Tilts, Bends, and Twists of Methylene Groups in Four-membered Rings. Evidence from the Microwave Spectrum of Trimethylene Sulphoxide

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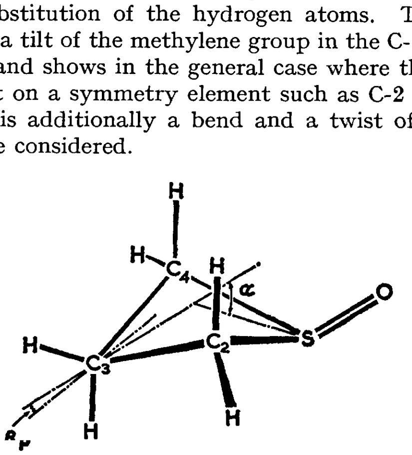
Summary Tilts, bends, and twists of the CH_2 groups in trimethylene sulphoxide derived from a complete r_S-structure (the first available for a 4-membered ring) are compared with those predicted on the basis of a recently proposed model.

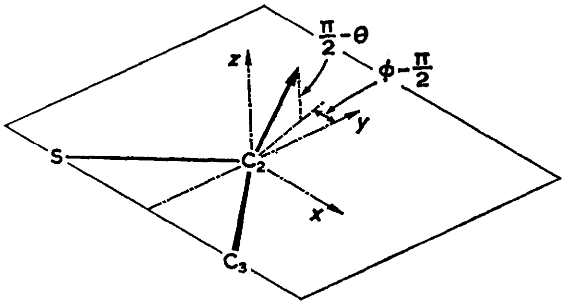
During the last decade knowledge has accumulated about the structure of molecules in the series of four-membered rings which has cyclobutane as the primary member, and there are now several examples where it is established whether the equilibrium structure of the four ring atoms is planar or puckered. The present position about the location of the hydrogen atoms for such rings is less clear, and in the absence of structural information the CH_2 groups have often been regarded as symmetrically disposed with respect to the neighbouring ring atoms, having the bisector of the methylene group coincident with the bisector of the angle formed by the three ring atoms of which the CH_2 group forms the apex. Recently theoretical[1] and experimental[2] investigations have indicated for cyclobutane that the CH_2 bisector is tilted out of the C–C–C plane. Bartell and Andersen[3] have related the angle of tilt to the ring dihedral angle using the idea of minimum tortuosity and Pasternak and Meyer[4] have similarly obtained a geometric relationship between the tilt, the dihedral angle, and hybridisation. Nevertheless there does not appear hitherto to have been a precise and complete experimental determination of the geometric structure for any four-membered ring based on cyclobutane. We now report a determination for one such molecule, namely trimethylene sulphoxide, for which a complete r_s structure has been obtained from a microwave spectroscopic investigation[5] which included isotopic substitution of the hydrogen atoms. The structure shows a tilt of the methylene group in the C-3 position (Figure 1) and shows in the general case where the carbon atom is not on a symmetry element such as C-2 (and C-4) that there is additionally a bend and a twist of the CH_2 group to be considered.



The experimental results show that the oxygen atom is in the equatorial position and that the dihedral angle $\alpha = 34°57'$. The experimentally measured configuration of the methylene groups can be described by reference to Figures 1 and 2. The CH_2 group at C-3 which lies in the plane of symmetry of the molecule is tilted so that the bisector makes an angle $\beta = 4°46'$ (see Figure 1) with respect to the C(2)C(3)C(4) plane.

The configuration of the CH_2 group at C-2 (or C-4) can be given in terms of Eulerian angles θ, ϕ, and χ. For this purpose, axes are located at C-2 with the y-axis along the bisector of the C(3)C(2)S angle, the x-axis in this plane, and the z-axis perpendicular to it as in Figure 2. The orientation of the CH_2 group can be described in terms of the bisector of the HCH angle as follows. The bisector falls in the $-++$ x,y,z octant and makes an angle θ with respect to the z-axis. Its projection in the xy plane makes an angle ϕ with respect to the x-axis while the CH_2 group is rotated by an angle χ about the bisector in the clockwise sense, as viewed along the bisector from the hydrogen atoms towards C-2. In terms of these angles the tilt is defined as $\pi/2 - \theta$, the bend as $\phi - \pi/2$, and the twist as χ. The measured values are a tilt of 7°36′, a bend of 5°3′, and a twist of 1°31′.

Following Bartell and Andersen[3] we may seek to understand the observed angles in relation to the bonding of the ring atoms. We begin by defining valence vectors for each of the ring atoms, taking angles between the vectors as the unstrained natural angles in open chain systems, and determine the relationships which exist between tilts, bends, and twists using the principle of co-planarity of valence vectors on neighbouring ring atoms. The principle is most conveniently applied in the present case by taking the observed orientation of the bisector for the CH_2 group at the C-2 position and using it to determine the orientations for the other ring atoms which satisfy co-planarity of valence vectors. This leads to a tilt of the CH_2 bisector at C-3 of 3°43′, which is in satisfactory agreement with the value of 4°46′ reported above. In applying the principle at the sulphur atom a question arises about the natural angles between the valence vectors. Suitably precise data exist only for dimethyl sulphoxide and thionyl fluoride, so dictating the choice of these as model molecules for this purpose.



For the former[6] the C–S–C angle is 96°23′ while the corresponding angle for the latter[7] is 92°40′. These lead through the principle of coplanarity of valence vectors to angles between the S=O bond and the C–S–C plane of 122°47′ and 120°19′ respectively which may be compared with the observed value of 120°7′. We note the possibility of a steric interaction between the methyl groups in dimethyl sulphoxide which may open up the valence angle and so thionyl fluoride is perhaps a better model.

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[1] J. S. Wright and L. Salem, *Chem. Comm.*, 1969, 1370.
[2] S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, 1970, **52**, 3857.
[3] L. S. Bartell and B. Andersen, *J.C.S. Chem. Comm.*, 1973, 786.
[4] P. Pasternak and A. Y. Meyer, *J. Mol. Structure*, 1974, **20**, 351.
[5] To be published.
[6] H. Dreizler and G. Dendl, *Z. Naturforsch.*, 1964, **19a**, 512.
[7] N. J. Lucas and J. G. Smith, *J. Mol. Spectroscopy*, 1972, **43**, 327.