Carbon-13 Chemical Shifts in Methylnaphthalenes

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

The carbon-13 n.m.r. spectra of some methylnaphthalenes have been determined and the individual resonances assigned. The effect of methyl substituents is additive except when in '*ortho*'-like relationship.

THE successful correlation of the ^{13}C chemical shifts of benzene and monocyclic 6π ions,[1] and those of azulene [2] with calculated π electron densities gave hope that this would make π electron densities observable quantities. In particular δ_c is increased by approximately 160 p.p.m. per unit increase of charge, and would appear to be a very sensitive means of assessing approximate wave functions. However, application of the Karplus–Pople [3] theory of chemical shifts in a relatively simple manner with neglect of a number of contributions presumed to be small, indicates a dependence not only on π charge density, but also on σ charge density and mobile bond order.[4]

Just as the study of naphthalene derivatives revealed a number of features of substituent effects on reactivity

[1] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 1961, 468.
[2] P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 1838.
[3] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.
[4] T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, 1966, **88**, 5397.

not apparent from the study of benzene derivatives,[5-7] one may anticipate that substituent effects on the ^{13}C chemical shifts in naphthalene will be valuable in the understanding of ground state substituent intractions and chemical shift theory.

TABLE 1

Effect of methyl substituent on naphthalene ring carbon-13 resonances (p.p.m.)

	Effect of 1-Me on				
C-1	−5·8 [a]	(±0·05) [b]	C-6	+0·6	(±0·1)
C-2	−0·9	(±0·2)	C-7	+0·4	(±0·05)
C-3	+0·5	(±0·2)	C-8	+4·0	(±0·1)
C-4	+1·6	(±0·05)	C-8a	+0·9_5	(±0·05)
C-5	−0·6	(±0·05)	C-4a	−0·1	(±0·05)
	Effect of 2-Me on				
C-1	+1·0	(±0·1)	C-6	+0·8	(±0·15)
C-2	−9·1	(±0·15)	C-7	+0·1	(±0·1)
C-3	−2·1	(±0·1)	C-8	+0·8	(±0·1)
C-4	+0·3	(±0·1)	C-8a	+0·1	(±0·1)
C-5	+0·3_5	(±0·05)	C-4a	+1·7_5	(±0·05)

[a] Mean of three estimates of chemical shift relative to naphthalene. [b] Mean deviation of estimates from mean.

TABLE 2

Effect of methyl substituent on benzene ring carbon-13 resonances (p.p.m.)

Reference	4	9	10	11	12
C-1	−9·1	−9·1	−9·3	−8·9	−9·4
C-2 (*ortho*)	−0·6_2	−0·3	−0·6	−0·7	−0·8
C-3 (*meta*)	+0·1_9	−0·3	0·0	+0·1	+0·1
C-4 (*para*)	+3·0$5_5$	+2·8	+3·1	+2·9	+2·9

TABLE 3

Carbon-13 chemical shifts in naphthalene relative to benzene (p.p.m.)

	Obs.	Lit.[4]
α-C (1,4,5,8)	+0·4(±0·1)	+0·4_4
β-C (2,3,6,7)	+2·6(±0·1)	+2·5_6
C-4a, -8a	−5·5(±0·1)	−5·2

that these effects are additive and characteristic at various positions, the spectra of substituted methylnaphthalenes provide the means of assignment of resonances in other monosubstituted naphthalenes.

EXPERIMENTAL

Proton-decoupled natural-abundance ^{13}C n.m.r. spectra were determined at 15·1 MHz on a modified [8] Varian HA 60 IL spectrometer controlled by a VDM 8K 620i computer. Samples were examined as neat liquids or saturated solutions in chloroform. In all cases cyclohexane was used as internal reference. Chemical shifts, positive when towards high field, are referred to benzene by taking benzene to be −101·4 p.p.m. from cyclohexane.

RESULTS AND DISCUSSION

Assignment of Resonances.—The observed chemical shifts of the ring ^{13}C atoms relative to those of benzene are given in Tables 3—7 together with the assignments and the chemical shifts calculated as described below.

As a starting point for making the assignments it was noted that those compounds giving a resonance at lowest field all have a β-methyl group. On this basis C-2 of 2-methylnaphthalene (2-MN) and 2,3-dimethylnaphthalene (23-DMN) were assigned. The remaining resonances at very low field in these compounds and two of the resonances in 2,3,6-trimethylnaphthalene (236-TMN) were then assigned to C-4a and C-8a. The difference between C-4a and C-8a in 2-MN can be associated with a *para*-like interaction of +1·6 p.p.m. with 2-Me (*cf.* 2·9 p.p.m. in toluene). The β-C and C-4a and -8a atoms of 13-DMN, 16-DMN, and 7-DMN were then assigned and the shifts of C-4a and C-8a due to the β-methyl group were found to correspond closely to those in 2-MN. The assignment of C-1 follows as the remaining resonance at very low field. It was noted that those compounds giving a resonance at highest field are those having an α-methyl-group. This resonance could most reasonably be assigned to C-8 or, less likely, to C-4.

TABLE 4

Observed and calculated chemical shifts (p.p.m. relative to benzene)

1-MN			2-MN			13-DMN			16-DMN			17-DMN		
Obs.	Asmt.	Calc.	Obs.	Asmt.	Calc.	Obs.	Asmt.	Calc.	Obs.	Asmt.	Calc.	Obs.	Asmt.	Calc.
−5·5	C-4a	−5·6	−6·8	C-2	−6·5_5	−5·9_5	C-3	−6·0	−6·0	C-6	−5·9	−6·3	C-7	−6·1$_5$
	C-1	−5·3_5	−5·6	C-8a	−5·4	−5·7	C-4a	−5·5	−5·7	C-4a	−5·5	−4·6_5	C-1	−4·6
−4·4_5	C-8a	−4·5_5	−3·6_5	C-4a	−3·7_5	−5·1	C-1	−5·1	−5·2	C-1	−5·1		C-8a	−4·4
−0·1	C-5	−0·2	+0·4_5	C-3	+0·5	−2·7	C-8a	−2·8	−2·7	C-8a	−2·8	−3·7	C-4a	−3·8
+1·9	C-2	+1·7	+0·7	C-4	+0·7	−0·2	C-2	−0·4	+0·8	C-5	+0·8	+0·1	C-5	+0·1
	C-4	+2·0		C-5		+0·6	C-5	+0·6		C-7	+0·8_5	+1·0_5	C-6	+1·1
	C-7	+2·9_5	+1·1	C-8	+1·2	+3·1	C-4	+3·0	+2·5	C-2	+2·5_5	+1·9_5	C-2	+1·8
+3·0	C-3	+3·1	+1·5	C-1	+1·4	+3·2_5	C-6	+3·3	+2·7_5	C-4	+2·8	+2·2_5	C-4	+2·3
	C-6	+3·2	+2·7	C-7	+2·7	+3·9_5	C-7	+3·8	+3·1	C-3	+3·4	+4·0	C-3	+3·9_5
+4·4_5	C-8	+4·4	+3·6	C-6	+3·4	+4·8	C-8	+4·7	+4·7	C-8	+4·7	+5·4	C-8	+5·4
Mean dev. 0·1			Mean dev. 0·1			Mean dev. 0·1			Mean dev. 0·1			Mean dev. 0·1		

As the first step in such a study, the effect of methyl substituents has been examined. Having demonstrated

[5] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **74**, 3539.
[6] P. R. Wells and W. Adcock, *Austral. J. Chem.*, 1965, **18**, 1365.
[7] P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 147.
[8] D. Doddrell, N. V. Riggs, and F. B. Hansen, *Austral. J. Chem.*, to be published.
[9] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.
[10] A. M. Ihrig and J. L. Marshall, *J. Amer. Chem. Soc.*, 1972, **94**, 1756.
[11] G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, 1972, **94**, 3089.
[12] D. Doddrell, B. Gupta, W. Adcock, M. Bullpitt, and W. Kitching, *J. Amer. Chem. Soc.*, in the press.

From a consideration of the spectra of 13-DMN, 16-DMN, and 17-DMN it is evident that this is indeed C-8 and not C-4. All the remaining resonances were assigned in a mutually consistent manner, assuming additivity of methyl group effects.

The results are summarised in Table 1. Data reported for the chemical shifts in toluene relative to benzene are given in Table 2 for comparison.

We shall defer detailed discussion of the pattern of substituent effects until we report our results for other substituted naphthalenes. However a few points may be noted. The pattern of shifts caused by a 2-methyl-substituent is essentially that expected bearing in mind the shifts in toluene and the predictions of naïve HMO theory. In particular C-4a, -6, and -8 are affected by the β-substituent, and C-2 responds in the same way as C-1 in toluene. On the other hand the 1-methyl substituent has a significantly reduced effect upon the adjacent carbon atom (C-1), a somewhat reduced effect on C-4 (*cf. para*), and a pattern of effects at C-5—C-7 quite unexpected on the basis of HMO theory. Most noteworthy is the large high field shift at C-8 and the smaller high field shift at C-8a.

TABLE 5

Observed and calculated chemical shifts (p.p.m. relative to benzene)

	14-DMN		15-DMN		26-DMN	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C-1, C-4	−3·5	−3·85				
C-2, C-3	+2·3	+2·25				
C-5, C-8	+4·0	+3·8				
C-6, C-7	+3·4	+3·6				
C-4a, C-8a	−4·4	−4·6				
C-1, C-5			−6·1	−6·05	+1·7	+1·7
C-2, C-6			+2·1	+2·3	−6·1	−5·7
C-3, C-7			+3·25	+3·5	+0·25	+0·6
C-4, C-8			+6·05	+6·0	+1·25	+1·5
C-4a, C-8a			−4·4	−4·6	−3·75	−3·6
	Mean dev. 0·2		Mean dev. 0·2		Mean dev. 0·2	

Chemical Shifts in Naphthalene.—One critical test of our assignments and of the applicability of the shifts given in Table 1 is the correct calculation of the spectrum of naphthalene. Note that chemical shift data for naphthalene itself has not been used except as a guide in the initial assignments. Employing the shifts given in Table 1 one may obtain from 1-MN and 2-MN eight estimates each of the α- and β-C shifts in naphthalene and four estimates of the C-4a and -8a shift. These are given in Table 3.

Comparison of Observed and Calculated Chemical Shifts.—The chemical shifts in the five compounds employed above were calculated using the data in Tables 1 and 3 and are compared with the observed results in Table 4. Agreement is seen to be very good and there is no obviously deviating entry. In each case the small deviations are random and show no bias such as might be ascribed to incorrect location of the reference resonance.

In Table 5 the observed and calculated shifts for three unhindered compounds not employed in the above analysis are compared and the agreement is quite satisfactory. This provides a further test of the treatment.

23-DMN and 236-TMN both contain methyl-groups in an '*ortho*' relationship for which the shifts given in Table 1 are inappropriate. The extent of the deviations in these compounds is given in Table 6. The reported[13] data for 18-DMN is also entered in this table. Only the ring containing the '*ortho*'-β-methyl-groups is affected

Methyl Substituent Effect.—Comparing appropriate carbons in 13, 16, and 17-DMN with 2-MN one obtains three estimates each of the effect of an α-methyl group on the various carbon atoms. Similarly the effect of a β-methyl group is obtained from comparisons with 1-MN.

TABLE 6

Observed and calculated chemical shifts (p.p.m. relative to benzene)

	Obs.	Calc.	Dev.
23-DMN			
C-1, C-4	+1·0	+1·7	−0·7
C-2, C-3	−6·9	−8·65	+1·7
C-5, C-8	+1·5	+1·55	
C-6, C-7	+3·5	+3·5	
C-4a, C-8a	−4·2	+3·6	−0·6
18-DMN *			
C-1, C-8	−7·1	−1·45	−5·7
C-2, C-7	−1·3?	+2·1	−3·4?
C-3, C-6	+0·1?	+3·7	−3·6?
C-4, C-5	+3·15	+1·4	+1·8
C-8a	−5·1	−3·6	−1·5
C-4a	−7·8	−5·7	−2·2
236-TMN			
C-1	+1·35?	+2·05	−0·7?
C-2	−5·75	−7·8	+2·1
C-3	−6·75	−8·5	+1·8
C-4	+1·6?	+2·5	−0·9?
C-5	+2·6	+2·55	
C-6	−5·75	−5·6	
C-7	+1·35	+1·4	
C-8	+1·8?	+1·9	
C-8a	−2·45	−1·85	−0·6
C-4a	−4·4	−3·5	−0·9

* Ref. 13.

TABLE 7

Methyl group chemical shifts (p.p.m. relative to cyclohexane)

Compound	α-Methyl	Compound	β-Methyl
1-MN	+8·2	2-MN	$+5·7_5$
13-DMN	+8·5	13-DMN	+6·0
16-DMN	$+8·2_5$	16-DMN	+6·0
17-DMN	$+8·2_5$	17-DMN	+5·5
14-DMN	+8·2	26-DMN	+5·6
15-DMN	$+7·5_5$	23-DMN	+7·2
18-DMN *	$+1·5_5$	236-TMN	$+5·6_5$, +7·3

* Ref. 13.

[13] A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchmann, *J. Amer. Chem. Soc.*, 1970, **92**, 2386.

by this presumed steric interference of the groups. A reasonable response to this interference would be a lengthening of the 2–3 bond and hence a reduction in the 2–3 bond order. This would lead [4] to a high field shift in the resonances of C-2 and C-3. The average deviation observed in the present case, +1·9 p.p.m., resembles the difference of *ca.* +2·5 p.p.m. between the reported [14] shifts in *o*-xylene and toluene. There will presumably be smaller, compensating increases in 1–2, 1–8a, and perhaps 4a–8a bond orders leading to low field shifts of C-1, -4, -4a, and -8a. In the case of 18-DMN, however, steric interference must be extremely serious and the whole molecule probably suffers considerable distortion from the normal naphthalene geometry.

Methyl Group Resonances.—β-Methyl groups in naphthalene undergo resonance at essentially the same chemical shift as those reported for the methyl groups of toluene (+6·0 p.p.m.) and *m*-xylene (+6·0_5 p.p.m.) The 2,3-dimethyl groups resemble those of *o*-xylene (+7·8 p.p.m.) and may presumably be accounted for in the same manner in terms of sterically induced charge polarization.[15] Methyl groups in α-positions are found some 2 p.p.m. to higher field and reflect the proximity of the hydrogen atom at C-8. In 18-DMN, however, there is a dramatic low field shift which again indicates a much more serious molecular distortion than encountered in other disubstituted naphthalenes.

We thank the Australian Research Grants Committee for financial support.

[2/2860 *Received*, 20*th December*, 1972]

[14] P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 1838.
[15] D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315.