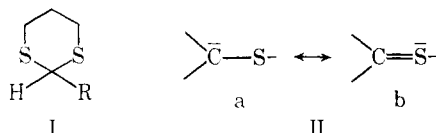


Communications to the Editor

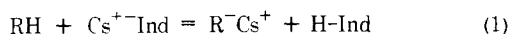
Equilibrium Ion Pair Acidities of Dithianes in Cyclohexylamine¹

Sir:

Abundant evidence based on qualitative metalation² and quantitative kinetic acidity³ studies shows that sulfur has a marked stabilizing effect on adjacent carbanions. Carbanions derived from 1,3-dithiane (I, R = H) have recently found important use in organic synthesis.⁴ The usual explanation given for this anion-stabilizing effect of sulfur involves conjugation expressed by the resonance structures, II, symbolic of back-donation of electrons into vacant sulfur d orbitals.



In this paper we present results of equilibrium acidity studies of dithiane and several substituted dithianes. These results provide the first quantitative equilibrium measures of such sulfur-enhanced carbon acids and bear directly on the proposed reasons for such stabilization. The method used, which has been published previously,⁵ involves addition of a known amount of the pure dithiane to a known mixture of a suitable indicator hydrocarbon and its cesium salt in cyclohexylamine. The reduction in concentration of the indicator cesium salt allows determination of the equilibrium constant for reaction 1.⁶ In the results summarized in Table I the equilibrium constants have been expressed as "pK values" relative to the "pK" of 9-phenylfluorene = 18.49. All of the cesium salts involved are expected to be contact ion pairs and these pK's actually express relative "contact ion pair acidities."



The substituents used were carefully chosen to provide measures of both inductive and conjugation effects. For example, the marked effect of $-\text{CH}_2\text{C}_6\text{H}_5$ compared to $-\text{CH}_3$ is equivalent in a $\rho^*\sigma^*$ correlation⁷ to $\rho^* = -20$, a value so large as to compel the conclusion that the carbanion is fully localized. For example, ρ^* is -5.7 for the pK's of $\text{YCH}_2\text{NH}_3^+$ in water and about -19 for the *gas phase* proton affinities of aliphatic amines;⁸ ρ^* is 4.6 for the comparable ion pair acidities of 9-alkylfluorenes⁹ in which the carbanions are delocalized.

The conclusion of a localized and, presumably pyramidal, carbanion ion pair in this system meshes with the observation of Eliel, Abatjoglou, and Hartman¹⁰ that metalation of 1,3-dithianes is exclusively equatorial. If our ion pairs are also equatorial carbanions, the pK's of the dithianes should be corrected to correspond to conformations with axial substituents in order to be mutually comparable. The corrected pK's in the last column of Table I are for equatorial C-H as derived from the equilibrium studies of Eliel and Hutchins.¹¹ Even with this correction, the effect of a methyl substituent on the acidity of I, $\Delta\text{pK} = 5.9$, is the largest yet known. We suggest that in this case of a pyramidal and lo-

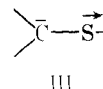
Table I. Equilibrium Acidities of 1,3-Dithianes toward Their Cesium Salts in Cyclohexylamine at 25°

1,3-Dithiane, I, R =	Indicator hydrocarbon ^a	No. of runs	pK of dithiane ^b	Corresponding pK's of R = axial ^c
H	TPM	11	31.1 ± 0.2	31.1
CH ₃	pMB	2	38.3 ± 0.2	37.0
C ₂ H ₅	pMB	4	≥ 38.6	≥ 37.5
CH ₂ C ₆ H ₅	DPM	3	34.0 ± 0.3	32.9
C ₆ H ₅	BDPM	5	29.6 ± 0.2	28.2
<i>p</i> -C ₆ H ₄ C ₆ H ₄	BDDA	1		
	PX	1	27.5 ± 0.2	26.1

^a Hydrocarbon symbols and corresponding pK's relative to 9-phenylfluorene = 18.49: TPM = triphenylmethane, 31.45; pMB = *p*-methylbiphenyl, 38.7; DPM = diphenylmethane, 33.4; BDPM = *p*-biphenyldiphenylmethane, 30.2; BDDA = 10-*p*-biphenyl-9,9-dimethyldihydroanthracene, 27.7; PX = 9-phenyl-xanthene, 28.47 (ref 6). ^b pK's in this column are on a per compound rather than a per hydrogen basis; these pK's are also "per hydrogen" if dithiane has effectively only a single acidic hydrogen. ^c Values used for ΔG° (axial-equatorial, kcal mol⁻¹; cf. ref 11) are CH₃, 1.8; C₂H₅ and CH₂C₆H₅, 1.5; C₆H₅ and *p*-C₆H₄C₆H₄, 2.0.

calized carbanion the normal carbanion-destabilizing effect in solution of a methyl substituent is not at all ameliorated by delocalization or rehybridization effects.

The foregoing substituent effects imply a highly localized carbanion with no significant role to be assigned to sulfur-delocalized structures such as IIb. We suggest instead that the principal mechanism of stabilization of carbanions by adjacent sulfur is by *polarization*. The effect of the induced dipole of polarizable sulfur electrons may be symbolized by III. This conclusion is in full accord with results of recent *ab initio* SCF calculations¹² and probably applies as well to carbanions associated with other second-row and higher elements.¹³



Finally, we note that no conclusion regarding the structure of the carbanion from I (R = C₆H₅) can be drawn from its relatively small substituent effect alone. However, the further effect of a *p*-phenyl substituent gives a $\Delta\text{pK} = 2.1$ which is almost as large as that of *p*-phenyl substitution on toluene ($\Delta\text{pK} = 2.3$).⁶ We conclude that the aryl-substituted carbanion is probably planar with delocalization of charge to the ring.

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Ab Initio SCF-MO Calculations of Thiomethyl Anion. Polarization in Stabilization of Carbanions¹

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 stabilized⁵ 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 $^-\text{CH}_2\text{SH}$ to complement our experimental results. The geometry of $^-\text{CH}_2\text{SH}$ was taken as that of methanethiol⁷ 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

Table I. SCF Calculations of Carbon Acidity

Basis set	Total energy, au		Proton affinities (kcal mol ⁻¹) ^a	
	CH_3SH	$^-\text{CH}_2\text{SH}$	$^-\text{CH}_2\text{SH}^b$	$^-\text{CH}_2\text{CH}_3$
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.

Table II. Mulliken Atomic Populations

Compound	Atomic populations for SS basis					
	X	Y ^a	C	X	H _{α}	H _{β}
CH_3SH	S	H	6.817	15.991	0.763	0.918
$^-\text{CH}_2\text{SH}$	S	LP	6.857	16.196	0.946	1.055
Δ			0.040	0.205	0.183	0.137
CH_3CH_3	$\text{CH}_2(\text{C})$	H	6.558	8.186 (6.558) ^b	0.814	0.814
$^-\text{CH}_2\text{CH}_3$	$\text{CH}_2(\text{C})$	LP	6.665	8.346 (6.520)	1.020	0.949
Δ			0.107	0.160 (-0.030)	0.206	0.135

^a LP \equiv lone pair. ^b Populations are given for CH_2 group (C + 2H) with population of C in parentheses.

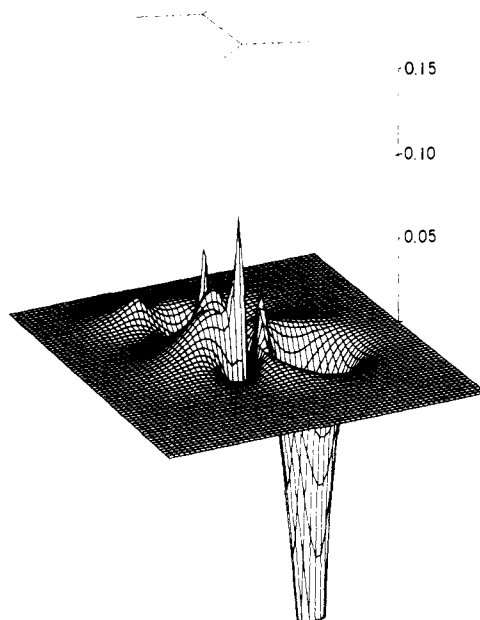


Figure 1. Electron density difference plot for deprotonation of ethane; $\rho(\text{CH}_3\text{CH}_2^-) - \rho(\text{CH}_3\text{CH}_3)$ for the (lone pair)-C-C-H plane (SS+d basis). The electron density, ρ , is plotted as the vertical axis in units of electrons au^{-3} with the molecular plane as the 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.

give proper perspective to the results, they are compared in Table I with similar data for deprotonation of ethane.

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 $\rho(\text{CH}_3\text{CH}_2^-) - \rho(\text{CH}_3\text{CH}_3)$ 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, $\rho(^-\text{CH}_2\text{SH}) - \rho(\text{CH}_3\text{SH})$, in Figure 2, shows ex-