

THE "SYN-EFFECT" IN SULFINES AND CARBONYL OXIDES:

CONFORMATIONAL PREFERENCES OF CH_3CHSO AND CH_3CHOO^1

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Theoretical calculations indicate that the preference of ethanethial S-oxide for syn-stereochemistry with a staggered HCCH conformation, as determined by microwave spectroscopy, is explained in terms of orbital and electrostatic interactions between the terminal oxygen and methyl hydrogen atoms.

Propanethial S-oxide (1), isolated from the onion or from synthetic sources, and its lower homologue ethanethial S-oxide (2) show a remarkable preference for (Z)- or syn-stereochemistry.² Thus, flash vacuum pyrolysis at 250-600°C of compounds 3-8 or treatment of sulfinyl chloride 3 with triethylamine at -20°C has been found by microwave spectroscopy to afford predominantly 1-Z and 2-Z with ¹H or ¹³C FT-NMR indicating the presence of no more than 1-5% of the (E)(anti)-isomer.^{1,2} We have found that the conformational behavior of 2, that is the relative energies of species 2a-2d, calculated with a restricted Hartree-Fock theory agree very well with the experimental results. This agreement has prompted our interpretation of the Hartree-Fock wavefunctions in terms of orbital and electrostatic interactions responsible for the observed syn conformational preference. This "syn-effect" is found in a number of compounds, e.g. theoretically in the valence isoelectronic carbonyl oxide methylperoxymethylene, CH_3CHOO (9)³ and experimentally in methylthionylimide, CH_3NSO ,⁴ among numerous other examples.⁵

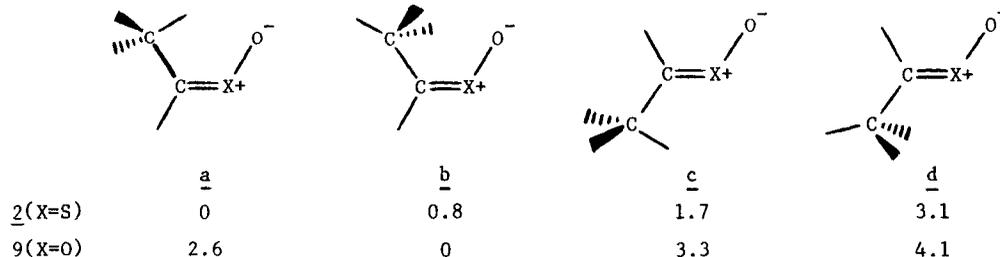
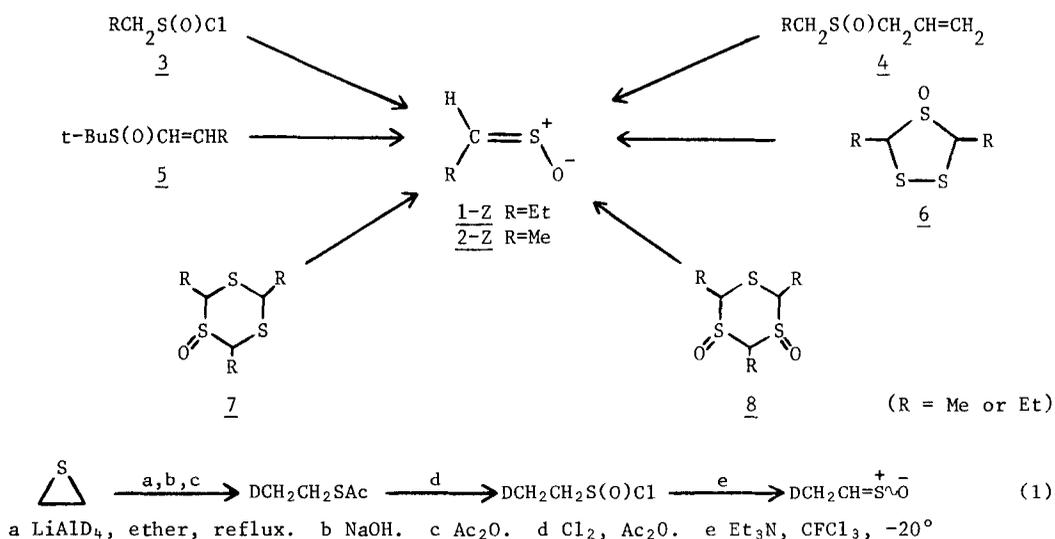


Fig. 1. Relative energies of conformers of ethanethial S-oxide(2) and methylperoxymethylene(9) (kcal/mol).

Restricted Hartree-Fock calculations on methylperoxymethylene (9) have shown that the syn-isomer 9b is more stable than the anti-isomer 9c by 3.3 kcal/mol.³ We now find that similar calculations for ethanethial S-oxide 2 using a variety of basis sets and employing both a rigid and non-rigid rotor model for the CH_3 -rotation⁶ show syn form 2a to be more stable than the anti form 2c by 1.7 (1.8 rigid rotor) kcal/mol. The barriers to three-fold rotation of these species

are 0.8 (0.9) kcal/mol for 2a and 1.4 (1.5) kcal/mol for 2c with maxima in the 2b and 2d conformers, respectively. Energy minima with respect to CH₃ internal rotation occur with the HCCS "eclipsed" conformation 2a. In a parallel microwave study of 2, the only conformation observed is 2a, being unambiguously distinguished from 2c or 2d by a comparison of observed and calculated rotational constants and from 2b by the rotational constants of the methyl-d₁ isotopically modified species (prepared according to eq 1). The absence of the anti isomer above ca. 5% suggests an energy of that species relative to 2a ≥ 2 kcal/mol. The methyl barrier to internal rotation is determined to be 0.83 kcal/mol. Although the methyl group internal rotation barrier is not available for the anti conformer, an apt comparison with the calculated value might be the observed 1.36 kcal/mol methyl barrier of ethanethial, CH₃CHS.⁷

Scheme 1



The conformational preferences for structures 2 and 9 can be explained in terms of orbital and electrostatic interactions between the terminal oxygen and methyl hydrogen atoms which are negligible in the anti form. For 9 in the absence of oxygen-hydrogen interactions the HCCO eclipsed anti form 9c is more stable than 9d by 0.8 kcal/mol. Going from the anti form to the syn form two types of interactions become important. These can be of the π -type, characterized by the formation of an "aromatic" 6π -electron system favoring 9b or of the σ -type, characterized by the formation of 6σ -MOs of which the HOMO is 1,5 bonding, favoring form 9a as depicted in Fig. 1 (X=O). Since 9b is more stable than 9d by 4.1 kcal/mol while 9a is more stable than 9c by only 0.7 kcal/mol the π -effect clearly outweighs the σ -effect in methylperoxymethylene.

The situation is similar in the case of sulfine 2 although modified by the longer C-X and X-O bonds and the increased polarity of the latter. By replacing the central oxygen atom in peroxymethylene by sulfur the distance between the terminal O atom and the closest methyl hydrogen atoms in 2a and 2b increases by about 0.3 Å to 2.5 Å (2a) and 3.0 Å (2b), respectively. The π -effect which, of course, is more sensitive to changes of the O \cdots H distance, becomes significantly smaller. We find a reduction of the (positive) O \cdots H overlap populations by more than

50% in 2b but just 45% in 2a when comparing the computed values of ethanethial S-oxide with those of methylperoxymethylene at the same level of theory.⁸ Also accompanying the replacement of oxygen by sulfur is a substantial increase in X-O electronegativity difference resulting in an accumulation of negative charge at the terminal oxygen atom which is twice as large in 2 as in 9 (see Table 1).⁹ Consequently besides the σ - and π -effect, we encounter a third effect in the syn forms 2a and 2b, namely an attractive electrostatic interaction between the positively charged methyl hydrogens and negatively charged terminal oxygen atom.⁹ Like the σ - and π -effects, this effect is missing in the anti forms 2c and 2d.

The relative values of the methyl barriers for the syn and anti forms of 2 and 9 can be explained with reference to Fig. 2. Both the anti to syn *decrease* in methyl barrier for 2 and the anti to syn *increase* in methyl barrier for 9 result primarily from the greater stabilization in going from form d to b than in going from form c to a.

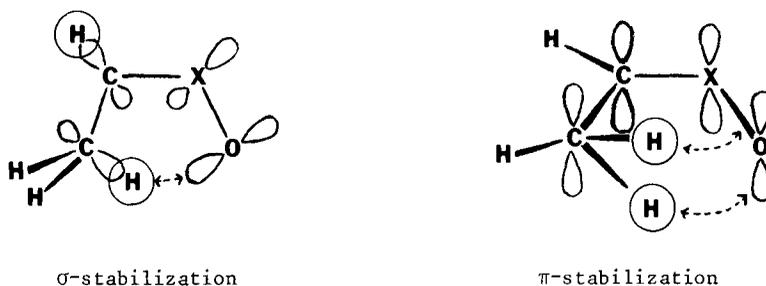


Fig. 1. Orbital interactions in ethanethial S-oxide(2)(X=S) and methylperoxymethylene(9)(X=O).

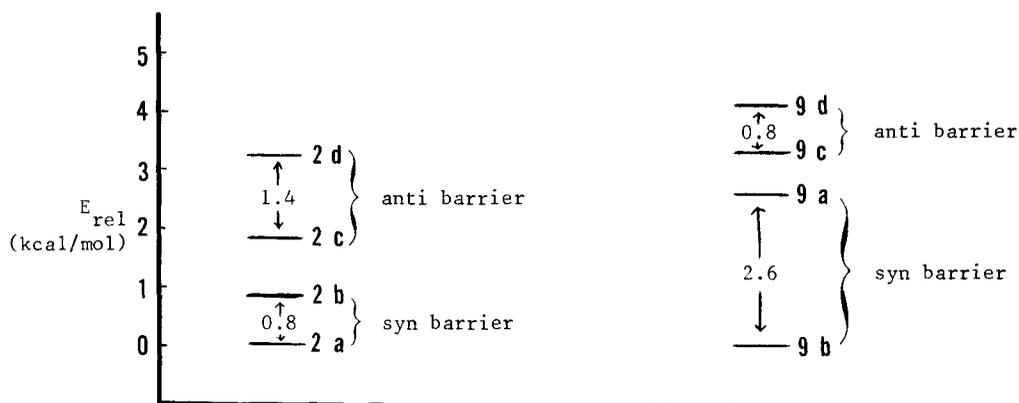


Fig. 2. Conformational barriers of ethanethial S-oxide(2) and methylperoxymethylene(9).

Table 1. Calculated charge distribution in ethanethial S-oxide (2) and methylperoxymethylene (9; in parenthesis) conformers

Atom	syn		anti	
	0° <u>2b(9b)</u>	60° <u>2a(9a)</u>	0° <u>2d(9d)</u>	60° <u>2c(9c)</u>
O ^a	-.4702(-.2405)	-.4748(-.2471)	-.4694(-.2415)	-.4727(-.2432)
S or O ^b	+.6282(-.0305)	+.6299(-.0288)	+.6327(-.0285)	+.6342(-.0273)
C ₁	-.2521(+.0995)	-.2486(+.1028)	-.2508(+.1017)	-.2488(+.1022)
C ₂	-.1807(-.1851)	-.1847(-.1938)	-.1824(-.1853)	-.1811(-.1858)
H ^c	+.0684(+.0945)	+.0675(+.0950)	+.0721(+.0986)	+.0719(+.0989)
H ^d	+.0669(+.0778)	+.0779(+.1107)	+.0700(+.0819)	+.0614(+.090)
H ^e	+.0698(+.0922)	+.0664(+.0806)	+.0639(+.0865)	+.0676(+.0826)

a terminal b inner c on C₁ d in plane, CH₃ e out of plane, CH₃

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References and Footnotes

1. a) This is paper 8 of the series "The Chemistry of Sulfoxes". For part 7, see E. Block, *Pure Appl. Chem.*, in press. b) Presented at the 9th International Symposium on Organosulphur Chemistry, Riga, USSR, June 9-13, 1980.
2. a) E. Block, A.A. Bazzi and L.K. Revelle, *J. Am. Chem. Soc.*, 102, 2490 (1980). b) E. Block, L.K. Revelle and A.A. Bazzi, *Tetrahedron Lett.*, 1277 (1980). c) L.K. Revelle, *Ph.D. Thesis*, University of Missouri-St. Louis, 1980.
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6. The full details of this study will be published elsewhere.
7. H.W. Kroto and B.M. Landsberg, *J. Mol. Spectrosc.*, 62, 346 (1976).
8. Actually, the reduction of bonding π -overlap between the terminal oxygen and the two hydrogens is 60% in 2b. However, this reduction is somewhat counterbalanced by σ -overlap also acting in form 2b.
9. The calculated gross atomic charges suggest that contrary to peroxymethylene the zwitterionic and not the biradical character is dominant in sulfine.

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