^{13}C NMR Chemical Shifts of Thiols, Sulfinic Acids, Sulfinyl Chlorides, Sulfonic Acids and Sulfonic Anhydrides

Fillmore Freeman* and Christos N. Angeletakis
Department of Chemistry, University of California, Irvine, California 92717, USA

^{13}C NMR spectra of thiols, sulfinic acids, sulfinyl chlorides, sulfonic acids and sulfonic anhydrides have been obtained. The data are discussed in terms of the additivity of the deshielding effects exerted by the sulfur functionality at the α- or β-position, and the shielding effects produced by the sulfur function at the γ-position.

INTRODUCTION

Although ^{13}C NMR spectroscopy has found important applications in organosulfur chemistry,[1-11] only limited data are available concerning the shielding effects, deshielding effects and ^{13}C NMR spectra of thiols,[6,8,11] sulfinic acids, sulfinyl chlorides[5] and sulfonic acids.[7] Knowledge of these data is useful for assessing the oxidation state of sulfur in hydrolytic studies or during the oxidation of disulfides, thiosulfinates and thiosulfonates.[12-22] This paper presents some systematic observations concerning the shielding and deshielding effects of thiols, sulfinic acids, sulfinyl chlorides, sulfonic acids and sulfonic anhydrides. The results are discussed in terms of the additivity of deshielding effects exerted by the sulfur functionality at the α- or β-position, and the shielding effects produced by the sulfur function at the γ-position.[23-28]

It was found useful to formulate two sets of analyses: first, by taking acyclic hydrocarbons as the reference compounds and examining the respective α, β and γ effects on the chemical shift differences from the same carbon atom in the alkane in which the heteroatom is replaced by a hydrogen atom; second, by taking the thiol as the reference molecule and comparing the substituent-induced chemical shift effects of the alkyl fragment caused by oxidation and/or conversion of the thiol to sulfinic acid, sulfinyl chloride, sulfonic acid and sulfonic anhydride. Although comparisons with acyclic alkanes permit correlations of previous data,[6,8,25] the use of thiols as reference compounds is more useful and informative.

RESULTS

α Effects

Table 1 presents the ^{13}C NMR chemical shifts for methane- (**1**),[8] ethane- (**2**),[6] propane- (**3**),[6] butane- (**4**),[6] 2-propane- (**5**), 2-methyl-2-propane- (**6**), 2,2-dimethylpropane- (**7**) and phenylmethanethiol (**8**). For the series **1**, **2**, **5** and **6**, when the three hydrogens of **1** are sequentially replaced by methyl groups the respective shielding of the carbon atom attached to sulfur is 12.6, 24.09 and 34.62 ppm. This structural change, thus, causes a deshielding of *ca* 12 ppm per methyl group. Increasing methyl substitution at C-α of thiols **1**, **2**, **5** and **6** also leads to an increase in the α effect when using acyclic alkanes as the reference compounds (see Table 1).

The ^{13}C NMR chemical shifts for methane- (**9**), ethane- (**10**), propane- (**11**), butane- (**12**), 2-propane- (**13**), 2-methyl-2-propane- (**14**), 2,2-dimethylpropane- (**15**) and phenylmethanesulfinic acid (**16**) are given in Table 2. Sequential replacement of hydrogens by methyls in **9**, to give **10**, **13** and **14**, leads to deshielding of 6.96, 10.93 and 12.29 ppm, respectively.

In contrast to thiols (Table 1), when compared with acyclic hydrocarbons sulfinic acids show a decrease in the α effect with increasing methyl substitution at C-α. This trend is also observed when thiols are used as reference compounds (Table 3).

Table 3 shows a comparison of the chemical shift differences of the carbons in sulfinic acids with the corresponding thiols. Oxidation of a thiol, in which the sulfur atom is attached to a primary carbon atom, to a sulfinic acid leads to an increase in deshielding at C-α by 32.2 to 36.4 ppm in **10**, **11**, **12**, **15** and **16**. The chemical shift differences for the α-carbons in **10**, **13** and **14** are 32.2, 24.6 and 15.5 ppm, respectively, downfield from the same carbon atoms in the corresponding thiols **2**, **5** and **6**. The average is a relatively constant 8.4 ppm per methyl group.

Table 4 gives the ^{13}C NMR chemical shifts for methane- (**17**), ethane- (**18**),[5] butane- (**19**), 2-propane- (**20**),[5] 2-methyl-2-propane- (**21**), 2,2-dimethylpropane- (**22**) and phenylmethanesulfinyl chloride (**23**). Sequential replacement of hydrogens by methyls in **17**, to give **18**, **20** and **21**, leads to deshielding of 6.02, 9.75 and 11.99 ppm, respectively. As with sulfinic acids, increasing methyl substitution at C-α leads to a decrease in the α effect in sulfinyl chlorides in comparison with acyclic alkanes.

* Author to whom correspondence should be addressed.

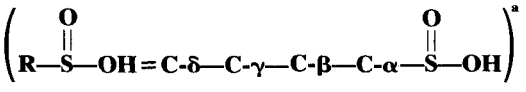
CCC-0030-4921/83/0021-0086$04.00

Table 1. ^{13}C NMR chemical shifts of thiols (R—SH = C-δ—C-γ—C-β—C-α—SH)[a]

R	Compound number	C-α		C-β		C-γ		C-δ	
		δ_C	α^b	δ_C	β^b	δ_C	γ^b	δ_C	δ^b
CH_3[c]	**1**	6.5	8.6						
CH_3CH_2	**2**	19.09	13.2	19.68	13.8				
$CH_3CH_2CH_2$[d]	**3**	26.4	10.8	27.6	11.5	12.6	−3.0		
$CH_3(CH_2)_2CH_2$[d]	**4**	24.6	11.4	37.1	12.1	22.3	−2.7	13.9	0.7
$(CH_3)_2CH$	**5**	30.59	14.5	27.59	12.0				
$(CH_3)_3C$	**6**	41.12	16.8	35.00	9.8				
$(CH_3)_3CCH_2$	**7**	38.79	10.9	31.79	0.3	28.06	0.2		
$C_6H_5CH_2$[e]	**8**	28.03	6.7						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding alkane.[25]
[c] In $CDCl_3$ at 15 MHz.[8]
[d] In CD_3OD solvent at 25.2 MHz.[6]
[e] δAr = 127.0–141.1 ppm.

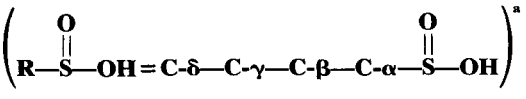
Table 2. ^{13}C NMR chemical shifts of sulfinic acids



R	Compound number	C-α		C-β		C-γ		C-δ	
		δ_C	α^b	δ_C	β^b	δ_C	γ^b	δ_C	δ^b
CH_3	**9**	44.30	46.4						
CH_3CH_2	**10**	51.26	45.36	5.41	−0.49				
$CH_3CH_2CH_2$	**11**	59.65	44.05	13.26	−3.84	15.32	−0.28		
$CH_3(CH_2)_2CH_2$	**12**	57.53	44.3	23.56	−1.4	21.88	−3.1	13.71	0.5
$(CH_3)_2CH$	**13**	55.23	39.1	13.79	−1.81				
$(CH_3)_3C$	**14**	56.59	32.3	21.35	−3.8				
$(CH_3)_3CCH_2$[c]	**15**	72.02	44.1	30.95	−0.5	29.79	1.9		
$C_6H_5CH_2$[c,d]	**16**	64.46	43.2						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding alkane.[25]
[c] In $CDCl_3$ at 22.63 MHz.
[d] δAr = 128.4–130.7 ppm.

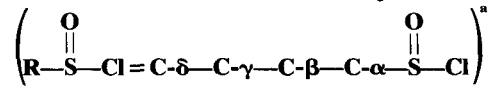
Table 3. Substituent-induced chemical shift effects in sulfinic acids



R	Compound number	C-α		C-β		C-γ		C-δ	
		δ_C	α^b	δ_C	β^b	δ_C	γ^b	δ_C	δ^b
CH_3	**9**	44.30	37.8	—	—	—	—	—	—
CH_3CH_2	**10**	51.26	32.2	5.41	−14.3	—	—	—	—
$CH_3CH_2CH_2$	**11**	59.65	33.3	13.26	−14.3	15.32	2.7	—	—
$CH_3CH_2CH_2CH_2$	**12**	57.53	32.9	23.56	−13.5	21.88	−0.4	13.71	−0.2
$(CH_3)_2CH$	**13**	55.23	24.6	13.79	−13.8	—	—	—	—
$(CH_3)_3C$	**14**	56.59	15.5	21.35	−13.7	—	—	—	—
$(CH_3)_3CCH_2$[c]	**15**	72.02	33.2	30.95	−0.8	29.79	1.7	—	—
$C_6H_5CH_2$[c,d]	**16**	64.46	36.4						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding thiol (Table 1).
[c] At 22.63 MHz.
[d] δAr = 128.38–130.65 ppm.

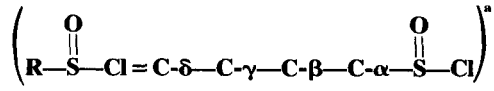
Table 4. ^{13}C NMR chemical shifts of sulfinyl chlorides



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b	C-δ δ_C	C-δ δ^b
CH_3	**17**	52.42	54.5						
CH_3CH_2[c]	**18**	58.44	52.5	5.72	−0.2				
$CH_3(CH_2)_2CH_2$	**19**	64.35	57.9	24.26	−0.2	21.68	−3.3	13.65	0.4
$(CH_3)_2CH$	**20**	62.17	46.1	14.46	−1.1				
$(CH_3)_3C$	**21**	64.41	40.1	22.47	−2.7				
$(CH_3)_3CCH_2$[d]	**22**	79.24	51.3	32.73	1.2	29.55	1.6		
$C_6H_5CH_2$[e]	**23**	71.12	49.8						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding alkane.
[c] In CH_2Cl_2 with solvent as internal standard at 22.63 MHz.[5]
[d] In $CDCl_3$ at 22.63 MHz.
[e] δAr = 128.6–130.8 ppm.

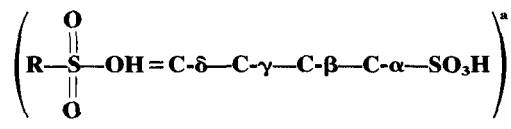
Table 5. Substituent-induced chemical shift effects in sulfinyl chlorides



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b	C-δ δ_C	C-δ δ^b
CH_3	**17**	52.42	45.9						
CH_3CH_2[c]	**18**	58.44	39.4	5.72	−14.0				
$CH_3CH_2CH_2CH_2$	**19**	64.35	39.8	24.46	−12.8	21.68	−0.6	13.65	−0.3
$(CH_3)_2CH$	**20**	62.17	31.6	14.46	−13.1				
$(CH_3)_3C$	**21**	64.41	23.3	22.47	−12.5				
$(CH_3)_3CCH_2$[d]	**22**	79.24	40.5	32.73	0.9				
$C_6H_5CH_2$[e]	**23**	71.12	43.1						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding thiol (Table 1).
[c] In CH_2Cl_2 with solvent as internal standard at 22.63 MHz.[5]
[d] In $CDCl_3$ at 22.63 MHz.
[e] δAr = 128.6–130.8 ppm.

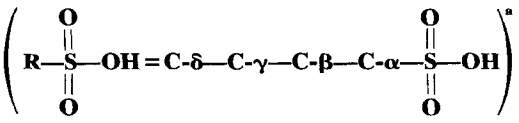
Table 6. ^{13}C NMR chemical shifts of sulfonic acids



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b	C-δ δ_C	C-δ δ^b
CH_3	**24**	39.06	41.16						
CH_3CH_2	**25**	46.62	40.52	9.2	3.3				
$CH_3CH_2CH_2$	**26**	53.73	38.13	18.8	2.7	13.7	−1.9		
$CH_3(CH_2)_2CH_2$	**27**	52.09	38.9	25.47	0.5	21.32	−3.7	13.41	0.2
$(CH_3)_2CH$	**28**	52.85	36.8	16.76	1.2				
$(CH_3)_3C$[c]	**29**	55.91	31.6	24.97	−0.2				
$(CH_3)_3CCH_2$[d]	**30**	63.39	35.5	30.89	−0.6	29.42	1.7		
$C_6H_5CH_2$[e,f]	**31**	58.36	37.1						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding alkane.
[c] In 20% (v/v) CD_3OD–$CDCl_3$.
[d] At 22.63 MHz.
[e] In 20% CH_3OH–$CDCl_3$.
[f] δAr = 128.0–134.3 ppm.

Table 7. Substituent-induced chemical shift effects in sulfonic acids



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b	C-δ δ_C	C-δ δ^b
CH_3	**24**	39.06	32.6						
CH_3CH_2	**25**	46.62	27.5	8.09	−11.6				
$CH_3CH_2CH_2$	**26**	53.73	27.3	17.41	−10.2	12.74	0.1		
$CH_3CH_2CH_2CH_2$	**27**	52.09	27.5	25.47	−11.6	21.32	−1.0	13.41	−0.5
$(CH_3)_2CH$	**28**	52.85	22.3	16.76	−10.8				
$(CH_3)_3C$[c]	**29**	55.91	14.8	24.97	−10.0				
$(CH_3)_3CCH_2$[d]	**30**	63.39	24.6	30.89	−0.9	29.42	1.4		
$C_6H_5CH_2$[e,f]	**31**	58.36	30.3						

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding thiol (Table 1).
[c] In 20% (v/v) CD_3OD–$CDCl_3$.
[d] At 22.63 MHz.
[e] In 20% (v/v) CH_3OH–$CDCl_3$.
[f] δAr = 128.02–134.28 ppm.

Table 5 shows that conversion of —SH, which is attached to a primary carbon atom, to —S(O)Cl causes an increase in shielding at C-α by 39.4 to 43.1 ppm in **18**, **19**, **22** and **23**. The α-carbons in the series **18**, **20** and **21** are 39.4, 31.6 and 23.3 ppm downfield from the same carbon atoms in the corresponding thiols **2**, **5** and **6**, respectively. This amounts to *ca* 8.1 ppm per methyl group, which is essentially the same value as observed for sulfinic acids (Table 3).

The ^{13}C NMR chemical shifts for methane- (**24**), ethane- (**25**), propane- (**26**), butane- (**27**), 2-propane- (**28**), 2-methyl-2-propane- (**29**), 2,2-dimethylpropane- (**30**) and phenylmethanesulfonic acid (**31**) are shown in Table 6. Sequential replacement of hydrogens by methyls in **24** to give **25**, **28** and **29** leads to deshielding by 7.56, 13.79 and 16.85 ppm, respectively.

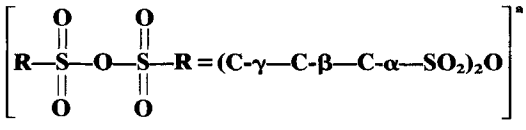
As with sulfinic acids and sulfinyl chlorides, increasing methyl substitution at C-α leads to a decrease in the α effect when compared with acyclic alkanes.

Table 7 shows that the α-carbons in the sulfonic acid series **25**, **28** and **29** are 27.5, 22.3 and 14.8 ppm downfield from the same carbon atoms in the corresponding thiols **2**, **5** and **6**, respectively. The average is 6.4 ppm per methyl group, which is *ca* 2.0 ppm less than the corresponding value from the comparison of sulfinic acids with thiols. Consequently, oxidation of a sulfinic acid to a sulfonic acid causes a shielding effect of −8.63 to −0.68 ppm at the α-carbon atom. The chemical shifts for α-carbons in the series **25**, **28** and **29** are −4.64, −2.38 and −0.68 ppm, respectively, relative to the same carbon atoms in the corresponding sulfinic acids **10**, **13** and **14**. The average is *ca* 2 ppm per methyl group.

Tables 8 and 9 show the ^{13}C NMR chemical shifts and substituent-induced effects for methanesulfonic anhydride (**32**), 2,2-dimethylpropanesulfonic anhydride (**33**) and phenylmethanesulfonic anhydride (**34**).

Table 9 shows that the α effects of sulfonic anhydrides **32**, **33** and **34** are 35.0, 28.1 and 32.4 ppm, respectively, relative to the corresponding thiols **1**, **7**

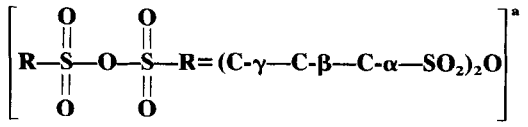
Table 8. ^{13}C NMR chemical shifts of sulfonic anhydrides



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b
CH_3	**32**	41.46	43.56				
$(CH_3)_3CCH_2$[c]	**33**	66.93	39.0	31.96	0.5	29.35	1.5
$C_6H_5CH_2$[d]	**34**	60.46	39.2				

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding alkane.
[c] At 22.63 MHz.
[d] δAr = 125.7–131.1 ppm.

Table 9. Substituent-induced chemical shift effects in sulfonic anhydrides



R	Compound number	C-α δ_C	C-α α^b	C-β δ_C	C-β β^b	C-γ δ_C	C-γ γ^b
CH_3	**32**	41.46	35.0				
$(CH_3)_3CCH_2$[c]	**33**	66.93	28.1	31.96	0.17	29.35	1.3
$C_6H_5CH_2$[d]	**34**	60.46	32.4				

[a] In $CDCl_3$ with TMS as internal standard at 62.89 MHz, except where noted.
[b] Chemical shift difference from the same carbon atom of the corresponding thiol (Table 1).
[c] At 22.63 MHz.
[d] δAr = 125.7–131.1 ppm.

and **8** (Table 1). The α effects are larger than those of the corresponding sulfonic acids **24**, **30** and **31** by 2.4, 3.5 and 2.1 ppm, respectively.

β Effects

Table 1 shows that the β effects for thiols **2–5** range from 11.5 to 13.8 ppm. It can be seen from Table 3 that the shieldings of the β-carbon atoms in sulfinic acids **10–14** are −14.3, −14.3, −13.5, −13.8 and −13.7 ppm relative to the corresponding thiols, respectively. The shielding of the β-carbon atoms in sulfinyl chlorides **18–21** are −14.0, −12.8, −13.1 and −12.5 ppm relative to the corresponding thiols, respectively (Table 5). Table 7 shows that the β effects for sulfonic acids **25–29** are −11.6, −10.2, −11.6, −10.8 and −10.0 ppm relative to the corresponding thiols, respectively.

DISCUSSION

Heretofore, it has been generally agreed that the α effect depends primarily on substituent electronegativity, the β effect is fairly constant and independent of the nature of the substituent and the δ effect is generally negligible in aliphatic systems.[23–28] However, in analysing the shielding and deshielding effects of sulfur functionalities, one has also to consider that a particular effect for a molecule is the combination of α, β and γ effects of the various atoms of which the substituent function is composed.[1,6,29–31]

The α, β and γ effects in straight-chain thiols (Table 1) are close to those of a carbon atom.[6,8,25] Introduction of methyl groups at the α-carbon leads to an increase in the α effect (Et → iso-Pr, 1.3 ppm) and a decrease in the β effect (iso-Pr → *tert*-Bu, −2.2 ppm). These values are appreciably smaller than the shift of *ca* 9.6 ppm per methyl group for the series ethane, propane and 2-methylpropane,[25] and suggest that increased methyl substitution at C-α of thiols does not lead to enhancement of the polarization of the C—S bond.

The data in Table 3 show that there is an increase in deshielding (32.2 to 36.4 ppm) at C-α of sulfinic acids **10**, **11**, **12**, **15** and **16** relative to the respective thiols. This may be due to the additive β effects of the two oxygen atoms, since the hybridization of tricoordinate sulfur in sulfinic acids is similar to the hybridization of sulfur in sulfoxides.

It may be that shielding effects are transmitted through a sulfur atom in a manner similar to that in alkanes.[6] For example, methylation of a thiol to give a methyl sulfide causes an increase of the α effect by approximately 10 ppm. This suggests that the β effect of the methyl group (9.4 ppm)[25] is transmitted through the sulfur atom. Further methylation of a methyl sulfide increases the α effect by an additional 10 ppm.[6] These hypotheses can be applied to the chemical shifts of the α-carbon atoms in sulfinic acids. That is, the monodentate oxygen atom of a sulfinic acid exerts a deshielding effect of 20 ppm (as in sulfoxides)[6] (an α effect of 20 ppm is caused by the oxidation of a dialkyl sulfide to the corresponding sulfoxide[6]), and the bidentate oxygen of 10 ppm. Although the comparison between alcohols and sulfoxides has little fundamental basis, it is of interest to note that the β effect of —OH is about 10 ppm in alcohols.[32]

The α effect in sulfinic acids **10**, **13** and **14** (Table 3) decreases with increasing methyl substitution at C-α. This decrease, which is approximately 8.4 ppm per methyl group, may be due to an increase in the polarization of the C—S bond as a result of the additional methyl groups. This enhancement of polarization may lead to a decrease in electron density at the carbon atom. (Although the reasons for this effect are not yet fully understood, it is clear that there is significant alteration in the electron distribution around the α-carbon atom.)

The increase in shielding at C-α in sulfinyl chlorides **18**, **19**, **22** and **23** by 39.4–43.1 ppm (Table 5) may be a combination of deshielding caused by the greater electronegativity of the polar sulfinyl chloride group and by the β effect of the chlorine atom.

The downfield shift of approximately 8.1 ppm per methyl group in sulfinyl chlorides **18**, **20** and **21** is

similar to the value of *ca* 8.4 ppm observed in sulfinic acids.

Interestingly, oxidation of a sulfoxide to a sulfone does not cause significant deshielding at C-α, the α effect of a sulfone appearing to be about the same as that of a sulfoxide.[6,31,33] However, oxidation of a sulfinic acid to a sulfonic acid causes a shielding effect of −8.63 to −0.68 ppm at C-α (Table 7). This is the opposite to that expected if the electronegativities of the sulfinyl and sulfonyl groups are compared.[1,6,34–37] [In contrast with the trend of ^{13}C shieldings, the α-proton shieldings vary according to the effective electronegativity of the sulfur atom.[1,3,4] For example, the α-protons of 2,2-dimethylpropanesulfinic acid (**15**) appear at δ2.85 and those of 2,2-dimethylpropanesulfonic acid (**22**) appear at δ2.98 in $CDCl_3$ solvent.]

An average deshielding of about 2.0 ppm per methyl group in sulfonic acids **25**, **28** and **29** relative to the respective sulfinic acids **10**, **13** and **14** is observed (Table 7). In contrast, sulfonic acid **30** has the highest shielding effect (8.63 ppm) relative to the corresponding sulfinic acid **15**. Thus, the increase of shielding at C-α for sulfonic acids, relative to sulfinic acids, may be attributed to bond angle widening caused by increased steric compression on the α-carbon by the sulfonic acid group relative to the sulfinic acid group.[25,31,38,39]

Oxidation of trivalent phosphorus also shows similar trends as noted above for sulfur. Namely, the effect on an adjacent carbon atom of a change in the oxidation state of phosphorus in acyclic phosphines and phosphinites has been found to be small or negative [$(\underline{C}H_3)_3P$, $\delta = 17.3$;[38] $(\underline{C}H_3)_3PO$, $\delta = 18.6$;[40] $\underline{C}H_3P(OCH_3)_2$, $\delta = 19.3$;[23] $\underline{C}H_3PO(OCH_3)_2$, $\delta = 9.8$[41]].

The downfield trend (Table 7) of about 6.4 ppm per methyl group at C-α, which is observed in sulfonic acids **25**, **28** and **29** relative to the respective thiols, can be explained as described above for sulfinic acids.[25,38,39]

The α effects of sulfonic anhydrides **32–34** (Table 8) are larger than those of the corresponding sulfonic acids **24**, **30** and **31** (Table 7) by 2.4, 3.5 and 2.1 ppm, respectively; this may reflect the inductive β effect of the bidendate oxygen atoms in **32–34**.

Except for neopentyl derivatives **15** and **22**, conversion of a thiol to a sulfinic acid or a sulfinyl chloride results in shielding at the β-carbon atom by −12.5 to −14.3 ppm (Tables 3 and 5). This shielding effect may be considered as mostly due to the sum of the γ effects of the monodentate oxygen (−6.7 ppm)[6] and bidentate oxygen or chlorine atom. The γ effect of OH or Cl is approximately −6 ppm.[25,32,38]

In comparison with the corresponding thiols, the shielding of the β-carbon atoms in sulfinic acids and sulfinyl chlorides (Tables 3 and 5) does not decrease significantly with increased methyl substitution at C-α. For example, the β effects for sulfinic acids **10**, **13** and **14** relative to the respective thiols are −14.3, −13.8 and −13.7 ppm. This is in contrast to the shielding trends observed at C-β with increased methyl substitution at C-α in acyclic sulfones,[10,31] and with γ effects which are transmitted through quaternary carbons by a variety of substituents.[42]

Oxidation of a thiol to a sulfonic acid causes an increase in shielding at the β-carbon atom by −10.00 to −11.6 ppm, except for the neopentyl derivative **30** (Table 7).

As observed for sulfinic acids and sulfinyl chlorides, increasing methyl substitution at C-α of sulfonic acids **25**, **28** and **29** does not significantly alter the shielding at the β-carbon atom (Table 7).

A number of explanations have been proposed to account for the origin of the upfield shifts at β-carbon atoms in sulfoxides and sulfones. Among these are: (1) γ-*gauche* steric interactions, causing polarization of the C—H bonds in such a way that the carbon nucleus is shielded.[43–53] (Although the shielding γ effect (*ca* 2 ppm) has been found to be particularly characteristic of alkanes,[24,44–47] the mechanistic origin of this effect remains unclear. Early attempts at identifying the origin of the γ effect involved a 'steric compression' between proximate C—H bonds. However, it is now recognized that this cannot be the sole source of the effect[28,48–53]); (2) linear electric field induced shifts causing a carbon atom to experience an upfield shift when a C—H bond is proximal to the negative end of an electric dipole such as S=O;[53] (3) hyperconjugative type interactions of free electron pairs with the S—C-α bond, accompanied by alternation of the electron density at the carbon atom situated *trans* with respect to oxygen;[31,54] (4) anisotropic shielding by the sulfoxide or sulfone group which is similar to that proposed for the nitro group.[31,55] However, these explanations do not fully account for the ^{13}C NMR shielding effects at the β-carbon atoms in sulfinic acids (Table 3), sulfinyl chlorides (Table 5) and sulfonic acids (Table 7).

The shieldings at the γ-carbon atom relative to butane for butanethiol (**4**) and its oxide derivatives **12**, **19** and **27** are essentially constant (−3 to −2 ppm). The γ effects for neopentyl-substituted compounds **7** (0.2 ppm), **15** (1.9 ppm), **22** (1.6 ppm), **30** (1.7 ppm) and **33** (1.5 ppm) are small. Interestingly, other sulfur functional groups [—S^-, —SCH_3, —$S(O)CH_3$, —SO_2CH_3, —$\overset{+}{S}(CH_3)_2$] exhibit the same γ effect of −3 to −2 ppm.[6]

The δ effects in the butanethiol (**4**) derivatives are also small (<1 ppm).

EXPERIMENTAL

^{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 35°, sweep width 15 000 Hz, acquisition time 0.5 s and 16K data points. The following parameters were used for the WH-90 FT spectrometer; pulse width 40°, sweep width 5000 Hz, acquisition time 1.5 s and 8K data points. Broad band decoupling was used.

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.[1–11]

The ^{13}C NMR spectra were obtained at *ca* 30 °C. The concentrations of the samples were 5–15% (w/w).

Thiols

Thiols **1–6** and **8** are commercially available and thiol **7** was prepared as previously described.[56]

Sulfinic acids

Sulfinic acids **12**,[57] **13**,[58] **14**,[59] **15**[16,18,60] and **16**[61] were prepared as previously described. The sodium or magnesium salts of the sulfinic acids were carefully acidified with 60% sulfuric acid in water at 0 °C, extracted three times with ether and dried ($MgSO_4$). The combined ether extracts were concentrated to give the sulfinic acids.[57,58,62]

Sulfinyl chlorides

Sulfinyl chlorides **17–20** and **22**[16,18] were prepared by the procedure of Douglass and Norton,[63] except that CH_2Cl_2 was used as the solvent. Sulfinyl chlorides **21**[59] and **23**[64] were prepared as previously described.

Sulfonic acids

Sulfonic acids **27–29** were obtained by the thermal decomposition of the corresponding sulfinic acids.[62] A typical procedure is the preparation of butanesulfonic acid (**27**). A round-bottomed flask containing butanesulfinic acid (**12**) (0.5 g, 4.1 mmol) in a nitrogen atmosphere was placed in an oil-bath which had been heated to 100 °C. After 1 h, the oil-bath was removed and the dark residue in the flask was dissolved in ether (10 ml). The ether solution was extracted with water (2×3 ml). The water extracts were combined and evaporated at 20–25 °C. The product (**27**) was dried by azeotroping off the remaining water with benzene, and weighed 0.12 g (64%). Sulfonic acid **31** was prepared[65] and purified[66] as described previously.

Sulfonic anhydrides

Sulfonic anhydrides **32**[67] and **34**[66] were prepared as previously described. Sulfonic anhydride **33** was prepared by the reaction of neopentanesulfonic acid (**30**) with *p*-tolylcarbodiimide in benzene.[66] Compound **33** was recrystallized from hexane in 31% yield, m.p. 79–80 °C. Calculated for $C_{10}H_{22}S_2O_5$: C, 41.93; H, 7.74; S, 22.39%. Found: C, 41.94; H, 7.78; S, 22.08%.

Acknowledgment

Thanks are due to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the National Science Foundation for partial support toward the purchase of the NMR spectrometers.

REFERENCES

1. F. Freeman, C. N. Angeletakis and T. J. Maricich, *Org. Magn. Reson.* **17,** 53 (1981).
2. E. Block, A. A. Bazzi, J. B. Lambert, S. M. Wharry, K. K. Andersen, D. C. Dittmer, B. H. Patwardhan and D. J. H. Smith, *J. Org. Chem.* **45,** 4807 (1980), and references cited therein.
3. T. Takata, Y. H. Kim, S. Oae and K. T. Suzuki, *Tetrahedron Lett.* 4303 (1978).
4. S. W. Bass and S. A. Evans, Jr., *J. Org. Chem.* **45,** 710 (1980).
5. D. Rinne and A. Blaschette, *Z. Anorg. Allg. Chem.* **428,** 237 (1977).
6. G. Barbarella, P. Dembeck, A. Garbesi and A. Fava, *Org. Magn. Reson.* **8,** 108 (1976).
7. Y. Kosugi and T. Takeuchi, *Org. Magn. Reson.* **12,** 435 (1979).
8. G. Dauphin and A. Cuer, *Org. Magn. Reson.* **12,** 557 (1979).
9. R. Davies and J. Hudec, *J. Chem. Soc., Perkin Trans. 2,* 1395 (1975).
10. A. H. Fawcett, K. J. Ivin and C. D. Stewart, *Org. Magn. Reson.* **11,** 360 (1978).
11. C. Nagata, J. Saito and S. Tanaka, *Bunseki Kagaku* **26,** 64 (1977); *Chem. Abstr.* **86,** 188602 (1977).
12. J. L. Kice, *Adv. Phys. Org. Chem.* **17,** 100 (1980).
13. F. Freeman, C. N. Angeletakis and T. J. Maricich, *Tetrahedron Lett.,* **22,** 1867 (1981).
14. F. Freeman and C. N. Angeletakis, *J. Org. Chem.* **46,** 3991 (1981).
15. F. Freeman and C. N. Angeletakis, *J. Am. Chem. Soc.* **103,** 6232 (1981).
16. F. Freeman and C. N. Angeletakis, *J. Am. Chem. Soc.* **104,** 5766 (1982).
17. F. Freeman, C. N. Angeletakis, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.* **104,** 1161 (1982).
18. F. Freeman, C. N. Angeletakis and T. J. Maricich, *J. Org. Chem.* **47,** 3403 (1982).
19. F. Freeman and C. N. Angeletakis, *J. Org. Chem.* **47,** 4194 (1982).
20. M. M. Chau and J. L. Kice, *J. Am. Chem. Soc.* **98,** 7711 (1976).
21. S. Oae, Y. H. Kim, T. Takata and D. Fukushima, *Tetrahedron Lett.* 1195 (1977).
22. S. Oae and T. Takata, *Chem. Lett.* 845 (1981).
23. L. D. Quin, M. D. Gordon and S. O. Lee, *Org. Magn. Reson.* **6,** 503 (1974).
24. D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.* **86,** 2984 (1964).
25. J. B. Stothers, *Carbon-13 NMR Spectroscopy,* Chapt. 3. Academic Press, New York (1972).
26. F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra,* Chapt. 2. Heyden, London (1976).
27. R. J. Abraham and P. Loftus, *Proton and ^{13}C NMR Spectroscopy.* Heyden, London (1978).
28. G. C. Levy, R. L. Lichter and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,* 2nd ed., Chapt. 3. Wiley, New York (1980).
29. J. B. Lambert, D. A. Netzel, H. Sun and K. K. Lilianstrom, *J. Am. Chem. Soc.* **98,** 3778 (1976).
30. J. Mason, *J. Chem. Soc. A* 1038 (1971).
31. S. S. McCrachren and S. A. Evans, Jr., *J. Org. Chem.* **44,** 3551 (1979).
32. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz and H. J. Reich, *J. Am. Chem. Soc.* **92,** 1338 (1970).
33. G. W. Gokel, H. M. Gerdes and D. M. Dishong, *J. Org. Chem.* **45,** 3634 (1980).
34. U. S. Mathews, J. E. Bares, J. E. Bartmess, F. G. Bordwell,

F. J. Cornforth, G. E. Drunker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, *J. Am. Chem. Soc.* **97,** 7006 (1975).
35. G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pendone and R. Albert, *J. Am. Chem. Soc.* **92,** 4002 (1970).
36. J. Julien, H. Stahl-Lavriere and A. Trautmann, *Bull. Soc. Chim. Fr.* 420 (1966).
37. J. Crosby and C. J. M. Stirling, *J. Am. Chem. Soc.* **90,** 6869 (1968).
38. Ref. 25, p. 158.
39. D. G. Gorenstein, *J. Am. Chem. Soc.* **99,** 2554 (1977).
40. G. A. Gray and S. E. Cremer, *J. Org. Chem.* **37,** 3458 (1972).
41. L. F. Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra,* Spectrum 12. Wiley–Interscience, New York (1972).
42. W. A. Ayer, L. M. Browne, S. Fung and J. B. Stothers, *Org. Magn. Reson.* **11,** 73 (1978).
43. B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.* **89,** 5319 (1967).
44. L. J. M. van de Ven and J. W. de Haan, *J. Chem. Soc., Chem. Commun.* 94 (1978).
45. M. Yamazaki, T. Takeuchi and K. Matsushita, *Kogyo Kagaku Zasshi* **74,** 656 (1971); *Chem. Abstr.* **75,** 71115a (1971).
46. E. L. Eliel, V. S. Rao and K. M. Pietrusiewicz, *Org. Magn. Reson.* **12,** 461 (1979).
47. L. P. Lindeman and J. Q. Adams, *Anal. Chem.* **43,** 1245 (1971).
48. R. Ditchfield and P. D. Ellis, in *Topics in Carbon-13 NMR Spectroscopy,* edited by G. C. Levy, Vol. 1, p. 1. Wiley, New York (1974).
49. E. L. Eliel and K. M. Pietrusiewicz, in *Topics in Carbon-13 NMR Spectroscopy,* edited by G. C. Levy, Vol. 3, p. 172. Wiley, New York (1979).
50. K. Seidman and G. E. Maciel, *J. Am. Chem. Soc.* **99,** 659 (1977) and references cited therein.
51. J. C. MacDonald, *J. Magn. Reson.* **34,** 207 (1979).
52. H. Beierbeck, J. K. Saunders and J. W. Apssimon, *Can. J. Chem.* **55,** 2813 (1977).
53. J. G. Batchelor, *J. Am. Chem. Soc.* **97,** 3410 (1975).
54. E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell and D. W. Cochran, *J. Am. Chem. Soc.* **97,** 322 (1975).
55. A. C. Huitric and W. F. Trager, *J. Org. Chem.* **27,** 1926 (1962).
56. F. G. Bordwell, B. M. Pittana and M. Kuell, *J. Am. Chem. Soc.* **73,** 5004 (1951).
57. P. Allen, *J. Org. Chem.* **7,** 23 (1942).
58. J. Fenton and E. Ingold, *J. Chem. Soc.* 2341 (1929).
59. D. Barnard, L. Bateman, M. E. Cain, T. Colclough and J. L. Cunneen, *J. Chem. Soc.* 5339 (1961).
60. M. Uchino, K. Suzuki and M. Sekiya, *Synthesis* 794 (1977).
61. J. L. Kice and R. H. Engebrecht, *J. Org. Chem.* **27,** 4654 (1962).
62. J. von Braun and K. Weissbach, Chem. Ber. **63,** 2836 (1930).
63. I. B. Douglass and R. V. Norton, *J. Org. Chem.* **33,** 2104 (1968).
64. M. L. Kee and I. B. Douglass, *Org. Prep. Proceed.* **2,** 235 (1970).
65. T. B. Johnson and J. A. Ambler, *J. Am. Chem. Soc.* **36,** 372 (1914).
66. J. F. King and M. Aslam, *Can J. Chem.* **57,** 3278 (1979).
67. H. G. Khorana, *Can J, Chem.* **31,** 586 (1953).

Received 17 July 1981; accepted (revised) 4 August 1982