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The Influence of the Number of Sulfur Atoms on the PMR Chemical Shifts in Aryl Polysulfides

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The proton magnetic resonance for sulfur compounds has received major study.[1] But limited information for aromatic proton signals has been offered among aromatic sulfur derivatives because the aromatic signals were generally complex.[2] A number of aromatic sulfur compounds have been synthesized in our laboratory on the study of iron-catalyzed aromatic sulfuration.[3] During the course of the study, the aromatic proton signals are found to be influenced by increasing the sulfur chain length in the compounds. In this paper, the results of such observation and discussion for them are reported.

The ortho protons to sulfur atoms of aryl poly-

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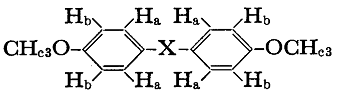
[1] S. R. Heller, "NMR Spectra of Sulfur Compounds," Intra-Science Chemistry Reports, Vol. 2, No. 4, Intra-Science Research Foundation, California (1968).

[2] C. Brown and D. R. Hogg, *J. Chem. Soc., B*, **1968**, 1315.

[3] T. Fujisawa, N. Ohtsuka, T. Kobori and G. Tsuchihashi, *Tetrahedron Lett.*, **1968**, 4533, 5071; *ibid.*, **1969**, 4291; T. Fujisawa and M. Kakutani, *J. Polym. Sci., B*, **8**, 19 (1970); T. Fujisawa, N. Ohtsuka and G. Tsuchihashi, This Bulletin, **43**, 1189 (1970).

TABLE 1. CHEMICAL SHIFTS OF

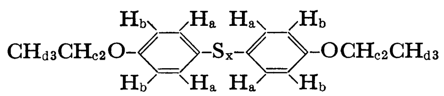


(δ in CCl_4)

X	H_a(d)	H_b(d)	H_c(s)	J_{ab}(Hz)
-S-	7.17	6.71	3.73	8.4
-SS-	7.30	6.71	3.74	8.4
-SSS-	7.39	6.71	3.76	8.5
-SO-	7.43	6.85	3.79	8.8
$-SO_2-$	7.80	6.89	3.79	9.0 ($CDCl_3$)

Abbreviations used: s, singlet; d, doublet.

TABLE 2. CHEMICAL SHIFTS OF



(δ in CCl_4)

X	H_a(d)	H_b(d)	H_c(q)	H_d(t)	J_{ab}	J_{cd}(Hz)
1	7.15	6.66	3.89	1.37	8.8	6.8
2	7.28	6.69	3.93	1.39	9.2	7.0
3	7.37	6.68	3.95	1.41	9.2	7.0

Abbreviations used: d, doublet; t, triplet; q, quartet.

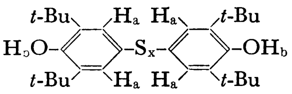
sulfides vary their PMR chemical shifts to lower field with increase of the number of the sulfur atoms. As shown in Tables 1 and 2, the number of the sulfur atoms exerts a considerable effect on the chemical shifts of H_a protons of anisole and phenetole derivatives in contrast with that of H_b. The slight shift of alkoxyl protons toward lower field was also observed. The similar effect of polysulfide linkage has already been reported in aliphatic series by Van Warzer and Grant,[4] although their data fit to an approximation based on the theory for the "neighbor anisotropy effect". The observation of the same tendency between aromatic and aliphatic protons is interesting because they often exist in different electronic circumstances. For example, in *p*-methoxyphenyl methyl sulfide, the signal for S-methyl protons (δ=2.36) appears at higher field than that for O-methyl protons (δ=3.70), but the situation is reverse in the chemical shift of ortho ring protons to oxygen (δ=6.69) and that to sulfur (δ=7.14). This is reasonably explained by inductive effect in aliphatics and by mobile π-electron system in aromatics. The chemical shift of the O-ortho protons moves considerably to higher field than that of benzene by electron releasing resonance by oxygen, whereas the signal of the S-ortho protons appears at about the same position of that of benzene because the conjugation between the ring and sulfur is suggested to be relatively small. In general, chemical shifts of ortho protons of substituted benzene ring are known to shift by influence of π-electron density and of anisotropy and/or inductive effect of the substituents.[5]

Signals for neighboring protons to electron-withdrawing group shift to lower field with the inductive order as shown in sulfide-sulfoxide-sulfone series (Table 1 and Ref. 6). Accordingly, it is reasonably assumed that as number of sulfur atoms in the polysulfide series increases, the strength of inductive effect becomes more intense. It is noteworthy that the same tendency has been also observed in the ultraviolet absorption spectra of di-*p*-tolyl polysulfides, in which as number of sulfur atoms increases, the shift toward the shorter wavelength occurs in primary band attributable to benzene ring and the absorbance becomes more intense.[7] This phenomenon suggests that the electron density of the benzene ring decreases by the localization of the electron to the center of polysulfide linkage with increasing chain length of sulfur atoms, coupled with the fact that the shift toward the longer wavelength occurs in secondary band attributable to linear sulfur–sulfur linkage. In other words, this is due to the electron-withdrawing effect of polysulfide linkage and strongly supports above inductive effect by polysulfide group.

A remarkable example of this tendency is found in the chemical shifts of thiobis(2,6-di-*t*-butylphenol) series as shown in Table 3. These chemical shifts of the ortho ring protons are particularly suited for the quantitative analyses of the mixture of the polysulfides with their integration ratio because independent singlet peaks for these absorptions can be assigned clearly.

As shown above, the data of the chemical shifts for polysulfides can be explained in terms of the inductive effect of polysulfide linkage, but a system illustrative of anisotropy effect was also observed. The chemical shifts of ortho protons of various

TABLE 3. CHEMICAL SHIFTS OF



(δ in CCl_4)

X	H_a(s)	H_b(s)	*t*-Bu(s)
1	7.02	4.98	1.40
2	7.21	5.06	1.41
3	7.31	5.13	1.42
4	7.38	5.22	1.46

Abbreviation used: s, singlet.

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[4] J. R. Van Warzer and D. Grant, *J. Amer. Chem. Soc.*, **86**, 1450, 3021 (1964). For methyl polysulfide: G. R. Pettit, I. B. Douglass, and R. A. Hill, *Can. J. Chem.*, **42**, 2357 (1964).

[5] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

[6] J. B. Hyne and J. W. Greidanus, *Can. J. Chem.*, **47**, 803 (1969).

[7] Y. Minoura, *Nippon Kagaku Zasshi*, **73**, 244 (1952).

TABLE 4. CHEMICAL SHIFTS OF S-ORTHO RING PROTONS OF AROMATIC SULFUR COMPOUNDS (δ in CCl_4)

Ar	ArSH	ArSAr	ArSSAr	ArSCl	ArSSCl
2,4-$(NO_2)_2C_6H_3$-	7.64 (d)*		8.45 (d)**	8.21 (d)	8.50 (d)
2-$NO_2C_6H_4$-	7.35 (m)		7.85 (q)*	8.00 (q)	8.31 (q)
4-$NO_2C_6H_4$-	7.32 (d)*		7.67 (d)	7.58 (d)	7.80 (d)
2-ClC_6H_4-	7.20 (m)		7.30 (m)	7.49 (q)	7.84 (q)
4-ClC_6H_4-	7.13 (s)	7.23 (s)	7.34 (d)	7.52 (d)	7.48 (d)
C_6H_5-	7.16 (m)	7.22 (m)	7.40 (m)	7.59 (m)	7.54 (m)
2-$CH_3C_6H_4$-	7.16 (m)	7.09 (m)	7.40 (m)	7.63 (d)	7.72 (t)
4-$CH_3C_6H_4$-	7.10 (d)	7.15 (d)	7.29 (d)	7.51 (d)	7.45 (d)
4-$CH_3OC_6H_4$-	7.17 (d)	7.17 (d)	7.30 (d)	7.63 (d)	

Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.
* in chloroform ** in tris(dimethylamino)phosphine oxide.

aromatic sulfur compounds are shown in Table 4. Of particular interest in the Table is sulfenyl chloride-thiosulfenyl chloride series. The chemical shifts in phenyl, *p*-tolyl and *p*-chlorophenyl derivatives move toward higher field as the number of sulfur atoms increases, which makes a marked contrast to the lower-field shift in polysulfide series. This tendency has been reported in methanesulfenyl chloride series.[4] This can be also explained in terms of the inductive effect attributable to the polarization of sulfur-chlorine bond as shown by $\overset{\delta+}{S}$—$\overset{\delta-}{Cl}$. On the other hand, the lower field shift was observed in ortho substituted benzenesulfenyl chloride series, which is accounted for by the anisotropy effect of sulfur-chlorine atoms because distance between the ortho ring proton and chlorodithio group becomes more close by the buttressing effect of ortho substituents. However, the chemical shifts in *p*-nitrophenyl derivatives move toward lower field with increasing chain length of sulfur atoms. This fact does not fit above explanation. The reason may be as follows: the ring protons may be affected mainly by anisotropy effect of chlorodithio group rather than by the inductive effect of chlorodithio group because strong electron-withdrawing effect of nitro group overshadows the inductive effect.

In summary, the above mentioned dependence of the chemical shifts of the aromatic protons on the chain length of polysulfide linkage, gives important informations for the qualitative and quantitative analyses of aromatic sulfur compounds by NMR.

Experimental

Materials. All known sulfur compounds used in this experiment were prepared by known methods or simple modifications thereof. 4,4′-Tetrathiobis(2,6-di-*t*-butylphenol) was prepared from the corresponding thiophenol and sulfur chloride, mp 106—107°C; found S, 23.52%, calcd S, 23.76%. Substituted benzenethiosulfenyl chlorides were prepared from corresponding thiophenols and sulfur dichloride. Bp (mp) and elementary analyses of sulfur (calcd.) of new thiosulfenyl chlorides are: 2,4-di-NO_2, (73—75°C), 23.66% (24.02%); 4-NO_2, (35—37°C), 29.03% (28.96%); 2-Cl, 77—79°C/0.2 mmHg, 29.97% (30.33%); 4-Cl, 73—74°C/0.08 mmHg, 30.12% (30.33%); 2-CH_3, 76—77°C/0.2 mmHg, 33.23% (33.60%); 4-CH_3, 67—68°C/0.1 mmHg, 34.07% (33.60%).

Measurement of the NMR. The PMR spectra were determined with a Varian HA-100 instrument. All the spectra without note were measured in carbon tetrachloride at a concentration of 10% (w/v) at room temperature with tetramethylsilane as an internal standard and the peak positions were expressed in δ-values.

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