Carbon-13 Chemical Shifts in Substituted Naphthalenes

By **Peter R. Wells** * and **Dennis P. Arnold**, Department of Chemistry, University of Queensland, St. Lucia, 4067, Australia
David Doddrell, Department of Organic Chemistry, University of New England, Armidale, N.S.W. 2351, Australia

The carbon-13 n.m.r. spectra of a number of substituted naphthalenes have been determined and individual resonances assigned. Substituent effects have been deduced and compared with corresponding effects in benzene. Some correlation with substituent parameters is evident but effects in the unsubstituted nucleus may arise less from conventional changes in electron distribution than from small molecular distortions.

HAVING assigned the ^{13}C resonances of the methylnaphthalenes, deduced the methyl substituent effects, and shown that in the absence of *ortho*-like interactions these are additive,[1] we can now analyse the spectra of a variety of monosubstituted naphthalenes by employing strategically placed methyl groups to locate the various carbon resonances.

EXPERIMENTAL

Proton-decoupled natural abundance ^{13}C n.m.r. spectra were determined at 15·1 MHz on a modified Varian HA60 IL spectrometer controlled by a VDM 8K 6201i computer. Samples were examined as saturated solutions in chloroform. In all cases cyclohexane was used as an internal reference. Chemical shifts, positive when towards low field,[†] are referred to tetramethylsilane by taking this to be −27·3 p.p.m. from cyclohexane. Off-resonance decoupling studies were not carried out, and unprotonated carbons could not be distinguished in our spectra by differences in nuclear Overhauser enhancements.

The preparation and purification of the samples was reported previously [2] with the exception of 1-methoxy-[4-^{2}H]naphthalene and 2-methoxy[6-^{2}H]naphthalene. The latter were prepared from the corresponding bromo-compounds by conversion into the lithium derivative followed by quenching D_2O.

RESULTS

Methylnaphthalenes.—Our previous results [1] are given together with other published results in Table 1. Johnson and Jankowski [3] give only partial assignments, while the assignments of Kitching *et al.*[4] are based on a study of 1-methyl[4-^{2}H]naphthalene.

TABLE 1

	1-Methylnaphthalene			2-Methyl-naphthalene	
	Ref. 1	Ref. 3	Ref. 4	Ref. 1	Ref. 3
C-1	134·2	133·5	134·3	127·2	126·7
C-2	126·8	126·4	126·8	135·5	135·1
C-3	125·7	125·3	125·6	128·2$_5$	127·9
C-4	126·8	126·3	126·8	128·0	127·5
C-5	129·7	128·4	128·8	128·0	127·6
C-6	125·7	125·3	125·5	125·1	124·8
C-7	125·7	125·5	125·7	126·0	125·7
C-8	124·2$_5$	123·9	124·2	127·6	127·1
C-8a	133·1$_5$	132·6	133·3	134·3	133·6
C-4a	134·2	134·0	134·3	132·3$_5$	131·7
CH_3	19·1	19·1	19·1	21·5$_5$	21·4

Nitronaphthalenes.—A comparison of the spectra of 2-nitronaphthalene and its 6-methyl and 3-methyl derivatives enabled the assignments given in Table 2 to be made, although it was evident that the shifts in the latter deviated from additivity especially for the substituted nucleus. The resonance at C-2 is very broad presumably due to the nitrogen quadrupole and could not be distinguished from noise in the case of 3-methyl-2-nitronaphthalene. The average deviation between observed and calculated spectra for 6-methyl-2-nitronaphthalene is 0·3 p.p.m., excluding the large deviation for C-6. However the deviations are all positive indicating that the location of the reference resonance in this case or the case of 2-nitronaphthalene could be in error by this amount. If this were so then the average deviation would be 0·1 p.p.m. and the deviation of C-6 1·45 p.p.m. The cause of this particular deviation is unclear, but of all the assignments this is the most secure. A calculated spectrum for the 3-methyl derivative was based upon that for 2,3-dimethylnaphthalene to give some allowance for the effect of proximate groups. Deviations remain for the substituted ring indicating that the nitro-group effect is more affected than that of the methyl group.

TABLE 2

2-Nitronaphthalene (2-NN) and derivatives

	2-NN Obs.	6-Methyl-2-NN Obs.	*Calc.*[a]	3-Methyl-2-NN Obs.	*Calc.*[a]	*Calc.*[b]
C-1	124·6	124·6	*124·2$_5$*	125·4	*124·3*	*125·0*
C-2	145·9	145·4	*145·1*		*148·0$_5$*	*146·3*
C-3	119·2	119·5$_5$	*119·1*	131·6 (131·2)	*128·6*	*126·5*
C-4	129·6$_5$	128·9$_5$	*128·8$_5$*	129·4	*128·5$_5$*	*129·3$_5$*
C-5	128·1	127·3$_5$	*127·1*	127·4	*127·4*	*127·3$_5$*
C-6	129·9 (130·1)	140·7$_5$	*139·1*	129·6$_5$ (129·4)	*129·9*	*129·9*
C-7	128·1	130·5$_5$	*130·2*	127·4	*127·1*	*127·3*
C-8	130·1 (129·9)	130·0$_5$	*129·7*	129·4 (129·65)	*129·7*	*129·7*
C-8a	132·05	130·5$_5$	*130·3*	131·2 (131·6)	*130·2*	*130·8$_5$*
C-4a	136·0	136·5$_5$	*135·9*	135·45	*136·1*	*136·4$_5$*

[a] Calculated from shift in 2-NN plus effect of methyl group.
[b] Calculated from shifts in 2,3-DMN *less* the effect of 2-methyl *plus* effect of 2-nitro-group.

Two sets of 1-nitronaphthalene derivatives were studied.

[†] In our previous publication [1] the opposite sign convention was employed for chemical shifts and these were referred to benzene. We make this change in conformity with most current publications.

[1] D. Doddrell and P. R. Wells, *J.C.S. Perkin II*, 1973, 1333.

[2] W. Adcock and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1351; P. G. E. Alcorn and P. R. Wells, *ibid.*, pp. 1377, 1391.

[3] L. F. Johnson, and W. C. Jankowski, 'Carbon-13 N.M.R. Spectra,' Wiley-Interscience, New York, 1972.

[4] W. Kitching, M. Bullpitt, D. Doddrell, and W. Adcock, *Org. Magnetic Resonance*, 1974, **6**, 289.

Those reported in Table 3 provide the bases for the estimation of the influence of an unhindered nitro-group. (There will be however some hindrance due to 8-H.) Results for compounds bearing a methyl group at C-2 are given in Table 4. The average deviation between observed and calculated for 4-methyl-1-nitronaphthalene is 0·1$_5$ p.p.m. excluding C-4 which again deviates by 1·75 p.p.m. Deviations in the case of the 6-methyl isomer appear to be rather more serious at C-2, -8, and -4a and again at C-6.

TABLE 3

Unhindered 1-nitronaphthalene (1-NN) derivatives

	1-NN Obs.	4-Methyl-1-NN Obs.	*Calc.*[a]	6-Methyl-1-NN Obs.	*Calc.*[a]
C-1	147·1		*145·5*	146·9$_5$	*146·7*$_5$
C-2	124·1	123·9	*123·7*	122·1$_5$	*123·3*
C-3	124·3	125·3	*125·1*	124·2	*124·1*
C-4	135·0	142·5$_5$	*140·8*	134·2	*134·2*
C-5	128·9	124·9	*124·9*	127·7	*127·9*
C-6	127·5$_5$	127·3	*127·1*$_5$	137·6	*136·6*$_5$
C-7	129·65	129·1	*129·0*$_5$	131·85	*131·7*$_5$
C-8	123·1$_5$	123·9	*123·7*$_5$	122·1$_5$	*122·8*$_5$
C-8a	125·2$_5$	125·5	*125·3*$_5$	123·6	*123·5*
C-4a	134·6$_5$	133·4$_5$	*133·7*	135·1	*134·5*$_5$

[a] Calculated from shifts in 1-NN plus effect of methyl group.

TABLE 4

Hindered 1-nitronaphthalene derivatives

	2-Methyl-1-NN Obs.	*Calc.*[a]	2,6-Dimethyl-1-NN Obs.	*Calc.*[b]	2,7-Dimethyl-1-NN Obs.	*Calc.*[b]
C-1	148·3	*146·1*	148·2	*147·9*$_5$	148·1	*147·5*
C-2	130·5$_5$	*133·2*	130·0	*129·7*$_5$	130·3	*130·45*
C-3	128·2[c]	*126·3*	128·2	*128·0*	127·3	*127·3*
C-4	or	*134·7*	127·1$_5$	*127·3*	128·1	*128·0*
C-5	127·9[c]	*128·5*$_5$	126·5$_5$	*127·1*	127·5	*127·8*
C-6	126·7$_5$	*126·7*$_5$	136·8	*135·8*$_5$	129·0$_5$	*128·8*$_5$
C-7	128·6	*129·5*$_5$	130·8$_5$	*130·7*	139·0	*137·7*
C-8	121·3	*122·3*$_5$	121·1	*121·0*	120·3	*120·3*
C-8a	124·8	*125·1*$_5$	123·1	*123·0*$_5$	125·1	*124·7*
C-4a	132·5	*132·9*	132·8	*132·4*	131·0	*130·7*$_5$

[a] Calculated from shifts in 1-NN with effect of methyl group. [b] Calculated from shifts in 2-methyl-1-NN with effect of methyl group. [c] Three resonances, 127·9, 128·2, 128·2, were not individually assigned.

TABLE 5

	1-Fluoronaphthalene			2-Fluoronaphthalene		
	Ref. 6	Ref. 4	This work	Ref. 6	Ref. 7	This work
C-1	161·8 (251·1)	159·5 (253·6)	157·3 (254·5)	117·6 (25·2)	116·2 (25·9)	116·2 (26)
C-2	111·8 (19·9)	109·8 (19·8)	109·2 (20)	151·9 (~246)	160·9 (248·8)	161·0 (248)
C-3	128·3 (8·2)	126·0 (8·0)	125·4 (8·5)	112·5 (20·4)	109·5 (21·0)	110·9 (21)
C-4	126·6 (4·0)	124·2 (4·6)	123·7 (4·5)	131·8 (8·8)	130·6 (10·1)	130·5 (~10)
C-5	128·7 (1·7)	126·6 (2·0)	126·1 (1·5) *	129·4 (0)	130·9 (~0)	130·8 (~0) *
C-6	129·8 (0·8)	127·3 (~0)	126·8 (0)	128·9 (0)	126·6 (2·8)	125·2 (2·5)
C-7	130·4 (3·2)	128·1 (3·0)	127·9 (3) *	128·6 (0)	128·1 (1·2)	128·0$_5$ (~0)
C-8	123·2 (5·1)	120·9 (5·0)	120·5 (4·5)	128·3 (0)	127·0 (~0)	126·9$_5$ (~0)
C-8a	126·8 (16·4)	124·3 (17·2)	124·0 (16·5)	135·7 (9·2)	134·8 (9·9)	134·7 (9·5)
C-4a	137·9 (4·8)	135·7 (5·0)	135·4 (4·5)	126·6 (2·5)	127·5 (5·1)	127·5 (5) *

* May require reverse assignments. See Discussion section.

A recently reported[5] spectrum of 1-nitronaphthalene, assigned on the basis of off-resonance proton irradiation, is in excellent agreement with that given in Table 3 except that each resonance is 0·55 p.p.m. to higher field.

A mutually consistent set of assignments for the hindered 1-nitronaphthalenes can be obtained in terms of a modified nitro-group effect in Table 16 and is indicated by the comparison of observed and calculated spectra for 2-methyl-1-nitronaphthalene (see Table 4).

Fluoronaphthalenes.—The spectra of both 1- and 2-fluoronaphthalenes have been reported previously[4,6,7] although the assignments were uncertain in the earlier work.[6] Comparison with 6-methyl-2-fluoronaphthalene[7] and fluoro[4-^{2}H$_{1}$]naphthalene[4] leads to the results given in Table 5. The scalar coupling constants $J(^{13}C-^{19}F)$ are given in parentheses. Comparisons of substituent induced shifts suggest that the assignments of C-5 and -7 in 1-fluoronaphthalene, and of C-5 and -4a in 2-fluoronaphthalene should be reversed (see Discussion section).

Acetylnaphthalenes.—The assignments for 1-acetylnaphthalene and its 7-methyl derivative are given in Table 6. The agreement between observed and calculated resonances is excellent (mean deviations 0·1 p.p.m.) employing the average shift due to the 1-acetyl group. Similarly the agreement in the case of 2-acetylnaphthalene and its 6-methyl derivative (mean deviations 0·15 and 0·2 p.p.m. respectively), also given in Table 6, is again excellent.

Bromonaphthalenes.—Table 7 summarises the assignments and chemical shifts of 2-bromonaphthalene with its 6-methyl and 6-methoxy-derivatives, and of 1-bromonaphthalene with its 4-methyl and 4-methoxy-derivatives. The mean deviations between observed and calculated spectra are excellent (±0·15, ±0·2, ±0·1, ±0·2, ±0·15, and ±0·1 p.p.m.). The carbon bearing the bromine atom is recognisable by its low intensity. The spectrum of 2-methyl-1-bromonaphthalene is given in Table 8 with

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[5] J. W. Emsley, J. C. Lindon, and D. Shaw, *J. Magnetic Resonance*, 1973, **10**, 100.

[6] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 2361.

[7] D. Doddrell, D. Jordan, N. W. Riggs, and P. R. Wells, *J.C.S. Chem. Comm.*, 1972, 1158.

results calculated by assuming additive substituent effects. Only C-1 and -2 deviate significantly.

Methoxynaphthalenes.—The resonances of 1- and 2-methoxynaphthalene were assigned from a comparison of these spectra with the 4-deuterio- and 4-bromo-, and with the 6-deuterio- and 6-bromo-derivatives respectively employing the bromo-substituent effect deduced above. Of the two reasonable assignments for C-1 and -3 in 2-methoxynaphthalene the one giving a significantly better comparison between observed and calculated shifts was preferred.

TABLE 6

Acetylnaphthalene (AcN) derivatives

	1-AcN Obs.	*Calc.*[a]	7-Methyl-1-AcN Obs.	*Calc.*
C-1	135·4$_5$	*135·5*	134·9	*134·7*
C-2	129·1	*129·2*	129·2	*129·1*
C-3	126·6	*126·6*	125·7$_5$	*125·8*
	or 126·5			
C-4	133·0$_5$	*133·0*	132·8	*132·6*$_5$
C-5	128·7	*128·7*$_5$	128·5	*128·4*$_5$
C-6	126·6	*126·5*	128·6	*128·6*
	or 126·5			
C-7	128·0	*128·3*$_5$	137·8	*137·4*$_5$
C-8	124·6	*124·6*	123·6$_5$	*123·6*
C-8a	130·6$_5$	*130·9*	131·0	*130·8*
C-4a	134·3$_5$	*134·4*$_5$	132·8	*132·7*
	2-AcN		6-Methyl-2 2-AcN	
C-1	128·1$_5$	*128·9*	129·4	*128·6*
C-2	135·0	*135·1*$_5$	134·3	*134·1*
C-3	124·3	*124·4*	124·3$_5$	*124·3*
C-4	128·8	*128·7*	128·0	*128·0*$_5$
C-5	128·8	*128·5*$_5$	127·2	*127·4*$_5$
C-6	129·9$_5$	*129·7*	138·9	*139·1*
C-7	127·1	*127·5*	129·7	*129·7*
C-8	130·4$_5$	*130·5*	130·3	*130·2*
C-8a	133·0	*133·0*	131·2	*131·2*
C-4a	136·0	*136·1*	136·3	*136·2*

[a] Calculated from the average shifts for the appropriate substituents.

Other Substituted Naphthalenes.—Results for 1-cyanonaphthalene and 2-hydroxynaphthalene were taken from ref. 4. Re-examination of these spectra suggests that the assignments given for C-3 and -7, and for C-8a and -4a in 1-cyanonaphthalene should be reversed. Of the two possible assignments for C-1 and -3 in 2-naphthol the one most closely resembling 2-methoxynaphthalene is preferred A preliminary result for C-1 in 1-chloronaphthalene is available.

TABLE 7

Bromonaphthalene (BrN) derivatives

	2-BrN Obs.	*Calc.*[a]	6-Methyl-2-BrN Obs.	*Calc.*[a]	6-Methoxy-2-BrN Obs.	*Calc.*[b]
C-1	130·2	*130·3*	130·1	*129·9*$_5$	128·9$_5$	*130·1*$_5$
C-2	120·0	*119·9*	119·1	*119·1*	117·5	*117·5*
C-3	127·1$_5$	*127·3*$_5$	127·2$_5$	*127·2*$_5$	128·9$_5$	*128·9*$_5$
C-4	129·8	*130·2*	129·6	*129·4*	128·9$_5$	*128·9*$_5$
C-5	128·0$_5$	*128·1*$_5$	127·2$_5$	*127·1*$_5$	106·3$_5$	*106·2*
C-6	126·4	*126·9*	136·6	*136·0*	158·6	*158·6*
C-7	127·2$_5$	*127·2*$_5$	129·4	*129·3*$_5$	120·2	*120·3*$_5$
C-8	129·4$_5$	*129·7*	129·6	*129·4*	130·6$_5$	*130·1*$_5$
C-8a	134·8	*134·8*	133·3$_5$	*133·0*$_5$	130·1	*130·6*
C-4a	132·1	*132·3*	132·6	*132·2*	133·5	*133·1*$_5$
	1-BrN		4-Methyl-1-BrN		4-Methoxy-1-BrN	
C-1	122·8$_5$	*122·1*	120·7$_5$	*120·5*	113·4$_5$	*113·6*
C-2	129·7	*129·7*	129·4	*129·2*	129·9$_5$	*130·0*
C-3	125·7$_5$	*126·0*	126·7$_5$	*126·9*	104·3	*104·3*
C-4	127·7	*127·9*	134·1	*133·7*	155·4	*155·8*
C-5	128·1	*128·3*	124·3	*124·3*	122·9$_5$	*122·9*$_5$
C-6	126·4	*126·5*	126·1$_5$	*126·1*	126·0	*126·0*
C-7	126·9$_5$	*127·2*	126·7$_5$	*126·6*	128·0	*128·1*
C-8	126·9$_5$	*127·1*$_5$	127·5$_5$	*127·7*$_5$	127·2$_5$	*127·1*$_5$
C-8a	132·0	*131·8*	131·8	*131·9*	133·0	*133·0*
C-4a	134·6	*134·7*	133·7	*133·7*$_5$	127·2$_5$	*127·1*$_5$

[a] Calculated from average shifts for the appropriate substituents.

TABLE 8

2-Methyl-1-bromonaphthalene

	Obs.	*Calc.*		Obs.	*Calc.*
C-1	124·1$_5$	*121·1*	C-6	125·4	*125·7*
C-2	135·7	*138·7*	C-7	127·0	*127·2*
C-3	127·9$_5$	*128·1*	C-8	127·0	*126·3*$_5$
C-4	127·0	*127·6*	C-8a	132·7	*131·7*
C-5	128·3$_5$	*127·9*$_5$	C-4a	133·2	*132·9*$_5$

TABLE 9

Methoxynaphthalene (MxN) derivatives

	1-MxN		4-Bromo-1-MxN		2-MxN		6-Bromo-1-MxN	
	Obs.	*Calc.*[a]	Obs.	*Calc.*[a]	Obs.	*Calc.*[a]	Obs.	*Calc.*[a]
C-1	156·1	*155·9*$_5$	155·4	*155·5*$_5$	106·2$_5$	*106·3*	106·3$_5$	*106·3*
C-2	104·1	*104·2*$_5$	104·3	*104·1*$_5$	158·3$_5$	*158·1*	158·6	*158·9*
C-3	126·5	*126·4*	129·9$_5$	*130·0*	119·1	*119·1*$_5$	120·2	*120·1*$_5$
C-4	120·7	*120·2*	113·4$_5$	*114·0*	129·6	*129·2*	130·1$_5$	*130·6*
C-5	128·0	*128·2*	127·2$_5$	*127·0*$_5$	128·1$_5$	*128·1*$_5$	130·1$_5$	*130·1*$_5$
C-6	126·9	*126·9*	128·0	*128·0*	124·0	*123·8*$_5$	117·5	*117·6*$_5$
C-7	125·5	*125·5*$_5$	126·0	*125·9*$_5$	127·2	*127·4*$_5$	128·9$_5$	*128·7*
C-8	122·7$_5$	*122·8*$_5$	122·9$_5$	*122·8*$_5$	126·8	*126·9*	128·9$_5$	*128·8*
C-8a	126·5	*126·6*	127·2$_5$	*127·1*	135·3	*135·3*$_5$	133·5	*133·4*$_5$
C-4a	135·6	*135·5*	133·0	*133·1*	129·9	*129·9*$_5$	130·6	*130·5*$_5$

[a] Calculated from the average methoxy- and bromo-shifts.

DISCUSSION

Substituent induced chemical shifts derived by comparison with the appropriate carbons of naphthalene are listed according to orientation * in Tables 10—15

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* Substituent orientation relative to the carbon atom under examination is labelled according to the substituent position by number and the carbon position (α or β). Thus for C-6, a β-carbon, in a 1-substituted naphthalene the interaction is labelled 5β (see ref. 8).

[8] S. Ehrenson, R. W. Taft, and P. R. Wells, *Progr. Phys. Org. Chem.*, 1968, **6**, 111.

TABLE 10

Substituent induced shifts at site of substitution

	ϕC-1	αC-1	βC-2
F	34·8	29·0	34·9
OCH_3	31·4	$27{\cdot}6_5$	31·7
OH	26·9		27·5
NO_2	20·0	18·8	19·8
$COCH_3$	9·1	7·1	$9{\cdot}0_5$
CH_3	8·9	5·8	9·0
CHO	8·6	5·1 *	
Cl	6·2	6·4	5·6
Br	−5·5	−6·0	−6·2
CN	−15·4	−18·0	

* From ref. 2.

TABLE 11

Substituents induced shifts at *para*-like positions

	ϕC-4 (*para*)	αC-4 (4α)	βC-4a
OCH_3	−7·7	−8·1	−4·2
OH	−7·3		−4·6
F	−4·5	−4·6	−6·7 (−3·4)
CH_3	−2·9	−1·6	$-1{\cdot}7_5$
Br	−1·6	−0·4	−1·9
CN	+3·9	+5·2	
$COCH_3$	+4·2	+4·8	+1·9
NO_2	+5·8	+6·7	+1·8
Aza	*+8·1*	*+7·7*	*+1·8*

TABLE 12

Substituent induced shifts at *ortho*-like positions

	ϕC-2 (*ortho*)	αC-2 (1β)	βC-1 (2α)	βC-3 (3β)	αC-8a	αC-8 (8α)
OCH_3	−14·4	$-21{\cdot}8_5$	$-21{\cdot}9_5$	−6·9	−7·6	$-5{\cdot}4_5$
OH	−12·7		−28·1	−8·1		
F	−12·8	−16·9	−12·1	−15·2	−9·8	−7·8
NO_2	−4·8	−1·9	−3·7	−6·9	$-8{\cdot}9_5$	$-5{\cdot}1_5$
$COCH_3$	+0·1	+3·1	+0·6	−1·7	−3·3	−3·7
CH_3	+0·7	+0·9	−1·0	+2·1	$-0{\cdot}9_5$	−4·0
Br	+3·4	$+3{\cdot}4_5$	+2·0	$+1{\cdot}2_5$	−2·3	−1·4
CN	+3·6	+2·7			−1·2	+4·5
Aza	*+21·9*	*+24·8*	*+24·8*	*+17·7*	*+14·8*	*+1·8*

TABLE 13

Substituent induced shifts at *meta*-like positions

	ϕC-3 (*meta*)	αC-3 (4β)	βC-4 (3α)	αC-4a	βC-8a
Br	+1·7	−0·1	+1·9	+0·6	+0·6
F	+1·4	−0·7	+2·2	+1·2	+0·5
OH	+1·4		+1·5		+1·5
OCH_3	+1·0	+0·3	+0·45	+1·3	+1·2
NO_2	+0·9	−1·9	$+1{\cdot}3_5$	$+0{\cdot}4_5$	$-2{\cdot}1_5$
CN	+0·6	−0·9		−0·5	
$COCH_3$	+0·0	+0·5	$+0{\cdot}4_5$	$+0{\cdot}2_5$	−0·7
CH_3	−0·1	−0·5	−0·3	+0·1	−0·1
Aza	*−3·8*	*−4·6*	*−7·5*	*−5·5*	*−5·2*

together with the corresponding data for substituted benzenes.[9] Data for the aza-substituent are from the studies on pyridine, quinoline, and isoquinoline.[10]

C-1 in substituted benzenes and C-2 in 2-substituted naphthalenes show within experimental uncertainty the same response to the substituent. C-1 in 1-substituted naphthalene is shifted to higher field than expectation by an amount roughly dependent upon the magnitude by the expected shift. Whether this is to be ascribed to a small molecular distortion arising from interaction with 8-H is unclear, since the effect of a 2-methyl group on the C-1 interaction of a nitro-group (see Table 16) is in the opposite direction.

TABLE 14

Substituent induced shifts at ' quinonoid ' positions

	βC-6 (6β)	βC-8 (7α)	αC-5 (5α)	αC-7 (8β)
OH	−2·6	−1·9		
OCH_3	−2·4	−1·25	−0·1	$-0{\cdot}5_5$
F	−0·9	$-1{\cdot}3_5$	−2·3 (−0·6)	+1·8 (0·0)
CH_3	−0·8	−0·8	+0·6	−0·4
Br	+0·8	+1·4	0·0	+1·0
$COCH_3$	+3·6	+2·2	$+0{\cdot}3_5$	$+2{\cdot}2_5$
CN			+0·7	+1·7
NO_2	+3·9	+1·7	+0·6	$+3{\cdot}5_5$
Aza	*+4·4*	*−0·4*	*0·0*	*+3·6*

TABLE 15

Substituent induced shifts at ' non-quinonoid ' positions

	βC-5 (6α)	βC-7 (7β)	αC-6 (5β)
OH	−0·6	+0·3	
OCH_3	−0·15	+1·6	+0·8
F	+2·6 (−0·8)	$+1{\cdot}9_5$	+0·7
CH_3	$-0{\cdot}3_5$	−0·1	−0·6
Br	$-0{\cdot}1_5$	$+1{\cdot}1_5$	+0·4
$COCH_3$	$+0{\cdot}2_5$	+1·3	+0·4
CN			−0·9
NO_2	−0·2	+2·0	$+1{\cdot}4_5$
Aza	*−2·1*	*+0·9*	*+1·6*

TABLE 16

Substituent induced shifts of ' methyl hindered ' nitro-group

		Δ			Δ
C-1	+21·3	+2·5	C-6	$+1{\cdot}6_5$	+0·2
C-2	−7·3	−9·2	C-7	+2·5	$-1{\cdot}0_5$
C-3	−0·1	+1·8	C-8	−6·2	$-1{\cdot}0_5$
C-4	+2·6	−4·1	C-8a	$-9{\cdot}2_5$	−0·3
C-5	−0·2	−0·8	C-4a	+0·3	$-0{\cdot}1_5$

Δ = (hindered) − (unhindered).

The 4α interaction in naphthalene closely resembles the *para*-interaction in benzene and both are well accounted for by the substituent parameters derived from reactivity and ^{19}F studies,[8] *i.e.*, δ_c *ca.* $3\sigma_I + 20\sigma_R^0$. C-4a is also in a *para*-like relationship to a β-substituent but is, of course, unobservable in other substituent effect studies. Reversing the assignments of C-5 and -4a in 2-fluoronaphthalene yields the shift given in parentheses in Table 11, in which case the data are well accounted for by δ_c *ca.* $10\sigma_R^0$. This indicates that conjugative effects reach this position but it is insensitive to inductive effects by whatever means they are transmitted. The aza-substituent, which is presumed to exert predominately an inductive effect, shows similar behaviour.

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[9] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972, p. 81.

[10] R. J. Pugmire, D. M. Grant, M. J. Robins, and G. W. Rhodes, *J. Amer. Chem. Soc.*, 1969, **91**, 6381.

The influence of substituents on the reactivity and physical properties of functions in *ortho*, *peri*, and related positions still defies quantitative analysis and it is clear that several factors are involved. The data of Table **12** indicate some similarities and some notable differences. There are indications of some relationships but these may be more apparent than real. We have resisted the temptation to suggest further dubious hypotheses, but hope others may be able to draw definitive conclusions from our data.

Much the same can be said of the shifts at *meta*-like positions given in Table **13** particularly since these are all quite small. It is interesting that the presumed inductive effect of the aza-substituent shows the alternation predicted by recent SCF–MO calculations, whereas most substituents still give rise to small lowfield shifts, although this is not always the case. Perhaps some of the interactions responsible for the shifts at *ortho*-like positions are not sufficiently attenuated to be negligible at the adjacent carbon atom.

The carbons of the unsubstituted ring of naphthalene can be divided into two sets, excluding the *ortho*-like 8α, according to whether or not naïve MO theory predicts an easy communication of conjugative interactions. The former (6β, 7α, 5α, and 8β) are described as ' quinonoid ' and the latter (6α, 7β, and 5β) as ' non-quinonoid '. Only in the case of the 6β-interaction can the data be satisfactorily fitted to the substituent parameters (δ_c *ca.* $3\sigma_I + 8\sigma_R{}^0$). In the other quinonoid cases, 7α and 8β, the substituent inductive and conjugative effects certainly play a role but this appears to be overlaid by some other effect. The ' quinonoid ' 5α-interaction on the other hand in most cases does not exceed experimental error. With the assignments of Table **5** the induced shifts of C-5 and -7 of 1-fluoronaphthalene are anomalous whereas if these are reversed as indicated in Table **14**, behaviour more in line with that of other groups is observed.

Relatively small substituent induced *shifts* would be expected for the non-quinonoid positions (6α, 7β, and 5β). Table **15** indicates that to some extent this is true especially with the reversed assignments in 2-fluoronaphthalene although several shifts are greater than those arising from 5α-interactions and exceed experimental uncertainties. Inductive effects appear to be dominant although these may again be overlaid by some other effect.

The results of steric crowding as evidenced by the results given in Table **16**, other results in the present study, and those on crowded polymethylnaphthalenes,[1] appear to be felt throughout the system and are not simply modifications of the normal substituent effect. This would arise if there were bond length and angle changes throughout the system in response to the primary distortion and if the carbon-13 chemical shifts are responsive to these changes. If such distortions also occur in monosubstituted naphthalenes, particularly those with α-substituents, these might be the cause of some of the shifts observed when other factors such as inductive and conjugative effects are not dominant.

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