

On the Substituent-induced Chemical Shifts of the Side Chain Carbons in the *para*-Substituted Propylbenzenes, 2-Methylpropylbenzenes, and 2,2-Dimethylpropylbenzenes

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The substituent-induced chemical shifts (SCS) for the side chain carbons in a number of the *para* substituted propylbenzenes (A), 2-methylpropylbenzenes (B), and 2,2-dimethylpropylbenzenes (C) were determined. The SCS of C₂ (β -position to the ring) of A showed clearly an inverse trend in the sense of the substituent electronic effect as good as SCS (¹³CH₃) of *p*-substituted ethylbenzenes. SCS (C₂) of B for electron attracting groups by resonance exhibited also an inverse trend while the magnitudes were very small. SCS (C₂) of C showed a normal trend. It was confirmed that the most important factor for the inversed SCS for SCS (C₂) for the ethylbenzenes, A, and B was the polarization of the C₂-H bond induced by the substituted phenyl moiety.

Introduction

The ring carbon shieldings of the substituted benzenes in NMR spectra are sensitive to the polar effect of the substituents.¹⁾ The substituent-induced chemical shifts (SCS) of the carbon-13 of the *para* position to substituents show a linear relation with the electron density²⁾ and are treated quantitatively by the extended Hammett equations since the contributing polar effects are composed of a blend of an inductive effect and a resonance effect.³⁾

On the other hand, SCS of the side chain atoms in the *para* substituted benzenes are small and the directions of SCS vary with the character of the side chain.^{3b),4)} Of particular interest, ¹³C resonance of the methyl groups in *p*-substituted ethylbenzenes,⁵⁾ 1-methylethylbenzenes (isopropylbenzenes),⁶⁾ and 1,1-dimethylethylbenzenes (*t*-butylbenzenes),⁷⁾ exhibited an inverse trend. Thus, the electron-attracting groups induce up field shift and the electron-donating groups down field shifts. SCS of the ¹³C resonance of the CH₃ group in these compounds were related to the original Hammett substituent constant σ values with

a negative slope rather than σ^0 constants. Inamoto and co-workers explained this phenomenon with a polarization of the C-H bonds of the methyl group induced by the charge on the substituted phenyl moiety.⁸⁾ In order to confirm their explanation, ^{13}C NMR spectra for the *p*-substituted propylbenzenes (A), *p*-substituted 2-methylpropylbenzenes (B, isobutylbenzenes), and *p*-substituted 2,2-dimethylpropylbenzenes (C, neopentylbenzenes) were examined in the present study.

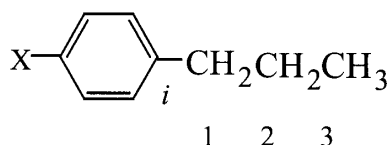
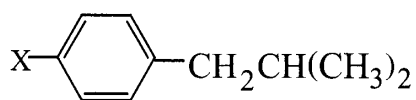
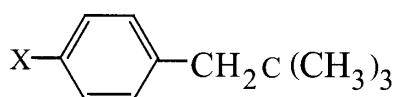
**A****B****C**

Table 1. SCS (in ppm) of *p*-Substituted Propylbenzenes (A) in Deuteriochloroform Solutions (Positive Values Represent Downfield Shifts)

Subst.	C-1	C-2	C-3	C- <i>i</i>
H	0(38.18) ^a	0(24.67) ^a	0(13.89) ^a	0(142.71) ^a
CH ₃ O	-1.00	0.16	-0.11	-7.95
CH ₃	-0.42	0.14	-0.03	-2.99
Br	-0.68	-0.18	-0.12	-1.03
Cl	-0.75	-0.21	-0.18	-1.52
CHO	-0.05	-0.39	-0.10	7.45
CH ₃ CO	-0.17	-0.45	-0.15	5.83
CH ₃ OCO	-0.15	-0.45	-0.18	5.47
C ₂ H ₅ OCO	-0.13	-0.40	-0.15	5.37
COCl	-0.10	-0.60	-0.18	8.73
NO ₂	-0.27	-0.58	-0.19	7.88

a) Chemical Shifts corresponding to the hydrogen substituent relative to TMS.

Table 2. SCS (in ppm) of *p*-Substituted Isobutylbenzenes (B) in Deuteriochloroform Solutions (Positive Values Represent Downfield Shifts)

Subst.	C-1	C-2	C-3	C- <i>i</i>
H	0.00 (45.59) ^{a)}	0.00 (30.35)	0.00 (22.46)	0.00 (141.72)
CH ₃ O	-0.95	0.10	-0.06	-7.78
CH ₃	-0.45	0.02	-0.02	-3.11
Br	-0.72	-0.12	-0.12	-1.04
CHO	-0.16	-0.32	-0.25	7.35
CH ₃ CO	-0.29	-0.32	-0.21	5.72
CH ₃ OCO	-0.13	-0.19	-0.11	5.57
C ₂ H ₅ OCO	-0.19	-0.22	-0.17	5.57
COCl	-0.16	-0.23	-0.14	8.80
CN	-0.22	-0.35	-0.30	5.59
NO ₂	-0.29	-0.11	-0.11	8.04

a) The values in the parentheses are chemical shifts corresponding to the hydrogen substituent relative to TMS.

Table 3. SCS (in ppm) of *p*-Substituted Neopentylbenzenes (C) in Deuteriochloroform Solutions (Positive Values Represent Downfield Shifts)

Subst.	C-1	C-2	C-3	C- <i>i</i>	C- <i>o</i> ^{a)}	C- <i>m</i> ^{a)}	C- <i>p</i>	others
H	0.00 (50.24) ^{b)}	0.00 (31.72)	0.00 (29.38)	0.00 (139.72)	0.00 (130.46)	0.00 (127.58)	0.00 (125.70)	
<i>p</i> -CH ₃ O	-0.95	-0.04	-0.11	-7.87	-0.43	-13.48	32.04	55.25
<i>p</i> -CH ₃	-0.50	-0.08	-0.06	-1.46	-1.09	0.95		21.17
<i>p-t</i> -C ₄ H ₉	-0.53	-0.01	-0.03	-3.07	-0.33	-3.14	22.68	31.44
<i>p</i> -Br	-0.68	-0.09	-0.13	-1.12	0.64	3.10	-6.00	
<i>p</i> -Cl	-0.73	-0.05	-0.13	-1.61	1.23	2.77	5.91	26.52, 197.96
<i>p</i> -CH ₃ CO	-0.08	0.22	-0.12	5.93	0.09	0.19	9.29	26.52, 197.96
<i>p</i> -CH ₃ OCO	-0.08	0.15	-0.05	5.58	-0.06	1.34	2.04	51.90, 167.23
<i>p</i> -COCl	0.00	0.40	-0.01	8.82	0.53	3.37	5.22	166.77
<i>p</i> -CN	0.01	0.24	-0.15	5.68	0.95	3.47	-16.04	119.14
<i>p</i> -NO ₂	-0.24	0.36	-0.08	7.97	-7.56	3.49	20.73	

a) Some assignments are interchangeable. b) The values in parentheses are the chemical shifts corresponding to the hydrogen substituent relative to TMS.

Results and Discussions

The obtained SCS of side chain carbons and the *ipso* carbons in A, B, and C are summarized in Table 1, 2, and 3 respectively. For C, SCS for all carbons are sited.

Magnitudes of the SCS(C₂, A) are almost same as those of SCS(¹³CH₃) in *p*-substituted ethylbenzenes. As expected, SCS(C₂) of A showed an inverse trend. Thus, the electron-donating substituents (CH₃O and CH₃) induced down field shifts and the electron-attracting substituents by resonance (CHO, CH₃CO, CH₃OCO, C₂H₅OCO, COCl, and NO₂; +R groups) induced up field shifts. It is noticeable that the sign of SCS(C₂, A) for the CH₃O and CH₃ are opposite to SCS(C₁, A). The magnitudes of SCS(C₂, A) of +R groups are larger than those for SCS(C₁, A). The following relation was obtained for the original Hammett σ_p constants.

$$\text{SCS}(C_2, A) = -0.79 \sigma - 0.02 \quad (r=0.99^9, s=0.03^{10})$$

These results suggest that the SCS(C₂, A) arise from the polar effect of the substituents and the effect transmitted through space.

A trend of SCS(C₂, B) is as well as that of SCS(C₂, A). However, the magnitude of the SCS(C₂, B) is smaller than that of the SCS(C₂, A) and the quantitative treatment is impossible.

It is noticeable that the trend of SCS(C₂, C) is clearly normal except for Br and Cl while the magnitudes are too small to carry out the quantitative analysis. The magnitude of SCS(C₂, C) is larger than that of the SCS(C₁, C) for +R groups. It appears that these phenomena arise from the hyper conjugation between the π orbital of the benzene ring and the C₁-C₂ bond.

Lambert and Singer reported SCS for the compound of a series of *p*-XC₆H₄CH₂M(CH₃)₃.¹¹⁾ They suggested an importance of the variation of the phenyl-C₁ bond due to the hyper conjugation between the benzene ring and the C₁-M bond for SCS of M. However, their assignments for chemical shifts of C₂ are erroneous. Trela pointed out that their measurements of the C_i-C₁ coupling constants were also erroneous.¹²⁾ The SCS of the methyl groups in isopropylbenzenes⁶⁾ and of *t*-butylbenzenes⁷⁾ also showed an inverse trend. Thus, a conformational effect is not important. It is concluded that the polarization of the C₂-H bond induced by phenyl moiety is the most important factor for the inverse SCS(C₂) in *p*-substituted ethylbenzenes, A, and B at least for the +R groups. The same explanation is applied to the inverse SCS for the ¹⁹F resonance in *p*-substituted benzylfluorides,¹³⁾ the ¹⁵N resonance in *p*-substituted benzylamines,¹⁴⁾ and ¹⁷O resonance in *p*-substituted benzylalcohols¹⁵⁾ and benzyl methyl ethers.¹⁶⁾ Here, lone pair electrons are drawn to the nuclei by the charge on the phenyl moiety. It may be presumed that an inversed trend of SCS(C₃) due to the +R groups arises from the same mechanism.

Experimental

All boiling points and melting points were uncorrected. The melting points were measured on a YANACO Mp hot stage melting-point apparatus. HPLC was carried out with a JASCO TRIROTAR-V with a Shodex RI SE-51 detector. A mixture of hexane and ethyl acetate was used as an eluent. The IR spectra were measured using a JASCO A100 spectrometer. The mass spectra were determined at 70 eV using a JEOL JMS-AX 50 5HA spectrometer. The ¹H NMR spectra were determined as a solution in deuteriochloroform with tetramethylsilane (TMS) as an internal standard on a JEOL Lambda 400 spectrometer at 400 MHz. The ¹³C NMR spectra were recorded on a JEOL Lambda 400 spectrometer at 100 MHz. The typical ¹³C NMR measurements were carried out under following conditions: concentration of the sample, 10% (V/V); tube bore, 5 mm; pulse length, 8.25 μs; number of data points, 16,384; spectral width, 27,100 Hz; digital resolution, 0.83 Hz; numbers of the scan, 2,000.

p-Substituted propylbenzenes. Most of these compounds were prepared and purified by the routine work. The boiling points were as follows: substituent, Bp (°C/mmHg); H, 55~57/22; CH₃O, 69/6; CH₃, 85/16; Br, 72/12; Cl, 54~58/16; CHO, 95/6; CH₃CO, 109/8; CH₃OCO, 90/6; C₂H₅OCO, 95/4; COCl, 95/6; NO₂, 125/13.

p-Substituted 2-methylpropylbenzenes. Most of these compounds were prepared by the usual method. *p*-Isobutylbenzaldehyde was a commercial product (TCI). The *p*-isobutylbenzotrile was obtained by heating the corresponding aldehyde, hydroxylamine hydrochloride, and *N*-methylpyrrolidone at 115 °C.¹⁷⁾ The boiling points were as follows; substituent, Bp (°C/mmHg); H, 171/760; CH₃O, 95/13; CH₃, 78/20; Br, 69/3.5; CH₃CO, 97/4; CH₃OCO, 109/3; C₂H₅OCO, 94/2.5; CN, 79/2.5; COCl, 86/4; NO₂, 90/3.

p-Substituted 2,2-dimethylpropylbenzenes. 2,2-dimethylpropylbenzene was obtained commercially (TCI). The *t*-butyl derivative was prepared by treating 2,2-dimethylpropylbenzene and 2-chloro-2-methylpropane (*t*-butyl chloride) with sodium. Other derivatives were synthesized by usual method. The boiling points and the melting points obtained were as follows; substituent, Bp (°C/mmHg), mp [°C]; CH₃O, 96/7; CH₃, 85/35; *t*-C₄H₉, 72/7; Br, 93/6.5; Cl, 110/20; CH₃CO, 105/3.5; CH₃OCO, [46]; COCl, 130/10; CN, 105/6.5.

References

- 1) a) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Chap. 5, Academic Press, New York (1972). b) G. E. Maciel, in "Topics in Carbon-13 NMR Spectroscopy," ed. by G. C. Levy, Wiley-Interscience (1974). c) E. Breitmaier and W. Voelter, "Carbon-13 NMR Spectroscopy," Chap. 4, p. 254, VCH, Weinheim (1987).
- 2) W. H. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.* Vol. 12, p. 159 (1976). R. T. C. Brownlee, and R. W. Taft, *J. Am. Chem. Soc.*, **92**, 7007 (1970).

- 3) a) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94**, 3089(1972). b) J. D. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.* Vol. 14, Chap. 1, p. 1. c) M. Sawada, Y. Takai, S. Yamano, S. Misumi, T. Hamafusa, and Y. Tsuno, *J. Org. Chem.*, **53**, 191(1988).
- 4) a) J. Bromilow, R. T. C. Brownlee, and D. J. Craik, *Aust. J. Chem.*, **30**, 351(1977). b) C. Dell'Erba, F. Sancassan, M. Novi, G. Petrillo, A. Mugnoli, D. Spinell, G. Consiglio, and P. Gatti, *J. Org. Chem.* **53**, 3564(1988).
- 5) L. F. Blackwell, P. D. Buckley, and K. W. Jolley, *Aust. J. Chem.*, **27**, 2283(1974); L. F. Blackwell, P. D. Buckley, and K. W. Jolley, *Aust. J. Chem.*, **29**, 2423(1976). Y. Kusuyama, *Wakayamadaigaku Kyoikugakubu Kiyō, Shizenkagaku (Bull. Fac. Edu. Wakayama Univ., Natur. Sci)*, **42**, 9(1992).
- 6) Y. Kusuyama, C. D. Brenzinger, and J. D. Roberts, *Org. Magn. Res.*, **13**, 372(1980).
- 7) C. D. Schaefer, Jr., J. J. Zucherman., and C. H. Yoder, *J. Organomet. Chem.*, **80**, 29(1974)
- 8) N. Inamoto and S. Masuda, *Kagakuoryōiki*, **33**, 198(1979).
- 9) Correlation coefficient.
- 10) Standard deviation.
- 11) J. B. Lambert and R. A. Singer, *J. Am. Chem. Soc.*, **114**, 10246(1992).
- 12) K. K. Trela, *Magn. Res. Chem.*, **33**, 406(1995).
- 13) J. Bromilow, R. T. C. Brownlee, and A. V. Page, *Tetrahedron Lett.*, **1976**, 3055.
- 14) Y. Kusuyama, *Chem. Express*, **8**, 317(1993).
- 15) a) P. Balakrishnan, A. L. Baumstark, and D. W. Boykin, *Tetrahedron Lett.*, **25**, 169(1984). b) Y. Kusuyama, *Wakayamadaigaku Kyoikugakubu Kiyō, Shizenkagaku (Bull. Fac. Edu. Wakayama Univ. Natur. Sci)*, **21**, 49(1999).
- 16) Y. Kusuyama, *Wakayamadaigaku Kyoikugakubu Kiyō, Shizenkagaku (Bull. Fac. Edu. Wakayama Univ. Natur. Sci)*, **29**, 49(1999).
- 17) H. M. S. Kumar, B. V. S. Reddy, and J. S. Yadav, *Syntheses*, **1999**, 586.

Corrections: Y. Kusuyama, *Wakayamadaigaku Kyoikugakubu Kiyō, Shizenkagaku*, **42**, 9(1992). P.12. scheme A. δ^+ should be replaced by δ^- and δ^- should be replaced by δ^+ .

和文題目及び要旨: 「パラ置換プロピルベンゼン(A)、2-メチルプロピルベンゼン(B)及び2,2-ジメチルプロピルベンゼン(C)の側鎖炭素化学シフトにおける置換基効果について」: 標記の化合物の炭素-1³C核磁気共鳴スペクトルを測定し、側鎖炭素の化学シフト(δ)を決定した。A, Bの2-位の炭素は置換基電子効果の解釈では逆の方向性を示し、Aにおいて顕著であった。他方Cの2-位の炭素は正の方向性を示した。A, BにおけるC₂の置換基効果は2位の炭素-水素結合の分極により生じたものである。