

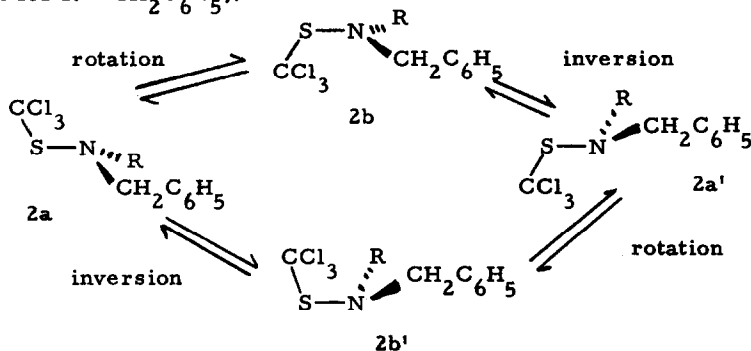
STEREOCHEMISTRY AT TRIVALENT NITROGEN III.<sup>1</sup>  
 EVIDENCE FOR A TORSIONAL BARRIER IN SULFENAMIDES<sup>2</sup>

Morton Raban, Freeman B. Jones, Jr.,  
 George W. J. Kenney, Jr.  
 Department of Chemistry  
 Wayne State University  
 Detroit, Michigan 48202 U. S. A.

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The chemical shift nonequivalence of diastereotopic<sup>3</sup> nuclei has been observed in many types of compounds<sup>4</sup> and has often provided valuable information concerning the symmetry and structure of the molecules in which it has been observed.<sup>5</sup>

The observation<sup>6</sup> of chemical shift nonequivalence of benzyl protons in sulfenamides 1 implies a chiral conformation such as 2a (or 2b) as the ground state for 1a, b, d, e. The coalescence of benzyl protons at elevated temperatures corresponds to the degenerate racemization of 1 (except for R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>).



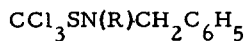
This process, 2a  $\rightleftharpoons$  2a', involves two transition states and two free energies of activation, corresponding to rotation around the N-S bond and inversion of the nitrogen pyramid. The free energy for degenerate racemization, as measured by the free energy of activation for exchange of diastereotopic protons, of necessity, corresponds only to the higher of the two transition states. We had earlier<sup>6</sup> pointed out that slow rotation due to p-d  $\pi$ -bonding does not offer a convincing rationale for the observed low temperature nonequivalence of diastereotopic protons in 1c. The assignment for the oxygen analogs, N, N, O-trialkylhydroxylamines,<sup>7</sup> and the extensive evidence that nitrogen inversion is dramatically slowed by the presence of an adjacent

heteroatom in three and four membered rings and bicyclic systems<sup>8</sup> suggested that slow nitrogen inversion due to lone-pair lone-pair repulsions could satisfactorily account for the observed n. m. r. behavior. We now report that further studies on the variable temperature n. m. r. spectra of 1 and 3 provides compelling evidence that this suggestion is in error and that the chemical shift nonequivalence of 1 results from an extraordinarily high barrier to rotation around the nitrogen-sulfur bond.<sup>1, 9</sup>

By contrast with the nitrogen pyramid in amines, amide nitrogen in succinimides is either planar, or very close to planar with a very small inversion barrier.<sup>10</sup> As a consequence, we can be sure that the barrier to inversion in N-trichloromethanesulfonyl-2,2-dimethylsuccinimide, 3, if one does exist, will be very small in comparison to those observed for the N, N-dialkylsulfenamides. The barriers to nitrogen inversion in N-acylaziridines are at least 10 kcal mole lower than those in alkyl aziridines.<sup>11</sup> The low temperature n. m. r. spectrum of 3 does, however, exhibit chemical shift nonequivalence of diastereotopic methyl groups. The free energy of activation for exchange in 3 is somewhat smaller than those for dialkylsulfenamides 1 (Table I) but the difference is far smaller than that to be expected were nitrogen inversion the process corresponding to coalescence. It may be concluded that a substantial barrier to rotation about the nitrogen-sulfur bond obtains in 3.

Evidence that slow rotation is responsible for the barrier to interchange of diastereotopic benzyl methylene hydrogens in 1, as well, lies in the steric effect on the barrier. Were slow inversion associated with coalescence, increase in the steric bulk of R would be accompanied by a decrease in the free energy of activation since steric hindrance is greater in the ground-state than in the transition state. The transition state for rotation, on the other hand, involves increased steric hindrance as the trichloromethyl group passes the alkyl group on nitrogen and steric deceleration is expected. Examination of the data for 1a-e (Table I) indicates that steric deceleration is observed.

These two independent experiments provide compelling evidence that a substantial torsional barrier exists in sulfenamides, probably as the result of lone-pair lone-pair interactions and suggest that torsional barriers may well be involved in the low temperature chemical shift nonequivalence in related compounds such as sulfinamides<sup>12</sup> and hydroxylamines.<sup>7</sup> Although it has been established that in cyclic (3 and 4 member ring) hydroxylamines the barrier to inversion is substantial, it should be noted that in these compounds the planarity (or near planarity) of ring system constrains the disposition of lone pairs of electrons on nitrogen and oxygen into a geometry of maximum interaction. However, the ground state in acyclic analogs, such as the sulfenamides discussed, is one in which the respective lone pairs of electrons can achieve a geometry of minimum interaction.



1

- a R = CH<sub>3</sub>  
 b R = CH<sub>2</sub>CH<sub>3</sub>  
 c R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 d R = CH(CH<sub>3</sub>)<sub>2</sub>  
 e R = C<sub>10</sub>H<sub>15</sub> (adamantyl)

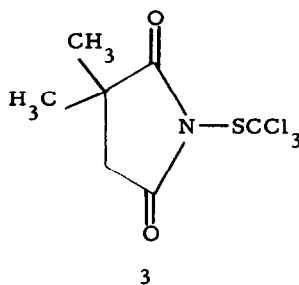


TABLE I

Compound	Solvent	$\Delta\nu_{\text{max}}^{\text{a}}$ in Hz	$J_{\text{AB}}$ in Hz	$T_{\text{c}}^{\text{b}}$ in degrees Kelvin	$\Delta G^{\ddagger \text{c}}$ in kcal mole
1a	CDCl <sub>3</sub>	8.5	14.5	290 <sup>o</sup>	14.4
1b	CDCl <sub>3</sub>	7.6	15.0	313 <sup>o</sup>	15.6
1c	CDCl <sub>3</sub>	8.6	14.8	301 <sup>o</sup>	15.3
1d	CDCl <sub>3</sub>	5.4	15.4	318 <sup>o</sup>	15.9
1e	Bromobenzene	20.9	15.9	341 <sup>o</sup>	17.0
3	CDCl <sub>3</sub>	3.3	----	220 <sup>o</sup>	11.8

<sup>a</sup> Spectra measured on ca. 10% solutions using a Varian A60-A spectrometer equipped with variable temperature accessory.

<sup>b</sup> Temperatures were calibrated using methanol spectra and are considered accurate to  $\pm 3^{\circ}\text{C}$ .

<sup>c</sup> Free energies of activation at the coalescence temperature were calculated using the equation of Kurland et. al. (R. J. Kurland, M. B. Rubin and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964) and the Eyring equation. The uncertainty in  $T_{\text{c}}$  results in an uncertainty in  $\Delta G^{\ddagger}$  of  $\pm 0.2$  kcal mole.

REFERENCES

1. a) Part II: M. Raban, G. W. J. Kenney, Jr., J. M. Moldowan and F. B. Jones, Jr., J. Am. Chem. Soc., 90, 2985 (1968).  
b) A portion of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, California, April 2, 1968.
2. Supported in part by grants from the Petroleum Research Fund of the American Chemical Society (No. 1139-G1) and the Research Corporation.
3. K. Mislow and M. Raban, in "Topics in Stereochemistry", Vol. 1, E. L. Eliel and N. L. Allinger, eds., Wiley-Interscience, New York, 1967. Chap. 1.
4. For recent reviews see ref. 3, and: a) M. L. Martin and G. J. Martin, Bull. Soc. Chim. France, 2117 (1966); (b) M. Van Gorkom and G. E. Hall, Chem. Rev., 22, 14 (1968).
5. For a recent elegant use of magnetic nonequivalence as a probe for molecular dissymmetry see: R. K. Hill and T. H. Chan, Tetrahedron, 21, 2015 (1965).
6. M. Raban, Chem. Commun., 1017 (1967).
7. a) D. L. Griffith and J. D. Roberts, J. Am. Chem. Soc., 87, 4089 (1965).  
b) R. E. Banks, M. G. Barlow, R. N. Haszeldine and M. K. McGreath, J. Chem. Soc., 7203 (1965).
8. a) W. D. Emmons, J. Am. Chem. Soc., 79, 5739 (1957).  
b) J. Lee and K. G. Orrell, Trans. Faraday Soc., 61, 2342 (1965).  
c) E. Fahr, W. Fischer, A. Jung, L. Sauer and A. Mannschreck, Tetrahedron Letters, 161 (1967).  
d) A. Mannschreck, R. Radeglia, E. Gründemann and R. Ohme, Chem. Ber., 100, 1778 (1967).  
e) J. E. Anderson and J. M. Lehn, J. Am. Chem. Soc., 89, 81 (1967).
9. Independent evidence that slow rotation rather than slow inversion is responsible for the exchange has been obtained by Dr. J. M. Lehn (private communication). Slow rotation also occurs in aminophosphenes. (A. H. Cowley, M. J. S. Dewar and W. R. Jackson, J. Am. Chem. Soc., 90, 4185 (1968).)
10. G. S. D. King, J. Chem. Soc., (B), 1224 (1966).
11. F. A. L. Anet and J. M. Osyany, J. Am. Chem. Soc., 89, 352 (1967).
12. H. J. Jakobsen and A. Senning, Chem. Commun., 617 (1967).