[Chem. Pharm. Bull. 27(8)1780—1791(1979)]

UDC 547.652.02.08 : 543.422.25.06

# Studies on $^{13}$C Magnetic Resonance Spectroscopy. XIV.[1] Interpretation of the $^{13}$C NMR Chemical Shifts of 2-Substituted Naphthalenes and Their 6-Methoxy Derivatives

HITOSHI TAKAI, AKIRA ODANI, and YOSHIO SASAKI

*Faculty of Pharmaceutical Sciences, Osaka University*[2]

(Received December 18, 1978)

The $^{13}$C chemical shifts of 2-substituted naphthalenes and their 6-methoxy derivatives are considered in terms of empirical parameters, charge densities, and screening tensors.

The $^{13}$C screening tensors were calculated theoretically using LCGI-MO theory, by the MINDO/2 method. The results were consistent with the experimental data. The 2p electron charge density, the predominant factor governing the calculated $^{13}$C chemical shift, also corresponded well with the experimental data.

**Keywords**——$^{13}$C magnetic resonance; chemical shift; 2-substituted naphthalene; charge density; MINDO/2; screening tensor; substituent effect

## Introduction

In the previous report of this series,[3] the chemical shifts of 2-substituted naphthalene derivatives (**1**) were assigned, and the substituent shielding parameters were shown to be useful for predicting the $^{13}$C chemical shifts of 2-substituted-6-methoxynaphthalene (**2**),[3b] 6-substituted quinoline and quinoxaline derivatives.[3a]

Many studies[4,5] have sought to correlate the substituent-induced $^{13}$C chemical shifts of conjugated systems to empirical parameters. However, for naphthalene derivatives, there have been few practical investigations[5] dealing with the total charge density calculated by the molecular orbital method, and simultaneously taking into account the electronic interaction between substituents and both the $\sigma$- and $\pi$-frameworks.

In this report, we first aimed to develop an empirical treatment of the $^{13}$C chemical shifts of **1** and **2**, and then the calculated $^{13}$C screening tensor was correlated to the $^{13}$C chemical shift.

According to Pople,[6] $\sigma^{\mathrm{A}}$ (the screening tensor of nucleus A) is given by Eq. 1.

$$\sigma^{\mathrm{A}} = \sigma_{\mathrm{d}}^{\mathrm{AA}} + \sigma_{\mathrm{p}}^{\mathrm{AA}} + \sum_{\mathrm{A} \neq \mathrm{B}} \sigma^{\mathrm{AB}} + \sigma^{\mathrm{A,ring}} \qquad (1)$$

The contribution of the paramagnetic term $\sigma_{\mathrm{p}}^{\mathrm{AA}}$ is a dominant factor (up to 90%) in the screening tensor of the $^{13}$C nucleus. The neighbor anisotropy term is unlikely to exceed a few ppm,[6] and moreover, when the values relative to naphthalene are being treated, the term $\sigma^{\mathrm{A,ring}}$ can be neglected. In this case, the screening tensor can be approximately expressed as follows.[7]

$$\sigma^{13}\mathrm{C}_{\mathrm{calcd.}}(\mathrm{A}) = \sigma_{\mathrm{d}}^{\mathrm{AA}} + \sigma_{\mathrm{p}}^{\mathrm{AA}} \qquad (2)$$

---

1) Part XIII: T. Tsujimoto, T. Nomura, M. Iifuru, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **27**, 1169 (1979).

2) Location: *Yamadakami 133-1, Suita, Osaka 565, Japan.*

3) *a*) H. Takai, A. Odani, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1672 (1978); *b*) *Idem, ibid.*, **26**, 1966 (1978).

4) G.L. Nelson and E.A. Williams, *Prog. Phys. Org. Chem.*, **12**, 229 (1976); and references cited therein.

5) For example, J.E. Bloor and D.L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

6) J.A. Pople, *Mol. Phys.*, **7**, 301 (1964).

7) M.J.S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).

Two factors are important in the term $\sigma_p^{AA}$; these are the contributions of the Slater 2p orbital of atom A, $<r^{-3}>_{2p}$, and the singlet-singlet excitation energy term $(E_k-E_j)$. The term $<r^{-3}>_{2p}$ depends primarily on the local electron density on the carbon and is given by Eq. 3,[8]

$$<r^{-3}>_{2p} = 1/(24a_0^3)\cdot[3.25-0.35(P_1-3)]^3 \tag{3}$$

where $a_0$ is the Bohr radius and $(P_1\text{-}3)$ is the excess charge density of the 2p electron. The difference $(E_k-E_j)$ may be approximated to $\Delta E$ and related to a mean excitation energy, normally taken as 10 eV. Indeed, two calculations have been carried out with (method a: Karplus–Pople equation)[8] and without (method b) this approximation.

Each term[7] in Ep. 2 can be evaluated from either *ab initio* MO or semi-empirical MO calculations. For relatively large molecules, semi-empirical methods are more practical at present,[9] and the MINDO/2 method was used in this work.

## Experimental

*p*-Substituted anisoles were obtained commercially. The $^{13}$C nuclear magnetic resonance (NMR) measurements were carried out as described in the previous report.[10]

For the HMO method, a set of "recommended" parameter values given by Streitwieser[11] was used, but in some cases, parameter values were determined on the basis that the calculated charges were linearly related to the $^{13}$C chemical shifts (*cf.* Table I).

Table I. Suggested Parameter Values for Ring Carbons and Substituents

| | Coulomb integral | Bond integral |
|---|---|---|
| Ring carbons | $h_C = 0.0$ | $k_{C1-C2} = 1.19$ |
| | | $k_{C9-C10} = 0.95$ |
| | | $k_{C1-C9} = 0.93$ |
| | | $k_{C2-C3} = 0.91$ |
| Substituents | | |
| $N(CH_3)_2$ | $h_N = -0.2$ | $k_{C-N} = 0.37$ |
| $NH_2$ | $h_N = 1.5$ | $k_{C-N} = 0.8$ |
| $OCH_3$; OH | $h_O = 2.0$ | $k_{C-O} = 0.8$ |
| $CH_3$ (heteroatom model) | $h_X = 2.0$ | $k_{C-X} = 0.5$ |
| $CH_3$ (inductive model) | $h_C = -0.12$ | $k_{C-C} = 0.0$ |
| $CH_3$ (conjugation model) | $h_C = -0.09$ | $k_{C-C} = 0.8$ |
| | $h_{H_3} = -0.5$ | $k_{C-H_3} = 3.0$ |
| F | $h_F = 3.0$ | $k_{C-F} = 0.7$ |
| Cl | $h_{Cl} = 2.0$ | $k_{C-Cl} = 0.4$ |
| Br | $h_{Br} = 1.5$ | $k_{C-Br} = 0.3$ |
| I | $h_I = 1.2$ | $k_{C-I} = 0.2$ |
| $COCH_3$ | $h_{\underline{C}O} = 3.5$ | $k_{C-CO} = 0.29$ |
| | $h_{C\underline{O}} = 1.0$ | $k_{C=O} = 1.0$ |
| | $h_C = 2.0$ | $k_{C-CH_3} = 0.5$ |
| $COOCH_3$ | $h_{\underline{C}O} = 3.5$ | $k_{C-CO} = 0.29$ |
| | $h_{C\underline{O}} = 1.0$ | $k_{C=O} = 0.8$ |
| | $h_O = 2.0$ | $k_{CO-O} = 0.8$ |
| CN | $h_{\underline{C}N} = 4.8$ | $k_{C-CN} = 1.6$ |
| | $h_N = 0.5$ | $k_{C-N} = 0.8$ |
| $NO_2$ | $h_N = 3.7$ | $k_{C-N} = 0.29$ |
| | $h_O = 1.0$ | $k_{N=O} = 0.7$ |

---

8) M. Karplus and J.A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

9) R. Ditchfield, *Mol. Phys.*, **27**, 789 (1974).

10) H. Takai, K. So, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1303 (1978).

11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemist," John Wiley and Sons, Inc., New York, 1961, p. 135.

MINDO/2 and INDO calculations were carried out on a NEAC 2200 computer, model S800, at the Computation Center of Osaka University using a program based on that of Kikuchi.[12)]

The geometries were assumed on the basis of the data for naphthalene,[13)] standard bond lengths and angles,[14)] and the corresponding mono-substituted benzene derivatives.[15)] The more stable geometry was employed when two different conformations of the substitutent might be considered.

## Results and Discussion

$^{13}$C chemical shifts of **1** are linearly correlated to empirical parameters such as substituent constants $\sigma_i$ or $\sigma_\pi$,[16)] substituent-induced chemical shifts (s.c.s.) of monosubstituted benzenes (**3**) ($\delta_{ipso}$, $\delta_{ortho}$, $\delta_{meta}$, and $\delta_{para}$) and/or linear combinations of these factors.[3)] Chemical shifts of **1** are, in turn, useful to predict the shifts of **2**. Chemical shifts of **2** can also be expressed in terms of one of the above parameters or a linear combination of them. However, the slopes of the linear relations obtained in these treatments are determined arbitrarily by the calculation. For a quantitative examination of the parameters determining the chemical shifts, a more detailed discussion is necessary.

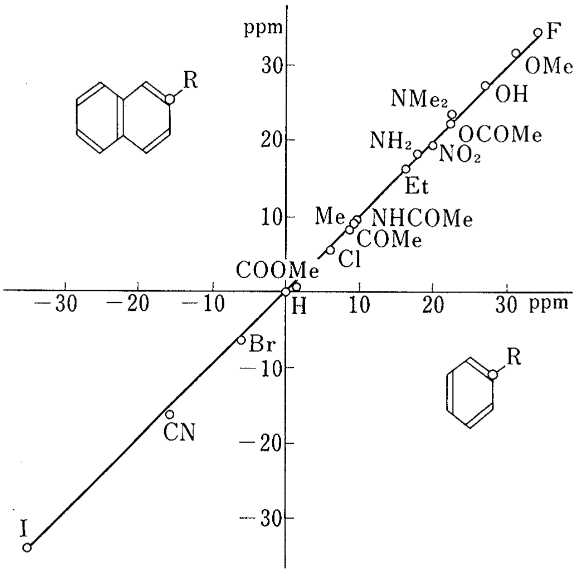


Fig. 1. Plot of s.c.s. at the *ipso* Position

C-2 of 2-substituted naphthalene *vs*. C-1 of monosubstituted benzene.

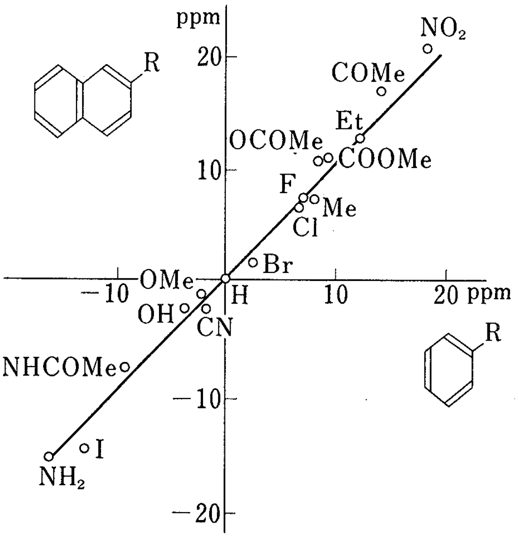


Fig. 2. Plot of the Sums of s.c.s. for 2-Substituted Naphthalene *vs*. Monosubstituted Benzene

---

12) O. Kikuchi, "Bunshi-Kido-Ho," Kodan-Sha, Tokyo, 1971.

13) V.I. Ponomarev, O.S. Filipenko, and L.O. Atavmyan, *Kristallografiya*, **21**, 392 (1976); A. Almenningen, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.*, **14**, 1056 (1961).

14) J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, 1970.

15) R=$N(CH_3)_2$: J.L. Boer and A. Vos, *Acta Crystallogr.*, **B28**, 835 (1972); L.V. Vilkov and T.P. Timaseva, *Dokl. Akad. Nauk. SSSR*, **161**, 361 (1965). R=$NH_2$: D.G. Lister and J.K. Tyler, *J. Mol. Structur.*, **23**, 253 (1974). R=$NHCOCH_3$: C.J. Brown, *Acta Crystallogr.*, **21**, 442 (1966). R=$OCH_3$: H.M. Seip and R. Seip, *Acta Chem. Scand.*, **27**, 4024 (1973): P. Diehl, H. Huber, A.C. Kunwar, and M. Reinhold, *Org. Magn. Reson.*, **9**, 374 (1977). R=OH: H.G. Pandraud, *Bull. Soc. Chim. Fr.*, **1967**, 1988. R=$CH_3$: W.A. Kreiner, H.D. Rodolph, and B.T. Tan, *J. Mol. Spectroscopy*, **48**, 86 (1973). R=$COCH_3$: Y. Tanimoto, H. Kobayashi, S. Nagakura, and Y. Saito, *Acta Crystallogr.*, **B29**, 1822 (1973). R=CN: J. Casado, L. Nygaard, and G.O. Sørensen, *J. Mol. Structur.*, **8**, 211 (1971). R=$NO_2$: J. Trotter, *Acta Crystallogr.*, **12**, 884 (1959). R=F: L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Structur.*, **2**, 209 (1968). R=$COOCH_3$: N.C. Baird and J.J.S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969). Changes of the endocyclic bond angle opposite the substituent: A. Dominicano, P. Mazzeo, and A. Caciago, *Tetrahedron Lett.*, **1976**, 1029.

16) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).

For the same substituents, the s.c.s. at C-2 of **1** and at the *ipso* carbon of **3** are nearly equal, so one can estimate the chemical shifts of **1** from the data for **3** (Fig. 1 [slope=1.01, $r^{18)}=1.000$]). The sum of the s.c.s. at C-1 and -3 (both adjacent to the *ipso* position) is equal to twice $\delta_{ortho}$. Among other positions, the quinonoidal ones (Wells' nomenclature),[17] C-6 and -8, and C-10, whose s.c.s. have a good correlation to $\sigma_\pi$, are governed mainly by the resonance effect of substituents,[3b,10] like the *para* position of **3**. The sum of s.c.s. of these *para*-like positions is approximately equal to $\delta_{para}$. That of the remaining C-4, -5, -7, and -9 is nearly equal to twice $\delta_{meta}$, so these positions are defined as *meta*-like positions. It can be concluded that the sum of the s.c.s. at all positions is the same for **1** and **3** (Fig. 2). s.c.s. is a suitable scale for the perturbation caused by the substituent. The sums of the perturbations of all ring carbons caused by substituents are the same for the naphthalene and benzene ring.

Substituent effects at corresponding positions in **1** and **3** show a similar tendency but are not equal quantitatively. For example, the range of the chemical shifts of C-1 and -3, both adjacent to the substituent, are not the same. Chemical shifts at C-1 or **1** range more widely than those at C-3. Both correlate to $\delta_{ortho}$ with independent slopes (slope=1.32, $r=0.984$ for C-1, and slope=0.65, $r=0.950$ for C-3). Plots of $\delta_{C-1}$ (s.c.s. at C-1) and $\delta_{C-3}$ *vs.* $\delta_{ortho}$ are somewhat irregular, namely, the points of nitro derivatives are located at opposite positions, and s.c.s. values of the methyl derivative have opposite signs ($\delta_{ortho}$ for $R=CH_3$ is $+0.72$ ppm). These irregularities afforded an ambiguous assignment of **1**, but the reason for them is not clear. Azzaro *et al.*[19] observed a variation in sensitivity to the substituent effect with respect to the unsaturated system, and treated it as a function of the number of $\pi$ electrons in the whole conjugated system. In our case this approach is not adequate. The apparent irregularity of s.c.s. at C-1 and -3 can be explained well in terms of the difference of double bond character,[20] which is an effective measure of the transmission of the substituent effect. Figure 3 shows that as the double bond character decreases, s.c.s. at the $\beta$-positions of an electron-donating ($-$R) substituent increases, whereas that at the $\beta$-positions of $+$R groups decreases. For halogens (Fig. 4), the plots cross as the double bond

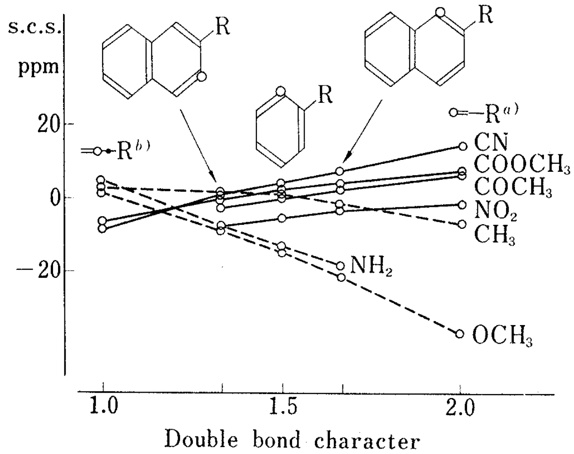


Fig. 3. Plot of s.c.s. against Bond Order of Parent Compounds

*a)* G. Miyajima, K. Takahashi and K. Nishimoto, *Org. Magn. Reson.*, **6**, 413 (1974).
*b)* T. Yonemoto, *J. Magn. Reson.*, **13**, 153 (1974).

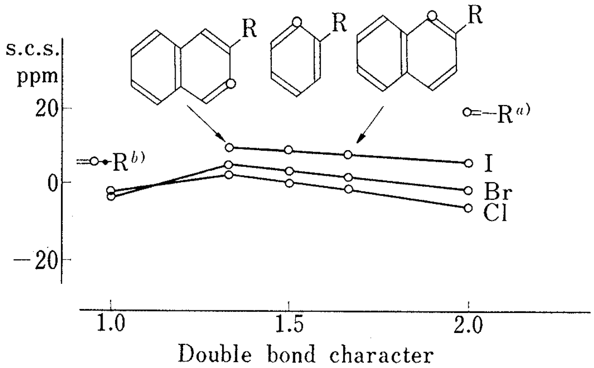


Fig. 4. Plot of s.c.s. against Bond Order of Parent Compounds

*a)* G. Miyajima, K. Takahashi, and K. Nishimoto, *Org. Magn. Reson.*, **6**, 413 (1974).
*b)* T. Yonemoto, *J. Magn. Reson.*, **13**, 153 (1974).

---

17) Correlation coefficient.
18) P.R. Wells, D.P. Arnold, and D. Doddrell, *J. Chem. Soc. Perkin II*, **1974**, 1745.
19) M. Azzaro, J.-F. Gal, S. Géribaldi, and N. Novo-Kremer, *Org. Magn. Reson.*, **9**, 181 (1977).
20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, New York, 1967, p. 183.

TABLE II. Substituent-Induced Charge Densities ($\Delta\rho_\pi$) Calculated by the HMO Method at Ring Carbons of 2-Substituted Naphthalenes

| Substituent | Carbon No. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $N(CH_3)_2$ | 0.1150 | −0.0935 | 0.0519 | −0.0084 | −0.0034 | 0.0201 | −0.0001 | 0.0198 | −0.0031 | 0.0280 |
| $NH_2$ | 0.0695 | −0.0484 | 0.0305 | −0.0049 | −0.0020 | 0.0124 | −0.0000 | 0.0122 | −0.0018 | 0.0171 |
| $OCH_3$ | 0.0609 | −0.0462 | 0.0272 | −0.0044 | −0.0018 | 0.0107 | −0.0000 | 0.0106 | −0.0016 | 0.0149 |
| $CH_3$[a] | 0.1045 | −0.1984 | 0.0534 | −0.0086 | −0.0031 | 0.0161 | −0.0001 | 0.0159 | −0.0036 | 0.0238 |
| $CH_3$[b] | 0.0438 | −0.0368 | 0.0202 | −0.0033 | −0.0013 | 0.0075 | −0.0000 | 0.0074 | −0.0013 | 0.0106 |
| $CH_3$[c] | 0.0272 | −0.0435 | 0.0135 | −0.0022 | −0.0008 | 0.0043 | −0.0000 | 0.0043 | −0.0009 | 0.0063 |
| H | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| F | 0.0315 | −0.0326 | 0.0152 | −0.0025 | −0.0010 | 0.0052 | −0.0000 | 0.0051 | −0.0010 | 0.0075 |
| Cl | 0.0147 | −0.0126 | 0.0068 | −0.0011 | −0.0004 | 0.0025 | −0.0000 | 0.0025 | −0.0004 | 0.0036 |
| Br | 0.0104 | −0.0076 | 0.0047 | −0.0008 | −0.0003 | 0.0018 | −0.0000 | 0.0018 | −0.0003 | 0.0026 |
| $COCH_3$ | −0.0898 | 0.0260 | −0.0322 | 0.0043 | 0.0020 | −0.0187 | 0.0001 | −0.0184 | 0.0013 | −0.0229 |
| $COOCH_3$ | −0.0664 | 0.0225 | −0.0248 | 0.0035 | 0.0016 | −0.0135 | 0.0000 | −0.0132 | 0.0011 | −0.0169 |
| CN | −0.2146 | 0.0109 | −0.0583 | 0.0023 | 0.0012 | −0.0519 | 0.0000 | −0.0516 | 0.0006 | −0.0541 |
| $NO_2$ | −0.1091 | −0.0485 | −0.0095 | −0.0093 | −0.0053 | −0.0341 | −0.0003 | −0.0358 | −0.0021 | −0.0253 |

a) Hetero atom model.
b) Inductive model.
c) Hyperconjugation model.

character changes. In this case, changes in the inductive and mesomeric effects both play an important role.

s.c.s. values of some carbons remote from the substituents are correlated[3b)] to the substituent constants.[16)] Ernst[21)] showed that good linear dependencies of s.c.s. *vs.* total charge density changes calculated by INDO MO theory exist for C-6, -8, and -10, but the observed slopes are not identical; they are 324, 209, and 187 ppm/e for C-6, -8, and -10, respectively. Excess $\pi$-electron charge density ($\Delta\rho_\pi$) calculated by the HMO method (Table II) reproduced the s.c.s. at C-6, -8, and -10 well with an identical slope, −261 ppm/e (Fig. 5). Moreover, quite similar relationships are found among $\delta_{para}$ and $\Delta\rho_\pi$ (Fig. 6). It is clear that

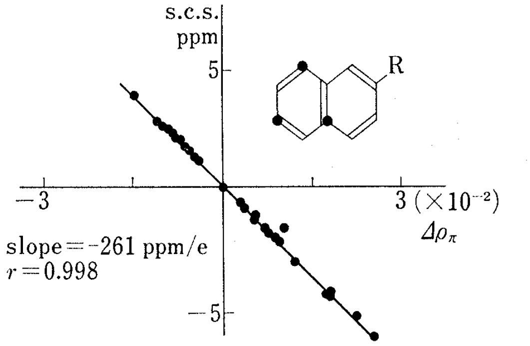


Fig. 5. Correlation between s.c.s. of 2-Substituted Naphthalenes and $\Delta\rho_\pi$[a)] Calculated by the HMO Method

*a*) $\pi$-Electron charge densities relative to naphthalene (R=H).

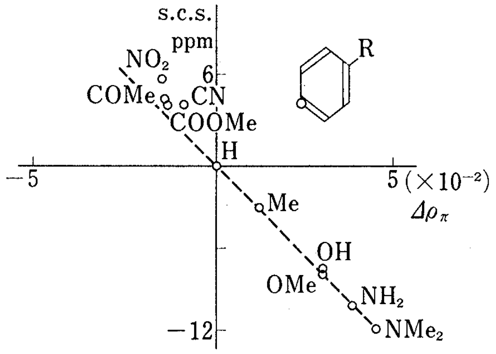


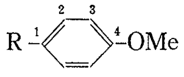
Fig. 6. Plot of s.c.s. *vs.* $\Delta\rho_\pi$[a)] Calculated by the HMO Method for Monosubstituted Benzenes

*a*) $\pi$-Electron charge densities relative to benzene (R=H).

Table III. $^{13}$C Chemical Shifts of *para*-Substituted Anisole Derivatives[a)]

| Substituent | Carbon No.[b)] 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $NH_2$ | 139.94 | 116.33 | 114.83 | 152.77 |
| NHCOMe | 131.25 | 122.08 | 114.05 | 156.37 |
| OMe | 153.79 | 114.65 | 114.65 | 153.79 |
| OH | 149.47 | 116.09 | 114.95 | 153.61 |
| OCOMe | 144.26 | 122.26 | 114.41 | 157.20 |
| Me | 129.82 | 129.82 | 113.69 | 157.50 |
| Et | 136.35 | 128.68 | 113.81 | 157.68 |
| H | 120.56 | 129.34 | 113.94 | 159.61 |
| F | 157.24 | 115.70 | 114.80 | 155.71 |
| Cl | 125.50 | 129.22 | 115.13 | 158.10 |
| Br | 112.79 | 132.15 | 115.67 | 158.64 |
| I | 82.65 | 138.15 | 116.33 | 159.42 |
| CHO | 130.00 | 131.85 | 114.29 | 164.52 |
| COMe | 130.53 | 130.53 | 113.69 | 163.44 |
| COOMe | 122.68 | 131.55 | 113.57 | 163.32 |
| CN | 104.04 | 133.89 | 114.77 | 162.84 |
| $NO_2$ | 141.50 | 125.80 | 113.99 | 164.58 |

*a*) In ppm downfield from internal TMS.
*b*) The numbering is as follows:



---

21) L. Ernst, *J. Magn. Reson.*, 22, 279 (1976).

s.c.s. values at *para*-like carbons are associated with the mesomeric effect of substituents and can be evaluated by rather empirical HMO calculation.

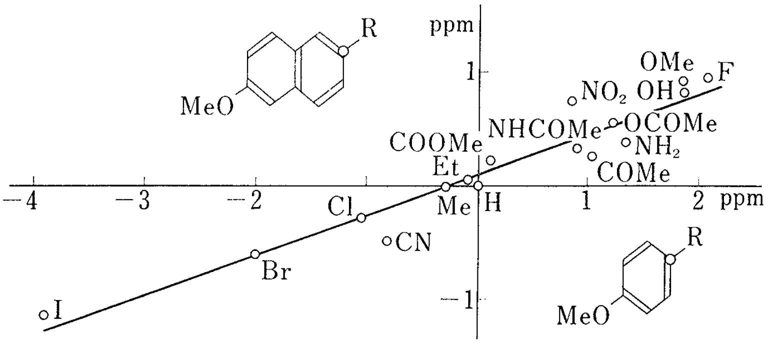


Fig. 7. Plot of Discrepancies[a] from the Additivity Rule at the *ipso* Position to the Substituent

2-Substituted-6-methoxy-naphthalene *vs*. *para*-substituted anisoles.

*a*) (Observed-calculated) chemical shifts.

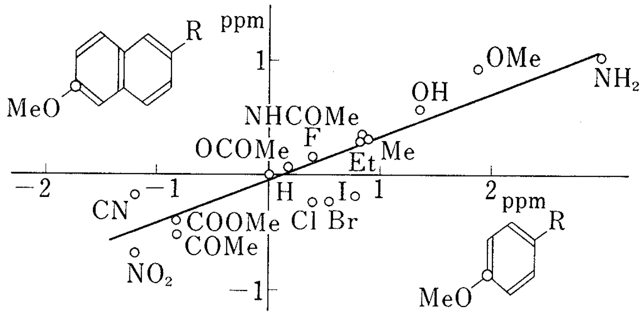


Fig. 8. Plot of Discrepancies[a] from the Additivity Rule

C-6 of 2-substituted-6-methoxynaphthalene *vs*. C-4 of *para*-substituted anisoles.

*a*) (Observed-calculated) chemical shifts.

The additivity of chemical shift of **2** holds satisfactorily,[3b] and the maximum derivation is within 1.1 ppm, though this is not negligible. Large discrepancies are found at C-2 and -6, indicating the existence of interaction between the two substituents.[3a,10] For comparison, *para*-substituted anisoles (**4**) with the same series of substituents were studied under identical conditions. Their chemical shifts relative to TMS are summarized in Table III. Discrepancies at C-2 and -6 of **2** correlate with those of **4** at the corresponding positions (Figs. 7 and 8), showing substituent-substituent interaction.

Table IV. Correlation between $^1$H s.c.s.[a] and Some Parameters for 2-Substituted Naphthalenes Calculated by the MINDO/2 Method[b]

| Position | $\Delta\rho^{H}$ c) | | $\Delta\rho_{\pi}$ f) | | $\Delta\rho_{total}$ g) | |
|---|---|---|---|---|---|---|
| | r d) | Slope e) | r d) | Slope e) | r d) | Slope e) |
| 1 | −0.676 | −28.9 | −0.981 | −7.17 | −0.967 | −7.33 |
| 3 | −0.031 | −1.41 | −0.902 | −11.9 | −0.896 | −9.23 |
| 4 | −0.740 | −14.5 | 0.845 | 4.41 | 0.840 | 4.58 |
| 5 | −0.945 | −21.7 | 0.888 | 7.97 | 0.841 | 8.08 |
| 6 | −0.830 | −41.3 | −0.972 | −8.27 | −0.970 | −11.6 |
| 7 | −0.945 | −20.1 | 0.610 | 7.93 | 0.668 | 10.1 |
| 8 | −0.780 | −36.0 | −0.928 | −9.84 | −0.937 | −10.8 |

*a*) V. Lucchini and P.W. Wells, *Org. Magn. Reson.*, **8**, 137 (1976).
*b*) R=N(CH$_3$)$_2$, NH$_2$, OCH$_3$, OH, H, COCH$_3$, COOCH$_3$, NO$_2$.
*c*) Electron charge density of the proton.
*d*) Correlation coefficient.
*e*) In ppm/e.
*f*) $\pi$-Electron charge density of the carbon to which the proton is attached.
*g*) Total electron charge density of the carbon to which the proton is attached.

To determine the structures of organic compounds, both $^{13}C$ and $^{1}H$ NMR are used. Thus, when $^{1}H$ chemical shift is correlated to the chemical shift of the carbon to which the proton is attached, it is convenient to predict one shift from the other. It is well known that the paramagnetic term is a dominant factor for the $^{13}C$ chemical shift but not for the $^{1}H$ chemical shift, so a general relationship may not exist. However, as an exceptional case, it was noted that the $\delta_{para}$ values are proportional to $\delta^{H}_{para}$. Hehre *et al.*[22] reviewed the charge distributions of **3** and compared the $^{1}H$ and $^{13}C$ chemical shifts. For **1** and **3**, as shown in Table IV, $^{1}H$ and $^{13}C$ chemical shifts of the two series are determined by $\rho_{total}$ and $\rho_{\pi}$ of carbons at *para*-like positions, and are proportional to each other (Tables V and VI).

TABLE V. Correlation between $^{13}C$ s.c.s. and $^{1}H$ s.c.s.[a] of Monosubstituted Benzenes[b]

| Position | $r$[c] | Slope[d] |
|---|---|---|
| *ortho* | 0.711 | 10.3 |
| *meta* | −0.341 | −1.27 |
| *para* | 0.993 | 17.0 |

*a*) K. Hayamizu and A. Yamamoto, *J. Mol. Structur.*, **28**, 89 (1968): The Abstract Papers of the 21th Annual Meeting of the Chemical Society of Japan, 1968, p. 284.
*b*) $R=N(CH_3)_2$, $NH_2$, $OCH_3$, OH, $CH_3$, H, Cl, Br, I, CHO, $COCH_3$, $COOCH_3$, CN, $NO_2$.
*c*) Correlation coefficient.
*d*) $^{13}C$ s.c.s./$^{1}H$ s.c.s.

TABLE VI. Correlation between $^{13}C$ s.c.s. and $^{1}H$ s.c.s.[a]

| Position | 2-Substituted naphthalenes[b] | | 2-Substituted-6-methoxynaphthalenes[c] | |
|---|---|---|---|---|
| | $r$[d] | Slope[e] | $r$[d] | Slope[e] |
| 1 | 0.895 | 13.3 | 0.902 | 15.4 |
| 3 | 0.490 | 4.35 | 0.541 | 5.08 |
| 4 | −0.361 | −2.21 | −0.480 | −4.47 |
| 5 | 0.610 | 1.17 | −0.464 | −4.11 |
| 6 | 0.990 | 15.7 | — | — |
| 7 | −0.748 | −4.29 | 0.331 | 1.89 |
| 8 | 0.969 | 9.18 | 0.975 | 11.4 |

*a*) V. Lucchini and P.W. Wells, *Org. Magn. Reson.*, **8**, 137 (1976); Y. Sasaki, M. Suzuki, T. Hibino, K. Karai, M. Hatanaka, and I. Shiraishi, *Chem. Phamr. Bull.* (Tokyo), **16**, 1367 (1968).
*b*) $R=N(CH_3)_2$, $NH_2$, $OCH_3$, OH, H, Br, $COCH_3$, $COOCH_3$, $NO_2$.
*c*) $R=NH_2$, $OCH_3$, $CH_2CH_3$, H, Br, $COCH_3$, $COOCH_3$.
*d*) Correlation coefficient.
*e*) $^{13}C$ s.c.s./$^{1}H$ s.c.s.

It is clear that the calculated charge distribution is generally useful to predict and to interpret the $^{13}C$ chemical shift. We therefore wish to postulate a less empirical method offering a better approach to these problems.

To calculate the screening tensor, the neighbor anisotropy term is neglected, and the contribution of ring current was evaluated by Pople's dipole approximation:[23] namely 1.3 ppm at the $\alpha$- and 0.5 ppm at the $\beta$-position, relative to benzene. We are interested in the

---

22) W.L. Hehre, R.W. Taft, and R.D. Topson, *Prog. Phys. Org. Chem.*, **12**, 159 (1976).
23) H.J. Bernstein, W.G. Schneider, and J.A. Pople, *Proc. Roy. Soc.*, **A236**, 515 (1956).

Table VII. Substituent-Induced Screening Tensor Changes Calculated by Method a[a] at Ring Carbons of 2-Substituted Naphthalenes (ppm)

| Substituent | Carbon No. 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $N(CH_3)_2$ | −15.26 | 43.06 | −10.34 | 3.42 | 1.58 | −2.13 | 1.09 | −2.18 | 4.24 | −4.76 |
| $NH_2$ | −11.57 | 39.80 | −7.43 | 2.45 | 1.19 | −1.29 | 0.86 | −1.31 | 2.95 | −3.29 |
| $NHCOCH_3$ | −9.44 | 37.10 | −7.43 | 1.89 | 0.73 | −0.74 | 0.47 | −0.46 | 2.49 | −2.43 |
| $OCH_3$ | −16.31 | 48.47 | −9.14 | 3.02 | 1.52 | −1.47 | 1.12 | −1.61 | 3.93 | −4.00 |
| OH | −14.43 | 46.12 | −8.02 | 2.88 | 1.39 | −1.20 | 1.07 | −1.31 | 3.40 | −3.51 |
| $CH_3$ | −2.51 | 15.78 | −1.32 | 0.48 | 0.34 | −0.41 | 0.25 | −0.47 | 0.90 | −0.89 |
| H | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| $COCH_3$ | 5.84 | 5.33 | −0.17 | −0.69 | −0.55 | 1.14 | −0.24 | 1.16 | −1.86 | 1.67 |
| $COOCH_3$ | 5.92 | 1.35 | 2.22 | −1.36 | −0.63 | 1.30 | −0.35 | 1.26 | −2.18 | 2.12 |
| CN | 0.61 | 12.82 | −0.16 | 0.20 | 0.05 | 0.81 | 0.37 | 0.56 | −0.62 | 0.70 |
| $NO_2$ | 2.30 | 13.60 | −1.00 | 0.34 | −0.08 | 1.77 | 0.36 | 1.45 | −1.62 | 1.71 |

[a] See the text.

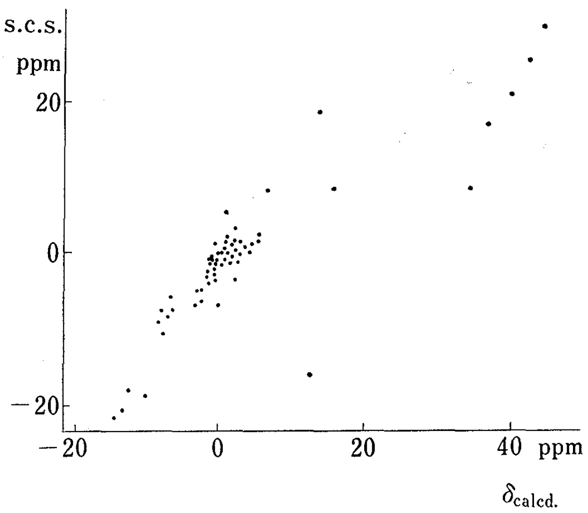


Fig. 9. Plot of s.c.s. of 2-Substituted Naphthalene *vs.* $^{13}C$ Screening Tensor ($\delta_{calcd.}$) Calculated from Eq. 2 (Method a)

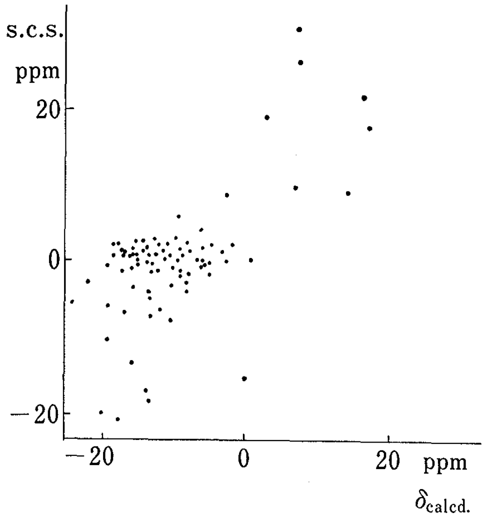


Fig. 10. Plot of s.c.s. of 2-Substituted Naphthalene *vs.* $^{13}C$ Screening Tensor ($\delta_{calcd.}$) Calculated from Eq. 2 (Method b)

Table VIII. Substituent-Induced Screening Tensor Changes calculated by Method b[a] at Ring Carbons of 2-Substituted Naphthalenes (ppm)

| Substituent | Carbon No. 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $N(CH_3)_2$ | −21.57 | 18.30 | −17.70 | −13.24 | −14.56 | −16.91 | −14.51 | −18.36 | −16.17 | −20.55 |
| $NH_2$ | −15.21 | 19.01 | −14.37 | −7.60 | −7.43 | −9.41 | −8.85 | −9.44 | −8.91 | −14.08 |
| $NHCOCH_3$ | −20.98 | 8.80 | −25.33 | −17.78 | −16.88 | −16.17 | −18.48 | −17.32 | −18.66 | −23.53 |
| $OCH_3$ | −19.85 | 10.03 | −18.29 | −10.40 | −7.63 | −10.08 | −9.54 | −11.54 | −7.16 | −14.08 |
| OH | −15.61 | 9.89 | −11.46 | −2.29 | −3.26 | −6.42 | −5.32 | −6.02 | −3.51 | −9.46 |
| $CH_3$ | −5.04 | 13.62 | −5.65 | −7.20 | −5.53 | −7.13 | −7.33 | −6.63 | −9.68 | −10.28 |
| H | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| $COCH_3$ | −8.36 | −4.66 | −13.96 | −16.11 | −16.32 | −15.27 | −15.43 | −12.02 | −20.43 | −18.33 |
| $COOCH_3$ | −10.07 | −11.24 | −13.98 | −17.13 | −16.09 | −15.85 | −18.05 | −14.60 | −23.68 | −18.87 |
| CN | −10.12 | −0.85 | −11.46 | −12.54 | −11.96 | −13.39 | −14.06 | −10.81 | −16.68 | −17.61 |
| $NO_2$ | −10.80 | 2.03 | −12.69 | −7.24 | −11.75 | −11.85 | −12.87 | −8.90 | −13.60 | −11.68 |

[a] See the text.

substituent-induced effect, and to cancel out the effect of ring current as a common term, shifts relative to those of ring carbons of naphthalene ($\alpha$-, $\beta$-, and ring junction) are considered.

For **1**, the relative $^{13}C$ chemical shifts ($\delta_{calcd.}$) calculated from Eq. 2 by method a (Table VII) were plotted against the observed s.c.s. (Fig. 9). The overall agreement is reasonable, with a correlation coefficient of 0.852; if the *ipso* carbon of naphthonitrile is ignored, the correlation coefficient becomes 0.902. The values of $\delta_{calcd.}$ calculated from Eq. 2 by method b (Table VIII) are plotted against s.c.s. in Fig. 10. They are based upon a treatment involving less approximation than that used in Fig. 9 (method a). Nevertheless, the correlation coefficient is only 0.652, and no systematic trend of errors can be seen. The contribution of $\sigma_d^{AA}$ to $\delta_{calcd.}$ is almost within the range of 1 ppm. Thus, the error due to $\sigma_p^{AA}$ must be large. In the calculation by method b, $\sigma_p^{AA}$ is estimated by considering the LCAO coefficient of the occupied and unoccupied MO, as well as the orbital energy. However, in the case of method a, only the occupied MO is considered. Assuming Koopmans' theorem $\varepsilon_i = -I_i$,[24] the photoionization potential gives information on the orbital energy of the ground state. Figure 11 shows that the orbital energies of the ground state agree well with the observed photoionization potentials.[25] The error due to the estimation of the term in Eq. 2 depends on the estimation of the wave function of the excited state.

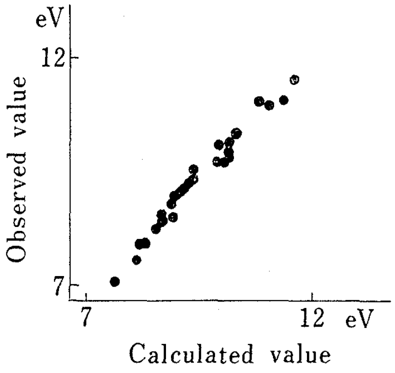


Fig. 11. Plot of Observed *vs.* Calculated Ionization Potentials of 2-Substituted Naphthalenes

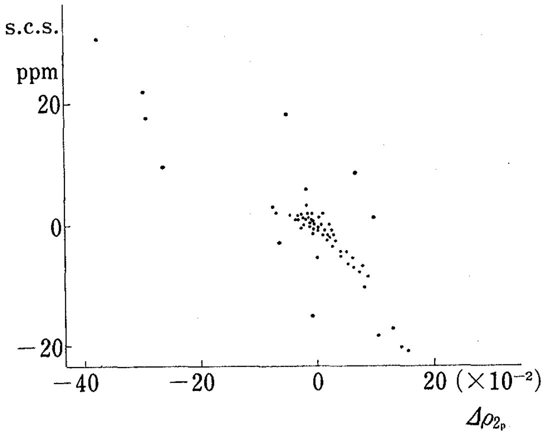


Fig. 12. Plot of s.c.s. of 2-Substituted Naphthalene *vs.* 2p-Electron Charge Densities ($\Delta\rho_{2p}$) Calculated by the MINDO/2 Method

To obtain $\sigma_p^{AA}$ from Eq. 2 by method a, $\Delta E$ is assumed to be constant, but this may not always be the case. When the different values of $\Delta E$ for each compound are evaluated, the correlation coefficients for (s.c.s.$-\sigma_d^{AA}$) *vs.* ($\delta_{calcd.}-\sigma_d^{AA}$) increase only slightly to 0.922 or 0.929 (without R=CN). This result suggests that the excitation energy is not always a predominant factor in s.c.s.

The term $\langle r^{-3}\rangle_{2p}$ estimated from the 2p electron charge density affects the values of $\sigma_p^{AA}$ and $\delta_{calcd.}$. The relationship between the variation of 2p electron charge density and $\delta_{calcd.}$ shows a correlation coefficient of 0.961. In this case, the slope of the line obtained by the least-squares method is −133 ppm/e, though *ipso* carbons deviate markedly from the line, especially when R=$COCH_3$, $COOCH_3$, and CN (more than 10 ppm). This was ascribed to a significant contribution of the bond order due to the hetero atom.

In any event, the change of 2p electron charge density contributes considerably to the variation of $\delta_{calcd.}$; in fact the relation between s.c.s. and the variation of 2p electron charge density represented in Fig. 12 shows a correlation coefficient of 0.847, which is comparable

---

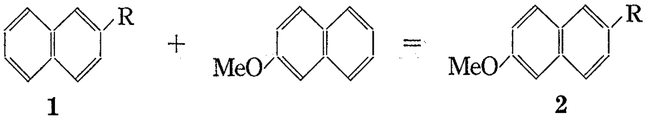
24) J. Koopmans, *Physica*, **1**, 104 (1934).

25) C. Utsunomiya, T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **48**, 1852 (1975); H. Boch, G. Wagner, and J. Kroner, *Chem. Ber.*, **105**, 3850 (1972); J.P. Maier, *Helv. Chim. Acta*, **59**, 994 (1974).

TABLE IX. Substituent-Induced Charge Densities ($\Delta\rho_{total}$ and $\Delta\rho_{\pi}$) Calculated by the MINDO/2 MO Method at Ring Carbons of 2-Substituted Naphthalenes

| Substituent | | Carbon No. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $N(CH_3)_2$ | Total | 0.1450 | −0.2959 | 0.1039 | −0.0436 | −0.0181 | 0.0225 | −0.0125 | 0.0201 | −0.0527 | 0.0502 |
| | $\pi$ | 0.1590 | −0.1197 | 0.0787 | −0.0381 | −0.0183 | 0.0313 | −0.0146 | 0.0254 | −0.0419 | 0.0592 |
| $NH_2$ | Total | 0.1030 | −0.2806 | 0.0687 | −0.0317 | −0.0139 | 0.0137 | −0.0099 | 0.0118 | −0.0373 | 0.0364 |
| | $\pi$ | 0.1101 | −0.0986 | 0.0551 | −0.0268 | −0.0124 | 0.0186 | −0.0121 | 0.0166 | −0.0269 | 0.0410 |
| $NHCOCH_3$ | Total | 0.0885 | −0.2562 | 0.0635 | −0.0265 | −0.0087 | 0.0075 | −0.0056 | 0.0026 | −0.0279 | 0.0291 |
| | $\pi$ | 0.0438 | −0.0439 | 0.0547 | −0.0161 | −0.0058 | 0.0100 | −0.0078 | 0.0051 | −0.0206 | 0.0281 |
| $OCH_3$ | Total | 0.1567 | −0.3930 | 0.0802 | −0.0355 | −0.0175 | 0.0160 | −0.0129 | 0.0155 | −0.0464 | 0.0439 |
| | $\pi$ | 0.1393 | −0.1130 | 0.0604 | −0.0351 | −0.0159 | 0.0215 | −0.0158 | 0.0210 | −0.0335 | 0.0478 |
| OH | Total | 0.1306 | −0.3669 | 0.0710 | −0.0324 | −0.0162 | 0.0130 | −0.0123 | 0.0124 | −0.0417 | 0.0392 |
| | $\pi$ | 0.1247 | −0.1032 | 0.0542 | −0.0332 | −0.0140 | 0.0170 | −0.0154 | 0.0181 | −0.0280 | 0.0421 |
| $CH_3$ | Total | 0.0238 | −0.0091 | 0.0112 | −0.0095 | −0.0038 | 0.0044 | −0.0027 | 0.0039 | −0.0121 | 0.0100 |
| | $\pi$ | 0.0356 | −0.0352 | 0.0167 | −0.0067 | −0.0035 | 0.0061 | −0.0032 | 0.0053 | −0.0085 | 0.0121 |
| H | Total | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| | $\pi$ | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| $COCH_3$ | Total | −0.0772 | 0.1308 | −0.0079 | 0.0041 | 0.0069 | −0.0125 | 0.0034 | −0.0131 | 0.0207 | −0.0179 |
| | $\pi$ | −0.0853 | 0.0667 | −0.0092 | 0.0114 | 0.0090 | −0.0177 | 0.0030 | −0.0136 | 0.0176 | −0.0246 |
| $COOCH_3$ | Total | −0.0817 | 0.1499 | −0.0344 | 0.0138 | 0.0077 | −0.0142 | 0.0042 | −0.0146 | 0.0244 | −0.0225 |
| | $\pi$ | −0.0870 | 0.0842 | −0.0299 | 0.0171 | 0.0100 | −0.0205 | 0.0043 | −0.0145 | 0.0236 | −0.0311 |
| CN | Total | −0.0291 | 0.0080 | −0.0152 | −0.0031 | −0.0005 | −0.0089 | −0.0039 | −0.0065 | 0.0067 | −0.0071 |
| | $\pi$ | −0.0257 | 0.0342 | −0.0010 | −0.0058 | 0.0023 | −0.0135 | −0.0061 | −0.0041 | 0.0075 | −0.0113 |
| $NO_2$ | Total | −0.0693 | 0.0183 | −0.0128 | −0.0065 | 0.0014 | −0.0193 | −0.0042 | −0.0178 | 0.0173 | −0.0158 |
| | $\pi$ | −0.0849 | 0.1138 | −0.0089 | 0.0009 | 0.0071 | −0.0288 | −0.0071 | −0.0121 | 0.0230 | −0.0293 |

to that between $\delta_{calcd.}$ and s.c.s. On the other hand, the correlation coefficient between s.c.s. and the variation of total electron charge density (calculated by MINDO/2 MO; Table IX) is 0.806. This result suggests that, instead of the total electron charge density, the $\pi$-electron approximation would be useful in conjugated systems if the $\pi$-electron charge density is easily affected. The correlation coefficient between s.c.s. and variation in $\pi$-electron charge density (calculated by MINDO/2 MO; Table IX) is 0.700.



1 2

Chart 1

For the observed chemical shifts of **2**, additivity (Chart 1) holds satisfactorily,[3b] and quantum chemical treatment also supports this rule, as shown in Tables X and XI.

TABLE X. Differences[a] between Calculated[b] and Predicted[c] $^{13}C$ Screening Tensors of 2-Substituted-6-methoxynaphthalenes

| Substituent | Carbon No. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $NH_2$ | 0.0 | −0.1 | 0.0 | 0.0 | 0.0 | −0.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| OMe | 0.0 | −0.2 | 0.0 | 0.0 | 0.0 | −0.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| OH | 0.0 | −0.1 | 0.0 | 0.0 | 0.1 | −0.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| Me | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| COMe | 0.0 | −0.1 | 0.0 | 0.1 | 0.0 | −0.1 | 0.1 | 0.0 | 0.1 | −0.1 |
| COOMe | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | −0.1 | 0.1 | 0.0 | 0.1 | −0.1 |
| CN | −0.1 | 0.0 | 0.0 | 0.1 | 0.1 | −0.2 | 0.1 | 0.0 | 0.2 | 0.1 |
| F[d] | 0.0 | 0.0 | 0.0 | 0.0 | −0.9 | −0.1 | 0.0 | 0.0 | 0.0 | 0.0 |

*a*) In ppm.
*b*) Calculated by Eq. 2 (method a) with the data obtained by MINDO/2.
*c*) Calculated from the additivity rule.
*d*) Calculated by Eq. 2 (method a) with the data obtained by INDO.

TABLE XI. Differences[a] between Calculated[b] and Predicted[c] 2p-Electron Charge Densities of 2-Substituted-6-methoxynaphthalenes

| Substituent | Carbon No. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $NH_2$ | 0.02 | 0.10 | −0.04 | 0.02 | −0.01 | 0.12 | −0.04 | 0.04 | −0.01 | 0.00 |
| NHCOMe | 0.03 | 0.04 | −0.02 | −0.03 | −0.04 | 0.07 | −0.01 | 0.02 | −0.01 | 0.01 |
| OMe | −0.01 | 0.14 | −0.05 | 0.04 | −0.01 | 0.14 | −0.05 | 0.04 | −0.02 | −0.02 |
| OH | 0.00 | 0.10 | −0.04 | −0.06 | −0.06 | 0.14 | −0.05 | 0.03 | −0.03 | 0.00 |
| Me | 0.03 | 0.02 | 0.00 | 0.01 | 0.02 | 0.05 | −0.03 | 0.03 | −0.03 | 0.02 |
| COMe | −0.02 | 0.03 | 0.03 | −0.03 | −0.08 | −0.01 | −0.05 | 0.00 | −0.07 | 0.07 |
| COOMe | −0.03 | 0.03 | 0.02 | −0.04 | −0.01 | −0.02 | −0.03 | −0.02 | −0.05 | 0.06 |
| CN | 0.03 | −0.04 | 0.04 | −0.07 | −0.22 | 0.07 | −0.07 | 0.01 | −0.08 | 0.09 |
| F[d] | 0.02 | 0.04 | 0.00 | −0.01 | −0.06 | 0.08 | −0.02 | 0.01 | 0.03 | 0.02 |

*a*) $\times 10^{-3}$ electron.
*b*) Calculated by the MINDO/2 method.
*c*) Calculated from the additivity rule.
*d*) Calculated by the INDO method.