Ab Initio Study of the Effect of Fluorination upon the Structure and Configurational Stability of α-Sulfonyl Carbanions: The Role of Negative Hyperconjugation†

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Received September 5, 1995. Revised Manuscript Received February 29, 1996⊗

Abstract: Ab initio calculations of the (methylsulfonyl)methyl anion (**1**), the ((trifluoromethyl)sulfonyl)methyl anion (**1T**), the (fluorosulfonyl)methyl anion (**1F**), and the (methylsulfonyl)isopropyl anion (**1D**) at the HF/6-31+G*//HF/6-31+G* level revealed a significant effect of fluorine substitution upon the structure and energy of α-sulfonyl carbanions. The C_α−S bond in **1T** and **1F** is shorter and the pyramidalization of the anionic carbon atom is less than in **1**. In the anions **1T** and **1F** the C_α−S bond is shortened and the S−CF_3(F) and the S−O bonds are lengthened as compared to the sulfones **3T** and **3F**. For all anions the staggered conformation (**1**, **1T**, **1F**, **1D**) is energetically more stable than the eclipsed conformation (**2**, **2T**, **2F**, **2D**). At the MP2/6-31+G*//HF/6-31+G* level the energy difference between the staggered and the eclipsed conformation is much larger for the fluorinated anions **1T** and **1F** than for **1** and **1D**. The rotational barriers about the C_α−S bond of the fluorinated species **1T** and **1F** are in accordance with related experimental results significantly higher than the barriers of the non-fluorinated species **1** and **1D**. A Fourier series analysis of the rotational potential curves shows the dominance of a positive V_2 term (conjugative overlap effects) which is much higher for **1T** and **1F** than for **1** and **1D**. Negative hyperconjugation ($n_C-\sigma^*_{SR}$) is an important mechanism which determines the conformation of the anions and particularly of the fluorinated anions. In the dimethyl anion **1D**, which has a strongly pyramidalized anionic carbon atom, the V_3 term (steric and torsional effects) also contributes significantly to the rotational barrier. The configurational stability of chiral α-sulfonyl carbanions thus depends on the height of the C_α−S rotational barrier which is determined by $n_C-\sigma^*_{SR}$ interaction and the steric contribution of the substituents. The calculations suggest that *S*-(trifluoromethyl) substitution of other *S*-stabilized carbanions should lead also to derivatives of a higher configurational stability.

Introduction

The structure and dynamics of the synthetically important α-sulfonyl carbanion salts **I**[1,2] has been studied extensively in recent years.[3−24] The dependence of the structure of **I** on the substituents (R^1−R^3), the cation (M^+), the ligand (L), and the aggregation number (*n*) has been revealed, in the crystal, by X-ray analysis,[3,4,7,9−11,13−16,18−20] whereas their structure in tetrahydrofuran solution has been inferred from cryoscopic experiments,[13,15,18] heteronuclear Overhauser enhancement NMR spectra,[13,15,18,20] hexamethylphosphoric triamide titration,[17] and acidity measurements of the corresponding sulfones **II**.[8]

$$\{[R^1R^2C_\alpha-SO_2R^3H]^-[M\cdot L_m]^+\}_n \qquad R^1R^2C(H)-SO_2R^3$$

I **II**

Although far from being complete, the following general picture about the structure of **I** can be drawn: (1) In the crystal they form solvated dimeric[3,4,7,9,10,13−16] or monomeric[11,20] contact ion pairs, depending on the nature of the ligand L, whereas in tetrahydrofuran solution they exist predominantly as solvated monomeric contact ion pairs.[13,15,18] (2) The contact ion pairs exhibit oxygen−metal and no carbon−metal bonds in the crystal

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† Presented in part at the 29th Symposium on Theoretical Chemistry; Sep 27−Oct 1, 1993, Oberwiesenthal, Germany, and at the 16th International Symposium on the Organic Chemistry of Sulfur, July 10−15, 1994, Merseburg, Germany.

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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S0002-7863(95)03034-4 CCC: $12.00

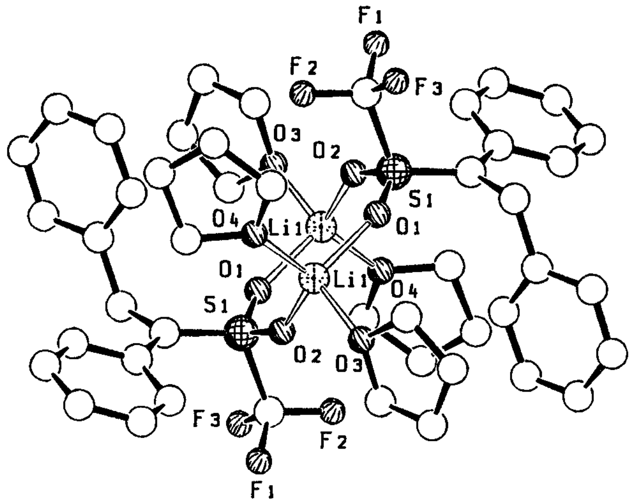

Figure 1. Crystal structure of (**Ia**·2THF)$_2$.

and, most probably, also in solution. (3) The anion prefers a staggered conformation in which the lone pair orbital at the C$_\alpha$ atom is gauche to both oxygen atoms. (4) A C$_\alpha$ atom bearing at least one aryl group is planar,[3,9,13–15] whereas the one having only alkyl groups is strongly pyramidalized.[9,16] (5) The C$_\alpha$−S bond of the anion is considerably shorter than the corresponding bond in the sulfone whereas the S−O bonds of the anion are only slightly longer than those of the sulfone. (6) Last but not least, there is no significant counterion effect of the oxygen-coordinated cation upon the bonding parameters of the anion.[9,15,16] The crystal structure of the fluorine-substituted salt {[PhCH$_2$(Ph)C-SO$_2$CF$_3$]Li·2THF}$_2$ ((**Ia**·2THF)$_2$)[13,15] depicted in Figure 1 illustrates the main structural features.

One of the most salient features of salts **I**, however, is their chirality[13,18,19] in the case of $R^1 \neq R^2$, which is related to the preferred staggered C$_\alpha$−S conformation of the anion[25,26,3] (*cf.* Figure 1). Currently there is a strong interest in the synthesis of configurationally stable chiral *S*-functionalized carbanions,[27–31] and a primary goal of the investigations in this laboratory is the synthesis of configurationally stable chiral carbanion salts **I**. We have found that deprotonation of α-chiral *S*-trifluoromethyl and *S*-*tert*-butyl sulfones **II** leads, with high enantioselectivity, to the corresponding carbanion salts **I** (R^3 = CF$_3$, *t*Bu) that are optically stable at low temperatures on the time scale of their reaction with electrophiles.[13,18,19] The racemization (enantiomerization) kinetics of **I**, as contact ion pair, as a solvent-separated ion pair, or as a counterion-free anion, has been determined by polarimetry and DNMR spectroscopy.[13,15,18–20] The results of these studies can be summarized as follows: (1) racemization is almost exclusively an enthalpic process; (2) the rate determining step is the rotation around the C$_\alpha$−S bond and not the inversion of a nonplanar C$_\alpha$ atom; (3) the height of the rotational barrier depends upon the nature of the substituent at the S atom as well as on number of the substituents at the C$_\alpha$ atom; and (4) the activation parameters do not significantly depend upon the nature of the ion pair.

Upon fluorine substitution, however, a significant alteration of the dynamics and the structure of **I** occurs. *S*-Trifluoromethyl α-sulfonyl carbanion salts **I** have a significantly higher racemization barrier than their analogous *S*-aryl and *S*-alkyl derivatives.[13,15,18] The enthalpy of activation for C$_\alpha$−S bond rotation of the *S*-trifluoromethyl-substituted compound [PhCH$_2$(Ph)C-SO$_2$CF$_3$]Li (**Ia**) in tetrahydrofuran has been determined to be 16.7 ± 0.3 kcal/mol whereas, for the corresponding *S*-*tert*-butyl substituted compound [PhCH$_2$(Ph)C−SO$_2$*t*Bu]Li (**Ib**), a $\Delta H^‡$ value of only 13.0 ± 0.3 kcal/mol was found. In order to fully appreciate this fluorine effect, one has to consider the greater steric contribution[32] of the *tert*-butyl group to the rotational barrier as compared to the trifluoromethyl group. The fluorine effect upon the optical stability of **I** is highly welcome synthetically since it allows for the preparation of derivatives of **I** (R^3 = CF$_3$) which are endowed with a half-life of racemization at −78 °C on the order of several days.[13,18,19] A manifestation of the structural alteration brought about by the introduction of fluorine is the shorter C$_\alpha$−S bond that *S*-trifluoromethyl carbanion salts **I** (R^3 = CF$_3$) appear to exhibit, as compared to their *S*-alkyl and *S*-aryl analogues.[13,15] Not surprisingly, fluorination also strongly affects the acidity of sulfones,[33] as shown by a comparison of the pK_a values of dimethyl sulfone (31.1), trifluoromethyl methyl sulfone (18.75), benzylsulfonyl fluoride (16.9), and benzyl phenyl sulfone (23.4).[12,33a] The (trifluoromethyl)sulfonyl group is one of the strongest neutral electron-withdrawing groups[34,33b] and an excellent nucleofuge, features which render the chemistry of trifluoromethyl sulfones very attractive.[13,15,35]

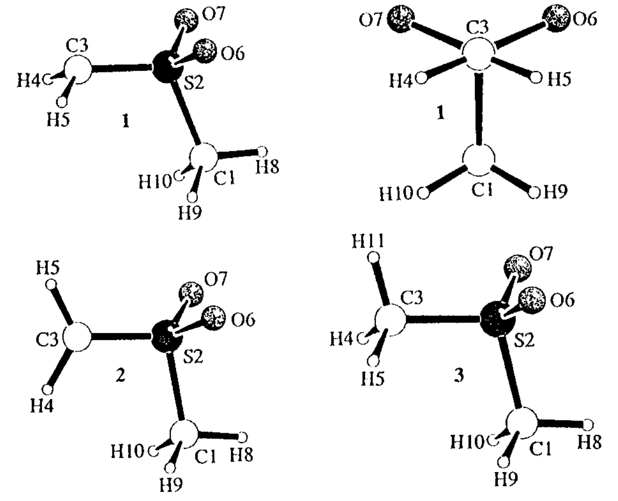

Figure 2. HF/6-31+G* optimized structures of molecules **1**, **2**, and **3**.

The structure and energetics of α-sulfonyl carbanions and their lithium salts **I** (M = Li) have also been addressed through theoretical studies. Ab initio calculations of the (methylsulfonyl)methyl anion (**1**) (Figure 2) were carried out by Wolfe et al.,[5] Streitwieser et al.,[6,21] Anders et al.,[22] and Wiberg et al.[23] The conformation with the lone pair orbital at the C$_\alpha$ atom

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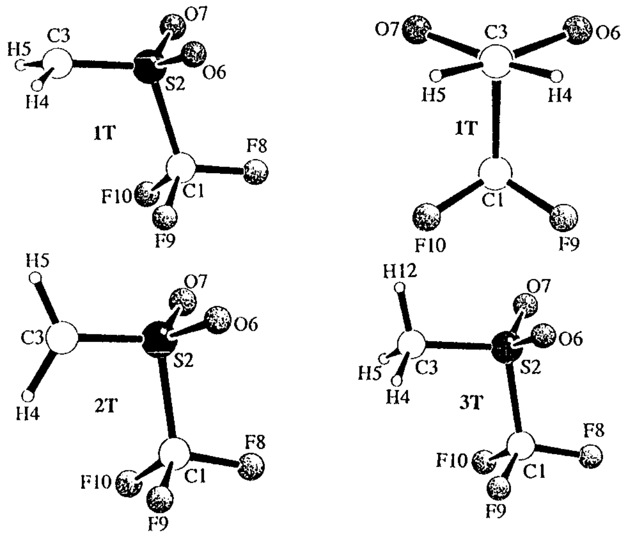

Figure 3. HF/6-31+G* optimized structures of molecules **1T**, **2T**, and **3T**.

gauche to both oxygen atoms (**1**) was found to be the most stable one. It was concluded that negative hyperconjugation[36,37] ($n_C-\sigma^*_{SMe}$)[5,38] is important in determining the minimum energy conformation.[5,6,21-23] The height of the rotational barrier of **1** was estimated to be about 9 kcal/mol,[6,22] and from a Fourier series analysis of the rotational potential curve a dominance of conjugative overlap effects was inferred.[6] Ab initio calculations of unsolvated monomeric (methylsulfonyl)methyllithium gave structures in which the cation is coordinated either to the anionic carbon atom and a single oxygen atom or only to both oxygen atoms of the (methysulfonyl)methyl anion (**1**).[5a,b,6,22] Thus far, however, for monomeric (and dimeric) solvated α-sulfonyl carbanion salts **I** coordination of the cation only to a single[20] oxygen atom or to both[11] oxygen atoms has been observed in the crystal.

In order to elucidate the effect of fluorine substitution on the structure and, in particular, on the configurational stability of α-sulfonyl carbanions, we performed ab initio calculations for the ((trifluoromethyl)sulfonyl)methyl anion (**1T**) and the fluorosulfonylmethyl anion (**1F**) (Figures 3 and 4) and compared the results with those obtained for the parent (methylsulfonyl)-methyl anion (**1**).[39,40] Another point of interest was the effect of alkyl substituents at the C_α atom upon the structure and dynamics of **I**, which has been studied experimentally[9,16,20] but not theoretically. We therefore performed further calculations for the (methylsulfonyl)isopropyl anion (**1D**) (Figure 5). To evaluate the structural differences between the anions and their conjugate acids, additional calculations were carried out for the parent sulfones: dimethyl sulfone (**3**), trifluoromethyl methyl sulfone (**3T**), methylsulfonyl fluoride (**3F**), and methyl isopropyl sulfone (**3D**) (Figures 2−5).

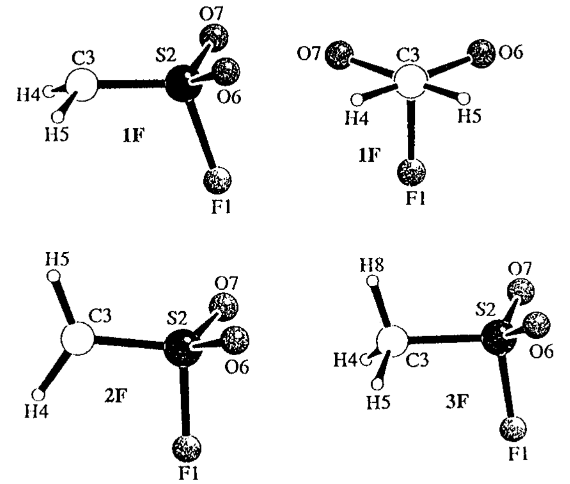

Figure 4. HF/6-31+G* optimized structures of molecules **1F**, **1F**, and **3F**.

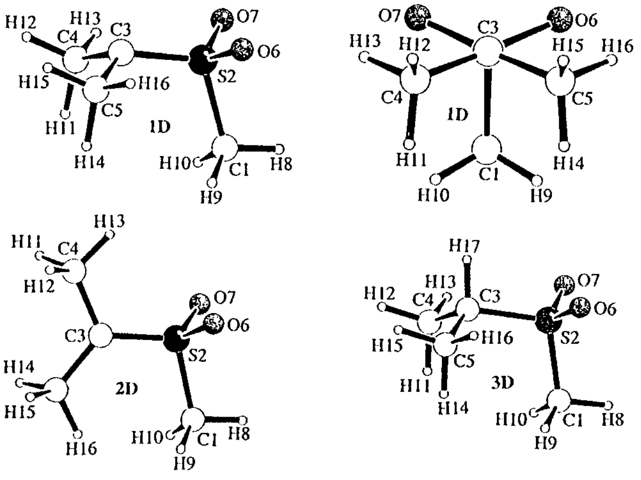

Figure 5. HF/6-31+G* optimized structures of molecules **1D**, **2D**, and **3D**.

Computational Methods

Calculations were carried out on the SNI5-600/20 and IBM 3090 facilities of the Rechenzentrum der RWTH Aachen and on a local VAX 3100 workstation employing either the GAUSSIAN 90[41] (SNI5-600/20) or GAMESS[42] (IBM 3090, VAX WS3100) packages of quantum chemical routines. All molecules under consideration were preoptimized with the 3-21G basis set[43-45] which was then augmented stepwise (3-21G(*),[45,46] 3-21+G(*),[47,48] 6-31G,[49-51] 6-31G*[52]) to 6-31+G*[47,48]

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Table 1. Selected Structural Parameters of **1**, **2**, and **3**[a]

parameter	1	2	3
C3−S2	1.670	1.663	1.774
S2−O6,7	1.462	1.472	1.438
S2−C1	1.807	1.789	1.774
H4−C3−H5	116.7	122.9	111.3
H4−C3−S2	113.2	118.4	109.6
H5−C3−S2	113.2	118.7	109.6
O6−S2−O7	117.3	110.6	119.9
O6,7−S2−C3	111.1	115.9	107.8
O6,7−S2−C1	102.0	105.2	107.9
C3−S2−C1	112.7	102.6	104.5
H4−C3−S2−C1	−67.9	0.0	−61.3
H4−C3−S2−O6	178.4	−114.0	−175.8
H4−C3−S2−O7	45.9	114.0	53.3
H5−C3−S2−C1	67.9	180.0	61.2
H5−C3−S2−O6	−45.9	66.0	−53.3
H5−C3−S2−O7	−178.4	−66.0	175.8
H11−C3−S2−O6			65.4
H11−C3−S2−O7			−65.4

[a] Bond lengths in Å, bond and dihedral angles in deg (HF/6-31+G*//HF/6-31+G*).

Table 2. Selected Structural Parameters of **1T**, **2T**, and **3T**[a]

parameter	1T	2T	3T
C3−S2	1.629	1.645	1.771
S2−O6,7	1.450	1.458	1.427
S2−C1	1.856	1.842	1.834
C1−F8	1.326	1.321	1.304
C1−F9,10	1.329	1.324	1.313
H4−C3−H5	120.9	123.3	111.8
H4−C3−S2	116.4	119.0	109.6
H5−C3−S2	116.4	117.7	109.6
O6−S2−O7	118.9	111.5	121.6
O6,7−S2−C3	113.0	117.4	109.6
O6,7−S2−C1	99.2	103.1	106.0
C3−S2−C1	111.6	101.3	102.3
H4−C3−S2−C1	76.3	0.2	61.5
H4−C3−S2−O6	−34.4	−111.1	−50.6
H4−C3−S2−O7	−173.0	111.6	173.6
H5−C3−S2−C1	−76.3	−179.8	−61.5
H5−C3−S2−O6	173.0	68.8	−173.6
H5−C3−S2−O7	34.5	−68.5	50.6
H12−C3−S2−C1			180.0
H12−C3−S2−O7			−67.9
H12−C3−S2−O6			67.9

[a] Bond lengths in Å, bond and dihedral angles in deg (HF/6-31+G*//HF/6-31+G*).

Table 3. Selected Structural Parameters of **1F**, **2F**, and **3F**[a]

parameter	1F		2F		3F
C3−S2	1.631	(1.639)	1.648	(1.646)	1.762
S2−O6,7	1.440	(1.477)	1.445	(1.485)	1.414
S2−F1	1.658	(1.772)	1.607	(1.689)	1.566
H4−C3−H5	119.1	(118.7)	124.6	(124.4)	111.5
H4−C3−S2	114.8	(113.9)	118.3	(118.8)	108.7
H5−C3−S2	114.8	(113.9)	117.2	(116.8)	108.7
O6−S2−O7	118.6	(119.6)	112.0	(111.9)	121.8
O6,7−S2−C3	113.5	(113.5)	117.7	(118.2)	110.7
O6,7−S2−F1	99.6	(98.8)	103.7	(103.5)	106.3
C3−S2−F1	109.5	(109.7)	98.8	(97.8)	98.2
H4−C3−S2−F1	−71.7	(−70.2)	0.0	(0.0)	−60.8
H4−C3−S2−O6	178.0	(−179.7)	−110.6	(−110.0)	−171.7
H4−C3−S2−O7	38.7	(39.3)	110.6	(110.0)	50.2
H5−C3−S2−F1	71.7	(70.2)	180.0	(180.0)	60.8
H5−C3−S2−O6	−38.7	(−39.3)	69.4	(70.0)	−50.2
H5−C3−S2−O7	−178.0	(179.7)	−69.4	(−70.0)	171.7

[a] Bond lengths in Å, bond and dihedral angles in deg (HF/6-31+G*//HF/6-31+G*). The values in parentheses have been optimized at the MP2/6-31+G* level.

Table 4. Selected structural parameters of **1D**, **2D**, and **3D**[a]

parameter	1D	2D	3D
C3−C4	1.513	1.500	1.529
C3−C5	1.513	1.504	1.529
C3−S2	1.677	1.660	1.801
S2−O6,7	1.461	1.475	1.441
S2−C1	1.809	1.788	1.776
C4−C3−C5	114.4	117.3	113.2
C4−C3−S2	115.4	125.9	112.2
C5−C3−S2	115.4	116.8	112.2
O6−S2−O7	117.2	110.1	119.4
O6,7−S2−C3	111.2	115.2	107.5
O6,7−S2−C1	102.2	104.4	107.3
C3−S2−C1	112.2	106.3	107.2
C1−S2−C3−C4	−68.5	0.0	−64.3
C1−S2−C3−C5	68.5	180.0	64.3
O6−S2−C3−C4	177.7	115.1	50.8
O6−S2−C3−C5	−45.2	−64.9	179.4
O7−S2−C3−C4	45.2	−115.1	−179.4
O7−S2−C3−C5	−177.7	64.9	−50.8

[a] Bond lengths in Å, bond and dihedral angles in deg (HF/6-31+G*//HF/6-31+G*).

quality by including polarization functions (*) and diffuse sp shells (+) at all atoms except hydrogen. Some optimizations were carried out under the constraint of C_s symmetry for which the mirror plane was defined by the C3−S−R^3 segment (vide infra). All stationary points were characterized by calculation of their normal frequencies. To obtain more reliable relative energies we included correlation effects by means of Møller−Plesset perturbation theory[53] to the second order on HF/6-31+G* optimized structures (MP2/6-31+G*//HF/6-31+G*). Additional geometry optimizations at the MP2/6-31+G* level were carried out for **1F** and **2F**.

Results and Discussion

Geometry. In the following discussion we will refer to **1**, **1T**, **1F**, and **1D** as the staggered and to **2**, **2T**, **2F**, and **2D** as the corresponding eclipsed conformers of the sulfonyl anions (Figures 2−5 and Tables 1−4). If not mentioned otherwise, the discussion refers to HF/6-31+G* optimized structures.

Substitution of one methyl group in dimethylsulfone (**3**) by a trifluoromethyl group or a fluorine atom results in a slight reduction of the S−CH_3 bond distance. The C1−S bond on the other hand, is 0.06 Å longer in the trifluoromethyl methyl sulfone (**3T**) than in **3**. The C3−S−R^3 angle is 104.5° in **3** and 102.3° in **3T** and thus only slightly decreases when the methyl group is replaced by the trifluoromethyl group. However, for the methylsulfonyl fluoride (**3F**) this angle is reduced by more than 6°. The O−S−O angle increases from 119.9° in **3**, to 121.6° in **3T**, and to 121.8° in **3F**. All S−R^3 bonds are longer in the anions than in the parent acids.

At the HF/6-31+G* level the R^1R^2C−S groups of the (methylsulfonyl)methyl anion (**1**), the ((trifluoromethyl)sulfonyl)methyl anion (**1T**), the (fluorosulfonyl)methyl anion (**1F**), and the (methylsulfonyl)isopropyl anion (**1D**) are more or less pyramidalized, and all of these structures turned out to be local minima. The sum of bond angles at the C_α atom can be used to define the degree of pyramidalization. The corresponding values are 343.1° in **1**, 353.7° in **1T**, 348.7° in **1F**, and 345.2° in **1D**. Except for **1T**, the H_2C−S segment of which is nearly planar, these values lie almost halfway between those for an ideal tetrahedron (328.4°) and a planar environment. Corresponding results for **1** were obtained by Anders et al.[22] These authors further showed that pyramidalization of the H_2C−S segment of **1** is retained when the optimization is carried out

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(53) Møller, C.; Plesset, S. *Phys. Rev.* **1934**, *46*, 618.

including MP2 corrections in the calculation of the gradients (MP2/6-31+G*//MP2/6-31+G*). To check whether this is also true when R^3 is an electronegative substituent, we performed an analogous optimization for **1F**. With a sum of bond angles at the anionic center of 346.5°, its deviation from planarity is even stronger than at the HF/6-31+G* level.

The optimized structure of the R^1R^2C-S segment critically depends on the quality of the basis set. Thus, similar to our results, Streitwieser et al.[6] obtained a significantly pyramidalized carbanion **1** using the 3-21G basis set augmented with a diffuse sp shell only on the C_α atom (3-21G+). Earlier calculations by other authors using a minimal basis set of Gaussian-type functions also resulted in lower energies for pyramidalized species.[5] In contrast, the 3-21G(*)+-optimized structure (d functions only on sulfur and a diffuse sp shell on the anionic carbon atom) is characterized by a planar H_2C-S group.[6] Moreover, we found local minima with essentially planar H_2C-S groups for **1**, **1F**, and **1T** with the 3-21+G(*) basis set which contains polarization functions only at sulfur but diffuse functions on all atoms except hydrogen.

Compared with the parent sulfones **3**, **3T**, **3F**, and **3D**, the $S-R^3$ bonds are longer in both the eclipsed and the staggered conformers of all anions. The fact that this elongation is more pronounced in the staggered than in the eclipsed conformer shows that the interaction of the anionic lone pair orbital with the $S-R^3$ part of the molecular backbone is more effective in staggered conformers.

The strong impact of fluorination on the properties of the anion is reflected by some remarkable differences in those structural changes that occur upon rotation about the C3$-$S bond. While the rotation converting either **2** into **1** or **2D** into **1D** results in increased C3$-$S and $S-R^3$ bond lengths, the C3$-$S bond lengths are reduced in the case of the fluorinated anions **1T** and **1F**. Thus rotation of the methylene group of the fluorinated anions from the eclipsed conformers to the staggered conformers causes a reduction of the C3$-$S bond length of 0.016$-$0.017 Å, and the elongation of the $S-CF_3$ bond is similar to that of the $S-CH_3$ bond in the case of the methyl anions **1** and **2**. At the HF/6-31+G* level, the most striking change in bond lengths occurs in the case of the *S*-fluoro compound. While the H_2C-S bond is 0.017 Å shorter in **1F** than in **2F**, the S$-$F bond distance in the staggered conformer exceeds that in the eclipsed conformer by 0.051 Å. We will see later how these changes in bond lengths can be easily explained in terms of $n_C-\sigma^*_{SR}$ hyperconjugation. The $C3-S-R^3$ bond angle is remarkably larger (by 6$-$11°) in the staggered (**1**, **1F**, **1T**, **1D**) than in the eclipsed anions (**2**, **2F**, **2T**, **2D**), and the same holds for the O$-$S$-$O angle which is about 7° larger in conformers **1**, **1F**, **1T**, and **1D** than in conformers **2**, **2F**, **2T**, and **2D**. Again the geometric changes upon rotation around the C3$-$S bond are strongly basis set dependent. While the HF/3-21+G(*) results qualitatively parallel the HF/6-31+G* data for the fluorinated anions, this is not the case for the methyl compound where the H_2C-S bond is 0.010 Å shorter in **1** than in **2** with the smaller basis set.

Energy. In accordance with the results of other authors,[5,6,21−23] we found that conformer **1**, in which the lone pair orbital of the methylene group bisects the O$-$S$-$O angle, is lower in energy than conformer **2** in which the hydrogen atoms of the methylene group are lying in the molecular plane defined by the C3$-$S$-$C1 segment (Table 5). This energetic order remains unchanged when the hydrogen atoms of the methylene segment are replaced by methyl groups. At the HF/6-31+G*//HF/6-31+G* level, the energy difference between **1** and **2** is 9.56 kcal/mol and inclusion of second-order Møller-Plesset corrections in single-point calculations at HF/6-31+G*-optimized geometries slightly lowers this value to 9.31 kcal/mol. When the hydrogen atoms of the methyl group are replaced by fluorine (**1T** and **2T**), this energy gap is significantly increased to 16.15 kcal/mol at the HF level. This value is only slightly reduced to 15.69 kcal/mol when MP2 corrections are included. The corresponding results for the fluoro compounds **1F** and **2F** are 14.61 (HF/6-31+G*//HF/6-31+G*) and 15.76 kcal/mol (MP2/6-31+G*//HF/6-31+G*), respectively. Finally, we obtained surprisingly high energy differences of 13.76 (HF/6-31+G*//HF/6-31+G*) and 13.97 kcal/mol (MP2/6-31+G*//HF/6-31+G*) between **1D** and **2D**.

Table 5. Relative Energies of **1**, **2**, **1D**, **2D**, **1T**, **2T**, **1F**, and **2F** in kcal/mol

method	E_{rel} (**2**−**1**)	E_{rel} (**2D**−**1D**)	E_{rel} (**2T**−**1T**)	E_{rel} (**2F**−**1F**)
HF/3-21G//HF/3-21G	7.09	13.14	9.98	
HF/3-21G(*)//HF/3-21G(*)	8.14	13.60	15.57	
HF/3-21+G(*)//HF/3-21+G(*)	7.69	11.46	16.85	13.91
MP2/3-21+G(*)//HF/3-21+G(*)	7.51	12.01	16.23	14.69
HF/6-31G//HF/6-31G	8.18	10.94	12.43	19.43
HF/6-31G*//HF/6-31G*	9.97	13.42	16.35	15.17
HF/6-31+G*//HF/6-31+G*	9.56	13.76	16.15	14.61
MP2/6-31+G*//HF/6-31+G*	9.31	13.97	15.69	15.76
MP2/6-31+G*//MP2/6-31+G*				16.08

It is interesting to note that the eclipsed conformers of all anions are characterized by two imaginary frequencies in the spectra of their normal vibrations and are therefore not true saddle points.[54] The eigenvector belonging to one of these frequencies corresponds to a rotation about the C3$-$S axis while the other indicates pyramidalization of the anionic center. Again, the HF/3-21+G(*) results are different, in that at this level the eclipsed anions are saddle points with a single imaginary frequency in the spectra of their normal modes. This mode corresponds to a rotation around the S$-$C3 bond.

To obtain approximate rotational barriers about the C3$-$S bond, we started from the staggered conformations (rotation angle $\phi = 0°$) optimized with the 6-31+G* basis set, increased ϕ in steps of 10°, and calculated total energies for 19 structures (Figure 6). These calculations were carried out in the rigid rotator approximation, which means that all structural parameters were held constant in each step. Taking into account the structural differences between the staggered and the eclipsed isomer, it is not surprising that the rotational barriers emerging from this process are significantly higher than the energy difference between the optimized rotamers. While the maxima of the curves for $R^3 = F$ and CF_3 are centered around 90°, that for $R^1 = R^2 = R^3 = CH_3$ is shifted to a value significantly smaller than 90°. To find an explanation for the different shapes of the potential curves, we analyzed them by applying Pople's Fourier series method.[55,56] Fitting the curves to a truncated Fourier series (1) by means of a non-iterative least-squares procedure, we obtained the results which are given in Table 6.

$$V(\phi) = {}^1/_2[V_1(1 - \cos(\phi)) + V_2(1 - \cos(2\phi)) + V_3(1 - \cos(3\phi))] \tag{1}$$

As found previously by Streitwieser et al. for **1**,[6] all series are dominated by a positive V_2 term, although the other components (V_1 and V_3) contribute significantly in some cases. We therefore

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(54) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.

(55) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

(56) Recently the physical basis of this analysis has been questioned, see: Salzner, U.; Schleyer, P. v. R. *J. Org. Chem.* **1994**, *59*, 2138.

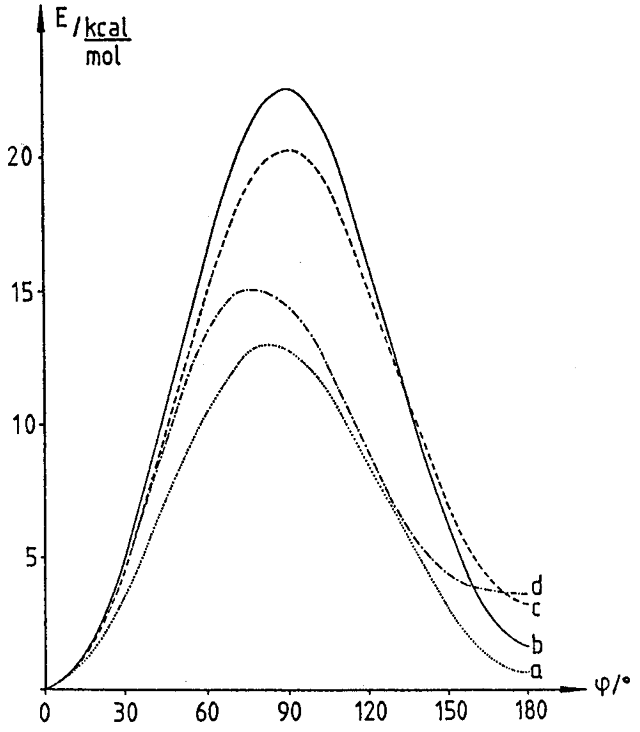

Figure 6. Barrier toward rotation about the C3−S axis of α-sulfonyl carbanions in the rigid rotator approximation (HF/6-31+G*//HF/6-31+G*). The staggered conformations (**1**, **1T**, **1F**, **1D**) correspond to $\phi = 0°$ (**a**: $R^1 = R^2 = H$, $R^3 = CH_3$; **b**: $R^1 = R^2 = H$, $R^3 = CF_3$; **c**: $R^1 = R^2 = H$, $R^3 = F$; **d**: $R^1 = R^2 = R^3 = CH_3$).

Table 6. Fourier Series Analyses of the Rotational Barriers Obtained by the Rigid Rotator Approximation Starting from the Staggered Conformations of **1**, **1T**, **1F**, and **1D**[a]

anion	V_1	V_2	V_3
1	−0.90	12.38	1.43
1T	0.74	21.38	0.47
1F	2.24	18.39	0.69
1D	−0.73	12.66	4.07

[a] The V_i are in kcal/mol (HF/6-31+G*//HF/6-31+G*).

conclude that the same effect, which is obviously an interaction of the anionic lone pair orbital with the orbitals of the C3−S−R^3 backbone, predominantly determines the rotational barriers in all anions under consideration. Since V_2 is greater for $R^3 = F$ and CF_3 than for $R^3 = CH_3$, this effect is amplified upon fluorination. Interestingly, V_2 is about the same for $R^3 = CH_3$, $R^1 = R^2 = H$, and $R^1 = R^2 = R^3 = CH_3$. Some additional features of the potential curves should be noted. In all cases positive V_3 values indicate that the preferred relative orientation of the SO_2-R^3 and the R^1R^2C group is staggered rather than eclipsed. While the contributions of the V_3 term (maxima at 60° and 180°) are less important for **1F** and **1T**, they play a non-negligible role for **1** and **1D**. The especially high value of V_3 in the case of **1D** is the most important reason for the shift of the maximum of the corresponding curve to a value of $\phi < 90°$. This high value of V_3 is most likely caused by repulsive interaction between the methyl groups of the C_α atom and the SO_2-CH_3 segment. While V_1 and V_3 are negligible compared with V_2 in the case of **1T**, a three times larger positive V_1 indicates a significant repulsive interaction for **1F** in the $\phi = 180°$ position, in which the S−F bond dipole moment and that due to the lone pair at C_α repel each other. For both **1** and **1D**, negative V_1 terms of comparable size might indicate a weakly stabilizing interaction in the $\phi = 180°$ position where the anionic lone pair orbital is *syn* to the S−R^3 bond.

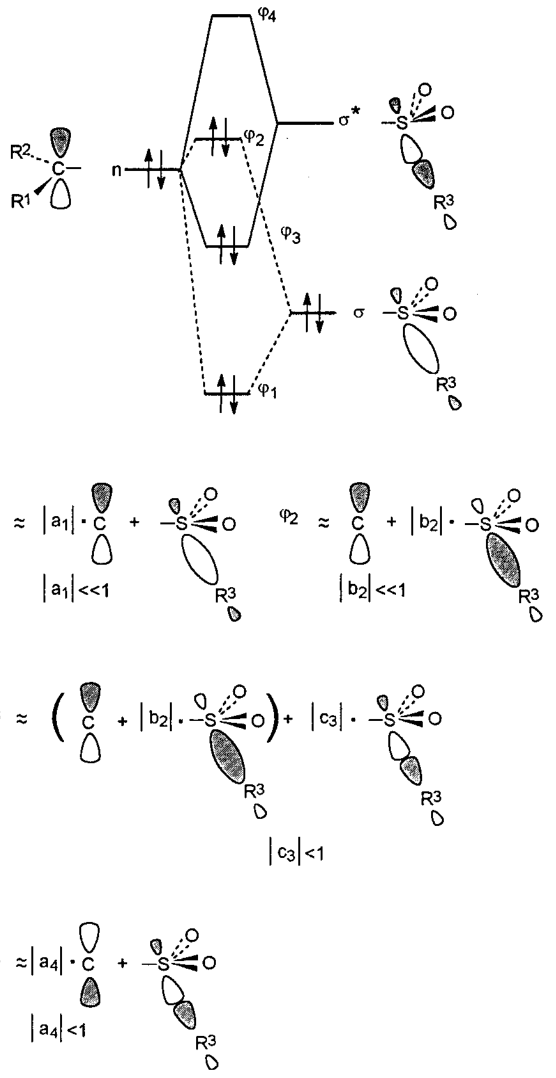

Figure 7. Schematic representation of negative hyperconjugation in α-sulfonyl carbanions.

Since in the more stable staggered rotamers the anionic lone pair orbital lies in the plane that contains the σ-orbitals of the C3−S−R^3 backbone, the stabilizing mechanism involves interactions between these σ-orbitals and the lone pair orbital. Qualitatively this stabilization can be explained in terms of negative (anionic) hyperconjugation, a model which has been used together with the results of ab initio calculations of $F-CH_2-CH_2^-$ and $CF_3-CH_2-CH_2^-$ by several groups[36,37,57−63] to explain the stabilization of the negative charge in these anions and their preferred conformation. Although compared with the deprotonation energies of the sulfones the energetic effects of such orbital interactions are small, they play a significant role in determining molecular conformations.[21,23]

In the staggered isomers the anionic lone pair orbital (n) interacts with the doubly occupied σ-orbital of the S−R^3 segment (σ), resulting in two doubly occupied orbitals: φ_1, which is bonding in the S−R^3 as well as in the C3−S region,

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[58] Stamper, J. G.; Taylor, R. *J. Chem. Res.* (*M*) **1980**, 1930.

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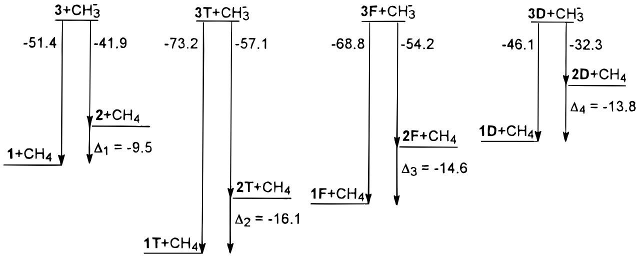

Figure 8. Schematic representation of hypothetical isodesmic proton transfer reactions of sulfones based on HF/6-31+G*//HF/6-31+G* energies. All values are in kcal/mol.

and φ_2, which lies somewhat above n and is also bonding in the S$-$R^3 but antibonding in the C3$-$S region (Figure 7). This two-orbital four-electron interaction (dashed lines) is destabilizing. Whether or not a net stabilization occurs depends on the degree to which the empty σ^* orbital of the S$-$R^3 bond participates. φ_1 is hardly affected by σ^*, while σ^* will interact with φ_2 resulting in orbitals φ_3 and φ_4. Electronegative substituents R^3 increase the coefficients at sulfur in the σ^* orbital and reduce the energy of this MO. Both effects enhance the $\varphi_2-\sigma^*$ interaction. As a result this energetically favorable interaction will be strong in the presence of electronegative substituents and will cause a net lowering of the total energy. Since the σ^* orbital adds antibonding contributions to the S$-$R^3 bond and bonding contributions to the C3$-$S bond, its participation will be reflected by the changes of the corresponding bond distances that occur upon rotation about the C3$-$S bond. With growing σ^* contributions one therefore expects decreasing C3$-$S and increasing S$-$R^3 bond lengths. These changes of interatomic distances coincide with the formal no-bond resonance description[64] of negative hyperconjugation which is expected to play an especially important role in charged or highly polar species.[36,37,40,57−63,65p,66,65q]

$$^{-}CH_2{-}X{-}R \leftrightarrow CH_2{=}X + R^{-}$$

If R^3 is an electropositive group, participation of σ^* is negligible and the unfavorable n$-\sigma$ interaction will now play the dominant role. This destabilizing and thus repulsive interaction is reduced by an increase of the C3$-$S bond length. As for **1** and **1D**, increased C3$-$S bond lengths compared with **2** and **2D** might be observed under such conditions.

We further calculated the changes of energy associated with the following (hypothetical) isodesmic proton transfer reactions 2−5, in which one H$^+$ is formally transferred from **II** to CH$_3^-$.[67]

$$CH_3{-}SO_2{-}CH_3 + CH_3^{-} \rightarrow \mathbf{1}, \mathbf{2} + CH_4 \qquad (2)$$

$$CH_3{-}SO_2{-}F + CH_3^{-} \rightarrow \mathbf{1F}, \mathbf{2F} + CH_4 \qquad (3)$$

$$CH_3{-}SO_2{-}CF_3 + CH_3^{-} \rightarrow \mathbf{1T}, \mathbf{2T} + CH_4 \qquad (4)$$

$$(CH_3)_2C(H){-}SO_2CH_3 + CH_3^{-} \rightarrow \mathbf{1D}, \mathbf{2D} + CH_4 \qquad (5)$$

The combined results are schematically represented in Figure 8. For R^3 = CH$_3$ and = CF$_3$ use of the total energies of the less stable conformers, **2** and **2T**, resulted in values of −41.9 and −57.1 kcal/mol, indicating that for these isomers the additional stabilization of the negative charge due to fluorination of the methyl group is about 15.2 kcal/mol. Calculation of the energies of the reaction employing the total energies of the more stable conformers **1** and **1T** yields values of −51.4 and −73.2 kcal/mol. Thus in this case the additional stabilization of the negative charge due to fluorination of the methyl group amounts to 21.8 kcal/mol. The height of the rotational barrier, approximated by the energy difference between the staggered and the eclipsed anion, reflects an additional stabilization of the anionic charge in the staggered isomer (**1**, **1T**). The difference between the barriers for the methyl and the trifluoromethyl compound shows that this additional stabilization is 6.6 kcal/mol more effective when an electronegative substituent is present. Therefore, somewhat more than two thirds of the 21.8 kcal/mol can be attributed to a conformationally independent inductive contribution. The remaining contribution (ca. 30%) originates from negative hyperconjugation operative only in the conformer where the anionic lone pair orbital is approximately in a plane with the S$-$R^3 bond. It is instructive to roughly estimate the relative importance of the two contributions to the overall stabilization of the negative charge for the fluoro compound **1F**. For the difference between the approximate rotational barriers of the methyl and the fluoro compound we obtained a value of 5.1 kcal/mol. The difference between the proton transfer energies using the less stable isomers **2** and **2F** is 12.3 kcal/mol. Thus we end up with the result that the mechanism active only in the staggered anions contributes about 29% to the net stabilization in the case of a single fluorine atom also. The relative importance of negative hyperconjugation and inductive contributions to the overall stabilization is therefore roughly the same for a single fluorine atom and a trifluoromethyl group. A similar analysis based on our 3-21+G(*) energies led to an almost identical result. These findings are in keeping with earlier computational results by Taylor et al.,[57,58] who calculated the energies of deprotonation of ethane, fluoroethane, and 1,1,1-trifluoropropane with the 4-31G basis set. Studying the conformational dependence of these energies, they concluded that negative hyperconjugation contributes significantly to the overall stabilization of the negative charge. Separating the net stabilization into a conformationally independent and a conformationally dependent component they attributed the latter to negative hyperconjugation and the former to inductive stabilization. As to the relative importance of these two contributions they assigned about 30% of the total stabilization to negative hyperconjugation. It has frequently been found that a β-fluorine atom and a β-trifluoromethyl group stabilize an adjacent anionic center to a similar extent.[57−59] Using the isodesmic proton

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[64] The concept of fluorine no-bond resonance was originally introduced to explain the orienting influence of the CF$_3$ group in electrophilic aromatic substitution reactions, see: Roberts, J. D.; Webb, R. L.; McElhill, E. A. *J. Am. Chem. Soc.* **1950**, *72*, 408.

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[67] For a calculation of the proton transfer equilibrium between trifluoromethyl methyl sulfone and CH$_3^-$ at the 3-21G*//3-21G* level of approximation, see: Taft, R. W. *J. Chim. Phys. Phys.-Chim. Biol.* **1992**, *89*, 1557.

transfer reaction 6, Apeloig[59] obtained reaction energies of −24.0 (R = F) and −25.8 kcal/mol (R = CF_3), indicating that the stabilizing effect of a trifluoromethyl group is indeed quite similar to that of a single fluorine atom.

$$H_3C-CH_2^- + R-CH_2-CH_3 \rightarrow H_3C-CH_3 + R-CH_2-CH_2^- \quad (6)$$

To see whether this is also true for α-sulfonyl carbanions we calculated the change of energy associated with the isodesmic reaction 3. Using the more stable conformer **1F**, we obtained a proton transfer energy of −68.8 kcal/mol which is 4.4 kcal/mol less favorable than that for the trifluoro compound. Thus although in α-sulfonyl carbanions the total stabilization of the negative charge by the trifluoromethyl group is somewhat more effective than that brought about by a single fluorine atom, the stabilizing effect of the two substituents is not very different. Comparable overall stabilities were also found for the anions CF_3^- and $CF_3CF_2^-$.[62]

Importance of d-like Orbitals in the Basis Set. The general importance of d-functions in the basis sets of second row elements has been discussed at length by other authors[5a,21,23,46,54,65] and the only aim of this brief section is to add some information to the abundant data presented in those papers. Omitting d-orbitals from the basis set results in drastic changes of the geometries. The average value of the S−O bond lengths in **1**, **1T**, **1F**, and **1D** is 1.654 Å with the 6-31G[49−51] basis set while it is reduced to 1.456 Å when the 6-31G* [52,65e] basis set is used. The average crystallographic S−O bond length of α-sulfonyl carbanion salts **I** is 1.452 Å.[3,4,7,9−11,13−16,18,20] Thus from the computational point of view, the importance of d-functions is self-evident.

In the case of the methyl compounds (**1**, **2**), lowering of the total energy by inclusion of d-functions is 1.8 kcal/mol more effective for **1** than for **2**, and this energy difference is approximately doubled for the trifluoro compound. In the case of the monofluoro species this order is reversed, in that **2F** is more strongly affected than **1F**, although the energy difference is almost the same. As a result, inclusion of d-orbitals changes the rotational barrier by not more than about 1.8 kcal/mol in the case of the methyl compounds, while this difference amounts to 4 kcal/mol for the fluorinated anions. As far as the methyl compound is concerned, we therefore agree with Streitwieser et al.[6] that d-orbitals do not play a significant role in stabilizing the anionic charge. Obviously they play a more important role when R^3 is an electronegative substituent, and the extent clearly depends on the relative orientation of the R^1R^2C group and the SO_2-R^3 segment.

Mulliken Population Analysis. In spite of its conceptual limitations, Mulliken population analysis[68] provides a tool to estimate the shifts of electron density that occur upon rotation of the R^1R^2C group about the C3−S axis (Figure 9). In the case of the fluorinated anions, the negative charge of the methylene group is stronger for the eclipsed conformers **2T** and **2F** than for the staggered conformers **1T** and **1F**, and the charge transferred to the SO_2-R^3 segment upon rotation about the C3−S axis is almost completely taken up by the SO_2 group.

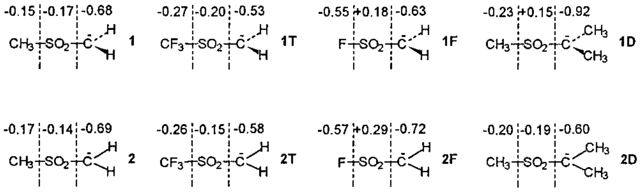

Figure 9. Mulliken charges of molecular fragments for anions **1**, **2**, **1T**, **2T**, **1F**, **2F**, **1D**, and **2D** (HF/6-31+G*//HF/6-31+G*). All values are in e_0.

The charge distribution in the methyl anions **1** and **2** is essentially independent of the relative orientation of the methylene group and the SO_2-R^3 segment. However, when both hydrogen atoms of the anionic center are replaced by methyl groups, the negative charge of the $(CH_3)_2C$ group is even stronger for the staggered than for the eclipsed conformer. These shifts of charge that accompany torsion of the C3−S bond correlate with the initially described changes of the C3−S bond length. Thus for **1** and **2**, the charge of the R^1R^2C group is approximately the same for both ions, and at 0.007 Å the elongation of the corresponding bond is indeed relatively small. Transfer of a significant amount of negative charge from the SO_2-R^3 segment to the R^1R^2C group is accompanied by an increase of the C3−S bond length of 0.017 Å when **2D** is transformed into **1D**. Finally, negative charge is transferred from the anionic center to the SO_2-R^3 group when the methylene group of the fluoro and the trifluoro compound is rotated from the eclipsed into the staggered position. In both cases this shift goes hand in hand with a reduction of the C3−S bond length.

Comparison to Experimental Results. Kinetic experiments revealed that the difference in the rotational barrier of a α-sulfonyl carbanion salt and the corresponding counterion free anion is only small. Thus, a qualitative comparison between experimental and computational results seems to be justified. The higher rotational barrier of the ((trifluoromethyl)sulfonyl)-methyl anion (**1T**) in comparison to the (methylsulfonyl)methyl anion (**1**) finds an experimental verification in the observation that the enthalpy of activation for $C_\alpha-S$ bond rotation of the monomeric O−Li contact ion pair $[PhCH_2(Ph)C-SO_2CF_3]Li$ (**Ia**) in tetrahydrofuran is 4.7 ± 0.3 kcal/mol higher than that of the monomeric O−Li contact ion pair $[PhCH_2(Ph)C-SO_2$*t*Bu]Li (**Ib**) (vide supra).[13,18,19] Undoubtedly, this difference should be even larger for **Ia** and its *S*-methyl analogue. The significant steric contribution of the methyl groups at the C_α atom to the rotational barrier of the anion **1D** in comparison to the anion **1** is not without experimental precedent either. The enthalpy of activation of the enantiomerization of $[PhCH_2(Me)C-SO_2CF_3]Li$ (**Ic**) is 4.5 ± 0.3 kcal/mol higher than that of $[PhCH_2(H)C-SO_2CF_3]Li$ (**Id**).[18,20]

A direct comparison between the calculated gas-phase structure and the solid state contact ion pair structure of α-sulfonyl carbanions is, in principle, not possible.[69] However, the X-ray crystal structure analyses of the O−Li contact ion pair $\{[PhCH_2(Ph)C-SO_2CF_3]Li\cdot 2THF\}_2$ (**Ia**·2THF)$_2$[13,15] and the ammonium salt $[PhCH_2(Ph)C-SO_2CF_3]NBu_4$ (**Ie**),[15] as well as of the O−Li contact ion pair $\{[Me_2C-SO_2Ph]Li\cdot diglyme\}_2$ (**If**·diglyme)$_2$[9] and the solvent-separated contact ion pair $[Me_2C-SO_2Ph]Li\cdot[2.1.1]$cryptand (**If**·[2.1.1]c),[16] showed that the influence of the oxygen-coordinated cation upon the structure of the anion as expressed by the bonding parameters is only small. Thus at least a rough comparison of certain structural parameters of the anions **1T** and **1D** with those of the anions of the salts (**Ia**·2THF)$_2$, **Ie**, (**If**·diglyme)$_2$, and **If**·[2.1.1]c, respectively, seems permissible. The pyramidalization of the C_α atoms in

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Table 7. Selected Cystal Structural Parameters[a] of (**Ia**·2THF)$_2$,[13,15] **Ie**,[15] and $PhCH_2C(Ph)SO_2CF_3$[18]

parameter	(**Ia**·2THF)$_2$	**Ie**	sulfone
O6−S2	1.447	1.449	1.427
O7−S2	1.449	1.443	1.426
C1−S2	1.859	1.826	1.850
C3−S2	1.620	1.638	1.807
C1−F	1.328	1.333	1.297
O6−S2−O7	117.4	118.2	119.9
O6−S2−C1	98.9	99.4	105.6
O6−S2−C3	112.0	112.0	112.3
C1−S2−C3	112.6	110.6	102.5
S2−C1−F[b]	110.9	113.0	109.9
F−C1−F[b]	107.3	105.8	108.9

[a] Bond lengths in Å and bond angles in deg. [b] Average values.

dimethyl-substituted species **1D**, (**If**·2THF)$_2$, and **If**·[2.1.1]c (345.2°, 346.5°, and 351.7°, respectively) is not much different. The lengths of the C3−S bonds in the lithium salts (**If**·diglyme)$_2$ and **If**·[2.1.1]c (1.640 and 1.625 Å, respectively) are comparable to that of the anion **1D** which is 1.677 Å. A comparison of the bonding parameters of the salts (**Ia**·2THF)$_2$ and **Ie** with those of the parent sulfone $PhCH_2(Ph)C(H)-SO_2CF_3$ on the one hand and of the anion **1T** and its parent sulfone **3T** on the other (Tables 7 and 3) shows that the calculations give a good qualitative picture of the changes that occur upon deprotonation. However, the calculated lengthening of the $S-CF_3$ bond in **1T** is not observed experimentally in the case of (**Ia**·2THF)$_2$ and **Ie**. To shed further light on this point, determination of the crystal structure of $[H_2C-SO_2CF_3]NBu_4$ (**Ig**) as the most reasonable model compound for **1T** would be desirable. Furthermore, with values of 1.670 and 1.608 Å, the $C_\alpha-S$ bond lengths of the anion **1** and of the O−Li contact ion pair $\{[H_2C-SO_2Ph]Li\cdot TMEDA\}_2$ (**Ih**·TMEDA)$_2$,[4] respectively, differ significantly. Here too, knowledge of the crystal structure of $\{[H_2C-SO_2Me]Li\cdot 2THF\}_2$ (**Ii**·2THF)$_2$ would be helpful.

Conclusion

The results presented above provide evidence that negative hyperconjugation plays a significant role in determining the conformation and the rotational barrier of α-sulfonyl carbanions. The changes in bond lengths that occur upon rotation of the R^1R^2C group are in keeping with its formal description as no-bond resonance. Structural changes as well as the conformational dependence of the stabilization energy might be explained in terms of an interaction between the anionic lone pair orbital on the one hand and the σ and σ^* orbitals of the molecular backbone on the other hand. This interaction is energetically especially favorable in the case of fluorine substitution either at the S atom or at the *S*-methyl group. As a result the rotational barrier increases significantly upon fluorine substitution. The calculations reveal also a significant steric contribution of the substitutents at the C_α atom to the rotational barrier of α-sulfonyl carbanions. Both effects, the increase in the rotational barrier by *S*-trifluoromethyl substitution and by the substituents at the C_α atom, have been verified experimentally. In this context it would be interesting to see if the introduction of a *S*-nonafluorobutyl instead of a *S*-trifluoromethyl group, which has a similar electronic but a larger steric effect,[33b] will lead to an even higher configurational stability of the α-sulfonyl carbanion. Finally, as far as the stabilization of α-sulfonyl carbanions is concerned, the calculations point, in accordance with previous findings,[5,6,22,23] to a major contribution by Coulombic interaction and to a minor one by hyperconjugation.[70]

Not only α-sulfonyl carbanions but also α-sulfonimidoyl, α-sulfinyl, and α-sulfenyl carbanions are stabilized by $n_C-\sigma^*_{SR}$[5a,23,27,71] hyperconjugation, and their configurational stability apparently depends too on the $C_\alpha-S$ rotational barrier.[29,72] Our calculations suggest that *S*-trifluoromethyl substitution may also lead in these cases to derivatives of a higher configurational stability.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The authors gratefully acknowledge the computing time for calculations on the SNI-S600/20 provided by the state Nordrhein-Westfalen (Project No. P104). We thank Prof. Dr. E. Anders for communicating his results to us prior to publication. We greatly appreciate Professor Dr. R. Woody's kindness in carefully reading the manuscript and correcting our English. This paper is dedicated to Professor Dr. H.-D. Scharf on the occasion of his 65th birthday.

Supporting Information Available: Full tables of structural parameters for sulfones **3**, **3T**, **3F**, and **3D** and anions **1**, **2**, **1D**, **2D**, **1T**, **2T**, **1F**, and **2F**, tables of total energies of anions **1**, **2**, **1D**, **2D**, **1T**, **2T**, **1F**, **2F**, and tables of total energies of sulfones **3**, **3D**, **3F**, **3T**, and auxiliary compounds (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA953034T

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