Non-Additivity of Carbon-13 Nuclear Magnetic Resonance Chemical Shift of Benzenesulfonic Acids

Yoshio KOSUGI

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464

Carbon-13 NMR spectra of a number of *m*- and *p*-substituted benzenesulfonic acids in basic deuterium oxide solutions have been obtained. Simple additivity rules for chemical shifts are totally useless for all carbons except for several carbons in *p*-CH₃, *p*-Et, and *p*-Cl derivatives. Deviations of a few ppm have been rationalized for 1,3- and 1,4-disubstituted benzenes, but deviations of 7 ppm are the largest among C-13 NMR chemical shifts data so far reported. The astonishing deviations are observed at the carbon attached to sulfo anion and at both adjacent carbons. The nature of the sulfo group changes according to the second substituent; it is not regulated by the substituent parameters which include various kinds of sigma values.

Keywords C-13 nuclear magnetic resonance, chemical shifts, additivity rule, non-additivity, benzenesulfonic acids

Peak assignments are the most important first step to analyze NMR spectra. Simple additive rules of the chemical shifts are frequently employed for the assignments in C-13 NMR. The Lindeman-Adams equation¹ for alkanes is a typical example. Empirical equations for alkanesulfonic acids have been proposed from this laboratory.² Substituent chemical shifts (SCS) on aromatic rings are not necessarily simple to correlate with various substituent parameters and physical constants. However, C-13 NMR chemical shifts of disubstituted benzenes are easily calculated by additivity of the increments with the two substituents. Ortho-interaction aside, the additivity calculations often determine the assignments for aromatic carbons.

Deviations of a few ppm between observed and calculated values are encountered in some 1,3- and 1,4-disubstituted benzenes.³⁻⁵ A reasonable explanation and calculations of electron density are given for these deviations, which stem from electronic interactions between two substituents.

During our investigation on organic acids and bases by C-13 NMR⁶⁻⁸ much larger deviations than previously reported have been found in a number of benzenesulfonic acids. The results would be useful not only for C-13 NMR data collection but also for structural studies on various sulfo-containing compounds.

Experimental

Chemicals

Chemicals of pure grade were purchased from Tokyo Kasei Kogyo Co. Ltd. All benzenesulfonates were

sodium salts.

NMR measurements

Natural abundance proton-decoupled C-13 NMR spectra at 25.16 MHz were recorded on an XL-100 spectrometer (Varian) equipped with a Varian Data 620i computer of 16K memory. Fourier transformed spectra were obtained using a spectral width of 5000 Hz with 12K data points. A pulse angle of about 30° was employed with a repetition rate of 3 s.

About 200 mg of the sodium benzenesulfonate and *ca.* 0.2 g of sodium hydroxide were dissolved in 3 ml of deuterium oxide containing a small amount of dioxane as an internal standard. Insoluble or sparingly soluble compounds, such as benzene and most of the monosubstituted benzenes, were dissolved in a mixture of deuterium oxide and methanol of 5–20%.

The chemical shifts were obtained by extrapolations to the point for 0% of methanol.

Chemical shifts and additivity calculations

Chemical shifts downfield from the internal standard were converted to the values from TSP-d₄ by adding 67.0 ppm for the chemical shift of dioxane.

The carbon attached to SO₃⁻ is defined as C_a. The C_b, C_c, ..., C_i are carbons along the shorter path towards the second substituent. The conventional numbering is discarded. Thus C_a, C_c and C_d in 5-sulfosalicylate are carbons bearing SO₃⁻, CO₂⁻ and O⁻, respectively. In order to apply the additivity rule, the same alphabetical letters are given to the carbons of monosubstituted benzenes corresponding to the benzenesulfonates. For example, in the additive calculation of *p*-toluenesulfonate based on the chemical shift of toluene, the carbons

bearing CH_3 groups in both compounds are C_c . On the other hand, the effects of SO_3^- on the chemical shifts of the ring carbons are given as increments which are obtained by subtraction of the chemical shifts of benzene (129.2 ppm) from those of benzenesulfonate (1).

Then chemical shifts are calculated by addition of the increments ($\Delta\delta_i=16.7, 3.3, -0.3, 5.9, -0.3, 3.3$ where i 's are a, b, c, d, e, f in this order) of benzenesulfonate to the observed values of the mono-substituted benzenes corresponding to the benzenesulfonates, or of the disubstituted benzenes in the case of trisubstituted benzenesulfonates.

Deviations are expressed by subtraction of the calculated values from the observed values.

Results and Discussion

Substituent additivity of C-13 chemical shifts of aromatic ring carbons has been examined for benzenesulfonic acids. The results are given in Table 1.

Three of the 1,4-disubstituted benzenesulfonates, 4, 5 and 6 are additive. The chemical shifts of some

carbons deviate by 2–3 ppm from the calculated values. These deviations are slightly larger than the case without sulfo group, but not unusual for 1,4-disubstituted benzenes.^{3,4}

In strong basic solutions, the chemical shifts were independent of concentrations. Therefore the deviations of a few ppm are accounted for by electronic interactions between sulfo anion and the second substituent.

A similar argument may be applied for the larger deviations in sulfanilate (2). Conjugative effects between the negative charged sulfo anion and the amino group move the chemical shifts to higher fields than expected, resulting in negative deviations. Negative deviations are found not only in the carbon attached to the sulfo group, but in the adjacent carbons. Thus all carbons in 1,4-benzenedisulfonate (7) produce deviations of about -4 ppm. The electron interaction suggests that π -electron localizes at the para carbons, that is, a resonance or conjugative polarization effect of the substituent operate mainly at C_a carbon and much less at C_b or other carbons.

Accordingly, the minor deviations observed for 1,3-disubstituted benzenes can be explained. However,

Table 1 Carbon-13 chemical shifts^a of benzenesulfonic acids and their deviations^b from calculated values

Benzenesulfonic acid ^c		C_a	C_b	C_c	C_d	C_e	C_f
Benzenesulfonic acid (1)	obs. ⁷	145.9	132.5	128.9	135.1	128.9	132.5
	incr. ^d	16.7	3.3	-0.3	5.9	-0.3	3.3
Sulfanilic acid (2)	obs.	135.0	129.8	118.0	152.5	118.0	129.8
	dev.	-2.3	-4.2	0.6	-1.3	0.6	-4.2
<i>p</i> -Phenolsulfonic acid (3)	obs.	127.9	130.2	121.0	172.7	121.0	130.2
	dev.	-5.9	-5.4	-0.2	-2.0	-0.2	-5.4
<i>p</i> -Toluenesulfonic acid (4)	obs.	144.7	131.9	127.9	142.2	127.9	131.9
	dev.	1.6	-1.8	-0.7	-2.7	-0.7	-1.8
<i>p</i> -Ethylbenzenesulfonic acid (5)	obs.	142.4	131.0	128.2	151.3	128.2	131.0
	dev.	0.5	-0.1	1.3	2.1	1.3	-0.1
<i>p</i> -Chlorobenzenesulfonic acid (6)	obs.	139.7	131.8	129.8	143.8	129.8	131.8
	dev.	0.6	-1.0	1.4	-1.1	1.4	-1.0
1,4-Benzenedisulfonic acid (7)	obs.	147.6	128.7	128.7	147.6	128.7	128.7
	dev.	-4.2	-3.5	-3.5	-4.2	-3.5	-3.5
Metanilic acid (8)	obs.	146.0	115.2	149.6	121.6	132.5	118.6
	dev.	-1.4	-5.8	-2.0	-2.0	2.1	-5.3
<i>m</i> -Phenolsulfonic acid (9)	obs.	146.0	117.7	169.5	124.6	132.6	113.6
	dev.	-3.0	-7.1	1.0	-2.8	0.6	-6.8
<i>m</i> -Sulfo benzoic acid (10)	obs.	142.9	129.4 ^e	137.7	132.4	129.7 ^e	126.1
	dev.	-5.3	-6.9	1.5	-5.6	-1.5	-5.1
1,3-Benzenedisulfonic acid (11)	obs. ⁷	146.9	129.5	146.9	132.6	133.5	132.6
	dev.	1.3	-6.3	1.3	-5.8	4.9	-5.8
<i>m</i> -Nitrobenzenesulfonic acid (12)	obs.	146.9	123.3	150.2	133.1	128.5	134.5
	dev.	-0.5	-4.4	0.8	2.8	-1.9	-4.7
5-Sulfosalicylic acid (13) ^e	obs.	131.6	128.9	128.0	170.7	123.1	130.3
	dev.	-0.3	-5.5	2.0	-1.0	2.7	-5.3
5-Sulfoisophthalic acid (14)	obs.	145.4	130.7	140.3	134.2	140.3	130.7
	dev.	-2.8	-7.7	1.1	-4.4	1.1	-7.7

a. Downfield (ppm) from TSP-d₄. b. Deviation (dev.)=observed value-calculated value. c. All measurements were done in deuterium oxide solutions containing excess amounts of sodium hydroxide. The carbon attached sulfo group is C_a ; e.g., for the compound 13, $\text{C}_a\text{-SO}_3^-$, $\text{C}_c\text{-CO}_2^-$, $\text{C}_d\text{-O}^-$. d. Increment (incr.)=observed chemical shift-chemical shift of benzene (129.2 ppm). e. Assignments could be reversed.

Fig. 1 Relationship between observed chemical shifts of benzenesulfonic acids and substituent constants. Black and white symbols are on σ_p and σ_m scales, respectively. Stars, circles, squares, triangles and ellipses correspond to C_a , C_b , C_c , C_d and C_f , respectively. Data of C_e are not given.

substituent effects other than resonance may be more important in the present experiments in polar solvents. Such an effect is profound in oxy anion (O^-) in 3. In spite of σ_p values similar to that of NH_2 , the largest deviations among 1,4-disubstituted benzenes ever reported have been found.

The curious nature of the sulfo group is manifested in 1,3-disubstituted benzenesulfonates (8–12) including trisubstituted derivatives, 13 and 14. Incredible deviations have been observed at C_b and C_f carbons. Some of the C_a and C_c carbons also deviate rather largely, but no unifying tendency is found. Bromilow *et al.*⁵ have recently reported that deviation of a few ppm found in 1,3-disubstituted benzenes are caused not only by electron demand but also by changes in the sensitivity of the chemical shifts. They have used a dual substituent parameter non-linear resonance (DSP-NLR) equation containing σ_R and σ_I to analyze the non-additivity nature of 1,3- and 1,4-disubstituted benzenes.^{4,5} We have also reported that substituted

benzoic acids are correlated with σ^o or σ^+ alone, or DSP analyses.⁶ Plotting the present data *versus* σ_m and σ_p gives Fig. 1. Neither other sigma values nor DSP analyses can give reasonable correlations.

Although no straight lines can be drawn in the figure, the plots of C_a (star marks) and C_b (circle marks) scatter around 140 ppm and 130 ppm, respectively. These results suggest that a sulfo group, as it changes its conformations, may keep its chemical shifts constant at C_a and C_b (and also C_f), where large deviations are observed.

The experimental results indicate an enormous amount of electrons are around C_a , C_b and C_f , which would be affected by the repulsion between two negative charged substituents. Electron flows to sulfo anion seem to be slow even if the second substituent is not charged. How slow depends on the substituent, and probably on the conformational changes of the sulfo group. Intermolecular interactions can be ruled out, because no concentration dependence has been observed; *e.g.*, a dilution of the concentration of the compound 13 to one tenth did not change the chemical shifts at all. Thus the additive rule is completely useless for sulfonic acids. The curious nature may be related with the fact that few sigma values of sulfo group are available in the literature and these are not yet definitive.⁹

The donation of sodium *m*-sulfophenolate and *p*-benzenedisulfonate by Prof. T. Kito (The Kyushu Institute of Technology) is gratefully acknowledged.

References

1. L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
2. Y. Kosugi and H. Konishi, *Bunseki Kagaku*, **33**, E47 (1984).
3. J. Bromilow, R. T. C. Brownlee, R. D. Topsom and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 2020 (1976).
4. J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek and R. W. Taft, *J. Org. Chem.*, **45**, 2429 (1980), and refs. 7a–z cited therein.
5. J. Bromilow, R. T. C. Brownlee, D. J. Craik and M. Sadek, *Magn. Reson. Chem.*, **24**, 862 (1986).
6. Y. Kosugi and Y. Furuya, *Tetrahedron*, **36**, 2741 (1980).
7. Y. Kosugi and T. Takeuchi, *Org. Magn. Reson.*, **12**, 435 (1979); *idem.*, *J. Magn. Reson.*, **32**, 83 (1978).
8. Y. Kosugi, Y. Yoshida and T. Takeuchi, *Anal. Chem.*, **51**, 951 (1979).
9. O. Exner, "Correlation Analysis in Chemistry", ed. N. B. Chapman and G. Shorter, Chapt. 10, p. 481, Plenum Press, New York (1978).

(Received March 19, 1988)

(Accepted April 28, 1988)