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UNUSUAL CHEMICAL SHIFTS IN ^{1}H- AND ^{13}C-NMR SPECTRA OF UNSYMMETRICAL DISULFIDES, THIOLSULFINATES AND THIOLSULFONATES

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Despite numerous reports, there has been no systematic study on ^{1}H- and ^{13}C-NMR of a series of disulfides[1)] and their oxidation derivatives such as thiolsulfinates[2)] and thiolsulfonates[3)], especially on ^{13}C-NMR of unsymmetrical disulfides, thiolsulfinates and thiolsulfonates.

In our course of study on the oxidation of unsymmetrical disulfides(A) to the corresponding monoxides(B) and dioxides(C), we have found that ^{1}H- and ^{13}C-NMR spectra[4)] of unsymmetrical disulfides(A), thiolsulfinates(B) and thiolsulfonates(C) showed unexpected chemical shifts, especially at α-position; namely, α-methyl or methylene protons of B showed larger downfield shifts than those of C, and α-carbons of B displayed the highest shifts among those of the three, A, B & C, while β'-carbons of B and C also showed higher field shifts than β-carbons of B and C. These unusual NMR behaviors have led us to study somewhat systematically the NMR chemical shifts of these sulfur compounds of different oxidation states by first synthesizing numerous unsymmetrical thiolsulfinates either by treatment of sulfinyl chlorides with thiols[5)] in the presence of t-amine, or by oxidation with H_2O_2-AcOH according to the methods of Isenberg[6)] (for 10, 10', 11, & 11'), and thiolsulfonates by oxidation of the corresponding thiolsulfinates with sodium metaperiodate[7)] (besides 11 & 11').

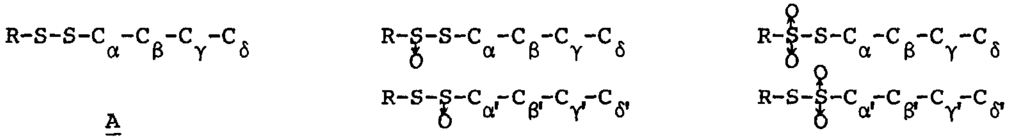

A B C

Fig. I

Generally the electron-withdrawing effect of sulfur group is considered to increase as the progress of the oxidation state of sulfur atom, i.e., sulfide $<$ sulfoxide $<$ sulfone, or sulfinate $<$ sulfonate(Table II).

Most of the α', β', γ', and δ'-protons of B and C are shifted substantially to downfield as expected (Table Ib). However, both α- and β-protons of B are shifted more to downfield than those of C despite the relatively weaker inductive effect of the -S(O)-S- than that of the -S(O)$_2$-S- group (Table Ia).

Table Ia ^{1}H-NMR Chemical Shifts of Unsymmetrical Disulfides, Thiolsulfinates and Thiolsulfonates in CDCl$_3$ at 27°, δ[ppm].

R-S(O)$_x$-S-R' (R'= $-C_\alpha-C_\beta-C_\gamma-C_\delta$), x=0, 1 & 2.

No.,	R= ,	R'=	x=0: R-S-S-R'				x=1: R-S(O)-S-R'				x=2: R-S(O)$_2$-S-R'			
			C_α	C_β	C_γ	C_δ	C_α	C_β	C_γ	C_δ	C_α	C_β	C_γ	C_δ
1	Ph	Me	2.39	*	*	*	2.53	*	*	*	2.48	*	*	*
2	"	Et	2.71	1.29	*	*	3.13$^{a)}$ 3.16	1.43	*	*	3.00	1.28	*	*
3	"	Pr	–$^{b)}$	–	–	*	3.12$^{a)}$ 3.09	1.80	1.03	*	2.97	1.62	0.90	*
4	"	Bu	[2.65]	–	–	[0.87]	3.14	–	–	0.92	2.99	–	–	0.83
5	"	p-Tol	–$^{c)}$				2.53[2.30]$^{c)}$				[2.22]$^{c)}$			
6	p-Tol	Me	–$^{c)}$		–$^{d)}$		2.38(2.12)$^{c)}$		2.53(2.30)$^{d)}$		(2.13)$^{c)}$		(2.21)$^{d)}$	
7	p-ClC$_6$H$_4$	Me	[2.26]$^{d)}$				2.40(2.33)$^{d)}$				(2.32)$^{d)}$			

Table Ib R-S-S(O)$_y$-R' (R'= $-C_{\alpha'}-C_{\beta'}-C_{\gamma'}-C_{\delta'}$), y=0,1 & 2.

No.,	R= ,	R'=	y=0: R-S-S-R'				y=1: R-S-S(O)-R'				y=2: R-S-S(O)$_2$-R'			
			C_α	C_β	C_γ	C_δ	$C_{\alpha'}$	$C_{\beta'}$	$C_{\gamma'}$	$C_{\delta'}$	$C_{\alpha'}$	$C_{\beta'}$	$C_{\gamma'}$	$C_{\delta'}$
1'	Ph	Me	2.39	*	*	*	2.90	*	*	*	3.12	*	*	*
2'	"	Et	2.71	1.29	*	*	3.10	1.41	*	*	3.16	1.41	*	*
3'	"	Pr	–$^{b)}$	–	–	*	3.09	1.86	1.08	*	3.14	1.91	1.01	*
4'	"	Bu	[2.65]	–	–	[0.87]	3.11	–	–	0.96	3.18	–	–	0.92
5'	"	p-Tol	[2.26]$^{c)}$				2.37$^{c)}$				2.40$^{c)}$			
8'	⟨H⟩	Me	2.32[2.33]$^{d)}$				2.95[2.86]$^{d)}$				3.32$^{d)}$			

* [ ]: Chemical shift in CCl$_4$ from TMS as an internal standard.

* ( ): Chemical shift in CD$_3$CO$_2$D-D$_2$O from TMS as an external standard.

a) Magnetically non-equivalent protons.
b) not determined.
c) for methyl protons of p-tolyl group.
d) for methyl protons of methyl group.

Oxidation of a disulfide, e.g., 3-methyl 1,2-dithiane (9) to the corresponding thiolsulfinate (e.g., 10) causes a normal downfield shift (from 41.4 to 57.4 ppm) at the α'-carbon due to the increase of the inductive effect (Fig. II & III). However, the ^{13}C-NMR chemical shifts of α- and β'-carbons of B (α-carbons: 34.9 in 10, 33.1 in 10', 27.6 in 13, and 35.1 ppm in 16; β'-carbons: 21.3 in 10, 22.4 in 10', 7.6 in 13' and 17.1 ppm in 16') are shifted to the highest fields among those of the three sulfur derivatives of different oxidation states, A, B and C.

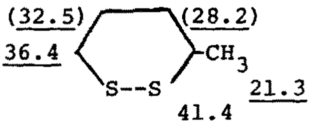
Oxidation of a thiolsulfinate (e.g., 10) to the thiolsulfonate (e.g., 11) also caused a downfield shift (from 57.4 to 65.1 ppm) at α'-carbon due to the electron-withdrawing inductive effect. But β'-carbons of C (24.8 in 11, 25.0 in 11', 8.3

Table II. ^{1}H-NMR Chemical Shift of Unsymmetrical Sulfinates and Sulfonates in $CDCl_3$ at 27°, δ[ppm].

$Ph{-}S(O)_z{-}O{-}R$ ($R = -C_1-C_2-C_3-C_4$)

R=	Me	Et		Pr			^{i}Pr		Bu		
	C_1	C_1*	C_2	C_1*	C_2	C_3	C_1	C_2*	C_1*	C_2C_3	C_4
Sulfinate z=1	3.44	3.70* 4.10	1.26	3.53* 3.97	1.62	0.89	4.57	1.22* 1.36	3.43* 3.94	- -	0.83
Sulfonate z=2	3.72	4.09	1.28	3.97	1.65	0.87	4.69	1.27	4.04	- -	0.86

* Magnetically non-equivalent protons.



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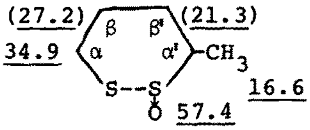

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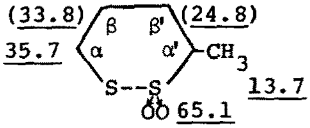

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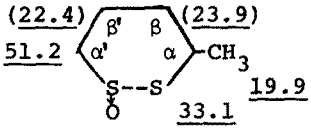
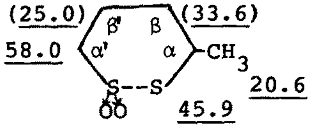


10'

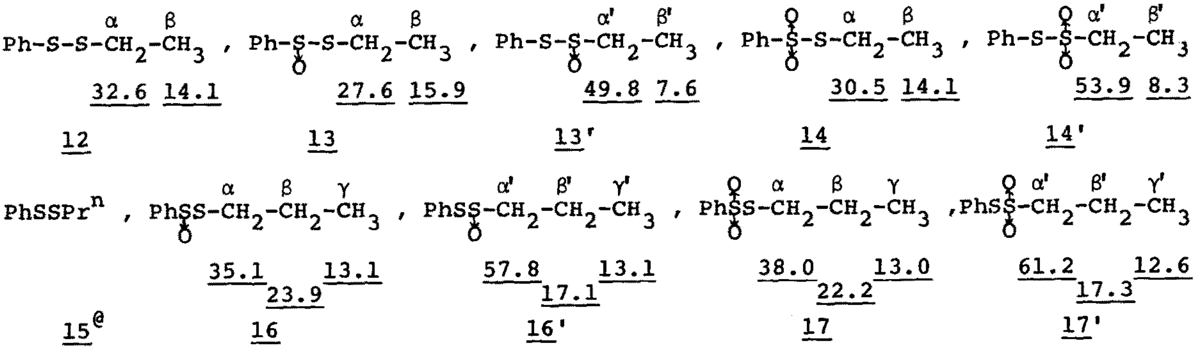


11'

Fig. II

* Chemical shifts, δ[ppm], in $CDCl_3$ from TMS as an internal standard at 27°.
* ( ): Assignments are not complete: see ref.8).

in 14', and 17.3 ppm in 17') are shifted to the highest field among those of the three derivatives , A, B and C. Particularly, the chemical shift of β'-carbon of 11 is the highest(13.7 ppm). This unusual chemical shift seems to indicate an increase of electron density on the carbon atom. Probably the methyl group of 11 is favorably located for a hetero steric compression of sulfonyl group due to the fixed six member ring of the dithiane.



$\mathrm{Ph{-}S{-}S{-}}\overset{\alpha}{\underset{32.6}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta}{\underset{14.1}{\mathrm{CH_3}}}$, $\mathrm{Ph{-}}\underset{O}{\mathrm{S}}\mathrm{{-}S{-}}\overset{\alpha}{\underset{27.6}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta}{\underset{15.9}{\mathrm{CH_3}}}$, $\mathrm{Ph{-}S{-}}\underset{O}{\mathrm{S}}\mathrm{{-}}\overset{\alpha'}{\underset{49.8}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta'}{\underset{7.6}{\mathrm{CH_3}}}$, $\mathrm{Ph{-}}\overset{O}{\underset{O}{\mathrm{S}}}\mathrm{{-}S{-}}\overset{\alpha}{\underset{30.5}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta}{\underset{14.1}{\mathrm{CH_3}}}$, $\mathrm{Ph{-}S{-}}\overset{O}{\underset{O}{\mathrm{S}}}\mathrm{{-}}\overset{\alpha'}{\underset{53.9}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta'}{\underset{8.3}{\mathrm{CH_3}}}$

12 13 13' 14 14'

$\mathrm{PhSSPr^n}$, $\mathrm{Ph}\underset{O}{\mathrm{S}}\mathrm{S{-}}\overset{\alpha}{\underset{35.1}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta}{\underset{23.9}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\gamma}{\underset{13.1}{\mathrm{CH_3}}}$, $\mathrm{PhS}\underset{O}{\mathrm{S}}\mathrm{{-}}\overset{\alpha'}{\underset{57.8}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta'}{\underset{17.1}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\gamma'}{\underset{13.1}{\mathrm{CH_3}}}$, $\mathrm{Ph}\overset{O}{\underset{O}{\mathrm{S}}}\mathrm{S{-}}\overset{\alpha}{\underset{38.0}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta}{\underset{22.2}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\gamma}{\underset{13.0}{\mathrm{CH_3}}}$, $\mathrm{PhS}\overset{O}{\underset{O}{\mathrm{S}}}\mathrm{{-}}\overset{\alpha'}{\underset{61.2}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\beta'}{\underset{17.3}{\mathrm{CH_2}}}\mathrm{{-}}\overset{\gamma'}{\underset{12.6}{\mathrm{CH_3}}}$

15@ 16 16' 17 17'

Fig. III

* Chemical shifts, δ[ppm], in $CDCl_3$ from TMS at 27°. @ not determined(15).

In the case of thiolsulfinates, the higher chemical shifts of α- and β'-carbons(γ-positions) of B are most likely resulted from a polarization of C-H bond(well known γ-effect9)). An interaction between the oxygen attached to sulfur atom and the protons of α- and β'-methyl or methylene group may also cause the α- or β'-carbon electron rich as shown in Fig. IV. This five member ring interaction is very likely to cause the larger downfield shifts of α- and β'-protons of B in ^{1}H-NMR spectra.

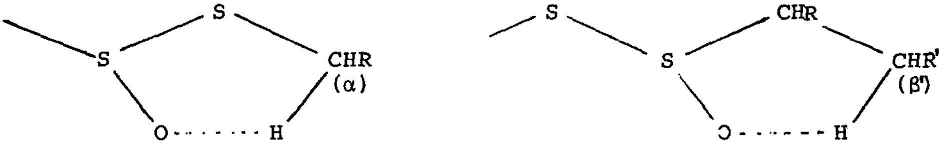


Fig. IV

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8) A mixture of 10 and 10', and also a mixture of 11 and 11' were used for the ^{1}H- and ^{13}C-NMR samples. No isomeric peak of methyl carbon of 10 and 10' was observed: only one peak(33.1 in 10' and 57.4 ppm in 10) which shows a rapid equilibrium of two diastereomeric isomers was confirmed by off-resonance NMR spectra: A quick cleavage and a recombination of the sulfur-sulfur bond of the thiolsulfinate may cause the rapid stereomutation as suggested by Koch and Fava; P.Koch & A.Fava, J. Am. Chem. Soc., 90, 3867(1968).
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