Table 2 in terms of parameters defined in Fig. 2.

*Table 1.* Calculated and measured structural parameters for the equatorial form of TMSO. Bond distances in Å, angles in degrees. Labelling of atoms in Fig. 1.

| Parameter | Calc. | Exp.[a] |
|---|---|---|
| $R$(C−C) | 1.559 | 1.542(5) |
| $R$(C−S) | 1.838 | 1.836(3) |
| $R$(S−O) | 1.484 | 1.475(3) |
| $R$(C−$H_2$) | 1.080 | 1.099(10) |
| $R$(C−$H_2'$) | 1.077 | 1.075(9) |
| $R$(C−$H_3$) | 1.077 | 1.087(7) |
| $R$(C−$H_3'$) | 1.079 | 1.098(8) |
| ∠CCC | 93.8 | 93.9(4) |
| ∠CCS | 90.0 | 89.6(8) |
| ∠CSC | 76.5 | 75.7(3) |
| ∠OSC | 114.4 | 113.4(5) |
| $\delta$[b] | 32.8 | 34.9(6) |

[a] Ref. 1. [b] Ring puckering angle.

The general impression of the data in Table 1 is that of a good agreement between measured and predicted structural parameters. Notable exceptions are the C−H bond distances. In this molecule there are four different C−H bond distances. According to our calculations these are virtually identical, the largest difference being 0.003 Å. Previous calculations of this kind have demonstrated that although the absolute values obtained for C−H bond distances are too short, the relative lengths are predicted with very high precision. This leads us to believe that the rather large difference between the measured values is not real. In particular we think that the experimental value of the C−$H_2'$ distance is too short. However, in view of the rather large

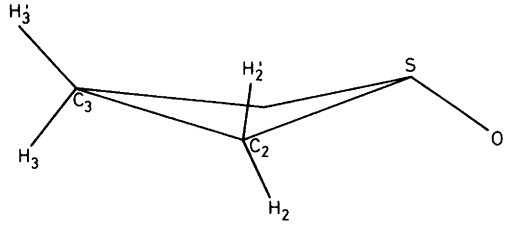


*Fig. 1.* Labelling of atoms in trimethylene sulfoxide (TMSO).

*Table 2.* Deformation of the geometries of the $CH_2$-groups in TMSO. Angles in degrees.

| Parameter | Group $C_2H_2H'_2$ | $C_3H_3H'_3$ |
|---|---|---|
| Calculated | | |
| $\phi_r$ | 5.5 | 3.0 |
| $\phi_t$ | 0.4 | |
| $\phi_w$ | 3.2 | |
| Exp. I | | |
| $\phi_r$ | 7.7(13) | 4.6(12) |
| $\phi_t$ | 1.5(8) | |
| $\phi_w$ | 5.1(15) | |
| Exp. II | | |
| $\phi_r$ | 6.3 | 3.1 |
| $\phi_t$ | 1.7 | |
| $\phi_w$ | 5.6 | |

uncertainties in the experimental values for these bonds (see Table 1) the measured bond lengths may be interpreted as equal. We will return to this point in the discussion of the $CH_2$-group deformations.

Another point of interest is that the predicted value of the ring-puckering angle is in very good agreement with the measured one. In a previous, identical calculation[2] of the corresponding parameter for azetidine we were in serious disagreement with results from an electron diffraction investigation,[14] the calculated and measured values being 15 and 34 degrees, respectively. It is gratifying that in the present case, where the molecule has a deep, well-defined potential minimum for the equatorial

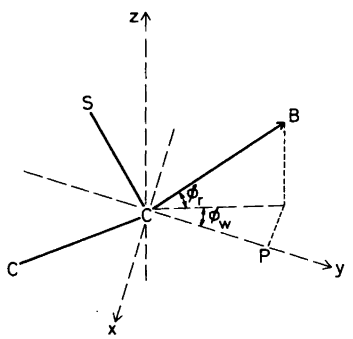


*Fig. 2.* Definition of deformation coordinates for the $C_2H_2H'_2$-group in trimethylene sulfoxide. The vector CB describes the bisector of the $H_2C_2H'_2$ angle. The twist of the group, $\phi_t$, is defined as the angle between the *yz*-plane and the plane BCP.

form, the calculated and measured minimum positions are in accordance. This lends support to the previously presented[2] assumption that the experimental value[14] of the puckering angle in azetidine probably is too large. One should, however, bear in mind that in TMSO one of the ring atoms has been furnished with *d*-functions. This might influence the predicted ring-puckering angle in a decisive way.

The bends, tilts and twists of the $CH_2$-groups were described in terms of Eulerian angles in the microwave study.[1] In order to facilitate a direct comparison between calculated and experimental values for these deformations, we have expressed them in terms of corresponding parameters. In Fig. 2 are defined the parameters $\phi_r$ and $\phi_w$ that express the rocking and wagging deformations, respectively. The twisting parameter, $\phi_t$, describes the angle between the $C_2H_2H'_2$-plane and the *yz*-plane. As shown in Fig. 2 these are related to the direction of the bisector of the HCH angle described by the vector CB. The ortogonal coordinate system is oriented such that the *y*-axis bisects the SCC angle, and the *xy*-plane coincides with the SCC plane. In Table 2 are given the calculated values of the deformation coordinates together with the experimental ones. As shown by the table, there are two experimental sets of parameter values labelled I and II, respectively. The values in set II are evaluated on the basis of atomic $r_s$-coordinates except that the principal axis coordinates c for the atoms $C_2$ and $C_3$ are calculated under the assumption that $R(C-H_2)=R(C-H'_2)$ and $R(C-H_3)=R(C-H'_3)$. In set I this constraint on the C–H bond distances has been removed. As mentioned above and confirmed by the data in Table 1, we predict the C–H bond distances to be virtually identical. Thus the calculated deformations should primarily be compared with those given in the experimental set II.

It is interesting to notice the complete agreement obtained for the $C_2H_2H'_2$ rocking parameter by this comparison, whereas the corresponding value in set I is significantly larger. One of the conclusions to be drawn from the data in Table 2 is the following. They demonstrate the capability of suitably chosen theoretical approaches to predict structural details with a precision that is sufficiently high to suggest preferences between alternative experimental parameter sets. This is a confirmation of previously gained experience.[2]

For the $CH_2$-group adjacent to the sulfur atom

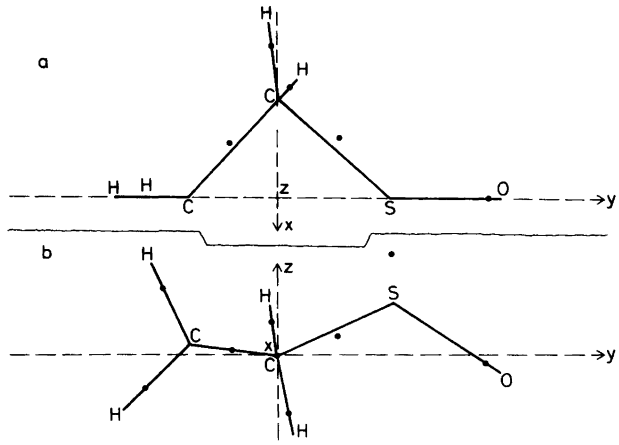


*Fig. 3.* Projection of trimethylene sulfoxide in (a) the *yx*-plane and in (b) the *yz*-plane. In (a) only the asymmetric part of the ring is included. Charge centers for localized orbitals are indicated by dots.

the picture is more complicated. The uncertainty estimates given for set I in the experimental work, and quoted in Table 2, indicate that the relative error is smallest for the rocking parameter $\phi_r$. It is interesting to notice that our predicted value for this parameter is closer to the one given by set II. For the other two parameters the measured values appear to be somewhat too high. However, by considering the uncertainty estimates given, it is impossible to distinguish between set I and set II and furthermore, it is doubtful whether the measured values are significantly different from the predicted ones. Also in this context it is pertinent to mention the importance of reliably predicted structural parameters as a support to experimental information.

In Fig. 3 are depicted some of the localized orbitals generated by the criterion of Boys.[13] The orbitals are characterized by dots placed at the positions for the center of gravity of their charges. For the sake of clarity the molecule is shown in two projections, in (a) the system is viewed from above the ring and in (b) the molecule is projected on its symmetry plane. In (a) only the asymmetric part of the molecule is included.

As revealed by the figure the localized orbitals describing the C–H bonds have their charge centers situated on the lines connecting atoms attached to each other. In this sense these bonds are normal, slightly polarized chemical bonds. The orbitals describing the C–C and C–S bonds show some interesting features. As demonstrated in Fig. 3 (a), the two inequivalent bonds are both clearly of the bent bond type characterized by charge centers outside the ring as described by straight lines between the ring atoms. This displacement is largest for the C–S bond. Fig. 3 (b) shows clearly that the C–C bonding orbitals are in the C–C–C plane. This does indicate that the predicted rocking of the group $C_3H_3H'_3$ is sufficient for satisfying the requirement of minimum bond tortuosity.[15] On the other hand the C–S bonding orbitals have their charge centers out of the C–S–C plane. They are located on the same side of the plane as the oxygen atom. This implies that the assumption of coplanar vicinal valence vectors for this part of the molecule is not confirmed by these localized orbitals. A possible rocking of the S=O group can be discussed under two different assumptions, *viz.* coplanarity of the vicinal valence vectors in the C–S–C plane and valence vectors pointing towards the predicted charge centers. In both cases, the rocking has been expressed in terms of a deviation from the bisector of the angle described by the S=O bond and the vector pointing towards the sulfur lone pair. Assuming coplanarity of vicinal vectors, we predict a rocking of the S=O group of $-2.9°$. If we relax this assumption, we predict a rocking of $-0.1°$ which implies that there is no significant rocking of the S=O group in this molecule.

*Acknowledgement.* This work has been supported in part by a grant from The Robert A. Welch Foundation.

REFERENCES

1. Bevan, J. W., Legon, A. C. and Millen, D. J. *Proc. R. Soc. London A 354* (1977) 491.
2. Skancke. P. N.. Fogarasi. G. and Boggs. J. E. *J. Mol. Struct. 62* (1980) 259.
3. Pulay, P. *Theor. Chim. Acta 50* (1979) 299.
4. Skancke, A. *J. Mol. Struct. 42* (1977) 235.
5. Skancke, A. and Boggs, J. E. *J. Mol. Struct. 50* (1978) 173.
6. Skancke, A. and Boggs, J. E. *J. Mol. Struct. 51* (1979) 267.
7. Pulay, P. *Mol. Phys. 17* (1969) 197.
8. Pulay. P.. Pang. F.. Fogarasi. G. and Boggs, J. E. *J. Am. Chem. Soc. 101* (1979) 2550.
9. Ditchfield, R., Hehre, W. J. and Pople, J. A. *J. Chem. Phys. 54* (1971) 724.
10. Hehre, W. J. and Lathan, W. A. *J. Chem. Phys. 56* (1972) 5255.
11. Pulay, P. *Program Description for TEXAS*, 1976.
12. Rohmer, M.-M. and Roos, B. *J. Am. Chem. Soc. 97* (1975) 2025.
13. Boys, S. E. In Lövdin, P. O., Ed., *Quantum Theory of Atoms, Molecules and the Solid State*, Academic, New York 1966, p. 253.
14. Mastryukov, V. S., Dorofeeva, O. V., Vilkov, L. V. and Hargittai, I. *J. Mol. Struct. 34* (1976) 99.
15. Bartell, L. S. and Andersen, B. *J. Chem. Soc. Chem. Commun.* (1973) 786.

Received October 29, 1979.