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Ab Initio SCF-MO Calculations of Thiomethyl Anion. Polarization in Stabilization of Carbanions[1]

Sir:

The acidity of C-H bonds is known experimentally to be significantly enhanced by attached sulfur.[2] The usual explanation is d-p π-bonding between the carbanion lone pair and sulfur 3d orbitals.[3] *Ab initio* SCF calculations on a related α-sulfinyl carbanion, however, have indicated that such d-orbital interaction is not important.[4] Recent calculations on $HSCH_2^-$ have shown that this carbanion is stabilized[5] but have left open the question of the mechanism of such stabilization.

As part of an extensive SCF study of carbanions,[6] we included *ab initio* calculations of CH_3SH and $^-CH_2SH$ to complement our experimental results. The geometry of $^-CH_2SH$ was taken as that of methanethiol[7] with the proton anti to the SH bond removed. Two basis sets were used: split shell (SS) and split shell plus d orbitals (SS+d).[8] To give proper perspective to the results, they are compared in Table I with similar data for deprotonation of ethane.

Table I. SCF Calculations of Carbon Acidity

Basis set	Total energy, au		Proton affinities (kcal mol⁻¹)[a]	
	CH_3SH	$^-CH_2SH$	$^-CH_2SH$[b]	$^-CH_2CH_3$
SS	−437.6218	−436.9481	423.5	453.0
SS + d	−437.6775	−437.0032	423.2	452.7

[a] Anion geometries reoptimized. [b] Reference 5 reports 422.3 kcal mol⁻¹.

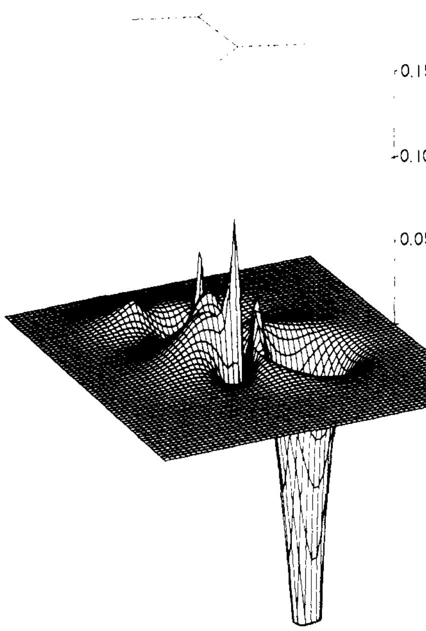


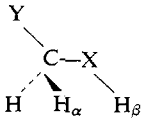
Figure 1. Electron density difference plot for deprotonation of ethane; $\rho(CH_3CH_2^-)$-$\rho(CH_3CH_3)$ for the (lone pair)-C-C-H plane (SS+d basis). The electron density, ρ, is plotted as the vertical axis in units of electrons au^{-3} with the molecular plane as the grid plane. The molecular structure is exactly superimposed above the figure. The long dotted line is the ionized C-H bond; the short dotted lines are methylene C-H bonds above and below the grid plane.

The results confirm the marked carbanion-stabilizing effect of sulfur. Introduction of 3d functions lowers overall energy by increasing the flexibility of the basis set but to the same degree for both the carbon acid and its conjugate anion; the d orbitals have essentially no effect on proton affinity.

Further insight is gained by inspection of electron density difference diagrams. The plot of $\rho(CH_3CH_2^-)$-$\rho(CH_3CH_3)$ in Figure 1 shows the polarizations that occur when a proton is removed from ethane. The deep well shows the electron density of the C-H bond ionized and the peak before the α-carbon shows how this C-H bond density has crowded in toward carbon to form the carbanion lone pair. In turn the C_α-H bond electrons are polarized toward the α-hydrogens and in the back-lobe region behind C_α. The C-C bonding electrons are polarized toward C_β and a concurrent polarization of C_β-H bond electrons occurs toward H_β.

The corresponding electron density difference plot for the sulfur case, $\rho(^-CH_2SH)$-$\rho(CH_3SH)$, in Figure 2, shows ex-

Table II. Mulliken Atomic Populations



Compound	X	Y[a]	Atomic populations for SS basis: C	X	H_α	H_β
CH_3SH	S	H	6.817	15.991	0.763	0.918
$^-CH_2SH$	S	LP	6.857	16.196	0.946	1.055
Δ			0.040	0.205	0.183	0.137
CH_3CH_3	$CH_2(C)$	H	6.558	8.186 (6.558)[b]	0.814	0.814
$^-CH_2CH_3$	$CH_2(C)$	LP	6.665	8.346 (6.520)	1.020	0.949
Δ			0.107	0.160 (−0.030)	0.206	0.135

[a] LP ≡ lone pair. [b] Populations are given for CH_2 group (C + 2H) with population of C in parentheses.

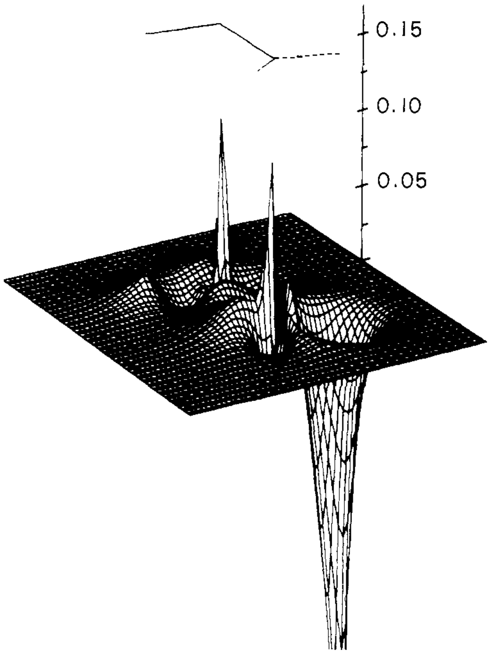


Figure 2. Electron density difference plot for deprotonation of CH_3SH; $\rho(HSCH_2^-)$-$\rho(HSCH_3)$, for H-S-C-(lone pair) plane (SS+d basis).

actly the same pattern, except that polarization at sulfur is stronger than at the C_β of ethyl anion. The pattern of these electron density difference functions suggests strongly that a SH substituent stabilizes a carbanion more than a methyl group because the SH group is more polarizable than CH_3. Arguments based on experimental p*K* measurements of substituted dithianes[2] have led to the same interpretation of the role of polarization; the Wolfe group[9] have independently arrived at the same conclusion from their SCF calculations.

These qualitative patterns of electron density difference functions may be compared with Mulliken atomic calculations summarized in Table II for the SS basis set. Mulliken population analyses are basis set dependent and relative values are more significant than the absolute populations.

For example, the increase in α-carbon population of only 0.107 electron for $CH_3CH_3 \rightarrow CH_3CH_2^-$ is much less than one would have anticipated for a developing carbanion. Of course, electrons have also polarized away from this carbon. The $CH_3SH \rightarrow {}^-CH_2SH$ case shows a similar pattern. The increase in C_α population is less, consistent with increased polarization, but the increases at H_α and H_β are comparable for both systems. Sulfur apparently gains electrons but the populations above do not tell us how. However, in the ethyl case the electrons gained by CH_2 as a whole are actually wholly on the hydrogens. The peculiarities of Mulliken populations allow us to see the polarization in the CH_2 group invisible in the S atom; that is, we expect the extra electron population in S to be also on outer fringes, exactly as shown in Figure 2.

We conclude that sulfur stabilizes carbanions by polarization rather than by d-orbital conjugation. We plan to explore the generalization of this result to carbanions stabilized by other second-row elements.

References and Notes

(1) This study was supported in part by NSF Grant No. 29383 and by USPH, NIH Grant No. GM-12855. Some of the computer time used was subsidized by the Computer Center, University of California.
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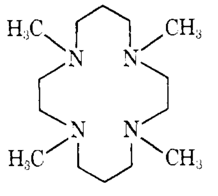
Structure of a Square Pyrimidal Pentacoordinate Complex of Ni(*N*-tetramethylcyclam)$^{2+}$. A Kinetically Determined Ligand Stereochemistry

Sir:

Earlier we reported the preparations of divalent nickel, copper, and zinc complexes of *N*-tetramethylcyclam (TMC, **1**).[1] These complexes, which are prepared by combining the metal salt with the free base in aqueous solution, have chemical behavior that is quite unlike that of the secondary amine analogs such as cyclam itself. They are quite labile, and pentacoordinate species are observed both in solution and in the solid state. Nmr data obtained on $[Zn(TMC)Cl]^+$ in nitromethane solution suggested that the macrocyclic ligand is coordinated in a planar fashion with all four methyl groups on the same side of the metal-nitrogen plane. It was assumed that the nickel and copper complexes also have this stereochemistry, which has been designated the trans I form by Bosnich, *et al.*[2] Kaden has suggested, on the basis of uv-visible spectral data, that the pentacoordinate nickel(II) complexes of TMC are trigonal bipyramidal, which requires that the ligand adopt a folded conformation.[3] An alternative synthesis of $Ni(TMC)^{2+}$, shown as reaction 1, yielded a second stereoisomer.[4] This



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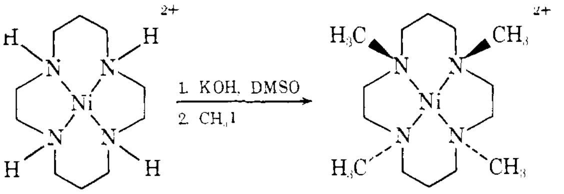

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(1)

reaction should yield the thermodynamically most stable of the five possible permethylated products. An X-ray structure determination on a derivative of the product of this reaction has shown it to have the set of nitrogen configurations shown in **2**.[4] This set of nitrogen configurations, the trans III form according to Bosnich,[2] is also the thermodynamically most stable form of metal complexes of the anal-