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The NMR Chemical Shifts of Aromatic Ring Protons. I. The Chemical Shifts of the Ring Protons of Mono-substituted Benzenes

Yasuhide YUKAWA, Yuho TSUNO, and Nobujiro SHIMIZU
The Institute of Scientific and Industrial Research, Osaka University, Yamada-kami, Suita, Osaka

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The ring protons of *mono*-substituted benzenes generally give complicated NMR spectra as a result of complex spin-spin coupling with their neighbors. This creates difficulties in determining the chemical shift of the respective ring protons and, subsequently, in examining effects. While recent computer analysis of ordinary spectra has provided a set of parameters,[1] the most practical method easily applicable in a laboratory of organic chemistry to solve this problem seems to be the deuterium-decoupling technique. Spiesecke and Schneider[2] and Schmid[2] determined the chemical shifts of ring protons of *mono*-substituted benzenes in a cyclohexane solution by means of deuterium substitution at specific positions. As a more convenient method, Garnett[3] suggested the application of massive deuteration.

Although the chemical shifts of the ring protons of benzene derivatives have been studied over a wide variety of substituents,[4,5] a comprehensive set of SCS data for *mono*-substituted benzenes under the same conditions is only available in carbon tetrachloride[1] and cyclohexane solutions.[2] Therefore, we determined the chemical shifts of *mono*-substituted benzenes in various solvents.

Our method of chemical-shift determination is essentially an application of Garnett's deuterium decoupling (massive deuteration). A statistical mixture of isomeric *mono*-substituted benzene-d_4, obtained by introducing a substituent to monoprotio deuteriobenzene, gives a highly simplified absorption pattern which consists of three singlets for the *o*-, *m*-, and *p*-proton. Thus, the chemical shifts of the respective protons were directly obtained from the spectra.

Mono-protio pentadeuteriobenzene was prepared from hexadeuteriobenzene by the bromination and subsequent reduction of the Grignard reagent with light water. This starting material was converted by direct substitutions and subsequent reactions to a series of *mono*-substituted monoprotio deuteriobenzenes.

The measurements were carried out with a Hitachi R-20 spectrometer operating at 60 MHz. The chemical shifts were determined relative to TMS as an internal standard at three concentrations below 5.0 mol% and were extrapolated to infinite dilution values. The shift values were determined rather precisely; the uncertainty involved in the infinite dilution values may be estimated as far less than ±0.5 Hz, except when the signals are coalesced. Since the relative intensity of the signals corresponds to the relative amounts of the existing protio-isomers, 2: 2: 1 for *o*-, *m*-, and *p*-isomers, the signals for *p*-protons could be assigned from their intensities without difficulty. The assignment of the *m*- and *o*-protons for most of the derivatives was confirmed by comparison with existing data.[1,2]

The SCS for the compounds for which no literature data were available were further confirmed by a study of the spectra of specifically-deuterated materials. The chemical shifts determined in carbon tetrachloride were in good accordance with those given by theoretical analysis; the discrepancy did not exceed ±0.5 Hz. This indicates the reliability of the present sets of data, obtained by the conventional method, as indicating the actual shifts of *mono*-substituted benzenes.

According to the results, the substituent chemical shifts (SCS values) appears to vary to a considerable extent depending on the solvents. Table 1 lists the SCS values in dimethylacetamide (DMA) as a representative polar solvent and in cyclohexane as a nonpolar solvent. The *meta*- and *para*-SCS values are magnified in DMA as compared with those in C_6H_{12}, but the *ortho*-SCS values remain approximately the same in both solutions. The SCS in C_6H_{12} is found to be proportional to that in CCl_4. On the contrary, no such linear correlation can be obtained between the SCS's in DMA and in C_6H_{12} or CCl_4. In a DMSO solution, practically the same SCS values as in DMA were reproduced within the order of experimental uncertainty. These findings suggest that the SCS should be treated independently in each solvent.

A number of studies of the correlation of the chemical shifts of substituted benzene dreivatives with the substituent parameters have been successfully made,[4–6] although actual correlations have always suffered from the significant deviations of the anisotropic substituents. However, the direct application of Hammett σ-constants does not necessarily result in satisfactory correlations.

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Table 1. Relative chemical shift of the ring proton of *mono*-substituted benzenes

Substituent	in DMA			in C_6H_{12}		
	$\Delta\delta_o$	$\Delta\delta_m$	$\Delta\delta_p$	$\Delta\delta_o$	$\Delta\delta_m$	$\Delta\delta_p$
NO_2	−55.7	−23.6	−32.6	−56.8	−11.9	−18.6
CN	−31.4	−17.0	−25.4	−16.9	− 6.0	−12.2
SO_2Cl	−49.7	−32.9	−38.9	−45.2	−14.9	−21.4
CH_3CO	−38.7	−11.7	−15.7	−39.7	− 7.4	−10.4
t-BuCO	−22.9	− 8.8	− 8.8	−26.6	− 3.2	− 3.2
CO_2Et	−40.1	−12.4	−19.4	−47.5	− 4.4	−10.1
CO_2H	−40.3	−10.1	−16.2	−54.2	− 8.9	−16.4
Br	−14.7	− 1.6	− 3.4	−12.0	6.0	3.7
I	−25.1	8.3	− 3.9	−25.0	15.0	1.8
$SiMe_3$	−10.4	0.6	0.6	−12.9	0.9	0.9
Me	10.5		10.5	11.1		11.1
t-Bu	− 3.7	2.8	10.2	− 4.5	2.8	10.3
neo-Pent.	14.1	6.4	16.1			
OPh	20.2	− 2.6	13.4	17.3	3.1	14.0
OMe	25.2	4.3	24.8	25.1	3.7	23.1
OH	32.5	12.1	36.1	31.6	7.0	25.8
NMe_2	37.2	12.9	43.1	35.1	8.2	32.4
NH_2	42.4	21.4	52.5	44.3	14.3	37.6

This failure should be attributed to the changes in the relative importance of the π-electronic delocalization (resonance) effect relative to the non-delocalization polar effect, changes depending on the structure of the systems and also on the nature of the detection variables (*i.e.*, the proton NMR chemical shifts compared to the pK_a of benzoic acids).

We have previously demonstrated[4,5] that the substituent effect on the chemical shift of side-chain protons can be described generally by Eq. (1):

$$\Delta\delta = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-) \qquad (1)$$

ρ is the reaction constant, and σ^0 is the standard substituent constant. $\Delta\bar{\sigma}_R^+$ and $\Delta\bar{\sigma}_R^-$ are the resonance substituent constants measuring the capacity of —R and +R groups respectively for electron donation and attraction through π-electronic delocalization. Either r^+ and r^- is the resonance reaction constant describing the extent of additional π-electronic interaction with conjugatively electron-donating(—R) or electron-attracting (+R) substituents.

Our linear Aromatic Substituent-Reactivity (**LArSR**) relationship (1) can be applied to the SCS's of the ring protons of *mono*-substituted benzenes. By the least-squares treatment, the following correlations were derived for the respective ring protons in DMA solution:

$$\Delta\delta_p = -39.6(\sigma_p{}^0 + 0.87\Delta\bar{\sigma}_R^+) + 0.24$$

$$(n=13,\ SD=2.81,\ R=0.995)$$

$$\Delta\delta_m = -34.5(\sigma_m{}^0 + 0.42\Delta\bar{\sigma}_R^+) - 0.61$$

$$(n=9,\ SD=2.03,\ R=0.993)$$

Equation (1) was also employed successfully for the SCS's in C_6H_{12} solution; $\sigma_p = -25.4$, $r_R{}^+ = 0.98$ and $\sigma_m = -18.9$, $r_m{}^+ = 0.48$. Halogens in the *meta*-correlation and dimethylamino group were not included in these calculations. The results are shown in Fig. 1 and 2 for *m*- and *p*-protons respectively. Yamamoto *et al.*[1] pointed out that the SCS values in CCl_4 were linearly correlated with σ^+ This means that the shifts in CCl_4 correlate with an $r_p{}^+$ value near unity.

From these results, it is evident that our **LArSR** Eq. (1) can be employed as a useful approximation to describe the physical properties mainly brought about

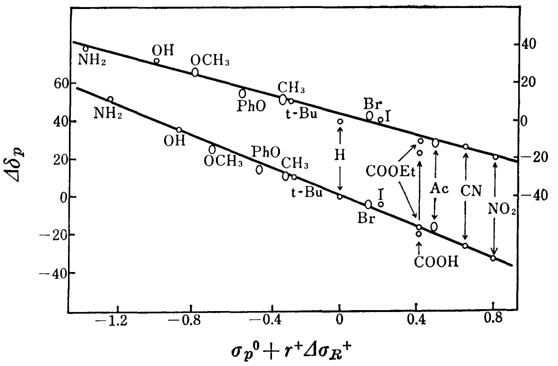

Fig. 1. Application of **LArSR** Eq. (1) to *para*-SCS values; Upper line, SCS in C_6H_{12}, and lower in DMA solutions.

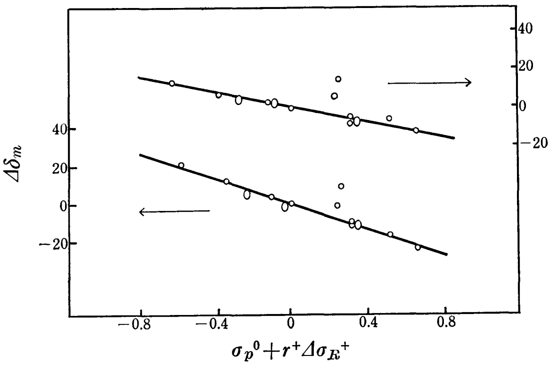

Fig. 2. Application of **LArSR** Eq. (1) to *meta*-SCS values; Upper in C_6H_{12} and lower in DMA solutions.

by the electronic distributions of the ground-state molecules.

In para correlations, the resonance contribution of the $-R$ substituents is remarkably exalted to give high r^+ values near unity, while the contribution of the $r^-\Delta\bar{\sigma}_R^-$ term is not significant; in effect, $r^-=0$. This suggests that the benzene ring works more effectively as a π-electron acceptor than as a π-electron donor in the π-delocalization in the ground-state *mono*-substituted benzenes. The change in r from one solvent to another may result in the non-linearity between the *para*-SCS values in different solvents. The significant solvent-variations of σ as well as of r values suggest that the simple sum treatment[1] should be applied only to data obtained in the same solvent or at least in a closely related group of solvents.

It should be noticed that the *meta*-correlation also requires exalted r^+-values, contraty to the negligible additional resonance term ($r_m^+=0$) in the ordinary *meta*-reactivity correlations. This might be caused by certain secondary contributions from the *ortho* and *para* π-charges.[8] Whatever the origin of the exalted resonance contribution,[8] the fact that the r_m value is just a half as much as the corresponding r_p value may be important, as the 1/2 ratio is a characteristic of the resonance contribution in the insulated σ^0-reactivity.

The substantial deviation of certain substituents might be attributed mainly to the specific magnetic effect. It is interesting to note that the effect of anisotropic substituents appears somewhat solvent-dependent (see Table 1). Dimethylamino group was not successfully correlated with the ordinary $\Delta\sigma_R^+$ value. In usual solvents, dimethylamino group was less electron-releasing than amino group, but it was more electron-releasing in carbon tetrachloride. No plausible explanation of this fact is available.

The chemical shift of the *ortho* proton can not be described simply by Eq. (1) alone. This is quite reasonable because the proximity of the *o*-proton to substituents may give rise to predominant non-electronic effects, such as anisotropic, local-field, and steric interactions. However, practically a linear correlation, $\Delta\delta_o=-55.3(\sigma^0{}_p+0.59\Delta\bar{\sigma}_R{}^+)$, can be obtained in DMA from selected well-behaving substituents. Similar results were obtained in other solvents. This means that the electronic effect predominantly controls the chemical shifts of the *o*-proton despite significant contributions of non-electronic factors.

The same method of determination and a similar type of SCS analysis have been used successfully in the study of particular solvent effects or of the complex formation of substituted benzenes and naphthalenes; the results will be reported in the near future.

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[7] For reference see G. W. Smith, *J. Mol. Spectroscopy*, **12**, 146 (1964).

[8] In a previous report[9] we have treated such an exalted π-electronic contribution of *meta* substituents in terms of the variation of the ring current by localized π-charges with substituents.[10]

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