

Proton Magnetic Resonance Spectra of Some Organosulfur Compounds

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Abstract

The proton magnetic resonance spectra of various sulfur derivatives of long-chain carboxylic acids have been studied. The types of compounds studied include those where the methylene chain is interrupted by a sulfide or a sulfone group and those where the carboxyl group has been replaced by $-\text{SO}_3-$ or $-\text{C}(=\text{O})\text{S}-$. The spectral effects produced by the sulfur-containing groups are discussed. The effect of the sulfur group in sulfides and sulfones is compared with the effect of an oxygen atom in a similar environment. The effect of the $-\text{SO}_3-$ and $-\text{C}(=\text{O})\text{S}-$ groups on neighboring methylene groups is compared with the effect of the carboxyl group.

Introduction

The proton magnetic resonance spectra of many types of organic compounds have been investigated in considerable detail and various correlation charts, which graphically describe the relation between chemical shift and intramolecular environment, have been published (1, 2, 3, 4). However, relatively little has been reported on saturated aliphatic compounds containing sulfur atoms. The spectra of two such compounds, methyl ethyl sulfide and methyl amyl sulfide, are included in the NMR spectrum catalog of Varian Associates (5). *Tau* values for methyl and methylene sulfide groups are reported by Nukada *et al.* (1) in their study of the classification of proton chemical shifts. Allen *et al.* have reported *tau* values for 1-dodecyl sulfide, disulfide, sulfoxide and sulfone (6). An early paper by Meyer *et al.* (3) presents chemical shift data for the protons of the thiol and sulfonic acid groups. Some dialkyl sulfides, sulfites, and sulfates are included in studies of the PMR spectra of alkyl derivatives by Dailey and Shoolery (7) and by Cavanaugh and Dailey (8 and 9). In studying long-range spin-spin coupling in alkyl sulfur compounds, van Meurs finds a small, but measureable, proton-proton coupling in dimethyl sulfide, sulfoxide, and sulfone (10). However, the corresponding coupling constant decreases with the replacement of one methyl group by a hetero or higher alkyl group. Replacement of both methyl groups reduces the long-range coupling constant to less than 0.2 cps.

The present study describes the spectral effects produced by introducing various sulfur-containing groups into long-chain molecules related to fatty acids. The various types of compounds studied included those where the methylene chain is interrupted by a sulfide or a

sulfone group. Also included were compounds where the carboxyl group has been replaced by $-\text{SO}_3-$ or $-\text{C}(=\text{O})\text{S}-$. Some derivatives which have a phenyl or a benzyl group attached to the sulfur atom of the sulfur-containing group were also investigated. Since the chemistry of organosulfur compounds is continuously growing in usefulness and interest, additional data are of value to supplement existing information regarding characteristic chemical shifts. Furthermore, a comparison of the effect of sulfur atoms with the effect of oxygen atoms in a similar chemical environment is of interest.

Experimental

The spectra of all samples were obtained on a Varian DP-60† nuclear magnetic resonance spectrometer at room temperature; i.e., $30 \pm 1^\circ\text{C}$ in the magnet air gap. The amplitude of the radio field was set at 60 db down from one-half watt so as to avoid saturation of the signal. The external magnetic field was swept at the rate of 0.5 to 1.0 cps/sec. Spinning 5-mm OD sample tubes were used to achieve maximum field homogeneity. Calibration of the spectra was accomplished by the usual side-band technique using a Hewlett-Packard 200 CD wide-band oscillator. Tetramethylsilane (K & K Laboratories, Inc., Jamaica, New York) was used as an internal reference.

Each spectrum was recorded two to four times to reduce the possibility of instrumental error. The chemical shift values given here are the average of those obtained from the several recordings of each spectrum. The delta scale was used to report chemical shifts where $\delta = 0.00$ for tetramethylsilane with positive values to low field. The chemical shifts of multiplets were taken at the midpoint.

Pure crystalline samples dissolved in carbon tetrachloride (Baker Analyzed Reagent, J. T. Baker Chemical Company, Phillipsburg, New Jersey) or deuteriochloroform (Varian Associates, Palo Alto, California) were used. The concentration range of the solutions was 0.1 to 0.2 M. The preparation and properties of the investigated samples have been described in the literature (11, 12, 13, 14, 15, 16, 17).

†Mention of commercial products does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

*Eastern Utilization Research and Development Division, ARS, USDA.

TABLE I. SPECTRAL ASSIGNMENTS

Compounds	Proton	Chemical Shifts	No. of Lines
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2-\text{S}-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-butylthioundecanoic acid	a b c d	0.91 1.29 2.34 2.50	3 1 3 3
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2-\text{S}-\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-amylthioundecanoic acid	a b c d	0.88 1.27 2.33 2.48	3 1 3 3
$\text{CH}_3(\text{CH}_2)_5\text{CH}_2-\text{S}-\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-heptylthioundecanoic acid	a b c d	0.89 1.30 2.35 2.49	3 1 3 3
$\phi-\text{CH}_2-\text{S}-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-benzylthioundecanoic acid	a b c d e	1.25 2.29 2.40 3.68 7.29	1 3 3 1 1
$\phi-\text{S}-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-phenylthioundecanoic acid	a b c d	1.27 2.34 2.90 7.26	1 3 3 complex
$\text{CH}_3-\text{S}(=\text{O})_2-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-methylsulfoundecanoic acid	a b c d	1.30 2.33 2.89 3.00	1 3 1 3
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2-\text{S}(=\text{O})_2-\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-butylsulfoundecanoic acid	a b c d	0.96 1.29 2.33 2.97	3 1 3 3
$\phi-\text{S}(=\text{O})_2-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH}$ 11-phenylsulfoundecanoic acid	a b c d	1.23 2.32 3.09 7.72	1 3 3 complex
$\phi-\text{CH}_2-\text{S}(=\text{O})_2-\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{O}-\text{CH}_3$ methyl 11-benzylsulfoundecanoate	a b c d e f	1.26 2.29 2.83 3.66 4.21 7.40	1 3 3 1 1 1
$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2-\text{S}(=\text{O})_2-\text{O}-\text{CH}_3$ methyl tetradecane sulfonate	a b	2.98 3.81	3 1

Results and Discussion

The structural formulae of the investigated compounds, the observed chemical shifts, and the number of observed lines are listed in Table I. Figure 1 exhibits a schematic correlation between characteristic chemical shifts and intramolecular environment. Some typical spectra are shown in Figures 2 and 3.

The PMR spectra of methyl esters of saturated, long-chain carboxylic acids, which could be regarded as the parent compounds of the investigated sulfur derivatives, exhibit four main peaks (18). The high-field triplet ($\delta = 0.88$ to 0.93) corresponds to the terminal methyl group. The chain methylene groups produce a broad band at $\delta = 1.25$ to 1.33 . The low-field triplet is produced by the alpha methylene group adjacent to the carboxyl group and falls in the range, $\delta = 2.25$ to 2.33 . The methoxy hydrogens of the methyl ester group produce a singlet in the range, $\delta = 3.55$ to 3.70 .

The introduction of a sulfide group into the methylene chain has a deshielding effect, with respect to the chain methylene groups, on the first methylene group on either side of the sulfur atom. Each methylene group is represented by a triplet at $\delta = 2.50$. This downfield shift (approximately 1.2 ppm) is considerably smaller than that produced by an oxygen atom in a similar environment (1); *i.e.*, the deshielding effect of an oxygen

atom in an ether is greater than the deshielding effect of a sulfur atom in a sulfide (thioether). Under the present experimental conditions, long-range proton-proton coupling through the sulfur atom was not observed. In 11-benzylthioundecanoic acid the presence of the phenyl ring causes slightly less of a downfield shift in the methylene group attached to the sulfur atom, but not to the ring ($\delta = 2.40$). However, in 11-phenylthioundecanoic acid the presence of the phenyl group enhances the downfield shift caused by the sulfur, so that the methylene group attached to the sulfur occurs at $\delta = 2.90$. Furthermore, the ring protons of 11-phenylthioundecanoic acid produce a complex multiplet centered about 7.26 ppm, whereas the ring protons of 11-benzylthioundecanoic acid produce only one observable line at 7.29 ppm.

The effect of a sulfo group on neighboring methylene protons is different from the effect of a sulfide group only in degree. The downfield shift is greater than in the sulfides but less than the shift produced by an oxygen atom in a similar environment. The first methylene group on either side of the $-\text{SO}_2-$ group is represented by a triplet in the range, $\delta = 2.9$ to 3.0 , a downfield shift of approximately 1.7 ppm from the chain methylene position. Under the present experimental conditions, long-range proton-proton coupling through the sulfo group was not observed. In methyl 11-benzylsulfo-

TABLE I. SPECTRAL ASSIGNMENTS (Continued)

Compound	Proton	Chemical Shifts	No. of Lines
$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2-\text{S}(=\text{O})_2-\text{O}-\text{CH}_3$ methyl hexadecane sulfonate	a b c d	0.93 1.31 2.98 3.81	3 1 3 1
$\text{CH}_3-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_3$ dimethyldithiosebacate	a b c	1.33 2.52 2.28	1 3 1
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ diamyl dithiosebacate	a b c d	0.93 1.32-1.55 2.49 2.83	3 3 3 3
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2-\phi$ benzyl thiostearate	a b c d e	0.88 1.25 2.48 4.03 7.18	3 1 3 1 1
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}(=\text{O})\text{S}-\phi$ phenyl thiostearate	a b c d	0.88 1.27 2.65 7.39	3 1 3 1
$\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2\text{CH}_2-\text{O}(\text{O}=\text{C})\text{CCH}_2(\text{CH}_2)_7\text{CH}_3$ 1-thiodecanoate-2-decanoate ethane	a b c d e f	0.90 1.31 2.27 2.55 3.11 4.18	3 1 3 3 3 3
$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2\text{CH}_2-\text{O}(\text{O}=\text{C})\text{CCH}_2(\text{CH}_2)_{13}\text{CH}_3$ 1-thiohexadecanoate-2-hexadecanoate ethane	a b c d e f	0.90 1.28 2.26 2.54 3.09 4.16	3 1 3 3 3 3
$\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{C}(=\text{O})\text{S}-(\text{CH}_2)_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_9\text{CH}_3$ 1,2-dithiododecanoate ethane	a b c d	0.90 1.28 2.52 3.01	3 1 3 1
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}(=\text{O})\text{S}-(\text{CH}_2)_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_{10}\text{CH}_3$ 1,2-dithiohexadecanoate ethane	a b c d	0.88 1.26 2.53 3.03	3 1 3 1
$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_{11}\text{CH}_3$ 1,3-dithiotetradecanoate propane	a b c d e	0.89 1.28 1.82 2.53 2.93	3 1 3 3 3
$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_{13}\text{CH}_3$ 1,3-dithiohexadecanoate propane	a b c d e	0.90 1.29 1.93 2.50 2.90	3 1 3 3 3
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}(=\text{O})\text{S}-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-\text{S}(=\text{O})\text{CCH}_2(\text{CH}_2)_{10}\text{CH}_3$ 1,4-dithiohexadecanoate butane	a b c d e	0.97 1.27 1.62 2.50 2.87	3 1 3 3 3

undecanoate the presence of the phenyl ring causes slightly less of a downfield shift in the methylene group attached to the sulfo group but not to the ring ($\delta = 2.83$). In comparing 11-phenylsulfoundecanoic acid with the phenylthio derivative supra, we found that the presence of the phenyl group causes less of a downfield shift in the phenylsulfo derivative than it does in the phenylthio derivative; i.e., 0.1 ppm as compared with 0.4 ppm. Again, when the phenyl group is attached to the sulfur-containing group, the ring protons produce a complex multiplet. For 11-phenylsulfoundecanoic acid the midpoint of the complex multiplet is at $\delta = 7.72$. With the interposition of a methylene group between the sulfur-containing group and the phenyl group, the ring protons produce only one observable line, which occurs at $\delta = 7.40$ for methyl 11-benzylsulfoundecanoate.

Next we shall compare the spectra of methyl esters of sulfonic acids with those of carboxylic acids. Since the sulfonic acid group is more electronegative than the carboxyl group, the protons of the methyl ester and alpha methylene groups are less shielded when these groups are adjacent to the sulfonic acid group ($-\text{SO}_3-$). In carboxylic methyl esters the chemical shifts of the alpha methylene and methyl ester groups are approximately 2.3 and 3.6 ppm, respectively. The chemical shifts of the same two groups in methyl tetradecane sulfonate and methyl hexadecane sulfonate are 2.98 and 3.81, respectively. The difference in the chemical shifts of the alpha methylene groups, as between the carboxylic methyl esters and the sulfonic methyl esters, is approximately 0.7 ppm, whereas the difference in the chemical shifts of the methyl ester groups is only 0.1 to 0.2 ppm.

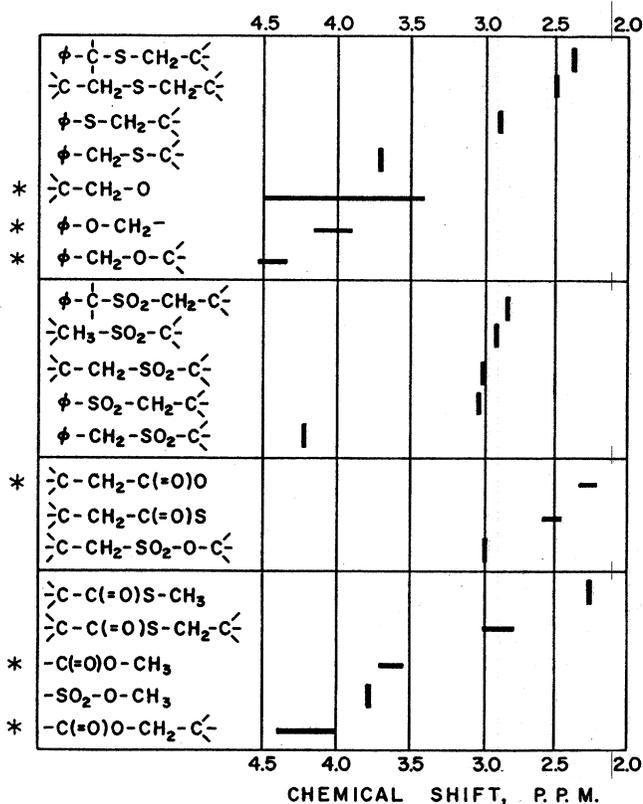


FIG. 1. CORRELATION BETWEEN CHEMICAL SHIFT AND INRAMOLECULAR ENVIRONMENT

*from ref. 1

Upon examination of the chemical shifts of the thiocarboxylic esters $[-\text{C}(=\text{O})\text{S}-\text{R}]$ we noted that the thiocarboxyl group causes less deshielding of an aliphatic methylene group (in the position marked "R") than does the carboxyl group. The downfield shift for the first methylene group of an alkyl thioester group is approximately 1.5 ppm from the aliphatic methylene position from about 1.3 to about 2.8 ppm. The first methylene group of an alkyl ester group ($\delta = 4.1$ to 4.2) is shifted approximately 2.9 ppm downfield from the aliphatic methylene position. In both methyl esters and methyl thioesters the singlet peak representing the carbomethoxy protons occurs 0.5 to 0.6 ppm upfield from the triplet (quartet in the case of an ethyl ester group) representing the first methylene group of higher alkyl esters and thioesters. In benzylthioesterate the methylene group between the sulfur and the phenyl group has a chemical shift of $\delta = 4.03$, which is nearly the same as that of the first methylene group of a carboxylic ester group for which $\delta = 4.1$ to 4.2 ppm. The combined deshielding effect of the sulfur and the phenyl groups on a methylene group between them is nearly equal to the deshielding with respect to an aliphatic methylene group which occurs at the first methylene group of an alkyl ester group. The ring protons in the spectra of both benzyl- and phenylthioesterate are represented by only one observed line. The triplet due to the alpha methylene group of the thiocarboxylic ester $[-\text{CH}_2-\text{C}(=\text{O})\text{S}-]$ falls in the range, $\delta = 2.48$ to 2.55 ppm. In this case the thiocarboxyl group causes greater deshielding with respect to an aliphatic methylene group than does the carboxyl group. The downfield shift is greater by 0.2 to 0.3 ppm.

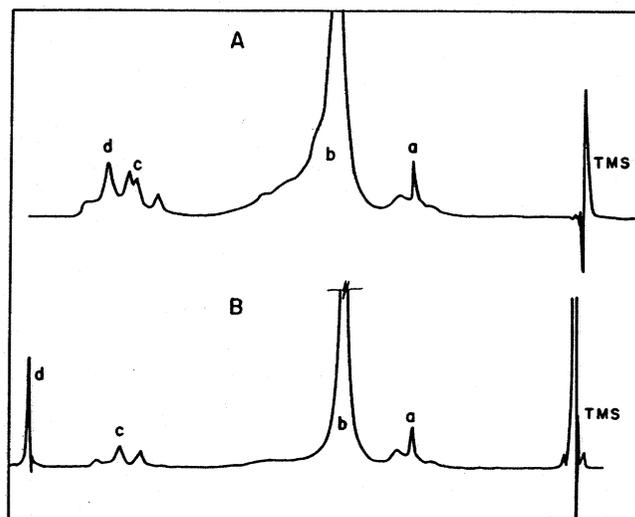
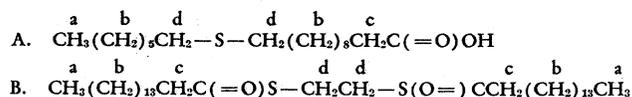


FIG. 2. PMR SPECTRA OF A SULFIDE AND A THIOCARBOXYLIC ESTER



Conclusions

Proton magnetic resonance can readily identify sulfur derivatives of long-chain carboxylic acids, distinguish them from their parent compounds, and, in many cases, from each other. Previous reports have suggested that in a qualitative manner the chemical shifts of protons in the alpha position increase with increasing effective electronegativity values of substituent groups (7, 19). In the investigated compounds the chemical shifts of protons in the alpha position decrease in the following orders:

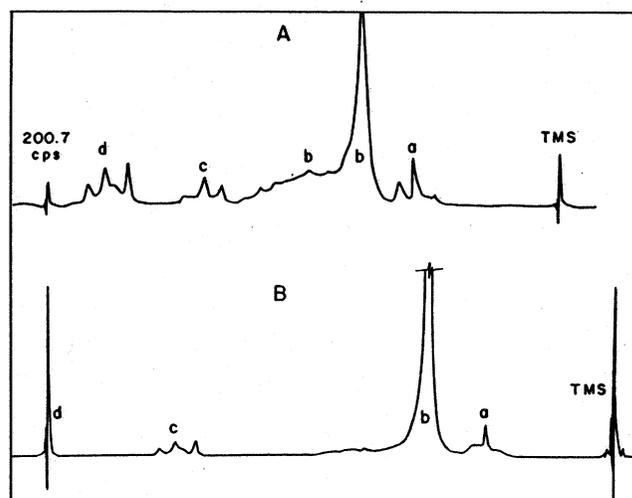
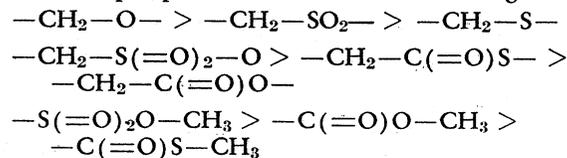
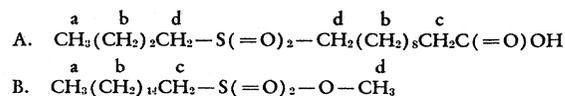


FIG. 3. PMR SPECTRA OF A SULFONE AND A SULFONATE



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