Tetrahedron. Vol. 25, pp. 5525 to 5533. Pergamon Press 1969. Printed in Great Britain

THE ELECTRONIC EFFECT OF THE METHYL AND METHOXYL GROUPS

PARTIAL RATE FACTORS FOR NITRATION OF SOME SUBSTITUTED NAPHTHALENES

D. T. CLARK* and D. J. FAIRWEATHER
Department of Chemistry, The University, Durham

(*Received in the UK* 4 *July* 1969; *Accepted for publication* 1 *August* 1969)

Abstract—Partial rate factors with respect to benzene have been obtained for the nitration of naphthalene, 2,6-dimethylnaphthalene and 2-methoxy-6-methylnaphthalene. These results together with previously published data for 2-substituted methyl- and methoxy-naphthalene are discussed in terms of cation localization energies, calculated within the Parisher–Parr–Pople framework. For both Me and OMe substituents it is shown that a good account of the reactivity of these molecules, which cover a range of 10^6 in partial rate factors, can be given by the simple SCF-MO treatment if due allowance is taken of sigma and pi inductive, and mesomeric effects.

INTRODUCTION

IT HAS been shown[1] that for Me substituted benzenes an adequate account of the electronic influence of the Me group on various physical and chemical properties can be given within the Pariser–Parr–Pople formalism if both inductive and mesomeric substituent effects are included.

In the light of the encouraging results obtained in accounting for the reactivity of Me substituted benzenes in electrophilic substitution (in particular partial rate factors for nitration)[1] it is of considerable interest to investigate perhaps a more stringent test of the model for the electronic effect of the Me group; the reactivity of substituted bicyclic aromatic systems. By contrast to the relatively weak interactions for the Me group, the OMe group attached to a conjugated system exerts a strong inductive *and* mesomeric effect. It has been shown[2] that an adequate account of the OMe groups electronic influence on electronic spectra and charge distribution requires that both sigma and pi inductive effects be taken into account. It is therefore of interest to investigate the application of this model to the reactivities of OMe substituted compounds.

Partial rate factors for nitration of mono substituted Me[3] and OMe[4] substituted naphthalenes have been obtained by Wells *et al.* and the 2-substituted compounds are of particular interest since for the OMe compounds the large rate enhancement at the 6 position provides a good test of any calculated reactivity parameters. A further test of the theory is provided by investigating the effect of a further substituent in the unsubstituted ring on the reactivities of various sites in the substituted ring.

We have therefore investigated the nitration of 2,6-dimethyl and 2-methoxy-6-methylnaphthalene and naphthalene itself to obtain partial rate factors with respect to benzene for these and the mono substituted compounds.

METHOD OF CALCULATION

The sigma and pi inductive effects have been incorporated into the standard PPP–SCF–MO method as previously described.[1, 2] The aromatic C—C bond lengths and angles were taken to be 1·39 Å and 120° respectively and the substituents located along the bisectors of the internal angles. The C—O bond length was taken to be 1·37 Å as in phenol.[5] Integral values and inductive parameters for the Me group have previously been given.[1] For the OMe group the relevant values are[2] $H_{\mu\mu} = -31{\cdot}51$ eV (unmodified for sigma and pi inductive effects) β_{C-O}Me $= -1{\cdot}680$ eV, $\gamma_{\mu\mu} = 19{\cdot}27$ eV.

The inductive parameters using the moenclature of Ref (2) are $\alpha C(X)_\pi$ 1·70 eV, $\alpha C(X)_\sigma$ 0·0 eV, $\alpha X(C)_\pi$ 1·70 eV, $\alpha X(C_\sigma)$ 1·00 eV, $\alpha C(X)$ 1·70 eV, $\alpha X(C)$ 2·70 eV.

RESULTS

Experimental. The nitration (HNO_3/CH_3COOH media 25°) of the 2-substituted methyl and methoxy-naphthalenes has been investigated in detail by Wells *et al.*,[3, 4] and partial rate factors determined with respect to naphthalene. To enable partial rate factors to be calculated with respect to benzene, competitive nitrations have been carried out between naphthalene and benzene. For 2,6-dimethyl naphthalene competitive nitrations were carried out with respect to 2-methylnaphthalene and for 2-methoxy-6-methylnaphthalene with respect to 2,6-dimethylnaphthalene. In the particular cases of naphthalene and 2,6-dimethylnaphthalene isomer distributions have been investigated in the range 25–100°, in order to obtain information on the relative importance of enthalpy and entropy effects in sites of varying steric requirement. In the nitration of 2,6-dimethylnaphthalene all of the three possible isomers were obtained and Table 1 shows the variation of isomer distribution with temp together with the results for naphthalene.

TABLE 1. VARIATION OF ISOMER DISTRIBUTION WITH TEMPERATURE FOR THE NITRATION OF NAPHTHALENE AND 2,6-DIMETHYLNAPHTHALENE IN HNO_3/CH_3COOH MEDIA

T°C	Naphthalene	2,6-dimethylnaphthalene	
	$[1\text{-}NO_2]/[2\text{-}NO_2]$	$[1\text{-}NO_2]/[4\text{-}NO_2]$	$[4\text{-}NO_2]/[3\text{-}NO_2]$
0	—	4·82 ± 0·07	39·5 ± 1·7
25	18·6 ± 0·6	4·36 ± 0·09	27·4 ± 1·1
50	15·0 ± 1·0	3·87 ± 0·07	18·8 ± 3·1
70	13·5 ± 0·3	3·57 ± 0·04	7·1 ± 3·1
100	11·2 ± 0·8	3·25 ± 0·01	8·80 ± 0·28

The activation energy differences are calculated to be $\Delta E_{(1-4)} - 0{\cdot}83 \pm 0{\cdot}10$ Kcal/mole and $\Delta E_{(4-3)} - 2{\cdot}92 \pm 0{\cdot}50$ Kcal/mole, and this indicates that entropy differences must also be quite small. As we have indicated, competitive nitrations were carried out at 25° between 2,6-dimethylnaphthalene and 2-methylnaphthalene, 2-methylnaphthalene and naphthalene and naphthalene and benzene. The competitive nitration between 2-methylnaphthalene and naphthalene reproduced within experimental error, those results previously reported by Alcorn and Wells.[3] The predominance of the 2-nitro isomer in the nitration of naphthalene is largely due to the lower activation energy $\Delta E_{(1-2)}$ – 1·49 ± 0·28 Kcal/mole, and although the substantial error in the latter does not justify any firm conclusions it would appear that the entropy difference must be quite small. The results are in good agreement with those previously reported by Alcorn and Wells (at 25°)[3], and Streitweiser and Fahey (50°, 100°).[6] Competitive nitrations between naphthalene and benzene at 25° gave an overall rate ratio of 149 ± 15, giving partial rate factors of 212 ± 22 and 11·4 ± 1·2 for the 1 and 2 position in naphthalene respectively. For 2,6-dimethylnaphthalene and 2-methylnaphthalene the overall rate ratio was calculated to be 9·9 ± 0·3; and from the partial rate factors of the latter and the isomer distributions, partial rate factors for 2,6-dimethylnaphthalene were calculated to be 92,400 ± 32,800, 1680 ± 820 and 21,200 ± 8070 for the 1, 3 and 4 positions respectively.

In the nitration of 2-methoxy-6-methylnaphthalene 3-mono nitro isomers were isolated and from their ^1H NMR spectra, with the aid of INDOR experiments, these were identified as the 1, 5 and 8 nitro 2-methoxy-6-methylnaphthalenes. Competitive nitrations with 2,6-dimethylnaphthalene and then extrapolation to benzene gave partial rate factors with respect to the latter of 3,050,000 ± 1,040,000, 114,000 ± 40,000 and 348,000 ± 129,000.

The rather large experimental errors arise from extrapolation from 3 sets of experimental data. The experimental results are collected in Table 2.

Theoretical. In applying the inductive mesomeric model to the localized intermediate cations, the inductive parameters for the Me and OMe groups and attached

TABLE 2. PARTIAL RATE FACTORS FOR NITRATION HNO_3/CH_3COOH MEDIA (25°).

Compound	position	partial rate factor (f)	Ref.
Benzene	–	(1)	
Naphthalene	1	2·12 ± 0·22 × 10^2	This work
	2	1·14 ± 0·12 × 10	This work
2-Methylnaphthalene	1	1·57 ± 0·75 × 10^4	Ref. (3)
	3	7·07 ± 3·4 × 10	Ref. (3)
	4	1·89 ± 0·90 × 10^3	Ref. (3)
	5	1·63 ± 0·78 × 10^3	Ref. (3)
	6	6·04 ± 2·9 × 10^2	Ref. (3)
	8	3·50 ± 1·67 × 10^3	Ref. (3)
2-Methoxynaphthalene	1	2·12 ± 0·31 × 10^6	Ref. (4)
	6	3·61 ± 0·86 × 10^5	Ref. (4)
	8	3·51 ± 1·23 × 10^5	Ref. (4)
2,6-Dimethylnaphthalene	1	9·24 ± 4·42 × 10^4	This work
	3	1·69 ± 1·07 × 10^3	This work
	4	2·12 ± 1·08 × 10^4	This work
2-Methoxy-6-methylnaphthalene	1	3·05 ± 1·04 × 10^6	This work
	5	1·14 ± 0·40 × 10^5	This work
	8	3·48 ± 1·29 × 10^5	This work

C atoms were modified as previously described.[1] Table 3 shows the cation localization energies $\Delta E_{\pi b}$ (as defined in Ref. 7) for the substituted naphthalenes and also the differences with respect to benzene taken as standard.

TABLE 3. CATION LOCALIZATION ENERGIES OF SUBSTITUTED NAPHTHALENES.

Compound	Position	$\Delta E_{\pi b}$ (eV)	$\Delta E_{\pi b}{}^{\circ} - \Delta E_{\pi b}$ (eV)
Benzene	-	22·512	(0)
Naphthalene	1	21·760	0·752
	2	22·095	0·417
2-Methylnaphthalene	1	21·047	1·465
	3	21·673	0·839
	4	21·682	0·830
	5	21·633	0·879
	6	21·656	0·856
	7	21·960	0·552
	8	21·378	1·134
2-Methoxynaphthalene	1	19·768	2·744
	3	20·921	1·591
	4	21·620	0·892
	5	21·410	1·102
	6	20·829	1·683
	7	21·806	0·706
	8	20·657	1·855
2,6-Dimethylnaphthalene	1	20·918	1·594
	3	21·536	0·976
	4	21·299	1·213
2-Methoxy-6-methylnaphthalene	1	19·621	2·891
	3	20·765	1·747
	4	21·228	1·284
	5	20·684	1·828
	7	21·297	1·215
	8	20·571	1·941

DISCUSSION

Qualitative discussion of the experimental results. The introduction of a Me substituent into the 2 position in naphthalene activates the adjacent sites the effect being much larger at the 1 than at the 3 position and this is consistent with the localization energy changes. The 1 and 8 positions are the most reactive sites and this is also clearly shown from the calculated localization energies. The 7 position in 2-methylnaphthalene is clearly the least reactive site by a substantial margin and this is consistent with the fact that the corresponding nitro isomer has not been detected experimentally.[3] In the nitration of 2-methoxynaphthalene only the 1, 6 and 8 nitro isomers were detected. This is consistent with the localization energies, however the latter suggest that the 3 nitro isomer should also be formed in detectable amounts. A striking feature of the results in Tables 2 and 3 is the large activation both observed and calculated for the 6 position. That this is due to some extent to the strong cross ring interaction in the Wheland intermediate cation can be inferred from the calculated electron population of the OMe substituent. The electron density transferred from the substituent to the ring system of the cations is 0·114, 0·099 and 0·088 for the highly activated 1, 6 and 8 positions respectively and this is to be compared with 0·058 for the site of lowest reactivity, the 7 position.

However the situation is by no means clear cut and the corresponding results for 2-methylnaphthalene are illuminating. For the 1, 6, 8 and 7 positions respectively the electron densities transferred from the pseudo pi system of the Me substituent are 0·089, 0·064, 0·059 and 0·044. This emphasizes the subtle interplay of the inductive

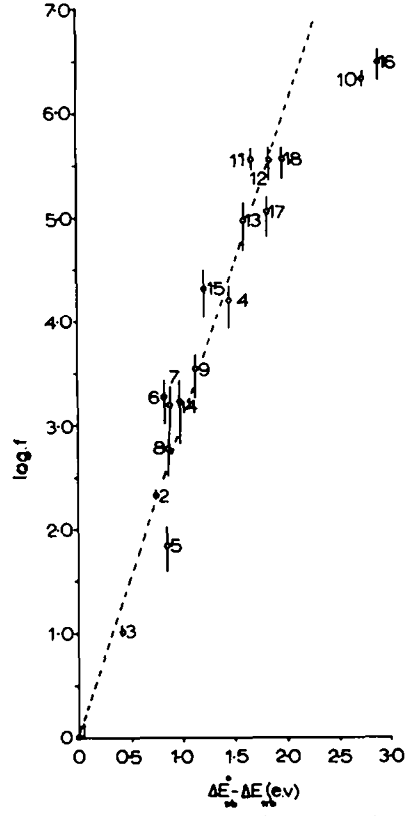

FIG. 1 Plot of $\Delta E_{\pi b}{}^{\circ} - \Delta E_{\pi b}$ (in eV) vs log *f* (partial rate factors for nitration (25°C HNO_3/CH_3COOH media).

Key.

1. Benzene.
2. Naphthalene 1 position.
3. Naphthalene 2 position.
4. 2-Methylnaphthalene 1 position.
5. 2-Methylnaphthalene 3 position.
6. 2-Methylnaphthalene 4 position.
7. 2-Methylnaphthalene 5 position.
8. 2-Methylnaphthalene 6 position.
9. 2-Methylnaphthalene 8 position.
10. 2-Methoxynaphthalene 1 position.
11. 2-Methoxynaphthalene 6 position.
12. 2-Methoxynaphthalene 8 position.
13. 2,6-Dimethylnaphthalene 1 position.
14. 2,6-Dimethylnaphthalene 3 position.
15. 2,6-Dimethylnaphthalene 4 position.
16. 2-Methoxy-6-methylnaphthalene 1 position.
17. 2-Methoxy-6-methylnaphthalene 5 position.
18. 2-Methoxy-6-methylnaphthalene 8 position.

and mesomeric contributions to the electronic effect of the substituent, since the theoretical model has the "built in" feature of increasing the importance of the mesomeric, relative to the inductive contributions in the charged species with respect to the neutral molecules. For 2,6-dimethyl naphthalene the order of reactivity $1 > 4 > 3$ is in agreement with the calculated localization energies. In the case of 2-methoxy-6-methylnaphthalene the reactivity indices are again in good agreement with the experimental order of reactivity $1 > 8 > 5$. It is of interest to compare the rate enhancements produced in one ring by a Me substituent in the other. For 2-methylnaphthalene with respect to naphthalene the rate enhancements at the 5 and 8 positions are 7·7 and 16·5 respectively. Unfortunately no figures are available for the 7 position. For 2,6-dimethyl naphthalene with respect to 2-methylnaphthalene the rate enhancements are 5·89, 11·25 and 2·38 respectively and this forms a consistent picture of the activating effect of the methyl substituent.

Quantitative discussion of the partial rate factor data. The partial rate factors cover a range of 10^6 and hence provide an exacting test of the theoretical model for the effect of the Me and OMe substituents. Fig. 1 shows a plot of $(\Delta E_{\pi b} - \Delta E_b)$ versus $\log f$ (partial rate factors for nitration HNO_3/HOAc, 25°). As we have pointed out, in obtaining partial rate factors with respect to benzene, extrapolation over several sets of experimental data is required so that the errors are rather large. With the noted exception of the 1 positions in the OMe substituted naphthalenes the correlation is amazingly good and confirms our previous results[1, 2] that an adequate account of physical properties and chemical reactivities of Me and OMe substituted aromatics can be obtained within the PPP formalism if correct cognizance is taken of the sigma and pi inductive and mesomeric effects of the substituents. The 1 positions in the methoxynaphthalenes fall furthest from a linear correlation and are much less reactive than suggested by the cation localization energies. However the calculations take no account of the interaction of the substituent with the entering electrophile in the intermediate cations, and in the case of the polar C—OMe bond in the OMe compounds such interaction will become important particularly in the close vicinity of the OMe group, i.e. at the 1 and 3 positions. This accounts for the lower than expected reactivity at these sites.

EXPERIMENTAL

Analytical and preparative scale nitration and the preparation of samples for analysis were as previously described.[1]

Materials. HNO_3 was purified as previously described.[1] British Drug Houses ANALAR acetic acid and benzene were used without further purification. Naphthalene m.p. 80·5–81·0°, 2-methylnaphthalene m.p. 31·5° and 2,6-dimethylnaphthalene m.p. 110–111° were vacuum sublimed before use and were chromatographically pure (GLC and TLC). 2-Methoxy-6-methylnaphthalene was prepared from 2-methylnaphthalene,[8] by sulphonation, fusion with KOH, and methylation of the 2-hydroxy-6-methylnaphthalene, (m.p. 77·5–78°) and was chromatographically pure (GLC and TLC).

Identification of products

Nitro 2-methylnaphthalenes. 1-Methylnaphthalene was nitrated by the method of Fierz–David and Manhaut.[9] The 1 nitro 2-methylnaphthalene obtained crystallized from EtOH as orange needles m.p. 80–81° (lit. 80–81°). The product from the preparative nitration of 2-methylnaphthalene carried out under the conditions of the analytical runs, was eluted down an 18 in × ¾ in column packed with alumina ("Camag", Brockmann activity 1), using CCl_4 as eluant. One fraction was obtained pure with the same GLC retention time and IR spectrum as authentic sample of 1 nitro-2-methylnaphthalene prepared as above. The major peak on the GLC trace from the analytical nitration of 2-methylnaphthalene had the same retention time.

TABLE 4. 100 MHz ^{1}H CHEMICAL SHIFTS (W R T TMS) AND COUPLING CONSTANTS FOR 2,6 DISUBSTITUTED NAPHTHALENES AND THEIR NITRO DERIVATIVES

Compound		1	3	4	5	7	8	J_{13}	J_{14}	J_{34}	J_{57}	J_{58}	J_{78}
2,6-Dimethylnaphthalene		744·0	715·6	751·8	744·0	715·6	751·8	1·6	<0·2	8·2	1·6	<0·2	8·2
2-Methoxy-6-methylnaphthalene		718·8	707·2	764·7	753·2	723·9	764·1	2·6	<0·2	8·6	1·8	<0·2	9·6
1 Nitro-2,6-dimethylnaphthalene		—	699·7	742·9	732·0	713·4	738·7	—	—	8·3	1·5	<0·2	8·8
4 itro-2,6-dimethylnaphthalene		770·1	791·6	—	820·7	730·5	763·1	1·5	—	—	—	<0·2	8·8
Nitro isomers of 2-methoxy-6-methylnaphthalene	(1)	—	718·1	769·8	748·3	732·8	748·8	—	—	9·2	1·5	<0·2	9·3
	(2)	804·0	712·6	763·0	789·5	770·5	—	2·2	<0·2	9·8	2·2	—	—

The peak areas for the other isomers agreed within experimental error, with the isomer proportions published by Alcorn and Wells[3] (although we did not characterize these peaks).

Nitro 2,6-dimethylnaphthalenes. The product from the nitration of 2,6-dimethylnaphthalene was eluted from an 18 in × ¾ in column packed with alumina ("Camag", Brockmann activity 1), using petroleum ether (b.p. 40–60°). Two fractions were obtained which were shown by GLC to be incompletely resolved. The two fractions were purified further by TLC using Kiselgel as stationary phase and cyclohexane as eluent. After recrystallization from EtOH, the two fractions had m.p's 66·0–66·5° and 78–79° (lit.[10] 1 nitro 2,6-dimethylnaphthalene 68°, Found C, 71·5; H, 5·4; 4 nitro 2,6-dimethylnaphthalene m.p. 84–85°,[11] Found C, 71·5; H, 5·4. Calc. for $C_{12}H_{11}NO_2$: C, 71·6; H, 5·5%). GLC analysis of the fraction m.p. 66·0–66·5° showed about 1% of a second isomer which had also been detected in the analytical runs. It seems reasonable to assign this as the 3 nitro 2,6-dimethylnaphthalene, although it did not prove possible to obtain a sample for identification. The identities of the other two isomers were established unambiguously by means of their ^{1}H NMR spectra. The ^{1}H 100 MHz NMR spectra of the two nitro isomers showed the Me resonances split by 0·04 ppm for the lower melting isomer (τ 7·72 and 7·68) and a single peak at τ 7·50 for the supposed 4 nitro isomer. The aromatic regions for both isomers consisted of overlapping ABC and AB systems, at τ 2·40–3·20 for the supposed 1 nitro isomer and τ 1·60–2·90 for the supposed 4 nitro compound. With the aid of INDOR experiments the lines associated with each AB system were unambiguously assigned to give J_{AB} = 8·1 Hz $\nu_0\delta_{AB}$ = 0·43 ppm and J_{AB} = 1·6 Hz $\nu_0\delta_{AB}$ = 0·22 ppm for the supposed 1 and 4 nitro isomers respectively. The magnitude of the chemical shift differences of the methyl resonances and coupling constants of the AB systems allow unambiguous assignments of these *structures*.

Nitro 2-methoxy-6-methylnaphthalene. The preparative scale nitration of 2-methoxy-6-methylnaphthalene gave three mono nitro isomers (with an isomer distribution of 87·2 ± 0·2% (1) 9·6 ± 0·1% (2) and 3·2 ± 0·1% (3)). On elution from an 18 in × ¾ in column packed with alumina ("Camag", Brockman activity 1), using CCl_4 as eluent, two fractions were collected, one of these was shown by GLC analysis to contain ≈90% of the major isomer (1), whilst the second fraction contained ≈80% of isomer (2) and 10% each of the other isomers. The first fraction was eluted on a thick layer plate (Kieselgel) using a 1:10 v/v mixture of $CHCl_3$ and CCl_4 as eluent. From this a pure sample of the major isomer (1) was obtained (m.p. 106–107°, Found C, 66·2; H, 5·0. Calc. for $C_{12}H_{11}NO_3$: C, 66·3; H, 5·1%). The ^{1}H (100 MHz) NMR spectrum of this compound (10% soln in CCl_4) consisted of overlapping AB and ABC systems in the region τ 2·30–2·82. With the aid of INDOR experiments the AB and ABC systems were analysed to give $\nu_0\delta_{AB}$ = 0·52 ppm J_{AB} = 9·2 Hz for the AB system and $\nu_0\delta_A$ = 732·8 Hz, $\nu_0\delta_B$ = 748·8 Hz, $\nu_0\delta_C$ = 748·3 Hz w r t TMS) with corresponding coupling constants J_{AB} = 9·25 Hz, J_{AC} = 1·5 Hz, J_{BC} < 0·2 Hz for the ABC system. The magnitude of the coupling constant for the AB system identifies the isomer as either the 1 or 5 nitro compound. The partial rate factors for the mono methoxy- and methyl-naphthalenes make it virtually certain that the major isomer is the 1 nitro isomer as do the localization energy calculations. This is strengthened by a consideration of the chemical shifts. The ^{1}H NMR spectra of 2,6-dimethylnaphthalene, and its 1 and 4 nitro derivatives and 2-methoxy-6-methylnaphthalene have been analysed in detail and a comparison of the chemical shifts of the ring protons are shown in Table 4. Unfortunately the chemical shifts of the 4 and 8 protons in 2-methoxy-6-methylnaphthalene are almost identical so that distinction between the 1 and 5 nitro isomers cannot be made on the basis of the effect of the *peri* nitro groups. However the close similarity in chemical shift of the B and C protons of the ABC system for the nitro derivative is best accommodated by assignment as the 1 nitro isomer.

Elution of the second fraction (thick layer, Kieselgel) enabled a separation of isomers (2) and (3) from (1), but none of the many eluents used would completely separate (2) and (3). GLC analysis showed the ratio of the isomers in the final fraction obtained to be 6:1 (Found C, 66·1; H, 5·0. Calc. for $C_{12}H_{11}NO_3$: C, 66·3; H, 5·1%). The ^{1}H 100 MHz NMR (10% solution in CCl_4) was complex, however with the aid of INDOR experiments the overlapping AB and ABC systems of the major component were identified. The only clear cut part of the spectrum attributable to the minor isomer was one half of an AB system J_{AB} 8·7 Hz centred at τ 2·97. The minor isomer is therefore identified as the 5 nitro compound. The analysis for the other component gave $\nu_0\delta_{AB}$ = 0·19 ppm, J_{AB} = 2·2 Hz for the AB system and $\nu_0\delta_A$ = 712·6 Hz, $\nu_0\delta_B$ = 763·0 Hz, $\nu_0\delta_C$ = 804·0 Hz, J_{AB} = 9·75 Hz, J_{AC} = 2·2 Hz, J_{BC} < 0·2 Hz for the ABC system (shifts w r t TMS). The magnitude of the coupling constant for the AB system identifies the isomer as the 4 or 8 nitro compound. From Table 4 it may be noted that for the 4 nitro isomer of 2,6-dimethylnaphthalene the *peri* hydrogen sandwiched between the Me and NO_2 groups exhibits a large downfield shift with respect to 2,6-dimethylnaphthalene. The high upfield shift (712·6 Hz) for the A proton and relatively small downfield shift (804·0 Hz) of the C proton in the ABC system is only compatible with assignment as the 8 nitro isomer.

Acknowledgement—D.J.F. wishes to thank the Hull Education Committee for the award of a maintenance grant. Thanks are due to Dr. J. W. Emsley for carrying out INDOR experiments and for many helpful discussions.

REFERENCES

[1] D. T. Clark and D. J. Fairweather, *Tetrahedron.* **25**, 4083 (1969).
[2] D. T. Clark and J. W. Emsley, *Mol. Phys.* **12**. 365 (1967).
[3] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.* **18**, 1377 (1965).
[4] P. G. E. Alcorn and P. R. Wells, *Ibid.*, **18**, 1391 (1965).
[5] H. Forest and B. P. Dailey, *J. Chem. Phys.* **45**, 1736 (1966).
[6] A. Streitweiser and R. C. Fahey, *J. Org. Chem.* **27**, 2352 (1962).
[7] M. J. S. Dewar and C. C. Thompson, *J. Am. Chem. Soc.* **87**, 4414 (1965).
[8] K. Dziewonski, J. Schienowna and E. Waldmann, *Ber. Dtsch. Chem. Ges* **58**, 1211 (1925).
[9] H. E. Fierz-David and E. Mannhaut, *Helv. Chim. Acta* **20**, 1024 (1937).
[10] F. Mayer and E. Alken, *Ber. Dtsch. Chem. Ges.* **55**, 2280 (1922).
[11] V. Vesely and F. Stursa, *Coll. Chem.* **4**, 21 (1932).