J. Org. Chem. **1996,** *61,* 1275−1283 **1275**

Effects of Conjugation and Aromaticity on the Sulfoxide Bond[1]

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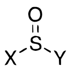
Received August 14, 1995[⊗]

An *ab initio* computational study on a series of sulfoxides is reported. The SO bond dissociation energy (BDE) of sulfoxides in which the sulfur atom is included in a formally aromatic ring (*e.g.*, thiophene sulfoxide) is found to be decreased by as much as 25 kcal/mol, compared to DMSO. A complementary effect is observed for sulfoxides in which the sulfur is included in a formally antiaromatic ring (*e.g.*, thiirene sulfoxide), in which SO BDEs are increased by as much as 15 kcal/mol. Both effects are attenuated by benzannulation. Examination of calculated geometries and isodesmic reactions with pure hydrocarbons leads to the conclusion that the observed effects are due to a severe disruption of the (anti) aromaticity of the sulfur-containing ring on oxidation. The cyclic sulfoxides appear to be neither significantly aromatic nor antiaromatic by energetic considerations. No significant SO bond strength effect is observed for simple conjugation. Inversion barriers for several sulfoxides are also calculated.

Introduction

During the course of our studies on the photochemistry and photophysics of aromatic sulfoxides,[2] we became quite interested in the SO bond strength of dibenzothiophene sulfoxide (**3**) and related compounds. Since the heat of formation of O atoms is well known, the sulfoxide bond dissociation energy (BDE) is accessible from the heats of formation for pairs of corresponding sulfides and sulfoxides. Though such data is available for a great number of sulfides, a literature search showed that experimental heats of formation are known for a very limited group of sulfoxides which consists only of a few simple dialkyl sulfoxides and diphenyl sulfoxide.[3] From this limited database has come the generalization that the SO bond strength is 87−90 kcal/mol.[3,4] Reliable sources of experimental and estimated thermochemical data had used these values to estimate the standard heat of formation of **3** and other unmeasured sulfoxides.[5] Nevertheless, it is clear from the literature that the bond dissociation energy of sulfur monoxides is subject to structural variation, and we had reason to believe that the SO BDE of dibenzothiophene sulfoxide is significantly weaker than those of DMSO or diphenyl sulfoxide.



Factors which appear to affect the nature and strength of the SO bond include (1) the electronegativities of X and Y, (2) the presence or absence of a conjugated unsaturation in X or Y, and (3) the aromaticity of any ring which includes the sulfur atom. The electronegativity effect is well documented for cases where X and Y are not carbon-based and can be rationalized by suggesting that a stronger bond results from electron donation from the O atom. For instance, the SO BDE of F_2SO is approximately 114 kcal/mol.[3,4] The effect of conjugation on SO bond energy is not quantified but is implied by literature IR data. Standard catalogues of IR frequencies[6] suggest that the SO stretching frequency (ordinarily about 1050 cm^{-1}) is dropped 10−20 cm^{-1} by conjugation. Lower stretching frequencies are usually taken as evidence of lower bond strengths for very similar compounds, though they are only an indirect indicator.

There are at least three indications that sulfoxides which include thiophene rings have special properties relative to other sulfoxides. In each case, the effect can be rationalized by appealing to the aromaticity of the thiophene ring and the apparent partial or complete loss of that aromaticity on oxidation to the sulfoxide. Historically, the first indication was the experimental determination[7] that chiral derivatives of thiophene sulfoxide (itself neither isolable nor chiral) racemize with distinctly lower barriers than other sulfoxides.[8−12] Intuitively, one expects the planar transition state for inversion in a thiophene sulfoxide to be preferentially stabilized by aromatic interaction of the sulfur lone pair electrons. In fact, the difference in activation energy for racemization of thiophene sulfoxides and diaryl sulfoxides approaches 20 kcal/mol. Another intriguing result was our recent finding that the dibenzothiophene sulfoxide−dibenzothiophene pair violated the otherwise consistent observation that oxidation of a sulfide to the sulfoxide *increased* the spectroscopic triplet energy.[13] (Neither thiophene nor benzothiophene derivatives were included in that study.) Finally, a restricted Hartree−Fock (RHF) *ab initio* computation with a moderate basis set[14] by Schlegel and co-workers on the isodesmic reaction (1) with thiophene sulfoxide and thiophene as the test

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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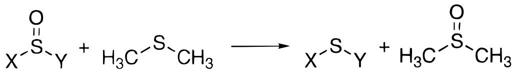
compounds indicated an SO bond strength 25.5 kcal/mol lower than that of DMSO.[15]


$$X{-}S(=O){-}Y + H_3C{-}S{-}CH_3 \longrightarrow X{-}S{-}Y + H_3C{-}S(=O){-}CH_3 \qquad (1)$$

In this paper we present the results of a computational study on a number of sulfoxides, using the isodesmic reaction (1) and others. We show that simple conjugation in fact does not significantly alter the BDE of sulfoxides. We confirm and expand substantially on Schlegel's finding that there is a dramatic effect on including the sulfur in a formally aromatic ring and show a complementary bond strengthening effect in thiirene systems. This effect derives from the strong aromatic stabilization or destabilization of the sulfide and the very much smaller stabilization/destabilization of the sulfoxide. A monotonic attenuation of the effect is observed on benzannulation of the aromatic or antiaromatic ring. We examine the calculated sulfoxide stretching frequencies, comparing bond strengths, experimental frequencies, and calculated intrinsic SO stretching frequencies. The expected gross trends are observed, but we are unable to validate a generalizable rule of thumb regarding conjugation and stretching frequencies at the relatively modest RHF/6-31G(d,p) level. Finally, we examine the energies of pseudoplanar transition states for several of the compounds as models for the inversion enthalpies.

Computational Methods

Computations were carried out using Spartan 3.1,[16] Gaussian 92,[17] and GAMESS.[18] Geometries were all fully optimized with each basis set at the RHF level, except for dibenzothiophene and dibenzothiophene sulfoxide. In those cases, geometries were optimized at RHF/3-21G-(d)[19,20] and RHF/6-31G(d)[21,22] and computations with the 6-31G(d,p) basis set were done using the RHF/6-31G(d) geometry. Stationary points were confirmed to have positive definite hessians at the RHF/3-21G(d) and RHF/6-31G(d,p) levels. All second (MP2) and fourth (MP4) order perturbation theory calculations[23−25] were done at the geometry obtained from the corresponding RHF calculation with the same basis set. For brevity, the designation for these calculations is usually compressed as below. The MP2/6-31G(d,p)//RHF/6-31G(d,p) calculation will be shown as MP2//6-31G(d,p) and others will be handled analogously. All computations using the 6-311G(d,p)[26,27] basis set were done at the RHF/6-31G-(d,p) geometry. Zero point energy corrections in Table 3 were calculated using the hessians determined at the RHF/3-21G(d) level. For nonrigid compounds, semiempirical conformation searches were used to determine starting geometries. A conformation very close to the crystal structure of methyl *p*-tolyl sulfoxide was used for the initial geometry for phenyl methyl sulfoxide.[28,29] The geometry of diphenyl sulfide was found to be C_2 and that of diphenyl sulfoxide was found to be C_S. Transition states for inversion of the sulfur center were calculated for several compounds by constraining the compounds to C_{2V} symmetry.

Intrinsic SO stretching frequencies were determined at the RHF/6-31G(d,p) level by the method of Boatz and Gordon.[30] In order to generate intrinsic frequencies that are the same for motions which are identical by symmetry, the chosen internal coordinates must both be complete and contain all the symmetry-identical incidences of a particular coordinate. However, correct intrinsic frequencies are determined for all nondegenerate vibrations with any complete set of internal coordinates. As our major interest was in the intrinsic SO stretching frequency, only the inclusion of the SO stretch in a complete set of internal coordinates was used as a criterion in its development.

Results and Discussion

The sulfoxides **1**−**13** chosen for study are illustrated in Scheme 1. The corresponding sulfides are designated by analogy with an "S" notation (*e.g.*, thiophene is **1S**). These structures were chosen to investigate several effects. The first was that of aromaticity of the sulfur-containing ring, as exemplified by thiophene sulfoxide (**1**). Benzothiophene sulfoxide (**2**) and dibenzothiophene sulfoxide (**3**) were chosen to examine any attenuation of the aromatic effect upon benzannulation, and because dibenzothiophene sulfoxide was the original molecule of interest.[2] Of these molecules, only **3** has actually been isolated and characterized. The others are too reactive for ordinary isolation. Simple alkyl substitutions on the thiophene ring of **2** are sufficient to allow isolation of its derivatives,[31,32] but quite bulky substitutions are necessary to achieve sufficient kinetic stabilization to isolate derivatives of **1**.[7] Compounds **4**−**7** were chosen to examine the effect of conjugation without aromaticity and to control for any strain effects because of ring size. These compounds are all known, and the infrared spectra of **4**−**6** are available. Thiirene oxide (**8**) was chosen to represent a situation in which the sulfur was contained in a formally antiaromatic ring, and the unknown sul-

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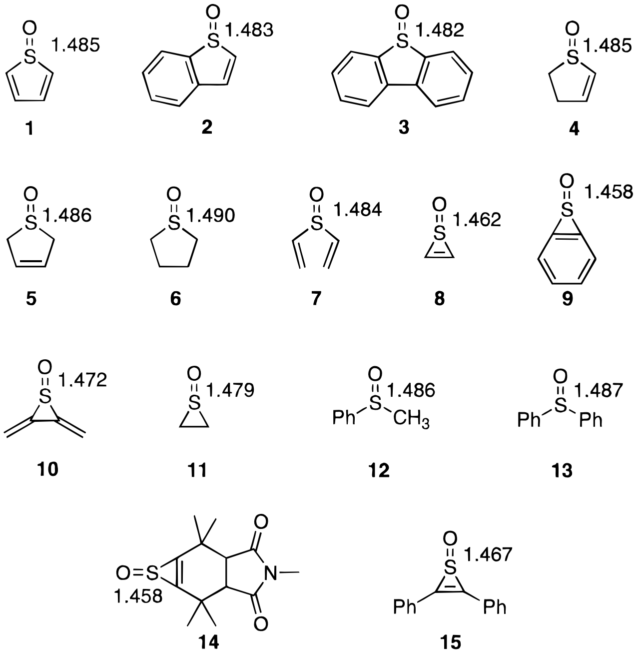
Scheme 1. Sulfoxides Used in the Study[a]



[a] Compounds **14** and **15** are the experimental models for compound **8**. Calculated SO bond lengths shown in the scheme are in angstroms. Those for **14** and **15** are from X-ray data.

foxide **9** is the formal benzannulation product, analogous to **2** and **3**. While **8** is not a known compound, compound **14** has been characterized by X-ray diffraction.[33] Diphenylthiirene sulfoxide (**15**) is also known[34] but is a poorer structural analog because of the extended conjugation. Radialene analog **10** is an additional control for the antiaromatic series. The tetramethyl derivative of **10** is a known, reasonably stable compound.[35] Thiirane oxide (**11**) was chosen as a control for the effects of the decidedly constrained geometry of a three-membered ring and because it is a well-characterized compound whose structure is known from microwave data.[36,37] Phenyl methyl sulfoxide (**12**) is a well known compound whose IR is available. It is another example of a simply conjugated system, and a crystal structure is known for the closely related *p*-tolyl methyl sulfoxide.[29] Diphenyl sulfoxide is the archetypal diaryl sulfoxide and also serves as a control for measuring effects on **3**. In addition, it is another compound whose SO bond energy is known. Of the sulfides, only **9S** is unknown, but **8S** is only very short lived, even in the gas phase.[38]

Computed and Experimental Geometries. Geometries were fully optimized for each of the structures **1**−**13** at the RHF level of theory using 3-21G(d), 6-31G(d), and 6-31G(d,p) basis sets. Several key geometrical parameters for the sulfoxides are presented in Table 1. An experimental crystal structure of methyl *p*-tolyl sulfoxide is available for comparison to **12**,[29] and microwave structures are available for DMSO[39] and **11**.[36,37] A crystal structure of **14** is available for comparison to the calculated geometry of **8**.[33] A partial structure of **13** is available from electron diffraction data.[40] Full calculated Cartesian geometries of all sulfides and sulfoxides are available as part of the supporting information. A salient observation which is not available from the table is that the sulfur atom in compounds **1**, **2**, and **3** resides slightly below the plane defined by the other atoms in the thiophene ring, with the O atom substantially above the plane.

As can be seen from Table 1, there are some significant differences (*e.g.*, up to 0.01 Å in bond length or 2.5° in angles) between the geometries obtained with 3-21G(d) and the two bases 6-31G(d) and 6-31G(d,p). However, the geometries calculated at RHF/6-31G(d,p) compare quite favorably to the experimental geometries of DMSO, **8** (**14**), **11**, and **12** (methyl *p*-tolyl sulfoxide). The largest bond length deviation is 0.007 Å. Aside from ∠CSC for DMSO (deviation = 1.2°), the largest angular deviation from experimental values is 0.6°. Given the size and number of molecules, use of larger basis sets to reach the RHF geometry limit was not considered practical, particularly in light of the good agreement with experiment. In Table 2 are selected geometrical parameters for the corresponding sulfides, calculated at the RHF/6-31G(d,p) level. Satisfactory agreement between experimental and calculated parameters has been obtained, with worst case deviations of 0.019 Å and 1.1°. These deviations are for dibenzothiophene (**3S**), for which the experimental uncertainty is ±0.01 Å. It should also be noted that the deviations from experiment for **1S** and **3S** are in the same direction and the trends are correctly followed.

Some interesting trends can be extracted from the geometry data. The first is actually the lack of a trend as can be seen in Figure 1, where the RHF/6-31G(d,p) SO bond lengths are plotted with 0.01 Å error bars. Only compounds **8** and **9** vary significantly from the others. These are the compounds in which the sulfur is contained in a formally antiaromatic ring and they sport a shortened SO bond. Computed values of 1.462 and 1.458 Å are well out of the normal range of about 1.48−1.49 Å. The calculated SO length of **8** well reproduces the experimental value of **14**, suggesting that these are not mere computational artifacts. Two control structures, **10** and **11**, show that the bond shortening is not simply the result of the three-membered ring, though the SO bond length of thiirane oxide (**11**) is on the short edge of the normal range at 1.479 Å. The SO length of **10** is slightly shorter still, at 1.472 Å. The ring atoms in **10** are of very similar hybridization to **8** and **9**, and given the results for **10** and **11**, perhaps about 0.01 Å (about half) of the

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[42] Experimental parameters refer to **14**, not **8**.

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Table 1. Calculated (RHF) and Experimental Geometrical Parameters of DMSO and Sulfoxides 1−13[a]

molecule	basis	r(SO)	$r(C_1S)$	$r(C_2S)$	$\angle C_1SO$	$\angle C_2SO$	$\angle$CSC	Θ
DMSO	3-21G(d)	1.490	1.791	1.791	107.8	107.8	96.6	62.7
	6-31G(d)	1.485	1.796	1.796	106.7	106.7	97.7	64.1
	6-31G(d,p)	1.485	1.795	1.795	106.7	106.7	97.8	64.1
	6-311G(d,p)[41]	1.483	1.796	1.796	106.4	106.4	98.1	64.4
	expt.[39]	1.485	1.799	1.799	106.7	106.7	96.6	64.9
1	3-21G(d)	1.492	1.763	1.763	115.0	115.0	90.0	53.3
	6-31G(d)	1.483	1.770	1.770	113.4	113.4	90.1	55.8
	6-31G(d,p)	1.483	1.770	1.770	113.4	113.4	90.1	55.7
2[b]	3-21G(d)	1.490	1.772	1.776	113.5	113.4	89.4	56.0
	6-31G(d)	1.483	1.780	1.784	112.1	111.9	89.5	58.1
	6-31G(d,p)	1.483	1.779	1.784	112.1	111.9	89.5	58.1
3	3-21G(d)	1.488	1.778	1.778	112.8	112.8	89.3	56.9
	6-31G(d)	1.482	1.787	1.787	111.5	111.5	89.3	59.0
4[c]	3-21G(d)	1.489	1.775	1.817	110.2	109.9	89.5	61.1
	6-31G(d)	1.485	1.781	1.818	108.6	108.9	89.6	63.1
	6-31G(d,p)	1.485	1.781	1.817	108.6	108.9	89.6	63.1
5	3-21G(d)	1.490	1.819	1.819	108.1	108.1	91.5	63.5
	6-31G(d)	1.486	1.821	1.821	107.0	107.0	91.9	65.1
	6-31G(d,p)	1.486	1.820	1.820	107.0	107.0	92.0	65.1
6	3-21G(d)	1.494	1.811	1.798	107.1	105.9	90.2	66.2
	6-31G(d)	1.490	1.824	1.807	106.4	106.1	91.2	66.4
	6-31G(d,p)	1.490	1.824	1.806	106.4	106.1	91.3	66.4
7	3-21G(d)	1.494	1.769	1.769	106.7	106.7	97.0	64.2
	6-31G(d)	1.484	1.780	1.780	107.6	107.6	97.6	62.7
	6-31G(d,p)	1.484	1.780	1.780	107.5	107.5	97.6	62.8
8	3-21G(d)	1.463	1.775	1.775	116.7	116.7	42.8	61.2
	6-31G(d)	1.462	1.765	1.765	114.8	114.8	42.7	63.3
	6-31G(d,p)	1.462	1.764	1.764	114.8	114.8	42.7	63.3
	expt[33,42]	1.458	1.772	1.772	114.2	114.2	42.8	63.9
9	3-21G(d)	1.449	1.711	1.711	113.7	113.7	48.7	63.8
	6-31G(d)	1.457	1.768	1.768	115.6	115.6	44.2	62.2
	6-31G(d,p)	1.458	1.768	1.768	115.6	115.6	44.2	62.2
10	3-21G(d)	1.476	1.775	1.775	117.7	117.7	47.5	59.5
	6-31G(d)	1.472	1.784	1.784	115.3	115.3	46.8	62.3
	6-31G(d,p)	1.472	1.784	1.784	115.3	115.3	46.8	62.3
11	3-21G(d)	1.482	1.785	1.785	113.5	113.5	50.2	63.9
	6-31G(d)	1.479	1.795	1.795	111.3	111.3	49.0	66.5
	6-31G(d,p)	1.479	1.794	1.794	111.3	111.3	49.0	66.5
	expt[36,37]	1.478	1.822	1.822	111.0	111.0	48.8	67.3
12[d]	3-21G(d)	1.494	1.792	1.778	106.3	106.3	97.0	64.6
	6-31G(d)	1.486	1.799	1.792	105.8	107.2	98.1	64.3
	6-31G(d,p)	1.486	1.798	1.792	105.8	107.1	98.2	64.3
	expt[29,43]	1.493	1.796	1.797	105.5	106.5	97.6	65.5
13	3-21G(d)	1.497	1.782	1.782	105.4	105.4	98.6	65.9
	6-31G(d)	1.487	1.796	1.796	106.2	106.2	99.5	64.4
	6-31G(d,p)	1.487	1.796	1.796	106.1	106.1	99.5	64.5
	expt[40]	1.489	1.804	1.804				

[a] The angle Θ is between the SO bond vector and the plane defined by the two CS bonds. All distances are in angstroms and all angles in degrees. [b] C_1 is the one not in the benzene ring. [c] C_1 is the unsaturated one. [d] C_1 is the methyl group.

shortening in **8** and **9** can be attributed to "simple" geometry effects deriving from the acute CSC angle. Experimentally, it is known that all of the bond lengths in the thiirene ring are shorter for **14** than for **15**.[33] This was attributed to delocalization of the double bond throughout the extended π-system in the latter compound. Also shorter in **14** than **15** is the SO bond. Given the delocalization of the π-system of **15**, it can safely be concluded that the shortening of the SO bond in derivatives of **8** is directly related to the π-electronic system of the ring.

Based on the naïve assumption that if there is to be an effect of aromaticity on these structures, it should be of the opposite sign for structures such as **1** and **8**, one might expect that the SO bond length of **1** would be longer than the rest of the "neutral" compounds. This is not observed, though other such complementary effects are found (*vide infra*).

An additional interesting structural feature of the sulfoxide series is illustrated in Figure 1. We define the angle Θ as that made between the SO bond vector and the CSC plane. Thus the value of Θ for a perfect

Table 2. CS Bond Lengths and ∠CSC Values Calculated at the RHF/6-31G(d,p) Level. Also Included Are Experimental Values Where Available[a]

molecule	$r(C_1S)$	$r(C_2S)$	$\angle$CSC
Me_2S	1.808	1.808	101.2
1S	1.725	1.725	91.3
1S (expt)[44]	1.714	1.714	92.1
2S	1.743	1.749	90.8
3S	1.759	1.759	90.4
3S (expt)[45]	1.740	1.740	91.5
4S	1.770	1.831	90.4
5S	1.829	1.829	94.6
6S	1.831	1.831	94.2
6S (expt)[46]	1.839	1.839	93.4
7S	1.767	1.767	102.6
8S	1.840	1.840	39.9
9S	1.791	1.791	43.7
10S	1.775	1.775	46.9
11S	1.811	1.811	48.0
11S (expt)[47,48]	1.815	1.815	48.3
12S	1.815	1.787	101.0
13S	1.789	1.789	102.7
13S (expt)[49]	1.771	1.771	103.7

[a] See Table 1 for identification of C_1 and C_2. All distances in angstroms and all angles in degrees.

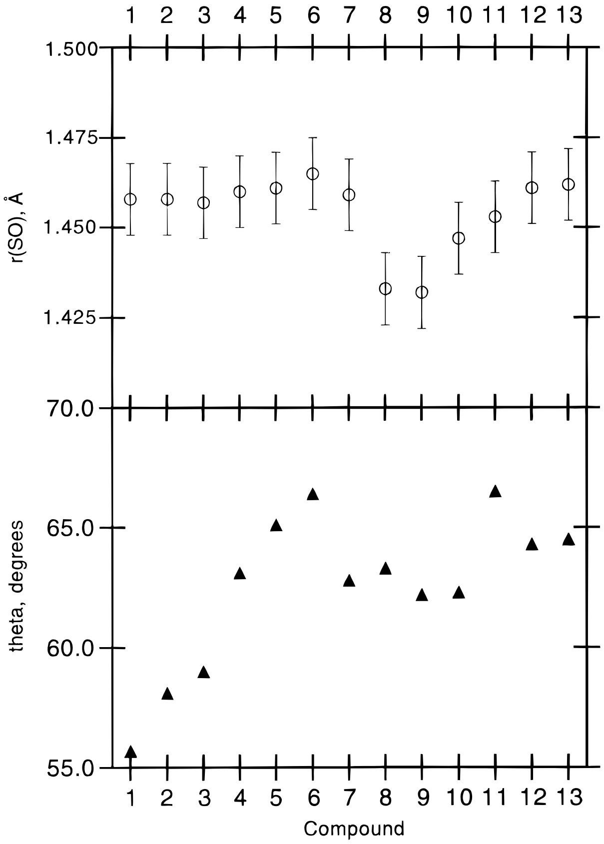

Figure 1. Calculated geometrical parameters of the sulfoxides. All parameters taken from RHF/6-31G(d,p) computations, except for **3**, where they are from RHF/6-31G(d).

tetrahedral center is 60°. A modest but clear trend is seen for compounds **1**−**3**. Given the absence of any significant differences in steric demand on the O atom for compounds **1**−**3**, the explanation for any trend must be electronic. Compounds **1**−**3** have $\Theta < 60°$, with a gradual increase in angle with benzannulation. All of the other conjugated sulfoxides, including **8** and **9**, lie in the region of 62−64°. All of the unconjugated ones have $\Theta > 64°$.

That aromaticity is significant to the structures of **1**−**3**, **7**−**10**, and particularly the corresponding sulfides and that benzannulation attenuates some of the effects are clear from a more detailed examination of the geometries. Structural distortions are observed which indicate avoidance of antiaromatic interactions and enhancement of aromatic ones. The expectation in such cases is that bond lengths around a ring will tend toward equality for aromatic systems (*e.g.*, benzene) and tend toward inequality in formally antiaromatic systems (*e.g.*, cyclobutadiene).

Consider, for instance, the CS bond length in the aromatic and antiaromatic sulfides, illustrated in Figure 2. The unusually long CS bond length calculated for **8S** (1.840 Å) can be considered analogous to the well known rectangular distortion in cyclobutadiene.[50] The corresponding bond length in **9S** is 1.791 Å, significantly attenuated by benzannulation, but still quite a bit longer than the control values of 1.767 Å for **7S** and 1.775 Å for **10S**. The trend is reversed for sulfides **1S**, **2S**, and **3S**, where shortening of the CS bond length corresponds to delocalization and aromatization. The experimental CS bond lengths for **1S** and **2S**, it should be noted, are 0.01 and 0.02 Å shorter than the calculated lengths but are still consistent with the trend we are pointing out. No experimental values are available for **7S** or **10S**, so it quite possible that all the CS bond lengths are slightly overestimated. For sulfoxides **1**−**3**, delocalization appears also to be the trend but to a much more limited extent. The calculated CS bond lengths for **8** and **9** are virtually identical. The difference in CS bond length for a given skeleton ($r_{\text{sulfide}} - r_{\text{sulfoxide}}$, see Figure 2) is slightly negative for the skeletons whose sulfides are nonaromatic, more negative for the aromatic sulfides, and positive for the formally antiaromatic sulfide skeletons.

The trends in the C_3−C_4 bond length in the five-membered rings of skeletons **1**−**3** is also indicative of the extent of delocalization in the system, where a shorter bond indicates increased delocalization. Figure 3 illustrates the calculated bond lengths for the sulfides and sulfoxides, using cyclopentadiene as a benchmark. The most consequential flaw of cyclopentadiene as a standard for comparison derives from the inherently longer CS bond of the other compounds, which may distort the rest of the ring. Nonetheless, we note that the computed geometries of the cyclopentadiene system show a slight bond contraction on benzannulation (indene, fluorene), and no significant variation is observed in the sulfoxides series. By contrast, the thiophene system shows a marked bond elongation on benzannulation, consistent with diminishing aromaticity in the thiophene ring. Also, the absolute bond lengths for the thiophene skeletons are the lowest among the three at each level of benzannulation. The experimental values for dibenzothiophene and fluorene suggest the computed geometries may underestimate the difference. The minimal variation of the C_3−C_4 bond length among the sulfoxides is consistent with a substantial loss in aromaticity, relative to the sulfides, which is supported by other findings discussed below.

Energies and Bond Strengths. In Table 3 are shown the bond strengths derived from the isodesmic reaction (1). These are based on the experimental bond dissociation energy of DMSO or diphenyl sulfoxide (**13**), the calculated electronic energies of the test compounds, and the calculated zero point energy differences. The SO bond energies of DMSO and **13** are based on the known heats of formation of DMSO, dimethyl sulfide, **13**, **13S**, and O(^{3}P), yielding a value of 86.8 kcal/mol for DMSO and 89.4 kcal/mol for **13**.

As expected, very little difference is observed between values calculated with 6-31G(d) and 6-31G(d,p) basis sets. In many cases, there is little difference between these and the 3-21G(d) values, as well, but the larger basis set has a significant effect for **3**, **7**, **9**, **10**, and **12**. Inclusion of the MP2 approximation of the correlation energy is significant ($\Delta E \geq 1.5$ kcal/mol) particularly for **1**−**3**, **8**, and **9**. Perhaps not surprisingly, the effect is to *lower* the bond strength in the "aromatic" series of **1**−**3** and to *raise* the bond strength in the "antiaromatic" series of **8** and **9**.

In order to check how close these results are to the HF limit, computations were done with the 6-311G(d,p) basis set in three cases. Practical considerations limited the extension of this basis across the whole series. Bond dissociation energies obtained at the RHF/6-311G(d,p)//RHF/6-31G(d,p) level are within 2.1 kcal/mol of those obtained at RHF/6-31G(d,p), with no particular pattern

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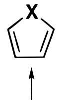
[50] The CS bond lengths for the **11** skeleton are also of interest, and the issue has been reviewed in reference 47.

[51] Brown, G. M.; Bortner, M. H. *Acta Crystallogr.* **1954**, *7*, 139.

skeleton	1	2	3	7	8	9	10
X = S	1.725	1.746	1.759	1.767	1.840	1.791	1.775
X = SO	1.770	1.782	1.787	1.780	1.772	1.768	1.784
difference	−0.045	−0.036	−0.028	−0.013	+0.068	+0.023	−0.009

Figure 2. Calculated CS bond lengths. All values are in angstroms.



skeleton	$X = CH_2$	X = S	X = SO
1	1.476	1.436 (1.42)	1.473
2	1.473	1.450	1.472
3	1.468 (1.50)	1.461 (1.44)	1.476

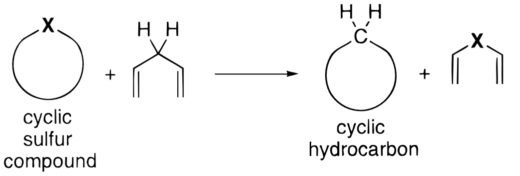
Figure 3. Calculated RHF/6-31G(d,p) and experimental CC bond lengths. Experimental values have reported errors of ±0.01 Å.[44,45,51]

observed. Corrections at the MP4 level are all within 2.5 kcal/mol of the MP2 calculations. Though the MP2//6-31G(d,p) data have apparently not quite converged, they are probably within a few kcal/mol of the ultimate values, and we believe that trends are probably quite reliable. One further proviso must be made for the flexible molecules; *ab initio* calculations were made based on semiempirical conformational searches. It is conceivable that there might be conformations of one or more of these molecules which are 1 or 2 kcal/mol lower than those used here.

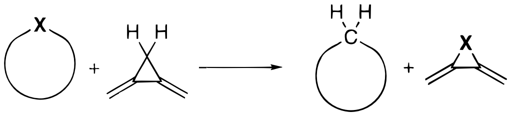
A reasonable test of the calculations is the prediction of the BDE of diphenyl sulfoxide, **13**. As can be seen from Table 3, the prediction based on DMSO and the MP2//6-31G(d,p) calculations is about 4 kcal/mol lower than the value of 89.4 kcal/mol obtained from experimental heats of formation. Because of this discrepancy, the values are also tabulated using **13** as a standard.

The BDEs calculated at the MP2//6-31G(d,p) and MP4/6-311G(d,p)//RHF/6-31G(d,p) levels are plotted in Figure 4. Clearly, the values for compounds **4**−**7** and **11**−**13** cannot be distinguished, especially considering reasonable error limits. These data are sufficient to conclude that simple conjugation of the sulfoxide to an unsaturation is not sufficient to significantly affect SO bond dissociation energy. Also, the effect of the severe geometry of a three-membered ring is apparently about equal for sulfides and sulfoxides, yielding an unaffected BDE.

Significant effects are clearly observed for compounds **1**−**3**, **8**, and **9**. The simplest explanation for this observation, especially given the geometric results already discussed, is that the (anti)aromaticity of the sulfides **1S**, **2S**, **3S**, **8S**, and **9S** is disrupted by oxidation of the sulfur. That is, if the sulfoxide is significantly less (anti)aromatic than the sulfide, then the SO bond strength is decreased (increased). However, in an older semiempirical and *ab initio* publication which considered several cyclopropene-like compounds (cyclopropene, cyclopropenone, etc.) it was concluded that **8** was a slightly *aromatic* system, on the basis of computations which isolated the C═C double bond from the third vertex of the ring.[52] As many authors have argued that the second sulfoxidic bond is ionic and dipole moments demonstrate significant positive charge at sulfur, we must also consider the possibility that **1** is slightly antiaromatic, by analogy to calling **8** slightly aromatic.



(2a)



(2b)

The bond dissociation data inherently show that **1**−**3** are less stabilized by aromatic interactions than are the corresponding sulfides; it is also clear that **8** and **9** are less *de*stabilized than their sulfide analogs. However, circumstantial evidence as to whether there is any residual aromatic stabilization (or antiaromatic destabilization) can be derived the isodesmic reactions shown in eqs 2a and 2b. These compare the energy of, for instance, thiophene and 1,4-pentadiene to that of cyclopentadiene and divinyl sulfide. The cyclic hydrocarbons for **1**, **2**, **3**, **8**, and **9** are cyclopentadiene, indene, fluorene, cyclopropene, and cyclopropabenzene, respectively. If the assumption is made that cyclopentadiene-like and cyclopropene-like structures are not subject to significant aromatic stabilization (or destabilization) in the ring of interest, then the heat of this reaction largely reflects the stabilization of the sulfur containing ring and differences in strain energy.

Figure 5 presents the results for the series **1**−**3** and **1S**−**3S**. We can make the assumption that the strain energy reflected in reaction 2a for these compounds is a constant across each series and represents only an offset of a few kcal/mol. Thus the *trend* of the energies across the series is bound to reflect primarily the difference in aromatic stabilization. As is reasonably expected, the aromatic stabilization across the thiophene series drops with benzannulation by about 6 kcal/mol for each benzo group. By contrast, the total energy difference for reaction 2a with **1** and **3** is only 1.2 kcal/mol, which is certainly within any reasonable estimate of present error limits of being identical. Evidently the sulfoxides cannot be classified as either strongly aromatic or antiaromatic.

A very recent paper by Schleyer and co-workers evaluated the aromatic stabilization energy of a series of C_4H_4X compounds.[53] By means of eq 3, they found aromatic stabilization energies of −56.7, 3.7, 22.4, and 28.8 kcal/mol for $C_5H_5^+$, C_5H_6, thiophene, and $C_5H_5^-$, respectively, at the MP2/6-31G(d) level. At the MP2//6-31G(d,p) level,

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(52) Hase, H.-L.; Müller, C.; Schweig, A. *Tetrahedron* **1974**, *34*, 2983−2993.

(53) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337−340.

Table 3. Calculated Sulfoxide Bond Strengths

method	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**[c]
RHF/3-21G(d)	66.4	73.7	78.4	85.6	85.0	86.8	90.0	100.6	97.7	81.0	82.8	90.0	91.6
	(64.3)	(71.5)	(76.3)	(83.5)	(82.8)	(84.6)	(87.7)	(98.4)	(95.5)	(78.9)	(80.7)	(87.9)	(89.4)
MP2//3-21G(d)	64.9	72.3	77.8	85.0	85.5	86.7	89.5	103.8	101.4	82.7	84.8	89.8	91.1
	(63.1)	(70.6)	(76.1)	(83.3)	(83.7)	(84.9)	(87.6)	(102.0)	(99.7)	(81.0)	(82.9)	(88.0)	(89.4)
RHF/6-31G(d)	66.2	72.5	76.3	85.2	845	85.6	85.9	101.4	95.7	78.3	82.1	87.1	85.7
	(69.9)	(76.1)	(80.0)	(88.9)	(88.1)	(89.3)	(89.3)	(104.7)	(99.3)	(82.0)	(85.8)	(90.8)	(89.4)
MP2//6-31G(d)	60.9	68.7	74.3	84.1	84.9	85.7	84.9	104.2	97.7	78.9	83.8	87.2	85.3
	(65.0)	(72.9)	(78.4)	(88.2)	(89.0)	(89.9)	(88.8)	(108.4)	(101.8)	(83.0)	(87.9)	(91.3)	(89.4)
RHF/6-31G(d,p)[b]	66.1	72.3	76.2	85.1	83.6	85.6	85.9	100.9	93.4	78.1	82.1	87.1	85.7
	(69.7)	(76.0)	(79.8)	(88.8)	(87.2)	(89.2)	(89.3)	(104.6)	(97.1)	(81.8)	(85.7)	(90.8)	(89.4)
MP2//6-31G(d,p)[b]	60.9	68.8	74.4	84.0	84.8	85.7	85.0	104.7	97.9	79.0	83.8	87.3	85.5
	(64.8)	(72.2)	(78.3)	(87.9)	(88.7)	(89.5)	(88.7)	(108.6)	(101.8)	(82.9)	(87.7)	(91.2)	(89.4)
MP4//6-31G(d,p)	63.3							104.3			84.6		
RHF/6-311G(d,p)[c]	64.0							99.7			82.2		
MP2/6-311G(d,p)[c]	58.1							106.2			86.5		
MP4/6-311G(d,p)[c]	60.6							106.1			87.3		

[a] All energies are in kcal/mol. Values without parentheses are based on DMSO; those in parentheses are based on diphenyl sulfoxide (**13**). Zero point energy corrections are included. The value of 86.8 kcal/mol was used for the bond strength of DMSO. The value of 89.4 kcal/mol was used for diphenyl sulfoxide. [b] Calculation performed at RHF/6-31G(d) geometry. [c] Single point energy calculations at the RHF/6-31G(d,p) geometry. [d] 89.4 kcal/mol is the experimental bond strength.

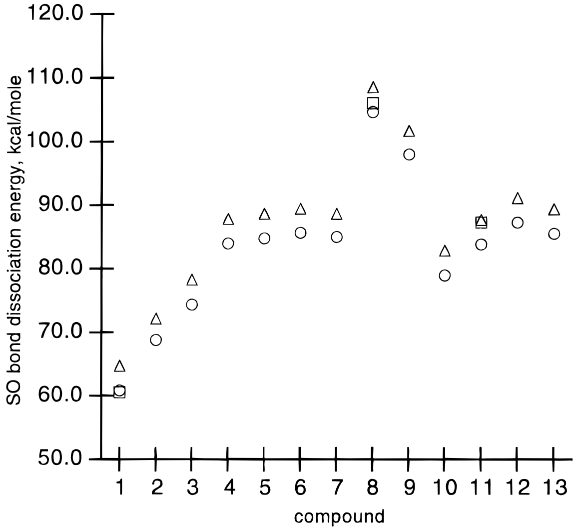
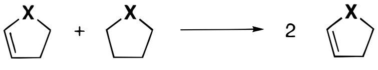


Figure 4. Calculated SO bond dissociation energies. Circles and triangles are MP2/6-31G(d,p)//RHF/6-31G(d,p) values, based on DMSO and **13**, respectively. Squares are MP4/6-311G(d,p)//RHF/6-31G(d,p) values based on DMSO.

we find 23.1 and 2.2 kcal/mol for thiophene and thiophene sulfoxide, respectively. Thus, a crude, but perhaps useful, analogy for the aromaticity can be made between the cyclopentadienide/cyclopentadiene pair and thiophene/thiophene sulfoxide.



(3)

A treatment of the **8** and **9** skeletons along the lines of Figure 5 is shown in Figure 6. A qualitative estimate of the strain component of reaction 2a was made by a study of reaction 4, which yields 13 and 10 kcal/mol more strain in the carbocycle than the heterocycle when X = S and SO, respectively. Because of the large strain offset apparent when using 1,4-pentadiene as the reacting hydrocarbon in reaction 2a, reaction 2b was also calculated, on the assumption that this would minimize the strain offset. Though this was not entirely successful, the striking parallel between the results for reactions 2a and 2b is excellent corroboration that the energies of **10** and **10S** are also not strongly influenced by aromatic interactions, and verifies their use as controls in the geometry study in Figure 2. In both reaction 2a and 2b, the energy difference between **8S** and **9S** is 7.5 kcal/mol, with less destabilization in the benzannulated sulfide. Like the **1**−**3** series, the difference in energy for reactions 2a and 2b are quite small for **8** and **9**, both under 1 kcal/mol.

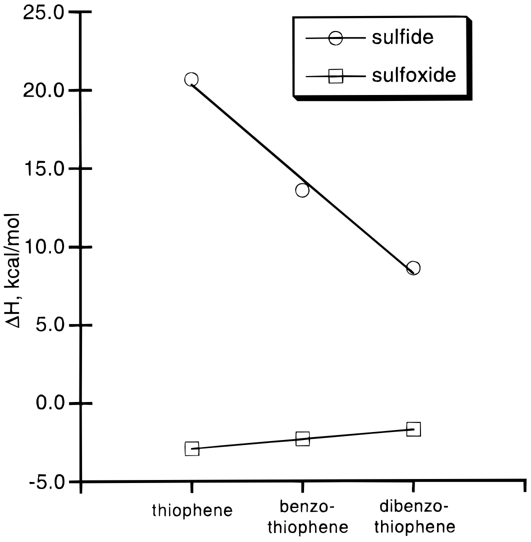
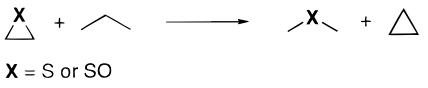


Figure 5. Heats of reaction for reaction 2a, calculated at MP2//6-31G(d,p) level.



(4)

Though not an aromaticity effect, the SO BDE of **10** also appears to be lower than that of the "ordinary" sulfoxides. Thiirane sulfoxide (**11**), the other small ring compound, also has a BDE on the low end of the main group. One may expect, then, that some SO bond weakening can be associated with differential strain for small ring sulfides and sulfoxides. A comparison of **7** and **10** sheds light on this issue. This is equivalent to running **10** and **10S** through reaction 2a. If we take the previous suggestion that neither **10** nor **10S** is significantly affected by aromaticity to be correct, this comparison confirms that the differential strain is responsible for the bond strength depression of **10**.

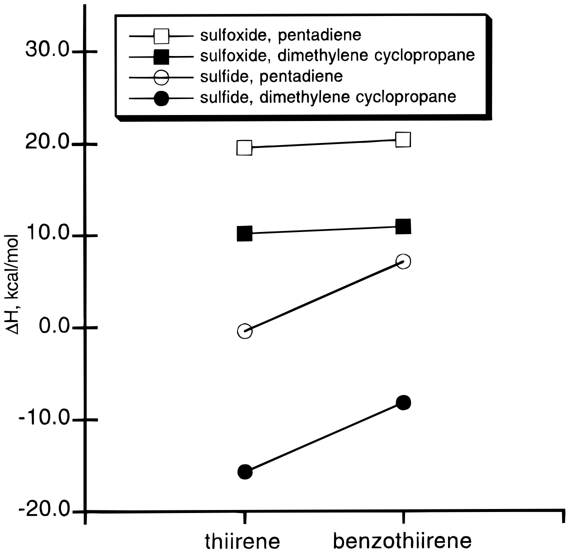


Figure 6. Heats of reaction for reaction 2a and 2b, calculated at MP2/6-31G(d,p) level.

SO Stretching Frequencies and IR Spectra. Nakanishi lists the characteristic sulfoxide stretching frequency as 1040−1060 cm^{-1}.[54] His text says that the stretch is dropped by 10−20 cm^{-1} upon conjugation or hydrogen bonding. Large environmental shifts are also observed—20 cm^{-1} lower in CCl_4 than in $CHCl_3$.[54] *The Chemist's Companion*[6] agrees with the range stated by Nakanishi, but points out that DMSO is out of the range at 1070 cm^{-1}. An examination of the spectra in the Aldrich collection[55] puts DMSO at 1057 cm^{-1} neat and 1102 cm^{-1} in the gas phase. Because of the unusually large environmental effects on the SO stretch, correlation of calculated and experimental frequencies is best done with gas phase data. However, given the high polarity of the sulfoxides, very little gas phase data actually exist. Thus we report spectra taken under neat or pseudoneat (KBr, Nujol) conditions. The experimental data appear to suggest that any 10−20 cm^{-1} shift on conjugation can easily be buried by other effects. For many compounds, even simple sulfoxides, more than one strong band is present in the 1000 to 1100 cm^{-1} range. Cairns *et al.* have examined this problem[56] and found that Fermi resonance between the sulfoxide stretch and other, sometimes unidentified, vibrations mix and shift the bands. Normal modes of vibration, calculated at RHF/6-31G(d,p) and visualized using the utility in Spartan, also showed significant coupling to other motions in several instances.

In order to search for correlations within the computations, the intrinsic SO stretching frequencies[30] were extracted from the hessian data calculated at the RHF/6-31G(d,p) level, also shown in Table 4. These values represent the predicted frequency of the SO stretch when completely decoupled from other molecular motions. As can be seen in Table 4, the calculated intrinsic frequencies correlate only grossly with calculated bond strength. The values for **8** and **9** are the largest, by about 60 cm^{-1}, and these are the compounds with the strongest SO bonds. However, though a stepwise increment in frequency is observed for the **1**−**3** series, as would be expected from the bond strengths of those compounds, all three frequencies are in the range defined by compound **4**−**7** and **10**−**13**. Though the experimental frequencies and the calculated intrinsic frequencies are not directly comparable, it is at least comforting to note that a similar pattern is observed. Among these compounds (or their closely related analogs) whose IR spectra are known, **8** is the one with the highest SO stretching frequency, while **2** and **3** are well within the pack.

Table 4. SO Stretching Frequencies[h]

sulfoxide	exptl freq[55−59a]	calcd intrinsic freq	calcd freq scaled by 0.89	calcd bond strength, RHF/6-31G(d,p)
DMSO	1065, ∼1020sh	1142	1016	
1		1130	1005	66.1
2	1025, 1065[b,c]	1137	1012	72.3
3	1026, 1072[c]	1146	1021	76.2
4	1020[d]	1144	1018	85.1
5	1020[d]	1137	1012	83.6
6	1021, 1095	1143	1017	85.6
7		1141	1015	85.9
8	1115[d,e]	1240	1104	100.9
9		1248	1111	93.4
10	1035[d,f]	1176	1046	78.1
11	1060[d,g]	1155	1028	82.1
12	1050, ∼1085, ∼1060	1137	1012	87.1
13	1037, 1088, ∼1020	1125	1001	85.7

[a] High intensity bands in 1000−1100 cm^{-1} region, all under neat or pseudoneat conditions listed from high intensity to low intensity. [b] 2-Methylbenzothiophene *S*-oxide. [c] Spectra from this laboratory. [d] Only band cited. [e] Compound **14**.[33] [f] Tetramethyl derivative, in $CDCl_3$.[35] [g] IR conditions not reported. [h] All frequencies are in cm^{-1}. All energies are in kcal/mol. Frequencies are calculated at RHF/6-31G(d,p) level, except for **3**, calculated at RHF/6-31G(d).

Given the data at hand, it cannot be concluded that there exists an experimentally verifiable correlation between conjugation of a sulfoxide and the SO stretching frequency. Whether this is simply an artifact of other, unpredictable molecular motions mixed into the normal modes and/or Fermi resonances cannot be determined without a much more extensive analysis, which must certainly use gas phase data. However, even the calculated RHF/6-31G(d,p) intrinsic frequencies, which are attempts to simulate the gas phase unperturbed stretch, do not show any correlation with bond strength.

Inversion Barriers. The experimental activation energies for pyramidal inversion of several sulfoxides are known.[9,11,12] Values for several aryl alkyl and diaryl sulfoxides are in the range of 36−38 kcal/mol, while adamantyl tosyl sulfoxide has a value of 43 kcal/mol. Also known is the inversion barrier for a dialkyl derivative of **1**; it is 15 kcal/mol.[7] Except in cases where alternate, lower energy bond-breaking pathways exist, it is assumed that thermal inversion of a sulfoxide center goes through a pseudoplanar transition state (planar at sulfur). Effects on the energy of the transition state for this conversion are relatively complex, particularly for cyclic systems, since the ideal C−S−C bond angle is significantly different for the pyramidal and planar geometries.

As models for this process, sulfur inversion structures were calculated for compounds **1**−**3**, **7**−**11**, **13**, and DMSO (Table 5). Genuine transition states (one imaginary frequency) were found for all but **8**, **9**, and **13**. The C_{2V} structure for **8** had CS lengths > 3 Å and a linear

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Table 5. Calculated Inversion Barriers and Selected Geometrical Parameters of the Transition States

compound	inversion barrier[a]	r(SO)[b]	r(CS)	∠CSC
DMSO	50.4	1.535	1.794	117.0
1	11.2	1.470	1.665	98.2
2[c]	23.9	1.494	1.693	97.2
3[d]	32.3	1.506	1.714	97.1
7	40.0	1.510	1.693	115.2
8[e]	31.8	–	–	–
9[e]	98.6	–	–	–
10	54.2	1.509	1.694	53.5
11	76.6	1.581	1.731	54.5
13[f]	43.7	1.522	1.757	118.1

[a] Calculated from the ground state energy and the energy of the C_{2V} transition state at the MP2//6-31G(d,p) level. ZPE corrections, calculated at RHF/6-31G(d,p), are included. [b] Geometrical parameters of the transition states. All lengths are in angstroms and all angles in degrees. [c] Transition state is C_S, not C_{2V}. [d] Calculated at MP2//6-31G(d) level. [e] Only a second order saddle point was found at C_{2V} symmetry. These are the energies of those second order transition states. [f] A C_2-symmetric second-order saddle point. See text for discussion.

H−C−C−H geometry, clearly showing it had decomposed to acetylene and SO, though the complex is a second order transition state in that symmetry. The C_{2V} structure for **9** had more ordinary looking bond lengths, but was also a second order saddle point. A second-order saddle point was also obtained for **13** in C_2 symmetry. A large imaginary frequency corresponded to the sulfur inversion, but a small one (*ca.* 25 cm^{-1} corresponded to disrotatory motion of the phenyl rings. However, exploration in that region of conformation space in C_1 symmetry showed the potential energy surface to be rather flat with respect to such rotations (<0.1 kcal/mol), and it was difficult to determine a true transition state. Therefore, the C_2 second-order saddle point was reluctantly accepted.

The calculated inversion barrier for DMSO (MP2//6-31G(d,p)) is 50.4 kcal/mol, and the CSC bond angle has opened up to 117° from 98° in the C_S ground state. The other acyclic cases, divinyl sulfoxide **7**, and diphenyl sulfoxide **13**, have significantly lower inversion barriers of 40.0 and 43.7 kcal/mol, respectively. Evidently, this is another place where conjugation *is* significant to physical parameters of the sulfoxide. The computed value for **13** is comparable to but significantly higher than the experimentally observed activation energy of 37.2 kcal/mol for phenyl tolyl sulfoxide.[12] The higher inversion barriers for **10** and **11** are attributed to the additional ring strain induced in the transition state.

In the thiophene sulfoxide series, inversion energies of 11.2, 23.9, and 32.3 are calculated for compounds **1**, **2**, and **3**. The value for thiophene sulfoxide compares favorably with the experimental activation energy[7] of 14.8 kcal/mol for a dialkylated derivative. Consistent with the notion that the sulfoxides in their most stable configuration are not aromatic, we attribute the lower inversion barriers to aromatic stabilization of the planar transition states. The stabilization energy falls off with benzannulation, just as is observed for **1S**, **2S**, and **3S**.

Summary

A computational study of the effects of conjugation and aromaticity on the bond dissociation energies and geometries of a number of sulfoxides has been reported. Bond dissociation energies were calculated at the MP2/6-31G-(d,p)//RHF/6-31G(d,p) level using an isodesmic oxygen atom transfer reaction with DMSO, whose SO BDE can be obtained from experimental heats of formation.

The data so obtained show that the sulfoxidic BDE is not particularly sensitive to unsaturated substitutions. However, if the corresponding sulfide is aromatic, then the BDE is dropped dramatically. The sulfoxidic BDE for thiophene sulfoxide, for instance, is estimated to lie in the range of 61−65 kcal/mol, compared to 87 kcal/mol for DMSO and 89 kcal/mol for diphenyl sulfoxide. Benzannulation of the thiophene ring moderates the effect (strengthens the SO bond). Complementarily, the sulfoxidic BDE in thiirene sulfoxide is estimated to be in the range of 104 to 109 kcal/mol. In this case, the corresponding sulfide suffers from antiaromatic interactions. The hypothetical benzannulated molecule **9** is estimated to have an SO BDE of about 102 kcal/mol. Analysis of CS bond-length trends and other isodesmic reactions involving nonaromatic hydrocarbons leads to the conclusion that the bond strength effect is derived almost entirely from the aromaticity of the sulfide, which is to say that aromatic/antiaromatic effects in molecules **1**−**3**, **8**, and **9** are at best marginal. The sulfoxides **1**−**3** show reduced barriers to inversion at sulfur; this is attributed to aromatic stabilization of the planar transition state.

Attempts to examine correlations between sulfoxide structure and infrared stretching frequencies were not particularly successful. Experimental values are unpredictably affected by Fermi resonance with other vibrations and the variation which depends on conditions of the measurement exceeds the empirically derived structural variation. Calculated inherent SO stretching frequencies grossly parallel the calculated bond lengths, but again, the expected accuracy is likely outside useful limits.

Acknowledgment. W.S.J. would like to acknowledge the Petroleum Research Foundation, administered by the American Chemical Society, the NSF (CHE 94-12964), the Research Corporation, and the donors of the Caldwell Endowment at Iowa State University for support of this research. M.S.G. acknowledges the support of the National Science Foundation (CHE 94-11911).

Supporting Information Available: Calculated Cartesian coordinates and energies calculated at RHF6-31G(d,p) and MP2/6-31G(d,p)//RHF6-31G(d,p) energies for all compounds (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951504W