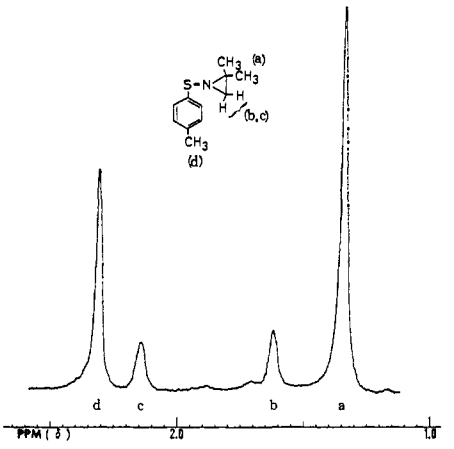

Figure 1. Low-temperature limit spectrum (−60°) of **1b** in methylene chloride.

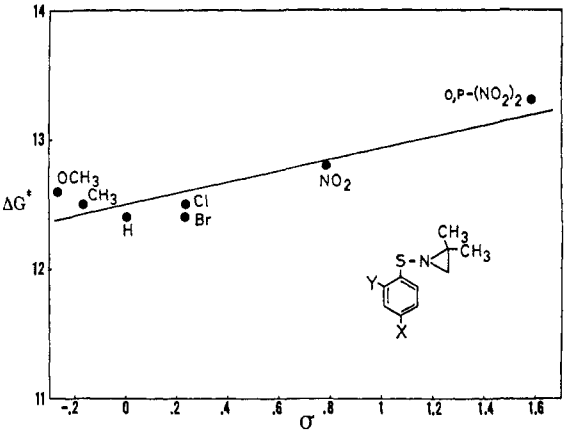

Figure 2. Hammett plot of free energies of activation for degenerate racemization in series **1**.

the temperatures for coalescence of the ring methylene singlets using the Eyring equation ($\kappa = 1$) and the expression $k_c = 2.22\Delta\nu$, since the chemical-shift differences were very large compared to the geminal coupling constants (Figure 1). The very small chemical shifts (<3 Hz) observed for the methyl singlets in most of these compounds preclude their use in determining accurate free energies of activation (*cf.* Figure 1).

As the data in the table indicate, a substantial decrease in the free energy of activation with increasing electronegativity is not observed. We may conclude that (p–d) π bonding does not substantially alter nitrogen inversion barriers in sulfenylaziridines even when a substantially electronegative group, *e.g.*, 2,4-dinitrophenyl, is present as a ligand at the sulfenyl sulfur atom. This, however, does not rule out the possibility of (p–d) π bonding in these compounds but requires only that the extent of (p–d) π bonding is not greatly different in the ground (pyramidal nitrogen) and transition (planar nitrogen) states.

Table I. Nmr Data for Arenesulfenylaziridines, **1**

Compd	X	Y	σ^a	$\Delta\nu$,[b] Hz	T_c,[b] °C	$\Delta G_c^{\ddagger}$, kcal/mol
1a	OCH_3	H	−0.27	30	−20	12.6
1b	CH_3	H	−0.17	31	−21	12.5
1c	H	H	0	32	−23	12.4
1d	Cl	H	0.23	31	−21	12.5
1e	Br	H	0.23	31	−24	12.4
1f	NO_2	H	0.27	30	−17	12.8
1g	NO_2	NO_2	1.58	23	−10	13.8

[a] Hammett substituent constants were taken from: H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953). The value for **1g** is the sum of ortho and para substituent constants. [b] Chemical shifts and coalescence temperatures refer to ring methylene signals. All spectra were measured on *ca.* 10% solutions in methylene chloride.

Analysis using the free-energy form of the Hammett equation, as previously described,[2b] afforded reaction constants and a correlation coefficient: $\rho' = -97 \pm 22$, $\rho_{300} = -0.3 \pm 0.1$, $r = 0.891$ (Figure 2). As in the previous study, the point for *p*-OCH_3 deviates positively from the linear least-squares line.

We do not feel that the trend indicated by the negative reaction constant is significant since the higher barrier for **1g** makes an important contribution to determining the magnitude of the reaction constant and steric factors may play a role for compounds with ortho substituents. When this point is excluded from the data set, the correlation is seriously affected: excluding **1g**, $\rho' = -49 \pm 37$, $\rho_{300} = -0.16 \pm 0.11$, $r = 0.554$. Thus, while we can be definite in excluding an explanation based upon a positive Hammett reaction constant, we are reluctant to rely heavily upon the small negative reaction constant obtained. A negative value is, however, in accord with the inductive effect predicted on the basis of theoretical investigations[1] or might be associated with increased rigidity in the carbon–sulfur single bond due to increased resonance interaction between the sulfur atom and the aromatic π system.[6]

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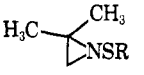
Stereochemistry in Trivalent Nitrogen Compounds. XX. Effect of σ–π Conjugation (Negative Hyperconjugation) on Nitrogen Inversion in Sulfenylaziridines

Sir:

The barrier to nitrogen inversion in trichloromethanesulfenylaziridine (**1a**) is very low (9.2 kcal/mol)



1a, R = CCl_3
b, R = CF_3

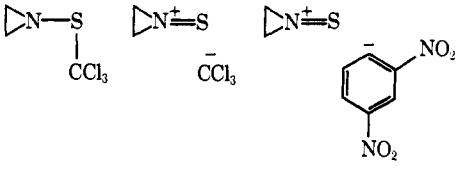
in comparison to barriers in arenesulfenyl and alkanesulfenyl analogs.[1,2] This cannot be due to a simple inductive effect nor due to (p–d) π conjugation.[3] Two other possibilities suggest themselves for this rate enhancement, steric acceleration and σ–π conjugation (negative hyperconjugation).[4]

(1) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).
(2) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 359 (1967).
(3) D. Kost, W. A. Stacer, and M. Raban, *ibid.*, **94**, 3233 (1972), and references therein.

Since congestion is greater in the pyramidal ground state than in the planar transition state for nitrogen inversion, aziridines with bulky ligands at nitrogen invert more rapidly, *caeteris paribus*, than those with less bulky substituents. Thus, the barriers to inversion in *N*-*tert*-butyl- (17.6 kcal/mol) and *N*-*tert*-butanesulfenyl- (12.2 kcal/mol) aziridines are substantially lower than those in their *N*-methyl (22.3 kcal/mol) and *N*-methanesulfenyl (13.3 kcal/mol) analogs.

Bystrov, *et al.*, suggested that overlap between the nitrogen lone-pair orbital and the C–O antibonding σ orbital (negative hyperconjugation) is responsible for the lower barriers in *N*-hydroxymethyl- and *N*-methoxymethylaziridines in comparison to those in *N*-alkylaziridines.[4] Similarly, nitrogen inversion is considerably more rapid in *N*-methoxymethylisoxazolidine than can be accounted for by steric considerations,[5] although changes in vicinal electron-pair repulsion might offer an alternate explanation in the isoxazolidine system.[6] The low barriers observed in some fluorine-substituted aziridines may also be evidence of this phenomenon.[7]

Bystrov, *et al.*, express σ–π hyperconjugation in aziridines by invoking a contribution from (n–σ*) π overlap. The same phenomenon can be viewed in a resonance framework by reference to canonical structures **2a** and **2b**. In either representation the inability



2a **2b** **3**

of the also highly electronegative 2,4-dinitrophenyl group to effect a rate acceleration comparable to that of the trichloromethyl group is understandable. Resonance stabilization of the carbanion orbital in **3** by the nitro groups is not possible since the σ bond (as well as the axis of the σ* orbital) lies in the nodal plane of the aromatic π system.

We have prepared compounds **1a** and **1b** and examined their barriers to topomerization by measuring the temperatures for coalescence of the methylene singlets. The chemical-shift differences, coalescence temperatures, and free energies of activation were: **1a**, $\Delta\nu$ = 30.5 Hz, T_c = −86°, $\Delta G_c^{\ddagger}$ = 9.2 kcal/mol; **1b**, $\Delta\nu$ = 35 Hz, T_c = −61°, $\Delta G_c^{\ddagger}$ = 10.4 kcal/mol. Geminal coupling is small enough that line broadening is negligible in comparison to the chemical-shift difference and the expression $k_c = \pi\sqrt{2}\Delta\nu$ provides an accurate measure of the coalescence rate.

(4) For discussions of σ–π conjugation and its effects on barriers to nitrogen inversion see: (a) ref 3, footnotes 1a,b,d; (b) R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, **94**, 220 (1972); (c) R. D. Baechler and K. Mislow, *Chem. Commun.*, 185 (1972); (d) J. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Yuzhakova, *Opt. Spectrosc. (USSR)*, **19**, 122 (1965); *Opt. Spektrosk.*, **19**, 217 (1965).

(5) (a) F. G. Riddell, J. M. Lehn, and J. Wagner, *Chem. Commun.*, 1403 (1968); (b) D. L. Griffith and B. L. Olson, *ibid.*, 1682 (1968); (c) M. Raban, F. B. Jones, E. H. Carlson, E. Banucci, and N. A. LeBel, *J. Org. Chem.*, **35**, 1496 (1970).

(6) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

(7) (a) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971); (b) J. M. Lehn, *Fortsch. Chem. Forsch.*, **15**, 311 (1970); (c) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 401 (1970).

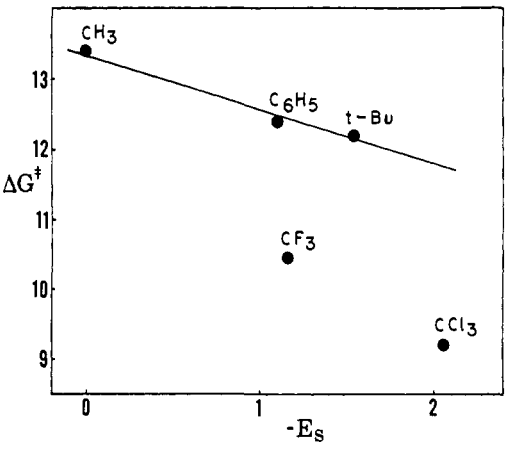


Figure 1. Plot of free energies of activation in sulfenylaziridines as a function of Taft's steric parameter, E_s.

These barriers are not in accord with an explanation based on steric factors alone. A plot of free energies of activation as a function of E_s,[8] a steric parameter (Figure 1) for **1a**, **1b**, and the comparable methanesulfenyl, benzenesulfenyl, and *tert*-butanesulfenyl compounds,[1a,9] indicates considerable deviations for **1a** and **1b**. Both compounds have energies of activation which are *ca.* 2–2.5 kcal/mol lower than those which would be predicted on steric grounds alone. Use of *A* values provides a similar estimate. On the basis of the *A* values given for methyl, phenyl, and trifluoromethyl,[10] the free energy of activation for **1b** deviates by about 2.5 kcal/mol from the line formed by the other two points. Although these calculations are admittedly crude, we may be confident in concluding that steric effects cannot account for the low barriers in **1a** and **1b**. Although estimates of the size of the CF_3 group vary (it is substantially larger than isopropyl on the E_s scale but slightly smaller than isopropyl on the *A*-value scale), under no circumstances would we imagine the trifluoromethyl group to be very significantly larger than *tert*-butyl as it would have to be if steric effects alone were responsible for the magnitude of nitrogen inversion barriers in sulfenylaziridines. By exclusion, then, our data suggest that negative hyperconjugation stabilizes the inversion transition state in **1a** and **1b** by about 2–3 kcal/mol.[11]

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(9) A value of 1.1 was estimated for $E_s(C_6H_5)$ since this value is about 40% larger than that for $E_s(C_6H_{11})$ and the *A* value for phenyl is 40% larger than that for cyclohexyl.[10]

(10) J. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(11) We thank Professor J. M. Lehn for a helpful discussion. This work was supported by the National Science Foundation and the U. S. Public Health Service.

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Preparation and Identification of CO and N_2 Complexes of NiF_2 and $NiCl_2$ by Matrix Isolation

Sir:

Although palladium(II) and platinum(II) carbonyl halides exist, no carbonyl halides of nickel(II) are