(O-*i*-Bu)-*p*. R_f values and spectral properties of the unprotected dinucleotide are shown in Table III. For analysis UpGp was degraded with pancreatic RNase to give Up (0.69 A_{260} unit) and Gp (0.76 A_{260} unit) which were separated by paper chromatography in solvent C and measured absorbance in water. The ratio found was 1.1:1.0. The undigested compound was not detected.

Adenylyl-(3′–5′)-uridylyl-(3′–5′)-guanosine 3′-Phosphate. The phosphoramidate resin VIIa (0.81 g, 14.6 μmol of dinucleotide) was treated with acetic anhydride (0.8 ml) in pyridine (2 ml) for 20 hr and detritylated with 8:2 acetic acid–chloroform (60 ml) at 30° for 24 hr. The resin VIII was washed and swelled in pyridine. Pyridinium *N*,2′,5′-*O*-triacetyladenosine 3′-phosphate (0.25 mmol) was added to the suspension of the resin and rendered anhydrous with added pyridine and triethylamine (0.55 mmol). The mixture was allowed to react with TPS (0.55 mmol) in pyridine (1.5 ml) and tri-*n*-butylamine (0.27 mmol) for 8 hr at room temperature. Aqueous pyridine (50%, 1.5 ml) was added and the resin was washed by the usual method. Liberation of the trinucleotide X from the resin was carried out with isoamyl nitrite (0.7 ml) in 1:1 pyridine–acetic acid (1.4 ml) for 10 hr at room temperature. The resin was removed by filtration and the filtrate and washings were combined and evaporated with aqueous pyridine. The trinucleotide X was precipitated from the pyridine solution with ether. The unprotected trinucleotide ApUpGp was isolated by paper chromatography in solvent C after treatment of X with 15 *N* methanolic ammonia for 20 hr. The yield was 49 A_{260} units, 1.49 μmol (10.2%) from VIIa. R_f values and spectral properties are given in Table III. ApUpGp was digested with RNase M to give Ap (0.741 A_{260} unit), Up (0.504 A_{260} unit), and Gp (0.62 A_{260} unit) as measured by corresponding spots on the paper chromatogram (solvent D). The ratio found was 0.94:0.97:1.00. Undigested compounds were not detected.

Synthesis and Isolation of the Dinucleotide Bz-C^{Bz}(OBz)-*p*-U(OBz)-*p*- by Gel Filtration. Phosphoramidate resin (Vb) (0.25 g, 0.08 mmol of nucleotide) was treated with acetic anhydride (5 ml) in pyridine (10 ml) for 48 hr. The resin was washed and treated with acetic acid–chloroform (8:2) at 30° for 24 hr. Pyridinium *N*,2′,5′-*O*-tribenzoylcytidine 3′-phosphate (1390 A_{260} units, 0.052 mmol) was allowed to react with the resin swelled with anydrous pyridine using TPS (0.295 mmol) in pyridine (0.5 ml) and tri-*n*-butylamine (0.29 mmol) for 8 hr. Tri-*n*-butylamine (0.07 ml) and 50% aqueous pyridine (10 ml) were added. After 1 hr the resin was washed and treated with isoamyl nitrite (0.67 ml, 5 mmol) in 1:1 pyridine–acetic acid (1.34 ml) at 25° for 24 hr. The resin was removed by filtration and the filtrate and washings were concentrated to 0.5 ml. The solution was applied to a column (1.2 × 108 cm) of Sephadex LH-20 preequilibrated with 90% ethanol. The elution pattern and conditions are shown in Figure 3. Fractions 40–50 (peak I) were combined and evaporated with pyridine. The protected dinucleotide was precipitated from the pyridine solution with ether. The spectral properties of Bz-C^{Bz}(OBz)-*p*-U(OBz)-*p* were $\lambda_{max}^{H_2O}$ 235.5, 262, 306 nm; $\lambda_{max}^{H^+}$ 235.5, 262, 314 nm; $\lambda_{max}^{OH^-}$ 234, 272, 318 nm; $\epsilon_{235}/\epsilon_{260}$ = 1.45 and $\epsilon_{260}/\epsilon_{305}$ = 3.37. The spectral properties of CpUp are shown in Table III. CpUp (*ca.* 2 A_{260} units) was degraded with pancreatic RNase. The mixture was applied to paper electrophoresis (0.05 *M* ammonium formate, pH 3.5, 700 V/40 cm) to separate Cp (0.98 A_{260} unit at pH 2, 0.14 μmol) and Up (1.27 A_{260} units at pH 2, 0.13 μmol). The ratio found was 1.1:1.0. The undigested material was not detected.

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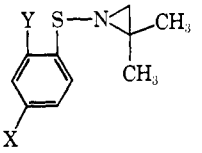
Communications to the Editor

Stereochemistry in Trivalent Nitrogen Compounds. XIX. Absence of a Rate Acceleration to Nitrogen Inversion in Sulfenylaziridines Due to d-Orbital Conjugation

Sir:

The possible effect of (p–d) π conjugation on barriers to nitrogen inversion has been a topic of some interest recently.[1] The early suggestion that (p–d) π conjugation lowers barriers in haloaziridines has been shown to be in error,[1e] and molecular orbital calculations have implied that planarity at nitrogen in silylamines is due to the low electronegativity of the silicon atom rather than d-orbital conjugation.[1a,1b] On the other hand, (p–d) π bonding has been suggested as a contributor to torsional barriers about sulfur–nitrogen bonds,[2] and a number of compounds with S–N bonds have been shown to be planar or nearly planar at nitrogen.[3] The low barriers to nitrogen inversion in sulfenyl-, sulfinyl-, and sulfonylaziridines[4] might have been due to d-orbital resonance since (p–p) π conjugation is known to lower aziridine nitrogen inversion barriers.[1]

Hammett analysis has demonstrated a substantial effect from polar substituents on torsional barriers in sulfenylsulfonamides and has indicated that the dependence observed was related to (p–d) π bonding between nitrogen and sulfur.[2b] A similar study of nitrogen inversion barriers would allow a determination of the importance of (p–d) π bonding in lowering nitrogen inversion barriers in sulfenylaziridines. We have examined nitrogen inversion barriers in a series of para-substituted benzenesulfenylaziridines, **1**. The free



1a, X = OCH_3; Y = H
b, X = CH_3; Y = H
c, X = Y = H
d, X = Cl; Y = H
e, X = Br; Y = H
f, X = NO_2; Y = H
g, X = Y = NO_2

energies of activation can be determined accurately[5] at

(1) For review articles which discuss this point see: (a) J. M. Lehn, *Fortsch. Chem. Forsch.*, **15**, 311 (1970); (b) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); (c) H. Kessler, *ibid.*, **9**, 219 (1970); (d) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971); (e) S. J. Brois, *Trans. N. Y. Acad. Sci.*, **31**, 931 (1969).

(2) (a) W. B. Jennings and R. Spratt, *J. Chem. Soc. D*, 1418 (1970); (b) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 2692 (1971).

(3) (a) T. Jordan, H. W. Smith, L. L. Lohr, and W. N. Libscomb, *ibid.*, **85**, 846 (1963); (b) R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *ibid.*, **93**, 924 (1971); (c) J. Kay, M. D. Glick, and M. Raban, *ibid.*, **93**, 5224 (1971).

(4) (a) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 359 (1967); (b) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967); (c) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).

(5) D. Kost, E. H. Carlson, and M. Raban, *J. Chem. Soc. D*, 656 (1971).

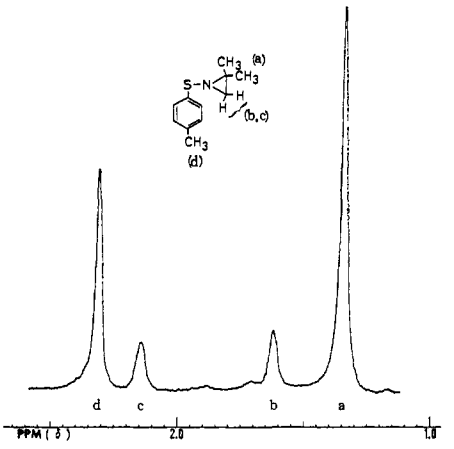


Figure 1. Low-temperature limit spectrum (−60°) of **1b** in methylene chloride.

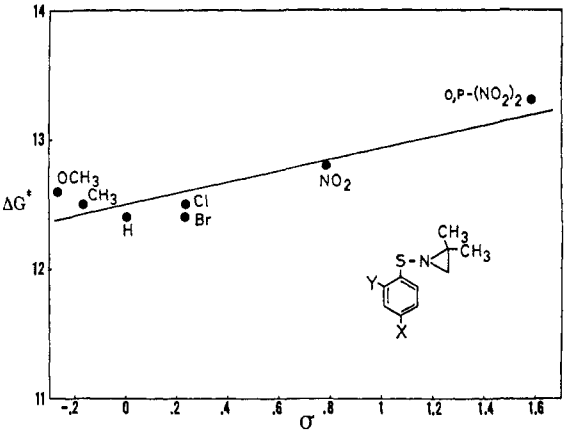


Figure 2. Hammett plot of free energies of activation for degenerate racemization in series **1**.

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]

(6) We are grateful to the National Science Foundation and to the United States Public Health Service for support of this work.

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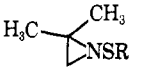
Stereochemistry in Trivalent Nitrogen Compounds. XX. Effect of σ–π Conjugation (Negative Hyperconjugation) on Nitrogen Inversion in Sulfenylaziridines

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.