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## Sulfur Anions: Comments upon Structure

Charles A. Kingsbury

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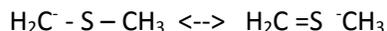
## Sulfur Anions: Comments upon Structure

Charles A. Kingsbury  
Department of Chemistry  
University of Nebraska  
Lincoln, NE 68588-0304, USA

Abstract: This work emphasizes the need for solvent simulation as well as a counterion in calculations concerning anions, although optimization may be difficult. Solvent and counterion both play a large role in conformation of the ion. Part of the reason for the success of sulfur anions in chemical reactions may be the ability of sulfone oxygen(s) to coordinate with the counterion (usually lithium). The “solvent” partially dissociates lithium from the carbanion center.

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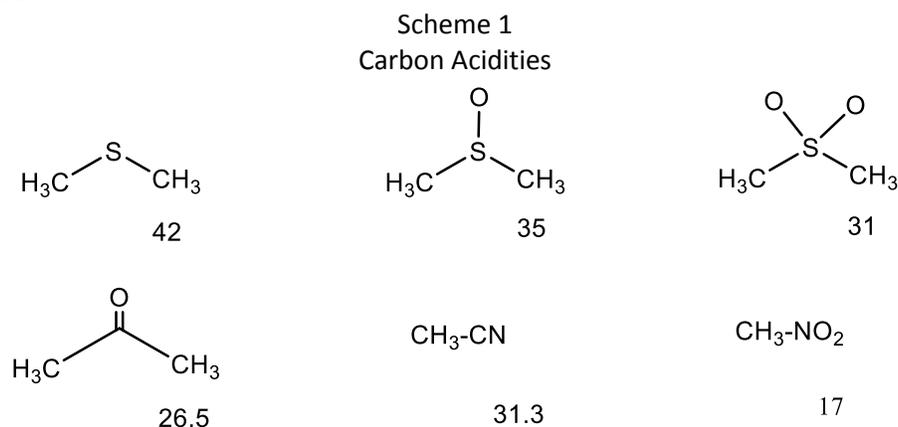
$\alpha$ -Anions derived from sulfones and some sulfides (e.g. dithiane) are commonly used in condensation and addition reactions.<sup>1-21</sup> Anions of sulfoxides are less commonly used.<sup>4</sup> Early work Wolfe, et al. seemed to favor sulfur *d* orbital involvement in the stability of the sulfur carbanions.<sup>22,23</sup> In 1994, two important papers appeared on the subject of structure and properties of these anions, one by Speers, Laidig and Streitwieser, and the other by Wiberg and Castejon.<sup>24,25</sup> Speers, Laidig and Streitwieser strongly disfavor *d* orbital involvement in stabilization of the sulfur anions.<sup>24</sup> Wiberg and Castejon used charge density difference plots. They conclude that *d* orbitals transfer charge from the lone pair to the bonding region, but do not affect energies.<sup>25</sup> A large increase of ( $\text{C}^-\text{H}_2\text{-S}$ ) bond order was found, along with a shortening of this bond. Of the three models to explain the enhanced acidity in reactions forming sulfur anions: (1) *d* orbital resonance, (2) polarization, (3) reverse hyperconjugation, Wiberg and Castejon seemed to favor a reverse hyperconjugation explanation (cf. structure shown directly below, following Schleyer and coworkers.).<sup>26,27</sup> Wiberg and Castejon also mention population of ( $\text{C}^-\text{H}_2\text{-S}$ )\*, although it is hard to see how this could shorten the covalent bond. Russian scientists indicated that the enhanced acidity of sulfides, sulfoxides and sulfones is related to the long C-S bond distance and the polarization/polarizability of that bond.<sup>28</sup> On the other hand, Bernasconi and Kittredge do not favor reverse hyperconjugation or *d* orbital resonance. They also favor the polarization/polarizability explanation.<sup>29</sup>



Wiberg and Castejon investigated the ( $\text{CH}_2^-$ -S) rotation barrier.<sup>25</sup> A large barrier, (6.7 to 12.5kcal) was found, depending on the basis set used for the calculation. On the other hand, the inversion barrier is small (<2 kcal). The sulfur affords little steric hindrance, and the ( $\text{CH}_2^-$ -S) bond, though shortened from 1.81Å (neutral structure) to 1.77Å (bare anion), is still quite long and unlikely to afford steric interactions anywhere in the rotation cycle. Thus, if this large barrier is in fact correct, are as yet dimly understood orbital considerations in effect?<sup>31-33</sup>

For the present, the question of how to represent sulfur oxygen bonds will be avoided.<sup>11,15,17,18</sup> The representation with sulfur **doubly** bonded to oxygen requires the involvement of *d* orbitals at sulfur.<sup>34-37</sup>

The acidities of representative cases are shown in Scheme 1. These data are from Bordwell and coworkers.<sup>38</sup> Bordwell used dimethyl sulfoxide as solvent, whenever possible, so that the anions are not heavily solvated



### Natural Bond Order (NBO) Data

The Natural Bond Orbital (NBO) option of the Gaussian calculation program, from Glendenning, Reed, Carpenter and Weinhold, provides a “second-order perturbative estimate of donor-acceptor (bond-antibond) interaction...”<sup>43,44</sup>

In the **sulfone** anion, the NBO program calculates the [C<sup>-</sup> - (S-O)\*] interaction (carbon anion to S-O bond interaction) as 30 kcal, but 10 kcal in the lithium salt.<sup>24</sup> These data are somewhat variable from run to run, depending upon precise structure. The [C<sup>-</sup> - (S-CH<sub>3</sub>)\*] is greater than [CH<sub>2</sub><sup>-</sup> - (S-O)\*]. The bond distance for the distal carbon to sulfur is also slightly lengthened (Scheme 2). The image of the HOMO shows a massive presence on CH<sub>2</sub><sup>-</sup>, but a small presence on the SO<sub>2</sub> oxygens. The latter resembles a *p* orbital in both the syn and the anti conformations (cf. Scheme 4). The “occupancy” of the αCH<sub>2</sub><sup>-</sup> is 1.81.

Other calculations give the interaction as 33 kcal, which points up the disturbing variability of these calculations. The NBO program identifies one sulfone oxygen lone pair interacting with the second (S-O)\* as ca. 30 kcal. This goes both directions. This sizable interaction may be one reason that sulfones are so stable.

For the **sulfoxide** anion, in the lone pair anti to S-O conformation, NBO provides a figure for the [CH<sub>2</sub><sup>-</sup> (S-O)\*] interaction of 14 kcal to 28 kcal (anti conformation, mp2 calculation). In several trials of the bare anion structure, the results were about evenly split between the ca. 14 kcal value and the ca. 28 kcal value. The image of the sulfoxide anions showed only minor variations in conformation between the 14 and the 28 kcal cases. Again, the image of the HOMO showed major presence on the carbanion carbon, although the oxygen is involved to a small extent. The NBO program also calculates the “occupancy” of (S-O\*) as 0.06 for the 14 kcal interaction, and 0.11 for the 28 kcal interaction. The lithium salt with the carbanion lone pair anti to (S-O)\* also shows a value of 16 kcal in the most favored

conformation. The “occupancy” of (S-O)\* is 0.06. The [ $\text{CH}_2^-$  - (CH<sub>3</sub>-S)\*] (carbanion interaction with the distal methyl-sulfur group) is 4 kcal.

These interaction energies are dwarfed by the findings for other stabilized anions. For the acetone anion case, the interaction of O<sup>-</sup> with the neighboring (C=C)\* is 133 kcal. For the acetonitrile anion, the “lone pair” on carbon shows a similar high interaction with (CN)\* of 107 kcal. For the anion derived from nitromethane, the interaction of lone pair on oxygen of the nitronate with (C=N)\* is 94 kcal for each oxygen. For dimethyl nitrosamine, (CH<sub>3</sub>)<sub>2</sub>N-N=O, the (N: - (N=O)\*) interaction is 130 kcal. It is noteworthy that this high value occurs in a neutral compound. Another neutral compound, formamide, shows a interaction energy of only 89 kcal for [N: - (C=O)\*]. A larger value might have been expected.

In the **sulfide** anion, the NBO program identifies the interaction of the lone pair associated with the carbanion to (S\*) as minute. The interaction with the distal (CH<sub>3</sub>-S)\* is 17 kcal in the bare anion, but only of 4 kcal in the lithium salt, the “real world” situation. Presumably the lone pair is more localized by lithium. The distal C-S bond distance increases slightly as well (cf. Scheme 2, bare anion). The NBO program identifies the [( $\text{CH}_2^-$  S)-CH<sub>3</sub>\*] interaction, i.e. carbanion sulfur bond to distal methyl, as minute. The carbanion lone pair interaction with all other atoms or bonds is similarly small. The “occupancy” of the carbanion carbon is 1.90.

For the **sulfoxide** (bare anion), the NBO treatment identifies a low value of 3 kcal for the (CH<sub>2</sub><sup>-</sup> - (CH<sub>3</sub>-S)\* (carbanion to distal methyl bond) interaction. The carbanion to (S-O)\* is larger, 14 kcal (anti conformation). The “occupancy” of the carbanion carbon is 1.84.

### Bond Distances

Schemes 2 and 3 show the bond distance determinations. These data, of course, are dependent upon method and basis set, and upon conformation. For example, dimethyl sulfide anion showed the **carbanion to sulfur** (C<sup>-</sup> -S) distance of 1.77Å at QCISD/6-31+G(d,p), and 1.75, 1.74, and 1.72Å for various calculations at mp2/6-31+G(d,p) (all with lone pair anti to the sulfur). Thus, it is not worthwhile to get too involved in bond distance data.

It is noteworthy that the **acetone** C<sup>-</sup> -C bond distance decreases from 1.52Å to 1.39Å upon forming the  $\alpha$  anion (Scheme 2). Undoubtedly, this is the effect of delocalization and “double bond character” in the C-C bond. The computer seems to regard the enolate, C-O<sup>-</sup>, as the principal anionic form (similar for the nitronate ion). In contrast the distal C-CH<sub>3</sub> group increases in bond distance from 1.51Å to 1.54Å. Similar bond distance increases are observed for the anions shown in Scheme 3.<sup>22,25,26</sup> In acetone, the C-O bond distance changes from 1.23Å in the neutral compound to 1.29Å in the anion, perhaps less than might have been expected (Scheme 2).

The conformation of the **sulfide** anion is unremarkable. The (C - S) bond distance moves from 1.81Å (neutral structure) to 1.77Å (bare anion), but back to 1.82Å in the case of the lithium salt. Then the same bond moves to 1.78Å in the PCM solvent simulation for the lithium salt. The S---Li distance is relaxed from 2.01Å (no solvent) to 2.22Å in the solvent simulation runs.<sup>25</sup> Some attraction of carbanion hydrogens for the sulfur nucleus may also be present in the bare anion. This seems to be lost in the PCM calculation.

The **sulfoxide** calculations showed somewhat greater gyrations (Scheme 3). The **C - S bond** changes from 1.82Å (neutral structure) to 1.70Å (bare anion) to 1.76Å or 1.73Å (two conformations of

the lithium salt) to 1.72Å or 1.69Å (PCM simulation. The **sulfone** anion changes in bond distance were also large, from 1.79Å (neutral structure) to 1.68Å (bare anion), but thereafter less pronounced. The PCM solvent simulation also gave 1.68Å.

For the **sulfoxide**, the **S-O bond distance** changes from 1.52Å (neutral structure) to 1.57Å (bare anion). Two C-Li conformations were found. In the conformation with Li anti to S-O, this distance is 1.53Å, but this increases to 1.60Å in the gauche conformation, where lithium is complexed to sulfoxide oxygen. With PCM solvent simulation, generally the same conformations were seen. The anti S-O structure displays a bond distance of 1.59Å.

The **sulfoxide** conformations are shown in Scheme 3 in somewhat more detail. The sulfoxide bare anion shows a somewhat similar conformation to the sulfide anion. It adamantly prefers the carbanion lone pair to be anti to S-O. The lone pair on carbon appears to be repelled by the lone pairs on oxygen. For the lithium salt, two conformations were located. The preference is for the carbanion lone pair (plus lithium) to be near S-O and favored by 28 kcal. The second conformation with the C—Li anti to S-O, is strongly disfavored, but in the PCM determination, the energy difference drops to only 1 kcal. The carbon—lithium and the oxygen—lithium distances vary substantially in the lithium salt (C—Li, 2.14Å, Li-O, 1.84Å vs. the lithium salt, PCM simulation (C—Li, 2.26Å or 2.41Å, most stable conformation).

The trimethylsulfonium anion bears some similarity to the sulfoxide anion (Scheme 3, lower level). The same disparity of bond distances is seen: although the shortening of the carbanion to sulfur bond distance is not as pronounced (CH<sub>3</sub>-S<sup>+</sup>) 1.80Å vs. (CH<sub>2</sub>-S<sup>+</sup>) 1.77Å, No distinctive NBO interactions were seen.

In dimethyl **sulfone**, the **S-O bond distances** increase from 1.47Å in the neutral compound to 1.50Å in the anion, similar to the sulfoxide. However, for the lithium salt, where lithium is complexed to one S-O, this S-O bond is longer at 1.53Å and the uncomplexed distal S-O distance is shorter, 1.48Å (Scheme 4). These S-O bond distances are generally shorter than for the sulfoxide.

Schemes 3 and 4 record the distances and angles between carbon, sulfur and oxygen as they change in the sulfur anions, lithium salt and PCM simulations. These changes are substantial. Hutchinson, Anderson, and Katritsky, and also Fraser, Schuber and Wigfield, studied the kinetics of exchange of hydrogens under basic conditions.<sup>32,33</sup> Fraser and coworkers found quite different results as solvent and base were varied. Both groups considered the geometry of the parent “acid” and the resulting carbanion to be the same. This seems to be correct only in general terms.

For the **sulfone anion**, two conformations were located (as shown in Scheme 4), in which the [CH<sub>2</sub> – (S-O)\*] distance is 1.68Å or 1.69Å. The lithium salt, occupies a third conformation with lithium complexed to one oxygen. The **C - S distance** then is 1.70Å (bare anion) and 1.68Å for the lithium salt with solvent simulation. The distal methyl (S-C) bond changes from 1.79Å (neutral structure), to 1.83Å or 1.81Å, in the bare anion (depending on calculation run) but returns to 1.79Å for the lithium case. The [CH<sub>2</sub> – (S-O)\*] interaction energy (about 4 kcal) is smaller than the [CH<sub>2</sub> – (CH<sub>3</sub>-S)] interaction (18 kcal).

In the progression from **sulfide to sulfoxide to sulfone**, the shortening of the **carbanion carbon to sulfur** bond is noteworthy. This shortening was also noted in early work by Wolfe, et al.<sup>22,23</sup> Part of this may be electrostatic For the **sulfide**, the C-S bond changes from 1.81Å (neutral compound), but diminishes to 1.78Å (lithium salt, PCM). The **sulfoxide** shows a **C - S distance** of 1.82Å (neutral) that

changes to 1.69Å (lithium salt, PCM). The **sulfone** changes from 1.79Å (neutral) to 1.68Å or 1.70Å (lithium salt, PCM)). This distance is generally shorter in the oxygen containing anions perhaps due to a larger attraction of the carbanion to the sulfur with its electronegative oxygen(s), although the reverse hyperconjugation argument of Wiberg and Castejon is another possibility. Although this ( $\text{C}^- - \text{S}$ ) extreme shortening might be taken as evidence for double bond character in the anion (similar to acetonide), this would require *d* orbital involvement, which Speers, et al deplored.<sup>24</sup> This would have to be greater in the sulfoxide and the sulfone, but it is not clear why the  $\text{C}-\text{S}$  distance should progressively diminish. A corresponding extension of the distal ( $\text{CH}_3-\text{S}$ ) bond occurs, though it is not pronounced.

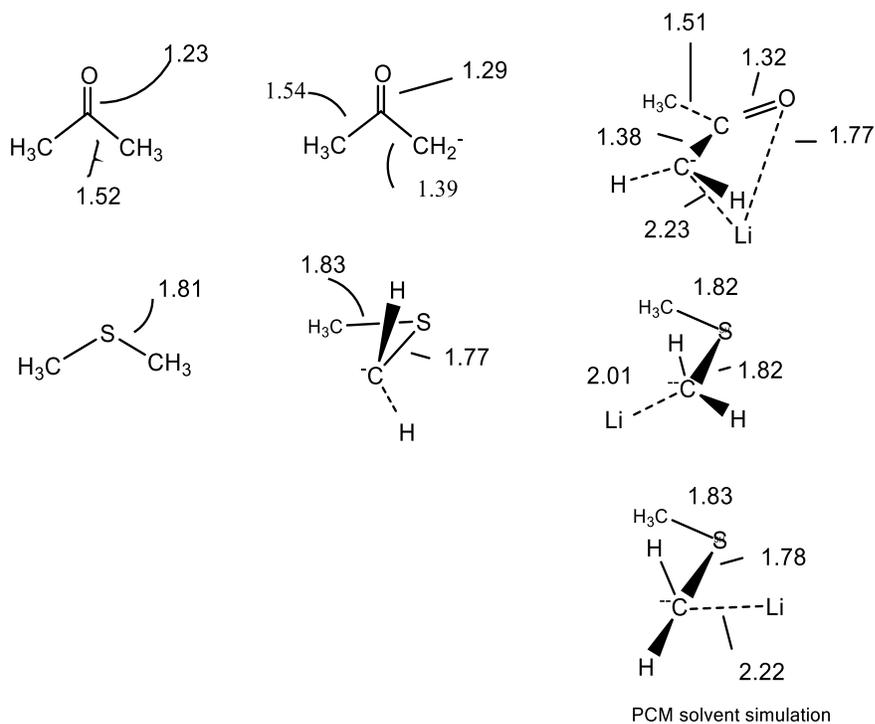
### Bond Angles

Scheme 5 records changes in **bond angles** on forming the anions. In **acetone**, the bond angle between the  $\text{C}^-$  and oxygen increases from 122° to 128°, whereas the distal carbon to oxygen angle diminishes to 115°. It is as if the partially negatively charged centers repel one another. A similar change occurs in the sulfoxide (Scheme 5), where the  $\text{C}^- - \text{S} - \text{O}$  angle changes from 106° (neutral structure) to 118° (bare anion), but 108° (lithium salt), and the same for PCM solvent simulation. The change in bond angle is smaller for the sulfone from 108° (neutral) to 110° or 113° (two conformations of the bare anion), to 102° or 107° depending on whether the lithium is cis (*gauche*) or trans to the oxygen in question. Other calculations optimize to a slightly different conformation and provide values of 103° or 112°.

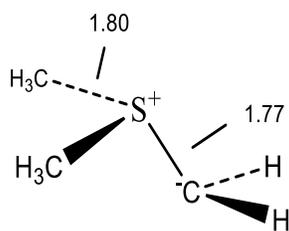
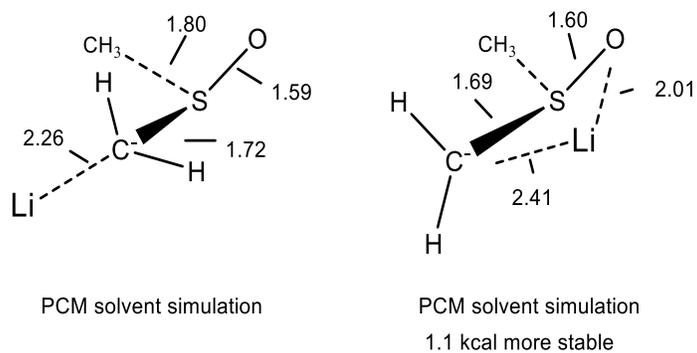
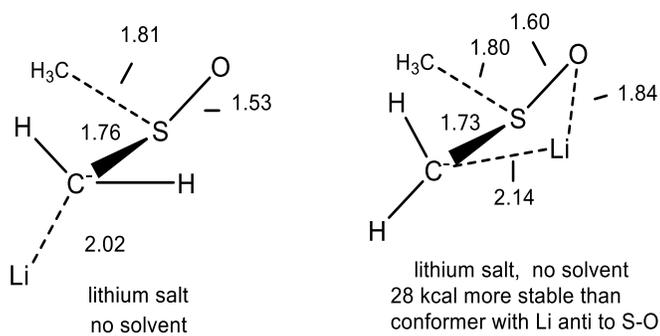
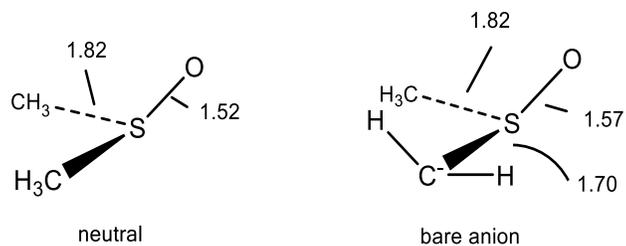
The degree of planarity is of interest for the carbon which has a formal negative charge. For the acetone anion, the H-C-H bond angle is calculated to be 118°. The carbon is essentially planar. The oxygen is calculated to have enhanced atomic charge density in the anion (-0.812) over the neutral precursor (-0.516) (cf. Scheme 6). This points to a high degree of anion delocalization. For the sulfide and sulfoxide anions, the H-C-H angles are not far from tetrahedral. The sulfone anion H-C-H angle is large at 117° or 116° (two different conformations). This diminishes to 114° in the lithium salt, and 115° in the PCM solvent simulation run, i.e. not much change. So, is the carbanion delocalized in the sulfone as in acetonide or somewhat so? The C-S-C bond angle increases upon going to the anion, for unknown reasons.

The **sulfone** anion ( $\text{C}^- - \text{S} - \text{O}$ ) bond angle changes from 108° (neutral structure) to 110° or 113° (bare anion). In the lithium salt, the ( $\text{C}^- - \text{S} - \text{O}$ ) bond angle moves to 102° for the complexed oxygen and 107° for the uncomplexed oxygen. This increases to 106° or 110° in the solvent simulation run. The looser association of lithium with carbon may affect chemical reactions, and may be one reason why THF is the preferred solvent for anionic reactions.

Scheme 2  
**Bond Distances** in Neutral vs. Anionic Species  
 Comparison of Acetone to Dimethyl Sulfide  
 (PCM solvent simulation mp2/6-31+G(d,p))

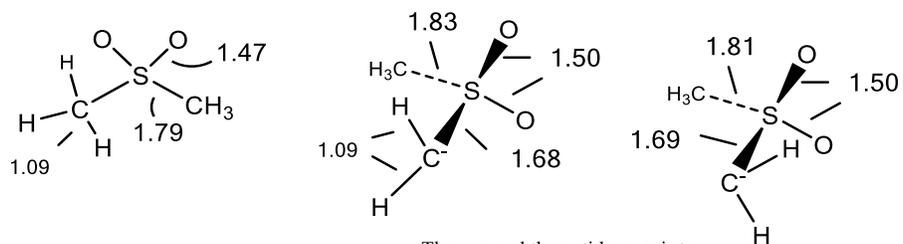


Scheme 3  
**Bond Distance Data for the Sulfoxide Anion**  
 Including PCM Solvent Simulation Data  
 (mp2/6-31+G(d,p))

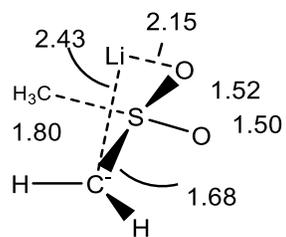
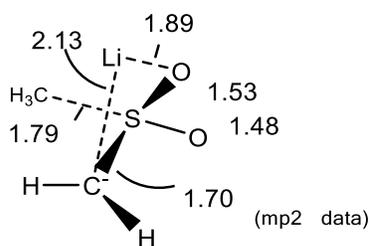


Trimethyl sulfonium anion

Scheme 4  
Bond Distances of Dimethyl Sulfone

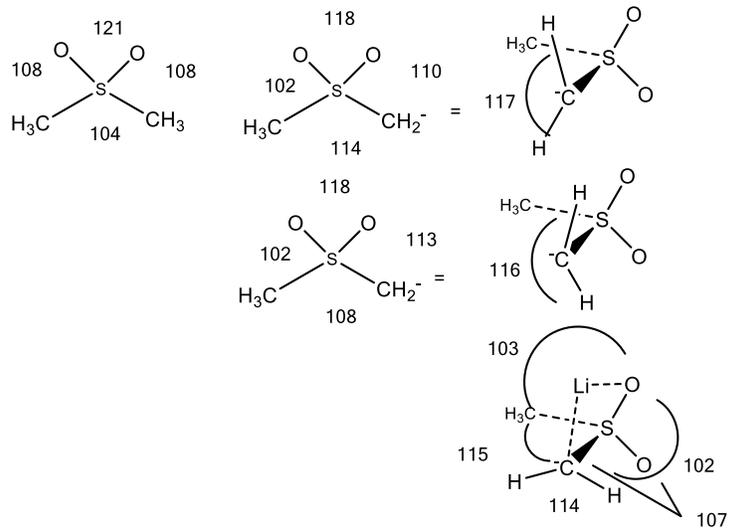
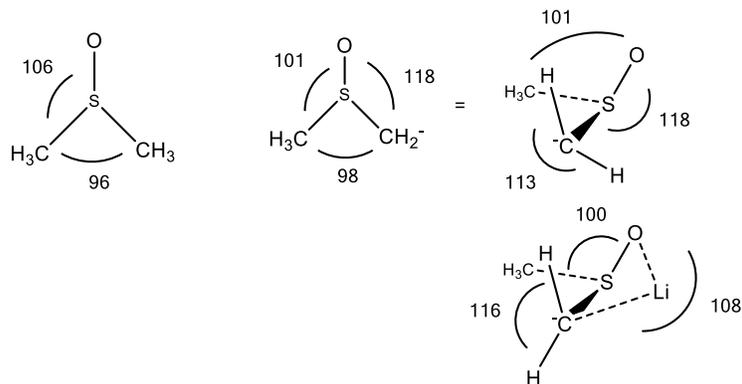
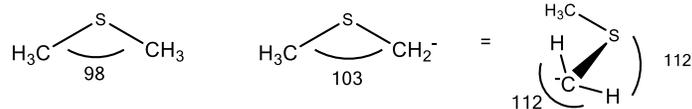
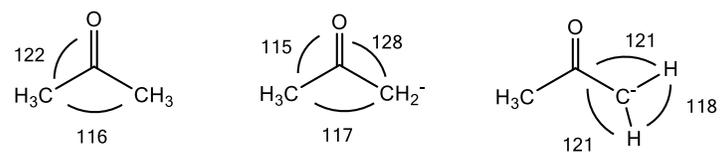


The syn and the anti lone pair to  
SO<sub>2</sub> conformations have  
very similar energies.



PCM solvent simulation  
mp2 data

Scheme 5  
 Bond **Angles** in Neutral vs (Bare) Anionic and Ion Paired Species  
 (no solvent simulation)

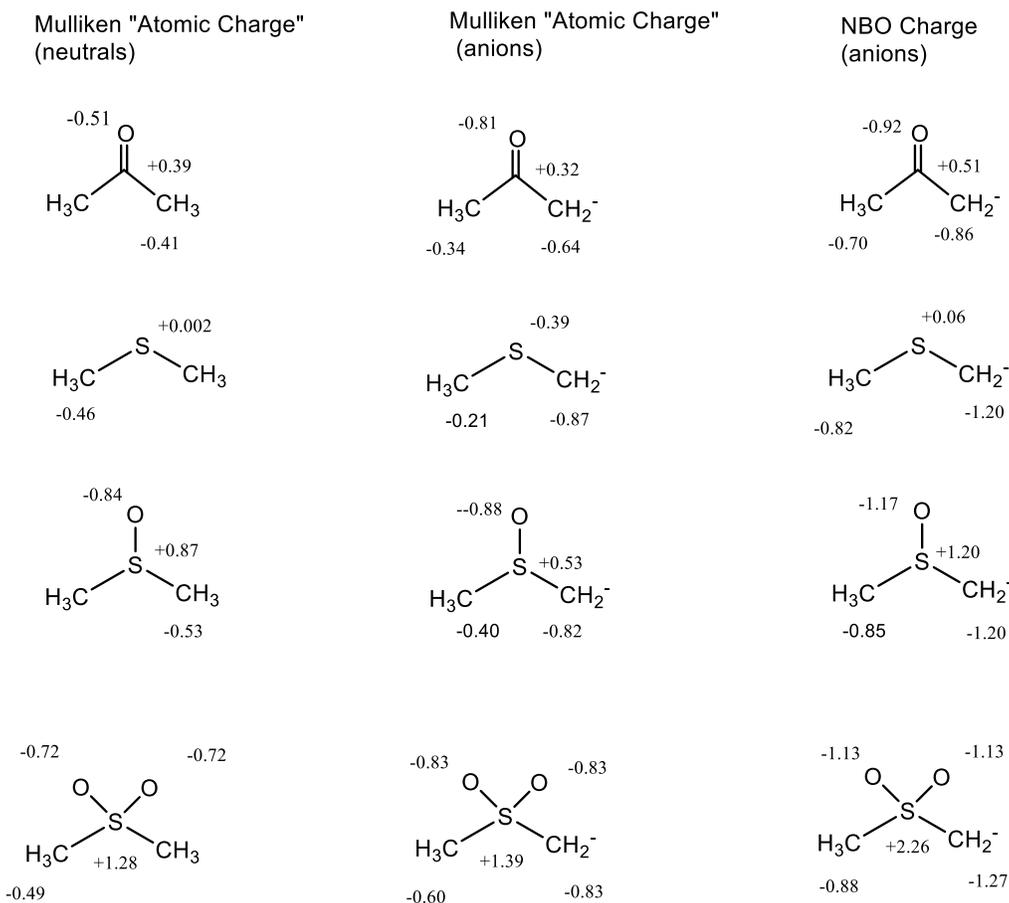


## Charge Densities

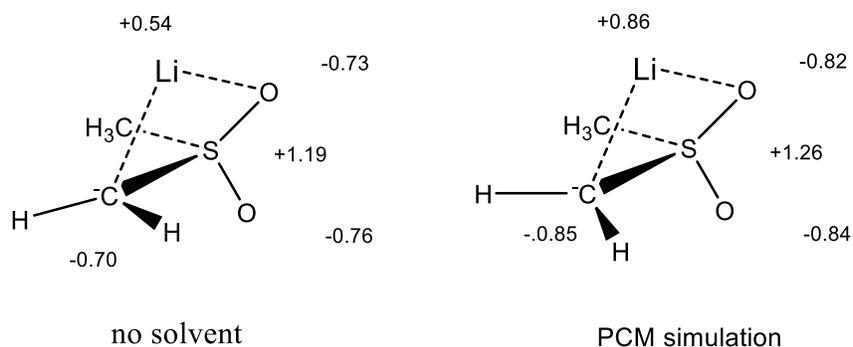
Calculated charge densities are not a particularly reliable guide to chemical phenomena. Different methods of determining charge density show widely different results, including sometimes different signs. Scheme 6 shows both the Mulliken approach to charge density and the NBO approach, which are quite different. The Mulliken charge density for the sulfoxide and the sulfone **oxygen(s)** increases to a relatively small degree, upon forming the anion. The charge density on **sulfide sulfur** changes from ca. 0 (neutral structure) to -0.39 (bare anion). The same large charge density occurs in the lithium salt, then drops slightly to -0.37 in the PCM solvent simulation. The **sulfide carbanion carbon** moves from -0.87 (bare anion) to -0.28 (lithium salt), then to -0.43 (PCM simulation mp2 data).

For the **sulfone**, the calculated atomic charge on **oxygen** increases from -0.72 (neutral structure) to -0.83 (anion). The charge at sulfur changes from +1.28 to +1.39, a surprising increase. For the carbanion carbon, the charge density changes from -0.83 (bare anion) to -0.70 (lithium salt), to -0.85 (PCM), all mp2 data (shown in part in Scheme 7). The change in charge density on **sulfur** on forming the anion, is quite significant.

Scheme 6  
Calculated Charge Densities  
QCISD/6-31+G(d,p)

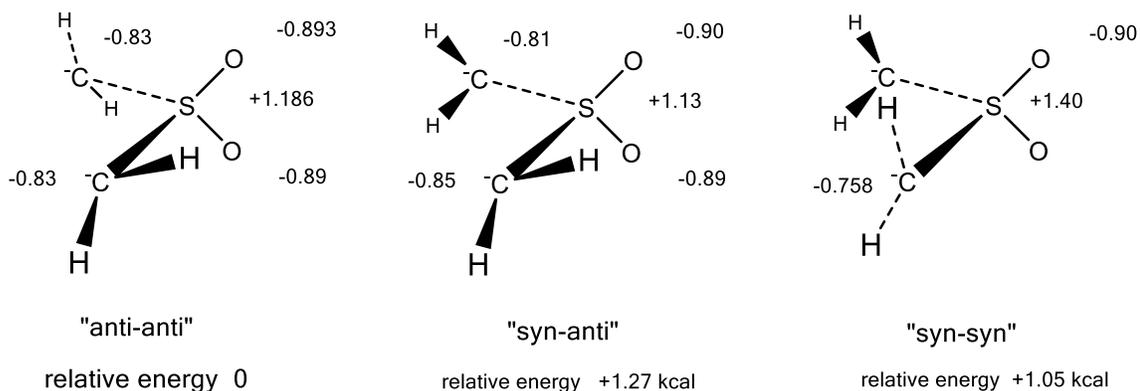


Scheme 7  
Mulliken Charge Densities in **Lithium Salts**.



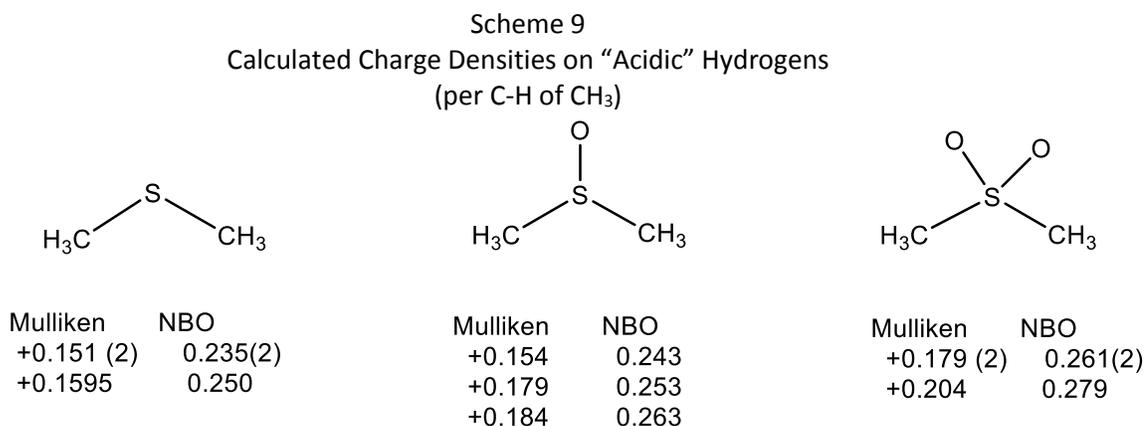
Computational data allow study of cases that would be difficult or impossible in the laboratory. An example is **dimethylsulfone dianion**, which gave the conformations shown in Scheme 8 along with Mulliken charge densities (mp2 calculations). Surprisingly, the anti-anti conformation is favored. This conformation shows one lone pair being canted downward and the other upward, evidently to reduce repulsion. Conformations with the carbon lone pair syn to sulfone oxygen(s) are disfavored, although not by much. These conformations are somewhat variable as optimization resulted in slightly different structures from run to run. Due to the structural variability, and the energy differences should not be taken as more than rough indications. The data from mp2 and qcisid calculations, are distressingly different

Scheme 8  
**Dianion** Conformations, Charge Densities and Relative Energies



## Addenda

Speers, et al emphasized the destabilization of the **parent “acid”** by sulfone or sulfoxide oxygen(s) as a major factor in the “acidity” of sulfides, sulfoxides, and sulfones. Calculations of charge densities of the hydrogens support Speers et al. contention (Scheme 9), as also noted in Speers publication. Speers et al considered the anion resulting from proton loss to occupy the same geometry as the parent “acid”, following earlier workers.<sup>30,31</sup> Although this might be true in a gross sense, the data of Schemes 2-4 of this study do not lend particular comfort to this idea.



Speers, et al. also mention “..the formation of the anion produces forces that are minimized by moving atoms away from one another...”. Some interatomic bond distances do lengthen going to the anion, but the most dramatic change is the **shortening** of the (C - S(O)) distance (Schemes 3 and 4).

Speers et al. stated quite emphatically that the oxygen(s) had **little effect** upon the **stability of the anion**. It is unclear what property of the two sulfone oxygens would destabilize the parent “acid”, but have little or no effect on the anion resulting from proton loss. One problem is that there seems to be no good independent measure of the stability of the anions themselves.

Does **stabilization** of the **anion** (by oxygens) resulting from proton loss occur? One possible measure, admittedly weak, of the stability of sulfur anions concerns the energy of the HOMO states. In theory, the lower the HOMO energy, the easier it should be to form this state. In the following table, the first row lists the HOMO energy of bare anions. The second row shows the bare anion plus the lithium cation, and the fourth row covers PCM solvent simulation. It is noteworthy that inclusion of the “solvent” results in a return of data toward that of the bare anion, as noted by Schleyer and coworkers, and by Wiberg and Castejon.<sup>19,20</sup> The **sulfone dianion**, where both methyl groups have lost a hydrogen, presumably suffers electrostatic repulsion, and shows higher energies. The sulfone dianion case involves two orbitals that are centered on the  $\alpha$  and  $\alpha'$  carbons, in both the H and H-1 cases. Charge repulsion in the **sulfone dianion** affects the HOMO energies in all conformations, making them dramatically higher than the monoanion case.

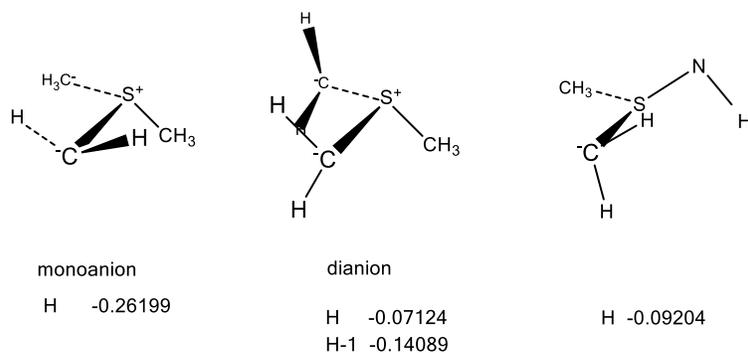
Scheme 10  
HOMO Energies  
Qcisd/6-31+g(d,p) except for PCM data and for Dianions (H and H-1)

	Sulfide	Sulfoxide	Sulfone
Bare <b>mono anion</b>	-0.04585	-0.10027	-0.12109
Sulfone bare <b>dianion</b>			+0.05069, +0.05020
Mono anion (lithium salt)			
	-0.29277	-0.331	-0.33994
Mono Anion (Li salt, PCM solvent simulation)			
	-0.28259	-0.29152	-0.32120

Quite likely, the lowering of the HOMO energy (mono anions) in the progression of sulfide to sulfone is the electronegativity effect of the oxygen(s). Computer aided visualization of the energy levels of the bare anion showed nothing at sulfur that resembled a classical *d* orbital.

The conformation of the trimethylsulfonium monoanion shows a tendency for the lone pair at carbon to distance itself from the lone pair at sulfur. The trimethylsulfonium **dianion** shows a higher HOMO energy but still less than zero, unlike the sulfone dianion. The conformation shows a tendency for the carbon lone pairs to distance themselves from one another and not from the sulfur lone pair. The conformation of the sulfilamine anion is similar to the sulfoxide anion. Compared to the sulfoxide anion, the sulfilamine HOMO energy is higher, presumably due to lower electronegativity of nitrogen. The downward orientation of the N-H is somewhat surprising.

Scheme 11  
HOMO Energies



It appears that the HOMO level is sensitive to destabilization due to charge repulsion in the sulfone dianion, but less so in the trimethylsulfonium dianion, where the net overall charge is a single negative. If sensitive to destabilization, the HOMO levels of all monoanions should also be sensitive to stabilization.

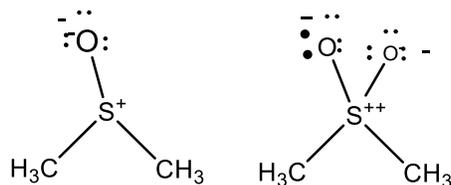
The data are consistent with a stabilization progressing from sulfide anion to sulfoxide anion to sulfone anion enabling them to be formed more easily. This occurs in addition to the destabilization of the starting “acid”, advocated by Speers, et al.<sup>24</sup>

The reason for the dramatic shortening of the ( $\text{CH}_2\text{-S}$ ) bond in the anions is unlikely to be reverse hyperconjugation, which seems relatively small.<sup>25</sup> In the case of the **sulfide** anion, the image of one lower energy orbital (H-4) resembles a classic ethylene pi bond, except that the carbanion carbon and sulfur are involved. This should shorten the ( $\text{CH}_2\text{-S}$ ) bond. Furthermore, it could partially explain the high rotation barrier found by Wiberg and Castejon.<sup>25</sup> Orbital H-8 also bonds the carbanion carbon and sulfur, although its effect on rotation would be small due to its resemblance to an s orbital. The bonding situation from calculations including the lithium ion is similar but more complex.

In the **sulfone** anion, it may be true that there is no *d* orbital resonance, but it is **not** true that there is no interaction of the carbanion carbon with oxygens. This occurs in both the syn and the anti conformations. In this regard, H-6, H-7, H-8, and H-9 display interaction of the carbanion carbon with sulfur and oxygens that could be considered as bonding. Many of the images of energy levels show what seems to be *p* orbital involvement at oxygen (and sulfur. Inclusion of the lithium counterion cases provided an additional complexity.

The situation with the **sulfoxide** anion is very complex. In the anion, H-4, H-5, H-6, H-8 and H-10 show a bonding interaction between the carbanion carbon and sulfur. H-8 shows a major involvement of oxygen with the carbanion carbon. It is easy to see why the sulfide anion undergoes less ( $\text{CH}_2\text{-S}$ ) shortening than the sulfoxide and sulfone anions. Unfortunately, we are at the mercy of the person(s) who programmed the images for an accurate depiction of overlap.

It is convenient to use simple “lines” or “sticks” to indicate bonding in chemical structures, particularly for undergraduate courses. The Lewis electron dot representations are likewise misleading for molecular properties.<sup>43</sup> The Lewis system places three lone pairs at oxygen and a formal negative charge. This high charge density should promote sulfone solubility in polar solvents, and high hydrogen bonding ability, which is not the case.<sup>44</sup> The sulfoxide shows the opposite characteristics, although the Lewis structure is similar. In the sulfones, one should not shy away from oxygen-oxygen bonding. Perusal of the images of the various energy levels clearly shows this interaction in H-4, H-7 and H-8. Some sulfur bonding with both oxygens (H-8) and even some carbon bonding to oxygens (H-6). This might enhance the stability of sulfones. However, the wide O-S-O bond angle argues against O-O bonding.



## Computational Details

Computations were made using Gaussian03, at either mp2/6-31+G(d,p) or qcisd /6-31+G(d,p).<sup>45</sup> Often, the calculations were repeated a number of times, which gave rise to slightly variable conformations and variable data. Frequencies were not always determined. The “SCRF” data were

obtained using "PCM" at dielectric constant 7.2 (tetrahydrofuran), often with difficulty (mp2 only). The calculated charge densities are shown in Scheme 6-8 for rough comparison purposes only. They are extremely sensitive to calculation method and basis set.

Calculations done at mp2/6-31+G(2d,2p) or at mp2/6-311+G(d,p) did not provide any additional useful data.

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