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PM3-MO Calculations of Monolithiated Sulfones, Sulfoxides, and 1,3-Dithianes: Comparison with *ab Initio* or X-ray Results

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Geometries of dimethyl sulfone, the methylsulfonyl anion, and its monolithiated isomers **3**−**6**, $CH_3-SO_2-CH_2Li$, were calculated by *ab initio* (MP2(full)/6-31+G*//MP2-(full)/6-31+G*) and semiempirical (MNDO and PM3) methods. d-Orbitals are not involved in the stabilization of the anion (NBO analysis). From calculation of the energy differences (MP4(sdtq)/6-31+G*//MP2(full)/6-31+G*, with inclusion of the ZPE correction) between the lithiated isomers, structure **3** (C_1, the Li^+ in contact with the C_a carbon, and one oxygen) turns out to be most stable. The second minimum, **4** (C_s, the Li^+ in contact with the two oxygens), is 6.5 kcal/mol less stable. The transition states **5** (23.5 kcal/mol above **3**) and **6** (4.9 kcal/mol above **3**) are associated with two different modes for the interconversion of **3** into its mirror image. The PM3 (but not the MNDO) results are in acceptable agreement with the energetic ordering and the structural data obtained from *ab initio* calculations. PM3 and MNDO were applied to a variety of known X-ray structures in which the sulfur atom is found in different oxidation states (**8**, $[Ph-SO_2-CHPhLi{\cdot}TMEDA]_2$, **9**, $[Ph-SO-CPh(Me)-Li{\cdot}TMEDA]_2$, and **10**, $PhC(S-(CH_2)_3-S-)Li{\cdot}TMEDA{\cdot}THF$). These complexes are described much better by PM3 than by MNDO.

Introduction

All the title compounds play an important role as reactive and easily accessible intermediates.[1] The well-known stabilization of carbanionic centers by adjacent sulfur groups[2] as found for example in metalated sulfones, $R^1R^2C^--SO_2R^3\ M^+$, has given rise to many theoretical[3] and additional experimental[4] studies. As pointed out by Bors and Streitwieser,[3e] there is now a certain agreement between both the experimental and theoretical research groups that this stabilization—at least in the sulfones—is dominated by an $n_C-\sigma^*_{S-R}$ interaction and not by d_S-p_C π-bonding.[2] Lately, the role of the counterion M^+ has gained more interest.[5]

Nevertheless, despite recent increases in computer capabilities, a dearth of high-level *ab initio* results for small model compounds and semiempirical results for larger systems (see below) is obvious. Model compounds (e.g. the lithiated sulfone system) have been calculated using the 3-21G basis set family.[3]

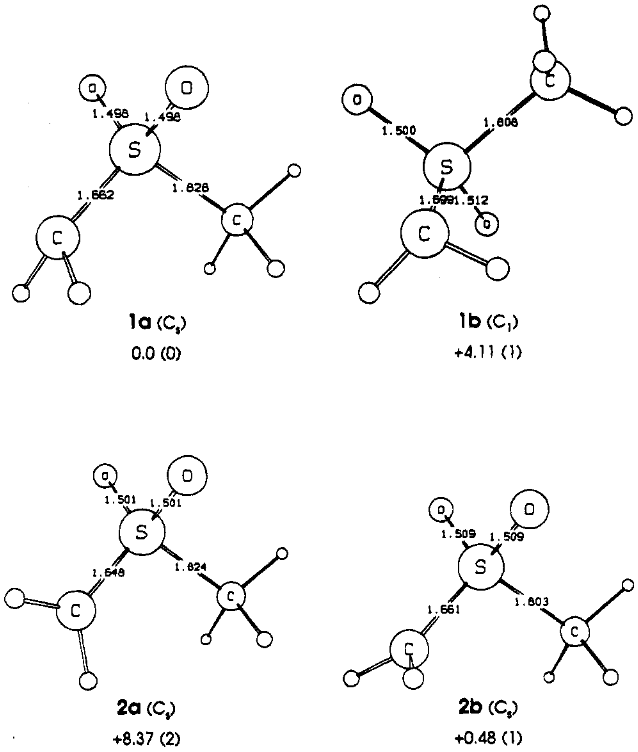

Figure 1. Methylsulfonylmethyl anion. (MP4(sdtq)/6-31+G*//MP2(full)/6-31+G* results; bond lengths in angstroms (Å); relative energies in kilocalories per mole (kcal/mol); number of imaginary frequencies in parentheses.)

To what extent are semiempirical calculations suitable for investigating sulfur-containing lithiated compounds—especially the larger species? Two "popular" methods are now available, MNDO and PM3: the latter was recently

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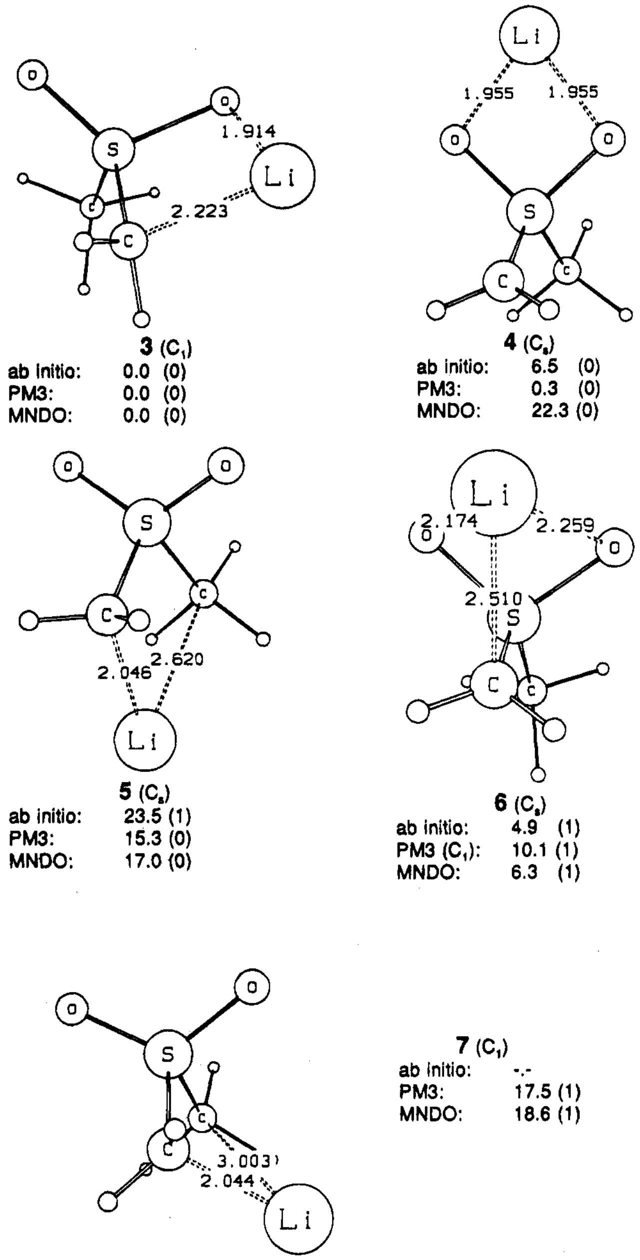
Table 1. Selected Bond Lengths [Å], and Bond and Dihedral Angles [Deg] of Dimethyl Sulfone and Its Anion

	6-31G*	6-31+G*	MP2(full)/ 6-31+G*	PM3	MNDO
			Dimethyl Sulfone		
S−O	1.437	1.438	1.472	1.468	1.534
S−C	1.774	1.774	1.783	1.793	1.815
C−H_t	1.082	1.082	1.092	1.099	1.104
C−H	1.081	1.081	1.091	1.098	1.103
O−S−O	120.1	119.9	120.9	118.2	114.9
C−S−C	104.3	104.5	103.8	100.0	105.9
H−C−H	111.2	111.3	111.6	106.6	110.5
H_t−C−S	106.5	106.4	106.1	112.0	107.9
S−(HCH)	121.7	121.5	121.4	124.8	120.2
			Dimethyl Sulfone Anion **1a**		
C_a−S	1.660	1.670	1.662	1.575	1.648
C−S	1.809	1.807	1.828	1.846	1.839
S−O	1.460	1.462	1.498	1.532	1.545
C_a−H_a	1.080	1.079	1.086	1.080	1.073
C−H	1.084	1.083	1.093	1.094	1.102
C−H_t	1.085	1.085	1.094	1.094	1.102
O−S−O	117.4	117.3	118.7	113.3	111.4
C_a−S−C	112.6	112.7	113.9	104.3	106.4
S−C−H_t	109.2	108.6	108.5	112.0	109.1
H_a−C_a−H_a	115.8	116.8	118.7	111.1	120.9
H−C−H	109.8	110.1	110.6	107.0	109.6
C_a−(OSO)	129.8	129.2	129.5	134.7	131.1
S−($H_aC_aH_a$)	132.3	134.1	139.7	177.8	177.6
S−(HCH)	120.0	119.6	118.8	122.3	120.3

extended to lithium by the development of an optimized parameter set.[6]

In order to assess the reliability of these semiempirical methods in calculating structures and energy relationships, we first focused our interest on the dimethyl sulfone system; that is the methylsulfonylmethyl anion, and a variety of its corresponding monolithiated structures ($CH_3-SO_2-CH_2Li$, Figures 1 and 2). Our orientating investigation[6] was based on the 3-21G(*) results published by Bors and Streitwieser.[3e] We recalculated this system with larger *ab initio* basis sets. On the basis of these results, we extended this investigation by semiempirical calculations on previously published X-ray structures of the dimeric complex of a lithiated sulfone,[7] [Ph−SO₂−CHPhLi·TMEDA]₂ (Figure 3), a dimeric sulfoxide,[8] [Ph−SO−CPh(Me)Li·TMEDA]₂ (Figure 4), and a monomeric 1,3-dithiane,[9] PhC(S−(CH₂)₃−S−)Li·TMEDA·THF (Figure 5). We are thus concerned with characteristic substance classes in which the sulfur atom is found in different oxidation states and for which typical lithium−cation coordinating solvent molecules will be considered. The general purpose of the following investigation is to provide a comprehensive assessment of the applicability of PM3.



3 (C_1)
ab initio: 0.0 (0)
PM3: 0.0 (0)
MNDO: 0.0 (0)

4 (C_s)
ab initio: 6.5 (0)
PM3: 0.3 (0)
MNDO: 22.3 (0)

5 (C_s)
ab initio: 23.5 (1)
PM3: 15.3 (0)
MNDO: 17.0 (0)

6 (C_s)
ab initio: 4.9 (1)
PM3 (C_1): 10.1 (1)
MNDO: 6.3 (1)

7 (C_1)
ab initio: -.-
PM3: 17.5 (1)
MNDO: 18.6 (1)

Figure 2. The lithiomethyl methyl sulfone system (Li/PM3-calculated structures; bond lengths in angstroms (Å); MP4-(sdtq)/6-31+G*//MP2(full)/6-31+G*-, PM3- and MNDO results; relative energies in kilocalories per mole (kcal/mol).)

Method

Ab initio calculations were performed using the Gaussian 92[10] program package. Semiempirical calculations were run using the program MOPAC6/PC.[11] All geometries were optimized at MNDO,[12] PM3,[13] HF/6-31G*,[14] HF/6-31+G*,[15] and MP2(full)/6-31+G* (including Møller−Plesset electron correlation[16] in the framework of full second order) levels, and characterized as minima, saddle points, etc. by calculation of vibrational frequencies. Energy calculations were performed on the MP2(full)/6-31+G* geometries using the 6-31++G** basis set (MP2(full) level) and the 6-31+G* basis set (MP4-(sdtq) level). Zero point energies were scaled by 0.91.[17] If MNDO or PM3 were used for the calculation of lithium-

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Table 2. Energies[a] and Total Energies[b]

species (point group)	PM3[a] (NIMAG)[c]	MNDO[a] (NIMAG)[c]	6-31G*//6-31G*[b]	6-31+G*//6-31+G*[b]	MP2(full)/6-31+G*//MP2(full)/6-31+G*[b]	MP2(full)/6-31++G**//MP2(full)/6-31+G*[b]	MP4(sdtq)/6-31+G*//MP2(full)/6-31+G*[b]	ZPE[d] (NIMAG)[e]
dimethyl sulfone (C_{2v})	−76.27(0)	53.72(0)	−626.391 730	−626.398 785	−627.203 886	−627.252 335	−627.238 336	57.51(0)
1a (C_s)	−90.62(0)	38.60(0)	−625.768 293	−625.789 204	−626.606 963	−626.650 113	−626.638 517	47.84(0)
1b (C_1)	−86.07(1)	44.0(1)	−625.760 966	−625.781 693	−626.598 390	−626.641 643	−626.631 083	47.34(1)
2a (C_s)	−85.06(1)	44.87(1)	−625.752 143	−625.773 967	−626.592 070	−626.635 135	−626.623 573	46.71(2)
2b (C_s)	−90.61(1)	38.61(0)	−625.766 729	−625.788 144	−626.605 961	−626.648 937	−626.637 025	47.34(1)
3 (C, O) (C_1)	−69.03(0)	26.14(0)	−633.277 754	−633.285 205	−634.104 437	−634.146 223	−634.132 779	50.35(0)
4 (O, O) (C_s)	−68.77(0)	48.47(0)	−633.265 243	−633.274 154	−634.095 212	−634.137 175	−634.121 418	49.63(0)
5 (C,C) (C_s)	−53.69(0)	43.14(0)	−633.237 282	−633.246 049	−634.064 061	−634.105 971	−634.094 826	50.02(1)
6 (TS **3**−**3**) (C_s)	−58.98(1)[f]	32.48(0)	−633.262 307	−633.273 726	−634.096 563	−634.138 070	−634.124 180	49.86(1)
7 (TS **3**−**5**) (C_1)	−51.49(1)	44.73(1)						

[a] Energies in kilocalories per mole (kcal/mol). [b] Total energies in atomic units (= 627.51 kcal/mol). [c] *N*umber of *IMAG*inary frequencies. [d] Zero-point energies in kilocalories per mole (kcal/mol) (6-31+G* calculations). [e] *N*umber of *IMAG*inary frequencies (6-31+G* calculations). [f] Transition state (C_1) **3** → **4**.

Table 3. Relative Energies[a]

species	PM3	MNDO	6-31G*//6-31G*	6-31+G*//6-31+G*	MP2(full)/6-31+G*//MP2(full)/6-31+G*	MP2(full)/6-31++G**//MP2(full)/6-31+G*	MP4(sdtq)/6-31+G*//MP2(full)/6-31+G*	corrected[b]
1a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1b	+4.55	+5.40	+4.60	+4.71	+5.38	+5.32	+4.66	+4.11
2a	+5.56	+6.27	+10.13	+9.56	+9.35	+9.40	+9.38	+8.35
2b	+0.01	+0.01	+0.98	+0.67	+0.63	+0.74	+0.94	+0.48
3 (C, O)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4 (O, O)	+0.26	+22.23	+7.85	+6.93	+5.79	+5.68	+7.13	+6.47
5 (C, C)	+15.34	+17.00	+25.40	+24.57	+25.34	+25.26	+23.82	+23.52
6 (TS **3**−**3**)	+10.05[c]	+6.34	+9.69	+7.20	+4.94	+5.12	+5.40	+4.95
7 (TS **3**−**5**)	+17.54	+18.59						

[a] Energies in kilocalories per mole (kcal/mol). [b] Zero-point energy corrected, see ref 17. [c] Transition state (C_1) **3** → **4**.

containing compounds, these methods are denoted Li/MNDO and Li/PM3.

Results and Discussion

To reveal inherent deficiencies of the semiempirical methods, we first calculated the methylsulfonylmethyl anion with several *ab initio* basis sets (see Tables 2 and 3), and then compared the results with semiempirical (MNDO and PM3) data. Further, our study of some isomeric lithiated structures of this anion allows both a comparison of the optimized geometries and relative energies.

Methylsulfonylmethyl Anion. We calculated four structures **1a** (C_s), **1b** (C_1), **2a** (C_s), and **2b** (C_s) (Figure 1). The first two (**1a** and **b**) differ in the nature of negative hyperconjugation[18] (**1a**, $n_C-\sigma^*_{S-C}$ interaction; **1b**, $n_C-\sigma^*_{S-O}$ interaction). The only minimum, **1a**, is found to be 4.11 kcal/mol more stable than **1b** which has one negative eigenvalue and thus indicates the predominant interaction of the carbon lone pair (n_c) with the antibonding σ^*-orbital of the S−CH_3 bond. This is further supported by an NBO analysis,[19] based on an MP4/6-31+G*//MP2(full)/6-31+G* single-point calculation: the $n_C-\sigma^*_{S-C}$ stabilization (33.9 kcal/mol) is found to be about 6 kcal/mol more effective than the corresponding $n_C-\sigma^*_{S-O}$ interaction (27.8 kcal/mol). The hyperconjugation causes a shortening of the C_a−S and a lengthening of the S−CH_3 bond, relative to the analogous bonds in dimethyl sulfone (Table 1). Structure **2a**,[4e] with the CH_2 moiety in the C_s plane, reveals two imaginary frequencies and lies 8.37 kcal/mol above **1a**.

These optimized geometries are in good agreement with preceding theoretical investigations.[3c,e] The only remarkable point is that the carbanion now (finally) turns out to be pyramidal with the hydrogens bent out of plane by 40.3° as indicated by the dihedral angle S−H_a−C−H_a in Table 1. However, the energy difference between the pyramidal minimum and the planar structure **2b** is calculated to be 0.48 kcal/mol. This difference is much too small to be considered of (experimental) significance. Bors and Streitwieser reported similar conclusions, they found the anionic carbon to be planar at the 3-21G(*)+ level.[3e] The pyramidal structure **1a** found in the course of our study makes d_S-p_C π-interaction for the stabilization of the carbanion unlikely. This is also supported by the NBO analysis of **1a**: the *d* character on sulfur in the σ bond orbitals is always less than 2%, too low to be of any significance.

Comparison of the MP2(full)/6-31+G* geometries of **1a** and the neutral molecule with those of the semiempirical methods is given in Table 1. The above-mentioned small influence of sulfur d-orbitals in stabilizing α-sulfonyl carbanions justifies the application of the semiempirical methods for energies, but, however, their effect on structures is well-known.[20] In the following we assess

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Table 4. Selected Bond Lengths [Å] and Bond and Dihedral Angles [Deg] of Monolithiated Dimethyl Sulfones

	6-31G*	6-31+G*	MP2/6-31+G*	PM3[a]	MNDO
3					
C_a—S	1.713	1.714	1.706	1.662	1.858
C—S	1.779	1.779	1.786	1.798	1.804
S—O_1	1.491	1.491	1.530	1.604	1.572
S—O_2	1.442	1.444	1.477	1.485	1.535
O_1—Li	1.870	1.858	1.851	1.914	2.067
O_2—Li	3.335	3.333	3.352	3.741	3.771
C_a—Li	2.116	2.128	2.115	2.223	1.992
S—C_a—Li	79.2	78.9	78.9	84.3	87.0
O—S—O	115.8	115.6	116.4	113.8	111.5
C_a—S—C	113.9	114.4	115.1	108.0	113.2
H_a—C_a—H_a	111.7	111.7	112.5	108.3	109.1
C_a—(OSO)	121.0	120.6	121.0	124.1	118.7
S—($H_aC_aH_a$)	123.0	123.1	124.3	145.5	117.5
4					
C_a—S	1.627	1.634	1.628	1.528	1.659
C—S	1.790	1.790	1.804	1.797	1.832
S—O	1.492	1.491	1.528	1.594	1.571
O—Li	1.893	1.888	1.890	1.954	2.076
C_a—Li	3.447	3.446	3.466	3.802	3.882
S—C_a—Li	36.3	36.3	35.2	30.7	36.4
O—S—O	106.3	106.2	106.9	96.6	97.8
C_a—S—C	118.2	117.8	119.1	109.0	114.2
H_a—C_a—H_a	119.4	119.5	120.4	108.2	122.0
C_a—(OSO)	123.1	122.9	123.3	127.4	120.9
S—($H_aC_aH_a$)	142.0	141.5	144.0	179.2	164.4
5					
C_a—S	1.749	1.748	1.744	1.703	1.817
C—S	1.785	1.785	1.805	1.852	1.842
S—O	1.446	1.448	1.483	1.488	1.532
O—Li	4.177	4.181	4.101	4.033	3.947
C_a—Li	2.020	2.012	2.005	2.045	1.915
C—Li	3.293	3.314	3.122	2.622	2.482
S—C_a—Li	120.5	121.1	115.1	108.1	101.7
O—S—O	119.1	118.9	120.3	116.3	113.3
C_a—S—C	106.9	107.2	106.7	98.7	98.6
H_a—C_a—H_a	107.8	107.8	108.9	107.0	108.6
C_a—(OSO)	128.9	128.7	130.1	134.2	133.8
S—($H_aC_aH_a$)	111.9	111.9	113.8	131.8	117.2
6					
C_a—S	1.697	1.697	1.683	1.601	1.909
C—S	1.796	1.777	1.786	1.779	1.788
S—O	1.467	1.467	1.506	1.580	1.565
O—Li	2.284	2.293	2.225	2.210	2.319
C_a—Li	2.169	2.185	2.227	2.510	2.040
S—C_a—Li	71.4	71.3	68.1	66.9	75.2
O—S—O	112.0	112.0	112.4	102.9	102.2
C_a—S—C	118.8	118.7	120.4	114.5	127.3
H_a—C_a—H_a	113.7	113.7	115.2	109.4	109.2
C_a—(OSO)	114.5	114.8	115.2	114.8	103.7
S—($H_aC_aH_a$)	127.5	127.7	130.8	161.8	117.3

[a] Compound **6**, the C_1-symmetrical transition state (**3** → **4**) cannot be compared with other structures.

the reliability of PM3 and MNDO in reproducing geometries. The CH_2 moiety of the most stable conformation **1a** is calculated to be (almost) planar, but, qualitatively bond length changes are well-represented by PM3 and MNDO (Table 1).

PM3 was found to be distinctly superior to MNDO because of the improved description of hypervalent molecules.[21] As expected, PM3 is in very good agreement with *ab initio* results for dimethyl sulfone, whereas MNDO gives too long S—O and S—C bonds. The description of the anionic species is less accurate. Both semiempirical methods reveal S—O bonds that are too long. Furthermore, the anionic C—S bond is calculated about 0.09 Å too short using PM3. Another significant difference is the near planarity of the carbanion in contrast to the 40° pyramidality predicted by *ab initio* results.

Table 5. Structural Data of [Ph—SO_2—CHPhLi·TMEDA]$_2$, 8

	X-ray[a]	PM3	MNDO
bond lengths (Å)			
C_1—S	1.641(5)	1.601	1.693
C_8—S	1.784(5)	1.804	1.793
S—O	1.465(4)	1.554	1.543
N—Li	2.136(10)	2.228	2.341
O—Li	1.890(9)	1.843	2.073
C_1—C_2	1.437(8)	1.428	1.424
bond angles (deg)			
O—S—O	115.4(2)	111.5	108.6
S—C_1—C_2	125.8(4)	131.0	128.6
dihedrals (deg)			
O—S—C_1—C_2	45.6(6)	39.3	45.9
	175.4(5)	167.3	167.9
C_8—S—C_1—C_2	70.4(6)	77.9	76.2
S—C_1—C_2—C	3.1(9)	0.1	12.2
	176.8(30)	179.7	169.0

[a] See ref 7.

Table 6. Selected Data of [Ph—SO—CPh(Me)Li·TMEDA]$_2$, 9

	X-ray[a]	PM3	MNDO
bond lengths (Å)			
Li—O	1.92(2)	1.965	2.222
Li—N	2.13(2)	2.285	2.445
Li—Li	2.65(4)	2.724	3.044
Li—C_1	4.00(3)	3.700	4.109
S—O	1.58(1)	1.666	1.567
S—C_1	1.63(1)	1.675	1.673
S—C_9	1.81(1)	1.819	1.756
C_1—C_2	1.44(2)	1.434	1.444
C_1—C_8	1.54(2)	1.491	1.491
bond angles (deg)			
O—Li—O	91(1)	91.3	93.5
Li—O—Li	87(1)	87.7	86.5
Li—O—S	148(1)	138.4	149.7
Li_a—O—S	123(1)	118.8	117.1
O—S—C_1	117(1)	110.1	113.3
O—S—C_9	101(1)	104.8	107.5
C_1—S—C_9	104(1)	104.6	106.9
S—C_1—C_2	120(1)	129.3	128.2
S—C_1—C_8	119(1)	112.2	110.9
C_2—C_1—C_8	118(1)	117.9	120.3

[a] See ref 8.

Table 7. Selected Data of PhC(S—$(CH_2)_3$—S—)Li·TMEDA·THF, 10

	X-ray[a]	PM3	MNDO
bond lengths (Å)			
Li—O	1.970	2.077	2.416
Li—N_1	2.148	2.244	2.440
Li—N_2	2.110	2.231	2.452
Li—C_1	2.280	2.203	2.153
C_1—C_5	1.468	1.471	1.490
C_1—S_1	1.776	1.789	1.718
C_1—S_2	1.769	1.788	1.718
bond angles (deg)			
O—Li—N_1	105.8	101.8	100.5
O—Li—N_2	108.8	106.7	109.8
O—Li—C_1	117.2	124.8	106.6
C_1—Li—N_1	119.8	117.5	134.7
C_1—Li—N_2	114.1	114.4	123.9
N_1—Li—N_2	86.9	83.8	77.4
C_5—C_1—Li	119.5	121.4	107.8

[a] See ref 9, $\sigma \geq 0.005$ Å and 0.1°, respectively.

Lithiomethyl Methyl Sulfone.[3d,e] The energy surface of the lithiomethyl methyl sulfone isomers was first explored with Li/PM3.[6] The resulting three structures were then optimized at the MP2(full)/6-31+G* level to

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[21] Stewart, J. J. P. *MOPAC—A Semiempirical Molecular Orbital Program*; ESCOM Science Publishers: Holland, 1990.

give the stationary points **3**−**5**. One might expect the lithium cation to prefer coordination to the three negatively charged centers, the oxygen atoms, and the carbanion. This is not the case. What appears to be the global minimum is the unsymmetrical (C_1) structure **3** with the lithium cation in contact with the anionic carbon and only one oxygen atom. A second minimum (**4**, C_s, +6.47 kcal/mol relative to **3**; MP4(sdtq)/6-31+G*//MP2-(full)/6-31+G*) locates the lithium in a "scissored" position in contact with the two oxygen atoms. Structure **5** (C_s, +23.52 kcal/mol), a species with one imaginary frequency, shows the Li^+ in the C_s plane in contact with the anionic center and can be interpreted to be the transition state for the interconversion of **3** into its mirror image by rotation of the lithiomethyl group *under* the C_a−S bond (Figure 2, *ab initio* results).

The alternative route to this mirror image is represented by a second transition state (**6**, C_s), with the Li^+ in contact with both the oxygen atom and the carbanionic center. Compared with the pathway via **5**, this interconversion via **6** is favored (see Table 3, energies relative to **3**: **5**, +23.52 kcal/mol; **6**, +4.95 kcal/mol). Both semiempirical methods fail to find a structure comparable to **6**. Li/MNDO predicts an additional C_s symmetrical minimum, which might be the result of the well-known overestimation of the Li−C interaction.[22] Li/PM3 suggests an interconversion mechanism via an unsymmetrical (C_1) transition state with the Li^+ facing the two oxygen atoms (relative energy +10.1 kcal/mol), but this pathway includes structure **4** as an intermediate. For completeness we also discuss the "semiempirical" structure **7**, which cannot be located by *ab initio* calculations. Because the isomer **5** is predicted incorrectly by Li/PM3 and Li/MNDO to be a minimum, both methods find a further transition state, **7**, which corresponds to the movement of Li^+ as located in **3** to give the minimum **5**. Obviously, both structures **5** and **7** are artifacts of the semiempirical methods. For further details, see Table 2 (relative energies).

In contrast to Li/MNDO, which predicts the second minimum **4** to be the least stable isomer (22.3 kcal/mol higher in energy than **3**), the *ab initio* relative ordering is reproduced by Li/PM3. Nevertheless, both semiempirical methods favor the correct inversion pathway of isomer **3** under exclusion of structures comparable with **5**. Li/PM3, however, seems to overestimate the Li−O interaction slightly. This is indicated by the stability of **4** (only 0.3 kcal/mol less stable than **3**) and the fact that the preferred conversion mode of **3** into its mirror image is characterized by the movement of the lithium atom from **3** to **4** with its two strong Li−O contacts.

In order to assess the performance of the semiempirical methods in describing geometries, some specific structural properties from *ab initio* and Li/MNDO and Li/PM3 calculations are summarized in Table 4. Compared with the methylsulfonylmethyl anion, the addition of the lithium cation leads to three significant structural changes. Contact of Li^+ with one or both oxygens results in a longer S−O bond (structures **3** and **4**), whereas a C_a−Li contact (as in **3** and **5**) lengthens the C_a−S and shortens the C−S bond. The third effect is the shortening of both the C_a−S and the C−S bonds in the case of a free C_a center (structure **4**). Li/PM3 is clearly superior to Li/MNDO in predicting these changes, although, as mentioned above, there are still some deficiencies resulting from the description of the free anion by MNDO and PM3. (The S−O bond length is overestimated; the "free" C_a−S bond results as too short; the angles around the sulfur atom are too small.) Note that Li/MNDO dramatically increases the C_a−S bond in case of an Li^+ attached to the C_a center. In general, the representation of Li−C and Li−O bonds is much more accurate with Li/PM3 than with Li/MNDO.

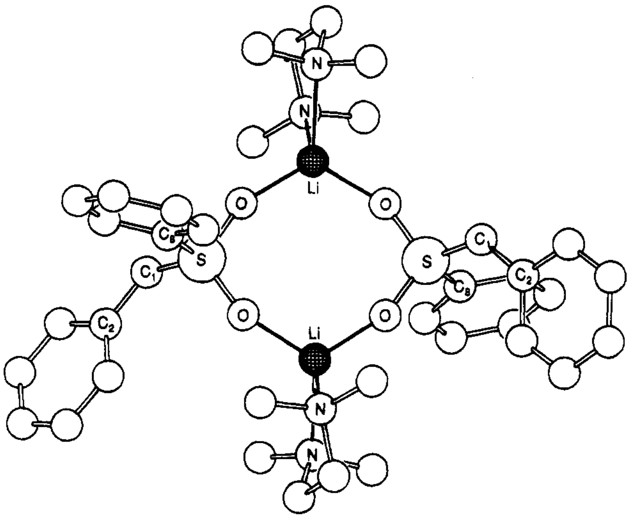

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Figure 3. Li/PM3-calculated structure of $[Ph-SO_2-CHPhLi\cdot TMEDA]_2$ (ref 7).

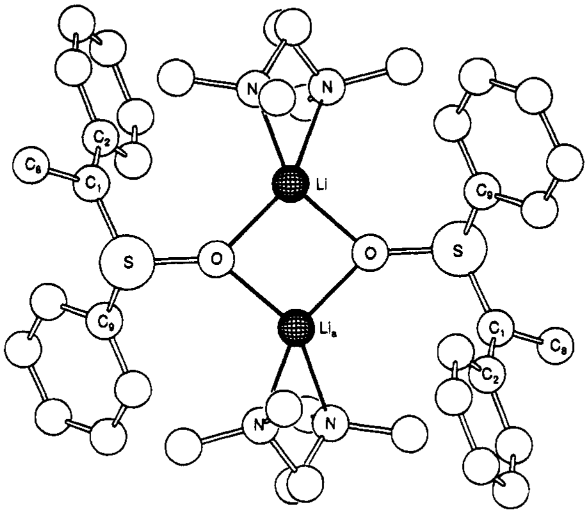

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Figure 4. Li/PM3-calculated structure of $[Ph-SO-CPh(Me)-Li\cdot TMEDA]_2$ (ref 8).

Comparison of Li/PM3 Results With X-ray Structures of Monolithiated Sulfur-Containing Compounds. Finally, in order to test the reliability of the Li/PM3 method in predicting geometries of larger systems, we calculated the compounds **8**−**10**. The X-ray structures of two TMEDA complexes **8**, a dimeric lithiated sulfone, and **9**, a dimeric lithiated sulfoxide, have been reported previously by Boche et al.[7,8] The X-ray structure **10** (reported by Amstutz, Dunitz, and Seebach[9]) was included because this monomeric lithiated dithiane contains TMEDA *and* THF in the complex. Both semiempirical methods find the essential features of the X-ray

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[22] Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *55*, 335.

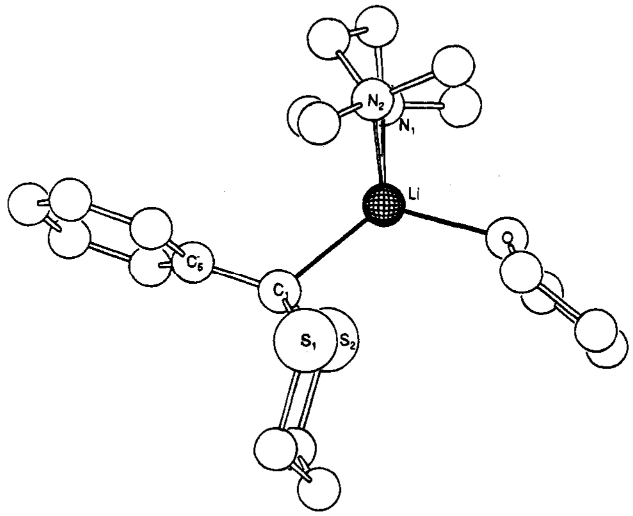

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Figure 5. Li/PM3-calculated structure of PhC(S−$(CH_2)_3$−S−)Li·TMEDA·THF (ref 9).

structures. Therefore, the following discussion is restricted to Li−O, Li−N, and Li−C distances. For further details compare the data collected in Tables 5−7. Some deficiencies can be tracked down to inherent errors of PM3 and MNDO as discussed for dimethyl sulfone and its anion (vide supra), e.g. for the S−O and C−S bond lengths, but most of them are reduced in the calculation of larger molecules.

[Ph−SO_2−CHPhLi·TMEDA]$_2$, 8. The central segment of the S, O, and Li atoms is a flat chairlike eight-membered ring system (Figure 3), the lithium cations are not in contact with the carbanionic centers C(1). In particular, the Li−O and the Li−N distances are reproduced better by Li/PM3 than by Li/MNDO (Table 5).

[Ph−SO−CPh(Me)Li·TMEDA]$_2$, 9. This dimeric species shows a central O/Li/O/Li four-membered ring system (Figure 4). Again, the lithium cations are not coordinated by the carbanionic centers C(1). Comparison of the Li−O, Li−N, Li−Li, and Li−C(1) distances indicate that this segment is much better described by Li/PM3 than by Li/MNDO (Table 6).

PhC(S−$(CH_2)_3$−S−)Li·TMEDA·THF, 10. This example belongs to the important class of the Seebach−Corey "Umpolung" reagents (Figure 5). This complex **10** is especially suitable for testing the reliability of any semiempirical method in predicting correct structures in this field: It contains contacts of the lithium cation to the carbanionic center, to the oxygen atom of THF, to two nitrogen atoms of TMEDA, and some characteristic C−S bond lengths. As summarized in Table 7, all these Li−O, Li−N(1), Li−N(2), Li−C(1) contacts and further details of the structure suggest that Li/PM3 performs significantly better than Li/MNDO.

Together with previous results,[6] these calculations support the superior applicability of Li/PM3 for the description of large molecules and X-ray structures.

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