white needles: mp 91–92 °C; NMR (CDCl₃) δ 6.04 (d of d, J_1 = 2, J_2 = 16 Hz), 1.89 (d of m, J_2 = 16 Hz); MS (isobutane), 329 (M + 1), 327 (100, M – 1).

Hydroboration of 5β-Chol-9(11)-ene. To a solution of 5β-chol-9(11)-ene (300 mg, 0.91 mmol) dissolved in THF (3 mL) was added BH₃·THF (1 mL, 1 mmol, 1 M). A portion (3 mL) of this was pressurized at 5000 atm and room temperature for 20 h. After release of the pressure, excess THF and BH₃ were evaporated, leaving an oily residue: IR (Nujol) 2500, 1555 cm⁻¹. The residue was dissolved in THF (2 mL) and oxidized by sequential addition of water (1 mL), 3 N NaOH (0.3 mL, 0.90 mmol), and 30% H₂O₂ (0.3 mL, 3 mmol), followed by heating at 40–50 °C for 2 h. The mixture was extracted with pentane, washed with water and brine, dried over Na₂SO₄, and evaporated, yielding an oil that crystallized from methanol/benzene (4:1): mp 65–66 °C; MS (EI) M⁺ 328

(M⁺). The solution, which was not pressurized (∼1 mL), was evaporated and yielded an oily residue: IR (Nujol) 2500 (w), 1555 (w) cm⁻¹. This was identical with the high-pressure product.

Carbon-13 Nuclear Magnetic Resonance Study of the Conformations of Disulfides and Their Oxide Derivatives[1,2]

Fillmore Freeman* and Christos N. Angeletakis

Department of Chemistry, University of California, Irvine, California 92717

Received February 2, 1982

The carbon-13 nuclear magnetic resonance spectra and substituent effects of several acyclic disulfides and their oxidized derivatives are reported. Oxidation of a disulfide to a thiosulfinate or a thiosulfonate has a deshielding effect on the α-carbon atom and a shielding effect on the α'-carbon atom. The chemical shifts of α- and α'-carbon atoms of sulfinyl sulfones can best be correlated with the shifts of the α- and α'-carbon atoms in the corresponding thiosulfinates. On the basis of ¹³C NMR shielding trends, it appears that conformational preferences of all the oxidized derivatives of disulfides are similar. A modified gauche effect is proposed to account for the difference in chemical shifts of the α-carbon atoms in the oxidized derivatives of disulfides.

The ¹³C NMR chemical shifts of selected model molecules in various groups of organic compounds have proved to be of great diagnostic value in the analysis of unknown mixtures or structures. Organosulfur compounds, as a class, are of particular interest owing to some of their unique conformational and stereochemical properties and to the various oxidation states of sulfur. Sulfur atoms participating in disulfide bonds have electron pairs available for covalent bonding with oxygen. The possible structures are shown below.

Although there are numerous scattered references in the literature concerning ¹³C NMR studies of organosulfur compounds,[2–4] there are only a few systematic studies of disulfides (1),[3,5–7] thiosulfinates (2),[2,5,6] and α-disulfoxides (3, not yet isolated).[8–11] The ¹H NMR spectra of 1,[3,5–7]

2,[3,5,6,12,13] 4,[3,5,6] and several α-disulfones (6)[14] have been reported. Thus, we have carried out a systematic study of the ¹³C NMR spectra of simple symmetrical acyclic disulfides and some of their oxide derivatives (2–6). These data and previous reports[2,3,5,6] are used to obtain useful ¹³C NMR chemical shift trends for 2–6 and to give some insight into the preferred conformations of these compounds in solution.

Results

The ¹³C NMR chemical shifts for a series of disulfides (7–15), thiosulfinates (16–24), thiosulfonates (25–33), sulfinyl sulfones (34–36), and α-disulfones (37–41) are shown in Tables I and II. The assignments were made by off-resonance decoupling techniques and by observation of the expected downfield shifts owing to changes in the electronegativity of divalent sulfur after oxidation.

The ¹³C NMR substituent effects of thiosulfinates (2) and thiosulfonates (4), which were calculated from the spectral data tabulated in Table I, are shown in Table III. The α_{SO} values [$\alpha_{SO} = \delta_{C_\alpha}$(thiosulfinate) – δ_{C_α}(disulfide)] vary from 13.18 to 19.30 ppm, and the α'_{SO} values [$\alpha'_{SO} = \delta_{C_{\alpha'}}$(thiosulfinate) – $\delta_{C_{\alpha'}}$(disulfide)] range from –9.03 to 2.30

(1) Abstracted from the Ph.D Thesis of C.N.A., University of California, Irvine, CA, 1982.
(2) Freeman, F.; Angeletakis, C. N. *Org. Magn. Reson.*, in press.
(3) Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *Org. Magn. Reson.* 1981, *17*, 53.
(4) Block, E.; Bazzi, A. A.; Lambert, J. B.; Wharry, S. M.; Andersen, K. K.; Dittmer, D. C.; Patwardham, B. H.; Smith, D. J. H. *J. Org. Chem.* 1980, *45*, 4807 and references therein.
(5) Takata, T.; Kim, Y. H.; Oae, S.; Suzuki, K. T. *Tetrahedron Lett.* 1978, 4303.
(6) Bass, S. W.; Evans, S. A., Jr. *J. Org. Chem.* 1980, *45*, 710.
(7) Dauphin, G.; Cuer, A. *Org. Magn. Reson.* 1979, *12*, 557.
(8) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* 1981, *103*, 6232.
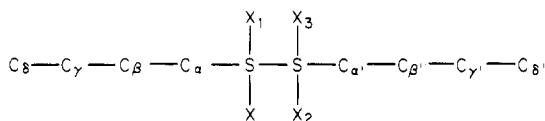(9) Freeman, F.; Angeletakis, C. N., unpublished data.
(10) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.*, in press.
(11) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.*, in press.
(12) Kato, A.; Numata, M. *Tetrahedron Lett.* 1972, 203.
(13) Legler, L. E.; Jindal, S. L.; Murray, R. W. *Tetrahedron Lett.* 1972, 3907.
(14) Farng, L. O.; Kice, J. L. *J. Am. Chem. Soc.* 1981, *103*, 1137.

disulfide	**1**, $X = X_1 = X_2 = X_3$ = lone pair electrons	
thiosulfinate	**2**, X = oxygen atom; $X_1 = X_2 = X_3$ = lone pair electrons	
α-disulfoxide	**3**, $X_1 = X_3$ = oxygen atom; $X = X_2$ = lone pair electrons	
thiosulfonate	**4**, $X = X_1$ = oxygen atom; $X_2 = X_3$ = lone pair electrons	
sulfinyl sulfone	**5**, $X = X_1 = X_2$ = oxygen atom; X_3 = lone pair electrons	
α-disulfone	**6**, $X = X_1 = X_2 = X_3$ = oxygen atom	

ppm. The α_{SO_2} values [$\alpha_{SO_2} = \delta_{C_\alpha}$(thiosulfonate) $- \delta_{C_\alpha}$(disulfide)] range from 16.59 to 25.69 ppm, and the α'_{SO_2} values [$\alpha'_{SO_2} = \delta_{C_{\alpha'}}$(thiosulfonate) $- \delta_{C_{\alpha'}}$(disulfide)] vary from −6.04 to 10.66 ppm.

Discussion

Disulfides and their oxidized derivatives show conformational preferences that are apparently governed by the gauche effect,[15] which is defined as a tendency to adopt a structure that has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds. Disulfides show dihedral angles close to 90°.[16,17] The dihedral angle in thiosulfinates (**2**),[18] thiosulfonates (**4**),[19] and α-disulfones (**6**)[18,20] has been predicted to be near 60° as a result of dipole moment measurements. This value is different than that observed in the solid state.[21-23] Ab initio molecular orbital calculations have been performed for the simplest homologues of thiosulfinates (**42**), α-disulfoxides (**43**), thiosulfonates (**44**), and α-disulfones (**45**).[24]
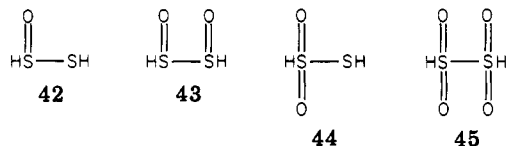

Dipole moment measurements[18,19] suggest that gauche interactions of the two C–S bonds in thiosulfinates (**2**) lead to **46a** as the preferred conformation. Since carbon and
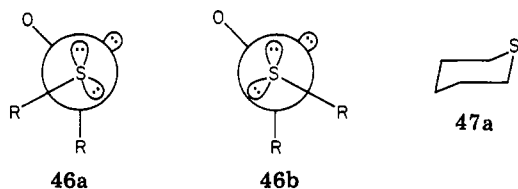

sulfur have approximately the same electronegativity,[25]

conformation **46b** might be expected to be favored over **46a** owing to the gauche effect.[15] However, it has been observed that the chemical shift of the α-carbon atom in thiane **47** does not correlate with the electronegativity of sulfur while a good correlation is obtained for several other heteroatom-substituted pentamethylene heterocycles.[26] It is also of interest to note that both ^{1}H NMR[27] and ^{13}C NMR[6] shift data for 1,2-dithiane 1-oxide suggest that **48a**
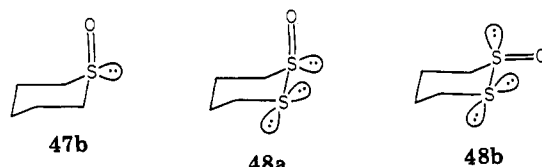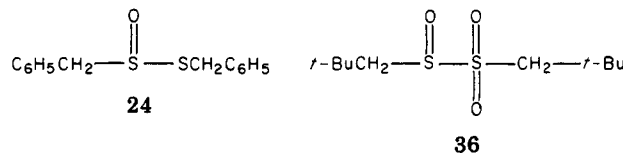

is >2 kcal mol⁻¹ more stable than the conformation with the equatorial sulfinyl oxygen atom (**48b**). Similar observations have been reported for thiane 1–oxide (**47b**).[28]

The gauche conformations of thiosulfonates (**4**), sulfinyl sulfones (**5**), and α-disulfones (**6**) are shown in structures **49**, **50**, and **51**, respectively.
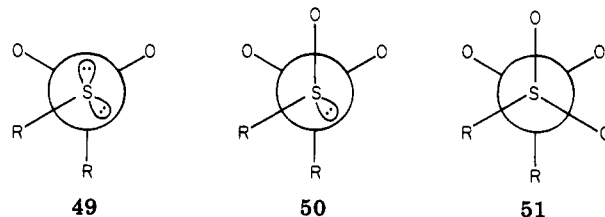
Inspection of molecular models shows that the α- and α'-carbons and hydrogens in thiosulfinate **46a** and thiosulfonate **49** are almost the same distance from the sulfinyl oxygen atom. Although coupling constants are not known to be affected significantly by through-space effects,[29] the similarity in coupling constants of the α- and α'-protons of *S*-phenylmethyl phenylmethanethiosulfinate (**24**; $\alpha = 13.1$ Hz, $J_{\alpha'} = 13.4$ Hz)[3] and 2,2-dimethylpropyl 2,2-di-

methylpropanesulfinyl sulfone (**36**; $J_\alpha = 13.8$ Hz, $J_{\alpha'} = 13.6$ Hz),[11] and other phenylmethyl- and 2,2-dimethylpropyl-

(15) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(16) Aroney, M. J.; LeFerre, R. J. W.; Pierens, R. K.; The, H. L. K. *Aust. J. Chem.* **1968**, *21*, 281.

(17) Boyd, D. B. *J. Am. Chem. Soc.* **1972**, *94*, 8799 and references therein.

(18) Dembeck, P.; vivarelli, P.; Jehlicka, V.; Exner, O. *J. Chem. Soc., Perkin Trans. 2* **1973**, 488.

(19) Exner, O.; Harpp, D. N.; Gleason, J. G. *Can. J. Chem.* **1972**, *50*, 548.

(20) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.

(21) Kiers, C. T.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 166.

(22) Noordik, J. H.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 156.

(23) Kiers, C. T.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 126.

(24) Freeman, F.; Angeletakis, C. N.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 1161.

(25) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

(26) Lambert, J. B.; Netzel, D. A.; Sun, H.; Lilianstrom, K. K. *J. Am. Chem. Soc.* **1976**, *98*, 3778.

(27) Harpp, D. N.; Gleason, J. G. *J. Org. Chem.* **1971**, *36*, 1314.

(28) Buchanan, G. W.; Durst, T. *Tetrahedron Lett.* **1975**, *21*, 1683.

(29) Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR Spectroscopy"; Heyden and Son Ltd.: London, 1978; Chapter 3.

Table I. ¹³C NMR Chemical Shifts (ppm) for Alkyl Disulfides and the Corresponding Thiosulfinates and Thiosulfonates[a]

Structures:

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-S-S-\overset{}{C}-\overset{}{C}-\overset{}{C}-\overset{}{C}\qquad (R,\ R')$$

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-\overset{O}{\underset{O}{S}}-\overset{\alpha'}{C}-\overset{\beta'}{C}-\overset{\gamma'}{C}-\overset{\delta'}{C}\qquad (R'',\ R')$$

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-\overset{O}{S}-S-\overset{\alpha'}{C}-\overset{\beta'}{C}-\overset{\gamma'}{C}-\overset{\delta'}{C}\qquad (R,\ R')$$

R [R', R'']	compd no.	¹³C chemical shifts, ppm							
		α	β	γ	δ	α'	β'	γ'	δ'
CH₃	7[b]	22.04							
	[16,[c] 25[b]]	[42.79,[c] 48.74]				[14.44,[c] 18.23]			
C₂H₅	8[b]	32.82	14.50						
	[17,[b] 26[b]]	[49.88, 56.94]	[7.67, 8.31]			[26.81, 30.54]	[16.26, 15.12]		
n-C₃H₇	9	41.26	22.56	13.12					
	[18, 27]	[58.15, 64.68]	[17.23, 17.63]	[13.21, 13.36]		[24.91, 38.36]	[24.29, 23.45]	[13.21, 12.89]	
n-C₄H₉	10	38.97	31.37	21.68	13.67				
	[19, 28]	[56.09, 62.53]	[25.50, 25.53]	[21.91, 21.76]	[13.53, 13.44]	[32.91, 35.97]	[32.62, 31.71]	[21.76, 21.32]	[13.68, 13.56]
i-C₃H₇	11[b]	41.14	22.60						
	[20,[b] 29[b]]	[55.26, 63.35]	[15.70, 16.26]			[38.27, 42.70]	[24.57, 24.22]		
t-C₄H₉	12[b]	45.63	30.51						
	[21,[b] 30[b]]	[58.81, 68.02]	[24.01, 23.74]			[47.93, 56.29]	[32.20, 31.52]		
i-C₄H₉	13[b]	48.60	28.21	21.78					
	[22,[b] 31[b]]	[65.18, 70.48]	[24.92, 25.21]	[21.58,[d] 22.48], 22.52		[41.54, 44.57]	[26.69, 28.90]	[21.66, 21.68]	
t-C₄H₉CH₂	14[e]	55.96	30.31	28.83					
	[23,[e] 32[e]]	[71.55, 74.95]	[32.07, 32.12]	[29.56, 29.76]		[46.93, 49.92]	[32.26, 33.47]	[28.72, 28.86]	
C₆H₅CH₂	15[f]	43.32							
	[24,[g] 33[h]]	[62.30, 69.01]				[36.07, 40.85]			

[a] The ¹³C NMR spectra of 9, 10, 16, 18, 19, 27, and 28 at 62.89 MHz and of 14, 15, 23, 24, 32, and 36 at 23.29 MHz. The solvent is CDCl₃. The shifts of the thiosulfinates and thiosulfonates are given, respectively, in brackets. [b] Reference 6. [c] Value from this work. Reference 6 gives values of 42.66 and 13.74 ppm for Cα and Cα'. [d] The γ-carbon atoms of 22 are diastereotopic. [e] Reference 10. [f] The chemical shift for phenyl is 126.9–137.4 ppm. [g] The chemical shift for phenyl is 127.7–136.7 ppm. [h] The chemical shift for phenyl is 127.8–134.9 ppm.

Table II. ^{13}C NMR Chemical Shifts (ppm) for Alkyl Sulfinyl Sulfones and Alkyl α-Disulfones^a

| R [R']	compd no.	^{13}C chemical shifts, ppm							
		α	β	γ	δ	α'	β'	γ'	δ'
CH$_3$	34	38.11				34.79			
n-C$_3$H$_7$	37	52.68	16.18	13.18					
n-C$_4$H$_9$	35 [38]	52.10 [50.82]	24.08 [23.97]	22.11 [21.82]	13.53 [13.32]	48.53	24.17	21.73	13.40
i-C$_3$H$_7$	39	56.36	16.06						
t-C$_4$H$_9$CH$_2$	36^b [40^b]	62.19 [59.35]	32.93 [33.00]	29.96 [29.82]		62.48	32.61	29.76	
C$_6$H$_5$CH$_2$	41^c	59.35							

^{a} Spectrometer frequency 62.89 MHz. Solvent is CDCl$_3$. Shifts for the alkyl α-disulfones are given in brackets. ^{b} Reference 10. ^{c} The chemical shift for phenyl is 124.26-131.79 ppm.

substituted thiosulfinates (J = 13-14 Hz)^3 can be rationalized in terms of the orientation of the protons toward the asymmetric center S=O.

Oxidation of a disulfide to the corresponding thiosulfinate results in deshielding at the α-carbon atom by 13.2-20.8 ppm. This α_{SO} effect [$\alpha_{SO} = \delta_C(-S(O)S-) - \delta_C(-SS-)$] results from the inductive effect of the partially positive sulfur and the β effect of the oxygen atom.^{26,30} Similarly, oxidation of a simple acyclic sulfide to a sulfoxide leads to an α_{SO} deshielding of 20 ppm.^{30} Increased congestion on the α- or β-positions in a thiosulfinate diminishes the α_{SO} effect, which is consistent with similar trends observed with acyclic hydrocarbons^{31,32} and sulfones.^{33}

Although oxidation of an acyclic sulfoxide to a sulfone has a small effect on the chemical shift of the α-carbon atom (<2 ppm),^{30,33,34} the α_{SO_2} deshielding effect is significantly more pronounced than the α_{SO} effect in disulfides (Tables I and II). Also, increased steric congestion around C$_\alpha$ or C$_\beta$ does not lead to smaller values of α_{SO_2}. This may be due to the favored conformation of thiosulfonates (**49**) which violates the Edward-Lemieux principle.^{35} Since this principle disfavors structures with a polar bond between two electron pairs, conformation **49** causes an increased β interaction between the α-carbon atom and the sulfonyl oxygens which increases α_{SO_2}.

Except for S-methyl methanethiosulfonate (**25**; α_{SO_2} = 26.7 ppm), the highest α_{SO_2} observed is with S-phenylmethyl phenylmethanethiosulfonate (**33**; α_{SO_2} = 25.7 ppm). Increased contribution from structures **52** and **53** (eq 1) may account for increased deshielding at the α-carbon atom of **33**.


$$ (1) $$
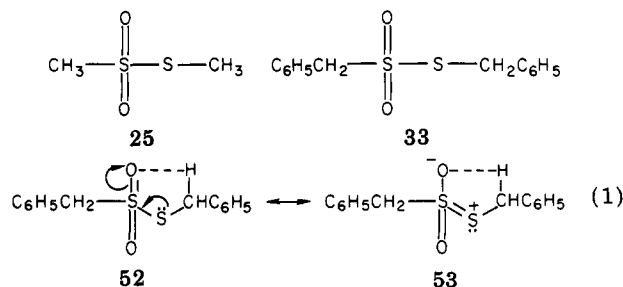
The β_{SO} and β_{SO_2} effects are shielding and essentially constant (-6.77 to -4.93, Table III) except for S-(2-methylpropyl) 2-methylpropanethiosulfinate (**22**), S-(2,2-
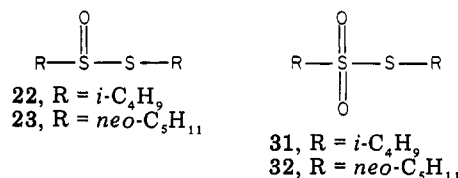
dimethylpropyl) 2,2-dimethylpropanethiosulfinate (**23**), S-(2-methylpropyl) 2-methylpropanethiosulfonate (**31**), and S-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfonate (**32**). These effects, which are similar to those found in sulfoxides and sulfones,^{30} may be attributed to the γ-effect of the sulfoxide oxygen atom or the sulfone oxygens (-6.7 ppm).^{30}

The α'_{SO} substituent effects are shielding and vary from -9.03 to -2.87 ppm, except for S-(2-methyl-2-propyl) 2-methyl-2-propanethiosulfinate (**21**) which has a deshielding α'_{SO} effect of 2.30 ppm.
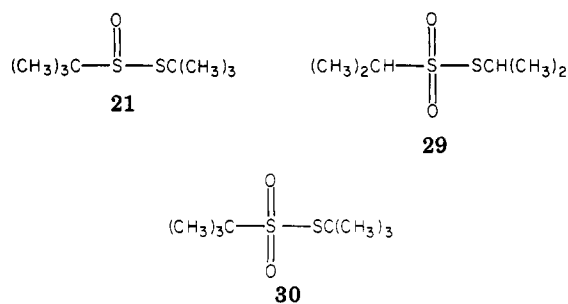
The α'_{SO_2} effects are shielding, but are less pronounced than the α'_{SO} effects, and vary from -6.0 to -3.0 ppm, except for S-2-propyl 2-propanethiosulfonate (**29**) and S-(2-methyl-2-propyl) 2-methyl-2-propanethiosulfonate (**30**) which show deshielding α'_{SO_2} values of 1.6 and 10.7 ppm, respectively.

Hyperconjugation and electron-pair back-donation into the carbon-sulfur σ orbital have been suggested as major factors in producing shielding α'_{SO} and α'_{SO_2} effects.^{6} However, comparison of the ^{13}C NMR spectra of thiosulfinates (**2**) and thiosulfonates (**4**) with those of sulfinyl sulfones (**5**) and α-disulfones (**6**) (vide infra) suggests that conformational effects also play a major role in determining the magnitude of α'_{SO} and α'_{SO_2}. The α'_{SO_2} values are smaller than the α'_{SO} values, presumably owing to the unfavorable trans interaction of the C—S and S=O bonds with an electron pair (**49**). This interaction can cause a greater distance between the sulfonyl oxygen atoms and

(30) Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* 1976, *8*, 108.

(31) Mason, J. *J. Chem. Soc. A* 1971, 1038.

(32) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* 1971, *43*, 1245.

(33) McCracken, S. S.; Evans, S. A., Jr. *J. Org. Chem.* 1979, *44*, 3551.

(34) Gokel, G. W.; Gordes, H. M.; Dishong, D. M. *J. Org. Chem.* 1980, *45*, 3634.

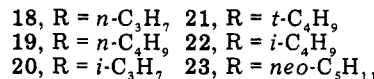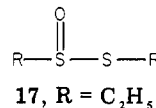(35) Wolfe, S.; Rauk, A.; Tel, L. M.; Csizmadia, G. I. *J. Chem. Soc. B* 1971, 136.

Table III. ^{13}C NMR Substituent Effects from the Oxidation of Disulfides to Thiosulfinates and Thiosulfonates[a]

R [R']	compd no.	α	β	γ	δ	α'	β'	γ'	δ'
CH₃	16 [25]	20.75 [26.70]				-7.60 [-3.81]			
C₂H₅	17 [26]	17.06 [24.12]	-6.83 [-6.19]			-6.01 [-2.28]	1.76 [0.62]		
n-C₃H₇	18 [27]	16.89 [23.42]	-5.33 [-4.93]	0.09 [0.24]		-6.35 [-2.90]	1.73 [0.89]	-0.46 [0.23]	
n-C₄H₉	19 [28]	17.12 [23.56]	-5.87 [-5.84]	0.23 [0.08]	-0.14 [-0.23]	-6.06 [-3.00]	1.25 [0.34]	0.08 [-0.30]	0.01 [-0.11]
i-C₃H₇	20 [29]	14.12 [22.11]	-6.43[b] [-6.34]			-2.87 [1.56]	2.03 [1.62]		
t-C₄H₉	21 [30]	13.18 [22.39]	-6.50 [-6.77]			2.30 [10.66]	1.69 [1.01]		
i-C₄H₉	22 [31]	16.58 [21.88]	-3.29 [-3.00]	0.27[b] [0.70]		-7.06 [-4.03]	-1.52 [0.69]	0.12 [-0.10]	
t-C₄H₉CH₂	23 [32]	15.59 [18.99]	1.95 [1.81]	0.73 [0.93]		-9.03 [-6.04]	1.76 [3.16]	-0.11 [0.03]	
C₆H₅CH₂	24 [33]	18.98 [25.69]				-7.23 [-2.47]			

[substituent effects; carbon skeleton diagrams for
$$\text{C}-\text{C}-\text{C}-\text{C}-\text{S}-\text{S}-\text{C}-\text{C}-\text{C}-\text{C}$$
$$\text{C}-\text{C}-\text{C}-\text{C}-\text{S}(=\text{O})-\text{S}-\text{C}-\text{C}-\text{C}-\text{C}$$
$$\text{C}-\text{C}-\text{C}-\text{C}-\text{S}(=\text{O})_2-\text{S}-\text{C}-\text{C}-\text{C}-\text{C}]$$

a The substituent effects are calculated as $\Delta\delta = \delta_C(-S(O)-S-) - \delta_C(-S-S-)$ or $\Delta\delta = \delta_C(-SO_2-S-) - \delta_C(-S-S-)$. Values for thiosulfonates are given in brackets. *b* The substituent effect is based on the average value for the diastereotopic methyl resonances.

$C_{\alpha'}$ than between the sulfinyl oxygen atom and $C_{\alpha'}$ (**46a**), which leads to an increase in the through-space component of the γ effect for **49** relative to **46a**.

The α'_{SO} value (-9.03 ppm) for **23** is larger than any of the values for the thiosulfinates listed in Table III. Moreover, the α'_{SO} effect of isobutyl-substituted **22** is deshielding by 1.00 ppm relative to the α'_{SO} effect of S-butyl butanethiosulfinate (**19**). These observations suggest

$$\text{R}-\overset{\overset{\displaystyle O}{\|}}{\text{S}}-\text{S}-\text{R}$$

17, R = C₂H₅
18, R = n-C₃H₇   **21**, R = t-C₄H₉
19, R = n-C₄H₉   **22**, R = i-C₄H₉
20, R = i-C₃H₇   **23**, R = neo-C₅H₁₁

that the γ-gauche shielding effect becomes more pronounced with increasing methyl substitution at C_β and $C_{\beta'}$. In contrast, the α'_{SO} effects for S-propyl propanethiosulfinate (**18**, -6.35 ppm), **19** (-6.06 ppm), S-2-propyl 2-propanethiosulfinate (**20**, -2.87 ppm), and **21** (2.30 ppm) decreases with increasing methyl substitution at C_α and $C_{\alpha'}$.

The UV absorption maxima of dialkyl disulfides[36,37] are displaced toward progressively shorter wavelengths in the series methyl (255 nm), ethyl (252 nm), isopropyl (245 nm), and *tert*-butyl (230 nm via extrapolation). The major factor in determining these shifts may be the increase in the dihedral angle (>90°), which results from an increase in the bulk of the alkyl group.[17] Although the α'_{SO} effect in primary thiosulfinates S-ethyl ethanethiosulfinate (**17**), **18, 19, 22**, and **23** is similar to the effect of a sulfinyl oxygen atom in a sulfoxide (~6 ppm),[30] α'_{SO} values of **20** and **21** are -2.8m and 2.30 ppm, respectively. The α'_{SO} values for **20** and **21** may be rationalized in terms of the size of the dihedral angle.

Increasing alkyl substitution at C_α and $C_{\alpha'}$ causes a decrease in the dihedral angle in bis(2-propyl) disulfide (**11**) and bis(2-dimethyl-2-propyl) disulfide (**12**) upon ox-

$$\text{R}-\text{S}-\text{S}-\text{R}$$

11, R = i-C₃H₇

12, R = t-C₄H₉
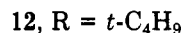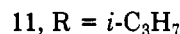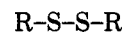
idation to thiosulfinates **20** and **21**, respectively, approaching 60° as for the primary derivatives (Table III). This decrease in the dihedral angle is accompanied by an increase in interactions between C—S and S=O (or SO₂) bonds and leads to deshielding of the α'-carbon atom.

The α- and α'-carbon atoms of sulfinyl sulfones (**5**), and α-disulfones (**6**, Table II) experience significant shielding compared to the α-carbon atoms of thiosulfinates (**2**) and thiosulfonates (**4**). In acyclic systems, oxidation of a sulfoxide to a sulfone does not produce significant further deshielding at C_α.[30] Of all the preferred conformations of the oxidized derivatives of disulfides (**1**), only **49** violates the Edward–Lemieux principle[35] and leads to distortions in the chemical shifts of C_α and $C_{\alpha'}$ in thiosulfonates (**4**). Thus, a comparison of the chemical shifts of the α-carbon atoms of thiosulfinates (**2**) with those of the corresponding sulfinyl sulfones (**5**) and α-disulfones will lead to a better understanding of the chemical shifts of the α- and α'-carbon atoms of **5** and **6**.

(36) Rosenthal, N. A.; Oster, G. *J. Am. Chem. Soc.* **1961**, *83*, 4445.
(37) Bergson, G.; Gleason, G.; Schotte, L. *Acta Chem. Scand.* **1962**, *16*, 1159.

Table IV. Comparison of the C_α and $C_{\alpha'}$ Chemical Shifts (ppm) of Sulfinyl Sulfones and α-Disulfones with the C_α Chemical Shifts of the Corresponding Thiosulfinates[a-c]
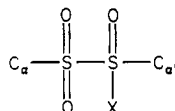

5, X = lone pair electrons
6, X = oxygen atom

compd	no.	$\delta_{C_\alpha}{}^{obsd} - \delta_{C_\alpha}{}^{calcd}$	$\delta_{C_{\alpha'}}{}^{obsd} - \delta_{C_\alpha}{}^{calcd}$
	34	2.92	−0.40
	35	2.07	−1.50
	36	−0.33	−0.04
	37	0.88	
	38	0.79	
	39	3.97	
	40	−3.17	
	41	4.28	

[a] $\delta_{C_\alpha}{}^{obsd}$ and $\delta_{C_{\alpha'}}{}^{obsd}$ from Table II. [b] $\delta_{C_\alpha}{}^{calcd} = \delta_{C_{\alpha'}}{}^{calcd} = \delta_C(-C-S(O)-S-C-) + \alpha'_{SO}$ from Tables I and II, where $\alpha'_{SO} = \delta_C(C-S(O)-S-C) - \delta_C(-C-S-S-C)$. [c] Assignment of α- and α'-carbon atoms is uncertain.

The chemical shifts of C_α and $C_{\alpha'}$ of 5 and 6 may be interpreted as being the sum of the shift of C_α of 2 and the α'_{SO} value of 2 (eq 2). The deviations of the chemical

$$\delta_C{}^{calcd} = \delta_{C_\alpha}(-C-S(O)S-C-) + \delta_{C_{\alpha'}}(-C-S(O)S-C-) - \delta_{C_\alpha}(-C-S-S-C-) \quad (2)$$

shift of C_α and $C_{\alpha'}$ of 5 and 6 ($\delta_C{}^{obsd}$) from the calculated value ($\delta_C{}^{calcd}$) are given in Table IV. The deviations are less than 3 ppm for the straight-chain alkyl compounds methyl methanesulfinyl sulfone (34), butyl butanesulfinyl sulfone (35), di-n-propyl disulfone (37), and di-n-butyl disulfone (38).
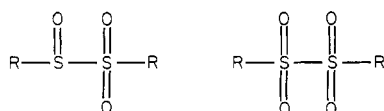
34, R = CH₃
35, R = n-C₄H₉

37, R = n-C₃H₇
38, R = n-C₄H₉
39, R = i-C₃H₇
40, R = neo-C₅H₁₁

The deviations listed in Table IV can best be rationalized in terms of the change in the dihedral angle between

the alkyl groups when 2 is oxidized to 5 and to 6. Although 5 and 6 are significantly more sterically congested than 2, the deviations from the predicted values are relatively small for 35, 37, and 38. This suggests that oxidizing a straight-chain alkyl thiosulfinate (2) to 5 or to 6 does not lead to a large change in the dihedral angle.

Interestingly, sulfinyl sulfone 36 shows the smallest deviation from the predicted value of the eight compounds listed in Table IV. Presumably increased steric congestion at C_β and $C_{\beta'}$ does not lead to much of a change in the environment of C_α on oxidation of 23 to 36.

The α-carbon of bis(2-propyl) disulfone (39) is deshielded relative to the predicted value of 3.97 ppm while C_α of bis(2,2-dimethylpropyl) disulfone (40) is shielded by −3.17 ppm. These data, and molecular models, suggest that increased steric congestion at C_α leads to an increase in the dihedral angle in the transformation of 2 to 6. The reverse appears to be true when C_β is congested.

It is also of interest to note that attempted preparation of 2-methyl-2-propyl 2-methyl-2-propanesulfinyl sulfone (54, eq 3) led only to the isolation of 2-methyl-2-propanesulfinic anhydride (55).[38-41]

(3)
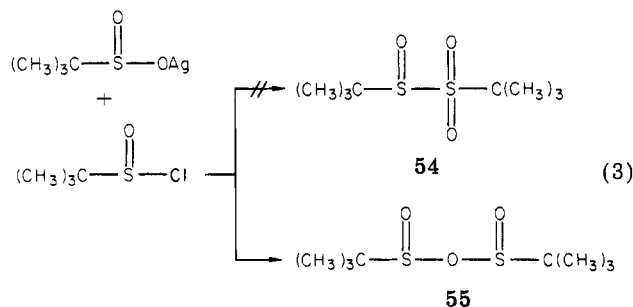
Although C_α is a secondary carbon atom, bis(phenylmethyl) α-disulfone (41) shows the highest deviation (4.28 ppm) among the compounds listed in Table IV. Presumably electronic effects play an important role in this system. Sulfonyl groups are known to increase the acidity of α-protons more so than sulfinyl groups. For example, the pK_a of dimethyl sulfoxide is 4 pK_a units larger than that of dimethyl sulfone.[42] The required geometry for removal of a proton from a carbon atom adjacent to a sulfonyl group is known[14,42-45] to be one in which the hydrogen lies on the bisector of the angle *between* the two oxygen atoms of the sulfonyl group. This would suggest structure 56 for 41. On the other hand, on the basis of the X-ray crystal structure of diphenyl α-disulfone,[21,23] the preferred conformation for 41 might be expected to be as in 57 (Newman projection along C-S bond). However, the acidity of the α-protons in 41 is expected to be particularly enhanced owing to the presence of a polarizable phenyl group and two adjacent sulfonyl groups. These effects are expected to lead to deshielding at C_α in 41 (cf. 56).

The β', γ, γ', δ, and δ' effects of thiosulfinates (2) and thiosulfonates (4) have been discussed.[3,6] The β- and β'-

(38) Kice, J. L.; Ikura, K. *J. Am. Chem. Soc.* 1968, 90, 7378.

(39) Campbell, J. Ph.D. Thesis, Oregon State University, Corvallis, OR, 1973.

(40) The formation of 55 rather than 54 may be the result of thermodynamic control, i.e., 55 is more stable than 54, because the reaction with other alkyl groups led to sulfinyl sulfones.[9,41]
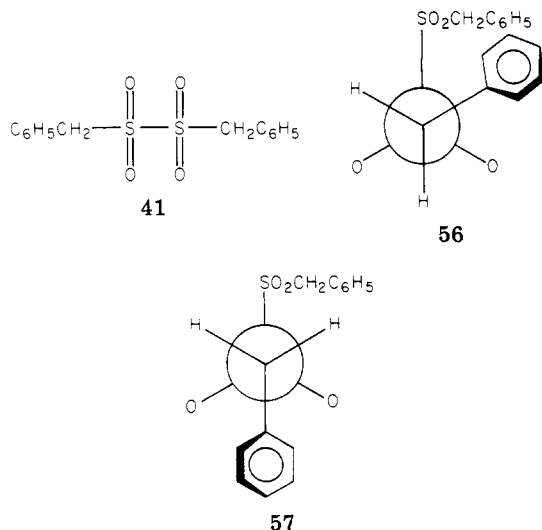
(41) Kice, J. L., private communication.

(42) Matthews, U. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* 1975, 97, 7006.

(43) Bordwell, F. G.; Doomes, E. *J. Org. Chem.* 1974, 39, 2526.

(44) Bordwell, F. G.; Phillips, D. D.; Williams, J. M. *J. Am. Chem. Soc.* 1968, 90, 426.

(45) Corey, E. J.; König, H.; Lowrey, T. H. *Tetrahedron Lett.* 1962, 515.

41

56

57

carbon atoms in sulfinyl sulfones (5) and α-disulfones (6) are generally more shielded than those of 2 and 4, but the effects are small.

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Elemental analyses were performed by Roberston Laboratory, Florham, NJ.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WH-90 and WM-250 Fourier transform NMR spectrometers which were controlled by B-NC-12 and Aspect 2000 computers, respectively. The following parameters were used for the ^{13}C NMR spectra obtained on the WM-250 spectrometer: pulse width 10.0 μs, pulse angle 35°, sweep width 15 000 Hz, acquistion time 0.5 s, 16K data points. The following parameters were used for the WH-90 FT spectrometer; pulse angle 40°, sweep width 5000 Hz, acquisition time 1.5 s, 8K data points. Broad-band decoupling was used.

IR spectra were obtained on a Perkin-Elmer 283 spectrometer.

Disulfides 7, 9, and 10 are commercially available.

Thiosulfinates 16,[16] **21** (reaction time 5 h),[46] and **24**[47,48] were prepared as previously described.

S-Propyl Propanethiosulfinate (18).[49] To a stirred solution of propyl disulfide (9; 3.0 g, 20 mmol) in 10 mL of CH$_2$Cl$_2$ at 0 °C was added dropwise (~1 drop/s) a solution of 4.24 g (20 mmol) of 81% MCPBA in 50 mL of CH$_2$Cl$_2$. The mixture was stirred for 15 min at 0 °C and filtered. The filtrate was washed with 20 mL of 5% NaHCO$_3$ and 20 mL of water and dried (Na$_2$SO$_4$), and

the solvent was evaporated. Pure **18** (2.55 g, 77%) was obtained after flash chromatography on silica gel. *The purification step was carried out as quickly as possible.*

S-Butyl butanethiosulfinate (19)[49] **and S-(2-propyl) 2-propanethiosulfinate (20)**[49] were obtained in 74% and 83% yields, respectively, by using the procedure for the preparation of **18**.

S-Propyl propanethiosulfonate (27) was prepared by the thermal decomposition of the corresponding sulfinic acid.[50] *n*-Propanesulfinic acid (2.0 g, 18 mmol) was placed in a round-bottomed flask and heated under nitrogen in an oil bath at 100 °C for 1 h when slight darkening occurred. The decomposition mixture was dissolved in ether and extracted with water. The ether layer was dried (MgSO$_4$) and evaporated. Flash column chromatography of the ether layer residue gave 0.73 g (32%) of **27** as a colorless oil.

S-Butyl butanethiosulfonate (28)[50] was obtained in 40% yield by using the procedure for the preparation of **27**.

Sulfinyl sulfones 34,[38,39] **35,**[51] and **36**[10] were prepared as previously described.

α-Disulfones 39,[14] **40,**[10] and **41**[14] were prepared as previously described.

Dipropyl Disulfone (37).[14] *S*-Propyl propanethiosulfonate (27; 0.73 g, 4.0 mmol) and 2.05 g (8.8 mmol) of 74% MCPBA were dissolved in 30 mL of CH$_2$Cl$_2$, and the solution was allowed to stand at room temperature for 4 days. The precipitate of *m*-chlorobenzoic acid was removed via filtration, and the filtrate was washed with 5% NaHCO$_3$ and then dried (MgSO$_4$). After removal of the solvent, the residue was recrystallized from ethanol to give 0.18 g (21%) of **37**: mp 47–48 °C; IR (CDCl$_3$) 1340 and 1120 cm^{-1} (s, >SO$_2$). Anal. Calcd for C$_6$H$_{14}$O$_4$S$_2$: C, 33.63; H, 6.59; S, 29.92. Found: C, 33.72; H, 6.74; S, 29.46.

Dibutyl Disulfone (38).[14] *S*-Butyl butanethiosulfonate (28; 0.83 g, 4.3 mmol) and 2.19 of (9.5 mmol) of 74% MCPBA were dissolved in 33 mL of methylene chloride. After being allowed to stand at 24 °C for 4 days, the product mixture was worked up as described above for **37**. Recrystallization from ethanol gave 0.37 g (39%) of **38**, mp 56–57 °C (lit.[14,52] mp 58–59 °C).

(46) Barnard, D.; Bateman, L.; Cain, M. E.; Colclough, T.; Cunneen, J. L. *J. Chem. Soc.* **1961,** 5339.

(47) Backer, H. J.; Bloosterziel, C. N. *Recl. Trav. Chem. Pays-Bas* **1954,** *73,* 129.

(48) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1981,** *46,* 3991.

(49) Block, E.; O'Connor, J. *J. Am. Chem.* **1974,** *96,* 3929.

(50) Von Braun, J.; Weissbach, K. *Chem. Ber.* **1930,** *63,* 2836.

(51) Kice, J. L.; Wu, S. M. *J. Org. Chem.* **1981,** *46,* 3193.

(52) Allen, P., Jr.; Karger, L. S.; Haygood, J. D., Jr.; Shrensel, J. *J. Org. Chem.* **1951,** *16,* 767.