Tetrahedron Letters No. 41, pp 3711 - 3714, 1976. Pergamon Press. Printed in Great Britain.

SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFTS OF SUBSTITUTED BENZENES. PERIODICAL DEPENDENCY OF SUBSTITUENT ELECTRONEGATIVITY EFFECTS UPON RING-CARBON CHEMICAL SHIFTS

Naoki Inamoto,* Shozo Masuda, Katsumi Tokumaru, Kazuo Tori,† Masayuki Yoshida and Yohko Yoshimura†

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, 113 Japan

and †Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

(Received in Japan 8 July 1976; received in UK for publication 23 August 1976)

In the preceding paper,[1] we reported that the relative substituent ^{13}C chemical shifts of meta-carbons (C_m-SCS) and ring-carbons directly bonded to a substituent (C_s-SCS) in a series of substituted benzenes are ruled by substituent electronegativities in the series of the second-period central atoms, but that halogen atoms such as chlorine and bromine as well as some other heavy atoms deviate from the relationship. Earlier workers explained this phenomenon in terms of the magnetic anisotropy of the halogen atoms in the case of the C_s-SCS.[2a]

Examining a number of selected literature data on ^{13}C-SCS in monosubstituted benzenes[3] and 4-substituted styrenes,[4] we found satisfactory periodical linear relationships between both C_s- and C_m-SCS and the substituent electronegativity of elements of the second through the sixth period.

FIGURES 1 and 2 respectively show the periodical linearity between C_s- and C_m-SCS and the group electronegativity of substituents (χ_X)[5] in monosubstituted benzenes.[3] Similar behavior is also demonstrated in the cases of C-2(6) (C_m) and C-4 (C_s) in substituted styrenes[4] as reproduced in FIGs. 3 and 4. Furthermore, similar periodical relationships of ^{13}C-SCS and χ_X were revealed on reexamination of the data reported in earlier studies of ^{13}C-SCS of monosubstituted methanes[2b] (see FIG. 5) and ethylenes,[6] although the use of substituents from the fourth through sixth periods is more restricted.

In these relationships, plots for the halogen atoms seem to belong to each period line. The deviation of plots for cyano and ethynyl groups from the second-period line (see FIGs. 1 and 3), as suggested in the preceding paper,[1] may arise from their anisotropy effects on the basis of recent calculation of the ^{13}C

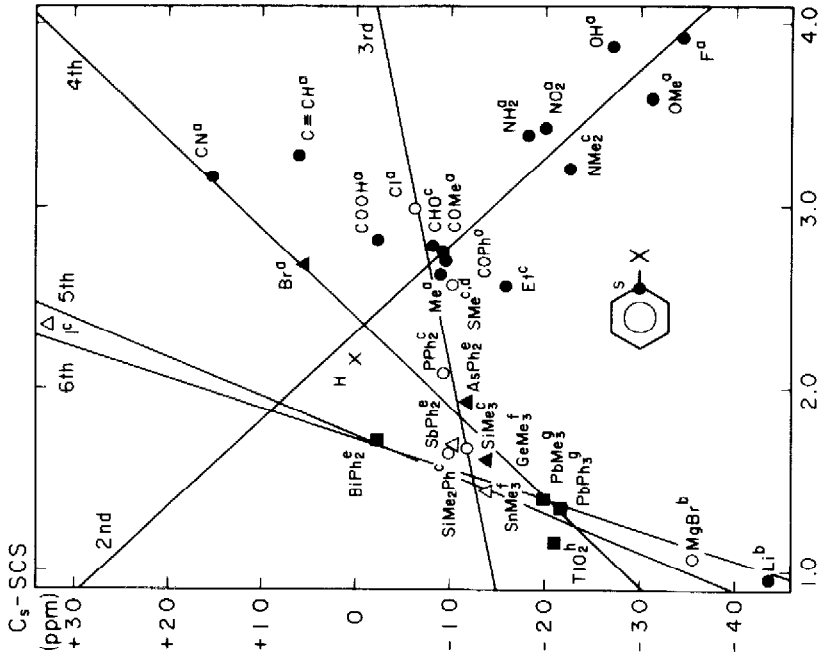

FIG. 1. Plots of C_s-SCS vs. substituent electronegativity (χ_X) for monosubstituted benzenes. Data taken from ref 3.

●, plots for substituents having a second-period element for the center atom: O, those for a third-period element; ▲, those for a fourth-period element; Δ, those for a fifth-period element; ■, those for a sixth-period element; X, that for the hydrogen.

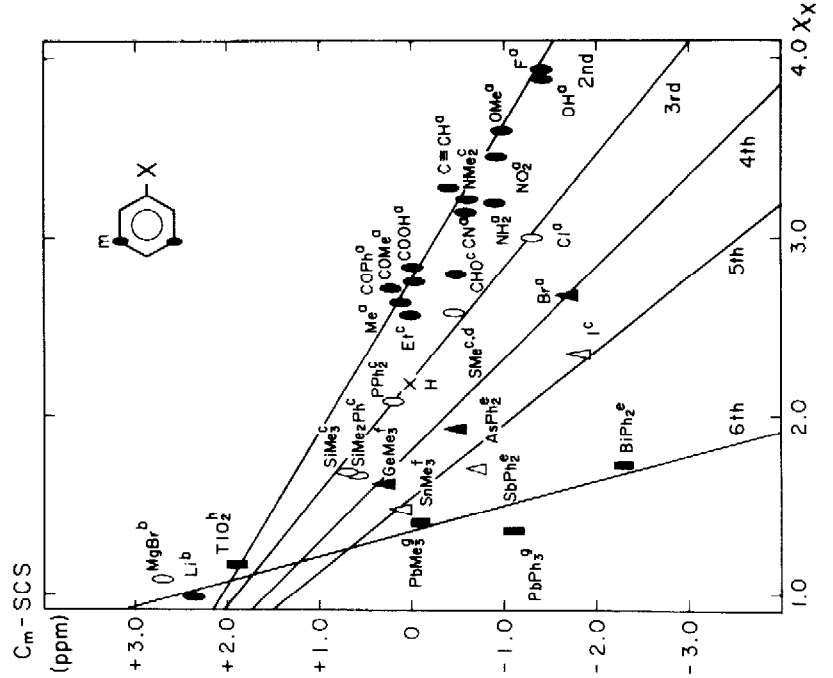

FIG. 2. Plots of C_m-SCS vs. substituent electronegativity (χ_X) for monosubstituted benzenes. Data taken from ref. 3.

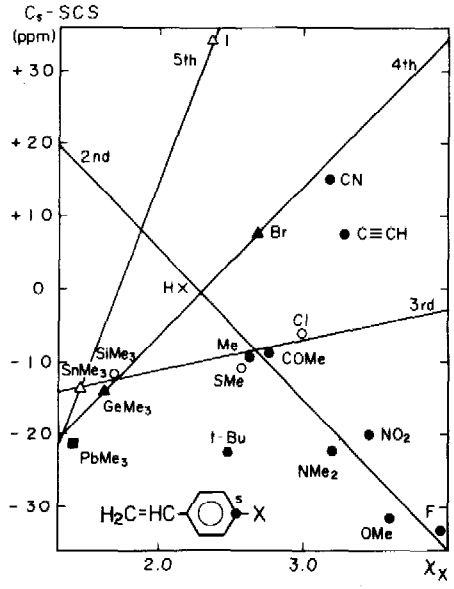

FIG. 3. Plots of C_s-SCS (C-4) vs. substituent electronegativity (χ_X) for 4-substituted styrenes. Data taken from ref 4.

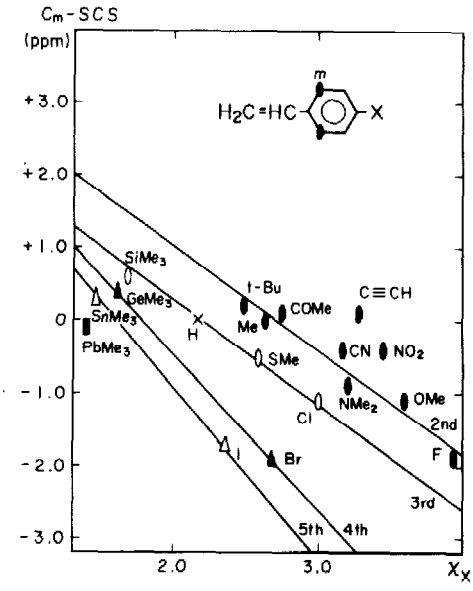

FIG. 4. Plots of C_m-SCS (C-2(6)) vs. substituent electronegativity (χ_X) for 4-substituted styrenes. Data taken from ref 4.

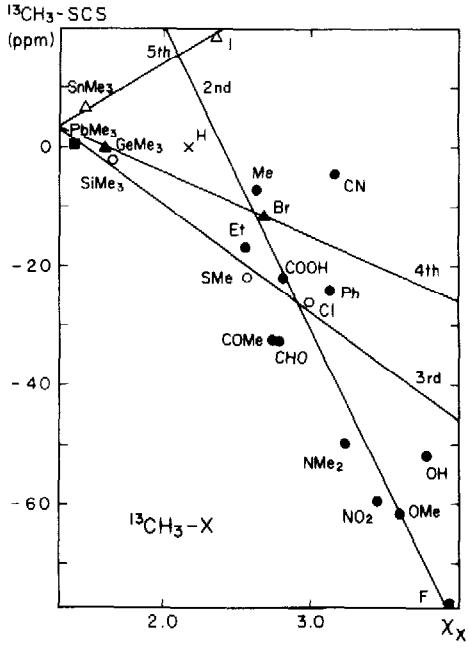

FIG. 5. Plots of ^{13}C-SCS vs. substituent electronegativity (χ_X) for monosubstituted methanes. Data taken from ref 2b.

chemical shift of acetonitrile.[7] The extremely large downfield shifts of C_s-Li and C_s-MgBr signals (see FIG. 1) have been suggested as resulting from the ionic character of their bonds.[3b]

Interestingly, the sign of the slopes from the third- to the sixth-period lines is the opposite of that of the second-period one in the relationships of C_s-SCS and χ_X (see FIGs. 1 and 3). The feature of the relationships of C_α-SCS and χ_X in monosubstituted ethylenes ($CH_2=C_\alpha HX$) is very similar to that in monosubstituted benzene. This inversion of the sign is also apparent for the slope of the fifth-period atoms in the relationships of monosubstituted methanes. However, similar

relationships between C_m-SCS and x_X show the same sign in each period line as indicated in FIGs. 2 and 4.

This periodical dependency of the electronegativity effect has also been reported for IR,[8] ^{1}H-SCS,[9] and $J_{^{13}C-H}$ data.[10]

REFERENCES

(1) N. Inamoto, S. Masuda, K. Tokumaru, K. Tori, M. Ysohida and Y. Yoshimura, the preceding paper.

(2) (a) H. Spiesecke and W. G. Schneider, J. Chem. Phys. 35, 731 (1961); (b) Idem., Ibid. 35, 722 (1961).

(3) (a) G. L. Nelson, G. C. Levy and J. D. Cargioli, J. Amer. Chem. Soc. 94, 3089 (1972); (b) A. J. Jones, D. M. Grant, J. G. Russel and G. Fraenkel, J. Phys. Chem. 73, 1624 (1969); (c) Our data measured for this study: for the measurement procedures, see the preceding paper. For the δ_C data on Et, CHO, NMe_2, PPh_2, $SiMe_3$, $SiMe_2Ph$, see also L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley-Interscience, New York (1972); J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972); or R. E. Rakita, J. P. Srebo and L. S. Worsham, J. Organometal. Chem. 104, 27 (1976); (d) A. C. Boicelli, R. Danieli, A. Mangini, A. Ricci and G. Pirazzini, J.C.S. Perkin II, 1343 (1974); (e) O. A. Gansow and B. Y. Kimura, Chem. Commun. 1621 (1970); (f) D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching and M. Bullpitt, Austral. J. Chem. 27, 417 (1974); (g) D. de Vos, J. Organometal. Chem. 104, 193 (1976); (h) W. Kitching, D. Praeger, C. J. Moore, D. Doddrell and W. Adcock, Ibid. 70, 339 (1974).

(4) G. K. Hamer, I. R. Peat and W. F. Reynolds, Can. J. Chem. 51, 897 (1973).

(5) (a) For atom electronegativity, see W. Gordy, Phys. Rev. 69, 604 (1946); (b) For group electronegativity, see J. K. Wilmshurst, J. Chem. Phys. 27, 1129 (1957).

(6) (a) G. E. Maciel, J. Phys. Chem. 69, 1947 (1965); G. Miyajima, K. Takahashi and K. Nishimoto, Org. Magn. Resonance 6, 413 (1974).

(7) I. Morishima, A. Mizuno and T. Yonezawa, Chem. Phys. Lett. 7, 633 (1970).

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Chapter 23, Methuen, London (1958).

(9) (a) P. Lazzeretti and F. Taddei, Tetrahedron Lett. 3025 (1969); (b) Idem., Org. Magn. Resonance 3, 113 (1971).

(10) (a) A. W. Douglas, J. Chem. Phys. 45, 3465 (1966); (b) S. Masuda and N. Inamoto, Chem. Lett. 655 (1973).