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# CONFORMATIONAL ANALYSIS—CXIV

## MOLECULAR MECHANICS STUDIES OF SULFOXIDES

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**Abstract**—The conformational characteristics of dimethyl sulfoxide and a number of 6-membered ring sulfoxides have been studied. The thiane, 1,3- and 1,4-dithiane and 1,3,5-trithiane ring systems with various oxide substitutions have been examined. It is found that the chair forms are more stable than the twist or boat in all cases. The energy profiles of the twist-boat manifold are in many cases highly unusual, and quite different from anything so far known experimentally. The axial-equatorial preference of the oxygen is highly variable, depending on the steric and electrostatic interactions found in the particular case.

The use of molecular mechanics or force fields for the calculation of structures, energies and other properties of hydrocarbons has become widespread in the last few years.[3] Similar studies have also been carried out[3,4] for a few kinds of functionally substituted molecules, and this paper represents an extension in some detail of the application of the method to the calculation of the conformational properties of sulfoxides.

The cyclohexane ring system has been quite thoroughly examined with respect to its conformational behavior.[5-8] When heteroatoms are introduced into the ring, the conformational properties of the resulting heterocycles may differ considerably from those of cyclohexane.[9] It is known, for example, that the oxygen in thian-1-oxide shows a preference for the axial position,[10] and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane prefers a twist, rather than a chair conformation.[4,11]

The 1973 hydrocarbon force field described previously[8] was used as a starting point to extend these force field calculations to a study of sulfoxides. A few additional parameters are needed and they are listed in Table 1. The force constants were either taken from the literature, or if we were unable to locate data for a particular structural feature, the constants from the analogous sulfide were used. The additional numerical values were derived by fitting structural data available for dimethyl sulfoxide[12] and for *trans*-1,4-dithiane-1,4-dioxide,[13] as reported in an earlier preliminary study.[14] The comparison with experiment for these compounds is given in Table 2. The electrostatics of the sulfoxide group was treated by using the C–S bond moment appropriate for sulfides,[15] and then assigning an S=O moment of 3·03 D, with the negative end toward oxygen, in order to fit the observed moment of dimethyl sulfoxide.[16a] The experimental and calculated results for the model structures are given in Table 3.

Having now the necessary force field to deal with sulfoxides, we first looked at thian-1-oxide. In this system it is known that the ring prefers a chair conformation with the sulfoxide oxygen in the axial position.[10,17] An early interpretation given by Johnson[17b] attributes the axial preference of the sulfoxide oxygen to an attractive interaction between the oxygen and the syn-axial hydrogens. We calculate that the chair form is more stable than the twist forms by more than 5 kcal/mole and for the chair, the axial conformation is more stable than the equatorial by 0·15 kcal/mole. The calculations are summarized in Table 4. Experimental values span quite a range (0·18–1·3 kcal/mole) depending on the circumstances of measurement, but they uniformly favor the axial.

Our calculations do not support the idea that there is an attractive interaction between the sulfoxide oxygen and the syn-axial hydrogens. Rather, there is a repulsion, which is largely relieved by bending the sulfur-$C_\alpha$–$C_\beta$ bonds, so that the oxygen moves outward away from the ring. As described earlier,[8] with our force field a hydrogen in the equatorial position is squeezed in between four vicinal hydrogens, while an axial hydrogen is subjected to only two such repulsions. This effect is the major contributor for the equatorial preference of small groups, such as methyl or halogen. An analogous situation is found here. The equatorial oxygen is squeezed between four vicinal hydrogens, while there are only two corresponding repulsions if it is in the axial position. This is the intepretation put upon the facts by our force field. Whether or not other force fields would give the same interpretation, we do not know. More importantly, whether or not this interpretation actually corresponds to physical reality is also uncertain. The significant point is that the calculations do predict correctly what is observed experimentally and hence may presumably be used to obtain correct predictions regarding other similar experimental measurements.

It has been demonstrated that in 3,3-dimethylthiacyclohexan-1-oxide, the ordinary slight axial preference of the sulfoxide oxygen is reversed into a pronounced equatorial one.[17a] The calculations indicate that the *e*-chair conformation of 3,3-dimethylthiacyclohexan-1-oxide is more stable than the equatorial form by 1·1 kcal/mole, the large repulsion between the syn-axial oxygen and methyl, together with the severe bending the molecule undergoes to relieve that repulsion, being the major contributors to this difference.

The relationship between cyclohexane and thian-1-oxide with respect to ring conformations is rather close although the symmetry in thian-1-oxide is much lower than that in cyclohexane. The calculated energies for the important conformations are summarized in Table 4.

Because of the lower symmetry in thian-1-oxide, two chair, three twist and four boat forms need to be considered, in contrast with cyclohexane where there is only one conformation of each type. Here, the energies of the twist forms are about 5 kcal/mole above that of the stable chair form. There is an energy barrier of about 10·5 kcal/mole separating the two forms. A twist conformation can pseudorotate through a boat conformation to

Table 1. Parameters for the geometry calculation

van der Waals Parameters for the Hill Equation

| Atom | $r^*$ (Å) | $\epsilon$ (kcal/mole) |
|---|---|---|
| S* | 2.00 | 0.184 |
| O | 1.65 | 0.046 |

Bond Stretching

| Bond | $l_0$ (Å) | K (mdyn/Å) |
|---|---|---|
| C-S* | 1.805 | 3.64 |
| S*-O | 1.480 | 5.00 |

Angle Bending

| Angle | $\Theta_0$ (deg) | K (mdyn Å/rad$^2$) |
|---|---|---|
| $C_{sp^3}$-S*-$C_{sp^3}$ | 93.5 | 0.90 |
| $C_{sp^3}$-$C_{sp^3}$-S* | 110.0 | 1.10 |
| H-$C_{sp^3}$-S* | 108.6 | 0.64 |
| S-$C_{sp^3}$-S* | 113.7 | 0.42 |
| $C_{sp^3}$-S*-O | 107.5 | 0.90 |
| S*-$C_{sp^3}$-S* | 113.7 | 0.42 |

Torsional Parameters

| Dihedral Angle | Torsional Constants (kcal/mole) |
|---|---|
| H-$C_{sp^3}$-$C_{sp^3}$-S* | 1.450 |
| $C_{sp^3}$-$C_{sp^3}$-$C_{sp^3}$-S* | 1.450 |
| $C_{sp^3}$-$C_{sp^3}$-S*-O | 1.450 |
| $C_{sp^3}$-$C_{sp^3}$-S*-$C_{sp^3}$ | 1.450 |
| S*-$C_{sp^3}$-$C_{sp^3}$-S* | 1.450 |
| H-$C_{sp^3}$-S*-$C_{sp^3}$ | 1.450 |
| S-$C_{sp^3}$-$C_{sp^3}$-S* | 1.450 |
| S*-$C_{sp^3}$-S*-$C_{sp^3}$ | 1.450 |
| S*-$C_{sp^3}$-S-$C_{sp^3}$ | 1.450 |
| S-$C_{sp^3}$-S*-$C_{sp^3}$ | 1.450 |
| S-$C_{sp^3}$-S*-O | 0.800 |
| S*-$C_{sp^3}$-S*-O | 0.800 |
| H-$C_{sp^3}$-S*-O | 0.800 |

Dipoles

| Atom Type | Bond Moment (D) |
|---|---|
| $C_{sp^3}$-S* | 1.20 |
| S*=O | 3.03 |

* Indicates a sulfur atom attached to a sulfoxide oxygen.

another twist, with the boat conformations being from about 0·7 to 4·1 kcal/mole in energy above the twist. The energy difference between the $C_s$ and $C_1$ boat forms (1·5–2·4 kcal/mole) is largely from the greater unfavorable H–C–C–H eclipsing effects found in $C_s$ symmetric form. Note that the simple symmetrical twist-boat manifold found in cyclohexane no longer holds in thiacyclohexan-1-oxide.

The same axial-chair preference of the 1-substituent is also found in the 1,2-dithian-1-oxide system,[18] but when one examines the 1,3-dithian-1-oxide molecule, it has been reported that the sulfoxide oxygen now prefers the equatorial conformation.[19] In looking at 2-*t*-butyl-1,3-dithian-1-oxide, Cook and Tonge[19] found the oxygen to be preferentially equatorial, the composition of equilibrium mixtures corresponding to a free energy difference of 0·5 kcal/mole, favoring the equatorial conformation. They suggested that intramolecular dipole-dipole interactions contribute in some measure to the observed equilibria. Recently, low temperature NMR[20] has given similar results concerning *a*-/*e*-chair equilibrium, the equatorial form being favored over the axial by 0·6 kcal/mole.

We examined the parent 1,3-dithian-1-oxide in order to determine the reason for the equatorial preference of the oxygen in these systems. The calculations indicate that although chair forms are still more stable than twist and boat forms, the relationship between the conformational characteristics of 1,3-dithian-1-oxide and cyclohexane is rather remote. It is in the twist-boat manifold that the major contrast with cyclohexane occurs, and first we note that the twist form is no longer always more stable than the boat form. In this case there are five energy minima and five maxima in the manifold, as opposed to six for cyclohexane. Two boat forms[21] which correspond to energy maxima in cyclohexane, are neither minima nor maxima in this case, but simply points on the sides of the potential well. One twist form[22] which corresponds to an energy minimum in cyclohexane, is an energy maximum in this case.

The calculations also show that the equatorial preference of the oxygen in the chair form of 1,3-dithian-1-oxide is largely due to a dipolar interaction. It is found that almost all of the 1·74 kcal/mole steric energy difference between the *a*- and *e*-chair conformations is due to the 1·63 kcal/mole higher dipole energy (using a dielectric constant of 1·0) that is present in the axial conformation. As the dielectric constant increases from 1·0 to 3·0, both the dipole-dipole interaction energy and the total energy difference between the *e*- and *a*-chair forms would decrease; from 1·74 to 0·61 kcal/mole and from 1·63 to 0·59 kcal/mole respectively. The calculated energy difference is in good agreement with the experimental value.

As expected, the introduction of a 5,5-dimethyl grouping in 1,3-dithian-1-oxide increases the original equatorial preference of the oxygen. The energy difference between *a*- and *e*-chair conformations here was calculated to be 2·7 kcal/mole, and it is mainly from bending (1·4 kcal/mole) and dipolar interactions (1·4 kcal/mole). The calculations are in agreement with the experimental findings. Van Acker and Antenunis[20] have shown by low temperature NMR that 5,5 - dimethyl - 1,3 - dithian - 1 - oxide exists exclusively in the equatorial conformation.

IR data[23] show that both *a*- and *e*-chair conformations of 1,4-dithian-1-oxide exist in solution in $CS_2$, but the *a*-chair is the only conformation found in solid state. Recently, NMR data[24] have disclosed that there is an equilibrium between chair conformations, the population ratio of *a* : *e* being 88 : 12, which corresponds to a free energy difference of about 0·8 kcal/mole. The chair conformations are calculated to be more stable than the others, with the axial conformation 1·1 kcal/mole lower in energy than the equatorial. Most of this energy difference is due to dipolar interactions.

The conformational characteristics of 1,4-dithian-1-oxide are qualitatively similar to those of cyclohexane, chair forms being more stable than twist forms, and boat forms being the transition states for the twist-twist pseudorotation. However, the barriers for the twist-twist transformations span quite a range depending on the starting and the final conformations; from essentially no barrier to as high as 8·4 kcal/mole. The extreme instability of the symmetrical boat form ($C_s$) is noteworthy. This seems to be mainly due to both the unfavorable H–C–C–H eclipsing effects and the short S . . S distances (3·1 Å here)

Table 2. Comparison of calculated and observed geometries

| | Calc. (Å or Deg.) | Obs. (Å or Deg.) M.W.[12a] | Obs. (Å or Deg.) X[12b] |
|---|---|---|---|
| Dimethyl Sulfoxide | | | |
| $C_{sp^3}$-S* | 1.809 | 1.799 ± 0.005 | 1.801 ± 0.010 |
| S*=O | 1.480 | 1.485 ± 0.006 | 1.471 ± 0.008 |
| $C_{sp^3}$-S*=O | 108.1 | 106.7 | 107.2 ± 0.6 |
| $C_{sp^3}$-S*-$C_{sp^3}$ | 96.9 | 96.6 | 97.9 ± 0.5 |
| trans-1,4-Dithiane-1,6-dioxide | | | X[13] |
| $C_{sp^3}$-S* | 1.809 | | 1.81 ± 0.02 |
| S*=O | 1.479 | | 1.48 ± 0.01 |
| $C_{sp^3}$-$C_{sp^3}$ | 1.537 | | 1.51 ± 0.03 |
| $C_{sp^3}$-S*-$C_{sp^3}$ | 97.9 | | 97.9 ± 0.8 |
| $C_{sp^3}$-$C_{sp^3}$-S* | 112.3 | | 112.3 ± 1.3 |
| $C_{sp^3}$-$C_{sp^3}$-S*=O | 107.5 | | 107.4 ± 0.8 |

Table 3. Calculated and observed dipole moments (Debye units)

| Dipole Moments | Calc. (D = 1.0) | Obs. |
|---|---|---|
| Dimethyl sulfoxide | 4.03 | 3.9 ± 0.1[16a] |
| Thiocyclohexan-1-oxide | 4.04 | 4.19[16b] |
| 1,3-Dithian-1-oxide (eq) | 3.48 | 3.74[a,19], 3.56[b,19] |
| " (ax) | 4.79 | 4.39[c,19] |
| 1,4-Dithian-1-oxide (eq) | 3.00 | |
| " (ax) | 2.92 | |
| 1,3,5-Trithian-1-oxide (eq) | 3.02 | |
| " (ax) | 5.52 | |
| trans-1,4-Dithiane-1,4-dioxide | 0.00 | |
| cis-1,4-Dithiane-1,4-dioxide | 5.08 | |
| trans-1,3,5-Trithiane-1,3-dioxide | 5.02 | |
| cis-1,3,5-Trithiane-1,3-dioxide | 2.80 | |
| cis-1,3,5-Trithiane-1,3,5-trioxide | 1.50 | |
| trans-1,3,5-Trithiane-1,3,5-trioxide | 4.01 | |

[a] This is the observed dipole moment for 2,2-dimethyl-1,3-dithian-1-oxide in benzene

[b] This is the observed dipole moment for trans-2-t-butyl-1,3-dithian-1-oxide

[c] This is the observed dipole moment for cis-2-t-butyl-1,3-dithian-1-oxide

in the symmetric boat forms. The former raises the energy difference between $C_1$ and $C_s$ forms by about 2 kcal/mole, and the latter an additional 3 kcal/mole. The origin of the 3·2 kcal/mole energy difference between the two $C_s$ boat forms is largely due to the highly unfavorable dipole-dipole interactions found in one case.

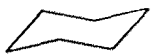
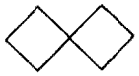
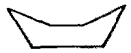
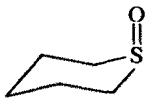
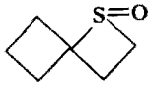
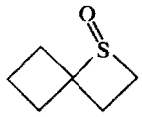
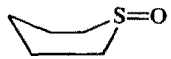
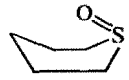
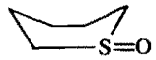
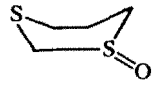
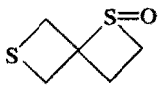
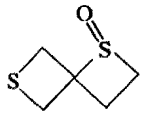
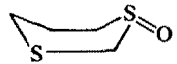
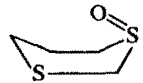
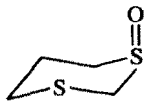
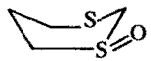
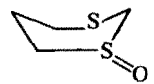
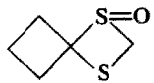
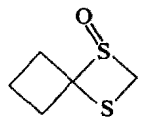
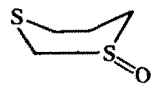
A logical extension of these calculations was to include the 1,3,5-trithian-1-oxide systems, which do not appear to be known experimentally.† As expected, the *e*-chair conformation is calculated to have 3·1 kcal/mole lower dipole energy and 3·5 kcal/mole lower total energy than the axial conformation, which are, respectively, about twice those found in 1,3-dithian-1-oxide.

The conformational characteristics of the twist-boat transformations of 1,3,5-trithian-1-oxide are rather similar to those of cyclohexane; the twist forms being energy minima and the boat forms energy maxima. The barriers are within the range of 0·5–1·7 kcal/mole, which are comparable to those found in cyclohexane, 1·5 kcal/mole.

We next turn our attention to the dioxides of the same basic heterocyclic rings. *trans*-1,4-Dithiane-1,4-dioxide, with a diaxial oxygen arrangement in the crystal,[13] seems to exist preferentially in the same conformation in solution.[25] Our calculations show that the chair with diaxial oxygens is the most stable conformation, being 4·7 kcal/mole lower in energy than that of the diequatorial chair form. The main energy difference between the diaxial and the diequatorial

†After this manuscript was submitted for publication, a paper describing NMR studies on this compound appeared (S. A. Kahn, J. B. Lambert, O. Hernandez and F. A. Carey, *J. Am. Chem. Soc.* **97**, 1468 (1965)). The authors concluded the compound existed as a single chair conformation. No firm conclusion could be drawn concerning the oxide conformation.

Table 4. Conformations and energies (kcal/mole) calculated for a dielectric constants of 1·0

| | Chair | Twist | | Boat | |
|---|---|---|---|---|---|
| Cyclohexane |  0·0 |  5·3 | |  6·8 | |
| Thian-1-oxide |  0·0 |  6·3 |  5·9 |  8·5 |  9·2 |
| |  0·2 |  5·1 | |  7·0 |  6·8 |
| 1,3-Dithiane-1-oxide |  0·0 |  4·9 |  7·3[a] |  6·1 |  6·7[b] |
| |  1·8 |  4·2 |  5·8 |  7·3 |  5·8[b] |
| | |  4·5 |  3·6 |  6·0 |  7·1 |

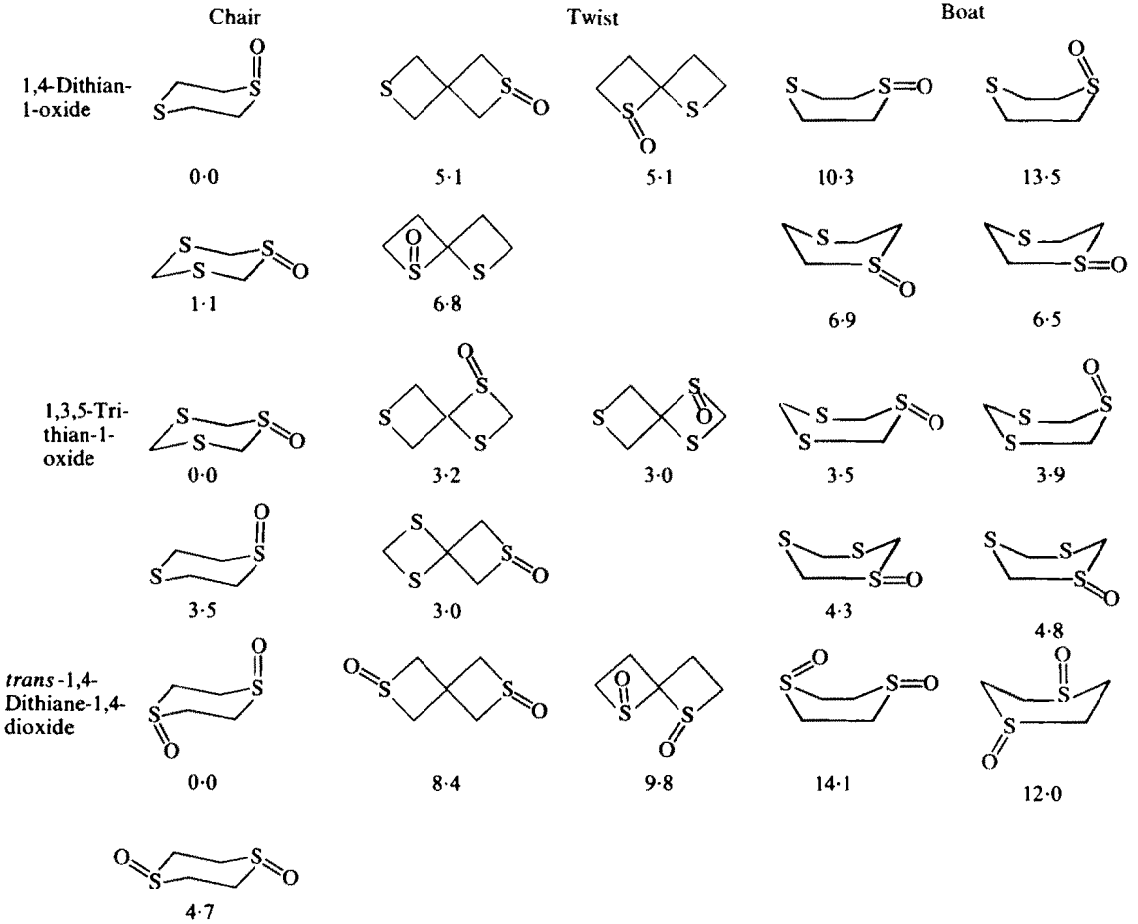
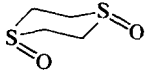
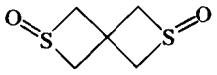
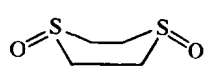
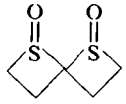
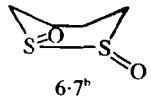
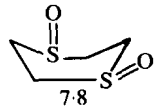
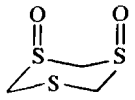
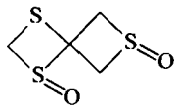
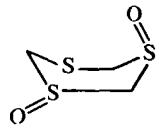
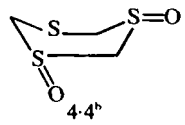
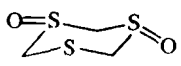
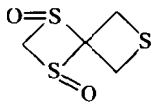
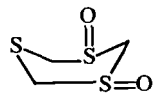
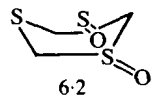
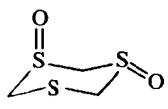
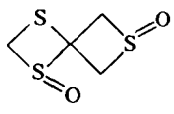
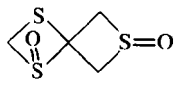
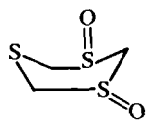
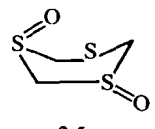
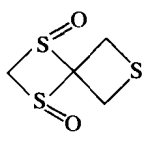
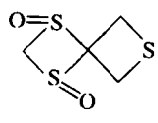
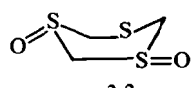
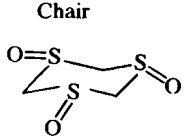
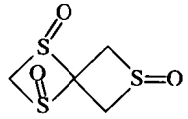
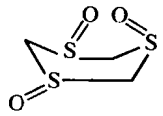
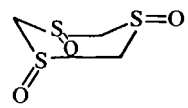
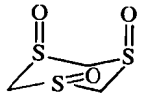
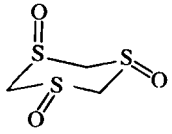
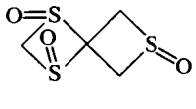
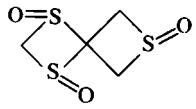
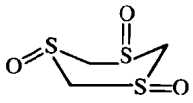
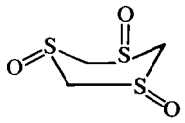
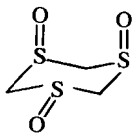
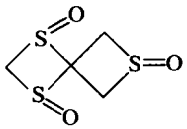
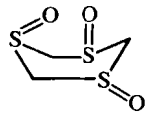
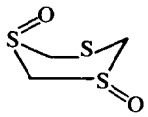

Chair
Twist
Boat
1,4-Dithian-1-oxide
0·0
5·1
5·1
10·3
13·5
1·1
6·8
6·9
6·5
1,3,5-Trithian-1-oxide
0·0
3·2
3·0
3·5
3·9
3·5
3·0
4·3
4·8
trans-1,4-Dithiane-1,4-dioxide
0·0
8·4
9·8
14·1
12·0
4·7

Table 4(*Contd*)

| | Chair | Twist | | Boat | |
|---|---|---|---|---|---|
| *cis*-1,4-Dithiane-1,4-dioxide |  0·0 |  5·9 |  7·4 |  20·4[a] |  11·5 |
| | |  20·3[b] | |  6·7[b] |  7·8 |
| *cis*-1,3,5-Trithiane-1,3-dioxide |  0·0 |  4·5[b] |  4·8 |  5·4 |  4·4[b] |
| |  8·0 |  4·1 | |  8·0 |  6·2 |
| *trans*-1,3,5-Trithiane-1,3-dioxide |  0·0 |  0·7 |  2·0 |  3·2 |  2·5 |
| | |  1·1 |  3·0 |  3·2 | |

| | Chair | Twist | Boat | |
|---|---|---|---|---|
| *cis*-1,3,5-Trithiane-1,3,5-trioxide |  0·0 |  6·0 |  7·0 |  8·4 |
| |  13·5 | | | |
| *trans*-1,3,5-Trithiane-1,3,5-trioxide |  0·0 |  5·5[b] |  2·7 |  6·8 |  5·4[b] |
| |  4·9 |  2·5 |  4·3 |  5·6 |

[a] a local energy maximum.
[b] a point on the side of a potential well.

chair conformations is from the dipole-dipole interaction. The conformational characteristics of *trans*-1,4-dithiane-1,4-dioxide are similar to those of cyclohexane.

The chair is the most stable conformation of *cis*-1,4-dithiane-1,4-dioxide, but the twist-boat transformations are rather different from any of those discussed above. In this case there are four energy minima in the manifold, as opposed to six for cyclohexane. The $C_2$ symmetrical boat forms (mirror images),[21] which correspond to energy maxima, and the $C_2$ symmetrical twist forms (mirror images)[21] which correspond to energy maxima and minima in cyclohexane, respectively are neither minima nor maxima in this case, but simply points on the sides of the potential well. The extreme instability of one of the $C_s$ symmetrical boat forms[22] is noteworthy. It results, of course, because of the highly unfavorable dipole-dipole interactions.

*cis*-1,3,5-Trithiane-1,3-dioxide has two distinguishable chair conformations. The chair with the diaxial arrangement of S=O groups is one of the more unstable conformations due to the unfavorable dipolar interactions. The conformational characteristics of the twist-boat transformations of *cis*-1,3,5-trithiane-1,3-dioxide are similar to those of *cis*-1,4-dithiane-1,4-dioxide. The twist-boat manifold here becomes four-fold. Two boat forms (mirror images)[21] and two twist (mirror images)[21] are again points on the sides of the potential well. The barriers span quite a range; 0·4–3·9 kcal/mole.

*trans*-1,3,5-Trithiane-1,3-dioxide has the conformational characteristics for the twist-boat transformations similar to those found for cyclohexane, although here the barriers are between 0·2 and 2·5 kcal/mole. However, the energy difference between the chair and twist forms is much smaller than found in cyclohexane (0·7 vs 5 kcal/mole in cyclohexane). Therefore, it may be anticipated that when appropriate substituents are introduced into the parent ring systems as in 4,4 - dimethyl - 1,3,5 - trithiane - 1,3 - *trans* - dioxide for example, the twist form will be more stable than the chair, as was found[4,11] in 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane.

Finally, for completeness we examined the trioxides. *cis*-1,3,5-Trithiane-1,3,5-trioxide has two possible chair conformations. The chair conformation with all three oxygens equatorial is the most stable conformation, and the one with all three oxygens axial is highly unstable. This extreme instability, of course, results largely because of dipolar interactions. The other conformational features are similar to those found in cyclohexane.

The conformational features of *trans*-1,3,5-trithiane-1,3,5-trioxide are also interesting. There is a single most-stable chair form. The twist-boat manifold is now only four-fold, just as *cis*-1,4-dithiane-dioxide or *cis*-1,3,5-trithiane-1,3-dioxide. The origin of four-fold transformations for those compounds is the same; two boat[21] and two twist[21] forms are simply points on the sides of the potential well instead of an energy minima or maxima.

In summary, we have examined the conformational idiosyncrasies of a number of sulfide and sulfoxide-containing 6-membered ring systems. For the parent ring systems, the chair is favored over other conformations, but this may not be true when substituents are introduced. The stereodynamics of twist-boat transformations are often quite different from those found in cyclohexane. These results, of course, arise from a delicate balance of the various steric and electrostatic effects. Many predictions are made, which await experimental test.

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[21]See footnote [b] under Table 4.

[22]See footnote [a] under Table 4.

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