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Substituent Effects on the ^1H NMR Spectra of Substituted Phenylthioacetic Acids

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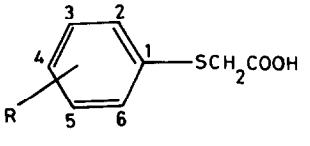
The study of the correlation between substituent-induced chemical shifts (SCS) of protons and the Hammett substituent constant for aromatic compounds is a subject of topical interest (*1–3*). The substituent alters the electron density of the aromatic ring by inductive and resonance interactions and these effects are relayed to the ring/side chain protons presumably by the polarization of the intervening σ or π bonds (*4*). In compounds of the type, R–C_6H_4T–H (where R is the substituent, C_6H_4T is the transmitting group, and H is the reaction site) the substituent and the terminal proton are sufficiently remote so that anisotropy, ring current effects, and van der Waals dispersion forces are negligible or at least constant. Therefore most of the shieldings and hence SCS observed are related to the electron density at the reaction site or nucleus. When T contains oxygen, nitrogen, a carbon–carbon double or triple bond or, in general, a group that conjugates readily with the aromatic ring, then the sensitivity of the chemical shift of the proton to remote substituents becomes pronounced (*5*).

In the present study the ^1H NMR spectra of several substituted phenylthioacetic acids (I) (*6*) have been measured in $CDCl_3$ (10% concentration or as saturated solutions using TMS as the internal standard) using a 90-MHz Perkin–Elmer R32 NMR spectrometer. The proton chemical shifts ($\Delta\nu$, Hz) for the methylenic and 3,5 protons in I are presented in Table 1 together with the



I

corresponding substituent constants σ and σ^+. The $\Delta\nu$ of methylenic protons of I has been plotted against σ and σ^+ values (Fig. 1). Although a good correlation is obtained with σ (0.948), the correlation with σ^+ is excellent. Similarly the chemical shifts of the 3,5 protons give better correlation with σ^+.

Ratios of inductive or field effects and resonance effects can be obtained by the analysis with the dual substituent parameter equations. There are several equations for this purpose, where parameters of inductive (*I*) or field (*F*), resonance (*R*) with

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TABLE 1

PROTON CHEMICAL SHIFTS ($\Delta\nu$) IN SUBSTITUTED PHENYLTHIOACETIC ACIDS

Substituent	$\Delta\nu_{CH_2}$ (Hz)	$\Delta\nu_{3,5}$ (Hz)	σ^a	σ^{+b}
1. 4-NH_2	313	590	−0.66	−1.3
2. 4-MeO	319	619	−0.27	−0.78
3. 4-NHCOMe	321	665	0	−0.6
4. 4-Me	324	641	−0.17	−0.31
5. 4-i.Pr	325	647	−0.15	−0.28
6. H	329	662	0	0
7. 3-MeO	329	—	0.12	0.047
8. 4-Cl	328	661	0.23	0.11
9. 4-Br	328	657	0.23	0.15
10. 4-NO_2	342	735	0.78	1.24[c]

[a] Values of σ defined by L. P. Hammett, *J. Am. Chem. Soc.* **59,** 96 (1937).
[b] Values of σ^+ defined by H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **80,** 4979 (1958).
[c] σ^- value is used for 4-NO_2 substituent.

weighting factors (a, b, f, r) are involved:

$$\Delta\nu = a_1\sigma_I + b_1\sigma_R^0 + \text{constant} \qquad \text{(Taft (7))}, \qquad [1]$$

$$\Delta\nu = f_2F + r_2R + \text{constant} \qquad \text{(Swain and Lupton (8))}, \qquad [2]$$

$$\Delta\nu = a_3\sigma^0 + r_3\Delta\sigma_R^+ + \text{constant} \qquad \text{(Yukawa and Tsuno (9))}. \qquad [3]$$

The results of the analyses using Eqs. [1] to [3] are given in Table 2 and the

TABLE 2

RESULTS OF CORRELATIONS OF ^{1}H CHEMICAL SHIFTS OF **I** WITH σ, σ^+, σ_I, σ_R^0, F, AND R PARAMETERS

Parameter	Type of constants	$r/100R^2$	b	c	SD/SE	n
$\Delta\nu_{CH_2}$	σ	0.948	19.2		0.26	10
	σ^+	0.995	11.3		0.08	10
	σ_I, σ_R^0	98.5	12.9	36.5	1.15	9
	σ, $(\sigma^+ - \sigma)$	99.1	9.97	12.8	0.817	10
	F, R	95.6	6.82	25.6	2.13	8
$\Delta\nu_{3,5}$	σ	0.962	94.7		0.11	9
	σ^+	0.992	55.6		0.06	8
	σ_I, σ_R^0	98.8	68.3	173	0.530	8
	σ, $(\sigma^+ - \sigma)$	98.7	42.4	72.8	0.564	8
	F, R	96.8	39.4	118	0.994	7

Notes. r = correlation coefficient; $100R^2$ = Percentage coefficient of determination; b, c = coefficients in the equations $\Delta\nu = a + b\sigma$, $\Delta\nu = a + b\sigma^+$, $\Delta\nu = a + b\sigma_I + c\sigma_r^0$, etc.; SD = standard deviation; SE = standard error of the regression in multiple correlations; n = number of substituents.

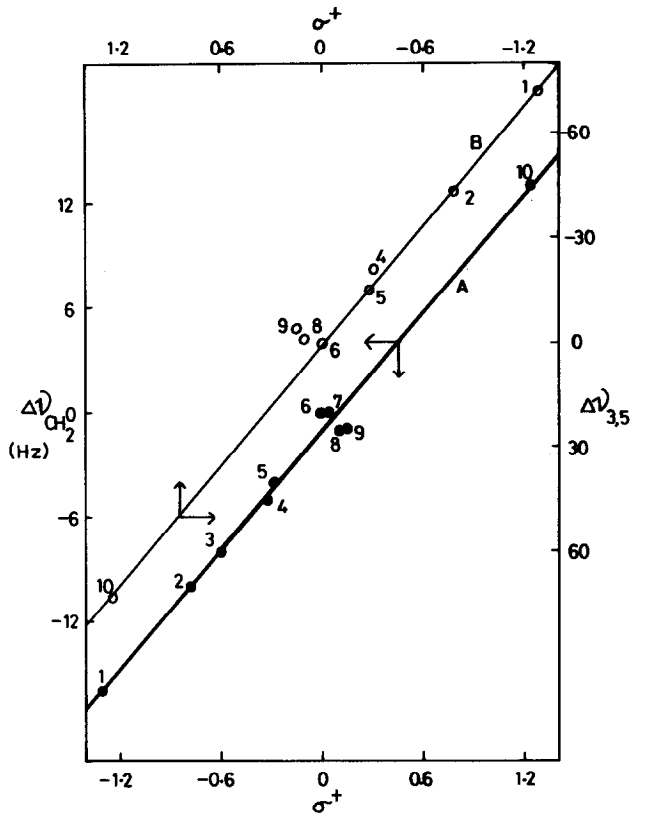

FIG. 1. Plots of (A) $\Delta\nu_{CH_2}$ and (B) $\Delta\nu_{3,5}$ against σ^+ for substituted phenylthioacetic acids (Nos. 1–10 as in Table 1). (A) Correlation coefficient 0.995. (B) Correlation coefficient 0.992.

goodness of fit was evaluated with $r/100R^2$. The data in Table 2 clearly demonstrate that the resonance contribution to the chemical shift predominates (>70%) over the field effect both for the CH_2 and 3,5 protons. The application of Eq. [3] indicates that r_3, the proportionality constant for the enhanced resonance, is greater than one.

In aryl families, R–C_6H_4T–H, as a substituent is moved down a chain from a terminal proton, the effect of R on the chemical shift ($\Delta\nu$) of the proton diminishes and the value of the reaction constant ρ, obtained from the correlation of $\Delta\nu$ with σ^+ characterizes T as well as the conditions of NMR measurements. Marcus *et al.* (*10*) found that the minimum attenuation factor per connecting atom is approximately 2 to 3 in CCl_4; thus they observed ρ (in Hz/σ) as 21.8 and 7.11 for thiophenols and aryl methyl sulfides, respectively, from the correlations of SCS with σ. The value of ρ in the present study is 11.3, which as expected is lower than the ρ value of thiophenols. But the ρ value of phenylthioacetic acids is higher than that reported for aryl methyl sulfides. This may be attributed to (i) a change in solvent and (ii) the additional deshielding caused by –COOH group in phenylthioacetic acids. Thus the ^{1}H NMR data for I confirm that ρ can be considered as an index of transmission efficiency (*10*).

The chemical shifts of the CH_2 protons in $C_6H_5XCH_2COOH$ (X = O, S, SO, or SO_2) have also been recorded. The observed values (in Hz) are: S: 329, SO: 339, SO_2: 367, and O: 421. This is in accordance with the electronegativity order S < SO < SO_2 < O. The most electronegative oxygen atom is responsible for the largest observed deshielding of the CH_2 protons in phenoxyacetic acid and hence absorbs at higher frequency (downfield). The observed order in the chemical shifts of the CH_2 protons in $C_6H_5XCH_2COOH$ is also consistent with the acidities of the acids.

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