Proton Magnetic Resonance Spectra of Some Methylnitronaphthalenes

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Chemical shifts and coupling constants for the ring protons of 3-, 6-, and 7-methyl-1-nitronaphthalene have been obtained by analysis of their 100 MHz spectra and employed in the successful computer simulation of the spectra. The nitro-group substituent effect has been deduced. A previously reported erroneous assignment has been corrected.

We reported some time ago the ^{1}H n.m.r. spectra of the nitronaphthalenes, some of their methyl derivatives, and some dinitronaphthalenes.[1] The spectra were obtained at 60 MHz and we were able to obtain only an approximate measure of the nitro-substituent effect. More recently a detailed analysis of the 100 MHz spectra of several 1-substituted naphthalenes and of 2-methylnaphthalene (5 mol % in carbon tetrachloride) was presented.[2] In this it was reported without comment that for 1-nitronaphthalene the resonance of H-5 is at lower field than that of H-4 (δ 8·004 and 7·860, respectively). Since we had found a rather modest effect of the nitro-group at H-5, more in keeping with other observations of the substituent effect at this position,[3] a re-investigation appeared to be warranted. Furthermore we required secure assignments for the protons of 1-nitronaphthalene in order to verify our analysis of the ^{13}C spectrum by double resonance studies.

Although 1-nitronaphthalene gives the least complex of the spectra of the monosubstituted naphthalenes, we chose to examine the simpler overlapping patterns of its 3-, 6-, and 7-methyl derivatives in the hope that the substituent effects would be additive, and in the belief that a comparison with 2-methylnaphthalene would give a better estimate of the nitro-group effect averaged over three compounds.

EXPERIMENTAL

The samples, prepared and purified as reported previously,[4] were examined as 0·8M solutions in carbon tetrachloride. The spectra were recorded on a JEOL PS 100 spectrometer in the frequency sweep mode scanning at 0·5 Hz s^{-1} with the field locked on the resonance of internal tetramethylsilane. Double irradiation and homonuclear INDOR studies were carried out by employing the built-in decoupling unit.

Calculated line spectra were obtained by using the NMRIT program, employing as input a set of chemical shifts and coupling constants derived from an approximate analysis of the spectra assisted by double irradiation and INDOR studies. This set was varied until the best fit on line positions and intensities for the methyl-group-decoupled spectra was obtained, after which a simulated spectral curve was generated.

RESULTS AND DISCUSSION

The 6- and 7-methyl derivatives yield relatively simple spectra with distinct multiplets for four of the protons and a complex two-proton multiplet at highest field. 3-Methyl-1-nitronaphthalene shows a one-proton multiplet at low field, a one-proton doublet at mid-field, and a complex pattern arising from four protons at high field. The assignments and chemical shifts for the best fit of the observed spectra are given in Table 1, and the coupling constants are given in Table 2.

TABLE 1

^{1}H Chemical shifts of 1-nitronaphthalene derivatives [δ values (±0·002 p.p.m.)]

	3-Methyl	6-Methyl	7-Methyl
H-2	7·874	7·994	8·001
H-3		7·339	7·276
H-4	7·680	7·830	7·856
H-5	7·683	7·535	7·651
H-6	7·440		7·263
H-7	7·501	7·364	
H-8	8·389	8·319	8·171

TABLE 2

^{1}H Coupling constants [in Hz (±0·2 Hz)] for 1-nitronaphthalene derivatives

	3-Methyl	6-Methyl	7-Methyl	Unsubst.[2]
$J_{2,3}$		7·6	7·5	7·4
$J_{6,7}$	6·9			7·7
$J_{3,4}$		8·0	8·7	8·1
$J_{5,6}$	8·3		8·3	8·6
$J_{7,8}$	8·7	8·7		9·3
$J_{2,4}$	1·8	1·3	1·4	1·1
$J_{5,7}$	1·8	1·8		0·9
$J_{6,8}$	1·6		1·6	1·0
$J_{5,8}$	0·7	0·7	0·7	0·2
$J_{4,8}$	0·8	0·8	0·9	0·5

There is an improvement in the resolution of these spectral patterns when the sample is irradiated at the methyl proton resonance frequency, since there is a small coupling ($<0·5$ Hz) with protons *ortho* to the methyl group and a smaller coupling to a proton *meta* to the methyl group. There also appears to be coupling involving protons in the ring not containing the methyl group.

By comparing the corresponding resonance positions of these three compounds one can deduce the relative chemical shifts in 2-methylnaphthalene and 1-nitronaphthalene by subtracting the effect of the nitro-group and of the methyl group, respectively. These are compared in Table 3 with the relative chemical shifts for these compounds reported in ref. 2. Agreement is good with the exception of H-4 and H-5 in 1-nitronaphthalene. Table 4 shows a second comparison based upon a

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[1] P. R. Wells, *J. Chem. Soc.*, 1963, 1967; P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1108; P. R. Wells, *ibid.*, 1964, **17**, 967.

[2] J. W. Emsley, S. R. Salman, and R. A. Storey, *J. Chem. Soc.* (*B*), 1970, 1513.

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

[4] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1377.

TABLE 3

Relative ^{1}H chemical shifts (p.p.m.)

2-Methylnaphthalene			Ref. 2	1-Nitronaphthalene			Ref. 2
H(1) − H(4)	−0·131	(±0·017)	−0·142	H(4) − H(5)	0·146	(±0·001)	−0·144
H(1) − H(5)	−0·197	(±0·021)	−0·211	H(4) − H(8)	−0·524	(±0·003)	−0·530
H(1) − H(8)	−0·149	(±0·001)	−0·176	H(2) − H(3)	0·692	(±0·030)	0·661
H(3) − H(6)	−0·129	(±0·009)	−0·107	H(2) − H(6)	0·593	(±0·025)	0·589
H(3) − H(7)	−0·152	(±0·025)	−0·138	H(2) − H(7)	0·480	(±0·029)	0·485

common chemical shift for H-8 and H-2, the resonances of which are the most readily located in the spectrum of 1-nitronaphthalene. It is evident that the H-5 signal has been incorrectly assigned in ref. 2, and it appears that the error may have arisen from giving the H-4,H-5 difference the wrong sign.

TABLE 4

Comparison of ^{1}H resonances of 1-nitronaphthalene

	Ref. 2	This work		Ref. 2	This work
H-8	8·390	(8·390)	H-2	8·122	(8·122)
H-4	7·860	7·866	H-3	7·430	7·461
H-5	8·004	7·720	H-6	7·533	7·529
			H-7	7·637	7·642

If we assume that the chemical shifts for 2-methylnaphthalene are correct, and these are substantiated by our studies of dimethylnaphthalenes, the chemical shift changes brought about by the nitro-group can be calculated. The results are given in Table 5 with corresponding ^{13}C and ^{19}F shifts for comparison.

TABLE 5

Nitro-group effect in p.p.m. (positive shifts to low field)

Position	^{1}H Shift	^{13}C Shift [a]	^{19}F Shift [b]
2	+0·70 (±0·01) *	−1·9	
3	+0·01 (±0·01$_5$)	−1·8	+0·79
4	+0·19$_5$ (±0·01$_5$)	+6·7	+12·77
5	+0·05 (±0·01)	+0·6	
6	+0·11 (±0·01$_5$)	+1·4$_5$	
7	+0·20$_5$ (±0·01$_5$)	+3·5$_5$	+6·76
8	+0·71 (±0·00$_5$)	−5·1$_5$	
ortho	+0·96$_5$ [c]	−4·8 [c]	−5·6 [d]
meta	+0·21 [c]	+0·9 [c]	+3·3 [d]
para	+0·33 [c]	+5·8 [c]	+10·8 [d]

* Mean deviation of two or three estimates.

[a] P. R. Wells, D. P. Arnold, and D. Doddrell, *J. C.S. Perkin II*, in the press. [b] W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1967, **89**, 379. [c] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731. [d] H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4809.

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