THE "SYN-EFFECT" IN SULFINES AND CARBONYL OXIDES:
CONFORMATIONAL PREFERENCES OF CH₃CHSO AND CH₃CHOO

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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, CH₃CHOO (9)³ and experimentally in methylthionylimide, CH₃NSO,⁴ among numerous other examples.⁵

![Diagram](https://via.placeholder.com/150)

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 CH₃-rotation 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 Zb and Zd 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 Za.

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 ethanethiol, CH₃CHS.

The conformational preferences for structures 2 and 3 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 3 in the absence of oxygen-hydrogen interactions the HCCO eclipsed anti form 3c is more stable than 3d 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 3b or of the σ-type, characterized by the formation of 6σ-MOs of which the HOMO is 1,5 bonding, favoring form 3a as depicted in Fig. 1 (X=O). Since 3b is more stable than 3d by 4.1 kcal/mol while 3a is more stable than 3c 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 ••• H distance, becomes significantly smaller. We find a reduction of the (positive) O ••• 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 \(\sigma\)- and \(\pi\)-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 \(\sigma\)- and \(\pi\)-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.

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

![Fig. 2. Conformational barriers of ethanethial S-oxide(2) and methylperoxymethylene(9).](image)
Table 1. Calculated charge distribution in ethanethial S-oxide (2) and methylperoxymethylene (9; in parenthesis) conformers

<table>
<thead>
<tr>
<th>Atom</th>
<th>0° 2b(9b)</th>
<th>60° 2a(9a)</th>
<th>0° 2d(9d)</th>
<th>60° 2c(9c)</th>
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<tr>
<td>C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-0.4702(-0.2405)</td>
<td>-0.4748(-0.2471)</td>
<td>-0.4694(-0.2415)</td>
<td>-0.4727(-0.2432)</td>
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<tr>
<td>S or O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+0.6282(-0.0305)</td>
<td>+0.6299(-0.0288)</td>
<td>+0.6327(-0.0285)</td>
<td>+0.6342(-0.0273)</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>-0.2521(+0.0995)</td>
<td>-0.2486(+1.028)</td>
<td>-0.2508(+1.017)</td>
<td>-0.2488(+1.022)</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.1807(-1.1851)</td>
<td>-0.1847(-1.1938)</td>
<td>-0.1824(-1.1853)</td>
<td>-0.1811(-1.1858)</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;</td>
<td>+0.0684(+0.0945)</td>
<td>+0.0675(+0.0950)</td>
<td>+0.0721(+0.0986)</td>
<td>+0.0719(+0.0989)</td>
</tr>
<tr>
<td>H&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>+0.0779(+1.107)</td>
<td>+0.0700(+0.0819)</td>
<td>+0.0614(+0.090)</td>
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<td>H&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>+0.0676(+0.0826)</td>
</tr>
</tbody>
</table>

a terminal  b inner  c on C<sub>1</sub>  d in plane, CH<sub>3</sub>  e out of plane, CH<sub>3</sub>

Acknowledgment. We thank R.W. Murray for helpful suggestions, acknowledge support from NSF (CHE 80-01490), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Missouri-St. Louis, and thank the Rechenzentrum Köln for providing computation time at the CDC CYBER 76, and J. Roderburg for technical assistance.

References and Footnotes

1. a) This is paper 8 of the series "The Chemistry of Sulfines". 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.


6. The full details of this study will be published elsewhere.


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.

(Received in USA 8 October 1980)