

366. *Proton Magnetic Resonance Spectra of Dinitronaphthalenes.*

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The proton magnetic resonance spectra of the ten dinitronaphthalenes have been measured for dilute dimethylacetamide solutions with benzene as internal reference. The individual protons of the symmetrical isomers (1,4-; 1,5-; 1,8-; 2,3-; 2,6-; and 2,7-) and two of the six different protons of the other isomers (1,2-; 1,3-; 1,6-; and 1,7-) have been identified. Naphthalene and 1,4-, 1,8-, and 2,3-dinitronaphthalene have also been examined in acetone and dimethylsulphoxide solutions.

The effects of a single nitro-group on the various ring-protons of naphthalene have been estimated and are discussed as measures of the nitro-substituent effect.

THE proton magnetic resonance spectra of a number of substituted benzenes have been examined by Corio and Dailey¹ and by Bothner-By and Glick.² A complex pattern of lines results from which, with varying degrees of certainty, the shifts for individual ring-protons can be deduced. Thus, in a concentrated cyclohexane solution the lines for the *ortho*-, *meta*-, and *para*-protons of nitrobenzene are estimated to have been shifted -0.97 , -0.30 , and -0.42 p.p.m., respectively, relative to benzene.¹ When extrapolated to infinite dilution in carbon tetrachloride, the *para*-proton shift² is -0.45 p.p.m. The spectra of the nitronaphthalenes are even more complex, but the symmetrically disubstituted naphthalenes yield much simpler spectra and these can often be readily and unambiguously analysed in terms of shifts for individual protons.

Taft³ has shown that chemical shifts, particularly of ¹⁹F, caused by substituents may be correlated by means of inductive and resonance substituent parameters. Spieske and Schneider⁴ have observed a correlation between proton and ¹³C resonance position and charge density from the spectra of the cyclopentadienyl anion, benzene, and the tropylium cation. An investigation of the proton magnetic resonance spectra of the dinitronaphthalenes was therefore undertaken to provide information concerning substituent effects in the naphthalene system.

EXPERIMENTAL AND RESULTS

The dinitronaphthalenes were crystallised from the appropriate spectroscopic solvent. Their purity was judged by m. p. and the absence of spurious peaks in their nuclear magnetic resonance spectra. Solvents were freshly distilled. Their purity was judged by their nuclear magnetic resonance spectra at high amplification, especially in the aromatic proton region. Proton magnetic resonance spectra were obtained with a Varian Associates A60 spectrometer. The chart paper was calibrated, frequency offset was checked, and isolated peaks were measured

¹ Corio and Dailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3043.

² Bothner-By and Glick, *J. Chem. Phys.*, 1957, **26**, 1651.

³ Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

⁴ Spieske and Schneider, *Tetrahedron Letters*, 1961, 468.

by using side bands generated by a Hewlett-Packard model 200CD wide-range oscillator. The locations of symmetrical, complex band centres were measured as the mean of the component lines. Chemical shifts, negative at low field, are quoted in parts per million relative to the resonance of benzene as an internal standard. Except where otherwise specified, the solutions were very dilute (*ca.* 0.5 mole %) with respect to both dinitronaphthalene and benzene and were recorded at spectrum amplitudes of 80–160 with a filter band width of 0.4 c./sec. and a radiofrequency field of 0.2 mG. The results reported are the mean values derived from at least two spectra. In favourable cases shifts are accurate to *ca.* 0.02 p.p.m.

Internal Standard, Benzene.—The resonance positions of the protons of acetone and of benzene relative to external tetramethylsilane both vary as the concentration of benzene in acetone is changed from one drop in 5 ml. (“infinitely dilute”) through intermediate concentrations to 20% v/v in accordance with the findings of Bothner-By and Glick.² Their difference, however, remains constant at 4.81 ± 0.01 p.p.m. This constancy was not observed for solutions of benzene in dimethylacetamide or dimethyl sulphoxide.

Naphthalene.—The proton magnetic resonance spectrum of naphthalene was determined in a series of acetone solutions ranging from 19 to 0.5 mole % of naphthalene. From the typical A_2B_2 pattern observed the position of the band centre (δ_0) and the spacing of the two most intense peaks (“main spacing”) were measured. The band centre shifts to high field on dilution, paralleling the benzene peak, such that their difference is essentially constant at $0.33_3 \pm 0.00_5$ p.p.m. The “main spacing” also remains constant with dilution. Less extensive checks for dimethylacetamide and dimethyl sulphoxide solutions indicated a constant chemical shift relative to benzene and a constant “main spacing.” The spectra were analysed as described by Pople, Schneider, and Bernstein^{5a} for an A_2B_2 system to yield the results given in Table 1. Included are the previously reported results^{5b} (indicated by *)

TABLE 1.
Dilute solutions of naphthalene in various solvents.
(Shifts from internal benzene in p.p.m.; coupling constants in c./sec.)

	Dimethyl sulphoxide	Dimethylacetamide	Acetone	CCl ₄		Dioxan *
				(a)	(b) *	
δ_0	-0.44	-0.37	-0.34	-0.30	—	—
δ_α	-0.64	-0.57	-0.54	-0.48	-0.50	-0.48
δ_β	-0.24	-0.16	-0.14	-0.16	-0.16	-0.16
$\delta_\alpha - \delta_\beta$	0.39	0.41	0.39	0.35	0.34	0.36
$J_{\alpha\beta}$	8.6	8.4	8.6	~8	—	8.6
$J_{\beta\beta}$	5.6	5.8	6.2	—	—	6.0
$J'_{\alpha\beta}$	1.1	1.2	1.2	—	—	1.4

* See text.

for infinitely dilute solutions in carbon tetrachloride and in dioxan. Since no significant differences were observed in the values of $\delta_\alpha - \delta_\beta$ and the coupling constant derived from solutions of various concentrations, these were computed from the better-resolved spectra of fairly concentrated (*ca.* 10 moles %) solutions.

The coupling constants are unaffected by solvent change. $J'_{\alpha\beta}$ ($= J_{1,3}$ or $J_{2,4}$) corresponds to the coupling between *meta*-protons in benzene derivatives. $J_{\alpha\alpha}$ ($= J_{1,4}$), corresponding to *para*-coupling in benzene, cannot be determined and has been assumed to be zero in order to yield $J_{\beta\beta}$ ($= J_{2,3}$).^{5b} In fact, the quantity listed in Table 1 as $J_{\beta\beta}$ is $J_{\beta\beta} - J_{\alpha\alpha}$. Provided that $J_{\alpha\alpha}$ is not greater than 2 c./sec., $J_{\beta\beta}$ will be less than $J_{\alpha\beta}$ ($J_{\alpha\beta}$ corresponds to *ortho*-coupling in benzene derivatives).

The chemical shift towards low field increases in passing from carbon tetrachloride or dioxan through acetone and dimethylacetamide to dimethyl sulphoxide. Since differences in bulk magnetic susceptibility are cancelled by the use of an internal standard, specific solute-solvent interactions must be responsible for these shifts. Such behaviour has been studied in detail by Bothner-By and Glick² with similar findings for several other solvents.

1,4-Dinitronaphthalene.—Provided that the heteronuclear α -protons resonate at low field

⁵ Pople, Schneider, and Bernstein, “High Resolution Nuclear Magnetic Resonance,” McGraw-Hill Book Co. Inc., New York, 1959, pp. (a) 147–149, (b) 248, (c) 268.

relative to the heteronuclear β -protons, all the observed lines of the spectrum of 1,4-dinitronaphthalene can be unambiguously assigned. The protons at positions 2 and 3 are responsible for a two-proton sharp singlet while the 5-, 6-, 7-, and 8-protons lead to a four-proton A_2B_2 pattern. That the chemical shifts of the individual protons vary with solvent relative to one another as well as to benzene is shown by the position of the sharp singlet relative to the A_2B_2 pattern. For deuteriochloroform solutions it appears almost at the A_2B_2 band centre; for acetone solutions it obscures the low-field 7,12-peak; and for dimethylacetamide solutions it obscures the lower-field 1,2-peak. The A_2B_2 pattern of peaks was numbered as for the spectrum of naphthalene described by Pople *et al.*^{5a}

The chemical shift of each pair of equivalent protons relative to benzene (δ_B) and to the α - or β -protons of naphthalene (δ_N), as appropriate, is listed in Table 2 for dimethylacetamide solutions. For both acetone and dimethylacetamide solutions the coupling constants obtained are listed in Table 3. For acetone solution $\delta_{2,3} = -1.05$ p.p.m. from benzene which is

TABLE 2.

Chemical shifts for dilute dimethylacetamide solution of nitronaphthalenes (in p.p.m. relative to benzene or naphthalene).

Posn. of NO ₂ groups	Proton nos.	δ_B	δ_N	Interactions	Equation no.*	δ_N (calc.)
1,4-	2, 3	-1.14	-0.98	$1\beta + 4\beta$	1	-1.01
	5, 8	-1.00	-0.43	$5\alpha + 8\alpha$	2	-0.76 §
	6, 7	-0.68	-0.52	$5\beta + 8\beta$	3	-0.52
2,3-	1, 4	-1.61	-1.04	$2\alpha + 3\alpha$	4	-1.35
	5, 8	-1.05	-0.48	$6\alpha + 7\alpha$	5	-0.73 _s
	6, 7	-0.63	-0.47	$6\beta + 7\beta$	6	-0.52
2,7-	1, 8	-2.12	-1.55	$2\alpha + 7\alpha$	7	-1.55
	3, 6	-1.10	-0.94	$3\beta + 6\beta$	8	-0.96
	4, 5	-1.10	-0.53	$3\alpha + 6\alpha$	9	-0.53 _s
1,8-	2, 7	-1.13	-0.97	$1\beta + 8\beta$	10	-1.06
	3, 6	-0.63	-0.47	$4\beta + 5\beta$	11	-0.47
	4, 5	-1.36	-0.79	$4\alpha + 5\alpha$	12	-0.75
1,5-	2, 6	-1.19	-1.05	$1\beta + 5\beta$	13	-1.00
	3, 7	-0.69	-0.53	$4\beta + 8\beta$	14	-0.53
	4, 8	-1.34	-0.77	$4\alpha + 8\alpha$	15	-0.93 §
2,6-	1, 5	-1.88	-1.31	$2\alpha + 6\alpha$	16	-1.30 _s
	3, 7	-1.22	-0.96	$3\beta + 7\beta$	17	-0.90
	4, 8	-1.35	-0.78	$3\alpha + 7\alpha$	18	-0.78
1,6-	3	-0.63	-0.47	$4\beta + 7\beta$	19	-0.47
	4	-1.51 †	-0.93 †	$4\alpha + 7\alpha$	20	-0.95
	5	-1.92	-1.35	$2\alpha + 5\alpha$	21	-1.35
1,7-	3	-0.68	-0.52	$4\beta + 6\beta$	22	-0.53
	8	-2.10	-1.53	$2\alpha + 8\alpha$	23	-1.53
	2	-1.62 †	-1.46 †	$1\beta + 3\beta$	24	-1.44
1,3-	4	-2.11 †	-1.54 †	$2\alpha + 4\alpha$	25	-1.52
	3		(-1.09) ‡	$3\beta + 4\beta$	26	-0.91
	4	-1.25	(-0.68)	$3\alpha + 4\alpha$	27	-0.75
2-	1	-1.57	-1.00	2α	28	-1.06

* Equations are set up with observed shift (δ_N) equated to the interactions involved, *e.g.*: no. 1, $1\beta + 4\beta = -0.98$. † Assignment based on comparison with predicted shift. ‡ Rejected on basis of predicted shift. § Observed shift considered abnormally low (see text).

equivalent to a shift of -0.91 p.p.m. for a naphthalene β -proton. $\delta_0 = -0.86$ p.p.m. from benzene and $\delta_\alpha - \delta_\beta = 0.40$ p.p.m. Therefore, $\delta_{5,8} = -0.52$ p.p.m. relative to a naphthalene α -proton, and $\delta_{6,7} = -0.52$ p.p.m. relative to a naphthalene β -proton. It is surprising that the protons *peri* (5,8) to the nitro-groups are affected to the same extent as the 6,7-protons in acetone solution and to a smaller extent in dimethylacetamide solution. Rough calculations from the spectrum of 1,4-dinitronaphthalene in deuteriochloroform (concentration *ca.* 7%) (Bhacca, Johnson, and Shoolery⁶) indicates that in this solvent the *peri*-protons suffer a considerably greater shift than the 6,7-protons. Calculations of individual proton shifts due to a single nitro-group (see Discussion) listed in Table 2 under δ_N (calc.) also suggest that the present value for $\delta_{5,8}$ is abnormally low, but it is not clear why.

⁶ Bhacca, Johnson, and Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, 1962, spectrum no. 245.

TABLE 3.
Coupling constants (c./sec.) for nitronaphthalenes.

Posn. of NO ₂ groups	Solvent	$J_{\alpha\beta}$	$J_{\beta\beta}$	$J'_{\alpha\beta}$
1,4-	NMe ₂ Ac	8.9	5.6 *	1.0
	COMe ₂	9.1 ₅	6.2 *	1.3
2,3-	NMe ₂ Ac	8.3	6.2 *	1.2
	Me ₂ SO	8.5	7 *	1.5
	COMe ₂	9.1	6.5 *	1.2
2,7-	Me ₂ NAc	—	—	1 to 1.5
1,5-	"	8	8 †	1
1,8-	"	8.2	7.8 †	1
	COMe ₂	8.4	7.2 †	1
	Me ₂ SO	8.3	7.5 †	1
	Me ₂ NAc	8	8 †	1.5
1,6-	"	7.5	7.5 †	—
1,7-	"	—	—	1.5
1,3-	"	—	—	—
1,2-	"	9.3	—	—
2-	"	—	—	1

* $J_{\beta\beta} - J_{\alpha\alpha}$. † $J_{\beta\beta}$ alone.

2,3-Dinitronaphthalene.—Like the 1,4-isomer, 2,3-dinitronaphthalene has a simple spectrum, displaying a two-proton singlet at low field due to protons 1 and 4, and an A₂B₂ pattern due to the heteronuclear protons. Chemical shifts for dimethylacetamide solution are given in Table 2, with coupling constants for three solvents in Table 3. The shifts relative to the appropriate naphthalene proton in acetone and dimethyl sulphoxide solution are: acetone, $\delta_{1,4} = -0.93$, $\delta_{5,8} = -0.46$, $\delta_{6,7} = -0.50$ p.p.m.; and dimethyl sulphoxide, -0.94 , -0.33 , and -0.34 , respectively.

2,7-Dinitronaphthalene.—The protons of 2,7-dinitronaphthalene constitute two identical ABC systems that are independent provided *peri*-coupling is negligible. The spectrum is considerably simplified since the 3-, 4-, 5-, and 6-protons resonate at the same field strength (-1.10 p.p.m. from benzene). If J_{13} were equal to J_{14} this would be an A₂B system.

The low solubility of 2,7-dinitronaphthalene in any suitable solvent precluded the production of a well-resolved spectrum, but its simplicity provided good measures of chemical shifts (Table 2) although the coupling constants could not be precisely determined.

1,8-Dinitronaphthalene.—The spectra of dimethylacetamide, dimethyl sulphoxide, and acetone solutions were analysed as ABX systems, the X-member being the high-field 3(= 6)-proton. The identification of the AB members followed from the coupling constants, since it is considered established that $\alpha\beta$ -coupling exceeds $\beta\beta$ -coupling. Chemical shifts for dimethylacetamide solution and coupling constants (three solvents) are listed in Tables 2 and 3, respectively. For acetone and dimethyl sulphoxide solutions, relative to the naphthalene α - or β -protons, we have: acetone, $\delta_{2,7} = -0.93$, $\delta_{3,6} = -0.40$, $\delta_{4,5} = -0.61$ p.p.m.; and dimethyl sulphoxide, -0.84 , -0.28 , and -0.52 , respectively.

1,5-Dinitronaphthalene.—1,5- and 2,6-Dinitronaphthalene are the least soluble of this series of fairly insoluble compounds. The spectrum in dimethylacetamide solution was resolved sufficiently to reveal the main features of the ABX system, resembling that of 1,8-dinitronaphthalene, but insufficiently well for determination of J_{23} or J_{34} . Thus, while the resonance of the 3- and 7-proton could be assigned, protons in the pairs 2,6 and 4,8 cannot be distinguished. However, one pair of assignments (given in Table 2) is in good agreement with the substituent interactions involved; the other pair is inadmissible, the shift for protons 2 and 6 being excessive and for protons 4 and 8 deficient. Even with the better assignment the 4,8-protons, like the *peri*-protons of 1,4-dinitronaphthalene, appear to be shifted less than would be expected.

2,6-Dinitronaphthalene.—Although the spectrum of 2,6-dinitronaphthalene was poorly resolved, an ABX pattern could be recognised with the X-member (protons 1 and 5) at low field. The AB band centre and an approximate value of $\delta_A - \delta_B$ gives two alternative assignments for the 3,7- and 4,8-pairs. One assignment was rejected in favour of that listed in Table 2 on the basis of too large a shift for protons 3,7 and too small for 4,8. Coupling constants could not be determined.

1,6-Dinitronaphthalene.—The spectrum of 1,6-dinitronaphthalene in dimethylacetamide results from the superposition of two different ABX systems due to protons 2,3,4 and 5,7,8.

However, one system has the X-part clearly visible at low field (proton 5) and the other at high field (proton 3). The two AB parts are overlapping, but two doublets ($J \sim 1$ c./sec.) separated by 8 c./sec. can be observed corresponding to the high-field portion of the AB spectrum of protons 2 and 4. The X-region provides sufficient information for computation of δ_A , which must refer to proton 4 (the shift is too large for proton 2). δ_3 and δ_5 can be determined unambiguously and approximate values obtained for the coupling constants. The separation of δ_3 and δ_5 is 1.28 p.p.m. For very dilute acetone solution the low-field and the high-field peak are separated by 1.17 p.p.m.

1,7-Dinitronaphthalene.—The spectrum of 1,7-dinitronaphthalene in dimethylacetamide closely resembles that of the 1,6-isomer. Proton 3 at high field and proton 8 at low field are clearly visible. δ_3 and δ_8 can thus be measured and approximate values of the coupling constants obtained. The separation of δ_3 and δ_8 is 1.42 p.p.m. For very dilute acetone solution two peaks separated by 1.43 p.p.m. can be seen.

1,3-Dinitronaphthalene.—The spectrum of 1,3-dinitronaphthalene in dimethylacetamide consists of two closely spaced doublets due to protons 2 and 4 separated from the ABCD pattern due to the protons 5, 6, 7, and 8. The doublet at higher field was attributed to the β -proton by comparison with its calculated position. The α -proton appears at lower field, being subjected to the combined effects of nitro-groups in what is equivalent to *ortho*- and *para*-positions. The coupling, $J'_{\alpha\beta}$, is about 1.5 c./sec. $\delta_4 - \delta_2 = 0.39$ p.p.m. for dimethylacetamide solutions may be compared with the separation 0.33 p.p.m. between the two low-field peaks of the poorly resolved spectrum of acetone solutions.

1,2-Dinitronaphthalene.—The low-field doublet ($J_{\alpha\beta} = 9.3$ c./sec.) due to proton 3 or proton 4 is clearly separated in the spectrum of 1,2-dinitronaphthalene. The other doublet is, however, superimposed on the ABCD pattern of the heteronuclear protons. The separated doublet appears shifted too greatly to refer to proton 3, but the shift is consistent with its reference to proton 4. A position for proton 3 can be predicted and two peaks are observed corresponding to a doublet having $J = 9.3$ c./sec. centred at this point.

2-Nitronaphthalene.—There are seven different protons in 2-nitronaphthalene, interacting as ABX in the substituted ring and ABCD in the other ring. The resonance for proton 1 appears, however, well separated at low field (a doublet with $J \sim 1$ c./sec.), corresponding to one-seventh of the total spectral area.

DISCUSSION

Coupling Constants.—For those dinitronaphthalenes for which accurate measures of coupling constants could be obtained (see Table 3) the following appear generally applicable: $J_{\alpha\beta} = 8.7 \pm 0.4$; $J_{\beta\beta} - J_{\alpha\alpha} = 6.4 \pm 0.3$; $J'_{\alpha\beta} = 1.4 \pm 0.2$; $J_{\beta\beta} = 7.5$ c./sec. Therefore, $J_{\alpha\alpha} \sim 1$ c./sec. These values do not differ significantly from those for naphthalene. Only for 1,4- and 2,3-dinitronaphthalene in acetone solution, and 1,2-dinitronaphthalene in dimethylamide, where $J_{\alpha\beta}$ appears somewhat increased, can the substituents be considered to have modified the coupling constants. There appears to be greater variation in coupling constants derived from substituted benzenes than is observed in the present investigations.

Pople, Schneider, and Bernstein^{5c} have examined the proton resonances in quinoline, isoquinoline, and some of their methyl derivatives which may be considered as extreme forms of substituted naphthalenes. They report $J_{3,4} = 7.3$, $J_{5,6} = 8.3$, $J_{2,3} = 5.0$, $J_{6,7} = 4.9$, and $J_{7,8} \sim 7$ c./sec. for quinoline, and $J_{2,3} = 6.0$ c./sec. for isoquinoline, which show differences that may be attributable to distortions in the ring system by the heteroatom.

Effect of the Nitro-group on Proton Resonance Position.—If the effects of each nitro-group on the resonance position of a particular proton are additive then the shifts listed in Table 2 can be analysed into components according to the relative disposition of proton and nitro-group. Thus positions 6 and 7 in 1,4-dinitronaphthalene, which are β -related, are each subject to 5β - and 8β -interactions. There are fourteen different interactions that are combined in different ways to produce the twenty-eight combinations of interactions listed in Table 2. So, sufficient results should be available to compute and check these individual interactions.

The following nomenclature is used to describe substituent-reacting side-chain dispositions. The reacting side chain, in the present case a proton, is described as α or β according to whether it is attached to an α - or β -position in naphthalene. The position of the substituent relative to the reacting side chain is then denoted by the appropriate number. Thus, in 6-chloro-1-methylnaphthalene the chloro-substituent interaction at the methyl group would be described as 6α -Cl; the methyl-substituent effect at the chloroatom would be described as 5β -Me. In terms of the old terminology, "para" becomes 4α ; "amphi" becomes 6β ; "peri" becomes 8α . The ambiguities of "ortho" for 2α and 1β , and of "meta" for 3α and 4β , are removed.

TABLE 4.
Individual interactions (p.p.m.) in nitronaphthalenes.

Interaction	Shift	Interaction	Shift	Interaction	Shift	Interaction	Shift
1β	-0.77	6β	-0.29	2α	-1.06	6α	-0.24 ₃
3β	-0.67	7β	-0.23	3α	-0.29	7α	-0.49
4β	-0.24	8β	-0.29	4α	-0.46	8α	-0.47
5β	-0.23			5α	-0.29		

Some isomers, particularly 2,3-, 1,8-, and 1,2-dinitronaphthalene, are expected to show some abnormalities due to the steric interference of the two nitro-groups. Other indications of abnormality have already been observed. Such results were not used as a primary source of individual interactions.

From equations 3, 14, 19, and 22 (Table 2) it can be seen that the 4β -, 5β -, 6β -, 7β -, and 8β -interactions are similar in magnitude, with $6\beta = 8\beta > 7\beta$. If it is assumed that $5\beta = 7\beta$, these five interactions can be computed. Equations 1 and 13 then give a value for 1β (-0.77 ± 0.03), and equations 8 and 23 a value for 3β (-0.67 ± 0.02). These results are listed in the first part of Table 4. The secondary results involving interactions at the β -position are:

	$3\beta + 7\beta$	$4\beta + 5\beta$	$1\beta + 8\beta$	$6\beta + 7\beta$	$3\beta + 4\beta$
Obs.	-1.06	-0.47	-0.97	-0.47	(-1.09 *)
Calc.	-0.90	-0.47	-1.06	-0.52	(-0.91 *)

* Rejected.

Agreement is satisfactory and the main difference indicates a reduced substituent effect, probably 1β , due to *peri*-nitro-interference. The observed shift for 2,6-dinitronaphthalene was uncertain and the estimate is clearly in error.

From the differences between equations 7 and 16, and 9 and 18, $7\alpha - 6\alpha = -0.24$ and -0.25 , respectively. Values for 7α and 2α can be computed from equation 7, and the difference between equations 20 and 25 ($-6\alpha = -0.245 - 7\alpha$) gives a check for 2α (-1.065). Values for 5α and 8α can be computed from equations 21 and 23. Two values for 3α (-0.29 and -0.285) are obtained from equations 9 and 18, while two values for 4α (-0.48 and -0.44) are obtained from equations 20 and 25. The unused data, all of the secondary type, are as follows:

	$5\alpha + 8\alpha$	$4\alpha + 8\alpha$	$2\alpha + 3\alpha$	$6\alpha + 7\alpha$	$4\alpha + 5\alpha$	$3\alpha + 4\alpha$
Obs.	-0.43 *	-0.77 *	-1.04	-0.48	-0.79	-0.68
Calc.	-0.76	-0.93	-1.35	-0.73 ₈	-0.75	-0.73

* Abnormally low (see text).

Further internal consistency of these results is indicated by the similarity of the pseudo-*meta*-positions (3α and 4β) and of the heteronuclear non-quinonoid positions (5β and 6α).

The most severe test of this analysis is the prediction of spectra. The observed and predicted spectra of 1,6- and 1,7-dinitronaphthalenes are shown in Figs. 1 and 2. The lines used to derive the individual interactions are marked with an asterisk. The main features of the two overlapping ABX systems are well reproduced in the calculated spectra

although slight errors (*ca.* 0.04 p.p.m.) in shifts have led to small displacements of the individual peaks.

Calculation of the shifts for protons 3 and 4 in 2-nitronaphthalene shows that they should resonate at the same field strength, to yield a strong doublet split by *ca.* 1 c./sec. The strongest peak in the spectrum exactly matches this prediction although the prediction for the low-field peak due to proton 1 is 0.06 p.p.m. low. The spectra of 1- and 2-nitronaphthalene are at present being investigated with the assistance of the spectra of their methyl derivatives. No inconsistencies have yet been observed.

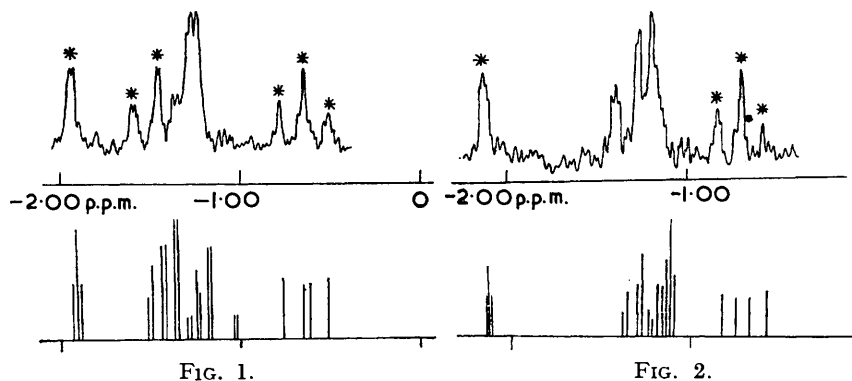


FIG. 1. Proton magnetic resonance spectra for (FIG. 1) 1,6- and (FIG. 2) 1,7-dinitronaphthalene. (* denotes predicted peaks.)

The spectra that have been obtained in solvents other than dimethylacetamide indicate that specific solvent-solute interactions make major modifications in the shifts of individual protons. For some other solvent a set of individual interactions would have been obtained markedly different from those listed in Table 4. Nevertheless these measures of nitro-substituent effect show some general features shared by other listings of substituent effects. There are additional features not indicated by other methods.

The nitro-group exerts its greatest influence in the ring containing it, especially at positions (2α , 1β , and 3β) corresponding to *ortho* in benzene. These shifts are in the order of the extent of interaction with the resonance effect of the nitro-group at these positions, *i.e.*, $2\alpha > 1\beta \gg 3\beta$. The 4α -interaction, corresponding to *para* in benzene derivatives, is, as expected, the largest for any proton not adjacent to the nitro-group (except 7α). The peaks for the heteronuclear non-quinonoid protons (6α , 5β , and 7β) are shifted by about the same extent as for the pseudo-*meta*-protons (3α and 4β), which indicates considerable internuclear interaction. This has been noted in the calculation of Hammett σ -values from reactivity data for substituted naphthalene derivatives.⁷ The quinonoid heteronuclear protons (5α and 6β) suffer approximately the same extra shift due to the resonance effect of the nitro-group. The *peri*-proton (8α) is heteronuclear and non-quinonoid, but is as close to the nitro-group as are the "*ortho*"-positions. Its peak is shifted considerably. The most unusual observation is the large shift for the 7α -proton. Unlike the other heteronuclear and "*meta*"-protons, but like the *peri*- and "*ortho*"-protons it is on the same side of the aromatic ring as the oxygen of the nitro-group; it may be for this reason that it suffers a proximity effect that has not been observed in studies of reactivity.

The effect of the nitro-group on the resonance positions of the naphthalene protons may be summarised as follows. There is a considerable general effect, presumably inductive, at all positions approximately equivalent to the *meta*-shift in nitrobenzene.

⁷ Wells and Ward, *Chem. and Ind.*, 1958, 528; Wells and Adcock, unpublished work.

Imposed on this is a considerably smaller mesomeric effect, and a very large proximity effect, due to direct magnetic shielding, acting through space as opposed to through the σ - or π -bond system.

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