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A Semi-empirical Calculation of the Substituent Effects on the ^{1}H Chemical Shifts of 1-Substituted Naphthalenes[1,2)]

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A semi-empirical equation for predicting the ^{1}H chemical shift induced by substituents in an aromatic system (J. Niwa, *Bull. Chem. Soc. Jpn.*, **48**, 118, 1637 (1975)) has been applied to the ring protons of 1-substituted naphthalenes. The predictions of the equation are tested against the available experimental data for six representative substituents and are also compared with those of the electric-field model.

The ^{1}H chemical shifts of a number of 1-substituted naphthalenes have been examined by Emsley, Lindon, Salman, and Clark[3)] in the light of some simple theories of the origins of substituent-induced chemical shifts (SCS). They have separately assessed the following models as the main factors governing the SCS values: (i) the local diamagnetic term of the relevant hydrogen atom; (ii) the magnetic anisotropy of the substituent group, calculated by using the expression developed by Pople for the paramagnetic part of the magnetic anisotropic tensor;[4)] (iii) the empirically established correlation between the SCS values and changes in the π or total electron density on the attached carbon atom;[5)] (iv) the modified equation of the correlation between the SCS values and changes in the π electron density, where the π electron densities on the attached and the next neighbor carbon atoms are considered,[6)] and (v) the electric-field model derived by Buckingham.[7)] It has been indicated by them that, although no one simple model can predict the SCS values of all the protons of 1-substituted naphthalenes, it is possible to predict some of the larger effects and to relate them to the structure, and that the electric-field model gives the best overall agreement with the observed SCS values.

In our preceding papers,[1,2)] we derived a semi-empirical equation (Eq. 2) for obtaining the SCS values of protons in substituted aromatic side-chains[1)] and monosubstituted benzenes[2)] by considering the ring-current effect ($\sigma^{A,\text{ring}}$) in addition to the diamagnetic term of the hydrogen atom, A (σ^{AA}_{dia}), in the C–H bond in question and that from its bonded carbon atom, B (σ^{AB}_{dia}):

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

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

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.[8)] We showed that Eq. 2 could reasonably reproduce the observed SCS values of protons in the aromatic side-chains and the benzenes.

The aim of the present paper is to demonstrate the validity of the predictions by Eq. 2 for a variety of substituents in the series of 1-substituted naphthalenes, to examine the range of applicability of this approach, and to determine its limitations. The advantage of the naphthalenes in examining the success of Eq. 2 is that they have seven protons situated in different magnetic environments. Second, we will discuss which approach, Eq. 2 or the electric-field model, is more appropriate for understanding and predicting the SCS values in 1-substituted naphthalenes.

Results and Discussion

The local diamagnetic term, σ^{AA}_{dia}, of the hydrogen atom of naphthalene has been calculated by using the expression given by Kajimoto and Fueno.[9)] The calculated values of σ^{AA}_{dia}, relative to the unsubstituted compound, are linearly correlated with the increments in electron densities on the hydrogen atoms:

$$\Delta\sigma^{AA}_{\text{dia}} = 16.1\Delta q^{A}. \qquad (3)$$

The diamagnetic contribution from the bonded carbon (σ^{AB}_{dia}) in the case of naphthalene can be calculated in the same way as in the cases of olefinic compounds[1)] and benzenes,[2)] because the C–H bond length is taken to be 1.08 Å and the ring proton also bonds to the sp^2-hybridized carbon atom. Thus, the σ^{AB}_{dia} term, relative to the unsubstituted compound, becomes:

$$\Delta\sigma^{AB}_{\text{dia}} = 8.70\Delta q^{B}. \qquad (4)$$

The paramagnetic term, $\sigma^{AB}_{\text{para}}$, of the B atom has been calculated according to Pople's expression.[4)] It remains almost constant for the series of 1-substituted naphthalenes so long as we assume the same average excitation energy and the same value of the integral $\langle r_{AB}^{-3}\rangle$. Accordingly, we can ignore the contribution of the paramagnetic term to the SCS.

In order to estimate the contribution of the ring-current effect ($\sigma^{A,\text{ring}}$) to the ring proton of naphthalenes, we have used the ring-current model presented by Pople,[10)] as Fig. 1 illustrates. The contribution of the "quinonoid" structure due to the introduction of a substituent into the A ring causes the decrease in the

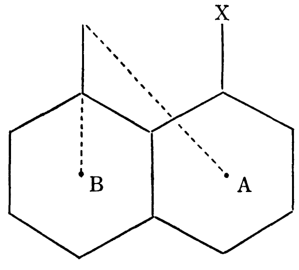


Fig. 1. The ring-current model for 1-substituted naphthalenes.

ring-current on the A ring. This contribution can be expressed by Eq. 5, which was derived for the ^{1}H chemical shifts in aromatic side-chains:[1,11)]

$$\Delta\sigma^{\mathrm{A,ring}} = -0.4f(\rho, z)|\sigma_\pi| \quad (5)$$

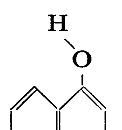
where $f(\rho, z)$ is the Johnson and Bovey ring-current shift in ppm, which is expressed as a function of the geometric factors for the proton located at the cylindrical co-ordinates, ρ and z, and where σ_π is the Yukawa-Tsuno parameter for measuring the resonance ability of the substituent. The "quinonoid" structure of the A ring may secondarily induce the localization of the π-electron system of the B ring. We may assume that the change in the ring-current induced on the B ring can be ignored, because the secondary effect may be considered to be very small compared with the contribution of the "quinonoid" structure of the A ring to the SCS value. Then, the ring-current effect due to the B ring cancels out the other in the calculation of the relative contribution of the ring-current effects in 1-substituted naphthalenes. Therefore, Eq. 5 can be applied, just as it is, to all the protons of the naphthalenes.

By combining Eqs. 3, 4 and 5, we obtain the following equation for the SCS of 1-substituted naphthalenes:

$$\delta_{\mathrm{calcd}} = 16.1\Delta q^{\mathrm{A}} + 8.70\Delta q^{\mathrm{B}} - 0.4f(\rho, z)|\sigma_\pi|. \quad (6)$$

The value of $f(\rho, z)$ for each proton of the naphthalenes has been graphically estimated by utilizing the table of the Johnson and Bovey ring-current shift.[8)] The values of $f(\rho, z)$ obtained are −1.50 ppm for the 2-, 3- and 4-protons, −0.60 ppm for the 5- and 8-protons, and −0.23 ppm for the 6- and 7-protons.

The geometry of naphthalene used in the calculation and that of the substituent group are taken from the standard compilations.[12)] The molecules of 1-nitronaphthalene, 1-naphthylamine, 1-naphthol, and 1-naphthaldehyde are assumed to be planar. The stable conformation of 1-naphthaldehyde may be I or II, or some equilibrium between the two. The calculation of the chemical shifts has been performed for both the I and II forms.



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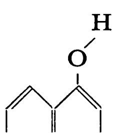
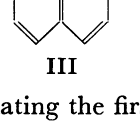
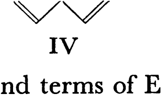


II

The 1-naphthol molecule may exist as an equilibrium between the two conformers, III and IV. These two conformers, however, give virtually identical predicted chemical shifts.



III



IV

In evaluating the first and second terms of Eq. 1, we have used the CNDO/2 formalism. In Table 1, the SCS values calculated by Eq. 6 are compared with the observed values. In Fig. 2, plots of the observed SCS values are shown against the calculated shifts. As may clearly be seen from Fig. 2, the calculated chemical shifts can reasonably reproduce the overall aspect of the SCS. However, Fig. 2 shows that Eq. 6 can not sufficiently reproduce such major features of the SCS as the large negative values for the 8-proton of 1-naphthaldehyde. In deriving Eq. 6, the long-range shielding effect of the substituent group has not been taken into consideration. Therefore, the magnetic anisotropy effect should also be considered for the 2- and 8-protons in the neighborhood of a substituent group which has a large magnetic anisotropy, as in the cases of 1-chloronaphthalene, 1-naphthaldehyde, and 1-nitronaphthalene.*

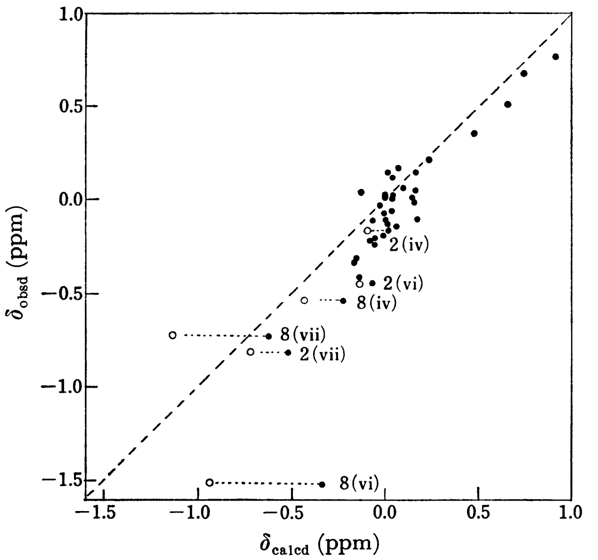


Fig. 2. Plots of δ_{obsd} against δ_{calcd} for ring protons of 1-substituted naphthalenes.
Numbered points correspond to entries in Table 1. Open circles are plotted against the chemical shifts corrected for the anisotropy effects of the substituent groups.

Unfortunately, no theoretical and empirical estimations of the magnetic anisotropy effects of these substituent groups are yet completely settled. The point magnetic dipole approximation[13)] is quantitatively not always reliable for the proton in the nearest neighborhood of the substituent group. Nevertheless, it may provide a qualitative basis for the discussion of the long-range shielding.

In the cases of 1-chloronaphthalene and 1-naphthaldehyde, we have attempted to estimate the magnetic

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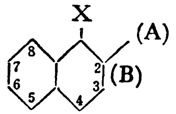
* On the whole, Eq. 6 correctly reproduces the SCS value of the 4-proton for the electron-donating substituent better than that for the electron-withdrawing substituent. A similar trend has also been obtained in the case of benzene.[2)] The insufficiency of Eq. 6 for the 3-proton may be mainly attributed to ignoring the magnetic contributions from carbon atoms neighboring the B atom, but that for the electron-withdrawing substituent may not be attributed to ignoring the magnetic anisotropy of the substituent group, because the anisotropy effect on the 3- and 4-protons is too small to correct the calculated SCS to the observed SCS. Accordingly, this shortcoming of Eq. 6 may show an inherent limitation of the present calculation.

TABLE 1. CALCULATED AND OBSERVED CHEMIAL SHIFTS OF RING PROTONS IN 1-SUBSTITUTED NAPHTHALENES[a)]



Proton	q^{A} b)	q^{B} b)	$\Delta\sigma^{AA}_{dia}$	$\Delta\sigma^{AB}_{dia}$	$\Delta\sigma^{A,\ ring}$	δ_{calcd}	δ_{obsd} c)	$\Delta\sigma_{E}$ c)
(i) 1-Naphthylamine								
2	1.0074	4.0730	−0.054	0.715	0.252	0.91	0.766	0.45
3	1.0143	3.9634	0.056	−0.238	0.252	0.07	0.167	0.01
4	1.0080	4.0486	0.038	0.362	0.252	0.65	0.507	0.28
5	1.0050	4.0144	−0.010	0.064	0.101	0.16	0.052	0.11
6	1.0118	3.9839	0.016	−0.060	0.039	0.00	0.018	0.03
7	1.0117	4.0005	0.014	0.084	0.039	0.14	0.009	0.04
8	1.0114	3.9952	0.093	−0.103	0.101	0.09	0.060	−0.14
(ii) 1-Naphthol								
2	1.0013	4.0705	−0.152	−0.693	0.204	0.74	0.676	0.40
3	1.0117	3.9672	0.014	−0.205	0.204	0.01	0.146	−0.01
4	1.0053	4.0378	−0.005	0.268	0.204	0.47	0.357	0.23
5	1.0042	4.0136	−0.022	0.057	0.031	0.07	−0.012	0.06
6	1.0108	3.9832	0.000	−0.066	0.031	−0.03	−0.031	0.04
7	1.0100	3.9994	−0.013	0.075	0.082	0.14	−0.064	0.00
8	0.9996	3.9924	−0.096	−0.127	0.082	−0.14	−0.410	−0.33
(iii) 1-Methylnaphthalene								
2	1.0117	4.0098	0.014	0.165	0.047	0.23	0.211	0.13
3	1.0120	3.9864	0.019	−0.038	0.047	0.03	0.124	0.02
4	1.0065	4.0164	0.014	0.082	0.047	0.14	0.155	0.11
5	1.0058	4.0084	0.003	0.012	0.019	0.03	0.021	0.03
6	1.0111	3.9893	0.005	−0.013	0.007	0.00	0.028	0.00
7	1.0112	3.9923	0.006	0.013	0.007	0.03	0.006	0.02
8	1.0044	4.0074	−0.019	0.003	0.019	0.00	−0.110	0.00
(iv) 1-Chloronaphthalene								
2	0.9927	4.0201	−0.290	0.255	0.042	0.01	−0.174	—
3	1.0057	3.9801	−0.082	−0.093	0.042	−0.13	0.035	—
4	1.0015	4.0155	−0.066	0.074	0.042	0.05	0.016	—
5	1.0029	4.0085	−0.043	0.130	0.017	−0.01	−0.071	—
6	1.0086	3.9856	−0.035	−0.045	0.006	−0.07	−0.115	—
7	1.0075	3.9917	−0.053	0.008	0.006	−0.05	−0.168	—
8	0.9947	3.9991	−0.174	−0.069	0.017	−0.23	−0.544	—
(v) 1-Naphthaldehyde (I)								
2	0.9996	3.9654	−0.179	−0.221	0.138	−0.26	−0.443	−0.63
3	1.0060	4.0007	−0.077	0.009	0.138	0.15	−0.102	0.15
4	1.0023	3.9911	−0.053	−0.138	0.138	−0.05	−0.218	−0.27
5	1.0040	4.0032	−0.026	−0.033	0.055	0.00	−0.060	0.08
6	1.0082	3.9916	−0.042	0.007	0.021	−0.01	−0.147	0.16
7	1.0081	3.9844	−0.043	−0.056	0.021	−0.08	−0.237	0.17
8	0.9988	4.0151	−0.109	0.071	0.055	0.02	−1.525	−0.006
(vi) 1-Naphtaldehyde (II)								
2	1.0085	3.9696	−0.037	−0.184	0.138	−0.08	−0.443	−1.72
3	1.0070	4.0018	−0.061	0.096	0.138	0.17	−0.102	−0.24
4	1.0025	3.9895	−0.050	−0.152	0.138	−0.06	−0.218	−0.52
5	1.0054	4.0047	−0.003	−0.020	0.055	0.03	−0.060	−0.14
6	1.0097	3.9910	−0.018	0.002	0.021	0.01	−0.147	0.15
7	1.0093	3.9847	−0.024	−0.053	0.021	−0.06	−0.237	0.21
8	0.9717	4.0241	−0.542	0.148	0.055	−0.34	−1.525	−0.65
(vii) 1-Nitronaphthalene								
2	0.9790	3.9965	−0.509	−0.211	0.204	−0.52	−0.807	−0.62
3	0.9973	3.9988	−0.216	0.070	0.204	0.06	−0.146	−0.05
4	0.9955	3.9830	−0.162	−0.209	0.204	−0.17	−0.335	−0.20
5	1.0090	4.0035	−0.075	−0.030	0.082	−0.02	−0.195	−0.06
6	1.0055	3.9874	−0.085	−0.030	0.031	−0.08	−0.218	−0.14
7	1.0041	3.9806	−0.107	−0.089	0.031	−0.16	−0.322	−0.14
8	0.9502	4.0274	−0.886	0.177	0.082	−0.63	−0.725	−0.58

a) All the values are relative to the unsubstituted compound. b) All the electron densities are calculated by the CNDO/2 method. The electron densies of naphthalene are: q^{A} (the 1-proton) $= 1.0056$, q^{A} (the 2-proton) $= 1.0108$; q^{B} (the 1-carbon) $= 4.0070$, q^{B} (the 2-carbon) $= 3.9908$ c) Cited from Ref. 3. The chemical shifts were measured in 5 mol% in CCl_4.

Table 2. The magnetic anisotropy effects of formyl, nitro, and chloro groups on the 2- and 8-protons

Substituent	χ_x	χ_y ($\times 10^{-30}$ cm^3 esu)	χ_z	2-proton	8-proton (ppm)
CHO(form I)[14]	28.8	34.6	18.0	−0.45	−0.08
CHO(form II)[14]	28.8	34.6	18.0	−0.04	−0.59
NO_2[16]	−18	−3.3	−23	−0.16	−0.54
		$\Delta\chi$			
Cl[12]		−7.5		−0.09	−0.16

a) x is in the direction of the C=O bond for the formyl group and in that of the C–N bond for the nitro group, and y and z are in- and out-of-plane respectively.

anisotropy effect on the 2- and 8-protons by using the values of the magnetic susceptibilities given by McConnell for the chlorine atom[12] and those given by Pople for the carbonyl group.[14] The respective values of the anisotropy effects obtained on the 2- and 8-protons are listed in Table 2. When these anisotropy effects are taken into account, the predicted SCS values in 1-naphthaldehyde become, respectively, −0.8 and −0.1 ppm for the 2- and 8-protons of Form I, while those of Form II become, respectively, −0.1 and −0.9 ppm. This result predicts that Form I may cause the considerable low-field shift in the 2-proton, whereas Form II causes that in the 8-proton. The present approach favors Form II over Form I for the aldehyde on the basis of the predicted SCS values for the 2- and 8-protons. Recently Hatano has indicated, on the basis of NMR measurements with the paramagnetic reagent technique, that Form II may be the stable conformer.[15] The present result corresponds with his indication.

With respect to the magnetic anisotropy of the nitro group, no theoretical estimation has been presented. Therefore, we have attempted to estimate the anisotropy effect by utilizing the values of the magnetic susceptibilities empirically obtained by Yamaguchi, who investigated the magnetic anisotropy effect of the nitro group on ortho methyl groups in nitrobenzene derivatives.[16] The values obtained for the 2- and 8-protons are shown in Table 2.

Emsley *et al.* have indicated that, among the simple models which they have assessed, the electric-field model (Eq. 7) gives the best overall agreement with the observed SCS values.[3] The electric-field model given by Buckingham[7] is:

$$\sigma_E = -AE_z, \qquad (7)$$

where A is calculated to be about 2×10^{-12} esu. E_z arises from point charges located on atoms; then E_z is given classically by Eq. 8, where q_B is the atomic charge:

$$E_z = \sum_{A \neq B} q_B \cos\theta_{AB}/r_{AB}^2. \qquad (8)$$

The θ_{AB} angle is that between the C–H and r_{AB}. In deriving Eq. 7, the rough approximation is originally used. Moreover, Emsley *et al.* introduced some assumption in applying Eq. 8 to the naphthalenes; they rather arbitrarily restricted the summation in Eq. 8 to charges which neighbor the proton, because of the difficulty of knowing how electric fields are transmitted within molecules.[3] The SCS values, $\Delta\sigma_E$, calculated by them are cited in Table 1. The correlation between the observed and the calculated SCS values is shown in Fig. 3. A comparison of Fig. 2 with Fig. 3 clearly shows that Eq. 6 can more correctly reproduce the observed SCS values than the electric-field model, even though Eq. 6 can not sufficiently reproduce the chemical shift of the 8-proton of 1-naphthaldehyde.

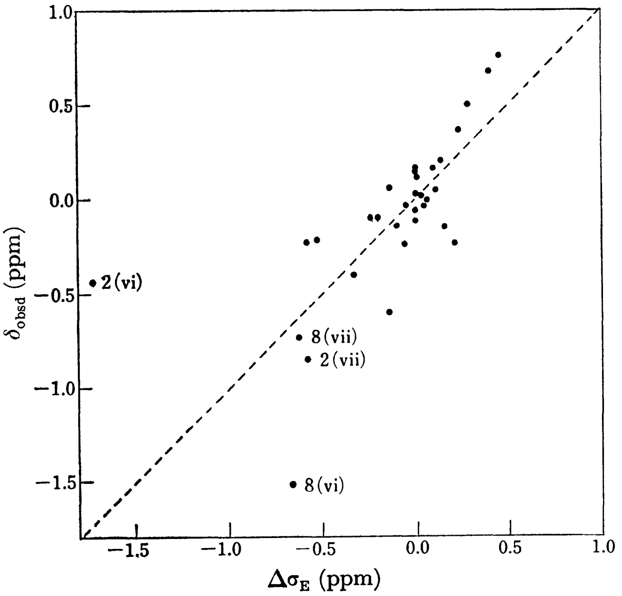


Fig. 3. Plots of δ_{obsd} against $\Delta\sigma_E$ calculated by Emsley *et al.*[3]
Numbered points correspond to entries in Table 1.

When the anisotropy effects are taken into consideration for the substituent groups, Cl, CHO, and NO_2, the shortcoming of Eq. 6 for the 2-protons of 1-chloronaphthalene, 1-naphthaldehyde, and 1-nitronaphthalene seems to be reasonably improved. However, the corrected chemical shift of the 8-proton of 1-nitronaphthalene seems to be overestimated, while that of 1-naphthaldehyde can not still sufficiently reproduce the observed SCS value. The improvement of Eq. 6 for the 8-protons of the two compounds remains a subject of future research, along with the exact estimation of the magnetic anisotropy effects of the substituent groups.

The CNDO/2 calculations were carried out on a FACOM-230 60 computer at the Nagoya University Computation Center.

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