# PROTON MAGNETIC RESONANCE SPECTRA OF NITRONAPHTHALENES IN DIMETHYLACETAMIDE SOLUTION

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#### Summary

Examination of the proton magnetic resonance spectra of some methyl and dimethyl derivatives of 1- and 2-nitronaphthalene has allowed assignments of spectral regions to the various ring protons to be made. The individual proton resonances and overall spectral patterns correspond well with those predicted from studies of the dinitronaphthalenes and dimethylnaphthalenes. Steric crowding in 2-methyl-1-nitronaphthalenes appears to reverse the proximity effect of the nitro group on the *peri*-hydrogen.

#### INTRODUCTION

A previous paper<sup>1</sup> reported the proton magnetic resonance spectra of the symmetrical dinitronaphthalenes. By assuming additivity the effects of a single nitro group on the various ring protons of nitronaphthalenes were deduced. The satisfactory prediction of the spectra of 1,6- and 1,7-dinitronaphthalenes indicated that the derived shift data are valid measures of nitro-substituent effects. This test has now been applied to the nitronaphthalenes and some methyl- and dimethyl-nitronaphthalenes.

## RESULTS AND DISCUSSION

### $\tau$ -Values for Dimethylacetamide Solution

Chemical shift data for dimethylacetamide solution were previously reported<sup>1</sup> relative to benzene as an internal reference. Benzene has now been measured in very dilute solution relative to tetramethylsilane thus enabling shifts to be expressed on the  $\tau$ -scale.

Benzene	$2 \cdot 625 \tau$	Naphthalene
		a-protons $2 \cdot 055 \tau$
Naphthale	ne band	${f Naphthalene}$
centre	$2 \cdot 255 \tau$	$\beta$ -protons $2 \cdot 465 \tau$

1-Nitronaphthalene.—The proton magnetic resonance spectrum of 1-nitro-NO<sub>2</sub>  $1^{2}$   $3^{1}\beta$   $3^{4}\beta$   $4^{\alpha}$   $3^{4}\beta$   $3^{4}\beta$   $3^{4}\beta$   $4^{\alpha}$   $3^{4}\beta$   $3^{4}\beta$  $3^$ 

were verified by examination of the spectra of the methyl-1-nitronaphthalenes. Using

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<sup>1</sup> Wells, P. R., J. Chem. Soc., 1963, 1967.

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the chemical shift and coupling constant data derived from the dinitronaphthalenes<sup>1</sup> it is possible to predict a spectrum for 1-nitronaphthalene. This is compared with the observed spectrum in Figure 1.

 $H_2$ ,  $H_3$ , and  $H_4$  approximate to an ABX-system the pattern for which is readily calculated (cf. Pople, Schneider, and Bernstein<sup>2</sup>).  $H_5$ ,  $H_6$ ,  $H_7$ , and  $H_8$  constitute an ABCD-system. As an approximation spectra were calculated for  $H_5$ ,  $H_6$ ,  $H_7$  and  $H_6$ ,  $H_7$ ,  $H_8$  as ABX-systems superimposing the two sets of  $H_6H_7$  peaks at half intensity. It is suspected that the peak positions will have only small errors but that the relative intensities may have substantial ones. Individual proton resonance positions have been estimated from the observed spectrum and compared in Table 1 with the



(a) Observed; (b) calculated.

calculated values. Agreement is satisfactory except for a general but slight (c. 0.05 p.p.m.) overestimation of the nitro-group effect. Figure 1 also indicates the calculated spectrum is overall some 0.05 p.p.m. too low.

3-Methyl-1-nitronaphthalene.—The spectrum observed for 3-methyl-1-nitronaphthalene consists of two regions. From  $2 \cdot 2$  to  $2 \cdot 4\tau$  is a 2-proton pattern assigned to H<sub>8</sub> and H<sub>7</sub>. From  $1 \cdot 5$  to  $1 \cdot 9\tau$  is a 4-proton complex assigned to H<sub>2</sub>, H<sub>4</sub>, H<sub>5</sub>, and H<sub>8</sub>. Allowing shifts of +0.2 for 2a, +0.15 for  $1\beta$ ,  $3\beta$ , no shift for 8a and +0.1 p.p.m.

<sup>2</sup> Pople, J. A., Schneider, W. G., and Bernstein, H. J., "High Resolution Nuclear Magnetic resonance." p. 134. (McGraw-Hill: New York 1959.)

for all other methyl groups and following the procedure adopted for 1-nitronaphthalene, calculated individual resonance positions (see Table 1) and a calculated spectrum may be obtained (estimates of the effect of a methyl group on the various ring protons were derived from the spectra of the 2,3-, 2,6-, 2,7-, and 1,5-dimethylnaphthalene in dimethylacetamide solution (see below). The high-field spectrum observed and calculated match well. The calculated low-field spectrum stretches from 1.6 to  $2.0\tau$ with an intense maximum at  $1.82\tau$  some 0.05 p.p.m. broad. A very intense broad peak is observed at  $1.80\tau$ .

4-Methyl-1-nitronaphthalene.—The spectrum of 4-methyl-1-nitronaphthalene shows two regions of approximately equal intensity assigned to  $H_3$ ,  $H_6$ ,  $H_7$  at high field (2·1 to 2·5 $\tau$ ) and  $H_2$ ,  $H_5$ ,  $H_8$  at low field (1·5 to 1·8 $\tau$ ). A doublet ( $J \approx 8$  c/s) centred at 2·46 $\tau$  can be extracted from the high-field region.  $H_3$  is calculated to yield a doublet ( $J_{2,3} = 7.5$  c/s) at 2·38 $\tau$ , and the high-field spectrum matches the

CHEMICAL SH	IFTS IN	I-NITRON	APHTHAL	ENES ( $\tau$	-VALUES	
Proton number 2 Nitro group	3	4	5	6	7	8
interaction $1\beta$	$4\beta$	4a	- 5a	$5\beta$	8β	8a
$\begin{array}{ccc} 1-\mathrm{NO}_2 & \mathrm{Obs.} & 1\cdot71_5\\ & \mathrm{Calc.} & 1\cdot71 \end{array}$	$\begin{array}{c}2\cdot 27_{5}\\2\cdot 23\end{array}$	$\begin{array}{c}1\cdot 71\\1\cdot 60\end{array}$	$\frac{1\cdot82_5}{1\cdot77}$	$2 \cdot 21$ $2 \cdot 23$	$\begin{array}{c}2\cdot 21\\2\cdot 18\end{array}$	$1 \cdot 64 \\ 1 \cdot 59$
$\begin{array}{c} 3-\mathrm{Me} \\ 1-\mathrm{NO}_2 \\ \end{array} \begin{array}{c} \mathrm{Obs.} & 1\cdot 81_5 \\ \mathrm{Calc.} & 1\cdot 86 \end{array}$		$\begin{array}{c}1\cdot 81\\1\cdot 80\end{array}$	$     \begin{array}{r}       1 \cdot 89 \\       1 \cdot 87     \end{array} $	$\begin{array}{c}2\cdot 28_{5}\\2\cdot 33\end{array}$	$\begin{array}{c}2\cdot28_{5}\\2\cdot28\end{array}$	$\frac{1\cdot 64_5?}{1\cdot 69}$
$\frac{4-\text{Me}}{1-\text{NO}_2} \begin{cases} \text{Obs. } 1\cdot77_5 \\ \text{Calc. } 1\cdot81 \end{cases}$	$\begin{array}{c}2\cdot 46\\2\cdot 38\end{array}$		$1 \cdot 75_5?$ $1 \cdot 77$	$\begin{array}{c}2\cdot 22_{5}\\2\cdot 33\end{array}$	$\begin{array}{c} 2 \cdot 22_5 \\ 2 \cdot 28 \end{array}$	$\begin{array}{c}1\cdot 62_{5}\\1\cdot 69\end{array}$
	$2 \cdot 29$ $2 \cdot 33$	$\frac{1\cdot 66_5}{1\cdot 70}$	$\begin{array}{c}2\cdot015\\1\cdot97\end{array}$		$\begin{array}{c}2\cdot 29\\2\cdot 33\end{array}$	$\frac{1\cdot 66_5}{1\cdot 69}$
$\begin{array}{c} \hline 7-\text{Me} & \left\{ \begin{array}{c} \text{Obs.} & 1\cdot76 \\ 1-\text{NO}_2 \end{array} \right\} \\ \hline \text{Calc.} & 1\cdot81 \end{array}$	$2 \cdot 35$ $2 \cdot 33$	$\begin{array}{c} 1 \cdot 64 \\ 1 \cdot 70 \end{array}$	$\frac{1\cdot82_5}{1\cdot87}$	$2 \cdot 42_5$ $2 \cdot 38$		$\frac{1\cdot72_5}{1\cdot74}$

			TABLE 1		
CHEMICAL	SHIFTS	IN	1-NITRONAPHTHALENES	$(\tau$ -VALUES)	ļ

calculated spectrum. A doublet  $(J \approx 7.5 \text{ c/s})$  centred at  $1.787\tau$  extracted from the low field spectrum matches H<sub>2</sub> (doublet,  $J_{2,3} = 7.5 \text{ c/s}$ , at  $1.81\tau$ ). The remainder of the low field spectrum is approximately as calculated.

6-Methyl-1-nitronaphthalene.—6-Methyl-1-nitronaphthalene gives a spectrum showing a 2-proton high-field pattern ( $H_3$ ,  $H_7$ ) 2·1 to 2·5 $\tau$  and a 3-proton low-field pattern ( $H_2$ ,  $H_4$ ,  $H_8$ ) 1·5 to 1·9 $\tau$  clearly separated from  $H_5$  at mid-field. No ABCD approximation is required as the spectrum may be calculated for superimposed ABX-systems. It is noteworthy that the observed and calculated spectra of this and the 7-methyl isomer show closer correspondence than for the other isomers. The pattern of peaks at low and high field is as calculated but shifted c. 0·03 p.p.m. to low field.  $H_5$  is calculated to lead to a tightly spaced quartet from 1·96 to 1·98 $\tau$ and is observed as a broad peak, partially resolved in some spectra, at 2·01<sub>5</sub> $\tau$ . 7-Methyl-1-nitronaphthalene.—The spectrum of 7-methyl-1-nitronaphthalene shows a 2-proton high-field region  $(H_3, H_6) 2 \cdot 2$  to  $2 \cdot 5\tau$ , resembling the 6-methyl isomer, and at lower field a series of peaks  $1 \cdot 6$  to  $1 \cdot 95\tau$  including an intense peak where the  $H_2$ ,  $H_4$ , and  $H_5$  patterns overlap the broad singlet of  $H_8$  at  $1 \cdot 72_5\tau$ . The observed and calculated spectra match well particularly at high field although  $H_2$ and  $H_4$  are observed c.  $0 \cdot 05$  p.p.m. lower than expected. Observed resonance positions were obtained by analysing the observed spectra as two superimposed ABX-systems. Coupling constants were found in good agreement with previous observations.

2-Methyl-1-nitronaphthalene.—Instead of a spectrum showing two 3-proton regions,  $H_4$ ,  $H_5$ , and  $H_8$  at low field and  $H_3$ ,  $H_6$ , and  $H_7$  at high field, only two protons comprise the low-field region  $(1 \cdot 8 \text{ to } 2 \cdot 0\tau)$  and four protons are responsible for the high-field region  $(2 \cdot 3 \text{ to } 2 \cdot 55\tau)$ .

The two doublets  $(J = 8 \cdot 7, 8 \cdot 6 \text{ cf. } J_{1,2} \approx 8 \cdot 7 \pm 0 \cdot 4 \text{ c/s}$  usually observed)<sup>1</sup> of the AB-system due to  $H_3$  and  $H_4$  can be extracted from the high-field and low-field patterns. The resonance positions of  $H_3$  at  $2 \cdot 48\tau$  (cf.  $2 \cdot 38\tau$  calculated) and especially  $H_4$  at  $1 \cdot 93\tau$  (cf.  $1 \cdot 77\tau$  calculated) are higher than calculated by an amount too great to be due to underestimation of the methyl interaction. A reduced nitrogroup effect appears to be at least partially responsible.

It seems unreasonable that  $H_5$  is the proton missing from the low-field region, i.e. transferred to the high-field region. Hence the resonance position of  $H_5$  is at  $1.96\tau$  (cf.  $1.90\tau$  calculated) again somewhat higher than calculated.  $H_6$ ,  $H_7$ , and  $H_8$  are together responsible for the most intense peak in the spectrum at  $2.32\tau$ (cf. 2.32, 2.28, and  $1.69\tau$  calculated respectively).

Compared with a naphthalene  $\alpha$ -proton  $(2 \cdot 055\tau)$  the nitro-group effect on  $H_8$  has been completely reversed to +0.27 p.p.m. in the presence of the methyl group at position 2 from -0.37 p.p.m. in its absence. This could arise if the nitro group, due to the steric effect of the methyl group, were twisted out of the plane of the aromatic system and had become perpendicular to it. Under these circumstances the effect of the magnetic anisotropy of the nitro group, affecting especially  $H_8$ , might change sign. In addition the influence of the resonance effect of the nitro group at other positions would be lost.

To examine this phenomenon further some methyl-substituted 2-methyl-1nitronaphthalenes were examined.

2,3-Dimethyl-1-nitronaphthalene.—Comparing the spectra of 2,3-dimethyl-1nitronaphthalene and 2-methyl-1-nitronaphthalene it is observed that the high-field region  $(2\cdot3 \text{ to } 2\cdot5\tau)$ , due to three protons has lost the doublet attributed to  $H_3$  and in the low-field region  $(1\cdot9 \text{ to } 2\cdot1\tau)$ , due to two protons, the  $H_4$  doublet has become a singlet at  $2\cdot04\tau$ . In comparison with the appropriate proton of 2,3-dimethylnaphthalene at  $2\cdot43\tau$  the  $4\alpha$ -nitro group has caused a shift to low field of  $0\cdot39$  p.p.m. (cf.  $0\cdot42$  p.p.m. see Table 5). The resonance position of  $H_5$  at  $c. 2\cdot0\tau$  corresponds to a nitro-group affect of  $c. 0\cdot3$  p.p.m. to low field (cf.  $0\cdot26$  p.p.m. see Table 5).  $H_6$ ,  $H_7$ , and  $H_8$  are all at  $c. 2\cdot4\tau$ . Nitro-group shifts for  $H_6$  and  $H_7$  are hence  $0\cdot27$ p.p.m. to low field (cf.  $0\cdot20$  see Table 5).  $H_8$  has been shifted  $c. 0\cdot1$  p.p.m. to high field (cf.  $0\cdot47$  p.p.m. to low field for an unhindered nitro group). 2,6-Dimethyl-1-nitronaphthalene.—The spectrum of 2,6-dimethyl-1-nitronaphthalene is the superposition of the patterns due to the AB-system of  $H_3$  and  $H_4$  and the ABX-patterns of  $H_5$ ,  $H_7$ , and  $H_8$ . As such it is amenable to complete analysis. Table 2 lists the peaks observed and their assignment.

SPECTRU	TAB JM OF 2,6-DIMET	LE 2 HYL-1-NITRON	APHTHALENE
Peak	Assignment	Relative Intensity	Coupling (c/s)
$2 \cdot 54 \tau$ $2 \cdot 41$ $2 \cdot 13$ $2 \cdot 03$ $1 \cdot 89$	$ \begin{array}{c} \\ H_{7}, H_{8} \\ H_{5} \\ H_{4} \end{array} \end{array} $	$\begin{array}{c} \sim 0 \cdot 3 \\ \sim 3 \\ \sim 0 \cdot 8 \\ \sim 0 \cdot 7 \\ \sim 0 \cdot 3 \end{array}$	

Analysis as an AB-system gives the resonance positions of  $H_3$  at  $2 \cdot 46\tau$  and  $H_4$  at  $1 \cdot 97\tau$ . The relative intensities in the doublets should be 36/64 as compared with approximately 3/7 observed. The observed coupling  $J_{3,4} \approx 8$  c/s has the value commonly observed  $(8 \cdot 7 \pm 0 \cdot 4)$ .<sup>1</sup> Compared with the resonance positions observed for 2,6-dimethylnaphthalene  $H_3$  is shifted  $0 \cdot 25$  p.p.m. (cf.  $0 \cdot 20$  p.p.m. see Table 5) and  $H_4$  is shifted  $0 \cdot 33$  p.p.m. (cf.  $0 \cdot 42$  p.p.m. see Table 5) both to low field.

Peak	Assignment	Relative Intensity	Coupling (c/s)
$\left.\begin{array}{c}2\cdot54\tau\\2\cdot49\\2\cdot40\end{array}\right\}\\2\cdot05\\1\cdot95\\1\cdot89\\1\cdot81\end{array}\right\}$	$ \begin{array}{c} H_{3}, H_{6}, H_{8} \\ \\ \\ H_{4} \end{array} \right\} H_{5} $	$ \begin{array}{c} \sim 2 \cdot 9 \\ \sim 0 \cdot 55 \\ \sim 0 \cdot 7 \\ \sim 0 \cdot 4 \\ \sim 0 \cdot 5 \end{array} \right\} $	$\begin{cases} J_{3,4} = 8 \cdot 3 \\ J_{5,6} + J_{5,7} = 9 \cdot 8 \\ J_{3,4} = 8 \cdot 5 \end{cases}$

 TABLE 3

 SPECTRUM OF 2,7-DIMETHYL-1-NITRONAPHTHALENE

 $H_5$ ,  $H_7$ , and  $H_8$  approximate closely to an AX<sub>2</sub> system with  $J_{AX} \sim 1 \text{ c/s} (J_{5,7} = 1.4 \text{ c/s} \text{ and } J_{5,8} \approx 1 \text{ c/s} \text{ are expected})$ . Thus  $H_5$  has been shifted 0.28 p.p.m. (cf. 0.28 p.p.m. see Table 5),  $H_7$  has been shifted 0.29 p.p.m. (cf. 0.20 p.p.m. see Table 5) both to low field while  $H_8$  is once again shifted 0.1 p.p.m. to high field.

2,7-Dimethyl-1-nitronaphthalene.—Like the 2,6-isomer a complete analysis of the spectrum of 2,7-dimethyl-1-nitronaphthalene is possible. Table 3 lists the observed peaks and their assignments.

The resonance position of  $H_8$  corresponds to a 0.12 p.p.m. shift to high field. 2-Nitronaphthalene.—The proton magnetic resonance spectrum of 2-nitronaphthalene in dimethylacetamide solution (Fig. 2(a)) can be divided into three  $7\alpha$   $2\alpha$  regions. At low field  $(1 \cdot 05\tau)$  the 1-proton broad peak is assigned  $7\beta\tau$   $1 \cdot 95\tau$ ) the 4-proton pattern is assigned to  $H_4$ ,  $H_5$ ,  $H_8$ , the remaining  $\alpha$ -protons, and  $H_3$ , a  $\beta$ -proton with adjacent nitro

group. The high-field 2-proton pattern  $(2 \cdot 1 \text{ to } 2 \cdot 35\tau)$  is assigned to the remaining  $\beta$ -protons H<sub>6</sub> and H<sub>7</sub>. These assignments are verified by the absence of the low-field peak from the spectrum of 1-methyl-2-nitronaphthalene and modification of the mid-field and high-field region for the 3-, 4-, and 6-methyl-2-nitronaphthalenes.

TABLE 4

СН	EMICAL SHIFT	s in 2-n	ITRONAP	HTHALEY	$tes (\tau - v)$	ALUES)	
Proton No. Nitro-group	1	3	4	5	6	7	8
interaction	2a	3β	3a	6a	6β	7β	7a
2-NO2	Obs. 1.05	1.78	1.78	1.78	$2 \cdot 25$	$2 \cdot 25$	1.69
-	Calc. 1.00	1.80	1.79	1.78	$2 \cdot 18$	$2 \cdot 24$	1.57
3-Me	Obs. 1.29		2.015	1.975	2.325	2.325	1.86
2-NO <sub>2</sub>	Calc. 1.10	-	1.99	1.88	$2 \cdot 28$	$2 \cdot 34$	1.67
4-Me	Obs. 1.23	1.93		?	2.28	$2 \cdot 28$	1.73
2-NO <sub>2</sub>	Calc. 1 · 10	1.95	-	1.78	$2 \cdot 28$	$2 \cdot 34$	1.67
6-Me	Obs. 1.04	1.825	1.825	$2.07_{5}$		2.39	1.76
2-NO <sub>2</sub>	Calc. 1.10	1.90	1.89	1.98		$2 \cdot 39$	1.67

Estimations of individual proton resonances from the observed spectrum are compared with calculations based on the dinitronaphthalene spectra in Table 4. The calculated and observed spectra are compared in Figure 2.

 $H_3$  and  $H_4$  are calculated to resonate at almost the same field strength and be only weakly coupled with  $H_1$ . The ABX-pattern for these protons is thus much simplified. The ABCD-system for  $H_5$ ,  $H_6$ ,  $H_7$ , and  $H_8$  was calculated as for the corresponding four spin system of 1-nitronaphthalene. The observed pattern for  $H_6$  and  $H_7$  resembles the high field half of an  $A_2X_2$ -pattern. Analysed as such much the same result for the mean resonance position of  $H_6$  and  $H_7$  is obtained. In addition  $J_{a8}+J'_{a8}$  is found to be approximately 10 c/s (cf. 9.8 c/s usually observed).<sup>1</sup>

1-Methyl-2-nitronaphthalene.—The outstanding feature of this spectrum is the absence of absorption below  $1.6\tau$ . The spectrum consists of an almost continuous series of peaks from 1.6 to  $2.3\tau$  from which no estimate of individual resonance positions could be made.

3-Methyl-2-nitronaphthalene.—The spectrum of 3-methyl-2-nitronaphthalene may be divided into three regions. The 1-proton peak at low field  $(1 \cdot 29\tau)$  is assigned

to  $H_1$ . The 2-proton pattern at high field  $(2 \cdot 3 \text{ to } 2 \cdot 3\tau)$  resembling that for 2-nitronaphthalene is assigned to  $H_6$  and  $H_7$ . The mid-field pattern  $(1 \cdot 7 \text{ to } 2 \cdot 1\tau)$  accounts for three protons  $H_4$ ,  $H_5$ , and  $H_8$  with the very intense peak observed for 2-nitronaphthalene much reduced ( $H_3$  absent).



Fig. 2.—Spectrum of 2-nitronaphthalene. (a) Observed; (b) calculated.

Comparison of observed and calculated resonance positions are given in Table 4. The observed spectral pattern is well reproduced by a calculated spectrum although  $H_1$  and  $H_8$  appear at higher field than calculated. This is suggestive of steric interaction

between the nitro and methyl groups but not to the extent observed for the 2-methyl-1-nitronaphthalenes.

4-Methyl-2-nitronaphthalene.—The spectrum of 3-methyl- and 4-methyl-2nitronaphthalene are very similar with the latter somewhat towards lower field. This arises from the similarity of  $H_3$  and  $H_4$  and the small couplings  $J_{1,4} \approx 1$  c/s and  $J_{1,3} = 1.4$  c/s. Again  $H_1$ , but not significantly  $H_8$ , appears at higher field than expected (see Table 4) but otherwise the observed and calculated spectra match well.

6-Methyl-2-nitronaphthalene.—The relatively large differences in resonance positions of  $H_5$ ,  $H_7$ , and  $H_8$ , of  $H_1$  and the approximate equivalence of  $H_3$  and  $H_4$  lead to a simplified spectrum due to two superimposed ABX-systems.  $H_1$ , at lowest field, is a broad 1-proton singlet  $(J_{1,3} = 1 \cdot 4; J_{1,4} \approx 1 \text{ c/s})^1$  at  $1 \cdot 04\tau$  partially resolved in some spectra.  $H_3$  and  $H_4$  appear as a broad singlet at mid-field  $(1 \cdot 82_5\tau)$  whose intensity exceeds two protons due to overlap of the higher doublet of the  $H_8$  quartet. The remaining  $H_8$  doublet gives a total intensity of three protons. From the approximate spacing of these two doublets  $J_{7,8} = J_{a\beta} \approx 9$  c/s.  $H_7$  at highest field  $(c. 2 \cdot 4\tau)$ 

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Interaction	Shift (p.p.m.)		Interaction	Shift (p.p.m.	.)
2a	$-1.03_{5}*^{+}$	(-1.06) <sup>‡</sup>	1β	$-0.74\pm0.02$	(-0.77)
3a	$-0.30*^{+}$	(-0.29)	38	$-0.70 \pm 0.01$	(-0.67)
4a	$-0.42 \pm 0.04$	(-0.46)	$4\beta$	$-0.20 \pm 0.02$	(-0.24)
5a	$-0.25_{5}\pm0.02$	(-0.29)	$5\beta$	$-0.28 \pm 0.04$	(-0.23)
6a	-0.22*	$(-0.24_{5})$	$6\beta$	$-0.20 \pm 0.02$	(-0.29)
7a	$-0.36_{5}\pm0.00$	(-0.49)	7β	$-0.20 \pm 0.03$	$(-0 \cdot 23)$
- 8α	$-0.47 \pm 0.03$	(-0.47)	8β	$-0.26\pm0.00$	(-0.29)
			1	1	

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INDIVIDUAL	SHIFTS	DUE	то	А	NITRO	GROUP

\* Two estimates only.

<sup>†</sup> Value from 3-methyl-2-nitronaphthalene decreased.

<sup>‡</sup> Values in parenthesis derived from dinitronaphthalenes.<sup>1</sup>

is a clearly separated 1-proton quartet giving  $J_{7,8} = 8 \cdot 7 \text{ c/s}$  (cf.  $8 \cdot 7 \pm 0.4 \text{ c/s}$  generally observed),  $J_{5,7} + J_{5,8} = J_{1,3} + J_{1,4} \approx 2 \text{ c/s}$  and  $J_{5,7} - J_{5,8} \approx 0$ . H<sub>5</sub> is observed between H<sub>7</sub> and H<sub>8,4</sub> as a broad 1-proton singlet at  $2 \cdot 07_5 \tau$  partially resolved in some spectra.

Dimethylnaphthalenes.—The spectra due to the aromatic protons of the 1,5-, 2,3-, 2,6-, and 2,7-dimethylnaphthalenes in dimethylacetamide solution were determined in order that an estimate of the effect of the methyl group could be obtained. More detailed investigations of the aromatic and methyl-proton resonances will be discussed in another publication.

Estimates of the effects of a methyl group on the various protons obtained from these and the methyl nitronaphthalene spectra are listed in Table 6.

Substituent Effects.—The effects of a single nitro group on the various protons of naphthalene as deduced from the relatively simple spectra of symmetrical dinitronaphthalenes<sup>1</sup> have proved to be satisfactory for the prediction of proton magnetic resonance spectra. Table 5 indicates little difference between our previous listing of individual shifts and a listing best fitting the spectra of the nitronaphthalenes and methyl nitronaphthalenes. Where more than three estimates of the shifts could be made the mean values and deviations are given. We are confident that these data could assist considerably in the determination of the structures of substituted naphthalenes, particularly of alkylnitronaphthalenes and of halogenonitronaphthalenes, where the halogen atom appears to have virtually no resultant effect on aromatic proton resonance position.

As a measure of nitro-substituent effect the main features previously reported can be seen, especially the dominance of proximity effects for 2a, 8a,  $1\beta$ , and  $3\beta$ . The effect of a 7a-nitro group does not appear to be as large as previously observed although an exceptional interaction with this proton is still evident. Most shifts are observed to vary approximately within the cumulative experimental errors (c. 0.04p.p.m. in favourable cases). Although there are indications of greater shifts of protons in quinonoid positions, an average value of  $-0.24\pm0.03$  p.p.m. for the 3a-, 5a-, 6a-,  $4\beta$ -,  $5\beta$ -,  $6\beta$ -,  $7\beta$ -. and  $8\beta$ -nitro-group effects is probably the most reasonable one to use.

Interaction	Shift (p.p.m.)	Interaction	Shift (p.p.m.)	Interaction	Shift (p.p.m.)
2a	+0.20	3a	+0.07	4β	+0.05
4a	(+0.2)	5α	+0.04	$5\beta$	+0.05
8a	-0.05	6a	+0.05	6β	+0.08
1β	+0.175	7a	+0.09	7β	+0.07
3β	$+0.08_{5}$	Mean	$+0.06\pm0.02$	8β	+0.04
·				Mean	$+0.06\pm0.01$

	2	LABLE	6 2			
INDIVIDUAL	SHIFTS	DUE	то	A	METHYL	GROUP

The combined steric effects of a methyl group at position 2 and the *peri*-hydrogen has a dramatic effect upon the influence of 1-nitro group. This is revealed especially by the resonance position of  $H_8$  in this type of compound where the normal shift of -0.47 p.p.m. becomes a shift of c. +0.1 p.p.m. The nitro group in 1-nitronaphthalene itself cannot be coplanar with the ring.<sup>3</sup> If twisting the nitro group until essentially perpendicular to the ring has reversed the proximity effect, then this effect must normally have been worth c. -0.3 p.p.m. and other effects, i.e. induction etc., worth c. -0.2 p.p.m., i.e. approximately the shift due to  $6a., 5\beta.$ , and  $7\beta$ -interactions which are also heteronuclear and non-quinonoid.

The longest wavelength ultraviolet absorption of ethanolic solution of 2-methyl-1-nitronaphthalene ( $\lambda_{\max} = 318 \text{ m}\mu$ , log  $\bullet = 3.284$ ) and 1-nitronaphthalene ( $\lambda_{\max} = 333 \text{ m}\mu$  log  $\epsilon = 3.319$ ) also indicate steric hindrance of coplanarity of the nitro group and the aromatic ring preventing conjugative interaction.

The effects of methyl groups on proton magnetic resonance position have been estimated approximately and are listed in Table 6. The shifts utilized for the

<sup>3</sup> cf. Le Fèvre, R. J. W. and Sundaram, A., J. Chem. Soc., 1962, 4756.

purposes of spectrum calculation, i.e. +0.2 for 2a, +0.15 for  $1\beta$  and  $3\beta$ , 0 for 8a, and +0.1 for all others, are seen to be somewhat excessive but reasonable. The effect of a *peri*(8a)-methyl group is noteworthy being a very small *low*-field shift.

#### EXPERIMENTAL

All melting points are corrected. Purity was checked in all cases by means of gas chromatography (15% QF-1 at 180° or 15% poly-3,5-dimethoxyphthalic glycol esters at 190°). Proton magnetic resonance spectra were determined in very dilute solution (c. 0.5 mole %) with a Varian Associates A60 spectrometer as previously described.<sup>1</sup>

(a) 2-Methyl-1-nitronaphthalene.—Prepared by the nitration of 2-methylnaphthalene essentially as described by Fierz-David and Mannhart<sup>4</sup> and obtained as yellow needles from ethanol, m.p.  $81^{\circ}$  (reported m.p.  $81^{\circ}$ ).

(b) 3-Methyl-1-nitronaphthalene.—2-Methyl-1-nitronaphthalene (30 g; 0.16 mole) was reduced to 2-methyl-1-naphthylamine with Raney nickel and hydrazine using the method of Adams and Dunbar<sup>5</sup> and acetylated using the method of Baker and Carlson.<sup>6</sup>

To a stirred and cooled ( $<20^{\circ}$ ) solution of N-acetyl-2-methyl-1-naphthylamine ( $14\cdot 2$  g; 0.07 mole) in acetic acid (100 ml) were added nitric acid ( $d = 1\cdot 5$ ;  $3\cdot 2$  ml; 0.08 mole). After warming to 80° during 2 hr the reaction mixture was poured on to ice, and the solid product ( $16\cdot 5$  g) collected and dried at c. 60°. The product was hydrolysed to give crude 2-methyl-4-nitro-1naphthylamine ( $12\cdot 5$  g, 85%). A pure sample (4 g), m.p.  $183^{\circ}$ , obtained by crystallization from benzene was deaminated by the method of Marion and McCrae<sup>7</sup> to yield 3-methyl-1-nitronaphthalene ( $2\cdot 1$  g, 56%), pale vellow needles, m.p.  $49\cdot 5-50^{\circ}$  (reported<sup>7</sup>  $49-50^{\circ}$ ).

(c) 4-Methyl-1-nitronaphthalene.—Prepared by the nitration of 1-methylnaphthalene essentially as described by Thompson<sup>8</sup> and obtained as fine yellow needles, m.p.  $71-72^{\circ}$  (reported  $71-72^{\circ}$ ).

(d) 7-Methyl-1-nitronaphthalene.-2-Methylnaphthalene (200 g) was acetylated in nitrobenzene solution by the method of Kon and Weller.<sup>9</sup> After removal of almost all of the nitrobenzene by vacuum distillation, gas chromatography indicated a mixture of two major and at least two minor component naphthyl methyl ketones. Fractional distillation under vacuum (10 mmHg) yielded: (i) unreacted 2-methylnaphthalene at b.p. 110°; (ii) impure 1-acetyl-7-methylnaphthalene (55 ml) at b.p. (170-174°; (iii) 2-acetyl-6-methylnaphthalene (c. 85% pure) as white solid (51 g) remaining undistilled. The 1-acetyl-7-methylnaphthalene was obtained as a series of fractions. (Fractions shown by gas chromatography to be rich in the minor isomers were set aside for further examination.) The crude ketone was converted to its oxime which was crystallized several times from ethanol to white needles, m.p. 119° (Dziewonski and Brand<sup>19</sup> report 120°). The oxime (20 g; 0.1 mole) was submitted to Beckmann rearrangement in polyphosphoric acid (400 g) by heating with stirring at 115° for 10 min after which time the yellow colour indicating the start of reaction had become very deep. The reaction product was poured into water (10 l.) and the white precipitated N-acetyl-7-methyl-1-naphthylamine (19.5 g., 95%) collected and thoroughly washed with water. Crystallization from ethanol gave white needles, m.p. 182° (Dziewonski and Brand<sup>10</sup> report m.p. 182-183°). Hydrolysis of the amide using sulphuric acid in aqueous ethanol<sup>11</sup> gave a 95% yield of 7-methyl-1-naphthylamine, m.p. 58-59° (reported<sup>9</sup> m.p. 58-59°) as white needles, after one crystallization from light petroleum, b.p. 40-60°. 7-Methyl-1-nitronaphthalene

<sup>4</sup> Fierz-David, H. E., and Mannhart, E., Helv. Chim. Acta, 1937, 20, 1024.

<sup>5</sup> Adams, R., and Dunbar, J. E., J. Amer. Chem. Soc., 1956, 78, 4744.

<sup>8</sup> Baker, B. R., and Carlson, G. H., J. Amer. Chem. Soc., 1942, 64, 2657.

<sup>7</sup> Marion, L., and McRae, J. A., Canad. J. Res. B, 1940, 18, 265.

<sup>8</sup> Thompson, H. W., J. Chem. Soc., 1932, 2310.

<sup>9</sup> Kon, G.A.R., and Weller, W. T., J. Chem. Soc., 1939, 792.

<sup>10</sup> Dziewonski, K., and Brand, M., Roczn. Chem., 1933, 12, 693; Chem. Abstr., 1933, 27, 4533.

<sup>11</sup> Ward, E. R., and Wells, P. R., J. Chem. Soc., 1961, 4859.

was obtained in low yield from the diazotized amine by the cobaltinitrite method of Hodgson *et al.*<sup>12</sup> as pale yellow needles, m.p.  $35^{\circ}$ , Vesely and Kapp,<sup>13</sup> report m.p.  $36-38^{\circ}$ ).

The fractions rich in minor isomers were converted to oximes and thence to N-acetylmethylnaphthylamines. From this mixture a sample of N-acetyl-2-methyl-1-naphthylamine, m.p. 191°, was obtained as shown by mixture melting point. The nature of the other minor isomers and a complete isomer distribution analysis for this reaction is under investigation.

(e) 6-Methyl-2-nitronaphthalene.—6-Acetyl-2-methylnaphthalene (see above) was crystallized to constant m.p. 66  $5^{\circ}$  as small white needles from ethanol, methanol, or light petroleum, b.p. 40–60° (no m.p. previously reported). The oxime, m.p. 180° (Dziewonski and Brand<sup>10</sup> report m.p. 181°) was converted using polyphosphoric acid at 90° for 10 min to N-acetyl-6-methyl-2-naphthylamine, m.p. 160° (Dziewonski and Brand<sup>10</sup> report m.p. 160°). 6-Methyl-2-naphthylamine, m.p. 129–130° (Vesely and Kapp<sup>13</sup> report m.p. 129–130°) was converted by the cobaltinitrite method in low yield to 6-methyl-2-nitronaphthalene, yellow needles, m.p. 119–120° (Vesely and Pac<sup>14</sup> report m.p. 119°).

(f) 6-Methyl-1-nitronaphthalene.---N-Acetyl-6-methyl-2-naphthylamine was nitrated as described for N-acetyl-2-methyl-1-naphthylamine and the product hydrolysed to give a high yield of 6-methyl-1-nitro-2-naphthylamine as orange needles from benzene, m.p. 166-167° (Found: N, 13.7%. Calc. for  $C_{11}H_{10}N_2O_2$ : N, 13.9%). The presence of a nitro group "ortho" to the amino group was indicated by the infrared spectrum.<sup>15</sup> Deamination<sup>7</sup> yielded 6-methyl-2-nitronaphthalene as yellow needles, from ethanol, m.p. 59-60° (Vesely and Pac<sup>14</sup> report m.p. 61-62°).

(g) 1-Methyl-2-nitronaphthalene.—Prepared according to Topsom and Vaughan,<sup>16</sup> as yellow needles, m.p.  $55^{\circ}$  (reported  $56^{\circ}$ ).

(h) 3-Methyl-2-nitronaphthalene.—Kindly supplied by Dr. J. Hyman, Hyman Laboratories, Inc., Berkeley, U.S.A.

(i) 4-Methyl-2-nitronaphthalene.—Prepared according to Vesely et al.<sup>17</sup> but using a modified deamination procedure<sup>18</sup> as yellow needles by sublimation, m.p.  $82^{\circ}$  (reported<sup>17</sup> m.p.  $81-82^{\circ}$ ).

(j) 2,3-Dimethyl-1-nitronaphthalene.—Prepared according to Willstaedt<sup>19</sup> as pale yellow crystals, m.p.  $112 \cdot 5^{\circ}$  reported m.p.  $111^{\circ}$ C).

(k) 2,6-Dimethyl-1-nitronaphthalene.—Prepared according to Mayer and Alken<sup>20</sup> as pale yellow crystals, m.p.  $68^{\circ}$  (reported m.p.  $68^{\circ}$ ).

(1) 2,7-Dimethyl-1-nitronaphthalene.—Prepared by nitration of 2,7-dimethylnaphthalene using the procedure that Mayer and Alken<sup>20</sup> applied to 2,6-dimethylnaphthalene as pale yellow needles, from ethanol, m.p. 80° (Found: N, 6.9%. Calc. for  $C_{12}H_{11}NO_2$ : N, 7.0%).

<sup>12</sup> Hodgson, H. H., and Marsden, E., J. Chem. Soc., 1944, 22; Hodgson, H. H., and Ward, E. R., J. Chem. Soc., 1947, 127.

<sup>13</sup> Vesely, V., and Kapp, J., Chem. Listy, 1924, 18, 201, 244.

<sup>14</sup> Vesely, V., and Pac, J., Collect. Czech., 1930, 2, 471.

<sup>15</sup> cf. Hathway, D. E., and Flett, M.St.C., Trans. Faraday Soc., 1949, 45, 818.

<sup>16</sup> Topsom, R. D., and Vaughan, J., J. Chem. Soc., 1957, 2842.

<sup>17</sup> Vesely, V., Stursa, F., Olejnicek, H., and Rein, E., Coll. Trav. Chim. Tchécosl., 1929, 2, 145.

<sup>18</sup> Clarke, H. T., and Taylor, E. R., Org. Synth. Coll. Vol., 1, 415.

<sup>19</sup> Willstaedt, H., Svensk Kem. Tidskr., 1942, 54, 223, 231.

<sup>20</sup> Mayer, F., and Alken, R., Chem. Ber., 1922, 55, 2278.