# Kinetic Acidity of Diastereotopic Protons in Sulfonium Ions. A Transition State Conformational Effect

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**Abstract:** The differential kinetic acidity of diastereotopic protons $\alpha$ to the sulfonium function has been studied in a series of conformationally biased or rigid thianium cation where the exocyclic $^+$S–C$_\alpha$ bond is equatorially set. The results show that the diastereotopic reactivity differential increases as the conformational mobility of the ring becomes more and more restricted. However, the stereoselectivity increase obtains from a continuous decrease of the reactivity of the axial $\alpha$ proton, that of the equatorial proton remaining essentially constant. The trend suggests that the conformation of the transition state for exchange of the axial proton, but not of the equatorial one, tends to differ considerably from the chair ground state. A PMO rationalization of the above trend is proposed, which focuses upon the two-electron two-orbital stabilizing interaction involving the lone pair at C$_\alpha$ (donor) and the vacant $\sigma^*$ S–C$_{\alpha'}$ and S–C$_{\alpha''}$ bond MOs (acceptors), occurring in the sulfonium ylides formed by removal of the equatorial or axial proton. In the ylide arising from removal of the equatorial proton, such interaction can occur without significant deformation of the ground state geometry; on the contrary, in the ylide arising from removal of the axial proton, a conformational change is required in order that the postulated interaction may occur. Ab initio SCF–MO computations support this rationalization.

Diastereotopic protons $\alpha$ to tricoordinated sulfur may be abstracted by base stereoselectively.[2] The phenomenon is important theoretically as well as practically insofar as the resulting carbanion, or ylide, may transfer chirality from sulfur to carbon.[3] A rationalization[4] of the differential acidity of diastereotopic protons in terms of the "gauche effect" theory[4] has not proven to be generally applicable[1,5] and the fundamental conformational factors presiding over this phenomenon are as yet obscure. The study we wish to report comprises the determination of the kinetic acidity differentials of $\alpha$ protons in conformationally biased or rigid thianium cations,[6] and a theoretical approach to the stability of diastereomeric sulfonium ylides. Our main conclusion is that the dependence of acidity on geometrical factors is related to the reacting system ability to achieve a conformation where the incipient lone pair orbital at C$_\alpha$ is either syn or anti aligned with one of the vicinal bonds at sulfur.

## Results and Discussion

The species whose exchange behavior we wish to report, **1–4**, populate largely or exclusively chair conformers where the



1    2    3    4
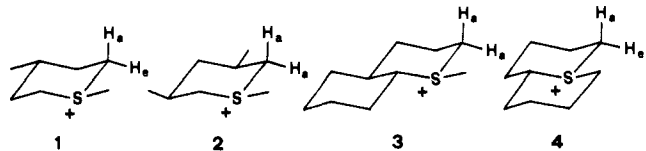
$^+$S–CH$_3$ (**1–3**) or $^+$S–CH$_2$ (**4**) bonds are equatorially set. They differ, however, for the position and nature of the conformation holding constraint.

The base-catalyzed H/D exchange rates of the individual $\alpha$ protons have been measured (D$_2$O, NaOD, 2 M or 5 M, 60 °C) by following the intensity decrease of their NMR signals at high field (270 MHz). The four cations above undergo stereoselective exchange, the pertinent rate factors, $k_{H_e}/k_{H_a}$, being 1, 0.5; 2, 2; 3, 5; 4, 35.

The figures indicate the diastereotopic reactivity differential increases as the ring becomes more rigid. It is remarkable, however, that this change of stereoselectivity obtains from a monotonic decrease of the reactivity of H$_a$, that of H$_e$ remaining essentially constant throughout the series (pseudo-

first-order specific rate, $k_{H_e} = 1.0 \times 10^{-5}$ s$^{-1}$). This trend suggests that the conformation of the transition state for exchange of H$_a$ tends to differ considerably from the chair conformation of the ground state. On the other hand, the constant reactivity of H$_e$, independent of constraint, indicates that the transition state conformation essentially coincides with the ground state.

A rationalization of the above trends can be attempted in terms of a perturbational molecular orbital (PMO) approach[8] coupled with SCF–MO ab initio computations. The PMO discussion focuses upon the diastereomeric sulfonium ylides, **5e, 5a**, formed by removal of the equatorial and axial proton,



5e        5a

respectively, which are supposed to be structurally and energetically close to the transition states leading to them, enough to provide a reliable criterion.[9] In particular we will consider the two-electron two-orbital stabilizing interaction involving the lone pair at C$_\alpha$ (donor) and the vacant $\sigma^*$ S–C$_{\alpha'}$ and S–C$_{\alpha''}$ bond MOs (acceptors).[14] The related stabilization energy is given by

$$\Delta E_{ij}^2 = 2K^2 S_{ij}^2/(E_i - E_j)$$

where $E_i$ and $E_j$ are the energies of the two interacting orbitals, $S_{ij}$ their overlap integral, $K$ a constant, and where the usual approximation for the interaction matrix element, $H_{ij} = KS_{ij}$, has been made.

Since the denominator is essentially independent of conformation, overlap becomes the key factor. Therefore the stabilization energy will increase with increasing overlap and be maximum for syn or anti alignment of the two interacting orbitals.

In **5e** the lone pair, arising from removal of the equatorial proton, is aligned anti to S–C$_{\alpha'}$; therefore the postulated interaction can occur without significant deformation of the ground state geometry and be independent of ring substitution. This is consistent with the constant reactivity of the equatorial $\alpha$ protons along the series **1–4**.

In **5a**, on the other hand, the lone pair is gauche to both the ring S–$C_{\alpha'}$ and the exocyclic S–$C_{\alpha''}$ bonds. Therefore the stabilizing interaction cannot operate without a conformational change allowing for the favorable syn or anti alignment to be achieved. The least expensive deformation capable of realizing such favorable arrangement is likely to be a torsion around the S–$C_\alpha$ bond toward the half-chair shown below, **7**, which brings the carbon lone pair and the S–$C_{\alpha''}$ bond MOs into syn alignment. Indeed this deformation obtains most easily when the conformation holding group is at $C_\gamma$ (**1**, position 4e), less easily when it is at $C_\beta$ (**2**, positions 3e, 3e'), still less easily when the constraint prevents any torsion at $C_{\alpha'}$–$C_{\beta'}$ (as in compound **3**), and is precluded in compound **4** owing to the heteroatom at the bridgehead. Thus the postulated interaction should decrease with increasing molecular rigidity along the series **1-4**, consistent with the observed reactivity decrease of the axial proton.

To provide quantitative support to the model, we have carried out ab initio computations at the STO-3G level[16,17] on the cationic ground state and the diastereomeric ylides derived from it. Such calculations have been extended to the *S*-methyl epimeric cation (where the exocyclic S–$C_{\alpha''}$ bond is axially oriented) and the corresponding ylides, **6a** and **6e**. The

geometries of the ylides were taken to be the same as those of the corresponding cations, equal in turn to those reported for *trans*- and *cis*-1-methyl-4-*tert*-butylthianium perchlorates, respectively.[18]

Because of the limitations of such computations (minimal basis set, no geometry optimization of the ylides) we limit our discussion to certain effects caused by the postulated interaction. A suitable index of its importance can be the total overlap population (TOP) of the vicinal S–C bonds: if the above interaction is operative, there is charge transfer from the carbon lone pair MO to the vacant antibonding $\sigma^*$ S–C bond MOs, and consequently the TOP of the S–C bonds involved should decrease. The relevant overlap populations are listed in Table I, and the values completely support the proposed model. Of the ylides derived from the S–$CH_3$ equatorial structure, only **5e** shows a significant TOP decrease in one of the vicinal S–C bonds, precisely that which is anti oriented with respect to the lone pair (the ring S–$C_{\alpha'}$). Instead, none of the S–C bonds shows such decrease in **5a**, in agreement with the gauche orientation of the lone pair orbital with respect to either S–C bond.

To check on the validity of our model we have carried out computations for the half-chair conformation (**7**), again

**7**
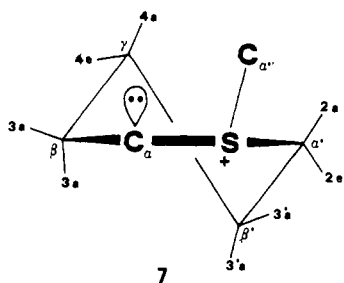
without geometry optimization, and found the following TOPs: S–$C_{\alpha'}$ = 0.2620, S–$C_{\alpha''}$ = 0.2459; these values confirm the postulated charge transfer to the vacant S–C bond MO which is syn coplanar with respect to the lone pair.

Both ylides derived from the S–$CH_3$ axial structure show

**Table I.** Total Overlap Populations (TOP) of the Vicinal S–C Bonds (STO-3G Level)

| Species | TOP (S–$C_{\alpha'}$) | TOP (S–$C_{\alpha''}$) |
|---|---|---|
| Equatorial cation | 0.2624 | 0.2615 |
| **5a** | 0.2619 | 0.2579 |
| **5e** | 0.2460 | 0.2635 |
| Axial cation | 0.2637 | 0.2696 |
| **6a** | 0.2674 | 0.2385 |
| **6e** | 0.2478 | 0.2689 |

a significant TOP decrease in one of the S–C bonds, that which happens to be anti to the lone pair orbital (S–$C_{\alpha'}$ for the equatorial ylide, and S–$C_{\alpha''}$ for the axial one). Indeed, the exchange of thianium cations in which the S–$CH_3$ group is axially oriented (namely, the *S*-methyl epimers of **1** and **2**) appears to be completely nonstereoselective,[19] in agreement with the circumstance that either proton is anti aligned with a S–$C_\alpha$ bond.

Thus the syn or anti coplanarity of the lone pair orbital with one of the vicinal S–C bond appears to stabilize the ylide and the transition state leading to it. We are aware, however, that the geometrical effect brought to light in this study may not be the only important one, just as the postulated stabilizing interaction may not be the sole important factor determining it. Additional experimental and theoretical work is in progress to provide further insight into this problem.

## Experimental Section

^{1}H NMR spectra were recorded on a Brucker WHF 270 instrument operating in the FT mode. The proton spectra of conformationally biased thianium cations have been recently described.[20] At high field the stereochemical assignment of the $\alpha$ protons is straightforward: in the $S^+$–$CH_3$ equatorial cations, the equatorial protons appear as doublets, because of the large $^2J$ (12–14 Hz) and the small $^3J$ (0–3 Hz), located some 0.5 ppm downfield to the geminal axial protons. The latter appear as triplets, $^2J$ and $^3J$ being both large.

^{13}C NMR spectra were recorded either on a Varian XL-100-15 or a Varian CFT-20 instrument, by the FT technique.

The rates of H/D exchange were determined for the various protons in a manner similar to that previously described.[1]

*trans*-1,4-Dimethylthianium (1) and *cis,cis*-1,3,5-trimethylthianium (2) were fluoroborate salts as previously described.[20]

*trans*-1-Thiadecalin was prepared via free-radical cyclization of *trans*-2-allylcyclohexanethiol obtained by Grignard reaction of cyclohexene episulfide with allylmagnesium bromide,[21] bp 110–111 °C (18 mm). Anal. ($C_9H_{16}S$) C, H. The ^{13}C spectrum was partially assigned through off-resonance experiments, residual splittings, and substituent effects: $\delta_{Me_4Si}$ (CDCl$_3$) 46.97 ($C_9$); 44.22 ($C_{10}$); 34.55, 34.35, and 32.55 ($C_4$, $C_5$, and $C_8$, interchangeable); 30.02 ($C_2$); 28.18, 26.73, and 26.31 ($C_3$, $C_6$, and $C_7$, interchangeable). The values are those expected on the basis of the shieldings of *trans*-decalin[22] and the known effects of the sulfur substituent,[23] leaving little doubt that the compound has the desired trans structure. Particularly informative is the shielding of the bridgehead carbon removed from the heteroatom ($C_{10}$) which has exactly the same $\delta$ as the bridgehead carbon of *trans*-decalin.[22] In the cis isomer $C_{10}$ would be expected to resonate in the neighborhood of $\delta \sim 37$.

**1-$\alpha$-Methyl-*trans*-1-thiadecalinium (3)** as iodide salt was obtained together with the $\beta$ isomer by iodomethylation of the corresponding sulfide. The $\alpha$ isomer (S–$CH_3$ equatorial) predominated in the crude product roughly in the proportion 10:1 and was obtained in pure form after two crystallyzations from EtOH/Et$_2$O, mp 148–149 °C dec. Anal. ($C_{10}H_{19}SI$) C, H, I. The ^{13}C NMR spectrum in D$_2$O essentially coincides (allowance being made for the different solvent) with that reported by Willer and Eliel.[24]

**cis- and trans-1-Thioniabicyclo[4.4.0]decane (4)** were obtained as a mixture of bromides by HBr cyclization of 1,9-diphenoxy-5-nonanethiol according to the procedure reported by Eastman and Kritchevsky.[25] The dry powder obtained sublimed between 243 and 250 °C (lit.[25] 266–267 °C). Metathesis with ammonium hexafluorophosphate in water gave a solid, mp 74–84 °C, obviously a mixture of isomers. Although recognizing the possibility of cis-trans isomer-

ism, the original authors[27] provided no evidence of which isomer was obtained. Apparently, in our hands the synthesis produced a mixture of isomers. This was clearly shown by the $^{13}C$ NMR spectrum which is fully consistent with a mixture of the trans and cis isomers in the ratio of about 2:1. The trans isomer has the following $^{13}C$ NMR ($\delta_{Me_4Si}{}^{26}$, $D_2O$): 55.2 ($C_6$), 39.8 ($C_2$, $C_{10}$), 31.0 ($C_5$, $C_7$), 24.8 ($C_3$, $C_9$), 23.9 ($C_4$, $C_8$). $^1H$ NMR ($D_2O$, 270 MHz): $\delta$ 1.5–2.4 (6 H, broad multiplet, $\beta$ and $\gamma$ protons), 3.2 (2 H, t, axial $\alpha$-methylene), 3.3 (1 H, q, $\alpha$-methyne), 3.6 (2 H, d, equatorial $\alpha$-methylene). The cis isomer has $^{13}C$ NMR $\delta$ 43.7 ($C_6$), 31.8 ($C_2$, $C_{10}$), 26.6 ($C_5$, $C_7$), 20.6 ($C_3$, $C_9$), 20.6 ($C_4$, $C_8$). $^1H$ NMR $\delta$ 1.5–2.4 (6 H, broad m, $\beta$ and $\gamma$ protons), 3.3 and 3.5 (5 H, broad m's, $\alpha$ protons).

Attempts to enrich the isomer mixture in the trans isomer (presumably the more stable thermodynamically) by thermal pyramidal inversion[27] were unsuccessful. Fractional crystallization of both the bromide and the hexafluorophosphate did not produce appreciable enrichment. Therefore the exchange was studied directly on the 2:1 isomer mixture. This caused no special difficulty since the $\alpha$ protons of the minor (cis) isomer turned out to exchange more than ten times faster than the more reactive proton of the trans isomer. The exchange of the latter could then be studied without interference.

## References and Notes

(1) (a) Laboratorio dei Composti del Carbonio Contenenti Eteroatomi del C.N.R.; (b) Università di Bologna.
(2) (a) G. Barbarella, A. Garbesi, and A. Fava, *J. Am. Chem. Soc.*, **97**, 5883 (1975); (b) ref 2–7 in ref 2a.
(3) (a) M. Cinquini, S. Colonna, and F. Montanari, *Chem. Commun.*, 1441 (1970); (b) P. Calzavara, M. Cinquini, R. Fornasier, and F. Montanari, *J. Am. Chem. Soc.*, **95**, 7431 (1973); (c) B. M. Trost and R. Hammen, *ibid.*, **95**, 962 (1973).
(4) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972).
(5) (a) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Am. Chem. Soc.*, **94**, 8794 (1972); (b) G. Barbarella, A. Garbesi, A. Boicelli, and A. Fava, *ibid.*, **95**, 8051 (1973); (c) R. Lett, S. Bory, B. Moreau, and A. Marquet, *Tetrahedron Lett.*, 3255 (1971).
(6) Thianium cations not possessing a strong conformational bias have been previously found to undergo exchange with little stereoselectivity if any.[7]
(7) (a) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 2297 (1971); (b) O. Hofer and E. L. Eliel, *J. Am. Chem. Soc.*, **95**, 8045 (1973).
(8) The fundamentals of perturbation theory may be found in several quantum mechanic texts; see, for example, H. Heilbronner and H. Bock, "Das Huckel MO Modell und Seine Anwendung", Verlag Chemie, Weinheim/Bergstr., Germany, 1968; R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.
(9) Recently Hunter[10] and Fraser[11] have warned against the possibility that H–D exchange rates may not be directly relatable to carbanion stability, because of internal return.[12] In aqueous solvent, however, internal return is undoubtedly negligible,[13] and Fraser's results themselves stand to prove it.[11]
(10) D. H. Hunter, Y. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis, *J. Am. Chem. Soc.*, **95**, 8327 (1973).
(11) R. R. Fraser and L. K. Ng, *J. Am. Chem. Soc.*, **98**, 4334 (1976).
(12) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, Chapters 3, 5.
(13) (a) J. Almy, D. C. Garwood, and D. J. Cram, *J. Am. Chem. Soc.*, **92**, 4321 (1970); (b) D. H. Hunter, "Isotopes in Organic Chemistry", E. Buncel and C. C. Lee, Ed., Elsevier, Amsterdam, 1975, p 135.
(14) A similar interaction ($n_C$–$\sigma^*{}_{S–H}$) has recently been found to be the major factor responsible for the preferred conformation and relative stability of oxy and thio carbanions.[15]
(15) N. D. Epiotis, R. L. Yates, F. Bernardi, and S. Wolfe, *J. Am. Chem. Soc.*, **98**, 5435 (1976).
(16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(17) All computations have been carried out with the Gaussian 70 system of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.
(18) E. L. Eliel and R. L. Willer, *J. Am. Chem. Soc.*, **96**, 3021 (1974).
(19) G. Barbarella, unpublished.
(20) G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Tetrahedron*, 1045 (1976).
(21) V. I. Dronov and V. P. Krivonogov, *Khim. Geterotsikl. Soedin.*, 622, 1186 (1972).
(22) D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973).
(23) (a) G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108, 469 (1976); (b) R. L. Willer and E. L. Eliel, *J. Am. Chem. Soc.*, **99**, 1925 (1977).
(24) E. L. Willer and E. L. Eliel, *Org. Magn. Reson.*, in press. We thank Professor Eliel for letting us know of their results before publication.
(25) R. H. Eastman and G. Kritchevsky, *J. Org. Chem.*, **24**, 1428 (1959).
(26) The internal standard was $(CH_3)_3SiCD_2CD_2Na$ ($Me_3SiPNa$); the shieldings have been converted to the $Me_4Si$ scale using the value $\delta_{Me_4Si}$ −1.8 ppm for the methyl carbon of $Me_3SiPNa$.[23a]
(27) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966); R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967); A. Garbesi, N. Corsi, and A. Fava, *Helv. Chim. Acta*, **53**, 1499 (1970).

# Electronic Structure of the π Donor Naphthalene 1,8-Disulfide[1]

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**Abstract:** Naphthalene 1,8-disulfide (**1**) was synthesized via known methodology and rigorously purified. TCNQ reacts with **1** to give a new donor–acceptor complex with a charge-transfer maximum at 925 nm and the electrical properties of an insulator. Ultraviolet photoelectron spectroscopy (UV PES) in the gas phase and solid state was used to study the molecular electronic structure of **1**; vertical ionization energies of 7.15 and 5.75 eV are observed in the gas and solid, respectively. The UV PES results are interpreted by means of perturbation molecular orbital (PMO) and CNDO/S2 calculations. It is found that the highest occupied molecular orbital structure is determined by π interactions between sulfur lone pairs and naphthalene π levels. The present work confirms an earlier suggestion that coplanar sulfur–sulfur lone pair interactions in disulfides should be ~2.0 eV.

## Introduction

The present study of the electronic structure of naphthalene 1,8-disulfide (**1**), a compound first isolated from the reaction of naphthalene and sulfur vapors in a hot iron tube,[2] was carried out in connection with our continuing interest in the chemical and physical properties of novel organochalcogen compounds, particularly with respect to relationships between

their molecular properties and novel solid-state phenomena.[3-6] Physical properties of **1** studied previously include its dipole moment,[7] the solution electron spin resonance of its cation radical[8,9] and its anion radical,[8] charge-transfer spectra,[8] and both solution and solid state Raman spectra.[10] Recently, the synthesis of the selenium and tellurium analogues of **1** has been reported;[11] the tellurium compound was reported to form a