851. *Polynitronaphthalenes. Part III.*[1,2] *A Quantitative Study of the Further Nitration of the Ten Dinitronaphthalenes.*

By E. R. Ward and C. D. Johnson.

A quantitative study has been made of the nitration in sulphuric–nitric acid, and in aqueous nitric acid alone, of all ten dinitronaphthalenes and of some trinitronaphthalenes. By the competition method 1- and 2-nitronaphthalene were found to be about equally reactive in nitration in sulphuric acid. The results are discussed in relation to current theories of aromatic nitration and good agreement has been found with theoretical predictions based on molecular-orbital theory.

For comparison, reaction of 1- and 2-nitronaphthalene with the brominium ion Br^+ has been investigated.

Naphthalene was first nitrated by Laurent as long ago as 1835 and its commercial development followed on Roussin's investigations into the properties of mono- and dinitronaphthalenes (1861). Nevertheless, not until the completion of the present investigation was it possible to describe, even qualitatively, all the polynitronaphthalenes that can arise from the direct nitration of naphthalene in sulphuric acid. These are now given in the scheme.

Our systematic studies of the further nitration of polynitronaphthalenes are now complete, with quantitative results for the nitration of all ten dinitronaphthalenes (and of some trinitronaphthalenes) in nitric–sulphuric acid, and, in some cases, in nitric acid alone. These are summarised in Tables 1—4.

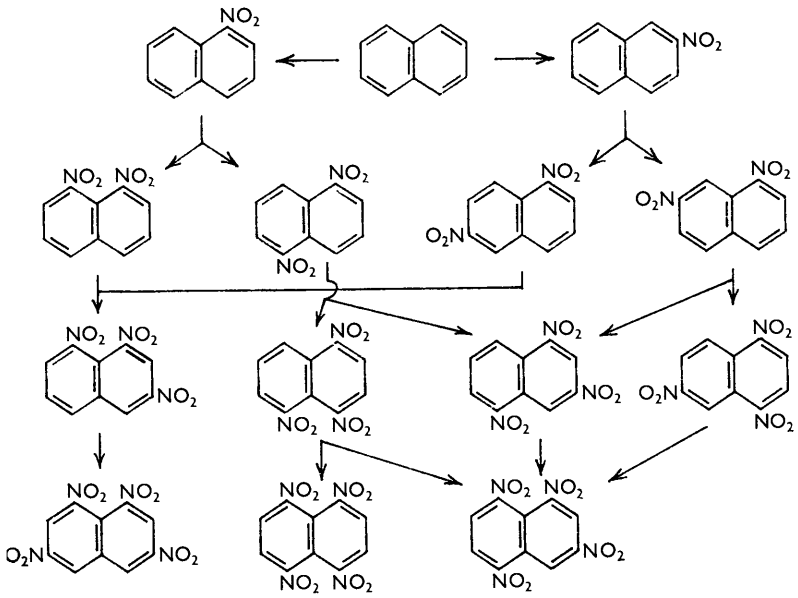
In confirmation of our previous work,[2] we have again found that for nitrations in aqueous nitric acid alone the amount of substitution in an α-position *peri* to an existing nitro-group is diminished, which we have suggested is due to increased reagent size in this medium.

In order to interpret more exactly the nitration of the polynitronaphthalenes we have made limited and preliminary studies of their relative reactivities by the competition method. Unfortunately difficulties in analysing the reaction products, except from the mononitronaphthalenes, enabled us to get only approximate values. 1- and 2-Nitronaphthalene were about equally reactive on nitration in either acetic anhydride or in sulphuric acid. For the dinitronaphthalenes relative reactivities were obtained which we considered sufficiently accurate to provide useful data and they have been published elsewhere.[3] It is hoped to make a much more detailed investigation based on the experience gained in these preliminary studies. However, it was found that 2,6- and 2,7-dinitronaphthalene are not the most reactive of the dinitronaphthalenes, as previously thought,[1] and that the difficulty in achieving mononitration only with these isomers may by due to the exceptional reactivity of the intermediate trinitronaphthalenes.

Bachman *et al.*[4] claimed that nitration of naphthalene by the boron trifluoride–nitrogen tetroxide complex in nitromethane at 80° produces a mixture of 1,5- and 1,8-dinitronaphthalene (products arising from 2-nitronaphthalene were not mentioned) in a ratio of *ca.* 1·7 : 1, in contrast to the usual ratio of 1 : 2 found for all other types of nitration. We have now nitrated 1-nitronaphthalene at −5° with Bachman's reagent and find an almost normal ratio of 39 : 61, based on a quantitative yield of dinitronaphthalenes. Hence this type of nitration is not peculiar and no special explanation is required to interpret the results (cf. Ward *et al.*[2,5]).

[1] Part I, Hodgson and Ward, *J.*, 1946, 533.
[2] Part II, Ward, Johnson, and Day, *J.*, 1959, 487.
[3] Johnson, Thesis, London, 1960.
[4] Bachman, Feuer, Bluestein, and Vogt, *J. Amer. Chem. Soc.*, 1955, **77**, 6188; Bachman and Vogt, *ibid.*, 1958, **80**, 2381.
[5] Ward, *Chem. and Ind.*, 1956, 195.

Evidence for the dipolar effect of a nitro-group in aromatic electrophilic substitution [6] (leading to substitution *ortho* or *peri* to an existing nitro-group) has been previously limited to nitration studies, and so does not exclude the possibility that this effect is peculiar to nitration. We therefore investigated the bromination, in sulphuric acid, of 1- and 2-nitronaphthalene by the brominium ion Br^+, using the method of Derbyshire and Waters.[7] The brominium ion might be expected to behave somewhat similarly to the nitronium ion,



although of course steric requirements will differ. Complete analysis of the products by column chromatography could not be achieved. Infrared spectroscopic analysis of the product from 1-nitronaphthalene gave the composition as 1-bromo-5-nitronaphthalene, 60 ± 10%; 1-bromo-8-nitronaphthalene, 15 ± 10%; 1-nitronaphthalene, 15 ± 10%; and *ca.* 10% of other material (probably a dibromonitronaphthalene but not 1,4-dibromo-5-

TABLE 1. *Mononitration of dinitronaphthalenes in sulphuric acid.*

Nitro-compound	Nitration (N1) * temp.	HNO_3 (mole)	Yield (%)	Product comp.*	Analysis *
1,2	35°	2	89	1,2,5- 44; 1,2,8- 56	C,P,S
1,3	25	1·5	89	1,3,8- 74; 1,3,5- 26	C,P
1,4	20	1·5	98	1,4,5-	C,P
1,5	30	1·5	94	1,4,5- 94; 1,3,5- 6	C,P,S
1,6	50	3·0	92	1,3,8-	C,P
1,7	25	1·5	91	1,3,5-; 1,4,6-; 1,3,6,8-	C,M
1,8 [a]	75	3·5	60	1,3,8-	
2,3 [b]	50	1·5	88	1,6,7-	
2,6	20	1·5	97	1,3,7-	C,P
2,7	30	1·5	91	1,3,6-	S

* For notes see Table 4.
[a] Hodgson, Ward, and Whitehurst, *J.*, 1945, 450. [b] Coulson, Thesis, London, 1955; Ward, Coulson, and Wells, *J.*, 1957, 4816.

nitronaphthalene). The preponderance of 1-bromo-5-nitronaphthalene was confirmed by paper chromatography and ultraviolet spectroscopy. For 2-nitronaphthalene the product composition by infrared spectroscopic analysis was 1-bromo-7-nitronaphthalene,

[6] Wells and Ward, *Chem. and Ind.*, 1958, 1172.
[7] Derbyshire and Waters, *J.*, 1950, 564, 573.

TABLE 2. *Nitration of some dinitronaphthalenes in aqueous nitric acid.*

Nitro-compound	Nitration (B1) * time (hr.)	Yield (%)	Product comp.*	Analysis *
1,2	3	57	1,2,5- 70; 1,2,8- 30	C,P
1,3	3	53	1,3,8- 58; 1,3,5- 29; 1,3,5,7- 13	P,M
1,4	3	76	1,4,5- 88; 1,4,6- 12	S,P
1,5	20	52	1,4,5- 34; 1,3,5- 47; 1,3,5,7- 19	P,M
1,6	3	60	1,3,6-; 1,3,8 †	P
1,8	3	66	1,3,8-	P
2,6	6	22	1,3,7-	C,P
2,7	3	—	Unchanged	P

* See Table 4 for notes. † Mainly 1,3,8-.

TABLE 3. *Dinitration of dinitronaphthalenes in sulphuric acid.*

Nitro-compound	Nitration (N1) * temp.	HNO_3 (mole)	Yield (%)	Product comp.*	Analysis *
1,2	80°	14		1,2,5,8-	P,S
1,3	80	17	50	1,3,6,8-	P
1,4	80	14	36	1,3,5,8- 50; 1,4,5,8- 50	P
1,5	80	14	51	1,3,5,8- 50; 1,4,5,8- 50	P
1,6	80	14	60	1,3,6,8-	
1,7	50	4	85	1,3,5,8-	
1,8	80	25	45	1,3,6,8-	
2,3 [a]	70	25	30	1,4,6,7-	
2,6 [b]	80	25	53	1,3,5,7- 81; 1,2,6,8- 16; (?)1,2,4,6- 3	SL
2,7 [b]	75	26	60	1,3,6,8-	

* For notes see Table 4.
[a] Coulson (see Table 1). [b] Chatt and Wynne, *J.*, 1943, 33.

TABLE 4. *Mononitration of some trinitronaphthalenes.*

Nitro-compound	Nitration conditions	HNO_3 (mole)	Yield (%)	Product comp.	Analysis
1,2,8	N1, 80°	9		1,2,5,8-	S
1,3,5	N1, 80°	25	60	1,3,5,8-	S
1,3,5	B1, 20 hr.		42	1,3,5,7-	P
1,3,7	N1, 80°	9		1,3,5,7-; 1,2,6,8-	SL, S
1,4,5	N1, 80°	14	37	1,3,5,8- 33; 1,4,5,8- 67	SL
1,4,5	B1, 12 hr.		51	1,3,5,8-	
1,4,6 [a]	N1, 80°	15	60	1,3,5,8-	

[a] Hardy and Ward, *J.*, 1957, 2634.

Notes on Tables 1—4. The initial compound and nitration products are described by the position of the nitro-groups.

Nitration conditions. N1, sulphuric acid (*d* 1·84)–nitric acid (*d* 1·5). B1, 70% w/w aqueous nitric acid (reflux, excess).

Yield. This represents the yield of polynitronaphthalenes isolated from the nitration product in relation to the original reactant and degree of nitration achieved. The product composition is based on the isolated polynitronaphthalenes.

C, Column chromatography. P, Paper chromatography. S, Infrared spectroscopy. M, Molecular complex formation. SL, Solvent separation.

40 ± 10%; 1-bromo-6-nitronaphthalene, *ca.* 10%; 2-nitronaphthalene, 25 ± 10%; 1,4-dibromo-6-nitronaphthalene, 25 ± 10%, supported by paper and column chromatography.

Since 5-substitution predominates in the case of 1-nitronaphthalene it appears that, possibly owing to its greater size, the brominium ion does not function here in a manner analogously to the nitronium ion. The extensive dibromination of 2-nitronaphthalene and the approximate nature of the analysis prevent us from drawing worthwhile conclusions for this compound.

Three new trinitro- and two new tetranitro-naphthalenes were prepared in these investigations. The mononitration product of 2,6-dinitronaphthalene must be 1,3,7-trinitronaphthalene, since by further nitration it affords 1,3,5,7-tetranitronaphthalene. The higher-melting trinitronaphthalene obtained from 1,2-dinitronaphthalene had a

dipole moment [8] of 3·65 D in benzene, showing it to be the 1,2,5-isomer. The lower-melting isomer was shown to be the 1,2,8-compound. On further nitration it gave the same product as the 1,2,5-isomer, showing the new tetranitronaphthalene to be the 1,2,5,8-isomer (which differs anyway from the known 1,2,6,8-isomer). The dipole moment of 1,2,8-trinitronaphthalene was 8·84 D. Although this dipole moment is well below the calculated value of 10·8 D (based on 4·0 D for a 1-nitro-group and 4·4 D for a 2-nitro-group [8]) it appears to exclude the 1,2,7-isomer, whose dipole moment would almost certainly be below 8·4 D.

Treating the tetranitronaphthalene from 1,6,7-trinitronaphthalene with sodium *p*-nitrothiophenoxide caused two nitro-groups to be displaced by nucleophilic attack. Since it has been established [9] that in such reactions only nitro-groups in 1,2-, 1,4-, or 2,3-positions in any nucleus are attacked, the 1,3,6,7-isomer is excluded, since this would have only one mobile group. Hence the tetranitronaphthalene is considered to be the 1,4,6,7-isomer, the alternative 1,2,6,7-compound being unlikely since *ortho*-nitration to an α-nitro-group has not been previously observed in the naphthalene series.

Experimental

Analytical Methods.—The procedures for column and paper chromatography were as previously described,[2] except that the alumina used was steeped in 2N-hydrochloric acid for 1 hr. with stirring, washed repeatedly with distilled water, and dried at 120—140° for 18 hr. Trinitronaphthalenes did not decompose on this neutral alumina, the columns usually showing no colour. Tetranitronaphthalenes, however, still suffered considerable decomposition with the production of highly coloured materials. The infrared spectral measurements were made and interpreted by Dr. D. H. Whiffen and Dr. K. Morgan (University of Birmingham).

Nitration Methods.—(a) *Mono- and di-nitration of dinitronaphthalenes* (*or mononitration of trinitronaphthalenes*) *in sulphuric acid* (N1). For mononitration the dinitronaphthalene (1·00 g.) was dissolved in warm sulphuric acid (*d* 1·84; 5 ml.) and then cooled, with stirring, to room temperature to obtain a finely divided suspension. A crystal of sodium nitrite was added and nitric acid (*d* 1·5) run in dropwise with vigorous stirring, the temperature being allowed to rise to, but not exceed, that indicated in Table 1. After 6 hours' stirring and a further 12 hours' storage the polynitronaphthalenes were precipitated by pouring the mixture on ice, collected, repeatedly washed with water, dilute aqueous sodium hydrogen carbonate, and again water, and dried in a vacuum at 60—90°.

For dinitration of dinitronaphthalenes or mononitration of trinitronaphthalenes a similar procedure was followed but during addition of nitric acid the temperature was allowed to rise to 50° and then raised, with vigorous stirring, to 75—90° for 1 hr., the mixture being cooled if frothing became excessive. The product was obtained by pouring the mixture on ice, or the reaction mixture was cooled to −5°; the whole was filtered through sintered glass, the solids were washed with decreasing strengths of aqueous sulphuric acid and finally with water (the filtrates from this were then poured on ice, and precipitates were washed as before).

(b) *Nitration in aqueous nitric acid* (B1). The dinitronaphthalene (1·00 g.) was refluxed with "AnalaR" nitric acid (*d* 1·42; 5 ml.) for 3 hr. and the product isolated by pouring the whole on ice, etc., as above. During refluxing copious brown fumes were evolved and the solution became dark brown.

Individual Nitrations.—These are only described where new compounds were formed or where unusual behaviour occurred which could not be indicated in the Tables.

(a) 1,2-*Dinitronaphthalene*. The product (0·433 g.) was chromatographed in benzene, fractions of 20 ml. being collected. The first five fractions contained 1,2,5-*trinitronaphthalene* (0·169 g.), m. p. 172°, [from ethanol–acetone (1 : 1) m. p. 178° (Found: C, 45·3; H, 1·4; N, 15·8. $C_{10}H_5N_3O_6$ requires C, 45·6; H, 1·9; N, 15·9%). Elution was continued with benzene–ethyl acetate (4 : 1) and the next seven fractions contained 1,2,8-*trinitronaphthalene* (0·214 g.), m. p. 168° (from benzene) (Found: C, 45·7; H, 1·9%). Coloured bands remained at the top of the column. Quantities up to 5 g. of product were separated in this manner.

[8] Richards, Sharpe, and Walker, unpublished work.

[9] Coulson, Thesis, London, 1955; Hodgson and Ward, *J.*, 1948, 2017; Ward and Day, *J.*, 1952, 4529.

The dipole moments of these compounds were measured (by Dr. S. Walker and Mr. A. N. Sharpe) in benzene solution at 25° ± 0·01°, by the method described by Cumper, Vogel, and Walker [10] and calculated by the method of Halverstadt and Kumler.[11] The dielectric constants were obtained by using a heterodyne capacitance meter based on a circuit described by Weissberger,[12] but incorporating a cathode-ray oscilloscope to detect the balance point.

1,2,5,8-*Tetranitronaphthalene* had m. p. 190—192° (Found: C, 39·7; H, 1·0; N, 17·5. $C_{10}H_4N_4O_8$ requires C, 39·0; H, 1·3; N, 18·2%).

(b) 1,3-*Dinitronaphthalene*. The reaction product from aqueous nitric acid (3·34 g.) was crystallised from benzene, giving pure 1,3,8-trinitronaphthalene (1·410 g.). The filtrate was treated with 2-naphthol (1·2 g.) in benzene (5 ml.), and the orange precipitate collected. Fractional crystallisation of this from chloroform gave first the red complex (0·49 g.) of 1,3,5,7-tetranitronaphthalene and then the orange complex (1·09 g.) of 1,3,5-trinitronaphthalene.

(c) 1,7-*Dinitronaphthalene*. A solution of the mononitration (N1) product (1·00 g.) in hot benzene (20 ml.) was treated with one of 2-naphthol (0·80 g.) in benzene (10 ml.). Cooling produced the red complex of 1,3,5-trinitronaphthalene, further crystallised from chloroform (0·51 g., 33% of 1,3,5-trinitronaphthalene in the original nitration product). Chromatography of the benzene filtrate gave 1,4,6-trinitronaphthalene (0·30 g., 30%), and paper chromatography showed this to be free from other polynitronaphthalenes. When the nitration product was chromatographed on alumina in benzene, paper chromatography of the fractionated product showed the presence of 1,3,5- and 1,4,6-trinitronaphthalene, and in the final fraction 1,3,5,8-tetranitronaphthalene.

(d) 2,3-*Dinitronaphthalene* (with T. M. Coulson). 1,4,6,7-*Tetranitronaphthalene* had m. p. 186° (from ethanol) (Found: C, 39·0; H, 1·4; N, 18·2. $C_{10}H_4O_8N_4$ requires C, 39·0; H, 1·3; N, 18·2%). It was dissolved in ethanol (12 ml.) and refluxed with *p*-nitrothiophenoxide (0·18 g.) in ethanol (2 ml.) containing sodium hydroxide (0·06 g.), for 30 min., the whole was cooled and poured on ice, and the solid collected. Chromatography on acid-washed alumina in benzene gave an almost quantitative yield of a *dinitrodi-*(p-*nitrophenylthio)naphthalene*, m. p. 126° (Found: C, 51·2; H, 2·98; N, 10·5; S, 11·7. $C_{22}H_{18}N_4O_8S_2$ requires C, 50·4; H, 2·29; N, 10·7; S, 12·2%).

(e) 2,6-*Dinitronaphthalene*. 1,3,7-*Trinitronaphthalene* had m. p. 155° (from alcohol–acetone, 1 : 1) (Found: C, 46·2; H, 2·0; N, 16·2%). With 2-naphthol in benzene, it gave a red complex (from chloroform), m. p. 120°. 1,3,5,7-Tetranitronaphthalene was separated from the nitration product of 1,3,7-trinitronaphthalene, and 1,2,6,8-tetranitronaphthalene (but not the 1,2,4,6-isomer [13]) detected in this by infrared spectroscopy.

Competitive Nitration of 1- *and* 2-*Nitronaphthalene*.—A solution of 1-nitronaphthalene (1·030 g.) and 2-nitronaphthalene (0·441 g.) in sulphuric acid (*d* 1·84; 12 ml.) was treated dropwise, with vigorous stirring, at 0° with a 4 : 1 v/v mixture of sulphuric acid (*d* 1·84) and nitric acid (*d* 1·42), 0·60 ml. being used, which was sufficient for *ca.* 25% of mononitration. The mixture was then poured on ice, the whole extracted with ether (3 × 75 ml.), the extract dried (Na_2SO_4, 5 g.; $NaHCO_3$, 5 g.) overnight, filtered through alumina, and evaporated (residue 1·573 g., 27% mononitration). This (0·392 g.) was chromatographed in benzene (20 ml.) on alumina (55 × 2 cm.) made up in 1 : 1 v/v benzene–light petroleum (b. p. 40—60°), and the yellow band of mixed mononitronaphthalenes eluted with this solvent (yield 0·260 g., 28·7% mononitration). Ultraviolet spectroscopy [14] showed the presence of 71% of 1- and 29% of 2-isomer. Hence 1·041 g. of unchanged mononitronaphthalenes contained 0·741 g. of 1- and 0·300 g. of 2-isomer. Hence the relative reactivities are 1-nitronaphthalene : 2-nitronaphthalene = 0·9 : 1. Repetition of the experiment gave a ratio 1·0. (The calculations were carried out as by Dewar *et al.*[15])

1- (0·728 g.) and 2-Nitronaphthalene (0·597 g.) in acetic anhydride (10 ml.) were nitrated, dropwise with vigorous stirring, at 0° with nitric acid (*d* 1·5; 0·10 ml.), and the solution then slowly raised to 60° and afterwards kept for 1 hr. The mixture was poured into water (500 ml.) containing sulphuric acid (*d* 1·84; 1 ml.), kept overnight, and extracted with chloroform (250 ml.). The extract was repeatedly washed with water, dried, filtered, and evaporated

[10] Cumper, Vogel, and Walker, *J.*, 1956, 3621.
[11] Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.
[12] Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publ. Inc., New York, 1938.
[13] Chatt and Wynne, *J.*, 1943, 33.
[14] Dewar and Urch, *J.*, 1957, 345.
[15] Dewar, Mole, and Warford, *J.*, 1956, 3576.

(residue 1·355 g., 8·6% mononitration). Chromatography, as above, indicated that 8·3% of mononitration had occurred, the composition of the mixed mononitronaphthalenes being 1-54·8% and 2-isomer, 45·2%, giving the relative reactivities as 1·1 : 1.

The authenticity of these experiments was verified as follows. Appropriate amounts of pure 1- and 2-nitronaphthalene, 1,5-, 1,6-, 1,7-, and 1,8-dinitronaphthalene were chromatographed in benzene on alumina. Separation of the mono- from the di-nitronaphthalenes was excellent. Infrared spectroscopy of the recovered mononitro-compounds showed the absence of dinitronaphthalenes and the composition was in reasonable agreement with that expected (Found: C, 69·7; H, 4·2; N, 7·8. Calc. for $C_{10}H_7NO_2$: C, 69·5; H, 4·05; N, 8·1%).

Bromination of 1- *and* 2-*Nitronaphthalene*.—1-Nitronaphthalene (2·0 g., 0·011 mole) and powdered silver sulphate (2·0 g.) in sulphuric acid (*d* 1·84; 10·4 ml.) and water (1·2 ml.) were treated with bromine (0·60 ml.; 0·011 mole) at −5° and shaken at room temperature for 3 hr., then poured on ice. The solids were collected, dried, and extracted with benzene. The extract was passed through a short alumina column; evaporation then gave a yellow oil which slowly solidified (2·46 g.) but was not separable by column chromatography. 2-Nitronaphthalene gave similar results but in this case pure 1,4-dibromo-6-nitronaphthalene was separated by column chromatography in benzene on alumina.

Discussion

Since the results given in Parts II and III of this series are based on improved nitration techniques and analytical methods this discussion largely ignores our earlier theoretical interpretations of the nitration of the polynitronaphthalenes.[1,16] The factors to be considered, in order of importance, are as follows.

(a) *The naphthalene polarisability*. This favours α- over β-substitution for all types of reaction (electrophilic, nucleophilic, and free-radical), as was implicit in the theories of Armstrong and Wynne,[17] Veselý and Jakeš,[18] and Hodgson *et al.*,[16] and has now received theoretical support from Dewar.[19]

(b) *The electronic effects of the nitro-group on the nucleus and their modification by the reagent*. For the nitro-group, inductive effects predominate (*i.e.*, I_σ, I_π, and direct field effects); the mesomeric effect is much smaller, and the *E*-effect negligible for electrophilic substitution.[20]

(c) *Steric effects*. If the deactivating influence of the nitro-group is exerted mainly through its inductive effect, rotation of the group out of the plane of the ring by steric interaction with a *peri*-hydrogen atom of a further nitro-substituent will not greatly diminish the magnitude of this influence or its effect on further nitration. The situation is complicated by the possible intervention of the *D*-effect.[2,6]

(d) *Miscellaneous factors*. We shall not discuss here factors such as temperature, modification of substrate and reagent by solvation, etc., except to point out the possible intervention of the nitric acidium ion in aqueous nitric acid nitrations already referred to.[2]

Attempts to make a comprehensive assay of the results in terms of classical electronic theory provided only a limited interpretation. Application of molecular-orbital theory, however, gave a much more satisfactory overall interpretation of both the qualitative and the quantitative results.

Dewar and Maitlis, using modified molecular-orbital theory, accounted satisfactorily for the nitration of quinoline, isoquinoline, cinnoline, quinoxaline, and quinazoline in sulphuric acid. The results parallel those for the further nitration of the mono- and di-nitronaphthalenes if we assume that the hetero-atom is replaced by the carbon atom

[16] Hodgson and Ward, *J. Soc. Dyers and Colourists*, 1947, **63**, 141, 177.
[17] Armstrong and Wynne, *J.*, 1877, **31**, 258.
[18] Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 925.
[19] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3355, 3357.
[20] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, 252; Wepster, "Progress in Stereochemistry," Butterworths, London, 1958, Vol. II; Jaffé, *Chem. Rev.*, 1953, **53**, 191; Roberts and Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

bearing the nitro-substituent. In any case, the equation [19] for the effect of a $+E$ substituent (Dewar's nomenclature) is too complicated for practical use; therefore, the effect of a substituent of this kind on the stability of the transition state may be taken as approximately Ca^2, where C is made equal to α, the "coulomb term" of the composite nitro-group and carbon to which it is attached.

Hence, the equation

$$\Delta E_\pi' = \Delta E_\pi + \Sigma\alpha_r a_{or}^2$$

may be applied (Dewar's paper [21] should be consulted for the terminology and method of application of this equation).

This treatment would be completely valid if the NMBO coefficients of the hetero-atom were zero, which would be the case if the C–N bond were entirely single. This is, of course, an approximation, but, as already pointed out, the nitro-group (and indeed all electronegative substituents) appear to have large inductive and only small mesomeric effects, the latter also being of diminished importance in the stabilisation of the transition state of an electrophilic substitution.

The results of the calculations by Dewar and Maitlis's method are tabulated here. A value of -4 kcal. mole^{-1} for β^* was assumed by Dewar and Maitlis for nitration in concentrated sulphuric acid and has been used here. A value of -5 kcal. mole^{-1} has been assumed for α, as this gives the best overall agreement with the experiments considered. Table 5 shows the calculated effects of the naphthalene polarisability and the 1- and 2-nitro-group on the naphthalene nucleus in the transition state of naphthalene substitution; Table 6 shows the results calculated for the dinitronaphthalenes when the effects of the nitro-groups are assumed to be additive.

TABLE 5. *Activation energies for nitration of the mononitronaphthalenes.*

Position of further substn. ...	1	2	3	4	5	6	7	8
Naphthalene	7·24	8·48	8·48	7·24	7·24	8·48	8·48	7·24
1-NO_2	—	2·50	0·42	1·82	0·46	0·42	0·63	0·30
1-Nitronaphthalene	—	10·98	8·90	9·06	7·70	8·90	9·11	7·54
2-NO_2	1·82	—	0·63	1·23	0·30	0·63	0·42	0·46
2-Nitronaphthalene	9·06	—	9·11	8·47	7·54	9·11	8·90	7·70

TABLE 6. *Activation energies for nitration of the dinitronaphthalenes.**

$(NO_2)_2C_{10}H_6$	1	2	3	4	5	6	7	8
1,2	—	—	9·5	10·3	**8·0**	9·5	9·5	**8·0**
1,3	—	11·6	—	10·9	*8·2*	9·3	9·7	**7·8**
1,4	—	11·4	11·4	—	**8·0**	9·5	9·5	**8·0**
1,5	—	11·4	*9·5*	**9·4**	—	11·4	*9·5*	**9·4**
1,6	—	11·6	9·3	9·5	9·5	—	9·7	**8·8**
1,7	—	11·4	9·5	**9·4**	**8·9**	9·5	—	9·4
1,8	—	11·6	**9·3**	9·5	9·5	**9·3**	11·6	—
2,3	10·3	—	—	10·3	**8·0**	9·5	9·5	**8·0**
2,6	9·4	—	9·5	**8·9**	9·4	—	9·5	**8·9**
2,7	9·6	—	9·7	**8·8**	**8·8**	9·7	—	9·5

* The figures for the positions where predominant nitration occurs are in bold types and those where a small amount of nitration occurs in italics.

The agreement with experiment is good. The figures are essentially the same as those of Sixma. The method of calculation in both cases is based on molecular-orbital theory, but Sixma assumes that the influence of the inductive effect of the nitro-group is due to the electrostatic field of the substituent (the direct field effect). As well as forecasting correctly the positions of further substitution, these results give the order of reactivity of the individual polynitronaphthalenes as follows (the trinitronaphthalenes being taken from Sixma's calculations):

$1 = 2 > 1,3 > 1,4 = 1,2 = 2,3 > 1,6 = 2,7 > 1,7 =$
$2,6 > 1,8 > 1,5 > 1,3,6 > 1,4,6 > 1,3,7 > 1,3,8 > 1,3,5 > 1,4,5 > 1,2,5 > 1,2,8 > 1,6,7.$

[21] Dewar and Maitlis, *J.*, 1957, 2521.

This order is in agreement with the preliminary experiments carried out. Moreover, the three most reactive trinitronaphthalenes are those given by the three dinitronaphthalenes (1,7-, 2,6-, and 2,7-) which appear to be most easily nitrated. However, it should be noted that no satisfactory reason can be given for the anomalous case of 2-nitronaphthalene, where mononitration yields a proportion of 5- to 8-substitution opposite to that expected on theoretical grounds.

The authors thank Mr. J. G. Hawkins, B.Sc., for some preliminary experiments, and the National Smelting Company (Avonmouth) for gifts of chemicals.

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE,
LEICESTER.

[*Received, September 22nd,* 1960.]