Studies on the Nuclear Magnetic Resonance Spectra in Aromatic Systems. V.¹⁾ Discussions on the 2-Substituted and 2-Substituted 6-Methoxynaphthalene Series

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The ring ¹H chemical shift in 2-substituted and 2-substituted 6-methoxynaphthalene series has been examined in the following items:

1. The shielding parameters of H₁, H₃ and H₄ in the above series have been estimated from the chemical shift ratios $\delta H_1/d_o$ (R), $\delta H_3/d_o$ (R) and $\delta H_4/d_m$ (R).
2. π -Electron charge density in C₆H₆ and naphthalene series.
3. Simple sum rule of π -electron charge density.
4. The correlation revised chemical shift with π -electron charge density.
5. Coupling constant and side chain chemical shift.

Introduction

The correlation among ring proton chemical shift in mono substituted benzene series—namely the substituent's shielding parameter—and π -electron charge density distribution has been examined by several groups of workers.^{3,4)} Moreover, above parameter has been widely used as simple sum rule⁵⁻⁷⁾ in poly-substituted benzene derivatives, but no extensive study concerning the above rule has yet been carried out in condensed aromatic system. In this work, we have examined the correlations among aromatic ring and side chain ¹H shift *vs* ρ value,⁸⁾ coupling constant and electronegativity of substituent group, ρ value estimation from ring ¹H chemical shift, *etc.* in 2-substituted- and 2-substituted-6-methoxynaphthalene series.

Experimental

The details of measurement are the same as described in the previous paper.⁶⁾ 2-Substituted naphthalene series are measured in <0.3 M C₆H₁₂ soln. except CHO, COOCH₃ derivatives (0.3 M CCl₄ soln.). Disubstituted series are measured in <0.3 M CCl₄ soln. except NH₂ derivate (0.3 M CH₂Cl₂ soln.). Positive shift indicates greater shielding, negative shift indicates lower shielding than that in C₆H₆. Side chain OCH₃ proton is referred to TMS. The number of positions in naphthalene nucleus are expressed as right.

1) **Materials Deuterium Exchange Reaction in 2-Substituted Naphthalene Series**—All materials (R=CH₃, Cl, Br, NH₂, OCH₃, COCH₃, CN) are of JIS grade. The deuterium exchange in H₁ position was carried out by CF₃CO₂H-D₂O method,⁹⁾ but unsuccessful in some cases (R=Br, COCH₃, CN). 2-Deutero-6-methoxynaphthalene was prepared from 2-bromo-6-methoxynaphthalene by Grignard method.

- 1) Part IV: *Chem. Pharm. Bull.* (Tokyo), **16**, 1193 (1968).
- 2) Location: Toyonaka, Osaka.
- 3) J.S. Martin and B.P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).
- 4) H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
- 5) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).
- 6) Y. Sasaki, M. Suzuki, T. Hibino, and K. Karai, *Chem. Pharm. Bull.* (Tokyo), **15**, 599 (1967).
- 7) M. Kondo, *Bull. Chem. Soc. Japan*, **38**, 1271 (1965).
- 8) π -electron charge density.
- 9) W.M. Lauer, G. Y. Matson, and G. Stedman, *J. Am. Chem. Soc.*, **80**, 6433 (1958).

2) **2-Substituted-6-methoxynaphthalene Series**—All materials ($R = \text{OCH}_3$, COCH_3 ,¹⁰ NH_2 , CO_2CH_3 ,¹¹ Br ,¹² C_2H_5 ,¹³) were prepared by authentic procedures from β -naphthol.

Assignment, Analysis and Inspection of Spectra

The assignment, analysis and inspection of spectra were carried out as 2 different 3 spin systems.¹⁴

1) **2-Substituted Naphthalene Series**—Owing to the mixing of 3 spin system (A ring) and 4 spin system (B ring) in the spectral pattern, it was impossible to assign the spectra intuitively, but we were able to assign the A ring pattern by deuterium exchange and spin decoupling technique. When $R = \text{NH}_2$ or OCH_3 , as a result of deuterium exchange occurred in H_1 , H_3 afforded doublet, followed by irradiating at H_3 , H_4 afforded singlet (cf. Fig. 1). When $R = \text{CH}_3$, Cl , Br , CN , by deuterium exchange no obvious alter-

Fig. 1. Spectra of 2-Methoxy Naphthalene

A: deuterated B: normal
C: decoupled

Fig. 2. Spectra of 2-Bromo Naphthalene

A: Normal B: decoupled

Fig. 3. Spectra of 2-Acetyl Naphthalene

A: normal B: decoupled

- 10) H.E. French and K. Sears, *J. Am. Chem. Soc.*, **70**, 1279 (1948).
- 11) G.W. Gray and B. Jones, *J. Chem. Soc.*, **1954**, 678; K. Fries and K. Schimmelschmidt, *Ber.*, **58**, 2835 (1925).
- 12) C.G. Koelsch, *Org. Synth.*, **20**, 18 (1940).
- 13) N.P. Buu-Hoi and D. Lavit, *J. Org. Chem.*, **22**, 912 (1957).
- 14) J.A. Pople, *Can. J. Chem.*, **35**, 1060 (1957).

nations were generally observed. Nevertheless, owing to the partial deuterium exchange in H_1 , H_3 signal sharpened appreciably, and by irradiating at which, the broad H_1 sharpened. Then, the deformed signal by deuterium exchange was assigned to H_3 , and H_4 signal became undiscernible (*cf.* Fig. 2). When $R=COCH_3$, deuterium exchange was unsuccessful. In the above case, we have assigned H_3 by irradiating the broad H_1 singlet at lowest field (*cf.* Fig. 3).

These results are summarized in Table I.

TABLE I. Ring Proton Chemical Shifts and Coupling Constants of 2-Substitutednaphthalene Series

Substituent	Ring proton ppm			J cps	
	H_1	H_3	H_4	1,3	3,4
NH_2	+0.43	+0.50	-0.29	2.7	9.0
OCH_3	+0.25	+0.16	-0.37	2.7	9.1
CH_3	-0.13	-0.09		2.1	
H	-0.50	-0.16	-0.50	1.4	8.6
Cl	-0.53	-0.18			
Br	-0.66	-0.26			
CN	-0.83	-0.32			
$COCH_3$	-1.12	-0.78	-0.49	1.8	8.7
CHO	-0.96	-0.66	-0.55		
$COOCH_3$	-1.23	-0.70	-0.44	2.2	8.7

2) 2-Substituted 6-Methoxynaphthalene Series—In these series, two 3 spin systems were analysed separately, and assigned from first order rule. These results are summarized in Table II, and inspected by dispersion method¹⁵⁾ (*cf.* Table III). The deviation— $\Delta_{calcd.}-\Delta_{exptl.}$ within 0.1 cps—supports correct analysis.

Fig. 4. Spectrum of 2-Acetyl-6-methoxy Naphthalene

15) T. Hirashima, T. Kameo, O. Manabe, and H. Hiyama, The Abstract Papers in the 19th Annual Meeting of the Chemical Society of Japan, 1, 94 (1966), *Bull. Chem. Soc. Japan*, in press.

TABLE II. Ring and Side Chain Proton Chemical Shifts and Coupling Constants of 2-Substituted 6-Methoxynaphthalene Series

Substituent	Ring protons ppm			J cps		Ring protons ppm				J csp	
	H ₁	H ₃	H ₄	1,3	3,4	H ₅	H ₇	H ₈	MeO	5,7	7,8
NH ₂	+0.44	+0.45	-0.12	2.2	8.9	+0.32	+0.34	-0.18	+3.43	2.5	8.8
OCH ₃	+0.32	+0.36	-0.30	2.5	9.3	+0.32	+0.36	-0.30	+3.40	2.5	9.3
CH ₃ CH ₂	-0.17	+0.08	-0.29	1.8	8.5	+0.29	+0.26	-0.29	+3.40	2.3	8.3
H	-0.44	-0.03	-0.33			+0.25	+0.16	-0.37	+3.39	2.5	8.0
Br	-0.56	-0.11	-0.29	2.1	9.1	+0.29	+0.22	-0.29	+3.40	2.5	9.1
COCH ₃	-0.98	-0.64	-0.36	1.8	8.8	+0.24	+0.16	-0.48	+3.36	2.5	8.4
COOCH ₃	-1.17	-0.68	-0.36	1.5	8.6	+0.23	+0.15	-0.51	+3.36	2.3	8.1

TABLE III. Results fo Dispersion Method (cps)

Substituent	A			B		
	Δ expt.	Δ calcd.	dif.	Δ expt.	Δ calcd.	dif.
NH ₂	5.35	5.37	0.02	4.78	4.83	0.05
OCH ₃	5.99	6.05	0.06	5.99	6.05	0.06
CH ₃ CH ₂	3.05	3.01	0.04	5.27	5.29	0.02
H				5.75	5.77	0.02
Br	3.69	3.66	0.03	5.07	5.08	0.01
COCH ₃	5.07	5.07	0	6.34	6.36	0.02
COOCH ₃	6.49	6.54	0.05	6.50	6.48	0.02

Result and Discussion

1) Chemical Shift Correlation among Benzene and Naphthalene Series

To estimate the chemical shift correlation among above 2 series and C₆H₆ series, H₁, H₃ and H₄ shifts were plotted against d_o (R) and d_m (R).¹⁶ The ¹H chemical shifts of A ring in 2-substituted naphthalene series are expressed as below and Fig. 5.

Fig. 5

A: —○— δH_1 , —□— δH_3 in 2-substituted naphthalene series/ d_o (R)
 B: —△— δH_4 in 2-substituted naphthalene series/ d_m (R)
 Ring current effect corrections in α - and β -positions in naphthalene series were +0.5 and +0.16 ppm¹⁷ respectively

$$\delta H_1 = 1.16d_o(R) - 0.40 \text{ ppm}$$

$$\delta H_3 = 0.83d_o(R) - 0.16 \text{ ppm}$$

$$\delta H_4 = 0.68d_m(R) - 0.42 \text{ ppm}$$

The intercepts represent ring current effects, respectively. The ¹H chemical shifts in 2-substituted 6-methoxynaphthalene series are as below:

$$\delta H_1 = 1.10d_o(R) - 0.33 \text{ ppm}$$

$$\delta H_3 = 0.80d_o(R) - 0.06 \text{ ppm}$$

$$\delta H_4 = 0.65d_m(R) - 0.32 \text{ ppm}$$

16) d_o (R), d_m (R) = *ortho* and *meta* shielding parameter in mono substituted C₆H₆ series.

17) J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, 1959, p. 252.

The influences of the substituent OCH_3 group to the ^1H chemical shifts of A ring are little in slopes, but rather large in intercepts.

From the gradients of 3 lines, the following conclusions were obtained: δH_1 , δH_3 and δH_4 in 2 naphthalene series were increase of 20%, decrease of 20% and 30%, compared with $d_o(\text{R})$ and $d_m(\text{R})$.

Formerly, Schaefer and Schneider¹⁸⁾ have concluded that the ^1H chemical shift is controlled mainly by a) ring current effect of neighboring system b) ρ value c) magnetic anisotropy of substituent, etc. Concerning a), it may be excluded by adding the neighboring ring participation 0.5 and 0.16 ppm to α - and β - ^1H . It may be described to IV 2) concerning b), to IV 4) concerning c).

2) π -Electron Charge Density Correlation¹⁹⁾ among C_6H_6 and Naphthalene Series

The $\rho^{20)}$ value distributions on ring carbon atom to which the ring proton is bonded and those on oxygen atom of OCH_3 group have been calculated by simplified LCAO MO method using Streitwieser's parameters.²¹⁾

Then we plotted $\Delta\rho$ values in 2-substituted- and 2-substituted 6-methoxynaphthalene series, against $\Delta\rho_o(\text{R})$ and $\Delta\rho_m(\text{R})$ ²²⁾ reciprocally. The results are summarised in the A ring

TABLE IV. HMO Calculations of Monosubstitutedbenzene Series

Substituent	<i>ortho</i>	<i>meta</i>	<i>para</i>
NH_2	1.03700	0.99826	1.02928
OCH_3	1.02528	0.99888	1.01960
CH_3	1.00452	0.99988	1.00326
Cl	0.979	1.001	0.987
Br	0.98400	1.00104	0.99040
CN	0.96462	0.00098	0.96886
CHO	0.93458	1.00148	0.94140
COOCH_3	0.94028	1.00160	0.94768
NO_2	0.94106	0.99766	0.93194

TABLE V. HMO Calculations of 2-Substitutednaphthalene Series

Substituent	C_1	C_3	C_4	C_5	C_7	C_8
NH_2	1.05386	1.02254	0.99646	0.99840	0.99986	1.00974
OCH_3	1.03662	1.01596	0.99730	0.99892	1.00004	1.00624
CH_3	1.00634	1.00290	0.99954	0.99976	1.00000	1.00110
Cl	0.97254	0.98538	1.00228	1.00078	0.99998	0.99622
Br	0.96820	0.98314	1.00270	1.00106	1.00008	0.99530
CN	0.94534	0.98072	1.00236	1.00124	1.00016	0.98864
CHO	0.89784	0.96548	1.00424	1.00208	1.00008	0.97858
COOCH_3	0.90802	0.96778	1.00430	1.00216	1.00000	0.98108

18) T. Schaefer and W.G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

19) Calculations were carried out on a NEAC-2208 computer in the Osaka University Computer Center. The authors are indebted to Assoc. Prof. Dr. H. Sayo, for his helpful advice in MO calculation.

20) $\rho_o(\text{R})$, $\rho_m(\text{R})$, $\rho_p(\text{R}) = \rho$ values in *ortho*, *meta*, *para* positions in mono substituted benzene series.

21) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John-Wiley and Sons, 1961, p. 135.

22) excess π -electron charge.

TABLE VI. HMO Calculations of 2-Substituted 6-Methoxynaphthalene Series

Substituent	C ₁	C ₃	C ₄	C ₅	C ₇	C ₈	C ₆ -O
NH ₂	1.05234	1.02282	1.00256	1.03440	1.01592	1.00694	1.94088
OCH ₃	1.03524	1.01580	1.00354	1.03524	1.01580	1.00354	1.94022
CH ₃	1.00506	1.00282	1.00588	1.03604	1.01576	0.99830	1.93964
Cl	0.97144	0.98544	1.00872	1.03724	1.01568	0.99334	
Br	0.97760	0.98838	1.00832	1.03704	1.01586	0.99440	1.93916
CN	0.94380	0.98068	1.00850	1.03682	1.01588	0.98578	
CHO	0.89728	0.96590	1.01000	1.03712	1.01570	0.97552	1.93546
COOCH ₃	0.90744	0.96792	1.01012	1.03738	1.01586	0.97836	1.93590

Fig. 6

—○— $\Delta\rho_{C_1}$, —□— $\Delta\rho_{C_3}$ in 2-substituted naphthalene series/ $\Delta\rho_o(R)$

$$\Delta\rho_{C_1} = 1.53\Delta\rho_o(R)$$

$$\Delta\rho_{C_3} = 0.56\Delta\rho_o(R)$$

$$\Delta\rho_{C_4} = 2.32\Delta\rho_m(R)$$

as follows: the $\Delta\rho$ values on C₁ and C₃ positions are increase and decrease of 50% compared with $\Delta\rho_o(R)$ (cf Fig. 6).

In B ring of 2-substituted 6-methoxynaphthalene series, ρ values on only C₈ position are seemed to be controlled by R.

3) Simple Sum Rule of π -Electron Charge Density

In the previous communication,²³⁾ the authors correlated ρ value vs. ring ¹H chemical shift in poly-substituted C₆H₆ series.

When above rule is applied to 2-substituted 6-methoxynaphthalene series, the ρ values are calculated by simple sum of $\Delta\rho$ values in 2-substituted and 6-methoxynaphthalene systems, as shown in Table VII, by adding the excess local charge densities on both series.

TABLE VII. Local Excess Charges of 2-Substituted 6-Methoxynaphthalene Series calculated by Simple Sum Method of ρ Value

Substituent	C ₁	C ₃	C ₄	C ₅	C ₇	C ₈
NH ₂	0.05278	0.02258	0.00270	0.03502	0.01582	0.00700
OCH ₃	0.03554	0.01600	0.00354	0.03554	0.01600	0.00354
CH ₃	0.00526	0.00294	0.00578	0.03638	0.01596	-0.00160
Cl	-0.02854	-0.01458	0.00852	0.03740	0.01594	-0.00648
Br	-0.03288	-0.01682	0.00894	0.03768	0.01604	-0.00740
CN	-0.05574	-0.01924	0.00860	0.03786	0.01612	-0.01406
CHO	-0.10324	-0.03448	0.01048	0.03870	0.01604	-0.02412
COOCH ₃	-0.09306	-0.03218	0.01054	0.03878	0.01596	-0.02162

4) Correlation among Revised Chemical Shift and ρ Value

The correlation among ring ¹H chemical shift and ρ value has been investigated experimentally as below:

23) Y. Sasaki, M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), 15, 1429 (1967).

When this relation is applied to the substituted aromatics, it is assumed

$$\delta = k \cdot \Delta\rho^{18)}$$

where δ = ring proton chemical shift

$$k = 10.7 \pm 0.2 \text{ ppm/e}$$

that several factors other than ρ value alternation afford serious contributions. In the previous papers,²⁴⁾ the contribution of shift due to ρ value alternation has been estimated in monosubstituted C_6H_6 series, and the revised parameter d_o rev. (R) and d_m rev. (R) have been submitted.

Just the same as before, the revised chemical shifts of the A ring in 2-substituted naphthalene series were obtained against σ_π . A slope through OCH_3 , CH_3 and H was obtained from the least square method and extended to electron attracting groups (cf. Fig. 7). Thus the revised parameters for substituents were taken so that the corresponding plots would fall on this straight line through the origin. The result was as below:

$$\delta H_1 \text{ rev. (R)} = 2.83 \sigma_\pi = 1.77 d_o \text{ rev. (R)}$$

$$\delta H_3 \text{ rev. (R)} = 1.16 \sigma_\pi = 0.72 d_o \text{ rev. (R)}$$

$$\delta H_4 \text{ rev. (R)} = 0.47 \sigma_\pi = 1.70 d_m \text{ rev. (R)}$$

Fig. 7

—○— δH_1 , —□— δH_3 and —△— δH_4 in 2-substituted naphthalene series/ σ_π

Fig. 8

—×— δH_6 , —△— δH_7 , —□— δH_8 in 2-substituted 6-methoxynaphthalene series/ σ_π

24) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull. (Tokyo)*, **16**, 1187 (1968).

TABLE VIII. Revised Chemical Shifts and ρ nmr of 2-Substitutednaphthalene Series

Substituent	Position	1	3	4
NH ₂	δ corr. ^{a)}	+0.96	+0.69	+0.24
	δ rev.	+1.18	+0.48	+0.20
	ρ nmr	1.1103	1.0449	1.0187
OCH ₃	δ corr.	+0.75	+0.32	+0.13
	δ rev.	+0.80	+0.32	+0.13
	ρ nmr	1.0748	1.0299	1.0121
CH ₃	δ corr.	+0.37	+0.07	
	δ rev.	+0.23	+0.09	+0.04
	ρ nmr	1.0215	1.0084	1.0037
Cl	δ corr.	-0.03	-0.02	
	δ rev.	+0.21	+0.08	+0.03
	ρ nmr	1.0196	1.0074	1.0028
Br	δ corr.	-0.16	-0.10	
	δ rev.	+0.15	+0.05	+0.03
	ρ nmr	1.0140	1.0047	1.0028
CN	δ corr.	-0.33	-0.16	
	δ rev.	-0.69	-0.28	-0.11
	ρ nmr	0.9355	0.9738	0.9897
COCH ₃	δ corr.	-0.62	-0.62	0.01
	δ rev.	-0.80	-0.33	-0.13
	ρ nmr	0.9252	0.9692	0.9879
COOCH ₃	δ corr.	-0.73	-0.54	+0.06
	δ rev.	-0.64	-0.26	-0.10
	ρ nmr	0.9402	0.9757	0.9907

a) Corrected for the induced currents in the neighbor ring ppm.

TABLE IX. Revised Chemical Shifts and ρ nmr of 2-Substituted 6-Methoxynaphthalene Series

Substituent	Position	1	3	4
NH ₂	δ corr.	+0.94	+0.61	+0.38
	δ rev.	+1.24	+0.61	+0.37
	ρ nmr	1.1159	1.0570	1.0346
OCH ₃	δ corr.	+0.82	+0.52	+0.20
	δ rev.	+0.86	+0.45	+0.30
	ρ nmr	1.0804	1.0421	1.0280
CH ₃ CH ₂	δ corr.	+0.33	+0.24	+0.21
	δ rev.	+0.29	+0.22	+0.21
	ρ nmr	1.0271	1.0206	1.0196
H	δ corr.	+0.06	+0.13	+0.17
	δ rev.	+0.06	+0.13	+0.17
	ρ nmr	1.0056	1.0121	1.0159
Br	δ corr.	-0.06	+0.05	+0.21
	δ rev.	+0.21	+0.18	+0.20
	ρ nmr	1.0196	1.0168	1.0187
COCH ₃	δ corr.	-0.48	-0.48	+0.14
	δ rev.	-0.74	-0.20	+0.04
	ρ nmr	0.9308	0.9813	1.0037
COOCH ₃	δ corr.	-0.67	-0.52	+0.14
	δ rev.	-0.58	-0.13	+0.07
	ρ nmr	0.9458	0.9879	1.0065

The result of the A ring in 2-substituted 6-methoxynaphthalene series was as below:

$$\delta H_{1\text{rev.}} = 2.63 \sigma_{\pi} + 0.10$$

$$\delta H_{3\text{rev.}} = 1.38 \sigma_{\pi} + 0.14$$

$$\delta H_{4\text{rev.}} = 0.07 \sigma_{\pi} + 0.19$$

In B ring, in order to estimate the resonance effect of the substituents R to the neighbor ring, slopes through all plots except NH_2 were obtained against σ_{π} (cf. Fig. 8).

$$\delta H_5 = 0.16 \sigma_{\pi} + 0.77$$

$$\delta H_7 = 0.34 \sigma_{\pi} + 0.38$$

$$\delta H_8 = 0.42 \sigma_{\pi} + 0.13$$

The influences of the substituents R to the ^1H chemical shifts of B ring were in the next order, namely, $H_8 > H_7 > H_5$. Moreover, δH_4 is under the least influence of R.

ρ_{nmr} of A ring in 2-substituted 6-methoxynaphthalene series was obtained using simple sum rule. δH_1 , δH_3 and δH_4 in $\text{R}=\text{H}$ was given by 2-deutero 6-methoxynaphthalene. They were added to the revised chemical shifts of 2-substituted naphthalene series.

Fig. 9. Correlation among OCH_3 Chemical Shift and σ_{π}

Fig. 10. Correlation among Coupling Constant and the Electronegativity of Substituent Group in 2-Substituted 6-Methoxynaphthalene Series

5) Correlation among OCH_3 Chemical Shift and σ_{π} in 2-Substituted 6-Methoxynaphthalene Series (cf. Fig. 9)

The deviation of ^1H chemical shift in OCH_3 group are within ± 0.04 ppm in this series, when $\text{R}=\text{H}$ is referred as a standard. These are not obvious, it may be that the resonance effect of R in A ring is negligible small to the side chain ^1H chemical shift in B ring.

6) Coupling Constant

In both naphthalene series, all J values can be linear with the electronegativity of substituent groups^{25,26} (cf. Fig. 10).

As shown in Fig. 10, $J_{7,8}$ is most influenced by R. It is interesting when compared with δH_8 .

25) J.R. Cavanaugh and B.P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

26) J.E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).