

at the saturated positions and stabilizing at the unsaturated 1-positions of the cyclohexadienes. NO_2 is stabilizing at all positions while NH_2 is destabilizing at all except the 1-position of 1,3-CHD.

F. Comparison of Kinetically and Thermodynamically Favored Sites of Protonation of Cyclohexadienyl Anions. In previous papers,^{4,65} we have compared kinetically preferred protonation sites (as reflected in minima, V_{min} , in molecular electrostatic potential⁶⁶ [MEP] maps) with thermodynamically favored sites (as indicated by relative product energies or protonation energies, ΔH_{prot}). Our present calculations show that in contrast to the protonation of benzene radical anions,^{3,4} the MEP preferred protonation sites of SCHD^- do not correspond to the thermodynamically favored sites. The MEP minima in the vicinity of SCHD^- are deepest near C(3) whereas the lowest energy cyclohexadiene isomer corresponds to protonation at C(1) or C(5).

Despite this situation, the correlation coefficient between V_{min} values for the SCHD^- 's and ΔH_{prot} for the reaction $\text{SCHD}^- + \text{H}^+ \rightarrow \text{SCHD}$ is 0.868, indicating a linear relationship (at the 95% confidence level).⁶⁷ This reflects an overall trend in the electrostatic contribution to the total protonation energy for the SCHD^- system. The regression line is $\Delta H_{\text{prot}} = 1.264V_{\text{min}} - 1206.3$

(66) Reviews: (a) Scrocco, E.; Tomasi, J. *Top. Curr. Chem.* **1973**, *42*, 95; (b) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 115.

(67) A full tabulation of the V_{min} and ΔH_{prot} values is presented in: Hinde, A. L. Ph.D. Thesis, Australian National University, 1979.

(kJ mol^{-1}) and is close to that found⁴ for protonation of SBz^- . The correlation coefficient is not as good as that for SBz^- , and this may reflect the greater variability in electronic environment in SCHD^- compared with SBz^- .

Conclusions

(1) In agreement with experimental results, 1,4-CHD is found to prefer a planar D_{2h} structure although distortions to nonplanar boat-type structures are not energetically costly. 1,3-CHD has a nonplanar C_2 structure.

(2) The energies of 1,4-CHD and 1,3-CHD are found to be quite similar.

(3) The 1-substituted 1,3-CHD isomer is uniformly preferred over all the other cyclohexadiene isomers for all the substituents examined. This is in agreement with experimental results in solution (under "equilibrium" conditions) for π -donor substituents, but for π -acceptor substituents the experimental situation is less clear-cut because of difficulties in achieving true equilibrium.

(4) A linear correlation exists between the MEP minimum values of SCHD^- and the corresponding protonation energies. The correlation is not as good as was obtained for SBz^- 's, a fact which can be attributed to the greater variability of the electronic environments in SCHD^- compared with SBz^- . The regression lines obtained for SBz^- and SCHD^- are similar and represent for these systems an overall trend, upon which additional electronic effects may be superimposed (as in SCHD^-).

Molecular Structure of Selected *S*-Methylthiophenium Tetrafluoroborates and Dibenzothiophene 5-Oxide

J. A. Hashmall, V. Horak,* L. E. Khoo, C. O. Quicksall, and M. K. Sun

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057. Received February 4, 1980

Abstract: Molecular structures of 5-methyldibenzothiophenium tetrafluoroborate (I), 1-methylnaphtho[2,3-*b*]thiophenium tetrafluoroborate (II), and dibenzothiophene 5-oxide (III) were determined by X-ray diffraction. The effect of increase of coordination at the sulfur atom (with respect to sulfur atom in thiophene-like molecules) was evaluated by examining the planarity of the structure, stereochemistry at the sulfur atom, CS bond distances, and the CC bonds alternation in the carbon atom framework. The experimental results parallel the results of MNDO semiempirical calculations of model species, i.e., thiophene (IV), the *S*-methylthiophenium ion (V), and thiophene *S*-oxide (VI). The changes of aromaticity of the thiophene-like molecules resulting from the substitution at the sulfur atom are discussed in terms of the perturbation theory by using HMO models.

The sulfur atom in thiophene-like molecules is characterized by exceedingly low reactivity compared to that of the sulfur atom in organic sulfides. For example, perbenzoic acid oxidized dibenzothiophene to the sulfoxide 100-fold more slowly than it oxidizes diphenyl sulfide.¹ The lack of reactivity of thiophenoid sulfur toward methyl iodide is even used to differentiate thiophenes from sulfides in coal analysis.² *S*-Alkylthiophenium salts can be prepared only by using the most vigorous alkylating agents, e.g., trialkyloxonium tetrafluoroborates³ or methyl iodide–silver tetrafluoroborate (or silver perchlorate).⁴

The products of reaction at an "aromatic" sulfur are less stable and much more reactive than those derived from sulfides. Thus, thiophene *S*-oxide undergoes spontaneous Diels–Alder dimeri-

zation.⁵ The reductive electrochemical deoxygenation of dibenzothiophene 5-oxide is about 0.6 V more positive than that of diphenyl sulfoxide under the same conditions.⁶ *S*-Alkylthiophenium ions exist only with nonnucleophilic counterions such as tetrafluoroborate or perchlorate anion⁴ in contrast to such ions as triphenylsulfonium ions which are stable even in the presence of bromides as contraion.⁷ Nonaromatic or antiaromatic character of thiophene *S*-oxides and *S*-alkylthiophenium ions has been postulated by Mock⁸ and Acheson,⁴ respectively, on the basis of interpretation of the NMR spectra which indicated the third ligand (O, alkyl) to be located off the molecular plane. Both the decrease of the aromatic stabilization and antiaromatic destabilization would explain the difference in properties of the thiophene-like molecules and their *S* derivatives.

(1) Horak, V.; Ponc, R. "Third International Congress of Heterocyclic Chemistry"; Sendai, 1971; p 585.

(2) Postovskii, J. J.; Harlamovich, A. B. *Fuel* **1936**, *15*, 229.

(3) Brumlick, G. C.; Kosak, A. I.; Pitcher, R. *J. Am. Chem. Soc.* **1964**, *86*, 5360.

(4) Acheson, R. M.; Harrison, D. R. *J. Chem. Soc. C* **1970**, 1794.

(5) Prochazka, M. *Collect. Czech. Chem. Commun.* **1965**, *30*, 1158.

(6) Lim, A. C. Thesis Georgetown, University, Washington, D.C., 1972.

(7) McKinney, P. S.; Rosenthal, S. *J. Electroanal. Chem.* **1968**, *16*, 261.

(8) Mock, W. L. *J. Am. Chem. Soc.* **1970**, *92*, 7610.

To examine this hypothesis, detailed structural studies of 5-methyldibenzothiophenium tetrafluoroborate (I), 1-methylnaphtho[2,3-*b*]thiophenium tetrafluoroborate (II), and dibenzothiophene 5-oxide (III) using X-ray diffraction have been carried out and are reported below.

To further aid in understanding the electronic structure differences between thiophenes and their *S*-alkonium and *S*-oxide derivatives, semiempirical molecular orbital calculations using the MNDO⁹ method were performed on thiophene, thiophene *S*-oxide, and the *S*-methylthiophenium ion.

Calculations

MNDO calculations on thiophene, thiophene *S*-oxide, and the *S*-methylthiophenium ion were performed by using a modified version of the available program¹⁰ including parameters for sulfur.¹¹ The geometries were optimized with the restrictions that thiophene be of C_{2v} symmetry, that thiophene *S*-oxide be of C_s symmetry, and that *S*-methylthiophenium be of C_s symmetry except that the methyl group rotation was not symmetry restrained.

The calculated heats of formation were as follows: thiophene, -30.0 kcal/mol (experimental, -27.6 kcal/mol); oxide, 75.2 kcal/mol; *S*-methylthiophenium, 226.5 kcal/mol.

The optimized geometries are in excellent agreement with experiment. For thiophene the critical calculated (experimental) parameters are as follows: $R_{S-C_2} = 1.692 \text{ \AA}$ (1.718 \AA); $R_{C_2-C_3} = 1.368 \text{ \AA}$ (1.352 \AA); $R_{C_3-C_4} = 1.455 \text{ \AA}$ (1.455 \AA); $\theta_{CSC} = 93.2^\circ$ (91.3°); $\theta_{SCC} = 111.8^\circ$ (112.6°); $\theta_{CCC} = 111.6^\circ$ (111.8°); $R_{C_3H} = 1.079 \text{ \AA}$ (1.085 \AA); $R_{C_4H} = 1.084 \text{ \AA}$ (1.073 \AA); $\theta_{SCH} = 118.5^\circ$ (119.2°); $\theta_{C_3C_4H} = 122.7^\circ$ (123.5°). The optimized geometry parameters for thiophene *S*-oxide and *S*-methylthiophenium are presented in structures IV, V, and VI.

The vibrational mode leading to inversion to the oxygen (or methyl group) through the plane of the ring was followed by altering the out of plane angle of the group on sulfur and calculating the energy of the structure with all other geometry parameters optimized. In both *S*-methylthiophenium and thiophene *S*-oxide the transition state for inversion was planar. The calculated enthalpies of activation for the inversion were 19.5 kcal/mol for *S*-methylthiophenium and greater than 30 kcal/mol for thiophenium *S*-oxide. (The barrier for thiophene *S*-oxide could not be calculated exactly because the MNDO SCF procedure did not converge for a planar configuration.)

Experimental

Melting points were determined with a Kofler hot state and were uncorrected. Microanalysis was performed by Huffman Laboratories, Wheatridge, Col. Dibenzothiophene (mp 97–100 °C) was obtained from Aldrich and was recrystallized from ethanol. Naphtho[2,3-*b*]thiophene was prepared following the four step synthesis after Carruthers et al.¹² The product recrystallized from ethanol–benzene mixture (1:1) showed mp 191–193 °C. Densities were measured by floatation in heptane–carbon tetrachloride mixtures.

5-Methyldibenzothiophenium Tetrafluoroborate (I). Following the procedure of Acheson⁴ 5 g of dibenzothiophene, 6 g of silver tetrafluoroborate, and 15 mL of methyl iodide in 70 mL of 1,2-dichloroethane yielded 5 g (89%) of I. The crude product was recrystallized from an acetonitrile–ether mixture; mp 149–150 °C.

1-Methylnaphtho[2,3-*b*]thiophenium Tetrafluoroborate (II). Analogously to I, 1.5 g of naphtho[2,3-*b*]thiophene, 3 g of silver tetrafluoroborate, and 7 mL of methyl iodide in 45 mL of 1,2-dichloroethane yielded 1.5 g (89%) of II. The crude product was recrystallized from an acetonitrile–ether mixture; mp 160–161 °C. Anal. Calcd for $C_{13}H_{11}BF_4S$: C, 54.5; H, 3.85; S, 11.19; F, 26.57. Found: C, 54.33; H, 4.04; S, 11.01; F, 26.13.

Dibenzothiophene 5-Oxide (III). Following the procedure of Fries and Vogt,¹² 3 g of chlorine gas was introduced into a solution of 7.5 g of dibenzothiophene in 75 mL of carbon tetrachloride. Addition of 80 g of ice yielded 7.58 g (93%) of III. The crude product was purified by repeated crystallization from benzene until no starting material or dibenzothiophene 5-dioxide could be detected by TLC; mp 188–190 °C.

Preparation of Crystals. Crystals of I and II which were suitable for X-ray investigation were grown from a minimum amount of redistilled acetonitrile to which ether was added just to the turbidity point. This mixture was then kept overnight in an ether atmosphere. X-ray quality crystals were separated by filtration and dried. Crystals of III suitable for X-ray investigation were grown from hot benzene solution by slow cooling in a Dewar flask.

Crystal Data for I: $C_{13}H_{11}BF_4S$, $M_r = 285.85$, space group $P2_1/c$ (C_{2h}^2), $a = 7.864$ (3) \AA, $b = 11.922$ (5) \AA, $c = 13.771$ (4) \AA, $\beta = 90.31$ (5)°, $V = 1291.08 \text{ \AA}^3$, $Z = 4$, $\rho(\text{calcd}) = 1.47 \text{ g/cm}^3$, $\rho(\text{obsd}) = 1.47 \text{ g/cm}^3$, $\mu = 2.82 \text{ cm}^{-1}$, $\lambda = 0.70930 \text{ \AA}$.

Crystal Data for II: $C_{13}H_{11}BF_4S$, $M_r = 285.85$, space group $P2_1/c$ (C_{2h}^2), $a = 10.134$ (3) \AA, $b = 8.431$ (3) \AA, $c = 16.029$ (3) \AA, $\beta = 106.91$ (5)°, $V = 1301.40 \text{ \AA}^3$, $Z = 4$, $\rho(\text{calcd}) = 1.46 \text{ g/cm}^3$, $\rho(\text{obsd}) = 1.46 \text{ g/cm}^3$, $\mu = 2.78 \text{ cm}^{-1}$, $\lambda = 0.70930 \text{ \AA}$.

Crystal Data for III: $C_{12}H_6SO$, $M_r = 200.26$, space group PT (C_i^1), $a = 12.252$ (4) \AA, $b = 8.538$ (2) \AA, $c = 9.530$ (3) \AA, $\alpha = 96.642$ (2)°, $\beta = 98.02$ (2)°, $\gamma = 105.12$ (2)°, $V = 940.65 \text{ \AA}^3$, $Z = 4$, $\rho(\text{calcd}) = 1.41$, $\rho(\text{obsd}) = 1.43$, $\mu = 26.4 \text{ cm}^{-1}$, $\lambda = 1.54056 \text{ \AA}$.

Collection and Reduction of X-ray Data. Diffraction data were collected at 22 °C on a Picker-FACS-1 automated diffractometer. Cell dimensions were determined by a least-squares refinement to fit the $\pm 2\theta$ values for 12 high angle reflections centered on the diffractometer. Integrated intensities were measured by the θ - 2θ scan techniques at a takeoff angle of 2.0°. The peaks were scanned from 1.5° on the low angle side of the $K\alpha_1$ peak to 1.5° on the high angle side of the $K\alpha_2$ peak at a rate of 1°/min. Stationary-crystal, stationary-counter background measurements of 10-s duration were taken at each end of the scan. The diffracted beams were counted by using a scintillation counter and were automatically attenuated with Ni foil whenever the count rate exceeded 8000 c/s. Zr-filtered Mo $K\alpha$ radiation was used for crystals I and II to collect hkl , $h\bar{k}l$, hkl , and $h\bar{k}l$ data forms to a maximum 2θ of 60°. Ni-filtered Cu $K\alpha$ radiation was used for crystal III to collect a hemisphere of data to a maximum 2θ of 128°. The intensities of three reflections were monitored as standards every 50 reflections, and slight isotropic decomposition was observed for crystals I and II. The intensities were corrected for background, decomposition, Lorentz, and polarization effects and then equivalent forms were averaged. No absorption corrections were applied. Of the 2360 (crystal I), 2469 (crystal II), and 2666 (crystal III) unique reflections measured for each crystal, respectively, only the 1681 (I), 1300 (II), and 1539 (III) reflections with ($I > 2\sigma(I)$) were used in the solution and refinement of the structures.

Solution and Refinement of the Structures. Structures I and II were solved by direct methods using the LSAM¹³ series of programs. Normalized structure factors were calculated, and the multiple-solution symbolic addition technique was applied to the 315 reflections with $|E| \geq 1.5$ (I) and the 332 reflections with $|E| \geq 1.4$ (II). The E maps computed from the sets of signs with the highest figure of merit revealed all nonhydrogen atoms. For structure III a Patterson function was computed which revealed the positions of the two crystallographically independent S atoms in space group PT . A difference Fourier synthesis, phased on these atoms, revealed all remaining nonhydrogen atoms. Full-matrix, anisotropic least-squares refinement converged smoothly for each structure. Hydrogen atoms were located from difference Fourier maps, but their positions were not refined. Instead, the hydrogen positions were fixed in their idealized positions with a C–H bond distance of 1.00 \AA. Final consistency indices, $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2}$, were 0.077 and 0.088 for I, 0.078 and 0.084 for II, and 0.061 and 0.062 for III. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where the weights, w , were taken as $4F_o^2/\sum^2(F_o^2)$. Atomic scattering factors were taken from standard tables.¹⁴ Final difference Fourier maps showed no feature above 0.3 e/\AA³. The lack of residual electron density and successful structure refinement support the choice of the centric space group PT for structure III.

Tables I, II, and III present the final positional and thermal parameters with their estimated standard deviations. Tables of final values for F_o and F_c are available as supplementary material.

Discussion

The molecular configurations of 5-methyldibenzothiophenium tetrafluoroborate (I) and 1-methylnaphtho[2,3-*b*]thiophenium

(13) Programs used for the structure solutions and refinements included local modifications of the ALFF Fourier program by Hubbard, Quicksall and Jacobson, the Busing–Levy ORFLS least-squares and ORFFE error function programs, Johnson's ORTEP plotting program, and the LSAM series by Main, Woolfson, and Germain, see: Stalick, J. K.; Quicksall, C. O. *Inorg. Chem.* **1976**, *15*, 1577.

(14) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(9) Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(10) Theil, W. *QCPE* **1978**, *11*, 353.

(11) Dewar, M. J. S.; McKee, M.; Reepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 3607.

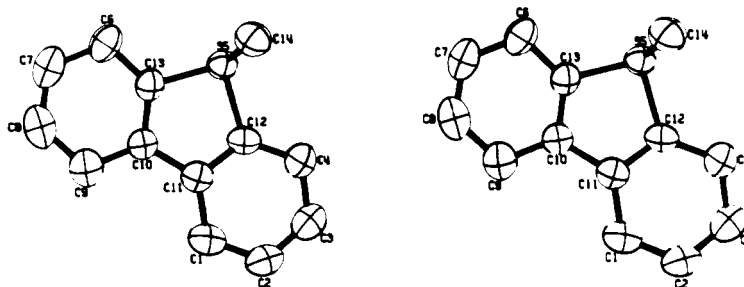
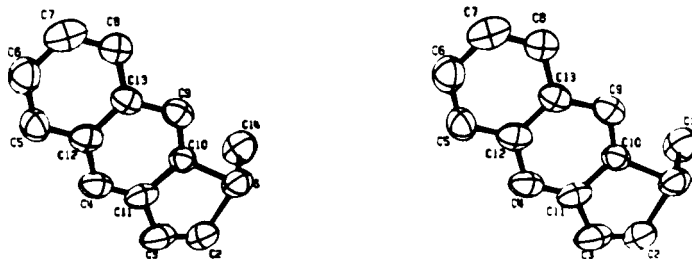
(12) Fries, K.; Vogt, W. *Justus Liebigs Ann. Chem.* **1911**, *381*, 341.

Table I. Final Positional and Thermal Parameters for 5-Methyldibenzothiophenium Tetrafluoroborate (I)

atom	fractional coordinates			anisotropic temp factors ($\times 10^4$) ^a					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(5)	0.2178 (2)	-0.0125 (1)	0.3146 (1)	130 (3)	73 (1)	68 (1)	8 (2)	-7 (1)	-0 (1)
C(1)	-0.2368 (8)	0.0498 (5)	0.4215 (4)	164 (12)	111 (6)	42 (4)	19 (7)	4 (5)	8 (4)
C(2)	-0.3235 (7)	-0.0503 (6)	0.4074 (4)	139 (11)	121 (7)	54 (4)	-9 (7)	-2 (6)	8 (4)
C(3)	-0.2501 (8)	-0.1406 (5)	0.3671 (5)	190 (14)	105 (6)	62 (4)	-33 (8)	-10 (6)	5 (4)
C(4)	-0.0839 (8)	-0.1379 (5)	0.3340 (4)	195 (13)	78 (5)	63 (4)	-13 (7)	-5 (6)	3 (4)
C(6)	0.3080 (10)	0.2035 (5)	0.3526 (5)	211 (14)	92 (6)	67 (4)	-25 (7)	-30 (6)	11 (4)
C(7)	0.1545 (10)	0.3113 (5)	0.3929 (5)	260 (17)	87 (6)	87 (6)	-38 (8)	-24 (8)	2 (5)
C(8)	0.0196 (8)	0.3356 (5)	0.4314 (5)	315 (19)	79 (6)	67 (5)	15 (9)	-15 (8)	-4 (4)
C(9)	0.0484 (7)	0.2574 (5)	0.4349 (4)	231 (14)	84 (5)	61 (4)	10 (8)	-21 (6)	3 (4)
C(10)	0.0484 (7)	0.1514 (5)	0.3938 (4)	153 (11)	71 (5)	40 (3)	3 (6)	-9 (5)	5 (3)
C(11)	-0.0675 (7)	0.0569 (5)	0.3895 (4)	147 (11)	76 (5)	43 (4)	14 (6)	-18 (5)	8 (3)
C(12)	0.0012 (7)	-0.0368 (5)	0.3467 (4)	140 (10)	79 (5)	46 (4)	13 (6)	2 (5)	10 (3)
C(13)	0.2039 (7)	0.1288 (4)	0.3559 (4)	161 (11)	69 (5)	55 (4)	1 (1)	-18 (6)	1 (3)
C(14)	0.2073 (8)	-0.0027 (5)	0.1844 (4)	213 (13)	118 (6)	65 (4)	-16 (8)	20 (6)	-15 (4)
B	-0.3069 (11)	0.1631 (7)	0.1440 (8)	200 (2)	91 (8)	138 (9)	10 (10)	25 (10)	36 (7)
F(1)	-0.4270 (5)	0.1159 (3)	0.1302 (4)	244 (9)	130 (4)	211 (5)	39 (5)	77 (6)	35 (4)
F(2)	-0.4270 (5)	0.0915 (4)	0.1756 (4)	297 (10)	155 (4)	162 (4)	-97 (6)	78 (5)	-18 (4)
F(3)	-0.2809 (7)	0.2405 (4)	0.2262 (4)	473 (14)	150 (5)	166 (5)	-68 (7)	46 (7)	-7 (4)
F(4)	-0.3511 (6)	0.2359 (4)	0.0752 (4)	385 (13)	223 (6)	144 (5)	78 (8)	2 (6)	62 (5)

atom ^b	fractional coordinates			atom ^b	fractional coordinates		
	x	y	z		x	y	z
H(1)	-0.2933	0.1150	0.4400	H(8)	0.1339	0.4135	0.4583
H(2)	-0.4386	-0.0545	0.4268	H(9)	0.0969	0.2766	0.4562
H(3)	-0.3134	-0.2069	-0.3610	H(1)	0.2022	-0.0715	0.0169
H(4)	-0.0290	-0.2038	0.3157	H(II)	0.0970	0.0527	0.1851
H(6)	0.4539	0.1829	0.3237	H(III)	0.3321	0.0459	0.0157
H(7)	0.3761	0.3761	0.3940				

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b For hydrogen atoms, the isotropic temperature factor was given at 5.0 Å². ^c Numbers in parentheses in this and succeeding table are estimated standard deviations in the least significant figures.

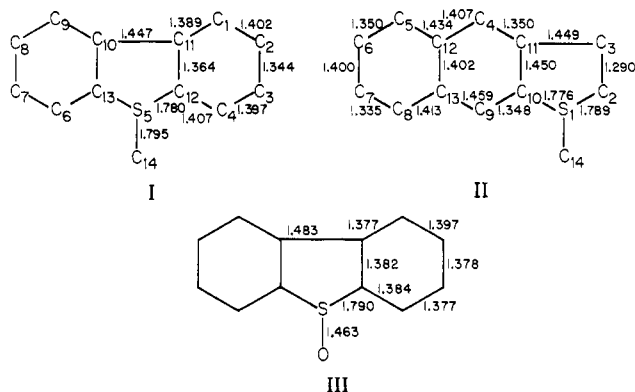
**Figure 1.** Stereoscopic representation of 5-methyldibenzothiophenium tetrafluoroborate (I).**Figure 2.** Stereoscopic representation of 1-methylnaphtho[2,3-*b*]thiophenium tetrafluoroborate (II).

tetrafluoroborate (II) are shown in Figures 1 and 2, respectively. The molecular configuration of dibenzothiophene 5-oxide (III) is practically indistinguishable from that for compound I. Selected bond distances and bond angles for all three compounds under investigation are listed in Tables IV, V, VI, and VIII with estimated standard deviations in parentheses. (The numbering system for compound III is identical to that used for compound I.) The

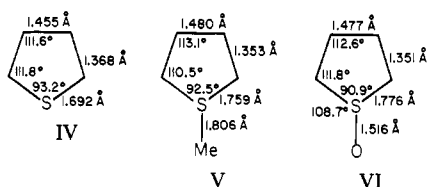
molecular diagrams below show bond distances for the three compounds in which chemically equivalent bonds are averaged for compound I and double averaged for compound III.

For characterization of the effect of attachment of a third ligand to the sulfur atom in thiophene-like molecules the planarity, sulfur atom bonding characteristics and geometry of the carbon atom framework of compounds I-III are examined. These results are compared with similar structural data previously reported for dibenzothiophene and related structures in the literature. The experimental results are also compared with those obtained for model structures, i.e., thiophene (IV), *S*-methylthiophenium ion (V), and thiophene *S*-oxide (VI), by using semiempirical MNDO

(15) Schaffrin, R. M.; Trotter, J. *J. Chem. Soc. A* 1970, 1561.(16) Burns, D. M.; Iball, J. *Proc. R. Soc. London, Ser. A* 1955, 227, 200.(17) Hargreaves, A.; Rizvi, S. H. *Acta Crystallogr.* 1962, 15, 3651.(18) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Restrup-Anderson, J. *J. Mol. Spectrosc.* 1961, 7, 58.



calculations.⁹⁻¹¹ The MNDO optimized geometries for IV, V, and VI are shown below.

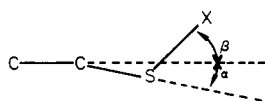


A small dihedral angle of 1.1° is found between the two planar benzene rings of compound I. The thiophene ring in this compound exhibits small but significant deviation from planarity with the sulfur atom protruding from the least-squares plane of the four carbon atoms for a distance of 0.05 Å. Similarly, the benzene rings do not lie in the same plane in compound III. In structure II a 2.1° angle is found between the plane of the heterocyclic ring (which is planar within experimental errors) and the plane of the naphthalene fragment.

For compounds I-III the local geometry around the sulfur atom and especially the situation of the third ligand is characteristic. Whereas the deviation of the sulfur atom with respect to the least-squares plane of the four carbon atoms in the heterocyclic ring is small or not detectable, the third ligands are located unequivocally off this plane. Thus the angle between the third ligand-sulfur bond—and the above-defined plane (β in the diagram below) is 68.9° for compound I, 68.2° for II, and 59.15° for III (averaged values). In compound I both the sulfur atom and the methyl group are located above the same face of the nonplanar heterocyclic ring. Molecular geometries, provided by MNDO calculations for structures V and VI, are similar to those obtained experimentally for compounds I-III.

The angles α and β for the MNDO optimized geometries are -5.0 and 64.2° for X = Me (compound V) and -4.3 and 64.3° for X = O (compound VI). Although no minimum exists with positive α for both these compounds (positive α corresponds to both the S and third ligand lying on the same side of the carbon plane), the geometries with positive α corresponding to the experimental values have, for both compounds V and VI, a MNDO energy less than 1 kcal/mole above the energy minimum. Further, no barriers to conversion are calculated.

This minor discrepancy between MNDO calculations could be due to the crystal forces, the differences between the parent compound and the dibenzo derivatives, or an inherent inaccuracy in the MNDO method which is generally thought to be reliable to about ± 5 kcal.



The C-S bond distances in structures I-III are significantly longer than the C-S bonds in dibenzothiophene (1.740 Å).¹⁵ Similar results are obtained for MNDO-optimized geometries. Methylation of thiophene results in a calculated 0.06°-Å elongation

of C-S bonds while oxidation results in a 0.07°-Å elongation of the corresponding bond length.

For examination of the carbon atom framework in structures I-III the A indices by Julg and Francois¹⁹ proved to be useful. This index quantifies the alternation of bonds in conjugated systems. Large values of A indicate relatively small bond alternation and correspondingly large delocalization, while small values of A indicate considerable bond alteration and correspondingly small delocalization. The A indices for structures I-III, dibenzothiophene, and related structures (fluorene, biphenyl) calculated by using experimental crystallographic C-C bond distances are presented in Table VIII. Also included is the A index of thiophene (IV) obtained by using experimental C-C bond distances based on microwave data.¹⁸ Finally, also are included A indices for structures IV-VI obtained by using C-C bond distances calculated by MNDO method. For polynuclear structures A indices were calculated both for the entire carbon atom framework and for the heterocyclic fragment alone. A indices for benzene ring fragments alone were also calculated for structures I, III, and dibenzothiophene. Averaged C-C bond distances for chemically equivalent bonds were used for all calculations. Particularly informative is the examination of A indices for structurally closely related compounds such as I, III, dibenzothiophene, fluorene, and biphenyl. The significantly lower value of the A indices of compounds I and III compared with those of dibenzothiophene for both the entire carbon atom framework and especially for the heterocyclic ring indicates a decrease in delocalization of π electrons as a result of increased covalency at the sulfur atom. The A indices for structures I and III are more similar to those of fluorene or biphenyl than those of the parent dibenzothiophene. When A indices calculated from MNDO optimized C-C bond distances are compared among the structures IV, V, and VI, a similar lower value is found for the three-coordinated sulfur compounds compared to thiophene itself. A indices calculated for compound II have particularly low values. The value of 0.35 calculated for the three C-C bonds of the heterocyclic moiety results from the annelation in this polycyclic structure as well as from inefficient conjugation of the three-coordinated sulfur atoms. The bond between the two shared carbon atoms of the heterocyclic ring and the naphthalene fragment maintains the character of "long" aromatic bonds in the naphthalene itself. However, the same bond in thiophene itself is a "short" aromatic bond. This substantial elongation of the "short" bond leads to a diametric shortening of the other "short" bond of the thiophene ring to a bond distance which cannot be characterized as an aromatic C-C bond any more. Thus, the bond distance 1.29 Å represents that of an especially short C-C double bond rather than that of an aromatic C-C bond. (Cf. 1.33 Å for an average C-C double bond and 1.37 Å for the corresponding C-C bond in thiophene.) This situation is certainly different from that in compounds I and III, in which the heterocyclic rings share their "short" bonds with benzene rings on which the substitution at sulfur shows practically no effect (A indices for benzene fragments are as follows: I, $A = 0.94$; III, $A = 0.99$; dibenzothiophene, $A = 0.98$). The major differences among the A indices of structures I, III, and dibenzothiophene reflect primarily the differences among the lengths of the C-C bonds connecting the two benzene rings.

The molecular geometries determined for three stable representatives of thiophene *S*-oxide and *S*-alkylthiophenium-like structures indicate a deterioration of the π -electron system with respect to the parent thiophene-like heterocycles. The increase in bond alternation including the elongation of the C-S bonds evidences a decrease in the π -electron delocalization resulting from a substitution at the S atom in the thiophene-like molecules. The orientation of the formal lone electron pair—which can be estimated from the orientation of the third substituent (O, Me) in I, II, and III—results in decreased overlap of this electron pair with the p_z orbitals of the adjacent carbon atoms compared to the overlap of the sulfur p_z electron pair in thiophene with the

Table II. Final Positional and Thermal Parameters for 1-Methylnaphtho[2,3-*b*]thiophenium Tetrafluoroborate (II)

atom	fraction coordinates			anisotropic temp factors ($\times 10^4$)					
	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.3275 (2)	0.6723 (2)	0.0384 (1)	171 (3)	187 (3)	47 (1)	18 (3)	33 (1)	-4 (2)
C(2)	0.2291 (10)	0.8006 (10)	-0.0456 (5)	200 (14)	259 (19)	54 (5)	8 (15)	46 (7)	9 (7)
C(3)	0.1015 (10)	0.8134 (10)	-0.0474 (5)	255 (17)	216 (17)	47 (4)	45 (15)	45 (7)	17 (7)
C(4)	-0.0590 (8)	0.7129 (9)	0.0365 (5)	176 (13)	179 (16)	40 (4)	22 (11)	18 (6)	-9 (6)
C(5)	-0.2010 (9)	0.6068 (9)	0.1265 (5)	146 (13)	217 (16)	55 (5)	-2 (11)	15 (6)	-4 (7)
C(6)	-0.2097 (8)	0.5220 (10)	0.1958 (6)	134 (13)	234 (17)	72 (5)	-3 (12)	26 (7)	-4 (8)
C(7)	-0.0933 (11)	0.4463 (9)	0.2508 (5)	254 (18)	191 (16)	59 (5)	-48 (15)	56 (8)	-2 (7)
C(8)	0.0272 (8)	0.4550 (9)	0.2347 (5)	138 (13)	207 (16)	51 (5)	7 (11)	24 (6)	17 (7)
C(9)	0.1762 (8)	0.5555 (8)	0.1450 (5)	158 (12)	136 (13)	46 (4)	-1 (10)	13 (6)	-1 (6)
C(10)	0.1811 (7)	0.6422 (8)	0.0762 (4)	123 (10)	151 (13)	37 (3)	20 (10)	11 (5)	3 (6)
C(11)	0.0634 (9)	0.7253 (9)	0.0200 (5)	202 (14)	163 (15)	36 (4)	-6 (12)	33 (6)	-9 (6)
C(12)	-0.0702 (9)	0.6231 (8)	0.1081 (5)	161 (13)	152 (14)	40 (4)	-1 (11)	17 (6)	-13 (6)
C(13)	0.0425 (8)	0.5418 (8)	0.1631 (4)	131 (11)	137 (13)	39 (4)	3 (10)	6 (6)	-6 (6)
C(14)	0.4335 (8)	0.8005 (9)	0.1200 (5)	185 (12)	272 (18)	73 (5)	-53 (13)	40 (6)	-18 (8)
B	0.4509 (13)	0.2293 (13)	0.1278 (7)	199 (20)	207 (23)	55 (6)	5 (18)	46 (9)	28 (9)
F(1)	0.3369 (5)	0.1772 (6)	0.1426 (4)	209 (8)	360 (12)	131 (4)	5 (8)	81 (5)	57 (6)
F(2)	0.4608 (6)	0.3898 (7)	0.1474 (4)	250 (10)	226 (10)	173 (5)	8 (8)	44 (6)	7 (6)
F(3)	0.5668 (5)	0.1552 (6)	0.1776 (3)	191 (7)	312 (10)	73 (3)	53 (8)	9 (4)	31 (5)
F(14)	0.4429 (6)	0.2139 (9)	0.0434 (3)	290 (10)	737 (22)	56 (3)	159 (12)	43 (4)	36 (6)

atom ^a	fractional coordinates			atom ^a	fractional coordinates		
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(2)	0.7082	0.1535	0.0716	H(8)	0.1147	0.4037	0.2684
H(3)	0.9670	0.1232	0.0919	H(9)	0.2183	0.4806	0.1771
H(4)	0.8392	0.7558	-0.0017	H(I)	0.4478	0.7402	0.1711
H(5)	0.7569	0.6632	0.0930	H(II)	0.5208	0.8302	0.1061
H(6)	0.7046	0.5237	0.2029	H(III)	0.3991	0.9044	0.1317
H(III)	0.8789	0.3865	0.2838				

^a For hydrogen atoms, the isotropic temperature factor was given at 5.0 Å².

Table III. Final Positions and Thermal Parameters for Dibenzothiophene 5-Oxide (III)

atom	fractional coordinates			anisotropic temp factors ($\times 10^4$)					
	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S ₁	0.0467 (2)	0.3784 (2)	0.2108 (2)	104 (2)	138 (3)	132 (3)	50 (2)	30 (2)	45 (3)
O ₁	0.0947 (4)	0.3382 (6)	0.3466 (5)	147 (7)	275 (12)	198 (9)	104 (8)	28 (7)	95 (9)
C ₁ (13)	0.0303 (5)	0.5802 (7)	0.2366 (6)	70 (7)	131 (12)	113 (10)	35 (8)	16 (7)	23 (9)
C ₁ (6)	-0.0426 (6)	0.6278 (9)	0.3183 (7)	94 (8)	201 (15)	141 (11)	37 (10)	17 (8)	36 (11)
C ₁ (7)	-0.0448 (6)	0.7886 (9)	0.3326 (7)	103 (9)	211 (17)	153 (12)	57 (10)	25 (8)	11 (12)
C ₁ (8)	0.0192 (6)	0.8986 (8)	0.2580 (8)	101 (9)	160 (9)	222 (14)	52 (10)	16 (9)	36 (12)
C ₁ (9)	0.0923 (6)	0.8483 (8)	0.1742 (7)	86 (8)	153 (14)	150 (11)	50 (9)	16 (8)	31 (10)
C ₁ (10)	0.0983 (5)	0.6895 (7)	0.1645 (6)	62 (6)	147 (13)	104 (9)	25 (8)	17 (6)	15 (9)
C ₁ (11)	0.1731 (5)	0.6116 (7)	0.0902 (6)	77 (7)	139 (12)	841 (8)	35 (8)	29 (6)	0
C ₁ (1)	0.2543 (6)	0.6830 (7)	0.0105 (6)	105 (8)	155 (14)	103 (9)	36 (9)	23 (7)	20 (9)
C ₁ (2)	0.3200 (6)	0.5872 (9)	-0.0440 (7)	128 (9)	194 (15)	120 (10)	45 (10)	48 (9)	11 (11)
C ₁ (3)	0.3047 (6)	0.4294 (9)	-0.0193 (7)	129 (9)	184 (15)	150 (12)	74 (10)	31 (9)	14 (11)
C ₁ (4)	0.2220 (6)	0.3557 (8)	0.0563 (7)	111 (9)	175 (15)	119 (11)	50 (10)	43 (8)	24 (10)
C ₁ (12)	0.1584 (15)	0.4511 (7)	0.1118 (6)	92 (8)	142 (13)	91 (9)	45 (9)	30 (7)	78 (9)
S ₂	0.4056 (2)	0.0403 (2)	0.2661 (2)	86 (2)	179 (4)	103 (3)	43 (2)	31 (2)	77 (3)
O ₂	0.3691 (4)	0.1072 (6)	0.1384 (5)	139 (6)	278 (12)	145 (8)	111 (8)	112 (6)	51 (8)
C ₂ (13)	0.5574 (5)	0.0742 (7)	0.2925 (6)	77 (7)	142 (13)	125 (10)	14 (8)	69 (7)	20 (10)
C ₂ (6)	0.6158 (6)	-0.0018 (8)	0.2043 (6)	114 (8)	189 (15)	104 (9)	76 (10)	37 (8)	27 (10)
C ₂ (7)	0.7317 (6)	0.0341 (9)	0.2396 (7)	95 (8)	227 (17)	161 (12)	61 (10)	48 (9)	68 (12)
C ₂ (8)	0.7919 (6)	0.1425 (9)	0.3638 (8)	83 (8)	232 (17)	170 (12)	39 (10)	30 (8)	60 (12)
C ₂ (9)	0.7320 (6)	0.2186 (8)	0.4528 (7)	697 (7)	206 (16)	130 (10)	10 (7)	10 (7)	26 (11)
C ₂ (10)	0.6159 (5)	0.1827 (8)	0.4194 (7)	622 (7)	174 (14)	130 (10)	25 (8)	11 (7)	51 (10)
C ₂ (11)	0.5354 (6)	0.2509 (8)	0.4942 (6)	85 (8)	175 (14)	98 (9)	34 (9)	26 (7)	33 (10)
C ₂ (1)	0.5624 (6)	0.3625 (8)	0.6213 (6)	99 (8)	175 (14)	82 (9)	28 (9)	15 (7)	9 (9)
C ₂ (2)	0.4728 (7)	0.4114 (8)	0.6699 (7)	114 (8)	191 (15)	105 (10)	36 (10)	31 (8)	2 (10)
C ₂ (3)	0.3622 (6)	0.3518 (9)	0.5996 (7)	96 (8)	235 (17)	122 (11)	65 (10)	35 (8)	16 (11)
C ₂ (4)	0.3351 (6)	0.2388 (8)	0.4731 (7)	79 (7)	207 (16)	152 (11)	44 (9)	32 (8)	25 (11)
C ₂ (12)	0.4252 (5)	0.1889 (7)	0.4254 (6)	65 (7)	141 (13)	110 (10)	7 (8)	5 (7)	21 (9)

atom	<i>x</i>	<i>y</i>	<i>z</i>	atom	<i>x</i>	<i>y</i>	<i>z</i>
H ₁ (6)	-0.0722	0.5588	0.3902	H ₂ (6)	0.5585	-0.0803	0.1046
H ₁ (7)	-0.0791	0.8279	0.4132	H ₂ (7)	0.7649	-0.0276	0.1706
H ₁ (8)	0.0377	1.0310	0.2684	H ₂ (8)	0.8987	0.1658	0.3897
H ₁ (9)	0.1585	0.9448	0.1366	H ₂ (9)	0.7968	0.3161	0.5521
H ₁ (1)	0.2643	0.8383	0.0015	H ₂ (1)	0.6651	0.4152	0.6830
H ₁ (2)	0.3917	0.6647	-0.0792	H ₂ (2)	0.5047	0.5334	0.7478
H ₁ (3)	0.3564	0.3473	-0.0281	H ₂ (3)	0.2836	0.3896	0.6143
H ₁ (4)	0.2067	0.2138	0.0787	H ₂ (4)	0.2380	0.1818	0.4048

^a For hydrogen atoms, the isotropic temperature factor was given at 4.0 Å².

Table IV. Selected Bond Lengths (Å) and Angles (Deg) for 5-Methyldibenzothiophenium Tetrafluoroborate (I) with Standard Deviation in Parentheses

atoms	lengths	atoms	angles
S-C ₁₄	1.795 (6)	C ₁₄ -S-C ₁₃	104.7 (3)
S-C ₁₃	1.777 (5)	C ₁₄ -S-C ₁₂	102.6 (3)
S-C ₁₂	1.782 (6)	C ₁₂ -S-C ₁₃	90.8 (3)
C ₁ -C ₂	1.384 (8)	C ₁₁ -C ₁ -C ₂	118.3 (6)
C ₁ -C ₁₁	1.413 (8)	C ₁ -C ₂ -C ₃	122.3 (6)
C ₂ -C ₃	1.338 (8)	C ₂ -C ₃ -C ₄	121.7 (6)
C ₃ -C ₄	1.383 (8)	C ₃ -C ₄ -C ₁₂	115.7 (5)
C ₄ -C ₁₂	1.385 (7)	C ₄ -C ₁₂ -C ₁₁	124.6 (5)
C ₁₂ -C ₁₁	1.371 (7)	C ₁₂ -C ₁₁ -C ₁	117.4 (5)
C ₆ -C ₇	1.420 (8)	S-C ₁₂ -C ₁₁	110.7 (4)
C ₇ -C ₈	1.349 (9)	S-C ₁₃ -C ₁₀	111.5 (4)
C ₈ -C ₉	1.410 (8)	C ₁₂ -C ₁₁ -C ₁₀	113.5 (5)
C ₉ -C ₁₀	1.400 (7)	C ₁₃ -C ₁₀ -C ₁₁	113.4 (5)
C ₁₀ -C ₁₁	1.447 (7)	C ₁₃ -C ₆ -C ₇	115.1 (6)
C ₁₀ -C ₁₃	1.356 (7)	C ₆ -C ₇ -C ₈	120.6 (6)
C ₁₃ -C ₆	1.393 (7)	C ₇ -C ₈ -C ₉	123.0 (6)
B-F ₁	1.339 (9)	C ₈ -C ₉ -C ₁₀	117.2 (6)
B-F ₂	1.344 (8)	C ₉ -C ₁₀ -C ₁₃	118.8 (5)
B-F ₃	1.471 (11)	C ₁₀ -C ₁₃ -C ₆	125.4 (5)
B-F ₄	1.327 (9)		

Table V. Selected Bond Lengths (Å) and Angles (Deg) for 1-Methylnaphtho[2,3-*b*]thiophenium Tetrafluoroborate (II) with Standard Deviation in Parentheses

atoms	lengths	atoms	angles
S-C ₁₄	1.791 (8)	C ₁₄ -S-C ₁₀	102.6 (3)
S-C ₂	1.789 (8)	C ₁₄ -S-C ₂	105.6 (4)
S-C ₁₀	1.776 (7)	C ₂ -S-C ₂	105.6 (4)
C ₅ -C ₁₀	1.348 (8)	C ₁₃ -C ₉ -C ₁₀	117.6 (6)
C ₁₀ -C ₁₁	1.450 (9)	C ₉ -C ₁₀ -C ₁₁	123.8 (7)
C ₄ -C ₁₁	1.350 (10)	C ₁₀ -C ₁₁ -C ₄	118.6 (7)
C ₄ -C ₁₂	1.407 (10)	C ₁₁ -C ₄ -C ₁₂	120.0 (7)
C ₁₂ -C ₁₃	1.402 (9)	C ₄ -C ₁₂ -C ₁₂	122.2 (8)
C ₁₃ -C ₉	1.459 (9)	C ₁₂ -C ₁₃ -C ₉	117.8 (7)
C ₅ -C ₁₂	1.434 (9)	C ₁₂ -C ₅ -C ₆	120.2 (7)
C ₅ -C ₆	1.350 (10)	C ₅ -C ₆ -C ₇	121.0 (8)
C ₆ -C ₇	1.400 (10)	C ₆ -C ₇ -C ₈	120.4 (8)
C ₇ -C ₈	1.335 (10)	C ₇ -C ₈ -C ₁₃	121.0 (8)
C ₈ -C ₁₃	1.413 (9)	C ₈ -C ₁₃ -C ₁₂	120.4 (7)
C ₃ -C ₁₁	1.449 (10)	C ₁₃ -C ₁₂ -C ₅	116.9 (7)
C ₃ -C ₂	1.290 (10)	S-C ₁₀ -C ₁₁	109.7 (6)
B-F ₁	1.319 (11)	C ₁₀ -C ₁₁ -C ₃	111.2 (8)
B-F ₂	1.387 (11)	S-C ₂ -C ₃	113.8 (7)
B-F ₃	1.364 (11)	C ₂ -C ₃ -C ₁₁	114.9 (8)
B-F ₄	1.339 (11)		

Table VI. Bond Lengths (Å) for Dibenzothiophenium 5-Oxide (III) with Standard Deviation in Parentheses

bond	molecule I	molecule II
S-O	1.460 (5)	1.465 (5)
S-C ₁₂	1.790 (6)	1.806 (6)
S-C ₁₃	1.780 (6)	1.783 (7)
C ₁ -C ₂	1.397 (9)	1.388 (9)
C ₂ -C ₃	1.464 (9)	1.362 (9)
C ₃ -C ₄	1.384 (8)	1.394 (8)
C ₄ -C ₁₂	1.380 (8)	1.397 (8)
C ₁₁ -C ₁₂	1.378 (8)	1.353 (8)
C ₁ -C ₁₁	1.392 (8)	1.390 (7)
C ₆ -C ₁₃	1.372 (8)	1.388 (8)
C ₆ -C ₇	1.373 (9)	1.357 (9)
C ₇ -C ₈	1.390 (8)	1.394 (8)
C ₈ -C ₉	1.396 (9)	1.405 (9)
C ₉ -C ₁₀	1.370 (8)	1.357 (8)
C ₁₀ -C ₁₁	1.475 (8)	1.491 (8)
C ₁₀ -C ₁₃	1.392 (7)	1.406 (7)

carbon orbitals. The lone-pair orientation does not, however, preclude participation of the sulfur atom in the π -electron system. The magnitude of decrease in π -electron participation remains in question. Does the substitution at the thiophenoid sulfur result in sufficient decrease of aromaticity to yield an antiaromatic π

Table VII. Bond Angles (Deg) for Dibenzothiophenium 5-Oxide (III) with Standard Deviation in Parentheses

angle	molecule I	molecule II
O-S-C ₁₂	110.3 (3)	110.0 (3)
O-S-C ₁₃	110.4 (3)	109.3 (3)
C ₁₂ -S-C ₁₃	88.5 (3)	88.7 (3)
S-C ₁₃ -C ₁₀	114.1 (5)	113.4 (5)
C ₁₃ -C ₁₀ -C ₁₁	111.3 (6)	111.3 (6)
C ₁₀ -C ₁₁ -C ₁₂	111.8 (6)	111.9 (6)
C ₁₁ -C ₁₂ -S	114.0 (5)	114.6 (5)
C ₆ -C ₁₃ -C ₁₀	121.7 (6)	121.4 (6)
C ₇ -H ₆ -C ₁₃	118.6 (7)	118.6 (6)
C ₈ -C ₇ -C ₆	120.7 (7)	121.2 (6)
C ₉ -C ₈ -C ₇	120.0 (7)	119.7 (6)
C ₁₀ -C ₉ -C ₈	119.3 (7)	119.7 (6)
C ₁₃ -C ₁₀ -C ₉	119.7 (6)	119.4 (6)
C ₄ -C ₁₂ -C ₁₁	122.0 (6)	122.2 (6)
C ₁₂ -C ₁₁ -C ₁	120.4 (6)	120.6 (6)
C ₁₁ -C ₁ -C ₂	117.7 (6)	117.4 (6)
C ₁ -C ₂ -C ₃	120.7 (7)	122.3 (6)
C ₂ -C ₃ -C ₄	122.1 (7)	120.2 (6)
C ₃ -C ₄ -C ₁₂	117.1 (6)	117.2 (6)

Table VIII. *A* Indices^a for Compounds I-III and Related Structures

no.	compd	entire structure	5-membered ring (or respective equiv bonds)
I	5-methyldibenzothiophenium-BF ₄	0.91	0.82
III	dibenzothiophene 5-oxide	0.91	0.75
	dibenzothiophene ¹⁵	0.96	0.97
	fluorene ¹⁶	0.92	0.87
	biphenyl ¹⁷	0.84	0.55
II	1-methylnaphtho[2,3- <i>b</i>]thiophenium-BF ₄	0.71	0.35
IV	thiophene ^b	0.93	0.93
V	1-methylthiophenium ^c	0.69	0.69
VI	thiophene 1-oxide ^c	0.69	0.69
	benzene	1.00	

^a Calculated by using a formula $A = 1 - (225/n)\sum_{rs}(1 - (d_{rs}/\bar{d}))^2$,¹⁹ where n = number of bonds, d_{rs} = individual (averaged for equivalent positions) CC bond length, \bar{d} = averaged bond length for all CC bonds for the structure under consideration. ^b Used bond length from microwave spectra.¹⁸ ^c Used bond length calculated by MNDO method.

Table IX. MNDO Calculated Bond Lengths for Thiophene, *S*-Methylthiophenium and Thiophene *S*-Oxide and Corresponding *A* Indices

bonds	S-C ₁	C ₁ -C ₂	C ₂ -C ₃	S-X	<i>A</i> index
thiophene (IV)	1.692	1.368	1.455		0.85
<i>S</i> -methylthiophenium (V)	1.759	1.353	1.480	1.806	0.69
thiophene <i>S</i> -oxide (VI)	1.766	1.351	1.477	1.516	0.69

system? A perturbation treatment based on HMO models sheds light on this question.

In this formalism the change in π -electron energy on ring closure of an open system



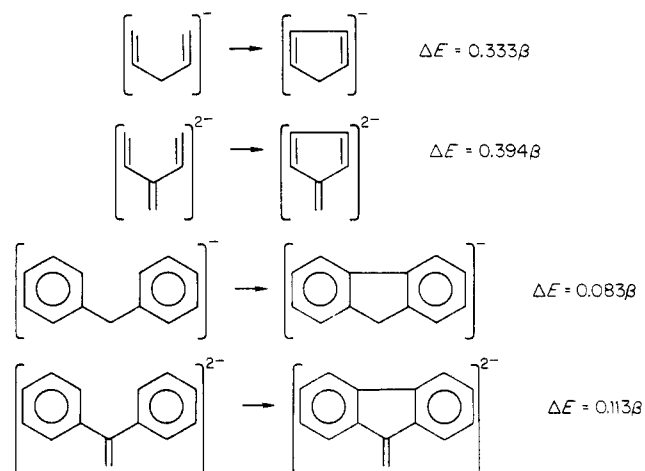
is given by

$$\Delta E = \beta_{rs} \sum_i c_{ir} c_{is} n_i$$

where β_{rs} is the R - S resonance integral, c_{ir} and c_{is} are the coefficients of the i th molecular orbital at atoms R and S, respectively, and n_i is the occupation number of the i th orbital. The sum is, of course, just the bond order p_{rs} , so

$$\Delta E = \beta_{rs} p_{rs}$$

ΔE can be easily evaluated by using data in existing tables^{20,21} for molecules with isoelectronic π systems to those in question. Thus



The topological effect of changing the five-membered aromatic rings to dibenzo derivatives is to markedly decrease the π -electron stabilization afforded by cyclization, e.g., to reduce the aromaticity

(20) Heilbronner, E.; Bock, H. "The HMO Model and its Application"; Wiley-Interscience: New York, 1976.

(21) Coulson, C. A.; Streitwieser, A., Jr. "Dictionary of π -Electron Calculations"; W. H. Freeman: San Francisco, 1965.

of the central ring. In the model isoelectronic hydrocarbon π systems the ones isoelectronic to the thiophene *S*-oxides are in both cases *more* aromatic than the ones isoelectronic to the thiophenes themselves! The result of replacing one or more carbon atoms in these systems with heteroatoms will decrease the ΔE values and, therefore, the aromaticity. Each of the π -orbitals has a plane passing through the heteroatoms. A heteroatom, more electronegative than carbon, will inductively polarize the π electrons toward it. This effect will be largest in π orbitals with non-zero coefficients at the heteroatom site. These, however, must by symmetry have coefficients with identical signs at the sites to be joined in the hypothetical cyclization. They must therefore contribute positive terms to the bond order. The inductive polarization will decrease the magnitude of these coefficients at the junction points, and thus this replacement will decrease the bond order and the aromaticity. The extent of this decrease can not be unequivocally determined. It will certainly be larger for *O*-substitution than for *S*-substitution because *O* is more electronegative (relative to *C*) than is *S*. The decrease will also be larger in magnitude for the smaller thiophene system than for the larger dibenzothiophene because the later has a larger π -electron source to disperse the charge. If the destabilization is sufficiently large to change the sign of the bond order the systems could be considered antiaromatic. The theoretical determination of aromaticity or antiaromaticity is very model dependent, and the question can only be finally settled by detailed thermochemical data which are now being determined.

Supplementary Material Available: Listings of structure factor tables for compounds I and II (34 pages). Ordering information is given on any current masthead page.

Optical Rotatory Dispersion Studies. 132.¹ Conformational Isotope Effect in Deuterium-Substituted Cyclohexanones

Shy-Fuh Lee, Günter Barth, and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received June 9, 1980

Abstract: The observed temperature dependence of the circular dichroism spectra of (3*R*)-2,2-dimethyl-3-deuteriocyclohexanone (**1**), (4*S*)-2,2-dimethyl-4-deuteriocyclohexanone (**2**), and (5*S*)-2,2-dimethyl-5-deuteriocyclohexanone (**3**) is interpreted as reflecting a conformational isotope effect which biases the equilibrium of the two chair conformers toward that conformation in which the deuterium substituent is axially oriented. With use of the estimates for the rotational strengths of the involved conformers as obtained from stereochemically rigid reference compounds, energy differences of -9.5, -4.2, and -2.7 cal/mol were calculated for the equilibria of **1**, **2**, and **3**, respectively. Empirical force field calculations show that the configuration of 2,2-dimethylcyclohexanone is slightly distorted from the symmetrical chair form. With use of the smaller nonbond interaction for C...D and H...D, energy differences were calculated for **1**, **2**, and **3** which are in qualitative agreement with the experimental ones.

Introduction

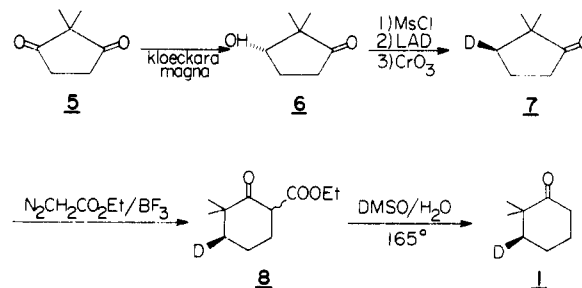
In two preliminary communications^{2,3} we have reported the temperature-dependent circular dichroism spectra of four deuterium-substituted cyclohexanones, (3*R*)-2,2-dimethyl-3-deuteriocyclohexanone (**1**), (4*S*)-2,2-dimethyl-4-deuteriocyclohexanone (**2**), (5*S*)-2,2-dimethyl-5-deuteriocyclohexanone (**3**), and (3*S*)-3-deuterio-4,4-dimethylcyclohexanone (**4**). We associated the observed temperature variation of the rotational strength with the presence of a steric isotope effect: in the chair \rightleftharpoons chair

(1) For preceding paper see: Sing, L. Y.; Lindley, M.; Sundararaman, P.; Barth, G.; Djerassi, C. *Tetrahedron*, in press.

(2) Lee, S.-F.; Barth, G.; Kieslich, K.; Djerassi, C. *J. Am. Chem. Soc.* **1978**, *100*, 3965-3966.

(3) Lee, S.-F.; Barth, G.; Djerassi, C. *J. Am. Chem. Soc.* **1978**, *100*, 8010-8012.

Scheme I



equilibrium the conformation with the deuterium in the axial positions becomes energetically preferred. We now report the