BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1637—1638 (1975)

A Semi-empirical Calculation of the Substituent Effect on the ^{1}H Chemical Shift of Benzene[1]

Jun Niwa

College of General Education, Nagoya University, Chikusa, Nagoya 464

(Received November 25, 1974)

Synopsis. The applicability of a semi-empirical expression for obtaining the relative ^{1}H chemical shifts in substituted aromatic side-chains, which was presented in the preceeding paper (J. Niwa, This Bulletin, **48**, 118 (1975)), has been examined for ring protons of monosubstituted benzenes.

In the preceeding paper,[1] we derived a semi-empirical expression for obtaining the relative chemical shifts (in ppm) of protons in substituted aromatic side-chains by considering the "ring-current" effect ($\sigma^{A,\,\mathrm{ring}}$) in addition to the diamagnetic contribution of the hydrogen atom, A, in the C–H bond of interest ($\sigma^{AA}_{\mathrm{dia}}$) and that from its bonded carbon, B($\sigma^{AB}_{\mathrm{dia}}$):

$$\delta_{\mathrm{calcd}}(\equiv\Delta\sigma^{A}) = \Delta\sigma^{AA}_{\mathrm{dia}} + \Delta\sigma^{AB}_{\mathrm{dia}} + \Delta\sigma^{A,\mathrm{ring}} \qquad (1)$$

$$= a\Delta q^{A} + b\Delta q^{B} - 0.4f(\rho, z)|\sigma_{\pi}| \qquad (2)$$

where the Δq's are the increments in electron densities on specified atoms, where a and b are, respectively, the constants particular to the hydrogen atom and the C–H bond, and where the third term is the modified Johnson and Bovey ring-current shift. We showed that Eq. (2) could correctly reproduce the relative chemical shifts of protons in substituted aromatic side-chains. In the present paper, we will examine to what degree of accuracy Eq. (2) can reproduce the relative chemical shifts observed for the ring protons of monosubstituted benzenes. In evaluating the first and second terms of Eq. (1), we have used the CNDO/2 formalism.

In order to calculate the local diamagnetic term ($\sigma^{AA}_{\mathrm{dia}}$) of the hydrogen atom, the expression (Eq. (3)) given by Kajimoto and Fueno[2a)] was applied to the case of the ring protons:

$$\sigma^{AA}_{\mathrm{dia}} = 17.75(-0.3q_{H}^{2}+1.5q_{H}) \qquad (3)$$

The calculated value of $\sigma^{AA}_{\mathrm{dia}}$, relative to the unsubstituted compound, is linearly correlated with the increment in the electron density on the hydrogen atom:

$$\Delta\sigma^{AA}_{\mathrm{dia}} = 16.0\Delta q^{A} \qquad (4)$$

In the preceeding paper,[1] we showed that the diamagnetic contribution from the bonded carbon ($\sigma^{AB}_{\mathrm{dia}}$) can be expressed as:

$$\sigma^{AB}_{\mathrm{dia}} = (e^{2}/3mc^{2})r_{AB}^{-1}q^{B} \qquad (5)$$

where r^{-1} is the inverse distance of the A atom from the point charge on the B atom and where q is the total (2s and 2p) electron density on the B atom. In the case of benzene, too, the contribution can be calculated in the same way as in the case of the olefinic proton,[1] because the ring proton also bonds to the sp^2-hybridized carbon atom and the C–H bond length is taken to be 1.08 Å. Thus, the $\sigma^{AB}_{\mathrm{dia}}$ term, relative to the unsubstituted compound, becomes:

$$\Delta\sigma^{AB}_{\mathrm{dia}} = 8.70\Delta q^{B} \qquad (6)$$

The paramagnetic term, $\sigma^{AB}_{\mathrm{para}}$, calculated according to Pople's expression,[2b)] remains almost constant for the series of monosubstituted benzenes so long as we assume the same average excitation energy and the same value of the integral $\langle r_{AB}^{-3}\rangle$.

In order to calculate the contribution of the "ring-current" effect relative to the unsubstituted compound, Eq. (7) derived by Yamada, Tsuno, and Yukawa[2d)] can be applied, just as it is, to all the ring protons in the present case:

$$\Delta\sigma^{A,\mathrm{ring}} = -0.4f(\rho, z)|\sigma_{\pi}| \qquad (7)$$

where the value of $f(\rho,z)$ is -1.50 ppm.[3)]

Using Eqs. (4), (6), and (7), we obtain the following equation for the relative chemical shifts of the ring protons:

$$\delta_{\mathrm{calcd}} = 16.0\Delta q^{A} + 8.70\Delta q^{B} + 0.6|\sigma_{\pi}| \qquad (8)$$

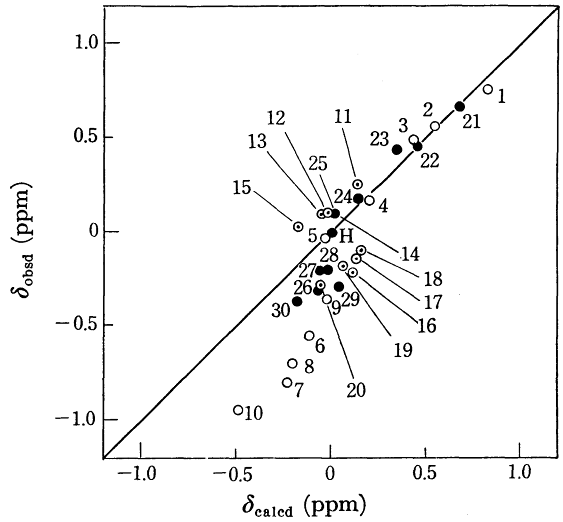
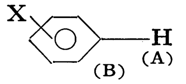


Fig. 1. Plots of δ_{obsd} against δ_{calcd} for ring protons of monosubstituted benzenes.
Numbered points correspond to entries in the Table 1.
○: *ortho*-substituent, ⊙: *meta*-substituent, ●: *para*-substituent.

The chemical shifts calculated by Eq. (8) are compared in the table with those observed for monosubstituted benzenes. In the figure, plots of the observed chemical shifts are shown against the calculated shifts. As may clearly be seen in the figure, the calculated chemical shifts can semi-quantitatively reproduce the trend of the substituent effects on the chemical shifts for protons at the position *para* to the substituents. This reveals that the three terms of Eq. (2) constitute the most important

Table 1. Calculated and observed relative chemical shifts of ring protons in monosubstituted benzenes[a]



Substituent	q^{A}[b]	q^{B}[b]	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,ring}$	δ_{calcd}	δ_{obsd}[c]
1. *o*-NH_2[e]	1.00317	4.05962	−0.054	0.576	0.288	0.81	0.746
2. *o*-OH	0.99422	4.05537	−0.197	0.539	0.192	0.53	0.558
3. *o*-OCH_3	0.99072	4.05168	−0.254	0.507	0.169	0.42	0.484
4. *o*-CH_3	1.00727	4.01035	0.011	0.147	0.047	0.21	0.17[d]
5. *o*-Cl	0.98833	4.01909	−0.292	0.223	0.042	−0.03	−0.026
6. *o*-CHO	0.99907	3.97829	−0.120	−0.132	0.138	−0.11	−0.561
7. *o*-CO_2H	0.99485	3.97353	−0.188	−0.173	0.150	−0.21	−0.8[d]
8. *o*-CO_2CH_3	0.99554	3.97386	−0.176	−0.170	0.168	−0.18	−0.713
9. *o*-CN	0.99888	3.98902	−0.123	−0.038	0.150	−0.01	−0.361
10. *o*-NO_2	0.97309	3.97933	−0.539	−0.123	0.204	−0.46	−0.952
11. *m*-NH_2[e]	1.00948	3.96844	0.046	−0.217	0.288	0.12	0.249
12. *m*-OH	1.00581	3.97105	−0.012	−0.194	0.192	−0.01	0.122
13. *m*-OCH_3	1.00368	3.97210	−0.046	−0.185	0.169	−0.06	0.093
14. *m*-CH_3	1.00775	3.98830	0.019	−0.045	0.047	0.02	0.09[d]
15. *m*-Cl	1.00067	3.98045	−0.094	−0.113	0.042	−0.17	0.022
16. *m*-CHO	1.00207	3.99905	−0.072	0.049	0.138	0.12	−0.221
17. *m*-CO_2H	1.00148	4.00019	−0.081	0.059	0.150	0.13	−0.14[d]
18. *m*-CO_2CH_3	1.00201	4.00024	−0.073	0.059	0.168	0.16	−0.109
19. *m*-CN	1.00118	3.99280	−0.086	−0.005	0.150	0.06	−0.182
20. *m*-NO_2	0.99169	3.99228	−0.238	−0.010	0.204	−0.04	−0.257
21. *p*-NH_2[e]	1.00880	4.03174	0.035	0.333	0.288	0.66	0.652
22. *p*-OH	1.00574	4.02194	−0.013	0.248	0.192	0.43	0.447
23. *p*-OCH_3	1.00379	4.01710	−0.045	0.206	0.169	0.33	0.439
24. *p*-CH_3	1.00740	4.00289	0.013	0.082	0.047	0.14	0.18[d]
25. *p*-Cl	1.00166	4.00085	−0.078	0.065	0.042	0.03	0.088
26. *p*-CHO	1.00260	3.97971	−0.069	−0.119	0.138	−0.05	−0.294
27. *p*-CO_2H	1.00243	3.97786	−0.066	−0.135	0.150	−0.05	−0.2[d]
28. *p*-CO_2CH_3	1.00288	3.97839	−0.059	−0.131	0.168	−0.02	−0.209
29. *p*-CN	1.00211	3.98908	−0.071	−0.038	0.150	0.04	−0.282
30. *p*-NO_2	0.99435	3.97395	−0.195	−0.169	0.204	−0.16	−0.378
31. H	1.00659	3.99341	0.000	0.000	0.000	0.00	0.000

a) All values are relative to the unsubstituted compound. b) All electron densities were calculated by the CNDO/2 method. c) Cited from the paper by Hayamizu *et al.*; K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **28**, 89 (1968); **28**, 422 (1968); **29**, 183 (1969). d) Cited from the monograph by Jackman *et al.* L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry" (International Series of Monographs in Organic Chemistry, Vol. 5) ed. by D. H. R. Barton and W. Doering, Pergamon Press, Oxford (1969), p. 202. e) A planar model was used for amino groups. f) The σ_π-values necessary to calculate the $\Delta\sigma^{A,ring}$ term, which have not been established, were obtained from the correlation line between *pi*-electron densities on the carbon atoms at the position para to the substituent and the known σ_π-values of the other substituents; σ_π(*p*-CHO): 0.23, σ_π (*p*-CO_2H): 0.25, σ_π(*p*-CO_2CH_3): 0.28.

factors determining the relative chemical shifts in the case of *para*-protons remote from the substituent. In the protons at the positions *meta* and *ortho* to the substituents, however, the correlation between the observed and the calculated chemical shifts collapses appreciably. The cause of the deviations in the case of *meta*-protons may be mainly ignoring the magnetic contributions from carbon atoms neighboring the B atom. In the case of *ortho*-protons, especially in carbonyl and nitro derivatives, one reason that the calculated chemical shifts do not well reproduce the observed shifts may be ignoring the magnetic anisotropy of substituent groups which cause a low-field shift in the proton.[4]

The CNDO/2 calculation was carried out on a FACOM-230 computer at the Nagoya University Computation Center.

References

1) J. Niwa, This Bulletin, **48**, 118 (1975).

2) a) O. Kajimoto and T. Fueno, *Chem. Lett.*, **1972**, 103; b) J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).

3) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "Hugh Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford (1965), p. 595; C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

4) For example, F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York (1969), pp. 75, 79.