normal mode, since the VCD intensities can be attributed to intrinsic contributions due to local oscillators. In applying the model, it is important to consider all possible rings including covalent, hydrogen-bonding, and alkyl/π or alkyl/lone pair interactions.

It is probable that the ring current mechanism is also important in generating the negative bias observed in the CH-stretching VCD of the aldohexose peracetates[11] and in the strong mid-infrared VCD band identified at $\sim$1150 cm^{-1} in Me$_2$SO-d_6 solutions of sugars.[12] Application of the model to the mid-infrared region requires a more accurate knowledge of the normal coordinates, since CC and CO stretches and CH deformation all contribute significantly.

The results of this study are significant from several points of view. First, a uniform explanation is provided for a broad class of VCD spectra. In addition, further evidence is established for the importance of the vibrational ring current intensity mechanism. Finally, this work forms a basis for a variety of stereochemical studies of sugars and related molecules in aqueous solution.

Acknowledgment. This work is supported by grants from the National Institutes of Health (GM-23567) and the National Science Foundation (CHE83-02416). We are grateful to A. S. Perlin (McGill University) and S. Abbate (Instituto per le Macromolecole olel C.N.R., Milano, Italy) for providing the D-glucose-2-d_1 sample.

Theoretical Study of Carbanions and Lithium Salts Derived from Dimethyl Sulfone

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Abstract: Theoretical ab initio studies of the anion of dimethyl sulfone using a modified 3-21G(*) basis set with subsequent electron density analysis reveal that d-p π conjugation is not an important factor in stabilizing the anion. Instead, simple coulombic interactions play a dominant role with significant charge polarization. Optimization of the related lithium salt gives two minima on the potential surface with the lithium cation location determined by electrostatic effects. Optimization of the dilithium salts of dimethyl sulfone shows that the α,α-dianion is 9.30 kcal mol^{-1} less stable than the α,α'-dianion.

Any thorough analysis of the factors influencing the stability of carbanions adjacent to sulfur groups must invariably address the continuing controversy over the role of sulfur d-orbitals. Early theorists suggested that overlap of the lone pair orbital on the anionic carbon with the empty d-orbitals on sulfur provides stabilization of the anion through charge transfer.[1,2] Others, however, objecting to the idea of substantial d-p π-bonding, argued that the empty sulfur 3d-orbitals are too high in energy and too diffuse to interact with the carbon p-orbitals.[3] Recent studies by Wolfe suggest that sulfur d-orbitals are important in lowering the energy by n-σ^* interaction.[4] Finally, charge polarization involving sulfur d-orbitals cannot be ruled out.[5d] While the subject is still debated, a consensus is forming among both theorists and experimentalists that sulfur d-orbitals have no substantial bonding interaction with α-carbanions for cases involving sulfides.[5]

For α-sulfinyl and α-sulfonyl compounds, on the other hand, the role of sulfur d-orbitals in the stabilization of carbanions is more controversial.[2,4,6] This is partly caused by the lack of sophisticated theoretical studies of these large molecular systems. Consequently, to provide more insight into this specific area, theoretical studies were performed on the anion of dimethyl sulfone. Analysis of the role of d-orbitals on the sulfur atom in

Table I. Optimized Geometries of Dimethyl Sulfone[a]

	3-21G	3-21G(*)	exptl
energy, au	−623.03238	−623.30361	
	Bond Lengths, Å		
S–O	1.592	1.438	1.431
S–C	1.831	1.756	1.777
C–H$_t$	1.079	1.083	
C–H	1.078	1.080	
	Angles, deg		
O–S–O	119.1	119.5	121.0
C–S–C	102.7	102.8	103.3
H–C–H	112.2	110.4	
H$_t$–C–S	106.8	107.6	
S–(HCH)[b]	124.4	127.9	

[a] Data taken from ref 13. C_2V symmetry assumed in all cases. Subscript t refers to the hydrogen that lies in the plane of symmetry. [b] Nomenclature signifies the angle between the first atom and the plane formed by the atoms in parenthesis.

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Table II. Optimized Geometries of Methylsulfonylmethyl Anion[a]

	basis set	
	3-31G+	3-21G(*)+
energy, au	−622.70219	−623.43182
	Bond Lengths, Å	
C_a–S	1.720	1.634
C–S	1.862	1.793
S–O	1.600	1.461
C–H_a	1.069	1.072
C–H	1.078	1.082
C–H_t	1.079	1.085
	Bond Angles, deg	
O–S–O	116.5	117.3
C_a–S–C	116.5	109.2
S–C–H_t	108.5	110.0
H_a–C_a–H_a	124.9	121.3
H–C–H	111.1	109.2
C_a–(OSO)[b]	135.9	136.3
S–($H_aC_aH_a$)	161.7	179.6
S–(HCH)	121.0	124.7

[a] Subscript a refers to anionic methylene group and t refers to hydrogen in the plane of symmetry. Both structures have C_s symmetry. [b] Nomenclature signifies the angle between the first atom and the plane formed by the three atoms in parentheses.

the stabilization of adjacent carbanions is approached in four ways: by examination of (1) gross structural changes upon formation of the anion, (2) the rotational potential surface for the anion, (3) proton affinity calculations using a basis set with and without sulfur d-orbitals,[5d] and (4) integrated spatial electron populations (ISEP)[7] to determine the electron distribution in the anion. Together, these four sources of evidence provide information that is helpful in distinguishing among the variety of possible mechanisms of stabilization in α-sulfonyl carbanions.

In addition to the study of the free methylsulfonylmethyl anion, it is also of obvious interest to examine the structural and electronic perturbations caused by the presence of a lithium cation. The structure of the lithium salt of $^-CH_2SO_2H$ was recently reported by Wolfe.[8] However, CH_3SO_2H does not exist in nature; it rapidly rearranges to methylsulfinic acid. Moreover, hydrogen is a poor model for a methyl group.[9] The methyl group is bulkier, more polarizable, and, of course, involves S–C rather than S–H bonds; thus, the structure found by Wolfe may be uncharacteristic of true compounds.

Finally, the study of α-sulfonyl carbanions is extended to the dianions of dimethyl sulfone. These dianions have recently become important synthetic reagents. Dimethyl sulfone is known to form a 1,3-dianion using *n*-butyllithium in THF.[10] When one of the sulfonyl substituents does not contain an α-hydrogen, 1,1-dianions have also been prepared under similar conditions.[10] Like the monoanion, the stabilization of the dianion has been proposed to involve charge transfer by conjugation to the sulfur atom.[11] To date, theoretical studies of the dianions have not been reported.

Results and Discussion

Calculations were performed on dimethyl sulfone, the corresponding anions and the lithium salts using the recently published 3-21G(*) basis set (d-orbitals on sulfur only).[12] Comparison of the reported optimized geometry of dimethyl sulfone with the experimentally determined geometry (Table I) shows good agreement and indicates that the 3-21G(*) basis set is adequate for the present work.[12]

Table III. Rotational Rigid-Rotor Potential Surface of the Sulfonyl Anion

rotation angle, deg	relative energy, kcal mol^{-1}
0	0.00
30	3.21
60	10.29
90	14.33
135	6.60
180	0.00

For calculations involving carbanions, the basis set was augmented with a diffuse sp shell (exponent = 0.06) on the anionic carbon atoms to aid in the description of the lone-pair electrons.[13] Unless specifically stated otherwise, this modified basis set was used in all anion calculations. Calculations were run either with GAMESS,[14a] GAUSSIAN 80,[14b] or GAUSSIAN 82[14c] on the Lawrence Berkeley Laboratory CDC 7600 or the Organic Chemistry VAX 11/750.[15] Electron density maps were calculated with the PROJ[14d] program.

Methylsulfonylmethyl Anion. The optimized geometry obtained in this study of the carbanion derived by deprotonation of dimethyl sulfone (**1**, Table II) confirms the geometry obtained by Wolfe, who used the same basis set but without the diffuse sp shell.[4] Comparison of this structure with that of the neutral molecule shows a shortened anionic C–S bond, longer S–O bonds, and a planar carbanion. These structural changes are consistent with but do not necessitate d-p π-bonding to the sulfur atom. Moreover, these structural changes are nearly identical with those obtained by using the 3-21G+ basis set (with a diffuse sp shell on carbon but no d-orbitals on sulfur). At both basis set geometries, the anionic C–S bond is shortened by about 0.011 Å in the anion, and the S–CH_3 bond is lengthened by about 0.034 Å. These similarities suggest that bond shortening cannot be caused by d-p π bonding but that n–σ* bonding or Coulombic interactions may be important.

One difference between the structures optimized at these two basis set levels is that the increase in the S–O bond lengths upon formation of the anions is not similar. At the 3-21G+ basis set level, the bond length increases by only 0.008 Å, whereas at the 3-21G(*)+ level the bond increases by 0.023 Å. In the latter case, as evidenced by the orbital coefficients, sulfur d-orbitals are involved in the description of the semipolar bond. Upon formation of the anion, the electrons in this bond revert to a lone pair on oxygen, which, in turn, effectively places more positive charge on the sulfur. At the 3-21G+ basis set level (no d-orbitals), the electrons that would have been involved in the semipolar bond are now part of the lone pair on oxygen in both the carbanion and the neutral molecule.

Another significant difference between the structures optimized with the two basis sets is that the carbanion at the 3-21G(*)+ basis set is planar, whereas the carbanion at the 3-21G+ level is pyramidal with the hydrogens bent out of the plane by 18.3°. Because the difference could be caused by some d-p π-bonding or n–σ* bonding in the carbanion, an attempt was made to determine the importance of the planarity of the anion as a criterion for possible conjugative stabilization. A calculation was performed to determine the energy difference between the planar (optimized) anion and a pyramidal structure. Specifically, the hydrogens attached to the anionic center were bent away from the oxygens

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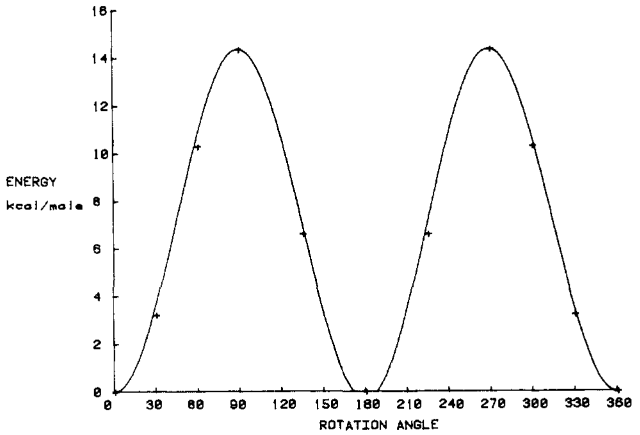


Figure 1. Rotational potential surface of the methylsulfonylmethyl anion calculated with a least-squares fit of the energies determined with a rigid-rotor approximation.

Table IV. Fourier Analysis of the Potential Surface

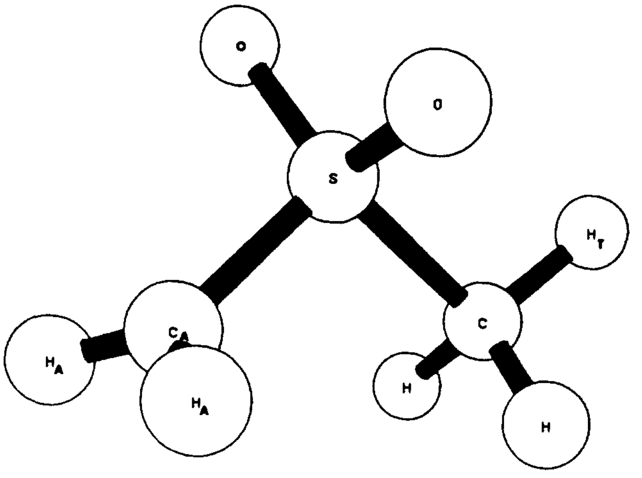
$V(\theta) = V_1/2(1 - \cos\theta) + V_2/2(1 - \cos 2\theta) + V_3/2(1 - \cos 3\theta)$

parameter[a]	potential[b] kcal mol^{-1}
V_1	-0.170
V_2	14.150
V_3	-0.134

[a] Reference 16. Parameter definitions: V_1 = dipole–dipole interactions, V_2 = conjugative overlap effects, and V_3 = steric and torsional effects. [b] Calculated with a least-squares iterative technique.

by 20° from planarity. The resulting increase in energy of this "pyramidal" anion over the planar form is 0.57 kcal mol^{-1}, too small to be considered of major significance. This small energy difference is in agreement with Chassaing's interpretation of J_{C-H} coupling constants measured for a variety of sulfones.[6h,4] Thus, a thorough analysis of structural changes that occur upon anion formation from dimethyl sulfone does not eliminate the possibility of conjugation, but, from an energetic standpoint, these interactions do not provide much stabilization.

The planar carbanion of the optimized structure is in agreement with the stereochemical studies of Corey that show that the configurationally stable carbanion is caused not by a barrier to inversion but by a barrier to rotation.[6a] However, Bordwell has suggested, based on acidity data, that, although the carbanion is planar, the conformation of the anion with the lone pair "gauche" to the two oxygens (**1**) may not be the most thermodynamically stable form.[6e] Instead, a minimum in the energy at the 90° rotated conformation was proposed. Accordingly, the rotational barrier of the anion of dimethyl sulfone was determined by using a rigid-rotor model. Figure 1 shows a graphical representation of this potential surface calculated by using a least-squares fit of the relative energies obtained at various rotation angles (Table III). These results show that the conformation in which the anionic lone pair is located between the oxygens (**1**, 0° orientation) is indeed a thermodynamic minimum on the potential surface that has a rotational barrier of over 14 kcal mol^{-1}, thus supporting experimental evidence concerning the chirality of α-sulfonyl carbanions. Bordwell's hypothesis was further checked by optimization of the 90° conformation using C_s symmetry. The resulting energy of this conformation (**2**), which is 9.31 kcal mol^{-1} higher in energy than the 0° conformation, compares well with the rotational barrier determined by using the rigid-rotor approximation (see Supplementary Material for geometries).

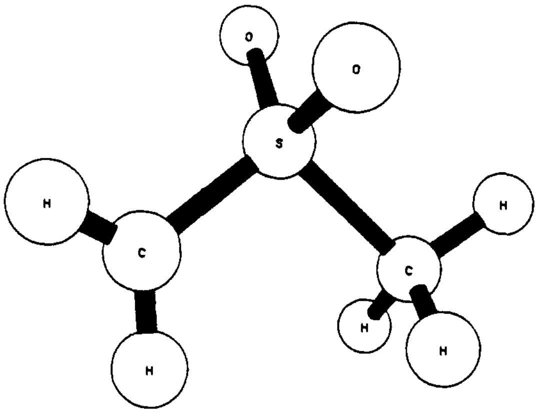


1

Table V. Proton Affinities of Methylsulfonylmethyl Anion

	energies, au	
basis set	3-21G+	3-21G(*)+
anion	−622.43838	−622.70671
neutral	−623.04480	−623.31270
proton affinity[a]	0.60642	0.60599

[a] Difference in proton affinities is 0.27 kcal mol^{-1}.



2

Pople's Fourier series analysis was applied to the rotational potential surface (Table IV).[16] The V_2 term dominates; neither dipole–dipole nor torsional effects are significant. The V_2 term can arise from conjugation, such as by d-p π-bonding or n–σ^* bonding, or by related interactions that do not involve charge transfer. An example is the "gauche effect" first proposed by Wolfe:[17] for molecules containing lone pairs and semipolar bonds on adjacent centers, the most stable conformation is that orientation that maximizes the number of gauche interactions between these types of bonds. Thus, the large V_2 for the anion of dimethyl sulfone could be caused by such a nonconjugative effect. Moreover, Coulombic stabilization aided by polarization of charge involving d-orbitals is also a V_2 effect. Consequently, no definitive information is gained about the role of sulfur d-orbitals in stabilizing the anion from examination of the rotational potential.

The difference in proton affinities of carbanion calculated at two different basis set levels, one with d-orbitals and one without d-orbitals on sulfur, is another measure of the importance of d-orbitals in any stabilization mechanism. If d-orbital participation is important, one would expect that the proton affinity calculated with d-orbitals would be lower in energy than the case without d-orbitals because of the extra stabilization of the anion afforded by the d-orbitals. This argument has been used to show that d-orbitals are not important in stabilizing anions formed from sulfides.[5d,18]

To eliminate superposition effects[19] in the proton affinity calculations, the energies of the anions were recalculated at the

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Table VI. Integrated Electron Populations Calculated with d-Orbitals

	molecule, geometry		
	neutral, optimized	anion, optimized	anion, neutral
CH_2^-		8.50	8.57
CH_3	8.93	9.04	9.06
S	13.80	13.98	13.93
O	9.15	9.24	9.22

Table VII. Integrated Electron Populations Calculated without d-Orbitals

	molecule, geometry		
	neutral, optimized	anion, optimized	anion, neutral
CH_2^-		8.53	8.49
CH_3	8.93	9.09	9.09
S	14.52	14.48	14.67
O	8.82	8.95	8.88

appropriate basis set level with hydrogen ghost orbitals located at the position of the hydrogen of the parent compound. Likewise, the energies of the neutral compounds were recalculated by using a basis set augmented with the diffuse sp shell on one of the carbon centers. In short, the energies of the anion and neutral compound used to obtain the proton affinity were calculated with the same number of basis functions at the 3-21G(*)+ basis set level. The proton affinity at the 3-21G+ basis set level was similarly determined. The energies presented in Table V show that the resulting difference in proton affinities is negligible and suggest strongly that d-orbitals are not important in any mechanism for the stabilization of an α-sulfonyl carbanions. These results agree with those suggested from analysis of the structural changes upon anion formation using both basis sets (vide supra).

Integrated spatial electron population (ISEP) analyses[14d] of dimethyl sulfone and its anion were also performed. Integration of the electron density around the anionic methylene group gives 8.50*e* (Table VI). Comparison of this electron count to that obtained from the methyl group (8.93*e*) in dimethyl sulfone shows a transfer of about 0.43*e* away from the anionic carbon. About 0.1*e* of this charge is assigned to the methyl group, 0.18*e* to the sulfur atom, and 0.18*e* to each of the two oxygen atoms. Evidence of this type of charge distribution has also been suggested based on force constants determined from IR and Raman studies of α-sulfonyl carbanions by Chassaing and co-workers.[6j] This charge distribution over the molecule suggests that some conjugative overlap may be occurring.

To determine the effect of sulfur d-orbitals on electron populations, a similar calculation was performed by using a 3-21G+ basis set that does not contain sulfur d-orbitals (Table VII). Charge transfer using this basis set shows much similarity; thus, the charge buildup on the oxygens and methyl group cannot be caused by d-p π-conjugation. Furthermore, because of this similarity in results, much care needs to be taken when invoking d-orbital participation in stabilizing α-sulfonyl carbanions.

A better approach to determine the fate of the electron density is by an integrated spatial electron density difference map. In this method, the electron density function of dimethyl sulfone is subtracted from that of the anion formed by removal of a proton without other changes in the geometry. Of course, this involves an approximation because the anion described in the difference map is not calculated at the optimized geometry but at the geometry of the neutral molecule. However, the similarity of the electron population of both forms of the anion (Tables VI and VII) shows that this approximation is not unreasonable.

The resulting electron density difference contour plot obtained by using the 3-21G(*)+ basis set (Figure 2a) shows the diffuse nature of the carbon lone pair. Furthermore, it reveals significant polarization of the electron density away from the anionic center. The polarization occurs along the S–CH_3 bond and near the S–O bond as denoted by an increase in charge density (solid contours) in these areas and a decrease near the sulfur nucleus. A secondary wave of polarization is indicated in the region around the hydrogens of the methyl group. These areas of polarized charge in the region of the oxygen and methyl group would account for the increase in electron population determined for these regions.

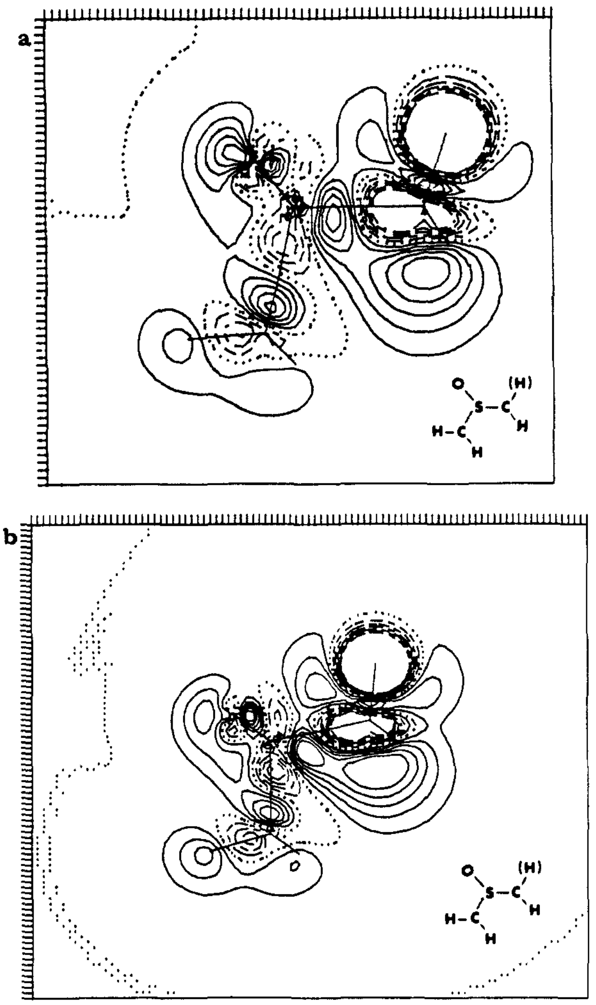

Figure 2. Electron density difference maps calculated by subtraction of the neutral compound from the anion formed by simple proton removal. Contour levels from −0.3 to +0.3 by 0.06 e au^{-2}. (a) using a 3-21G(*)+ basis set; (b) using a 3-21G+ basis set (no d-orbitals).

The increase in electron density near oxygen resembles the lone pair p-orbital. In the anion, the S–O bond becomes even more polarized than in the neutral molecule by shifting electron density from the bond to the p-orbital on oxygen, essentially forming the lone pair on oxygen. This, in turn, creates a higher positive charge on sulfur. This conclusion is supported by analysis of the orbital coefficients in the anion and neutral molecules and is also reflected in the structural changes as mentioned previously. The polarization of charge density along the S–CH_3 bond may be a result of simple charge polarization or of sulfur d-orbital interaction with the σ^* orbital, as first suggested by Wolfe using PMO analysis.[4] However, examination of the electron density difference map at the 3-21G+ basis set (Figure 2b) shows an extraordinarily similar pattern of charge polarization. As concluded from analysis of the proton affinity calculations, this similarity shows that sulfur d-orbitals are not important in stabilizing the anionic charge.

The dominating mechanism of carbanion stabilization can be described as a classical polarization involving the SO_2 group. Polarization along bonds is greater than transverse polarization.[20] An important molecular orbital mechanism that provides such polarization involves interaction with σ^* orbitals. That is, n–σ^* orbital interactions provide the quantum mechanical mechanism

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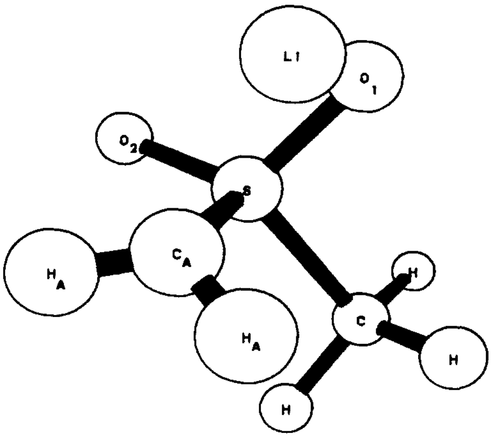
Table VIII. Important Parameters of Lithium Salt Structures[a]

	structure		
	3	**4**	**5** (Li fixed)
energy, au	−630.16760	−630.16585	−630.15098
	Bond Lengths, Å		
C_a–S	1.684	1.605	1.674
C–S	1.767	1.773	1.761
S–O_1	1.500	1.501	1.470
S–O_2	1.446	1.501	1.470
O_1–Li	1.816	1.879	2.273
O_2–Li	3.374	1.879	2.273
C_a–Li	2.170	3.519	[2.000][b]
	Bond Angles, deg		
S–C_a–Li	78.50	34.0	74.07
O–S–O	115.2	104.5	111.6
C_a–S–C	112.2	116.0	118.0
H_a–C_a–H_a	113.7	121.8	113.9
C_a–(OSO)[c]	125.5	140.8	117.5
S–($H_aC_aH_a$)	142.5	171.5	140.8

[a] See figures for subscript explanations; see supplementary material for the complete parameter set. [b] Bond length is fixed. [c] Nomenclature signifies the angle between the first atom and the plane formed by the three atoms in parentheses.

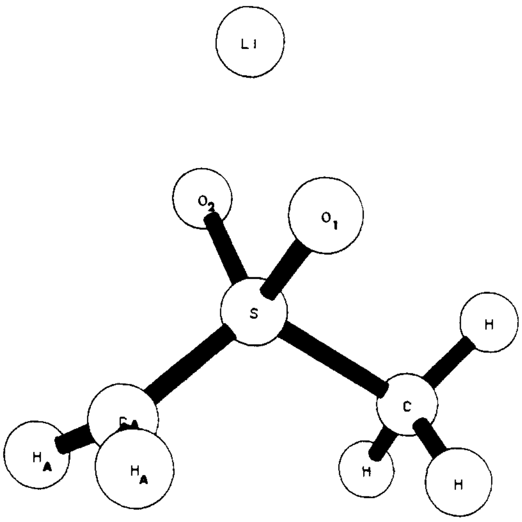
for implementing classical charge polarization, and these effects provide the dominating role in stabilization of a carbanion by an SO_2 group.

Lithiomethyl Methyl Sulfone. These studies were extended to the lithium salt of the carbanion formed from dimethyl sulfone. Optimization of the geometry (**3**, Table VIII) of this compound resulted in a structure similar to the structure of $Li^+ \, {}^-CH_2SO_2H$ obtained by Wolfe in which the lithium cation is clearly associated with the anionic carbon and only one oxygen.[8] Wolfe also reports, however, that the geometry he obtained is the only minimum on the potential energy surface. Optimization of the structure of the methylsulfonylmethyllithium gives another minimum of unusual structure that is 1.1 kcal mol^{-1} higher in energy. This structure (**4**) has C_s symmetry in which the lithium is now associated with the two oxygens atoms rather than the anionic carbon (a C–Li distance of over 3.5 Å compared to 1.88 Å for the O–Li distance). Note that this energy difference reflects gas-phase energies with no inclusion of the effect of zero-point vibrations.



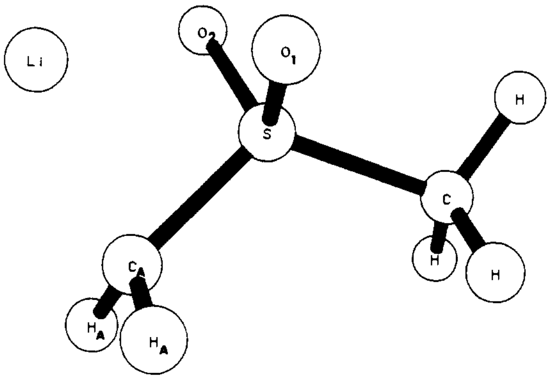
3

To eliminate the possibility that the oxygen atoms are simply using the empty valence shell of lithium to aid in the description of its electron-rich centers, both lithium salts were also optimized with the addition of a diffuse sp shell on the oxygens (exponent = 0.08435).[21] The resulting geometries (Supplementary Material) show that the lithium atom does not move significantly and eliminate the suggestion of possible superposition effects. However, the difference in energy of the two structures increases to 4.3 kcal mol^{-1}.



4

What is surprising about the optimized structures of the lithium salts is the location of the cation. Based on the electron population calculated for the anion, both oxygen atoms and the carbanion represent the most negatively charged centers. Thus, one might expect that the cation would be located in an area that is adjacent to all three centers. However, this was found not to be the case. An indication of the relative stability of the optimized structures relative to this proposed structure is given by the calculation in which the C–Li bond distance was fixed at the normal C–Li bond distance.[22] The resulting partially optimized structure **5** at the basis set that does not include diffuse functions on oxygen is 10.3 kcal mol^{-1} higher in energy than the fully optimized structure at the same basis set.



5

The cause for the preferred association of the lithium cation with the carbon and oxygen atoms instead of above the center of the triangle of the three negatively charged centers can be explained by simple electrostatic effects. This is demonstrated by a plot of the electrostatic potential that was calculated for a grid of points in the plane of symmetry of the higher energy structure of the anion. The resulting contour map of these points (Figure 3a) clearly shows three distinct potential wells: one near the oxygens, and one on either side of the carbanion center. Although the deeper potential wells are associated with the anionic carbon, placement of the lithium cation at a normal C–Li distance of 2.0 Å[22] (as marked in Figure 3a) shows that the cation cannot be located at the electrostatic minimum. Applying a similar treatment for the potential well near the oxygens, using the O–Li distance found for the ion pair, shows that the cation is located essentially on the same contour level in both potential wells. An

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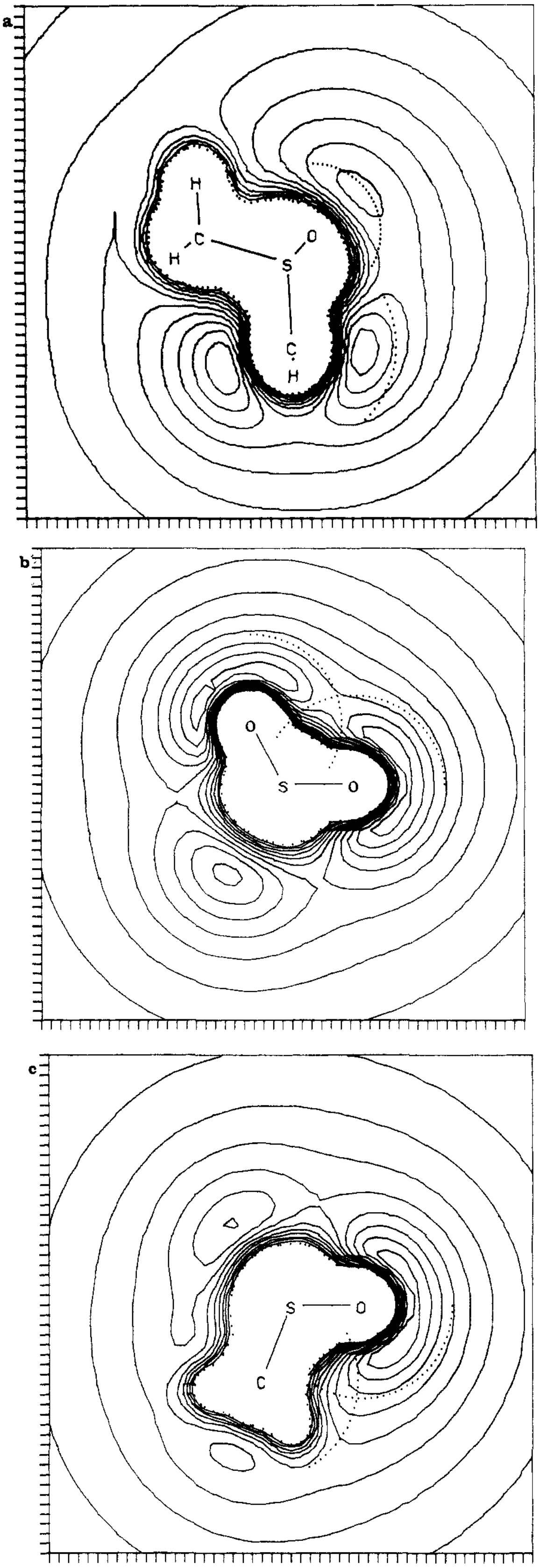

Figure 3. Electrostatic potential contour maps for the carbanion derived from dimethyl sulfone. Contour levels by 15 kcal mol^{-1}: (a) CSC plane; (b) OSO plane; (c) CSO plane. Dotted lines show normal O–Li and C–Li distances.

electrostatic potential plot in the O–S–O plane with a similar treatment involving the standard O–Li bond lengths shows that the cation is also located at an electrostatic minimum in this plane (Figure 3b). Thus, on the basis of purely electrostatic interactions, the lithium cation is about equally stable in either potential well.

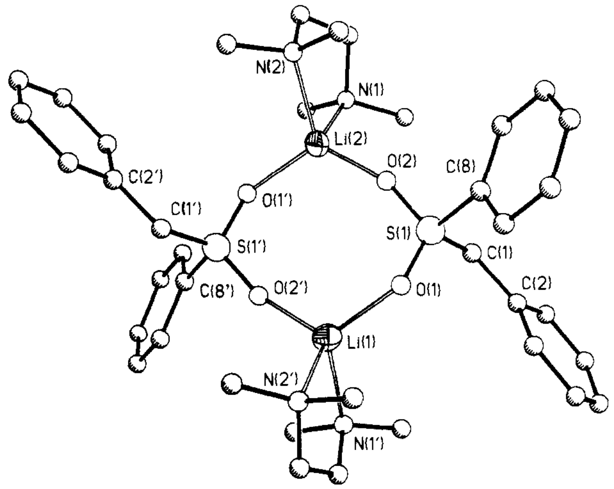

Figure 4. Crystal structure of $(PhSO_2CHC_6H_5^-Li^+/TMEDA)_2$ reported by Boche. Reprinted with permission from ref 23. Copyright 1985 VCH Verlagsgesellschaft.

The preference of the cation for the potential well near the oxygens results from perturbations in the geometry of the anion caused by the nearness of the lithium to the oxygens. These changes can be examined by comparing the optimized geometry with that geometry in which the lithium is set at a fixed C–Li distance of 2.0 Å (Table VIII). The optimized geometry has a significantly shorter anionic C–S bond length, a longer S–O bond, and a more planar anion, and the angle between the OSO plane and the anionic carbon is much greater (by 23.3°). Thus, the stability of having the lithium salt associated only with the oxygens probably results from a release in strain in the angle between the OSO plane and the anionic C–S bond.

Similarly, this explanation based on electrostatic effects can also apply to the slightly more stable structure in which the lithium cation is associated with the anionic carbon and one oxygen. The electrostatic potential plot calculated in the plane of the anionic carbon and the S–O bond shows a potential well about equidistant from the carbon and the oxygen (Figure 3c). Although the lithium does not actually lie in this plane, it is sufficiently close so that comparison of the potential minimum with the actual lithium location shows that the two are essentially in the same place.

In light of these theoretical results, it is interesting to examine the crystal structure of the Li/TMEDA salt of benzyl phenyl sulfone reported by Boche.[23] This salt is dimeric with each lithium bridging an oxygen on each of the sulfonyl anions (Figure 4). The structure is conceptually similar to **4** and suggests that the overall molecular energy is not strongly dependent on the location of a lithium cation. This concept extends to even larger cations. For example, examination of the electrostatic plots suggests that cesium with an ionic radius of 1.66 Å[24] is located sufficiently far from the deep potential wells to be only loosely associated with any particular location.

In summary, the results presented here are consistent with a purely electrostatic interaction involving the lithium cation and demonstrate that covalent interaction between carbon and lithium is unimportant. The structure in which the lithium is simultaneously associated with the three centers of negative charge is not electrostatically most favored. Instead, the stable minima on the potential surface arise from electrostatic interactions of the cation with only two negatively charged centers. Although electron density analysis cannot be performed on the lithium salts, the lack of importance of conjugative bonding in the lithium salt is demonstrated by the pyramidal carbanion center, a longer C–S bond length than was evidenced in the bare anion, and a rotation of

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(23) Boche, V. G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem.* **1985**, *97*, 577–578. We are indebted to Professor Boche for a preprint of his manuscript and for permission to reproduce Figure 4.

(24) Pauling, L. *J. Am. Chem. Soc.* **1927**, *49*, 765.

Table IX. Important Parameters of the 1,3 Dilithium Salts[a]

	structure		
	6	7	8
energy, au	−637.02331	−637.00843	−637.00074
symmetry[b]	C_2	C_{2v}	C_{2v}
	Bond Lengths, Å		
C–S	1.703	1.712	1.697
S–O	1.507	1.510	1.526
$C-Li_1$	2.157	2.107	2.205
$C-Li_2$	2.157	3.648	2.205
$O-Li_1$	1.805	1.867	2.105
$O-Li_2$	3.440	3.711	2.105
	Bond Angles, deg		
C–S–C	118.0	108.6	134.8
O–S–O	109.9	103.8	100.2
	Dihedral Angles,[c] deg		
X–S–C–Li	51.9	0.0	0.0
$X-S-C-H_1$	159.6	116.9	114.6
$X-S-C-H_2$	−69.0	−116.9	−114.6
$S-(H_1CH_2)$[d]	100.7	130.9	135.6

[a] See Supplementary Material for complete structural parameters. [b] Symmetry enforced during the calculation. [c] X corresponds to a dummy atom located halfway between the oxygen atoms—given to show dihedral angles. [d] Corresponds to the angle between the first atom and the plane formed by the three atoms in parentheses.

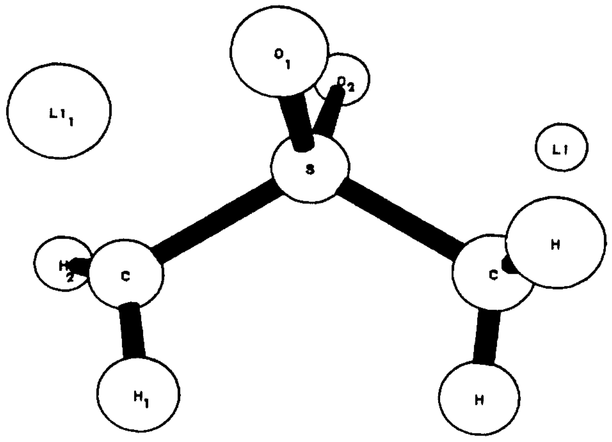
the anionic methylene center to a more stable structure. Finally, the optimized structure of the lithium salt suggests that the cation may play an important electrostatic role in determining the stereochemistry of the reaction of Schiff bases, isocyanates, and carbonyl-containing compounds with sulfones.[25] The lithium cation is in a position to stabilize the anionic intermediates formed in these reactions, thus causing a preference for attack at the anionic carbon from the side containing the cation.

Dilithium Salts of the Dimethyl Sulfone Dianions. After obtaining the somewhat unexpected structure for the lithium salt of dimethyl sulfone, it was of decided interest to determine the structures of the dilithium salts of the dianions of dimethyl sulfone. Reactions of dilithium salts are achieving more importance in synthetic sequences.[26] Because of the large number of basis functions required for these optimizations, the potential energy surface was first explored at the semiempirical MNDO level. The three resulting structures at the energy minima were then optimized at the ab initio level to give structures **6**, **7**, and **8** (Table IX).

The two structures of lowest energy are direct extensions of the stable lithium salts of the monoanion. In structure **6**, each cation is associated with one anionic carbon and differing oxygen atoms. The next most stable structure is similar to **7** in that the cation is associated with both oxygen atoms with the second cation associated with both carbanion centers. The least stable of these three structures has the lithiums associated with one carbanion and both oxygen atoms.

The overall changes in the structure of the ion triplet **6** compared to the ion pair are minimal. However, in structure **7**, the hydrogens undergo an inversion at the carbanion centers upon removal of the second hydrogen to form the dilithium salt. In structure **8**, the bond lengths and angles change dramatically upon the second deprotonation. Specifically, the S–O bond increases by almost 0.2 Å, and the C–S–C angle increases by almost 17° compared to structure **2**.

Thermodynamically, the second lithiation is obviously much more difficult than the first lithiation of dimethyl sulfone. The second negative charge is not stabilized as effectively as the first. From simple symmetry considerations, polarization of the charge along the S–C bond to stabilize the anion is no longer possible. Furthermore, increased polarization of the S–O bond does not seem to be important in the dianions. On the basis of the similar S–O bond lengths of the mono- as well as the dilithium salts, it would appear that the maximum polarization along this bond already occurs upon formation of the monolithium salt.



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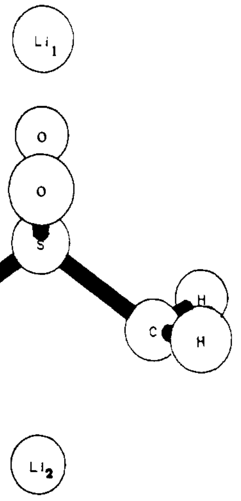

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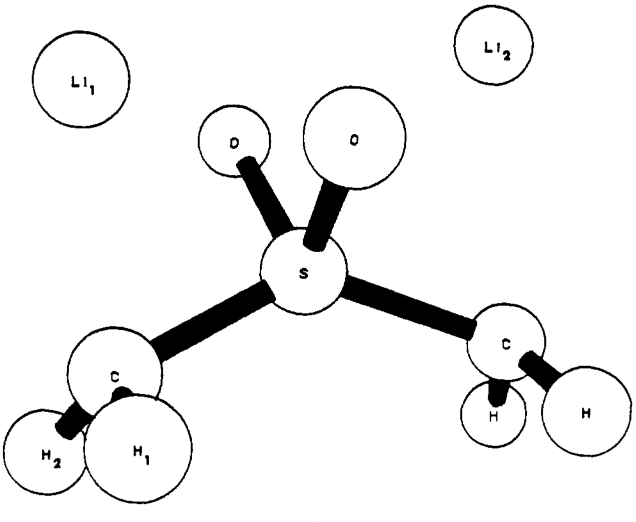

8

Another aspect of the dilithium salts concerns the disproportionation energy of the monolithium salt into the neutral sulfone and the dilithium salt as shown in eq 1. Summation of the

$$2\ CH_3SO_2CH_2^-Li^+ \rightleftarrows CH_3SO_2CH_3 + LI^{+-}CH_2SO_2CH_2^{-+}Li \quad (1)$$

energies on both sides of the equation show that the equilibrium

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(25) (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345. (b) Becker, H. D.; Russell, G. A. *J. Org. Chem.* **1963**, *28*, 1896. (c) House, H. O.; Larson, J. K. *J. Org. Chem.* **1968**, *33*, 61. (d) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 866. (e) Russell, G. A.; Becker, H. D. *J. Am. Chem. Soc.* **1963**, *85*, 3406.

(26) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

Table X. Optimized Geometry of the 1,1-Dilithium Salt **9**[a]

Bond Lengths, Å	
C_a-S	1.633
C-S	1.767
S-O	1.510
C_a-Li	2.132
O-Li	1.830
Li-Li	3.596
Bond Angles, deg	
C_a-S-C	118.1
H-C_a-S	116.4
Li-C_a-S	78.2
O-S-O	109.3
Li-C-Li	115.0
C_a-(OSO)[b]	125.6

[a] Energy = -637.03027 au. C_s symmetry enforced during the calculation; see Supplementary Material for complete structural parameters. [b] Angle between the first atom and the plane formed by the atoms in parentheses.

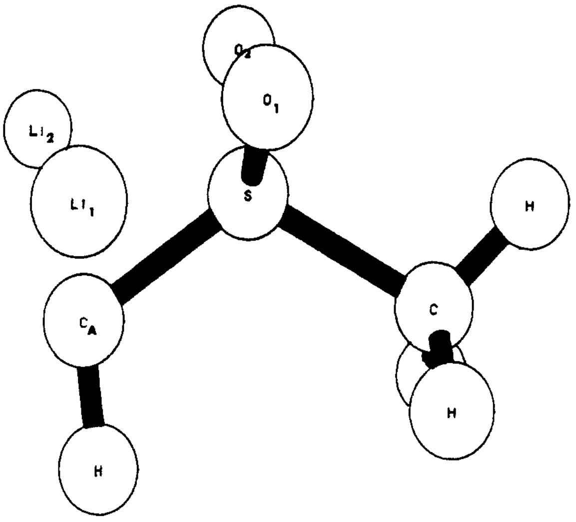
Table XI. Comparative Stabilities of the Dilithium Salts[a]

structure	energy, au	relative energy, kcal/mol
6	-637.13947	0.0
7	-637.12663	8.06
8	-637.12173	11.13
9	-637.12465	9.30

[a] 3-21G*+ basis set with d-orbitals on all heavy centers (except lithium) and diffuse functions on both carbon atoms.

favors the monolithium salt by 14.56 kcal mol^{-1}. Thus, without consideration of the entropy term, the amount of dilithium salt in equilibrium with the monolithium salt is negligible.

Solution-quenching studies show that the 1,3-dilithium salt is the stable species in tetrahydrofuran.[10] However, if one substituent lacks α-hydrogens, generation of the lithium salt of the 1,1-dianion is possible.[26] The search for the structure of this compound on the potential surface was accomplished by using MNDO methods. Only one stable structure resulted, which was further optimized at the ab initio level to give the structure shown (**9**, Table X). Note that in an effort to accommodate the extra charge on the anionic carbon, the basis set of this carbon was augmented with a set of d-orbitals (exponent = 0.65) in addition to the diffuse sp shell.



9

Once again, this structure is an extension of the lithium salt of the monoanion with each lithium associated with one carbanion center and one oxygen atom. In order to compare stabilities of the 1,1-dianion with the 1,3-dianions, the energies of all four lithium salts were calculated by using a larger basis set with the same number of basis functions for each structure. That is, the 3-21G*+ basis set (d-orbitals on all centers except lithium) was augmented with diffuse functions on the anionic centers. The resulting energies (Table XI) show that the dilithium salt of the 1,1-dianion is 9.30 kcal mol^{-1} higher in energy than that of the most stable 1,3-dianion. This value coincides with the lack of products from the 1,1-dianion found from solution-quenching studies.

Acknowledgment. This research was supported in part by NIH grant No. GM-30369. We are indebted to Steven Bachrach for suggesting the application of electrostatic potentials.

Supplementary Material Available: Table of complete optimized structures for structures **2–9** (4 pages). Ordering information is given on any current masthead page.

Isomers of $C_2H_4N^+$ and the Proton Affinities of CH_3CN and CH_3NC

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Received May 17, 1985

Abstract: The relative proton affinities of CH_3CN (acetonitrile) and CH_3NC (methyl isocyanide) were determined by using the Selected Ion Flow Tube technique. Two distinct species were observed for the $C_2H_4N^+$ ion: one produced from CH_3CN and one from CH_3NC. The two $C_2H_4N^+$ isomers were readily distinguished in the flow tube by their different reactivity. The association product, $C_2H_4N^+$, of the ion-molecule reaction between CH_3^+ and HCN was shown to be present in both isomeric forms in the ratio 85% protonated acetonitrile and 15% protonated methyl isocyanide.

The proton affinity (PA) of CH_3CN (acetonitrile) has been established by several techniques[1-3] as 788 ± 8 kJ mol^{-1}, whereas that of CH_3NC (methyl isocyanide) has been less well-characterized. Illies et al.[4] quote measurements by Aue et al. of 828 kJ mol^{-1} [5] for the proton affinity of methyl isocyanide. From the known heats of formation of CH_3CN and CH_3NC[23] and their respective proton affinities, the heats of formation of the isomers

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(4) Illies, A. J.; Shuying Liu; Bowers, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5674.

(5) Inferred from the data given in ref 4 and assuming a proton affinity for CH_3OH of 759 kJ mol^{-1}.

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