Linear Free Energy Relationship in Naphthalene System—Substituent Effects on Carbon-13 Chemical Shifts of Substituted Naphthyl Methyl Sulphides

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Correlation analyses of the ^{13}C NMR chemical shifts of the methylthio and the *ipso* carbons of several substituted naphthyl methyl sulphides in CDCl$_3$ using Hammett and dual substituent parameter equations have been performed. These studies reveal normal and inverse substituent effects for the *ipso* and methylthio carbons respectively. A comparison of the regression coefficients (ρ_I and ρ_R) of the 4-substituted 1-naphthyl methyl sulphides (4,1-series) with those of 6-substituted 2-naphthyl methyl sulphides (6,2-series) shows that the transmission of substituent effects is greater in the 4,1-series, in accord with rate studies.

In naphthalene systems, studies on the influence of substituents are mainly concerned with transition state (kinetic studies)[1a]. It is, therefore, of interest to gain information of the effect of substituents on the ground state electronic properties[1b] of the naphthalene derivatives. We have recently reported the results of correlation analysis on the rates of oxidation of naphthyl methyl sulphides[2-4]. The title investigation has been undertaken (i) to understand the substituent effects on the ^{13}C chemical shifts of *ipso* and methylthio carbons of 4-substituted 1-naphthyl (4,1-series) and 6-substituted 2-naphthyl (6,2-series) methyl sulphides and (ii) to compare the transmission of electronic effects of the 4,1-series with those of 6,2-series.

Materials and Methods

All the substituted naphthyl methyl sulphides were prepared as reported elsewhere[2,3]. Carbon-13 NMR spectra of these substrates were recorded on a JEOL FX-100 spectrometer in the pulse fourier transform mode at 25.05 MHz. A spectral width of 5000 Hz, 2s pulse duration and 8K time-domain data points were used; the peak positions obtained in δ(ppm) (with solvent CDCl$_3$ as the reference) are expressed relative to TMS. All the spectra were taken in CDCl$_3$ at sufficiently low concentrations (~ 0.1 mol dm^{-3}) so that solvent and intermolecular effects were negligible.

Results and Discussion

Both proton noise-decoupled and off-resonance decoupled ^{13}C NMR spectra have been recorded for all the sulphides. The method of numbering the carbons is shown in I. The proton noise-decoupled spectrum of methyl 1-naphthyl sulphide (1-MNS) displays eleven signals due to the eleven different carbons. The quartet at 15.35 ppm in the off-resonance decoupled spectrum is assigned to the methylthio carbon. Among the ten remaining signals, the low intensity singlets at 135.6, 133.2 and 131.2 ppm are due to three quaternary carbons of 1-MNS. The ^{13}C data of benzene[5] (II), methyl phenyl sulphide[6] (III) and naphthalene[7] (IV) in CDCl$_3$ have been used to make specific assignments of the singlets of 1-MNS. The ^{13}C chemical shifts of II and III indicate that the methylthio group causes dowfield shift of *ipso* (10.0ppm), *meta* (0.2ppm), and upfield shift of *ortho* (-1.8ppm) and *para* (-3.6ppm) carbons. The singlet at 135.6 ppm of 1-MNS is assigned to the C-1 bearing the methylthio group. The large downfield shift (135.6 $-127.9 = 7.7$ ppm) compares favourably with that obtained for the *ipso*-carbon (10.0 ppm) in III. Another singlet at 133.2 ppm in 1-MNS is assigned to the C-4a (which is in the *meta*- relationship to the methylthio substituent) with a small upfield shift (133.2 $-133.6 = -0.4$ ppm) as with III where the *meta* carbon suffers a small shift (0.2 ppm). The remaining singlet at
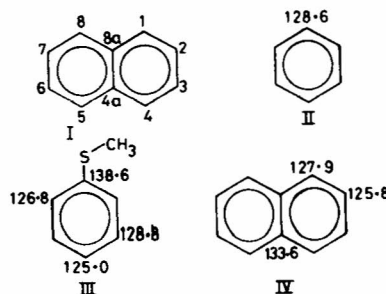
Table 1—Carbon-13 Chemical Shift Data of 1-MNS and 2-MNS

[Solvent: CDCl$_3$]

Carbon	δ(ppm)	
	1-MNS	2-MNS
1	135.6	125.5
2	123.8	136.0
3	125.2*	123.2
4	122.8	128.1
5	128.1	127.6
6	125.8*	125.1
7	125.7*	126.4*
8	125.3*	126.7*
4a	133.2	131.1
8a	1312	133.8
S—CH$_3$	15.35	15.59

*Signals may be interchanged.

Table 2—Chemicals Shifts of Methylthio and *ipso*-Carbons of Substituted Naphthyl Methyl Sulphides

Substi-tuent	δ(ppm)	
	ipso-carbon	S—CH$_3$
4-Substituted 1-naphthyl methyl sulphides		
H	135.6	15.35
MeO	126.1	18.37
Me	133.2	15.84
Et	133.2	15.94
F	130.5(3.5)[a]	16.37
Cl	135.1	15.40
Br	136.0	15.20
COMe	143.2	14.81
6-Substituted 2-naphthyl methyl sulphides		
NHAC	130.9	15.84
Me	134.8	15.89
Et	134.9	16.03
H	136.0	15.59
I	137.1	15.50
COMe	140.0	14.91

(a)$^{13}C - ^{19}F$ coupling constant.

131.2 ppm of 1-MNS is assigned to the C-8a. On the basis of similar arguments, and calculations based on the correlation equations reported by Kitching *et al.*[8] the assignments shown in Table 1 have been made for 1-MNS. The chemical shift data of methyl 2-naphthyl sulphide (2-MNS) are also included in Table 1. These assignments are also supported by the fact that good agreement between the calculated and observed chemical shifts of substituted naphthyl methyl sulphides are found when additivity calculations are made using the data of 1-MNS, 2-MNS (Table 1) and other appropriate monosubstituted naphthalenes[9,10]. The chemical shifts of methylthio and *ipso* carbons of 4,1- and 6,2-series of methyl naphthyl sulphides, presented in Table 2, show that the chemical shifts of the *ipso* carbons have a wide range compared to the methylthio carbons in both the series. This can presumably be ascribed to the fact that the *ipso* carbon but not the methylthio carbon can enter into direct conjugation with the substituents and that the *ipso* carbon is separated from the substituents by a lesser number of bonds relative to the methylthio carbon.

Correlation analysis of the chemical shifts in Table 2 have been performed using Hammett and dual substituent parameter (DSP) equations (1-3) with a view to understanding the nature and composition of the substituent effects on the chemical shifts.

$$\delta = \rho\sigma + \delta_0 \qquad \ldots (1)$$

$$\delta = \rho_I\sigma_I + \rho_R\sigma_R + \delta_0 \qquad \ldots (2)$$

$$\delta = fF + rR + \delta_0 \qquad \ldots (3)$$

In Eq. (1), both naphthalene [$\sigma_{41}(FM)^{11}$ and σ_{41}^{+12}] and benzene (σ_p, σ_p^+ and σ_p^-)[13] substituent parameters have been employed as these constants are known to afford good correlations of the reactivity data of naphthalene derivatives[1a,2,3]. In Eqs (2) and (3) the

constants[13,14], σ_I, σ_R^0, σ_R, σ_R^+, σ_R^-, F and R have been used. The results of all the best correlations are presented in Table 3. The DSP treatment seems to give good correlations. The F and R parameters do not afford better correlations than those obtained with constants such as σ_I, σ_R^0, σ_R, σ_R^+ and σ_R^-. For all the DSP correlations in Table 3, the confidence levels of F-tests are $> 99.5\%$ and the confidence levels of the susecptibility parameters, ρ_I and ρ_R, in the t-test are $> 98\%$. The following features emerge from the results of DSP analysis:

(i) The susceptibility parameters, ρ_I and ρ_R, of the 4,1-series are higher than those of the 6,2-series, suggesting a greater efficiency of the 4,1-series in the transmission of both inductive and resonance effects. Similar observations have been made in the correlations of the rate data of oxidation of these sulphides with peroxydisulphate, peroxydiphosphate and hexavalent chromium[2-4], and spectral data of substituted naphthalenes[8].

(ii) It is found that in both the series $\rho_R > \rho_I$, suggesting that the resonance effect dominates over the inductive effect.

(iii) The positive ρ_I and ρ_R values for the *ipso* carbon in both the series indicate a 'normal' substituent effect—electron-releasing substituents shield the carbon while electron-withdrawing ones deshield it.

(iv) The negative ρ_I and ρ_R values of the methylthio carbons show an 'inverse' substituent effect.

In view of the 'inverse' substituent effect for methylthio carbons, the reported ^{13}C chemical shifts of methylthio carbons of 4-substituted phenyl methyl

Table 3—Results of Best Fits of *ipso*- and Methylthio Carbon Chemical Shifts with Substituent Parameters

Series	Carbon	Substituent constant	Hammett equation			
			ρ^a	r^b	s^c	n^d
4,1	*ipso* (C-1)	σ_p^+/σ_p^-	10.0	0.942	1.78	8
	$S-CH_3$	σ_{41}^+	-2.55	0.955	0.395	6^e
6,2	*ipso* (C-2)	σ_p^+	7.48	0.973	0.769	6
	$S-CH_3$	σ_p	-1.44	0.947	0.145	6
			DSP equation			
			ρI^a	ρR^a	R^b	S_E^f
4,1	*ipso* (C-1)	σ_I, σ_R	16.3	24.4	0.997	0.457	8
	$S-CH_3$	σ_I, σ_R^+	-1.99	-3.10	0.969	0.321	8
6,2	*ipso* (C-2)	σ_I, σ_R	9.32	17.4	0.968	0.641	6
	$S-CH_3$	σ_I, σ_R^0	-1.06	-2.14	0.985	0.089	6

(a) Susceptibility constants; (b) correlation coefficients; (c) standard deviation; (d) number of data points; (e) ethyl and acetyl substituents are not included in the correlation; and (f) standard error of the estimate.

sulphides[6] have also been analysed by the DSP treatment and the results are expressed by Eq. (4).

$$\delta = -1.21\,\sigma_I - 2.23\,\sigma_R^+ + 15.9 \qquad \dots (4)$$
$$\pm 0.29 \quad \pm 0.21$$

$$R = 0.983; \quad F = 58.3; \quad n = 7$$

The above correlation is justified by $>99.9\%$ confidence level of the F-test while the inductive and resonance contributions are justified by $>99\%$ and 99.9% confidence levels in the t-test respectively. In both 4,1-naphthalene and benzene series, the ^{13}C chemical shifts of the methylthio carbons afford (i) good coorelations with σ_I and σ_R^+ constants, (ii) negative ρ_I and ρ_R constants and (iii) nearly equal blending factors $(\lambda = \rho_I/\rho_R)$. However, the origin of the 'inverse' substituent effect in not clear.

References

1 Charton M, *Correlation analysis in chemistry—Recent advances*, edited by N B Chapman and J Shorter (Plenum, New York) 1978, (a) ch. 5; (b) ch. 8.

2 Srinivasan C, Perumal S & Arumugam N, *J chem Soc Perkin Trans-2*, (1984) 2065.

3 Srinivasan C, Perumal S & Arumugam N, *Indian J Chem*, **24A** (1985) 56.

4 Perumal S, *Studies in kinetics of oxidation of organic compounds*, PhD thesis, Madurai Kamaraj University, Madurai, November, 1984.

5 Ewing D F, *Org Magn Reson*, **12** (1979) 499.

6 Buchanan G W, Reyes-Zamora C & Clarke D E, *Can J Chem*, **52** (1974) 3895.

7 Adcock W & Cox C P, *J org Chem*, **44** (1979) 3004.

8 Kitching W, Bullpitt M, Gartshore D, Adcock W, Khor T C, Doddrell D & Rae I D, *J org Chem*, **42** (1977) 2411.

9 Ernst L, *Z Naturforsch B*, **30** (1975) 788, 794.

10 Wells P R, Arnold D P & Doddrell D, *J chem Soc Perkin Trans-2*, (1974) 1745.

11 Dewar M J S & Grisdale P J, *J Am chem Soc*, **84** (1962) 3548.

12 Bancroft K C C & Howe G R, *Tetrahedron Lett*, **43** (1967) 4207.

13 Exner O, *Advances in linear free energy relationships*, edited by N B Chapman and J Shorter (Plenum, New York), 1972, ch. 1.

14 Swain C G & Lupton E C, *J Am chem Soc*, **90** (1968) 4328.