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Computational Investigation of Vicinal Disulfoxides and Other Sulfinyl Radical Dimers

Daniel D. Gregory[*,†] **and William S. Jenks**[*,‡]

Department of Chemistry, St. Cloud State University, St. Cloud, Minnesota 56301-4498,
and Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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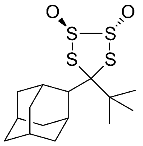
The structure and energetics of the simplest *vic*-disulfoxide $CH_3S(O)S(O)CH_3$ and its key isomers are reported. Computational methods include a CASSCF[2,2] treatment with a large basis set on sulfur and oxygen, followed by multireference MP2 refinement, and also the hybrid density functional B3LYP. Calculations at the G3 level were also carried out. In contrast to previous reports, a weak bond does exist for both *vic*-disulfoxide diastereomers. A bond enthalpy near 20 kcal mol^{-1} is reported. The isomeric sulfenylsulfinate is slightly lower in energy than the *vic*-disulfoxide. The B3LYP structure obtained for 5,5-di-*t*-butyltetrathiolane-2,3-dioxide reproduces the essential structural parameters of the one experimentally known *vic*-disulfinyl compound, 5-(1-adamantyl)-5-*tert*-butyltetrathiolane-2,3-dioxide.

Introduction

Vicinal disulfoxide[1] is a surprisingly rare functional group. Only recently has a vicinal disulfinyl compound (**1**) been isolated and thoroughly characterized,[2−4] though true α-disulfoxides have been characterized by NMR.[5]



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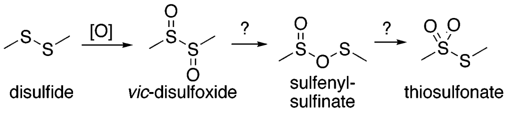
vic-Disulfoxides have been proposed as intermediates in a number of reactions, including, for instance, the oxidation of disulfides with electrophilic agents.[6] The consistent result of such oxidations, along with reactions that result in the coupling of sulfinyl radicals (RSO•),[7] is the formation of thiosulfonates (RSO_2R'), which are the global minimum on the potential energy surface. Given the ease of simple adduct formation and the amount of bond reorganization required to go from two sulfinyl radicals to a thiosulfonate, it is very likely that *vic*-disulfoxides and/or sulfenylsulfinates are formed first. These radicals are thought to undergo facile secondary chemistry to yield the thiosulfonates.[5−11] The mechanisms of these transformations are not well understood but are often postulated to involve the homolysis of the *vic*-disulfoxide and sulfenylsulfinate.



The relative instability of *vic*-disulfoxides has been a troubling problem for a number of years. In 1989 and 1991, the great organosulfur chemist Oae published a pair of papers in which he listed the important unsolved problems in organosulfur chemistry, and the instability of *vic*-disulfoxides was among these.[12,13] Though the repulsion of two positively charged sulfur atoms is an attractive hypothesis, it is belied in the relative *stability* of *vic*-disulfones. Herein, we present a computational study that addresses the $CH_3(S_2O_2)CH_3$ energy surface in general and the *vic*-disulfoxide in particular. We will conclude by siding with Kice, who suggested[11]—almost two decades before Oae declared the problem unsolved—that the paucity of *vic*-disulfoxides and several related phenomena can be related to the inherent stability of the sulfinyl radical.

Although several previous studies on *vic*-disulfoxides exist,[8,9,14,15] they are marred by the use of levels of theory and basis sets that are inadequate to describe the problem properly on even a qualitative basis. Indeed S−S "bond lengths" of 2.7 and 3.8 Å have been reported, well beyond the 2.3 Å we now know to expect from compound **1**. We establish a reasonable level of theory to describe these difficult molecules, address the issue of the relative stability of the possible dimers of CH_3-SO•, and explore these methods with larger molecules that are models for very recently obtained structures.

Computational Methods

All calculations were carried out with the GAMESS,[16] Gaussian 94,[17] or Gaussian 98[18] suites of programs. The G3[19−21] calculations and the B3LYP[22,23] calculations reported in Figures 1 and 2, with the exception of those involving the G3Large basis set,[21] were made using Gaussian. All other calculations, including the B3LYP calculations using the G3Large basis set and all B3LYP calculations not reported in Figures 1 and 2, were made using GAMESS. Note that GAMESS uses the VWN5 functional[24] as part of its B3LYP hybrid. MP2 and CCSD(T) calculations were made using the frozen-core approximation, except when the G3Large basis set was used. In those cases, "full" MP2 or MRMP2 calculations were made. Molecular structures and orbitals were viewed using the graphical interface program MacMolPlt.[25] All calculations are uncorrected for temperature (i.e., are effectively at 0 K). Harmonic frequency calculations were carried out for each

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[*] E-mail: dgregory@stcloudstate.edu; wsjenks@iastate.edu.
[†] St. Cloud State University.
[‡] Iowa State University.

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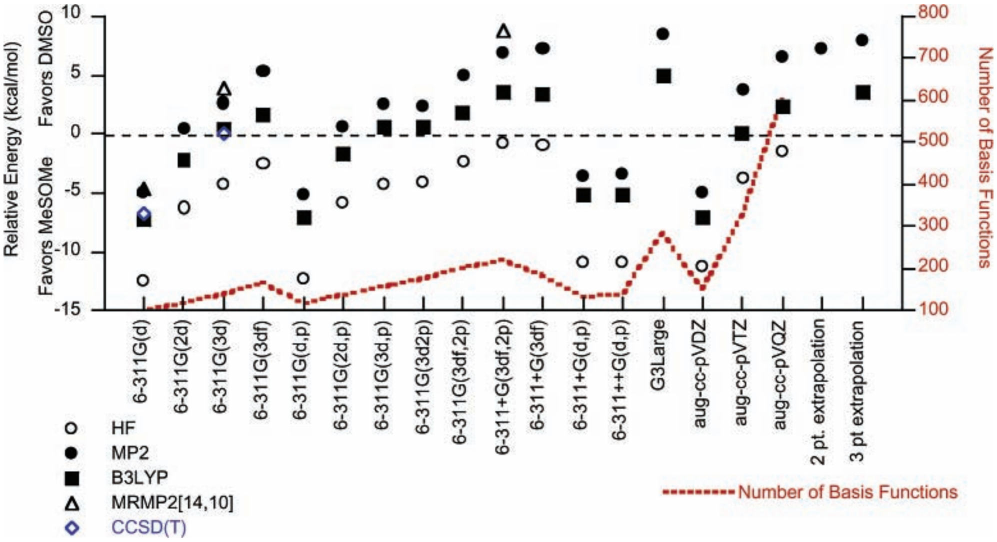


Figure 1. Relative energies of DMSO (**2**) and sulfenic ester methyl methanesulfenate (**3**) calculated at various levels of theory. The geometry for all of the calculations was obtained at MP2/6-311+(3df,2p). The G2(0 K) and G3(0 K) energy differences are 4.8[37] and 5.7 kcal mol^{-1}, respectively.

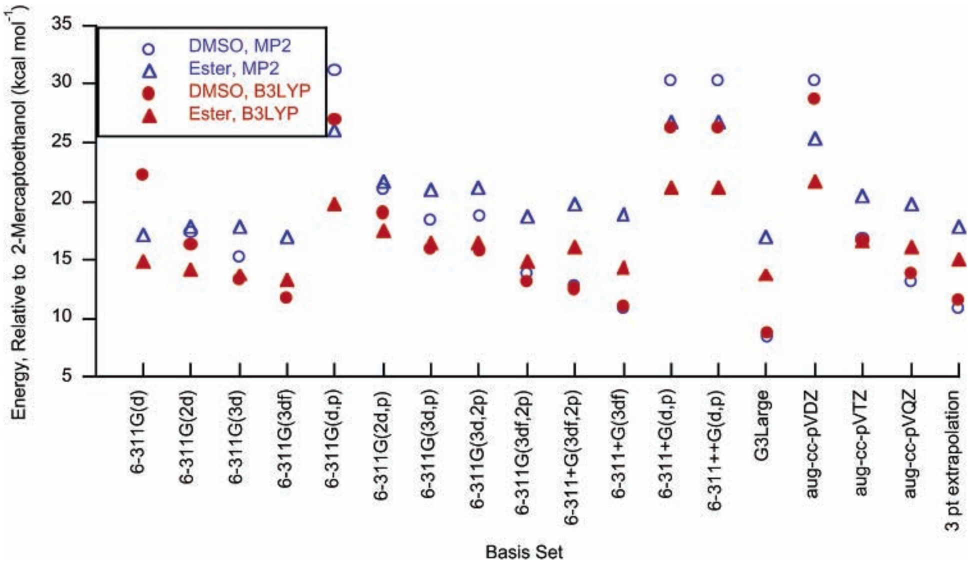
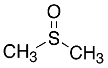


Figure 2. Energy differences between 2-mercaptoethanol (**4**) and DSMO (**2**) or sulfenic ester **3**, respectively. Circles show data for DMSO, and triangles, for the sulfenic ester. Open symbols are for MP2 calculations, and filled ones are for B3LYP. All data were obtained at the MP2/6-311+G(3df,2p) geometries. The energy differences at the G3(0 K) level are 12.8 and 18.5 kcal mol^{-1} for DMSO and sulfenic ester **3**, respectively.

optimized minimum or transition state but not at every level of theory. Both triple split-valence Pople-type and Dunning augmented correlation-consistent polarized valence basis sets[26,27] (aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ) were used, as indicated in the text. All 3D-rendered structures in the text are from B3LYP/6-311G(3df)mix optimizations unless otherwise noted. See section 2 for a definition of this basis set.

Results and Discussion

1. Basis Set Study. Computational studies on compounds containing oxidized sulfur often show large basis set effects.[28−30] In fact, it is well known that obtaining accurate thermochemistry on SO_2 is one of the most challenging problems among common small, stable molecules made of main group elements.[21,31−35] Because one of the principal goals of this work is to compare the energies of relatively large molecules with the formula $C_2H_6O_2S_2$ that have 0, 1, or 2 sulfur atoms in the sulfinyl or sulfonyl oxidation state, it was critical to understand just how large a basis set would be required and what parts of large basis sets might be truncated to economize on other calculations. To choose the smallest reasonable basis set to study the RSO dimers, we studied the relative energies of three isomers of C_2H_6OS: DMSO (**2**), methyl methanesulfenate (**3**), and 2-mercaptoethanol (**4**). These three compounds also appear in Turecek's related and important work.[29]


$CH_3S(=O)CH_3$

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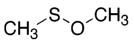

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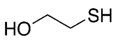

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The geometry of each of the isomers was optimized at MP2/6-311+G(3df,2p), and these fixed geometries were used for all subsequent calculations. Harmonic frequency calculations showed that each of the stationary points was a minimum, and the final geometries of all three isomers compared well with those previously reported.[29,36−38] For 2-mercaptoethanol, only the conformer shown by Turecek[29] to have the lowest energy was used after also checking others with MP2/6-311+G(3df,2p). Methods surveyed include Hartree−Fock (HF), density functional theory using Becke's hybrid functional (B3LYP), Møller−

Plesset perturbation theory truncated at second order (MP2), and complete active space self-consistent field (CASSCF) with an MP2 correlation correction added (MRMP2).[39,40] The CASSCF calculations had an active space consisting of 14 electrons in 10 orbitals (CASSCF[14,10]); for compounds **2** and **3**, this corresponds to a full valence treatment, save for the C−H bonds. These bonds are not expected to play a significant role in the chemistry of interest and in any case are expected to behave similarly in both molecules. Starting orbitals were obtained from RHF calculations utilizing the population localization (POP)[41] and modified virtual orbitals methods.[42]

Basis set extrapolations were calculated using two different techniques. The first method was described by Truhlar and coworkers.[43,44] Here, the optimized values of $\alpha = 3.4$ and $\beta = 2.2$ were used for the MP2 calculations. The second method was that described by Helgaker and co-workers.[45]

1.1. Computed Energy Differences between DMSO (2) and Methyl Sulfenic Ester (3). Figure **1** shows the relative energy between **2** and **3** for a series of basis sets and methods, all calculated at the MP2/6-311+G(3df,2p) geometry. The small variation between the single- and multireference MP2 energy differences did not appear to justify attempting a similar near-full valence treatment of larger compounds. Practical limitations also kept the number of CCSD(T) calculations to a minimum. An examination of Figure 1 reveals that for the limited number of cases shown the CCSD(T) data are better reproduced by B3LYP. At 6-311+G(3df,2p), we have five reasonable methods to compare: MP2, MRMP2, B3LYP, and the G2 and G3 methods (with their own basis set combinations), though the latter two are not shown in the Figure. Since we are comparing zero-spin isomers with equal numbers of paired electrons, the “higher-level corrections” of the Gn methods cancel, removing the empirical component of such calculations. The energy differences are 6.9, 8.7, 3.5, 4.8, and 5.7 kcal mol^{-1}, respectively. Depending on whether the G3 or the MRMP2 calculation stands as one’s state of reference, the performance of the MP2 calculations is comparable to or better than that of B3LYP.

The most striking feature of the data is that the trends for the relative energies of the species with basis set are followed at all levels of theory. The greatest effect among the Pople-type basis sets is that an increase in the number of d-polarization functions stabilizes the sulfoxide relative to the sulfenic ester. The addition of diffuse functions and an f function to the heavy atoms continues this trend, albeit less dramatically. It has been advocated that core polarization on S and O is important in obtaining accurate thermochemical data for SO_2 and related compounds.[33,34] The G3Large basis set is of similar size to 6-311+G(3df,2p) but adds core polarization functions (p and d for C and O, d and f for S). A slight stabilization of DMSO relative to **3** is observed for MP2, B3LYP, and G3 (vs G2), which suggests that this is a true basis set effect.

A relative stabilization of DMSO with larger basis sets is also reflected in the cc basis sets. In MP2 calculations, DMSO is more stable than **3** by 3.6 and 6.6 kcal/mol using aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively. The three-point extrapolation of these data to an infinite basis set extends the separation slightly to 7.9 kcal/mol.

A few words need to be said pertaining to the number of basis functions associated with each basis set. Figure **1** shows that both the MP2 and B3LYP methods achieve very similar energy differences using relatively large Pople basis sets and the quadruple-ζ cc basis set. However, there are 218 and 600 basis functions in the 6-311+G(3df,2p) and the aug-cc-pVQZ, respectively. The large number of basis functions associated with the aug-cc-pVQZ basis set, considering the size of our dimer molecules and the other molecules that we investigated, effectively eliminates this basis set as an option, but Figure 1 gives confidence that, within the limitations of the theoretical model chosen, 6-311+G(3df,2p) data will give data very comparable to the extrapolated aug-cc-pVXZ limit. However, the aug-cc-pVXZ basis sets do not include core polarization, which appears to be necessary for the most accurate calculations of relative energies. Although there are basis sets in the cc-pVXZ series that have added core polarization functions, it was decided that the G3Large basis set, being similar in size to 6-311+G(3df,2p) if not counting the core polarization, would be used for final energy calculations.

1.2. Computed Energy Differences between DMSO (2), Sulfenic Ester 3, and 2-Mercaptoethanol (4). Given the dramatic basis set effect on isomer energy differences and the quantitative differences observed between MP2 and B3LYP, it is worthwhile to understand whether this is derived from a problem calculating the energy of DMSO, the sulfenic ester, or both molecules. Thus, their energies were compared to that of another isomer, 2-mercaptoethanol, as illustrated in Figure 2.[29]

Among the Pople-type basis sets, the energy difference between **3** and **4** is relatively insensitive to d, f, and diffuse polarization functions on the heavy atoms but quite sensitive to polarization functions on H. The latter effect is expected because of the OH and SH bonds in **4**. In contrast, the energy difference between DMSO and **4** depends strongly on the heavy-atom polarization functions. The contrast in behavior between **2** and **3** is not as obvious with the aug-cc basis sets because the polarization functions are added onto the H and heavy atoms in a concerted fashion and not in the isolated manner of the Pople-type bases. It follows from these data that the basis set dependence of the energy difference between DMSO and the sulfenic ester (Figure 1) is largely due to the need for extensive polarization functions to describe the sulfinyl function adequately.

One other point should be noted. Figure 2 shows that B3LYP and MP2 give very similar energy differences between DMSO and 2-mercaptoethanol, especially as the basis sets get larger. By contrast, the B3LYP and MP2 energy differences between the sulfenic ester and 2-mercaptoethanol do not converge, with B3LYP giving a relatively more stable sulfenic ester by 3−4 kcal mol^{-1}. If it is assumed that, among these three compounds, it is most straightforward to obtain a reliable energy for 2-mercaptoethanol (in all respects save for the need for polarization functions on H), we can conclude that the disagreement between MP2 and B3LYP on ΔE in Figure 1 is due to the mishandling of the sulfenic ester by one of the methods rather than the mishandling of the sulfoxide.

Which method is more likely to be the accurate one for **3** must be addressed since experimental values are not available. Our bias is away from the density functional methods because of occasional very poor performance in related systems[37,46,47] and because the very weak bonds involved and computational difficulties (vide infra) point toward some of the structures not being well represented by a single-reference wave function. It has become fairly widely accepted, if not well documented, that for single-reference problems the natural progression of ab initio methods is HF → MP2 → CCSD(T) and the CCSD(T) value is the standard by which other methods should be judged. To establish whether the sulfenic ester is acceptably described by a single-reference wave function, the natural orbital occupation numbers in the active space of the CASSCF calculations were examined. All were ≥1.97 or ≤0.03, indicating that the single-reference approximation is reasonable.

With this conclusion in hand, an examination of Figure 1 in the two cases in which CCSD(T) energy differences are plotted reveals that the B3LYP values are in close agreement with them whereas the MP2 values are about 3 kcal mol^{-1} higher. As a result, it is likely that the B3LYP method yields relative energies for **3** that are more accurate than those from MP2 and MRMP2. Thus, although most of the structures in the sections below were initially explored with CASSCF and MRMP2 methods, B3LYP energies are reported in all appropriate cases.

2. Dimers of CH_3SO. The dimerization of methanesulfinyl ($CH_3SO\bullet$, **5**) may plausibly occur in three modes because there is significant spin density on both the sulfur and oxygen atoms.[5−9,14,15,37,48] These consist of an O−O dimer (**6**), an S−O dimer (**7**), and an S−S dimer (**8**). O−O dimer **6** is made reasonable-seeming by the transient existence of tetroxides[49] and the plethora of polysulfides. Sulfenylsulfinate **7** might be the anticipated initial adduct because the sulfinyl radical has a significant dipole along the S−O bond, leading to favorable electrostatic interactions in the transition state for radical coupling. Disulfoxide **8** consists of a pair of diastereomers, chiral **8rr** (and its antipode) and meso **8rs**. The expected isolated product, thiosulfonate **9**, is also included.

$CH_3SO\bullet$

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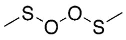

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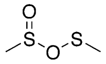

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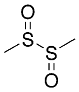

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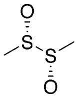
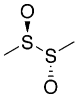
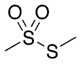


8rr



8rs



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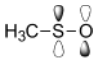
In this section, we consider each dimer in turn. To begin with, however, a useful observation can be made. All calculations on dimers **6** and **8** have in common the result that the HOMO and LUMO are constructed from bonding and antibonding combinations of the SOMO of radical **5**, which is a π^* orbital shared between S and O, illustrated schematically here:



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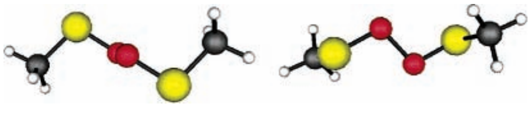
Presumably because of the weakness of the various key bonds connecting the dimers, it was found that the most reliable correlated method for getting sensible optimized structures for **6** and **8** was CASSCF optimization with a small active space consisting of just the two electrons in the HOMO and LUMO. (This also corresponds to a one-pair GVB run. This method, although time-saving in principle, did not lead to converged orbitals in practice.) Because the HOMO and LUMO were constructed from the same starting fragment orbitals, we felt confident about comparing the energies obtained from such structures, especially after adding the MRMP2 correction to the data.

Also, a great many different optimizations were run. To make the computer time manageable, mixed basis sets on which modest basis sets were used for the less critical parts of the molecules were used. For such runs, the methyl groups were treated with the 6-31G(d) basis set, and the sulfur and oxygen were treated with the 6-311+G(3df) or 6-311G(3df) basis.[50] Such basis set runs will be noted as 6-311+G(3df)mix or 6-311G(3df)mix, respectively. Precisely analogous mixed basis sets using G3Large instead of 6-311+G(3df) will be indicated in the same way, G3Lmix.

2.1. O−O Dimer (6). To the best of our knowledge, there is no direct experimental evidence for the formation of an O−O dimer from sulfinyl radicals, as represented by compound **6**. Lacombe, however, reviews several instances in which they have been proposed as transient intermediates or transition states.[8,9] Speaking in their favor is the ubiquitous existence of the polysulfide linkage, the most obvious being elemental sulfur S_8. Also known, at least as transient species, are tetroxides, through the work of Russell and the mechanisms for peroxyl radical decomposition.[49]

However, as we have argued previously,[37] the sulfinyl radical is specially stabilized, relative to peroxyl or perthiyl radicals, because the difference in electronegativity between S and O encourages effective mixing between the lone pair on S and the single electron on O that leads to the three-electron π-system. In this sense, the sulfinyl radical is closely related to its analogue, the nitroxide ($R_2NO\bullet$), which does not form an O−O dimer. This special stabilization of the sulfinyl radical should lead to a weakening of the O−O bond in **6**, relative to that in a tetroxide, which is already only a transient species. Another analogy can be made to ONOONO, a recently proposed intermediate in the oxidation of nitric oxide by O_2 to NO_2.[51] The lowest-energy conformation of ONOONO is calculated (CBS-QB3) to be about 11 kcal mol^{-1} more energetic than the separated NO_2 radicals. There is a barrier of 2.4 kcal mol^{-1} calculated for its dissociation.

The optimization of **6** at RHF/6-31G(d) results in the observation of the illustrated structure with C_i symmetry and an O−O bond length of 1.60 Å. Two views are shown for clarity. From the illustration, it can be envisioned that the C_i structure will directly correlate with a pair of ground-state $CH_3SO\bullet$ radicals through an elongation of the O−O bond. When the RHF structure was subjected to MP2 refinement, the result was the catastrophic separation of the molecule into two $CH_3SO\bullet$ fragments where the ever-increasing distance between the fragments led to correspondingly lower energies. Clearly, this nonphysical result can be attributed to the inappropriate use of spin-restricted MP2. As the fragments separated, the single-reference approximation inherent in the MP2 calculations became worse and worse.



To approach this molecule more realistically, a series of optimizations as a function of a constrained O−O distance were carried out at CASSCF[2,2]/6-31G(d). The active space represented the bonding and antibonding combinations of the sulfinyl SOMO, which corresponded well to the HOMO and LUMO of these structures, as mentioned above. The O−O distances ranged from a minimum of 1.60 Å (the RHF bond length) to a maximum of 4.24 Å, a distance to which an optimization that had begun with a 3.66-Å O−O distance had optimized. The results of this are shown in Figure 3, and it can be seen that the RHF structure is apparently residing in the barest of minima. However, when MRMP2 energies were obtained at each of these points, it became clear that O−O dimer **6** was probably not a minimum on the potential energy surface. Because of the energy dependence of sulfinyl systems on basis sets, MRMP2/6-

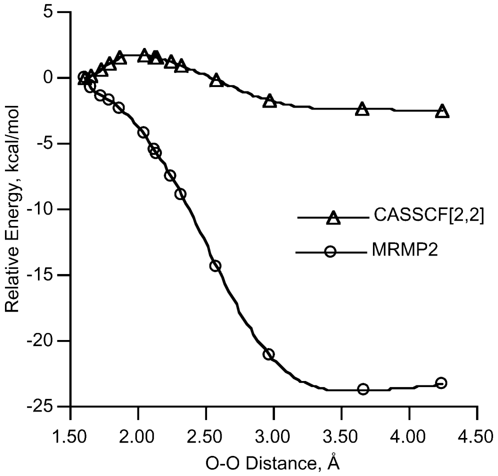
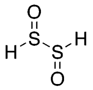


Figure 3. Relative energies of $CH_3SO-OSCH_3$ structures as a function of O−O distance. Energies were obtained from CASSCF[2,2]/6-31G(d) optimizations subject only to the O−O distance constraint. MRMP2 energies were obtained at the CASSCF geometries.

311+G(3df,2p)//CASSCF[2,2]/6-31G(d) energies were obtained with O−O distances of 1.60 and 4.24 Å. The latter of these was still the more stable, this time by 48 kcal mol^{-1}. It was thus concluded that compound **6** either is not a minimum on the true $C_2H_6O_2S_2$ surface or resides in a very shallow minimum, similar to the case described by Olson and Houk for ONOONO.[51]

2.2. O−S Dimer (7). In contrast to **6**, experimental evidence for structures such as **7** is known.[5] No indications were found that this molecule was as difficult to handle computationally as some of the others discussed herein. However, the molecule has one more meaningful bond-rotational degree of freedom than disulfoxide **8**. We did not do an exhaustive high-level conformational search on **7** but instead concentrated on a structure whose energy was 1.7 kcal mol^{-1} lower than that of a previously reported conformation,[9] when both were refined at the MP2/6-311G(3d,p) level. Attempts were made to make the same sort of CASSCF[2,2] calculations as reported in section 2.1, but the HOMO and LUMO of this compound do not correspond as well to the ± combinations of the $CH_3SO\bullet$ SOMO. As a result, the optimized orbitals in the active space drift over to other parts of the molecule. This makes direct comparisons of the energies of isomers **6** and **8** (vide infra) to that of **7** impossible using this level of theory. Instead, as reported below, G3 and B3LYP/G3Large energies were obtained.

2.3. S−S Dimer: *vic*-Disulfoxides 8rr and 8rs. In addition to the experimental work that has appeared documenting *vic*-disulfoxides, at least three groups have published ab initio computations on this subject. Freeman and Hehre, as early as 1982, published HF/6-31G(d)//HF/3-21G(d) calculations on the oxides of HSSH.[10] For the meso diastereomer of **10**, these authors found an S−S bond length of 2.14 Å and an equilibrium O−S−S−O dihedral angle of 180°. An identical S−S distance was found for the dl diastereomer, with an O−S−S−O dihedral of 174° in a conformation in which the two hydrogen atoms are nearly eclipsed. Subsequent authors[14] took the CASSCF approach that we have duplicated above but obtained the rather nonphysical S−S "bond" distance for **10** of 3.83 Å using the 3-21G(d) basis set. They later obtained an S−S distance of 4.31 Å for **8rs** using the same method, CASSCF[2,2]/3-21G(d), and characterized **8rs** as "two isolated radicals kept at equilibrium distance."[15]



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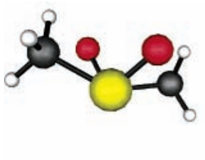
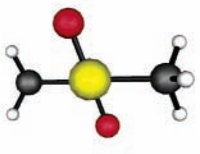
In 1998, another study was reported in which MP2/6-31G(d) optimizations were carried out on **8**.[9] For meso structure **8rs**, an S−S bond length of 2.30 Å was obtained. This, as we shall see, is close to the expected experimental value. However, for the dl isomer, these same authors obtained nonphysical S−S distances of 2.69 and 2.74 Å for different conformations. These authors again argued that **8rr** is "a complex between two close sulfinyl radicals held by sulfur−sulfur interaction and hydrogen bonding with the oxygen."[9]

We investigated these two diastereomers as well and optimized them as a function of the constrained internal rotation of the S−S bond. Initial structures were prepared with O−S−S−O dihedral angles from 0 to 360° in 15° increments for **8rr** and from 0 to 180° for meso **8rs**. Because of the symmetry, only half of the rotation is required for the latter compound. As expected, HF constrained optimizations proceed smoothly. Given the nonphysical results of MP2 optimizations in previous studies, it was not surprising to see some small negative natural orbital occupation numbers in some trial MP2 runs. At this point, MP2 was abandoned as a method, and we returned to CASSCF[2,2] for structural refinement.

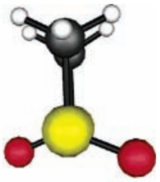
In these optimizations, a guess Hessian of at least HF quality was required to avoid poor first steps away from the HF geometries. Such runs usually resulted in fruitless dissociative optimizations. It is quite conceivable that this was the critical error in some previous work. However, even with good starting Hessians, reasonable geometries could not be obtained at some dihedral angles at CASSCF[2,2]/6-31G(d). However, this problem resolved itself when larger basis sets were used. The HF/6-31G(d) geometries and Hessians became input for CASSCF[2,2]/6-311G(3df)mix optimizations, followed by MRMP2 energy refinement. The results of these calculations are shown in Figures 4 and 5 for **8rr** and **8rs**, respectively. The zero energy is set for the lowest energy of the two diastereomers at each level of theory. Note that the dl compound is slightly lower-energy at MRMP2, but the meso compound is slightly lower-energy at CASSCF. The lowest-energy conformations are illustrated in Newman-type projections immediately below. The high-energy conformer of **8rr** is denoted as **8rr-max**.



8rr



8rs



8rr-max

For the dl compound, the MRMP2/6-311G(3df)mix barrier to rotation (neglecting zero-point energy) is nearly 10 kcal mol^{-1} at this level of theory. It is about 6.5 kcal mol^{-1} for the meso compound. Extremely similar barriers were obtained at MRMP2-(full)/G3Lmix//CASSCF[2,2]/6-311G(3df)mix. (See Supporting Information.) This is not unexpected in that core polarization contributions should be similar for rotamers of the same compound. At B3LYP/G3Lmix//CASSCF[2,2]/6-311G(3df)mix, the barriers are 8.5 and 8.0 kcal mol^{-1}. Because the bond energy is ≤20 kcal mol^{-1} (vide infra), this presumably explains the difficulty of some of the optimizations. The CASSCF energy profile for **8rs** is in qualitative agreement with a partial profile

TABLE 1: Absolute and Relative Energies of Compounds 5−10

	B3LYP[a]		G3 (0 K)	
	absolute (H)	relative[b] (kcal mol^{-1})	absolute (H)	relative (kcal mol^{-1})
CH_3SO• (**5**)	−513.24607		−513.063182	
$CH_3S(O)OSCH_3$ (**7**)	−1026.52188	17.1 (−18.4)	−1026.161427	19.5
$CH_3S(O)S(O)CH_3$ (**8rs**)	−1026.51954	18.8 (17.7)	−1026.156116	22.8
$CH_3S(O_2)SCH_3$ (**9**)	−1026.54913	0	−1026.192509	0
$CH_3S(O_2)$• (**11**)	−588.45566		−588.238108	
CH_3S• (**12**)	−438.01453		−437.865180	
2 CH_3SO•	−1026.49214	35.8 (31.2)	−1026.126364	41.5
$CH_3S(O_2)$• + CH_3S•	−1026.47019	49.5 (45.9)	−1026.103288	56.0

[a] B3LYP/G3Large, RO−B3LYP/G3Large for radicals. [b] Parenthetical values include unscaled RHF zero-point energies.

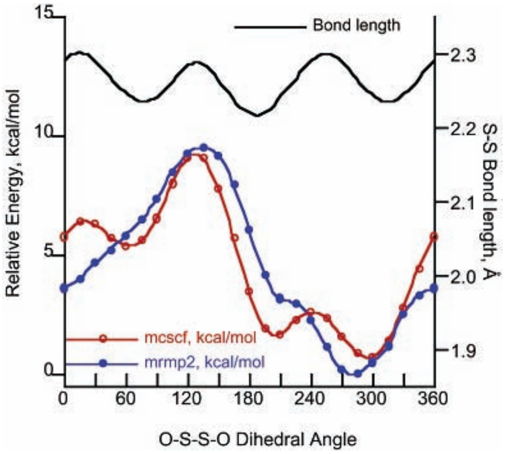


Figure 4. Relative energies of **8rr** as a function of the O−S−S−O dihedral angle. Structures are fully optimized, save for the single constraint, at CASSCF[2,2]/6-311G(3fd)mix. MRMP2 energies are taken at these structures. The lines are cubic spline fits to the data points.

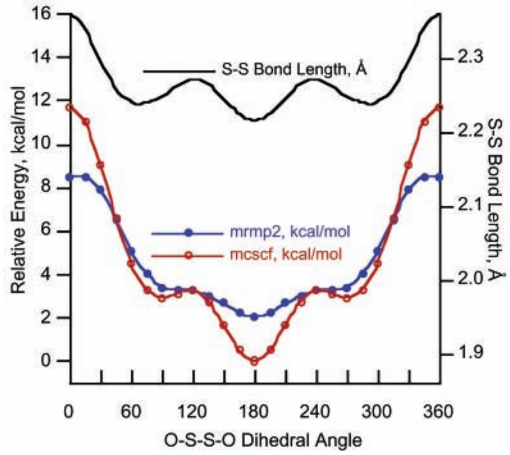
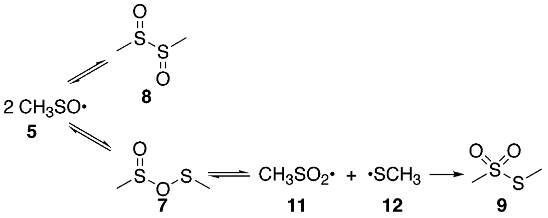


Figure 5. Relative energies of **8rs** as a function of the O−S−S−O dihedral angle. Structures are fully optimized, save for the single constraint, at CASSCF[2,2]/6−311(3df)Gmix. MRMP2 energies are taken at these structures. The lines are cubic spline fits to the data points.

reported previously at the HF/6-31G(d) level.[14] The low-energy meso isomer is favored by 5.0 kcal mol^{-1} in the B3LYP calculations, in contrast to the ~2 kcal mol^{-1} preference for the dl compound with MRMP2.

The S−S bond length in **8rr** and **8rs** is obviously one of the important issues, given the previous reports. The ordinary S−S bond length in a disulfide is about 2.05 Å, and the S−S bond length in thiosulfonates is near 2.10 Å.[52] The only S(O)−S(O) bond length known experimentally is that of compound **1**, which is neither quite a *vic*-disulfoxide nor as structurally unperturbed as **7**. Nonetheless, it must be taken as the benchmark at this time, and its S(O)−S(O) bond length is 2.301 Å.[4] To that extent, the calculated bond lengths of 2.215 (meso) and 2.265 Å (dl, 285°) significantly underestimate the length of this weak bond. Full optimization of these structures at B3LYP/6-311G(3df)-mix gave very reasonable results, with a dihedral angle of 180° and an S−S bond length of 2.312 Å for **8rs**. An O−S−S−O dihedral angle of 284° and a longer S−S distance of 2.387 Å were obtained for fully optimized **8rr**.

SCHEME 1: Possible Mechanistic Route to Thiosulfonates



Whether the CASSCF[2,2] or B3LYP S−S bond lengths are more accurate in an absolute sense, it is clear that there is no longer any reason to believe that these are unbound species held together in the gas phase by only weak intermolecular forces. The S−S bond in a *vic*-disulfoxide is weak, but it is real.

2.4. Energy Differences among Compounds 5−9. Table 1 shows the absolute and relative energies for the essential compounds in this series. Moreover, because the question of how one goes from **7** or **8** to **9** is an important one, we include the energies of a pair of sulfinyl radicals **5** and the energies of CH_3S• and CH_3SO_2•. A plausible pathway involving these radicals is illustrated in Scheme 1.

No MRMP2 energies are included in the Table because of difficulties associated with matching the active-space orbitals in one compound compared to the others. However, Figures 1 and 2 suggest that B3LYP may be more accurate among the closed-shell species given the combination of sulfenyl, sulfinyl, and sulfonyl oxidation states, and there is obviously no localization problem in such calculations as was encountered in the CASSCF calculations. B3LYP/G3Large and G3 data are shown. Though there is a significant quantitative difference in the relative energies obtained using these two methods, the general conclusions to be drawn from them do not differ. It should also be pointed out that, in contrast to the closed-shell comparisons made above, the empirical “HLC” corrections contained within the G3 numbers do not cancel out when comparing the closed- and open-shell species.

Although Scheme 1 is attractive, at least one part of it can be dismissed as experimentally irrelevant given the results in Table 1. Structures of type **7** are extremely rare[5] and have never been shown to be stable near room temperature, instead yielding thiosulfonates at the higher temperatures. Thus, we do not find it credible that homolytic cleavage, with a barrier near 30 kcal

TABLE 2: Energies and Structures of 13−15

	13	**14a**	**14b**	**15**[e]	**1** (X-ray)
MRMP2[a]				−2089.34748	
energy (H)	−1859.12112	-1859.12778	-1859.10853		
relative energy (kcal mol^{-1})	4.2	0	12.1		
S(O)-S(O) distance (Å)[b]	2.251	2.397	2.264	2.169	2.301
O−S−S−O dihedral angle[c]	184.6°	0°	51.7°	170.1°	165.5°
B3LYP[d]					
energy (H)	−1860.83444	-1860.83411	-1860.82723	-2094.81266	
relative energy (kcal mol^{-1})	0	0.2	4.5		
S(O)−S(O) distance (Å)	2.380	2.478	2.375	2.347	2.301
O−S−S−O dihedral	186.9°	0°	51.2°	168.5°	165.5°

[a] MRMP2(full)/G3Lmix//CASSCF[2,2]/6-311G(3df)mix. [b] All levels of theory reproduced the experimental 2.05-Å S−S(O) bond length. [c] Angles less than 180° imply that the S−O bond vector points slightly away from the ring whereas angles greater than 180° imply that the S−O bond vectors point slightly back toward the ring. [d] B3LYP/G3Lmix//B3LYP/6-311G(3df)mix. [e] CASSCF[2,2] only. See text for basis set.

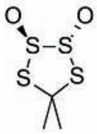
mol^{-1} or higher, is a plausible mechanism; there must be some other mechanism by which the isomerization of sulfenyl sulfinates to thiosulfonates occurs. Solvent intervention, bimolecular reactions, acid catalysis, and other nonhomolytic pathways are possibilities. Considerable effort was put into finding unimolecular transition states that connected **7** to **9** by low-energy pathways but without success.[53] We thus conclude that one of these other mechanisms is most likely involved. In contrast, the S(O)−S(O) bond in the *vic*-disulfoxide has a dissociation energy on the order of ≤20 kcal mol^{-1} (18.7 kcal mol^{-1} at G3(0 K)), a value consistent with rapid reactions near room temperature and the lack of isolation of these compounds in general.

Another important result shown in Table 1 is that the meso *vic*-disulfoxide and the sulfenylsulfinate are nearly isoenergetic. This makes Harpp's suggestion[5] that the various disulfoxides and sulfenylsulfinates in his bicyclic systems can interconvert and sometimes, depending on the exact structure, all be observed simultaneously seem reasonable. It also indirectly supports the notion that in the case of bimolecular combination of sulfinyl radicals the sulfenylsulfinate is the likely major primary adduct. With only a small difference in adduct energies, the potential energy surface leading to bond formation ought to be dominated by the electrostatic interactions that favor the formation of **7** and its analogues. Finally, the equilibrium

$$2CH_3SO\bullet \rightleftharpoons CH_3SO_2\bullet + \bullet SCH_3 \qquad \Delta H \approx 15 \text{ kcal mol}^{-1}$$

supports our hypothesis[37] that the sulfinyl radical is especially stabilized in this series and is the essential reason for the instability of the *vic*-disulfoxide.

3. Calculations on Other Representative *vic*-Disulfoxides. To test whether our calculations related well to experimental results, we took on calculations of systems that were models of compound **1**. The experimentally determined[2] structure of **1** has a few notable features including asymmetric S−O bond lengths of 1.41 and 1.46 Å, S−S(O) bond lengths of 2.05 Å, a S(O)−S(O) bond length of 2.30 Å, and an O−S−S−O dihedral angle of 165.5° with the oxygen atoms pointing slightly away from the ring. The appearance of the pair of sulfinyl groups is pseudodiaxial. Undoubtedly, the large alkyl groups in **1** affect the structure, compared to a simpler tetrathiolane-2,3-dioxide, but to what extent it is not known. We settled on dimethyl derivative **13** as an initial model because preliminary calculations on the parent tetrathiolane-2,3-dioxide showed that the "diaxial" conformation was a transition state rather than a minimum. In structure **13**, however, it is a minimum. Since the diaxial conformation most closely models that of **1**, no other conformation was sought.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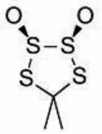
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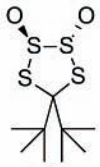
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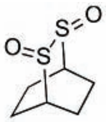
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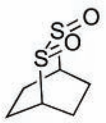
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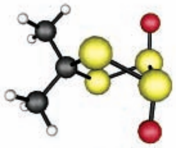
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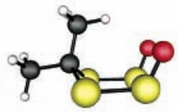
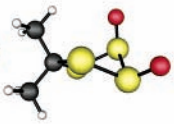
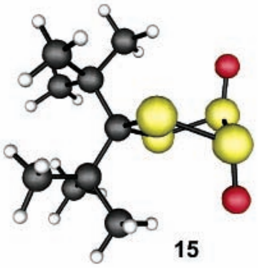

14a


14b


15

It has been assumed by most authors that the anti stereochemistry illustrated in **1** and **13** should be lower in energy than the syn stereochemistry illustrated in **14** because of the alignment of the S−O dipoles. Such considerations presumably contribute to the relatively large S−S rotational barriers in **8rr** and **8rs**. To test this hypothesis, compound **14** was investigated. Two conformations (**14a** and **14b**) that were energetic minima were found. As usual, these structures were optimized with CASSCF-[2,2]/6-311G(3df)mix calculations with the caveat that the nonoxidized sulfur atoms were also treated at 6-31G(d). They were also optimized at B3LYP/6-311G(3df)mix. Final energies were obtained in both cases using G3Lmix. Several structural and energetic parameters are given in Table 2. Surprisingly, **13** and eclipsed conformation **14a** have nearly the same energy at B3LYP whereas the eclipsed compound is of lower energy with MRMP2. The S(O)−S(O) distance in eclipsed **14a** is greater than in **13**, perhaps as a compensation to minimize the anticipated unfavorable dipole−dipole interaction. Conformer **14b** is probably of sufficiently high energy to be unimportant in solution. However, it should be noted that this conformer, in which the SO bond vectors are not aligned, does not share the elongated S(O)−S(O) bond with **14a**.

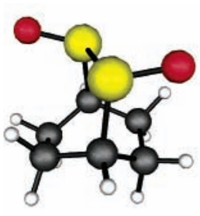
Compound **15** was examined to understand how much the structural parameters change with the addition of the large substituents and to model **1** closely. To make calculations on

TABLE 3: Structural Parameters for 16 and 17

	16	17
S−S distance (Å)	2.360	2.394
O−S−S−O dihedral angle	153.0°	4.0°
B3LYP/G3Lmix//B3LYP6-311G(3df)mix (H)	−1181.21723	1181.21414
relative energy (kcal mol^{-1})	0	1.9

this compound feasible, we used a slight variation on the CASSCF[2,2]/6-311G(3df)mix method in which the ring atoms were treated identically in **13**−**15** but in **15** the *tert*-butyl groups were reduced to the 3-21G basis set. The illustrated C_2-symmetric conformation was confirmed as a minimum with a harmonic frequency calculation at the HF level (which, naturally, had slightly different geometrical parameters). The S−S bond length and O−S−S−O dihedral angle are closer to the experimental values using B3LYP than using the CASSCF[2,2] method. To be fair, it should be noted that the latter treats every bond save the S(O)−S(O) bond in a Hartree−Fock manner, and this may result in some distortion of the ring. B3LYP has the clear advantage of treating all of the bonds equally and in a cost-efficient manner while giving results that are in good agreement with experiment. For further reference, the B3LYP S−O bond length is 1.467 Å, which compares to 1.461 and 1.409 Å for the two S−O bonds in **1** from the X-ray data. The CASSCF[2,2] length is 1.432 Å, quite near the average of the two experimental values. It should be noted that the computed S(O)−S(O) length is longer for **13** than it is for **15**. This lends further credence to the S(O)−S(O) bond lengths calculated with B3LYP for **8**, which were slightly longer than the experimental values for **1**.

The low energy of eclipsed structure **14a** was surprising to us. We thought it was possible that this had to do with the relative floppiness of the five-membered ring and issues of ring strain in different conformations. Thus, we also modeled compounds **16** and **17**. The C_2-symmetric optimized structure of **16** is a minimum, but the C_S structure for **17** is a transition state between two slightly asymmetric (C_1) structures. The low symmetry of **17** made the CASSCF[2,2]/6-311G(3df)mix jobs impractically time-consuming, so we rely on B3LYP/6-311G-(3df)mix structures and B3LYP/G3Lmix energies at those geometries. As can be seen in Table 3, the energies of the two structures are again similar. However, even with this relatively rigid framework, it is clear that some distortion occurs with **17** to avoid the perfect dipole alignment. First, there is the slight displacement of the dihedral angle and concomitant twisting of the [2.2.2] framework. Additionally, there is a slight lengthening of the S−S bond from 2.36 to 2.39 Å.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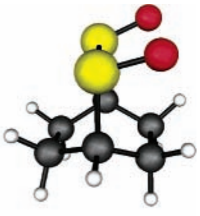
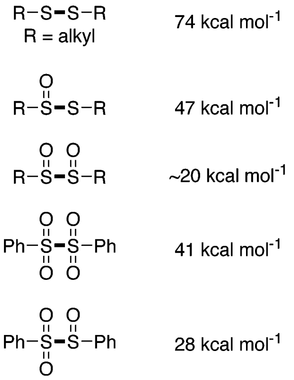

17

Experimental evidence for simultaneous observation of syn and anti bicyclic *vic*-disulfoxides is available from Harpp's oxidation of [3.2.1] systems where the two-atom bridge is the S−S linkage.[5] In this case, three isomers were observed at low temperature by NMR: an anti isomer and two syn isomers in which the pair of O atoms faced the two different bridges. Thus, in retrospect, it should not be surprising that the energy differences calculated here are not great. Of course, the experimental observations are also tied to the rate of formation and the rate of secondary chemistry, neither of which is directly addressed here. A computational examination of the oxidation of thiosulfinates by performic acid has appeared[54] and could have a bearing on the formation of syn and anti isomers in bicyclic systems. An important result to come from this work is that the dipole moments of the transition states for various oxidations in model systems are very different, meaning that solvent has a dramatic quantitative effect on the relative energies of the transition states compared to those of the gas phase, tending to level them.[54] Beyond that, though, we hesitate to draw further conclusions because of the aforementioned difficulties with certain S−S bond distances.

SCHEME 2: Representative S−S Bond Strengths[55−57]



Summary and Conclusions

vic-Disulfoxides are observed experimentally only rarely and have produced difficulties for computational and experimental chemists alike. With this paper, we show that the weak bonds in these and related systems can be treated with at least reasonable chemical accuracy with appropriately chosen levels of theory. The enthalpy difference between sulfenylsulfinates (e.g., **7**) and *vic*-disulfoxides is only a few kilocalories/mole in keeping with the analogous results for (mono-)sulfoxides and sulfenic esters. Furthermore, an investigation into cyclic and bicyclic *vic*-disulfoxides **13**−**17** suggests that the avoidance of aligning the SO bond dipoles is only one of several considerations leading to lower energy and that it may not be easy to pick the lowest-energy conformer/isomer of such molecules on inspection. We find no evidence for bound O−O sulfinyl radical dimers.

For the first time, we estimate that the S(O)−S(O) bond strength in acyclic *vic*-disulfoxides is on the order of 20 kcal mol^{-1}. To put this in context, we illustrate several representative S−S bond strengths in Scheme 2.[55−57] Clearly, oxidation of a sulfenyl sulfur to sulfinyl weakens the S−S bond considerably. An interesting feature, however, is that the first oxidation of a disulfide weakens the bond by ∼27 kcal mol^{-1}. A very similar (or only slightly elevated) destabilization of the S−S bond is found for the second oxidation, depending on the precise BDE value adopted. (The G3(0 K) BDE is 18.7 kcal mol^{-1}.) Furthermore, a destabilization of 27 kcal mol^{-1} is just a little larger than that effected upon the C−S bonds of dimethyl sulfide when the sulfur is oxidized to sulfoxide.[55,56]

Another way of explaning these data is that the disproportionation of the thiosulfonate to disulfide and *vic*-disulfoxide is nearly thermoneutral if we adopt the G3 energies as the most reliable (and only slightly endothermic with the B3LYP data.) It thus does not appear that there is a large destabilization of the *vic*-disulfoxide that would not be predicted outside of simple

Benson-style additivity arguments. Instead, the energetics are consistent with what is already known about monosulfinyl systems. Simply put, the weakness of the S(O)−S(O) bond is derived from the unusual stability of the two product sulfinyl radicals. Similarly, one may draw evidence for the special stability of sulfinyl radicals from a completely different reaction. Homolytic dissociation of the OH bond in methanesulfenic acid CH_3SOH also leads to $CH_3SO\bullet$. Compared to the 104 kcal mol^{-1} O−H BDE for CH_3OH, calculated values of 69 kcal mol^{-1} (G2) and 71 kcal mol^{-1} (G3//MP2/cc-pVTZ) have been reported by us[58] and others.[59]

These qualitative chemical conclusions being made, the quantitative disagreements among the methods should be addressed. The B3LYP calculations produce longer S(O)−S(O) bond lengths, but a comparison of the known structure of **1** to the calculated structure of **15** suggests that the longer bond lengths may be more accurate. However, there is considerably less certainty about the quantitative energetic aspects. A recent series of papers on the heat of formation for sulfine (H_2CSO)[60−64] illustrates the reason for our hesitation. CBS-QB3 and B3LYP calculations with large basis sets gave values of ΔH_f that varied by approximately 10 kcal mol^{-1}. This problem was compounded by uncertainty in the experimental value. Eventually, a consensus was reached, but not until very carefully chosen isodesmic reactions were considered on the density functional side. The simple comparison of the energies of radicals to those of molecules is plainly neither isodesmic nor isogyric. Although there are hints discussed in section 2 that the B3LYP energetics may be more accurate for R−S−O−R′ compounds than simple MP2 calculations with the same basis set, in the absence of other evidence to the contrary, we suggest that the G3 calculations are to be taken as more reliable[19] for the bond dissociation energies that are derivable from Table 1.

Acknowledgment. We thank the National Science Foundation (CHE 9708327 and CHE 0213375) and The Research Corporation (Cottrell Scholar award to W.S.J.) for their support of this research. We also thank the Minnesota Supercomputing Facility for a grant of computer time on their system on which we carried out calculations using Gaussian 98. We are also grateful to Alicia Spychala for her work in trying to find low-energy transition states.

Supporting Information Available: Coordinates, zero-point energies, and absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Notation for sulfoxides is ambiguous. The commonly used S═O notation does not reflect the true electronic structure, which is best represented by the ylide notation. However, for clarity, we adopt S−O in this paper, except in instances where indications of stereochemistry are required.

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