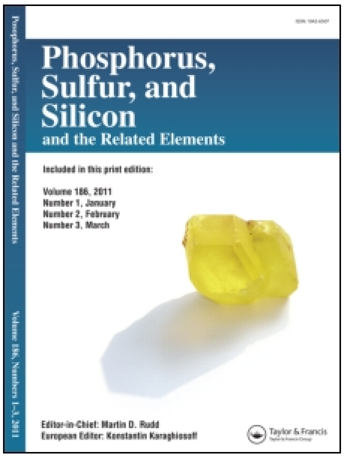

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AB Initio Calculations on Sulfonylmethyl Anions

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AB INITIO CALCULATIONS ON SULFONYLMETHYL ANIONS

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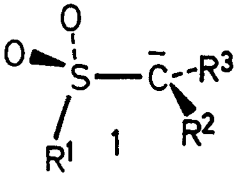
Abstract The role of negative hyperconjugation in the title compounds is elucidated by the results of quantum chemical ab initio calculations.

RESULTS AND DISCUSSION

Our results are briefly summarized in Table I. ΔE_{21} is the energy difference(MP2/6-31+G*//6-31+G*) between 2 and 1,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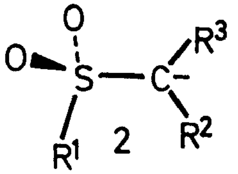
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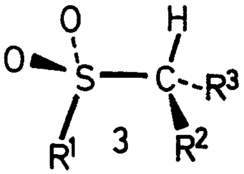
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$\Delta r_{R^1\text{-}S}$ and $\Delta r_{S\text{-}CR^2R^3}$ are the differences between the lengths of corresponding bonds in 1 and 2, and ΔE_r is the change of energy (6-31+G*//6-31+G*) associated with the isodesmic proton transfer reaction

$$3 + CH_3^- \longrightarrow 1 + CH_4$$

TABLE I. Computational results(GAUSSIAN 90). Energies in kcal/mol, Δr in Å.

	R^1	R^2	R^3	ΔE_{21}	$\Delta r_{R^1\text{-}S}$	$\Delta r_{S\text{-}CR^2R^3}$	ΔE_r
A	CH_3	H	H	9.3	+0.018	+0.007	-51.4
B	F	H	H	15.8	+0.051	-0.017	-68.8
C	CF_3	H	H	15.7	+0.014	-0.016	-73.2
D	CH_3	CH_3	CH_3	14.0	+0.021	+0.017	-46.1

The energies of reaction calculated by means of the isodesmic proton transfer reaction show that electronegative substituents stabilize the anionic charge by an amount of 17-22 kcal/mol more effectively than a methyl group. A detailed analysis[1] reveals that approximately two thirds of this energy difference are conformationally independent, while the remaining part is due to an additional process active only in 1, where the anionic lone pair lies in the plane defined by the R^1-S-C segment. Fourier analysis($V(\phi)=\frac{1}{2}[V_1(1-\cos(\phi))+V_2(1-\cos(2\phi))+V_3(1-\cos(3\phi))]$) of the potential curves[2] obtained upon rigid rotation of the CR^2R^3 group in 1(ϕ=0°) about the S-C bond indicates that the barriers for all combinations of substituents (A, B, C, and D) are dominated by the same effect(V_2; negative hyperconjugation[3]), which is stronger in presence of electronegative substituents R_1. Although for A and D the maxima of the curves are shifted to values $\phi<90°$, ΔE_{21} is still an approximation to the rotational barrier about the S-CR^2R^3 bond. It increases when $R^1=CH_3$ is replaced by an electronegative substituent. The surprisingly high ΔE_{21} for D is caused by a significant positive value of V_3 which is much lower in the other cases[1], while V_2 is about the same as for A. For all substitution patterns the R^1-S bonds are longer in 1 than in 2. This is also true for the S-CR^2R^3 bonds of A and D. However, when $R^1=CF_3$ and F these bonds are shorter in 1 than in 2. A complete account of our results will appear elsewhere[1].

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