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CHEMICAL SHIFTS IN DONOR SUBSTITUTED POLYCYCLIC AROMATICS[1]

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Abstract—The proton chemical shifts for 29 methoxy, dimethylamino and methylthio substituted polycyclic aromatics are reported. A strong deshielding effect on α-protons due to peri substitution is always found. This effect appears to increase in going from the nitrogen to the oxygen derivatives and is largest for the sulfur compounds. In 9,10-bis-(methylthio)anthracene where the S-Me is constrained to lie out of the plane of the rings, the peri effect is largest. A combination of charge distribution, ring current and peri effects reproduces the measured aromatic proton chemical shifts with reasonable accuracy.

INTRODUCTION

THE proton chemical shifts in aromatic molecules reflect the electronic environment of the protons and provide experimental clues to the electronic structure of such molecules. Many studies have shown that a fair empirical correlation exists between proton chemical shifts and calculated pi-electron density on the proton-bearing site for benzene derivatives and for some heterocyclic aromatics.[2] Effects such as local magnetic anisotropy, ring current, electric field effects, and others also contribute to the proton chemical shifts.

Because of this, and because of the generally inadequate accuracy of molecular wavefunctions in molecules containing heteroatoms, the use of simple algebraic summation of substituent constants appropriate to various substituents and orientations remains in many situations as practical a method of predicting proton chemical shifts as molecular orbital calculations.[3]

Strongly interacting substituents with strong donor or acceptor properties greatly perturb the pi-electron distribution in alternant hydrocarbons resulting in a relatively large spread of the aromatic proton chemical shifts, and the importance of other influences relative to the charge density effect is thus decreased.[4]

In connection with other investigations, a number of naphthalenes and other polycyclic aromatic hydrocarbons substituted with strongly interacting donor groups were prepared.[5] The NMR spectra of these compounds not only confirmed their identity and purity, but in most cases were well-enough resolved to allow complete analysis of the various proton chemical shifts. Few systematic NMR studies of substituted polycyclic hydrocarbons have been made. The most extensive work has been

[1] *Cumulative Influence of Conjugated Substituents in the π-system Properties of Aromatic Hydrocarbons.* Part XII.

[2] For a review cf. G. G. Hall, A. Hardisson and L. M. Jackman, *Tetrahedron* **19**, *Suppl.* 2, 101 (1963).

[3] T. K. Wu and B. P. Dailey, *J. Chem. Phys.* **41**, 3307 (1964); J. S. Martin and B. P. Dailey, *Ibid.* **39**, 1722 (1963).

[4] A. Zweig, J. E. Lehnsen, J. E. Lancaster and M. T. Neglia, *J. Am. Chem. Soc.* **85**, 3940 (1963).

[5] A. Zweig, A. Maurer and B. G. Roberts, in press.

done by Wells,[6,7] who has reported on the chemical shifts of a number of nitronaphthalenes. Dudek[8] had earlier noted the importance of peri interaction in 1,4-dimethoxynaphthalene and in several other types of naphthalene derivatives, treating the effect as a hydrogen-bond paramagnetic displacement.

EXPERIMENTAL

Preparation of the compounds was previously reported.[4] The chemical shifts reported in Table 1 were obtained at room temp from 5 molar solns of the compounds in CCl_4 to which small amounts

TABLE 1. PROTON CHEMICAL SHIFTS OF DONOR SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS

	Methyl resonance	Ring position	Ring proton resonance	δ C.D.[c]
1-Methoxynaphthalene	6·04	2	3·30	+0·083
		8	1·80	−0·002
2-Methoxynaphthalene	6·14	1	3·00[a]	+0·056
1,3-Dimethoxynaphthalene	6·07	2	3·61	+0·126
	6·16	4	3·40	+0·142
		8	1·91	−0·011
1,4-Dimethoxynaphthalene	6·11	2,3	3·47	+0·076
		5,8	1·87	0·000
		6,7	2·60	+0·012
1,5-Dimethoxynaphthalene	6·03	2,6	3.27	+0·081
		3,7	2·73	+0·008
		4,8	2·24	−0·052
1,6-Dimethoxynaphthalene	6·08	2	3·46	−0·097
	6·15	8	1·92	−0·015
		?	2·83[a]	[d]
		5[a]	3·05[a]	[d]
1,7-Dimethoxynaphthalene	6·05	[a]	3·33	[d]
	6·10	[a]	2·40	[d]
1,8-Dimethoxynaphthalene	6·11	2,7	3·28	+0·095
		3,6	2·78	+0·008
		4,5	2·78	+0·071
2,3-Dimethoxynaphthalene	6·11	1,4	3·02	+0·085
		5,8	2·43	+0·014
		6,7	2·79	+0·015
2,6-Dimethoxynaphthalene	6·15	1,5	3·04	+0·082
		3,7	2·96	+0·038
		4,8	2·47	+0·008
2,7-Dimethoxynaphthalene	6·14	1,8	3·05	+0·100
		3,6	3·13	+0·053
		4,5	2·45	+0·007
1,4,5,8-Tetramethoxynaphthalene	6·21	2,3, 6,7	3·28	+0·086
1-Methylthionaphthalene	7·52	8	1·72	+0·007
2-Methylthionaphthalene	7·50		2·2–2·9[b]	--

[6] P. R. Wells, *J. Chem. Soc.* 1967 (1963).
[7] P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.* **16**, 1108 (1963).
[8] G. O. Dudek, *Spectrochim. Acta* **19**, 691 (1963).

	Methyl resonance	Ring position	Ring proton resonance	δ C.D.[c]
1,4-bis(Methylthio)naphthalene	7·53	2,3	2·71	+0·062
		5,8	1·71	+0·002
		6,7	2·50	+0·010
1,5-bis(Methylthio)naphthalene	7·52	2,6	~2·61	+0·066
		3,7	~2·61	+0·007
		4,8	1·88	+0·045
1,8-bis(Methylthio)naphthalene	7·56	2–7	2·3–2·9[b]	[f]
2,3-bis(Methylthio)naphthalene	7·53	1,4	2·52	+0·069
		5,8	2·42	+0·012
		6,7	2·71	+0·013
2,6-bis(Methylthio)naphthalene	7·48	1,5	2·52	+0·067
		3,7	2·75	+0·029
		4,8	2·44	+0·008
2,7-bis(Methylthio)naphthalene	7·52	1,8	2·62	+0·082
		3,6	2·82	+0·042
		4,5	2·46	+0·006
1-Dimethylaminonaphthalene	7·17	2	3·10	+0·157
		8	1·88	−0·011
			2·33	
2-Dimethylaminonaphthalene	7·07	1	3·23	+0·168
		3	3·02	+0·060
1,5-bis(Dimethylamino)naphthalene	7·17	2,6	3·06	+0·152
		3,7	2·71	+0·021
		4,8	2·12	+0·115
2,6-bis(Dimethylamino)naphthalene	7·10	1,5	3·28	+0·161
		3,7	3·06	+0·063
		4,8	2·60	+0·021
2,7-bis(Dimethylamino)naphthalene	7·06	1,8	3·31	+0·066
		3,6	3·22	+0·029
		4,5	2·55	+0·088
9,10-Dimethoxyanthracene	6·01	1,4,5,8	1·79	—
		2,3,6,7	2·63	—
9,10-bis(Methylthio)anthracene	7·64	1,4,5,8	1·02	—
		2,3,6,7	2·47	—
1,6-bis(Dimethylamino)pyrene	7·03	2,7	2·40	—
		3,8	2·07	—
		4,9	2·16	—
		5,10	1·75	—
1,6-bis(Methylthio)pyrene	7·38	2,7	2·04	
		3,8	2·08	
		4,9	2·06	
		5,10	1·51	

[a] Assignment not certain.
[b] All ring H's in these limits.
[c] Parameters employed: $h_o = 1·86$; $h_m = 0·93$; $h_p = 1·14$; $k_{co} = 0·70$; $k_{cm} = 0·73$; $k_{cp} = 0·48$.
[d] Other δ C.D.: (3) −0·006; (4) +0·076; (5) +0·095; (7) +0·054.
[e] Other δ C.D.: (2) +0·084; (3) +0·008; (4) +0·059; (5) +0·005; (6) +0·037; (8) +0·074.
[f] Other δ C.D.: (2) +0·078; (3) −0·006; (4) +0·061.

of TMS had been added. Dilution studies in the methoxybenzene series indicated no significant concentration dependence.[4] The PMR spectra were obtained on a Varian Associates A-60 spectrometer. The calibration of the spectrometer was frequently checked by means of the standard $CHCl_3$–TMS sample. Spectra were also checked on a Varian DP60 spectrometer in those cases where signal-to-noise was somewhat poor.

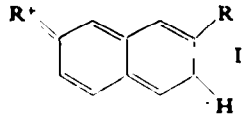
DISCUSSION

A. *General*

Although the spectra of the mono-substituted naphthalenes and the unsymmetrical dimethoxynaphthalene were too complex to be completely resolved, in several instances—especially where there was an alpha substitution—a band system for a single proton appeared at low field (or at high field) to which a chemical shift could be assigned. Complete analysis of the proton spectra of the symmetrically substituted naphthalenes unequivocally demonstrated that the low field proton is always on the *alpha* position *peri* to the substituent. The high field proton identifications are less certain and our assignments must be regarded as tentative. This *peri* downfield effect and the extent to which it may be counterbalanced by the upfield shielding *para* resonance effect of the pi-electron system is clearly illustrated in the 1,4 and 1,5-dimethoxy and 1,4 and 1,5-bis(methylthio)naphthalene spectra. In unsubstituted naphthalene the α and β protons have τ 2·22 and τ 2·56 respectively. In the 1,4-disubstituted compounds, the *peri* effect predominates at the 5,8 positions resulting in chemical shifts of τ 1·87 and τ 1·71 for the methoxy and methylthio compounds respectively. In the 1,5-disubstituted cases the strong intra-ring *para* resonance effect counters the *peri* effect, and results in the intermediate values of chemical shifts at the 4,8 positions of τ 2·24 and τ 1·88 respectively. The *peri* effect is larger with the sulfur compounds and as anticipated from previous studies[5,9] the countering upfield resonance effect is larger with the oxygen compounds.

Generally the effect of inter-ring interactions on chemical shifts is regarded as weak. Thus, the A_4B_4 naphthalene system is considered as two independent AA'BB' sets. However, the NMR studies of 2,6 and 2,7-disubstituted naphthalenes show that in these cases inter-ring resonance effects are far from negligible. Thus, the protons at the 3 position of the 2,7-disubstituted compounds is shifted up-field by 0·17 ppm in the dimethoxy and bis(dimethylamino) substituted naphthalenes and 0·07 ppm in the bis(methylthio) substituted naphthalenes relative to the 2,6-disubstituted compounds.

This proton shift due to change in position of the substituent in the *other* ring must be due to greater resonance interaction of the 3 and 6 positions relative to the 3 and 7 positions. In valence bond terms, this just means that the contributing



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resonance structure I has a significant effect. This conclusion is also in agreement with the results of MO calculations.

The chemical shift of the *peri* protons in 9,10-dimethoxyanthracene is about the same as in 1,4-dimethoxynaphthalene, but 9,10-*bis*(methylthio)anthracene shows a far

[9] A. Zweig and J. E. Lehnsen, *J. Am. Chem. Soc.* **87**, 2647 (1965).

larger *peri* effect than anticipated from a comparison with 1,4-bis(methylthio)naphthalene. The methyl groups are prevented from being in the plane of the aromatic rings in the anthracene derivatives, but not in the naphthalene compounds. This indicates that there is an anisotropic influence on the *peri* effect in the sulfur compounds which is dependent on the sulfur bond angle relative to the plane of the aromatic system. This effect also appears to influence the methyl proton chemical shifts as seen in the 1,8-bis(methylthio)naphthalene spectrum.

B. *Molecular orbital calculations*

The deviations from unit charge density at proton bearing sites in the naphthalene series (δ C.D.) are also reported in Table 1. The charge densities were calculated by the Hückel molecular orbital method using a special set of internally consistent heteroatom parameters derived from a study of the polarographic oxidation potentials of methoxy, methylthio, and dimethylamino substituted benzenes.[9] The charge densities were taken as double the sum of the squares of the eigenvectors of the filled molecular orbitals.

If one uses the well-established value of 10 ppm proton chemical shift per unit pi electron charge with the base values of τ 2·22 and τ 2·56 respectively for the *alpha* and *beta* protons of naphthalene (thus making an empirical correction for the "ring current") and adds to this a suitable correction for the *peri* effect,[10] agreement of predicted and measured chemical shifts $\pm 0{\cdot}1$ ppm, is found for 28 aromatic protons in the methoxynaphthalene series. The standard deviation is about double this for 16 aromatic protons of methylthio substituted naphthalenes. As the smaller number of alpha-dimethylamino substituted compounds available also suffer steric hindrance, no statistically significant data can be derived from them. The results were in accord with the results in the benzene series where Hückel parameters chosen from best fits with eigenvalue related data were used to examine data which relates to the eigenvectors of the secular determinant.[4] There too, the oxygen parameters showed more accuracy in describing the electronic distribution than did the sulfur parameters.[4]

The chemical shift of any aromatic proton in the methoxynaphthalene series may be expressed by the simple equation

$$\delta H = d_0(OCH_3) + d_p(OCH_3) + d_{alpha} + d_{peri}.$$

This equation gives the positions of the proton chemical shifts relative to benzene (τ 2·76) when the applicable additive corrections (d's) are made. The best values for these constants are $d_0(OCH_3) = +0{\cdot}59$ ppm, $d_p(OCH_3) = +0{\cdot}37$ ppm, $d_{alpha} = -0{\cdot}32$ ppm (a ring current correction for all α-naphthyl protons) and $d_{peri} = -0{\cdot}86$ ppm. including alpha correction. Better than 0·05 ppm accuracy for most of the methoxynaphthalene aromatic protons is achieved.

[10] Values used were $-0{\cdot}40$ ppm for methoxy, $-0{\cdot}43$ ppm for methylthio and $-0{\cdot}32$ ppm for dimethylamino.