Concerning the Configurational Stability at Nitrogen in *N*-Sulfonyloxaziridines

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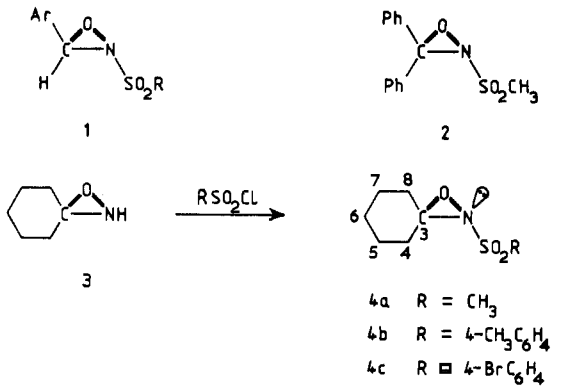
In recent years, *N*-sulfonyloxaziridines **1** have been extensively developed by Davis and co-workers[1] as synthetically useful chiral oxidants. The nitrogen atom in these compounds has been considered to be configurationally stable, and the view has been expressed[2a] that "the 2-arenesulfonyl group apparently does not significantly lower the nitrogen inversion barrier in these oxaziridines" (relative to the high barriers, 31–33 kcal mol^{-1}, obtaining in 2-alkyloxaziridines[3,4]). More recently, Torre et al.[5] concluded on the basis of NMR observations that the 2-methanesulfonyloxaziridine **2** had an "enantiomeric structure, stable at the pyramidal nitrogen atom at room temperature". The inability to obtain **2** in optically active form by oxidation of an *N*-sulfonyl imine precursor with optically active peroxyacid was therefore attributed to stereomutation of a long-lived intermediate.[5]



We now present evidence that an *N*-sulfonyl group *does* greatly reduce the configurational stability at nitrogen in oxaziridines, to the extent that they may undergo spontaneous stereomutation at ambient temperature.

Hitherto, *N*-sulfonyloxaziridines have been obtained by peroxyacid oxidation of *N*-sulfonyl imines. Almost all of the *N*-sulfonyloxaziridines prepared to date possess a 3-aryl group as in **1**. A search for alternative routes to these and related compounds has led us to obtain the new 3,3-dialkyl-2-sulfonyloxaziridines, **4a–c**, by reaction of 1-oxa-2-aza-spiro[2.5]octane (**3**) with the appropriate alkyl or aryl sulfonyl chloride in the presence of pyridine.[6,7] The yields are rather low (~15% with respect to **3**), though gram quantities of **4a–c** can be obtained from inexpensive starting materials (cyclohexanone and hydroxylamine-*O*-sulfonic acid).

Table I. Rate Constants and Free Energies of Activation for Nitrogen Inversion[a]

compd	temp, °C	k,[b] s^{-1}	T_1,[c] s	$\Delta G^{\ddagger}$, kcal mol^{-1}
4a	62	0.26	5.2	20.6
4b	62	0.46	2.0	20.2
4c	62	0.73	2.2	19.9

[a] Determined on a Jeol GX-270 spectrometer with use of 50% w/v solutions in benzene-d_6. [b] The analysis of magnetization transfer between two equally populated sites gave the rate constant k and mean relaxation time T_1 by graphical analysis of the sum and difference of the peak intensities as a function of time following selective inversion, see: ref 8 and 13. [c] Effective longitudinal relaxation time for the exchanging ring carbons (C-4 and C-8) determined in undegassed samples.

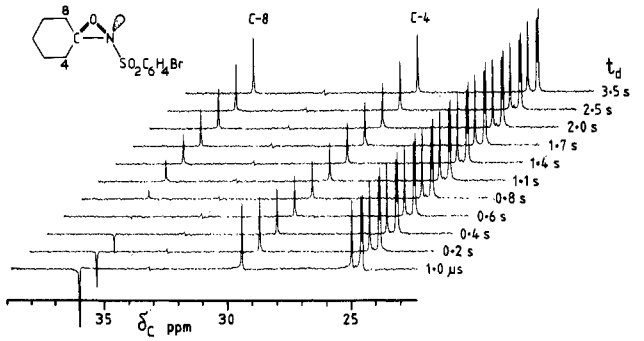


Figure 1. $^{13}C\{^1H\}$ NMR spectra (67.8 MHz) of oxaziridine **4c** (alkyl region) as a function of evolution time, t_d, in a DANTE selective (C-8) 180°-t_d-90° (unselective) pulse sequence showing magnetization transfer between C-8 and C-4.

Oxaziridines **4a–c** are well suited to an investigation of the configurational stability at nitrogen since they are symmetrically substituted at C-3 and are thermally stable up to ~80 °C. Furthermore the C-4 and C-8 resonances were found to be widely separated (by 6.6–6.8 ppm) in the ^{13}C NMR spectra recorded at ambient temperature. By using a DANTE[8] composite pulse to invert the lower field[9] α-carbon resonance (C-8) the configurational instability at nitrogen was demonstrated by inversion transfer experiments, and the rates of nitrogen inversion were thereby determined at 62 °C.

The results (Table I) clearly establish that the nitrogen inversion barrier in *N*-sulfonyloxaziridines is dramatically lower than that obtaining in *N*-alkyloxaziridines where $\Delta G^{\ddagger}$ ~32 kcal mol^{-1}.[3] The large decrease in the inversion barrier, ~12 kcal mol^{-1}, can be attributed largely to an unusually poor π-interaction between the oxaziridine nitrogen lone pair electrons (which have high s-character) and sulfur in the ground state. This is reflected in a highly pyramidal nitrogen atom and a long S–N bond as shown by X-ray crystal structures.[3,10] Hence the ground state in *N*-

(1) See, for example: Davis, F. A.; Jenkins, R. H., Jr.; Awad, S. B.; Stringer, O. D.; Watson, W. H.; Galloy, J. *J. Am. Chem. Soc.* **1982**, *104*, 5412. Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123. Davis, F. A.; McClauley, J. P.; Chattopadhyay, S.; Harakal, M. E.; Towson, J. C.; Watson, W. H.; Tavanaiepour, I. *J. Am. Chem. Soc.* **1987**, *109*, 3370. Davis, F. A.; Haque, M. S.; Ulatowski, T. G.; Towson, J. C. *J. Org. Chem.* **1986**, *51*, 2402.

(2) (a) Davis, F. A.; Lamendola, J., Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R., Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, *102*, 2000. (b) Chen, J. S.; Watson, W. H.; Davis, F. A.; Lamendola, J. F., Jr.; Nadir, U. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2861. (c) Kimura, M.; Watson, W. H.; Davis, F. A.; Lamendola, J. F., Jr.; Nadir, U. K. *Ibid.* **1979**, *B35*, 234.

(3) (a) Bjørgo, J.; Boyd, D. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1575. (b) Mannschreck, A.; Linss, J.; Seitz, W. *Liebigs Ann. Chem.* **1969**, *727*, 224. Montanari, F.; Moretti, I.; Torre, G. *Chem. Commun.* **1969**, 1086.

(4) Somewhat lower inversion barriers are found in oxaziridines containing very bulky *N-tert*-alkyl substituents, see: ref 3.

(5) Bucciarelli, M.; Forni, A.; Moretti, I.; Torre, G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 923.

(6) Oxaziridine **3** was prepared in dichloromethane solution at 0 °C from cyclohexanone and freshly prepared hydroxylamine-*O*-sulfonic acid as described by the following: Schmitz, E.; Schramm, S. *Chem. Ber.* **1967**, *100*, 2593. Schmitz, E.; Ohme, R.; Schramm, S. *Chem. Ber.* **1964**, *97*, 2521. The solution of **3** was dried (K_2CO_3) and assayed by iodometric titration (yield typically 30–35%).

(7) Pyridine (1.1 mol equiv) in dichloromethane and the sulfonyl chloride (1.0 mol equiv) in dichloromethane were simultaneously added dropwise to the stirred solution of **3** in dichloromethane at 0 °C. After 6 h the solution was washed 5 times with water and dried (K_2CO_3). The 2-methanesulfonyl- and 2-arenesulfonyl-1-oxa-2-aza-spiro[2.5]octans (**4a–c**) were purified by flash column chromatography on silica gel and characterized by ^{13}C NMR which showed characteristic quaternary C-3 resonance at δ 90.9 (**4a**), 91.8 (**4b**), and 92.2 (**4c**) in $CDCl_3$. These compounds liberated iodine from aqueous potassium iodide and gave satisfactory microanalytical data (±0.4% for C, H, N): compound **4a**, mp 44–46 °C; **4b**, mp 57–60 °C; **4c**, mp 68–70 °C.

(8) Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433.

(9) A ^{13}C nucleus trans to the oxaziridine nitrogen lone pair is shifted to higher field: Jordan, G. J.; Crist, D. R. *Org. Magn. Reson.* **1977**, *9*, 322.

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sulfonyloxaziridines is energetically destabilized relative to the transition state for nitrogen inversion where the nitrogen is trigonal and its p-type lone pair can interact well with sulfur via an n-σ^* π-bond.[11]

The kinetic data for **4a-c** can be extrapolated[12] to give estimated half-lives for racemization at 25 °C of ~70 s (**4a**), ~40 s (**4b**), and ~20 s (**4c**). While one should in principle be cautious in extending these results to other *N*-sulfonyloxaziridines, data for *N*-alkyloxaziridines indicate that changing the 3-substituents from alkyl to aryl has little effect on the inversion barrier.[3] Accordingly, it is likely that attempts to obtain symmetrically 3-substituted *N*-sulfonyloxaziridines in optically active form[5] may only be successful if the reaction and workup are performed at low temperature where racemization by nitrogen inversion is slow. Additionally, the reported[2] exclusive formation of a single (trans) diastereoisomer of unsymmetrically 3-substituted *N*-sulfonyloxaziridines **1** may reflect thermodynamic product control rather than a kinetic preference since cis → trans isomerization in these compounds by nitrogen inversion could also be fairly fast at ambient temperature.[14] The trans configuration should be favored on thermodynamic grounds for oxaziridines of type **1** as it minimizes steric interactions. Nevertheless, the present observations suggest that the possibility of configurational inversion at nitrogen should be borne in mind when considering reactions performed at, or above, ambient temperature.

(10) Forni, A.; Moretti, I.; Torre, G.; Bruckner, S.; Malpezzi, L. *J. Chem. Soc., Perkin Trans. 2* **1987**, 699.

(11) For a discussion of N-S n-σ^* bonding as an alternative to the traditional concepts of p_π-d_π bonding and negative hyperconjugation, see: Raban, M.; Kost, D. *J. Am. Chem. Soc.* **1972**, *94*, 3234. Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1982**, *104*, 2960.

(12) The extrapolation assumes that $\Delta G^{\ddagger}$ remains essentially constant over the temperature range 62 → 25 °C. This is a reasonable assumption bearing in mind the relatively small temperature range of the extrapolation and the fact that $\Delta S^{\ddagger}$ has been shown to be very small for nitrogen inversion in oxaziridines (ref 3a). The rate of racemization is twice that for nitrogen inversion.

(13) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 411.

(14) We would concur with the suggestion by a referee that the trans → cis inversion barriers in *N*-sulfonyloxaziridines **1** derived from aldehydes could be somewhat higher than those determined in **4**, due to reduced steric interactions in trans **1** where the sulfonyl group is syn to a ring hydrogen atom.

The H_3O^+ Cation in Aromatic Solvents. Synthesis, Structure, and Solution Behavior of $[H_3O^+ \cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]$

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The interaction of the oxonium ion, H_3O^+, with polar solvents has been extensively reviewed in the broader context of hydrogen bonding.[1] The first report of a complex of H_3O^+ and a macrocycle was an infrared spectroscopic study in 1972.[2] More recently, several reports have appeared.[3-8] This has proved to be a method of isolation of H_3O^+ from higher hydrated species, $H_3O^+(H_2O)_n$.[9] The structures of two complexes of H_3O^+ coordinated to macrocycles have been reported, one which lends strong support for pyramidal H_3O^+,[10,11] and one which may be interpreted in terms of planar H_3O^+.[12] In the extensive literature of the oxonium ion, evidence for the species in aromatic solution has not been presented. Here we report that the oxonium ion coordinated to 18-crown-6 does indeed have a stable existence in aromatic media.

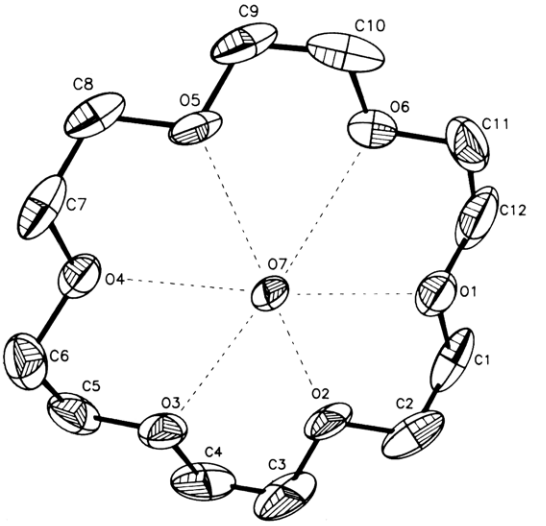

Figure 1. Structure of the $[H_3O^+ \cdot 18\text{-crown-6}]^+$ cation. The hydrogen atoms of the oxonium ion could not be located. The O(7)···O separations range from 2.70 to 2.85 Å.

We have long been interested in the interaction of salts with aromatic solvents. The formation of two liquid layers by such systems has been the subject of recent reviews.[13,14] Since this "liquid clathrate effect" has been shown to provide extra stabilization for ionic species in aromatic solutions,[15] we initially attempted to protonate 18-crown-6 by bubbling HCl(g) through an aromatic suspension of the macrocycle.[16] Under anhydrous conditions no reaction was observed. However, when HCl(g) was passed through a vessel open to the atmosphere, two liquid layers quickly resulted. Colorless crystals were collected and the complex was found to be $[H_3O^+ \cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]$.[17] Subsequently,

(1) *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North Holland: Amsterdam, 1976; Vol. I-III.

(2) Izatt, R. M.; Haymore, B. L.; Christensen, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1308.

(3) Behr, J.-P.; Dumas, P.; Moras, D. *J. Am. Chem. Soc.* **1982**, *104*, 4540.

(4) Heo, G. S.; Bartsch, R. A. *J. Org. Chem.* **1982**, *47*, 3557.

(5) Kolthoff, I. M.; Wang, W.-J.; Chantooni, M. K., Jr. *Anal. Chem.* **1983**, *55*, 1202.

(6) Jagur-Grodzinski, J. *Isr. J. Chem.* **1985**, *25*, 39.

(7) Buschmann, H.-J. *Inorg. Chim. Acta* **1986**, *118*, 77.

(8) Chenevert, R.; Rodrigue, A.; Chamberland, D.; Ouellet, J.; Savoie, R. *J. Mol. Struct.* **1985**, *131*, 187.

(9) Kochanski, E. *J. Am. Chem. Soc.* **1985**, *107*, 7869 and references therein.

(10) The structure of $[H_3O^+ \cdot 18\text{-crown-6(COOH)}_4]Cl^-$ is reported in ref 3. The oxonium oxygen atom resides 0.61 Å out of the plane of the three crown oxygen atoms to which it is hydrogen bonded. (The X-ray diffraction data yielded the positions of the hydrogen atoms.)

(11) This Journal has hosted several manuscripts, both experimental and theoretical, which have been concerned with pyramidal versus planar geometry for H_3O^+. See: Rodwell, W. R.; Radom, L. *J. Am. Chem. soc.* **1981**, *103*, 2865 and references therein.

(12) Shoemaker, C. B.; McAfee, L. V.; Shoemaker, D. P.; DeKock, C. W. *Acta Crystallogr.* **1986**, *C42*, 1310. The oxonium oxygen atom lies within 0.1 Å of the plane of the crown oxygen atoms, although disorder of the oxonium oxygen atom was not ruled out.

(13) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; pp 395-405.

(14) Atwood, J. L. In *Chemical Separations*; Navratil, J. D., King, C. J., Eds.; Litarvan: Arvada, Colorado, 1986; pp 335-354.

(15) For example, the superoxide ion, O_2^-, is stable in refluxing toluene in the complex $[K \cdot 18\text{-crown-6}][O_2(AlMe_3)_2]$: Hrncir, D. C.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 4277.

(16) Protonation of simple crown ethers in more polar solvents such as 1,2-dichloroethane has been studied: see ref 6. Protonation of pyridine-containing crown ethers has also been investigated: Gokel, G. W.; Garcia, B. J. *Tetrahedron Lett.* **1977**, 317. Grootenhuis, P. D. J.; Uiterwijk, J. W. H. M.; Reinhoudt, D. N.; vanStaveren, C. J.; Sudholter, E. J. R.; Bos, M.; van Eerden, J.; Klooster, W. T.; Kruise, L.; Harkema, S. *J. Am. Chem. Soc.* **1986**, *108*, 780.

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