or **4**.[10] To check a possibility that high pressure induces a crossover from a chair-preferred to a boat-preferred transition state, the pressure effect on the stereoselectivity was examined at room temperature in the range 3–12 kbar. Although the conversion was low at low pressure, the erythro/threo ratio was obtained by HPLC analysis. The results are summarized in Figure 1. Quite interestingly, a remarkable pressure effect is observed. At low pressure (3–5 kbar), the reaction of **2** with nitrobenzaldehyde produces the threo isomer predominantly while **4** gives the erythro isomer with slight preference. Therefore, the stereoselectivity at low pressure is in agreement with a chair transition state. It is reasonable to assume that $\Delta V^{\neq}$ is different for both chair and boat transition states and a boat transition state is favored at high pressure because of its tight character.

In conclusion, (i) $TiCl_4$ plays an important role for controlling the stereoselectivity in the Mukaiyama reaction. As recognized in several recent papers,[11] here also, Lewis acid serves as a stereosteering group as well as an activator of carbonyl groups. (ii) High pressure creates the stereoselectivity via a boat transition state, while low pressure produces the stereoselectivity via a chair transition state.

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[10] It is usually thought that enolates bearing a bulky group at the β-position, such as *tert*-butyl group, proceed through a boat-preferred transition state.[3a] See also: Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1983**, 3343.

[11] (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. (b) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *Ibid.* **1980**, *102*, 7595. (c) Danishefsky, S.; Kato, N.; Askin, D.; Kerwin, J. F., Jr. *Ibid.* **1982**, 104, 360. (d) Oppolzer, W.; Chapuis, C.; Dao, G. M.; Reichlin, O.; Godel, T. *Tetrahedron Lett.* **1982**, 4781. (e) Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667.

First Example of an Isolable σ-Sulfurane with an Apical Alkyl Group Effected by Transannular Bond Formation between the Amino and the Sulfonio Groups

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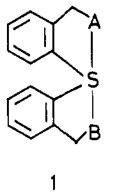
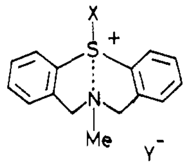
Whereas a variety of σ-sulfuranes of type **1** have been synthesized and the structures have been determined by X-ray crystallographic analysis,[1] every compound bears electron-withdrawing apical groups such as A and B due to the electron-rich and polarizable nature of the apical three-center 4-electron bond.[2]



1

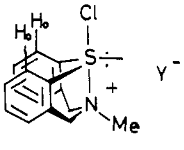


2, X = O⁻
3a, X = Me
b, X = Et
c, X = MeO
d, X = EtO
e, X = Cl

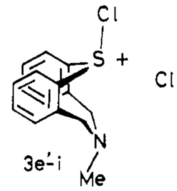
Hence there has been no example of an isolated σ-sulfurane with an electron-donating alkyl group at the apical position. Now we report the transannular bond formation between the amino and the sulfonio groups[3] of S-substituted *N*-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium salt (**3**), which afforded the first example of such σ-alkylsulfuranes as **3a** and **3b**, although σ-sulfurane with an equatorial methyl group was reported by Lau and Martin.[4]

Sulfoxide **2**[5] was converted to *S*-chloro chloride **3e-i** (Y = Cl) with excess thionyl chloride in benzene at room temperature quantitatively. Treatment of the suspension of the chloride with lithium dimethyl cuprate (1.2 equiv) in ether–THF at −78 °C furnished *S*-methyl hexafluorophosphate **3a** ($Y = PF_6$).[6] **3a** was converted to *S*-ethyl hexafluorophosphate **3b** ($Y = PF_6$) by reaction of methyl iodide with the intermediate sulfonium ylide, which was generated from **3a** with *n*-butyllithium in THF at −78 °C. **3e** was hydrolyzed with aqueous sodium carbonate to give back **2** quantitatively. **2** was alkylated with Meerwein reagent in dichloromethane to afford *S*-alkoxy hexachloroantimonates **3c** ($Y = SbCl_6$) and **3d** ($Y = SbCl_6$).

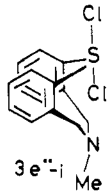
The reasonable structure of **3e** was assigned as σ-ammonio-*S*-chlorosulfurane, and not as **3e′** nor **3e″**, on the basis of the following facts: (i) ^{1}H NMR spectrum of **3e-i** (Y = Cl) shows singlets at δ 3.13 (NMe) and at 4.65 (CH_2) in CD_3CN, and no change is observed when the chloride ion is exchanged for hexachloroantimonate (**3e-ii**, $Y = SbCl_6$) or hexafluorophosphate (**3e-iii**, $Y = PF_6$), (ii) the chemical shift of NMe of **3e** is close to that of the corresponding *N*,*N*-dimethylammonium sulfide (**5**: δ 3.16) of *TB* or *BB* form, (iii) aromatic ortho hydrogens of **3e** appear at lower field (δ 8.23–8.63, m, 2 H) than other aromatic hydrogens (δ 7.22–8.02, m, 6 H), probably due to the effect of the polarizable apical bond.[7]



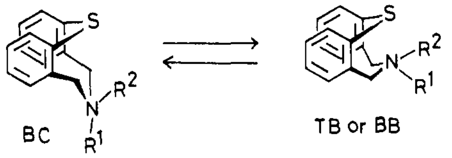
3e



3e′-i



3e″-i



BC TB or BB

4, R^1 = alkyl; R^2 = lone pair electron
5 (ammonium salt), $R^1 = R^2$ = Me

S-Methyl (**3a**) and *S*-methoxy (**3c**) compounds also show one type of singlets for the NMe and the methylene groups, i.e., **3a** δ 2.53, 4.06 (in CD_3CN) and **3c** δ 2.77, 4.25. ^{1}H NMR spectra of **3a**, **3c**, and **3e** did not show any temperature dependence between 70 and −30 °C.

Conformational analyses of *N*-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (**4**) and related compounds were investigated in detail by Ollis et al., Leonard et al., and Mehta et al.[8] In equilibrium (1), the boat-chair (*BC*) conformation has

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[1] (a) Kapovits, I.; Kalman, A. *J. Chem. Soc., Chem. Commun.* **1971**, 649. (b) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5519. (c) Adzima, L. J.; Chiang, C. C.; Paul, I. C.; Martin, J. C. *Ibid.* **1978**, *100*, 953. (d) Kapovits, I.; Rabai, J.; Ruff, F.; Kucsman, A. *Tetrahedron* **1979**, *35*, 1869; *Ibid.* **1979**, *35*, 1875. (e) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591. (f) Michalak, R. S.; Martin, J. C. *Ibid.* **1982**, *104*, 1683.

[2] Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54 and references cited therein.

[3] There has been no intended discussion on the interaction between the amino and the sulfonio groups, see: Ohara, Y.; Akiba, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1508. The result of theoretical treatment of this bonding will be published elsewhere by K. Morokuma, M. Hanamura, and K. Akiba.

[4] Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5490.

[5] Tanaka, S.; Watanabe, H.; Ogata, Y. *Yakugaku Zasshi* (*Tokyo*) **1973**, *93*, 997.

[6] The reaction mixture was quenched with an aqueous solution of potassium hexafluorophosphate and ammonium chloride (5:1 by weight). Products (**3a–d**) were recrystallized from ether–acetonitrile.

[7] Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390. Granoth, I.; Martin, J. C. *Ibid.* **1981**, *103*, 2711.

0002-7863/83/1505-6965$01.50/0

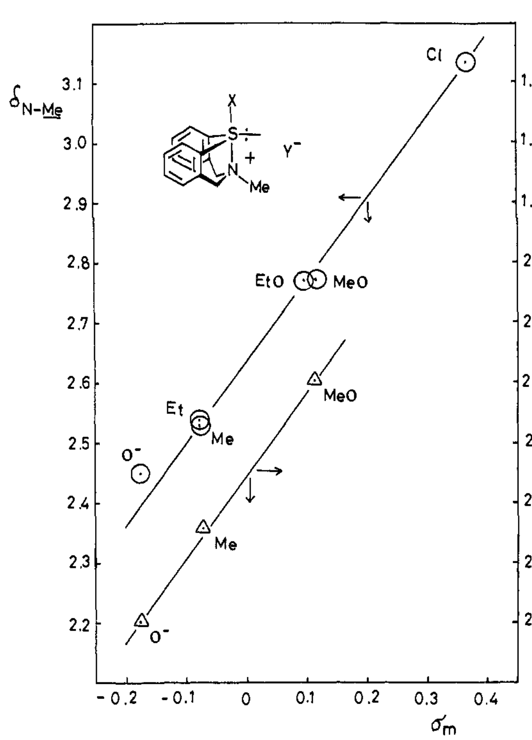

Figure 1. Hammett plot against σ_m of ^{1}H NMR chemical shifts of the NMe group and S–N bond distances of **3**.

been shown to be more stable and rigid than twist-boat (*TB*) and/or boat-boat (*BB*) conformations. By considering these results, we realized that there is a definite attractive force between the amino and the sulfonio groups of **3** which is strong enough at least to fix the conformation as *TB* or *BB*, exclusively.

A Hammett plot of chemical shifts of NMe of **3** against σ_m shows a very good straight line with positive ρ value ($\delta_{NMe} = 1.35\sigma_m + 2.63$, $r = 0.999$, $n = 5$) as shown in Figure 1. This fact further indicates that these compounds maintain the same conformation in solution and that the electron-withdrawing effect of the substituent at the sulfur is transmitted to the NMe group through the N–S bond.

X-ray crystallographic analysis established the proposed structures of **2**, **3a**, and **3c**.[9] The molecular structure of *S*-methylsulfurane **3a** is shown in Figure 2.[10] Since the geometry around the sulfur is essentially trigonal bipyramidal,[9] **3a** is concluded to be the first example of the stable σ-alkylsulfurane with an apical methyl group.

The S–N bond distances of three compounds also fit the same Hammett relationship as chemical shifts of the NMe group (Figure 1), and the bond distance becomes shorter as the electron-withdrawing effect of X increases.

Formation of iodosulfuranes as intermediates is proposed on the basis of kinetic study of the oxidation of the sulfur of methionine[11] and 5-methyl-1-thia-5-azacyclooctane.[12] The present study offers strong support for these observations.

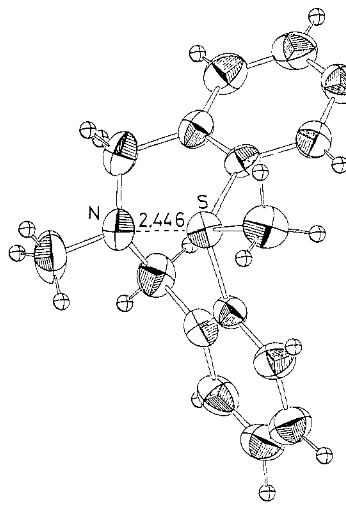

Figure 2. ORTEP drawing of *S*,*N*-dimethylammonioalkylsulfurane **3a**.[10]

Registry No. 2, 87532-42-1; **3a** (Y = PF_6), 87532-44-3; **3b** (Y = PF_6), 87532-46-5; **3c** (Y = $SbCl_6$), 87532-48-7; **3d** (Y = $SbCl_6$), 87532-50-1; **3e-i** (Y = Cl), 87532-51-2; **3e-ii** (Y = $SbCl_6$), 87532-53-4; **3e-iii** (Y = PF_6), 87532-54-5.

Supplementary Material Available: ORTEP drawings of **2**, **3a**, and **3c** and tables of crystal data and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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(8) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913. (b) Renaud, R. N.; Bovenkamp, J. W.; Franser, R. R.; Roustan, J. L. A. *Can. J. Chem.* **1977**, *55*, 3456. (c) Leonard, N. J.; Ōki, M.; Chiavarelli, S. *J. Am. Chem. Soc.* **1955**, *77*, 6234. (d) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630.

(9) X-ray data of **2**, **3a**, and **3c** concerning the following items are shown below: (i) the distance between the sulfur and the nitrogen, (ii) the distance between the sulfur and the X atom, (iii) the angle ∠X–S–N, (iv) the angle $\angle N\text{–}S\text{–}C_e$, (v) the angle $\angle C_e\text{–}S\text{–}C_e$. **2** (i) 2.609 Å, (ii) 1.501 Å, (iii) 179.4°, (iv) 75.6°, (v) 98.9°; **3a** (i) 2.446 Å, (ii) 1.804 Å, (iii) 176.9°, (iv) 79.7°, (v) 104.6°; **3c** (i) 2.206 Å, (ii) 1.658 Å, (iii) 175.3°, (iv) 81.7°, (v) 107.7°. Sum of the van der Waals radii of S and N is 3.35 Å. There are several interesting points in these structures, and full details will be published elsewhere by F. Iwasaki and K. Akiba.

(10) Johnson, C. K. ORTEP Report ORNL-3794, 1965, Oak Ridge National Laboratory, TN.

(11) Young, P. R.; Hsieh, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 7121.

(12) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1981**, *103*, 1159. Doi, J. T.; Musker, W. K.; deLeeuw, D. L.; Hirschon, A. S. *J. Org. Chem.* **1981**, *46*, 1239.

(13) All new compounds **3a–e** except **3e-i** (Y = Cl) gave correct elemental analyses. The melting point (°C) and yield (%) of **3** are listed: **3a**, 195–197, 16; **3b**, 195–198, 35; **3c**, 148–151, 49; **3d**, 176–178, 61; **3e-ii**, 170–173, 57; **3e-iii**, 145–155 dec, 34.

(14) Partial support of this work was provided by a Grant-in Aid for Scientific Research (No. 57430006) administered by the Ministry of Education, Science and Culture of Japanese Government.

Optical Activity due to Exciton Interaction between ^{1}B Transitions of Benzene Chromophores

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Dipole–dipole interactions between the ${}^1B_b$ transitions of naphthalene or anthracene chromophores[2] in chiral molecules have been shown to cause distinct CD couplets in agreement with expectations from the exciton theory. However, the exciton approach has thus far been regarded as unsuitable for analyzing CD spectra associated with the ^{1}B transition of *benzene chromophores*[3]

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(1) Present address: Suntory Institute for Biomedical Research, Wakayamadai, Shimamoto-cho, Mishima-gun, Osaka, 618 Japan.

(2) (a) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671. (b) Harada, N.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 4029. (c) Shingu, K.; Imajo, S.; Kuritani, H. *J. Am. Chem. Soc.* **1982**, *104*, 4272.

(3) See, e.g.: Snatzke, G.; Kajtar, M.; Snatzke, F. In "Fundamental Aspects and Recent Developments in Optical Dispersion and Circular Dichroism"; Ciardelli, F., Salvadori, P., Eds.; Heiden and Son: London, 1973; p 148. They pointed out also that some molecules containing only one benzene chromophore show couplet features in the ^{1}B region. We think, however, that such features are possibly caused by the small splitting of the degenerate levels due to the perturbation effect of the substituents. Only a positive CD was observed for (*S*)-3-*tert*-butyl-1,1-dimethylindan, which is the monomer of the spiro compounds illustrated in this paper. Its intensity was much weaker than the CDs arising from the exciton coupling of two benzene chromophores.[7]