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Effect of the Number of Sulfur Atoms on the Chemical Shifts of Mercapto Protons in Aralkyl Hydropolysulfides

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Chemical shift of group X in organic polysulfides $X(S)_nY$ has been observed to be sensitive to the character of far distant group Y and the number of sulfur atoms.[1-5] This phenomenon is useful for the analyses of polysulfide mixtures.[2-4] However, little information is available on protons directly attached to sulfur except for that on sulfanes[6] $[H(S)_nH]$. We wish to report on the PMR study on aralkyl hydropolysulfides $[R(S)_nH, n=1—3]$.

TABLE 1.[a] CHEMICAL SHIFTS OF $R(S)_nH$ (n=1—3)

No.	R	Thiols, RSH	Hydrodisulfides, RSSH	Hydrotrisulfides, RSSSH
1	$C_6H_5CH_2$	1.51[b]	2.74[d]	3.38
2	$(C_6H_5)_2CH$	2.05[b]	2.72[d]	3.17
3	$(C_6H_5)_3C$	2.90[c]	2.48	2.63

a) Values are in δ ppm, 7 w/w% in CCl_4. All SH peaks of course disappear by addition of D_2O. In benzyl and benzhydryl hydrodisulfides, each singlet peak accompanies beats, from which long range coupling constants with methylene or methine proton, J=0.4 and 0.6 Hz, are estimated. In hydrotrisulfides, peaks are singlet.

b) J. Tsurugi, T. Horii, T. Nakabayashi, and S. Kawamura, *J. Org. Chem.*, **33**, 4133 (1968).

c) J. Tsurugi, Y. Abe, T. Nakabayashi, S. Kawamura, T. Kitao, and M. Niwa, *ibid.*, **35**, 3263 (1970).

d) S. Kawamura, Y. Abe, and J. Tsurugi, *ibid.*, **34**, 3633 (1969).

Table 1 shows the PMR data obtained for dilute carbon tetrachloride solutions; chemical shifts of sulfhydryl groups of thiols, hydrodisulfides and hydrotrisulfides, in which R groups are the series of benzyl, benzhydryl and triphenylmethyl. Fig. 1 presents a graphical explanation of the results. In thiols, the chemical shift of benzhydryl compound is in a lower field than that of benzyl, triphenylmethyl being in the lowest, whereas a reverse relation is noted in hydrotrisulfides. As to the triphenylmethyl derivatives, their chemical shifts are not lowered with the increase of the number of sulfur atoms.

We see that at least two factors are required for explanation of the relation of the chemical shifts. One which clearly originates from the length of sulfur chain is anisotropy or inductive effect by sulfur atoms, and the other anisotropy and/or inductive effect of R group. In the PMR study of alkyl polysulfides or analogous compounds, Van Wazer and Grant[1] reported on C_y and C_z values (These are defined as follows; for the molecule $X(S)_nY$, C_y is the shift contribution of the terminal group Y separated from the group X, containing the magnetic nucleus, by n sulfur atoms, and C_z is the shift contribution of each sulfur atom.), which is calculated based on the theory for so-called "neighbor anisotropy effect." For our data, a similar calculation is possible.[7] In Table 2 are cited C_y values for each aralkyl group and C_z. The relation of the chemical shifts to calculated curves is also shown in Fig. 1.

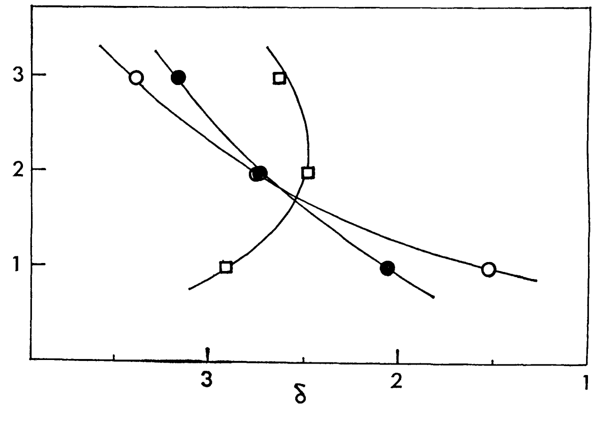

Fig. 1. Relationship between the chemical shifts and the number of sulfur atoms(n).
○ $C_6H_5CH_2(S)_nH$ ● $(C_6H_5)_2CH(S)_nH$ □ $(C_6H_5)_3C(S)_nH$
—— Calculated curve

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1) J. R. Van Wazer and D. Grant, *J. Amer. Chem. Soc.*, **86**, 1450 (1964).

2) D. Grant and J. R. Van Wazer, *ibid.*, **86**, 3012 (1964).

3) D. J. Martin and R. H. Pearce, *Anal. Chem.*, **38**, 1604 (1966).

4) T. L. Pickering, K. J. Saunders, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **89**, 2364 (1967).

5) T. Fujisawa and G. Tsuchihashi, This Bulletin, **43**, 3615 (1970).

6) E. Muller and J. B Hyne, *J. Amer. Chem. Soc.*, **91**. 1907 (1969).

7) C_y and C_z values were obtained by computer-programmed calculation. The computation was performed by the least mean square method, using the following linear equation,

$$\Delta\delta = C_y(1)\cdot U_1(n) + C_y(2)\cdot U_2(n) + C_y(3)\cdot U_3(n) + C_z\cdot V(n) \qquad (1)$$

where $\Delta\delta=\delta_2-\delta_n$, and $C_y(1)$, $C_y(2)$, $C_y(3)$ and C_z correspond to coefficients which designate the magnitudes of neighbor anisotropy effects of benzyl, benzhydryl, and triphenylmethyl groups, and of sulfur atom, respectively. Variables $U_i(n)$ and $V(n)$ which are the functions of the number of sulfur atoms n are derived from the Van Wazer's equation;[1]

$$U_i(n) = 1/R^3_{n+1} - 1/R_3{}^3$$

$$V(n) = \sum_{j=1}^{n} 1/R_j{}^3 - \sum_{j=1}^{3} 1/R_j{}^3$$

where R denotes the distance between the center of contributing group or atom and the nucleus in question, which is obtained by the random-flight calculation. In Eq. (1), $U_i(n)$ is taken as zero, except when the chemical shifts of a series of compounds are referred to. As an example, when the value of $\Delta\delta$ of α-toluenethiol, $2.74-1.51=1.23$, is replaced in Eq. (1), one would obtain $1.23=C_y(1)\cdot U_1(1)+0.0+0.0+C_z\cdot V(1)$.

Table 2. Anisotropic parameters for R(S)H (n=1—3)

No.	R	C_y	C_z
1	$C_6H_5CH_2$	−8.0	−9.7
2	$(C_6H_5)_2CH$	−12	−9.7
3	$(C_6H_5)_3C$	−21	−9.7

The large negative C_z value in Table 2 means that divalent sulfur atoms markedly deshield the directly attached neighboring protons. The fact that the value of C_y is also negative and increases in its absolute value with the number of benzene nucleus in the aralkyl group may imply that the sulfhydryl proton is mainly present near the plane of benzene nucleus. The reverse winding of the curve for triphenylmethyl series in Fig. 1 or the large negative C_y value of triphenylmethyl group compared with that of benzyl or benzhydryl, seems to suggest a sterically significant relation. In benzyl or benzhydryl derivatives, sulfhydryl protons have the chance to project over the surface of benzene nuclei. On the other hand, an extremely restricted rotation of benzene nuclei in triphenylmethyl groups diminishes the possibility, or the bulky groups prevent the real random-flight motion, and chemical shifts might be much lowered.

Van Wazer's equation gives an excellent fit for the relative position of the chemical shifts, but does not determine their absolute values. Therefore, some other effects such as the inductive effect should be taken into consideration to elucidate the fact that the chemical shift of diphenylmethanethiol is lower than that of α-toluenethiol, *etc.*

Experimental

PMR spectra were taken on a JNM 3H-60 spectrometer with tetramethylsilane as an internal standard (7 w/w% in CCl_4). Values of C_y and C_z in Table 2 were obtained by computer-programmed least squares calculation using Eq. (1) in Ref. 7 and data in Table 1. Benzyl,[8] benzhydryl,[8] and triphenylmethyl[9] hydrodisulfides, and benzyl[10] and triphenylmethyl[9] hydrotrisulfides were prepared by known procedures. Benzhydryl hydrotrisulfide (86% purity) was obtained as a carbon tetrachloride solution by the following procedure. To a solution of acetyl benzhydryl trisulfide (1 g) in *n*-propyl alcohol (20 m*l*) was added 1N *n*-propyl alcoholic hydrogen chloride (5 m*l*). The solution was kept at 29°C for 1 hr. Volatiles were evaporated under reduced pressure, and carbon tetrachloride was added to the residual oil. Acetyl benzhydryl trisulfide was prepared by the same method as that given in literature.[9] 77% of crude material, mp 53—57°C was obtained. This was purified by repeated recrystallization from ether to obtain white crystals, mp 57—58.5°C.

Found: C, 58.49; H, 4.82; S, 31.64%. Calcd for $C_{15}H_{14}OS_3$: C, 58.79; H, 4.60; S, 31.38%.

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10) H. Böhme and G. Zinner, *Ann. Chem.*, **585**, 152 (1954).