Charge-transfer Nitration of Naphthalene and the Methylnaphthalenes. Part 1. Direct Comparison with Electrophilic Aromatic Nitrations†

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The various nitronaphthalenes formed in high yields from the selective photoexcitation of the EDA complexes of the naphthalene and methylnaphthalene donors (ArH) with the *N*-nitropyridinium and tetranitromethane acceptors are ascribed to *charge-transfer nitration*, arising as they do from the cation-radical pairs [$ArH^{\bullet+}$, NO_2]. The nitration products from such an electron-transfer pathway are quantitatively compared with those from the *electrophilic nitration* (thermal), under otherwise the same conditions. The mechanistic implications to electrophilic aromatic substitution are discussed.

The mechanism of electrophilic aromatic substitution represents a critical cornerstone in the development of physical organic chemistry, stemming as it has from the pioneering and seminal studies by Ingold and co-workers.[1] Among the various substitution processes, aromatic nitration has elicited broad mechanistic interest from the early identification of the nitronium ion as the active electrophile in nitration with nitric acid.[2] Indeed a wide variety of nitronium 'carriers' NO_2–X have been employed, with their nitrating activity paralleling the base (nucleofugal) strength of X generally in the order:[3] OH_2 (nitracidinium ion) > Cl^- (nitryl chloride) > NO_3^- (dinitrogen pentaoxide) > OAc^- (acetyl nitrate) > OH^- (nitric acid) > py (*N*-nitropyridinium ion) > OCH_3^- (methyl nitrate) > $C(NO_2)_3^-$ (tetranitromethane).

In a more geneal context, the nitronium ion and its carriers are all electron-deficient and can potentially serve as effective electron acceptors (A) in common with other nitro compounds.[4] A characteristic property of the latter is their ability to form electron donor–acceptor or EDA complexes with different types of electron-rich donor, including aromatic hydrocarbons (Ar),[5,6] eqn. (1).

$$NO_2X + Ar \rightleftharpoons [NO_2X, Ar] \quad (1)$$

Such EDA complexes are also referred to as charge-transfer or CT complexes,[7] since they are sometimes coloured and show intermolecular absorption bands ($h\nu_{CT}$) that were spectroscopically characterized by Mulliken.[8,9]

We recently showed that the aromatic EDA complexes with tetranitromethane as the electron acceptor can lead to the nitration of various anisole donors (AnH) at ambient temperatures by the deliberate (actinic) irradiation of their charge transfer bands ($h\nu_{CT}$), eqn. (2).[10,11] Such a photo-induced

$$AnH + C(NO_2)_4 \rightleftharpoons [AnH, C(NO_2)_4] \xrightarrow{h\nu_{CT}} AnNO_2 + HC(NO_2)_3 \quad (2)$$

aromatic nitration has been demonstrated to proceed *via* an initial electron transfer.[12,13] As such, it raises the parallel questions as to (*a*) whether other nitronium carriers can be similarly activated and (*b*) what is the relationship of the electron-transfer process to the more conventional electrophilic aromatic nitration. Accordingly, we focus in this study on *N*-nitropyridinium ion as the common nitronium carrier in both electrophilic and electron-transfer activation of aromatic nitration under otherwise comparable reaction conditions. Naphthalene and its methyl derivatives were selected as the aromatic donors of choice for this purpose owing to the central role they play in the continuing dialogue of nitration mechanisms.[14–18]

Table 1 Charge-transfer spectral data of arene complexes with the *N*-nitropyridinium acceptor[a]

Arene donor	E_i/eV	λ_{CT}/nm[b]	Colour
Hexamethylbenzene	7.85	403	Yellow
1,4-Dimethylnaphthalene	7.78	425	Wine-red
9-Methylanthracene	7.25	506	Pink
9,10-Dimethylanthracene	7.11	534	Purple

[a] In CH_3CN at 0 °C with [$pyNO_2^+BF_4^-$] = 0.1 mol dm^{-3} and [Donor] = 0.05 mol dm^{-3} or saturated solution. [b] At band maximum.

Results

Naphthalene and its 1-methyl and 1,4-dimethyl derivatives are excellent aromatic donors by virtue of their ionization potentials (E_i) of 8.15, 7.96 and 7.78 eV,‡ in comparison with the higher and lower polycyclic analogues 9-methylanthracene and hexamethylbenzene with E_i = 7.25 and 7.85 eV, respectively.

Aromatic Charge-transfer Complexes of the N-*Nitropyridinium Acceptor.*—When a colourless solution of *N*-nitropyridinium tetrafluoroborate in acetonitrile was added to 1,4-dimethylnaphthalene (DMN), the mixture immediately turned wine red. The colour slowly bleached when the solution was allowed to stand at room temperature, but it persisted indefinitely when the solution was simply cooled to −40 °C. The absorption spectrum that corresponded to the colour change is shown in Fig. 1(*a*) as a low-energy shoulder (λ > 400 nm) tailing well into the visible spectral region. Fig. 1(*a*) also includes the similar spectral change attendant upon the treatment of DMN with the related acceptor tetranitromethane under comparable conditions. The charge-transfer character of the new absorption in Fig. 1(*b*) was readily assigned by the monotonic red (bathochromic) shift (Table 1), when DMN was replaced by the better aromatic donors 9-methylanthracene and 9,10-dimethylanthracene. Moreover, the blue (hypsochromic) shift in Table 1 with the poorer donor hexamethylbenzene is in complete accord with the predictions of Mulliken theory.[8,9]

The monotonic increase in the absorbance A_{CT} of the new charge-transfer band from the *N*-nitropyridinium acceptor

† Submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.
‡ 1 eV = *ca.* 1.602 × 10^{-19} J.

Table 2 Formation constants of the charge-transfer complexes of the naphthalenes with nitro acceptors[a]

Naphthalene donor	Nitro acceptor	Solvent	K/dm^3 mol^{-1}	ε/dm^3 mol^{-1} cm^{-1} [b]
1-Methyl	$C(NO_2)_4$	CH_2Cl_2	0.24 ± 0.02	280 ± 2
2-Methyl	$C(NO_2)_4$	CH_2Cl_2	0.27 ± 0.01	208 ± 4
1,4-Dimethyl	$C(NO_2)_4$	CH_2Cl_2	0.35 ± 0.01	253 ± 4
1,4-Dimethyl	$C(NO_2)_4$	CH_3CN	0.23 ± 0.01	288 ± 3
1,4-Dimethyl[c]	$pyNO_2^+BF_4^-$[d]	CH_3CN	1.07 ± 0.14	190 ± 21

[a] Measured at 25 °C, unless indicated otherwise. [b] Evaluated at 450 nm. [c] Measured at 0 °C. [d] As the tetrafluoroborate salt.

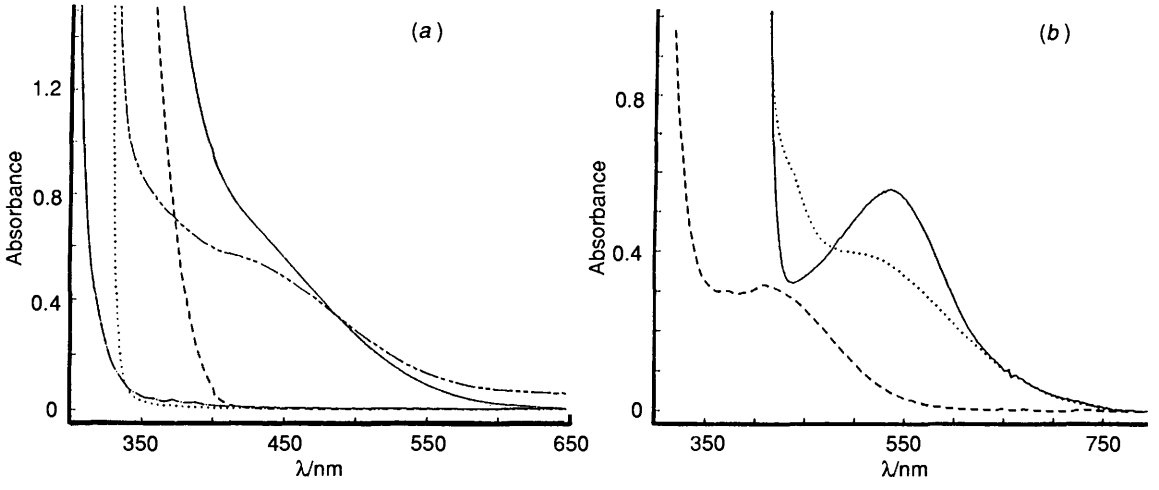
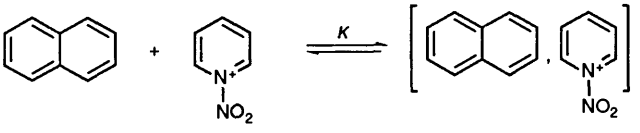


Fig. 1 (*a*) Charge-transfer spectrum from 0.13 mol dm^{-3} 1,4-dimethylnaphthalene and 0.02 mol dm^{-3} $pyNO_2^+BF_4^-$ in MeCN (—••—) or 0.05 mol dm^{-3} 1,4-dimethylnaphthalene and 0.14 mol dm^{-3} $C(NO_2)_4$ in CH_2Cl_2(——), relative to the spectrum of the uncomplexed acceptor, 0.02 mol dm^{-3} $pyNO_2^+BF_4^-$ (— • —) or 0.14 mol dm^{-3} $C(NO_2)_4$ (– – – –) and the uncomplexed donor, 0.05 mol dm^{-3} DMN. (*b*) Charge-transfer spectra of 0.1 mol dm^{-3} $pyNO_2^+BF_4^-$ with 0.05 mol dm^{-3} hexamethylbenzene (— — — —), 9-methylanthracene (••••••) and 1,4-dimethylanthracene (——) in MeCN.



(3)

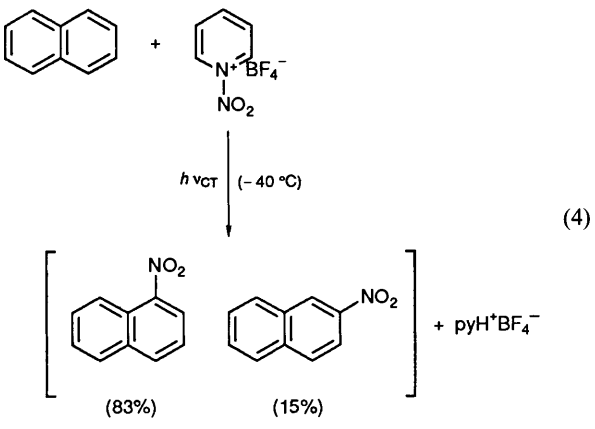
(NP) was quantitatively evaluated at various concentrations of the aromatic donor (Ar) as

$$\frac{[NP]}{A_{CT}} = \frac{1}{\varepsilon_{CT}} + \frac{1}{K\varepsilon_{CT}[Ar]}$$

according to the procedure of Benesi and Hildebrand.[19,20] The formation constant K and the extinction coefficient ε_{CT} of the 1:1 complex measured in this way were comparable to those of the analogous EDA complexes with tetranitromethane. The limited magnitude of K in Table 2 indicates that the naphthalene complex with the nitropyridinium acceptor, eqn. (3), like that with tetranitromethane, is best classified as weak.[7,8]

Photo-induced Nitration of Naphthalenes with N-*Nitropyridinium Tetrafluoroborate.*—Since naphthalene was efficiently nitrated by the *N*-nitropyridinium acceptor in the dark at room temperature (*vide infra*), the photo-induced nitrations were examined at −40 °C. The control experiment carried out with a solution of 0.05 mol dm^{-3} naphthalene and 0.1 mol dm^{-3} $pyNO_2^+BF_4^-$ in acetonitrile showed no apparent change at −40 °C when protected from light, even adventitious room-light. Naphthalene was quantitatively recovered intact upon work-up of the reaction mixture after a 3 h period. Accordingly, the solution of naphthalene (0.15 mmol) and $pyNO_2^+BF_4^-$ (0.3 mmol) in acetonitrile was deliberately irradiated for 3 h at $\lambda > 425$ nm with the output from a 500 W mercury lamp passed through a Pyrex sharp cut-off filter (Corning CS-3-72). Inspection of the absorption spectrum in Fig. 1 ensured that such filtered light could selectively excite only the charge-transfer absorption band of the complex. Thus there was no ambiguity about either the adventitious local excitation of the uncomplexed arene donor[21] (or the *N*-nitropyridinium acceptor[22]), or the generation of intermediates which did not result from the direct charge-transfer excitation of the EDA complex. The subsequent gas chromatographic analysis of the photolysate indicated the presence of unchanged naphthalene (0.054 mmol, 36%), together with a mixture of 1-nitronaphthalene (0.080 mmol) and 2-nitronaphthalene (0.014 mmol), the yields of which corresponded to 83 and 15%, respectively, based on the recovered naphthalene. In order to differentiate the nitration of naphthalene by actinic activation, eqn. (4), under conditions in which the thermal (electrophilic) reaction in the dark was too slow to compete (*vide infra*), it is hereafter designated as *charge-transfer nitration.*

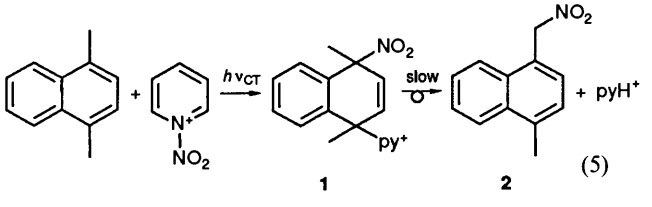
The charge-transfer nitration of 1-methylnaphthalene with the *N*-nitropyridinium acceptor was also carried out in acetonitrile at −40 °C, a temperature at which the control experiment established the thermal reaction to be insignificant. Selective irradiation of the bright yellow solution at $\lambda > 425$ nm led to the monotonic decrease in the charge-transfer absorbance. Gas chromatographic analysis of the photolysate after 3 h indicated the presence of a complex mixture of nitronaphthalenes including the 2-, 3-, 4-, 5- and 8-isomers in 30,



(4)

2, 52, 8 and 8% yields respectively (see the Experimental section for details).

The charge-transfer nitration of 1,4-dimethylnaphthalene with *N*-nitropyridinium cation was carried out at 0 °C. No thermal reaction was observed at this temperature for >16 h. Irradiation of the red–brown solution of the EDA complex from DMN (0.10 mol dm^{-3}) and $pyNO_2{}^+BF_4{}^-$ (0.10 mol dm^{-3}) with visible light ($\lambda > 425$ nm) led to gradual bleaching. After 3 h, the solvent was removed *in vacuo* from the yellow solution, and the inspection of the ^1H NMR spectrum of the metastable concentrate **1** showed the appearance of new singlet resonances at δ 2.29, 2.24, 2.21 and 2.06 in the methyl region, downfield singlets at δ 6.45 and 6.42 for a pair of vinylic protons, and aromatic multiplets centred at δ 8.75 and 8.10. The latter, together with its insolubility in diethyl ether suggested **1** to be a *syn*/*anti* mixture of pyridinium adducts which were structurally related to those obtained from CT nitration of DMN with tetranitromethane (*vide infra*). Upon standing overnight at room temperature, the adducts were quantitatively converted into a single product **2** of side-chain nitration,* eqn. (5), as

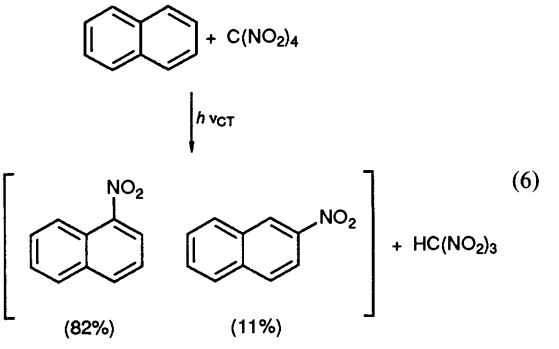


(5)

established by spectral comparison with that of an authentic sample.[23] There was no evidence for 1,4-dimethyl-2-nitronaphthalene as the product of ring nitration.

Charge-transfer Nitration of Naphthalenes with Tetranitromethane.—The red–brown solution of naphthalene (0.15 mmol) and tetranitromethane (2.5 mmol) in acetonitrile was stable at room temperature, as shown by the persistence of the charge-transfer absorption band for prolonged periods. Irradiation of the solution with visible light at $\lambda > 425$ nm for 17 h led to a yellow solution containing nitroform (0.085 mmol) as indicated by its characteristic absorption at $\lambda_{max} = 350$ nm ($\varepsilon_{max} = 14\,000$ dm^3 mol^{-1} cm^{-1}).[11] Gas chromatographic analysis of the photolysate indicated the presence of unchanged naphthalene (0.060 mmol), together with 1-nitronaphthalene (0.074 mmol) and 2-nitronaphthalene (0.010 mmol), which corresponded to 82 and 11% yields, respectively, based on the naphthalene consumed, eqn. (6).

The charge-transfer complexes of the methylnaphthalenes



(6)

with tetranitromethane were also persistent in acetonitrile. The deliberate irradiation of the red–brown solution containing 1-methylnaphthalene (0.30 mmol) and tetranitromethane (2.5 mmol) for 14 h at $\lambda > 425$ nm afforded nitroform (0.090 mmol) and a mixture of nitro-1-methylnaphthalenes consisting of the 2-, 3-, 4-, 5- and 8-isomers in 10, 15, 59, 9 and 7% yields, respectively, based on 1-methylnaphthalene consumed.† Similarly, the charge-transfer nitration of 2-methylnaphthalene under the same conditions led to nitroform (63%) and a complex mixture of four isomeric nitro-2-methylnaphthalenes‡ (see the Experimental section for details).

Although the red solution of 0.2 mol dm^{-3} 1,4-dimethylnaphthalene (DMN) and 0.4 mol dm^{-3} tetranitromethane in acetonitrile remained unchanged upon standing for prolonged periods, the products of charge-transfer nitration were temperature dependent. For example, when the red solution was irradiated with visible light ($\lambda > 425$ nm) at −30 °C for 2 h, the adduct **3** was observed as a 1:3 mixture of *syn*/*anti* isomers by the appearance of a characteristic set of resonances in the ^1H and ^{13}C NMR spectrum (*vide infra*). In order to confirm the structure and assign the stereochemistry of the adduct, the charge-transfer nitration was repeated in dichloromethane and the volatile solvent removed *in vacuo* at 0 °C. Single crystals of the major isomer **3a** suitable for X-ray crystallography were grown by the slow diffusion of hexane into a saturated ethereal solution of the crude adduct. The ORTEP diagram of the adduct **3a** in Fig. 2 revealed the *ipso* addition of O_2N–$C(NO_2)_3$ to 1,4-dimethylnaphthalene to occur with *anti* stereochemistry. The ^1H NMR spectrum of **3a** consisted of a pair of singlet resonances at δ 2.10 and 2.20, an AB system at δ 6.24 and 6.67 (J = 10.7 Hz), and a multiplet centred at δ 7.75 for the aromatic protons, with the correct intensity ratios of 3:3:2:4 for the structure in Fig. 2.§ Careful examination of the ^1H NMR spectrum of the crude product indicated the presence of additional resonances due to the minor adduct **3b**, presumably the *syn* isomer, with identical splittings but slightly displaced at δ 1.96, 2.06, 6.41 and 6.62. Most importantly, the mixture of *syn*/*anti* adducts in acetonitrile was slowly converted, upon standing at room temperature, quantitatively into the single product **2** of side-chain nitration,[23] eqn. (7a,b)

When the charge-transfer nitration of 0.2 mol dm^{-3} DMN and 0.4 mol dm^{-3} TNM in acetonitrile was repeated at 25 °C, it afforded a mixture of the same adduct **3** and the side-chain

* We thank Professor L. Eberson for an authentic sample of 1-methyl-4-nitromethylnaphthalene (**2**).

† Inspection of the ^1H NMR spectrum of the crude reaction mixture also indicated the presence of additional weak resonances in the alkene region at δ 6.5 and 6.4 and methyl resonances at δ 2.02 and 2.07 suggestive of the presence of small amounts of adducts similar to **1** and **3**.

‡ The lack of *ipso* attack on 2-methylnaphthalene leading to adduct formation was indicated by the absence of additional vinylic and methyl resonances in the ^1H NMR spectrum of the crude reaction mixture.

§ For comparison, the ^1H NMR spectrum of the analogous O_2N–OAc adduct isolated by Fischer *et al.*[24] consisted of similar resonances at δ_H 1.61 (s, 3 H), 1.95 (s, 3 H), 2.01 (s, 3 H, OAc), 6.11 (d, 1 H, J = 10.3 Hz), 6.34 (d, 1 H, J = 10.3 Hz) and 7.43 (m, 4 H).

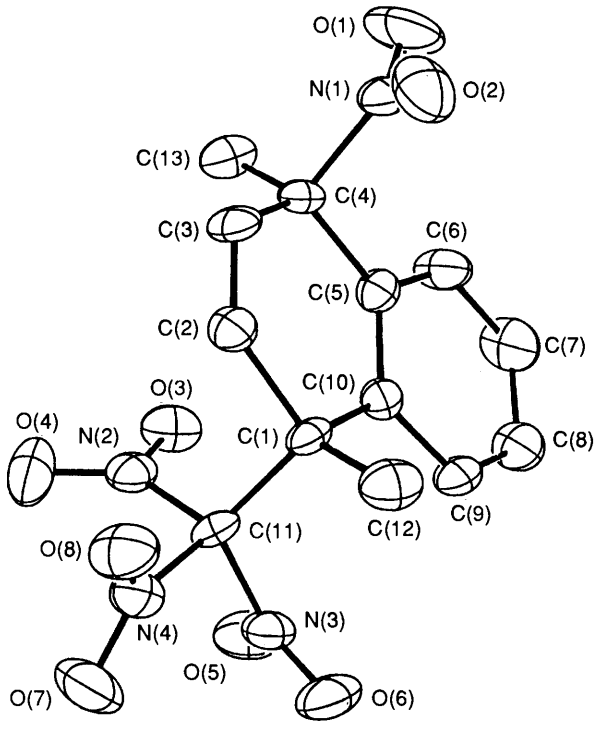
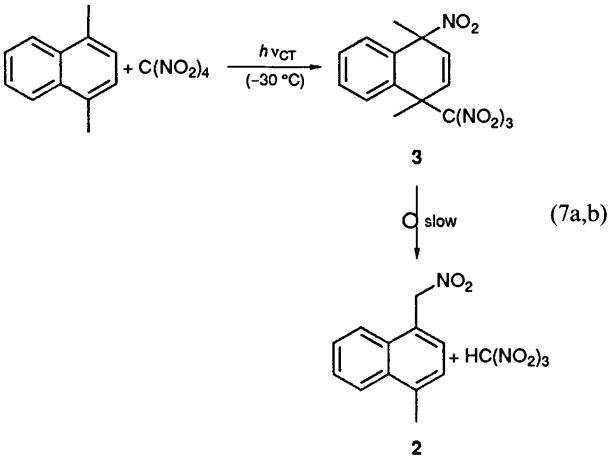
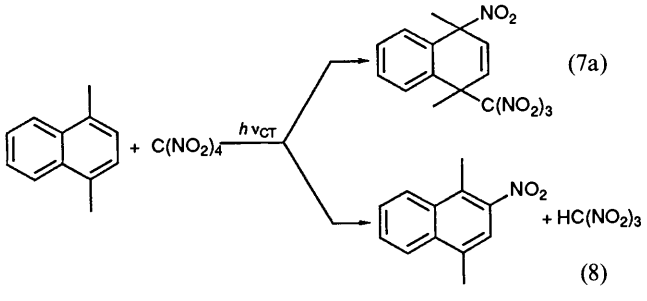


Fig. 2 ORTEP diagram of the *ipso* adduct **3** from the charge-transfer nitration of 1,4-dimethylnaphthalene and tetranitromethane showing *anti* stereochemistry

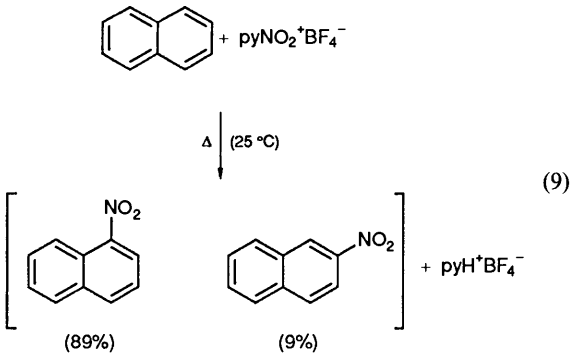


product **2** in 43 and 40% yields, respectively, together with a small, but discrete amount (9%) of 1,4-dimethyl-2-nitronaphthalene. Charge-transfer nitration at an intermediate temperature of 0 °C afforded more adduct (65%) at the expense of the side-chain product **2** (23%), but the same amount (8%) of 1,4-dimethyl-2-nitronaphthalene. Observation of the latter, together with the clean decomposition of the metastable adduct **3** to the side-chain product **2** in eqn. (7b), suggested that adduct formation and ring nitration were competitive processes, eqns. (7a) and (8).



Electrophilic (Thermal) Nitrations of Naphthalenes.—Aromatic nitrations were carried out with the *N*-nitropyridinium acceptor thermally at room temperature in the dark under conditions designed to simulate as closely as possible those employed in charge-transfer nitration. For comparison, aromatic nitrations were also carried out with the pure nitronium salt,[25] $NO_2^+BF_4^-$, as well as the nitrating agent prepared from anhydrous nitric acid in acetic anhydride[26] to represent the more conventional reagents for electrophilic nitration.

When a colourless solution of 0.1 mol dm^{-3} $pyNO_2^+BF_4^-$ was added to 0.05 mol dm^{-3} naphthalene in acetonitrile at 25 °C, a fleeting bright yellow colour appeared and slowly faded within an hour. The acetonitrile solution was triturated with ether, and the colourless precipitate was identified as pyridinium tetrafluoroborate by spectral (^{1}H NMR and IR) comparison with an authentic sample. Concentration of the filtrate *in vacuo* afforded a mixture of 1-nitronaphthalene (89%) and 2-nitronaphthalene (9%), eqn. (9). Similarly, the treatment

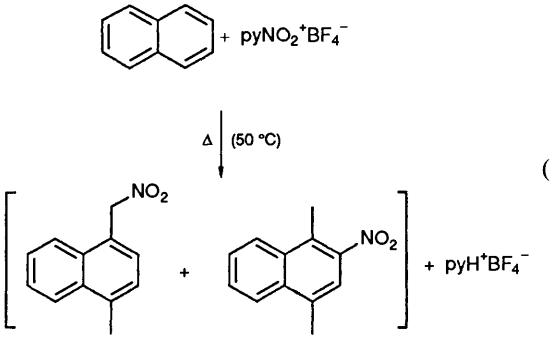


of naphthalene with 2 equiv. of purified nitric acid in acetic anhydride at 0 °C afforded 1-nitro- and 2-nitro-naphthalenes in 94 and 6% yields, respectively. Repetition of the experiment with added sodium azide[27] (0.5 equiv. relative to naphthalene) at −20 °C afforded the 1- and 2-nitronaphthalenes in 95 and 4% yields, respectively, under conditions that avoided the complications from the nitrous acid catalysis.[28,29]

Addition of 1-methylnaphthalene to an ice-cold solution of $pyNO_2^+BF_4^-$ in acetonitrile gave a bright yellow solution, which upon being warmed to room temperature slowly faded to a pale yellow solution within an hour. The pyridinium tetrafluoroborate was removed as described above, and gas chromatographic separation of the crude reaction mixture (after solvent removal *in vacuo*) indicated a mixture of nitro-1-methylnaphthalenes consisting of the 2-, 3-, 4-, 5- and 8-isomers in 31, 2, 52, 8 and 7% respectively. Each of the mono-nitro derivatives in the mixture was identified by GC–MS analysis in comparison with that reported by Eberson and Radner[16] (see the Experimental section). 1-Methylnaphthalene was also nitrated with anhydrous nitric acid in acetic anhydride at 0 °C. Chromatographic separation of the crude reaction mixture on neutral alumina yielded pure fractions consisting of 1-methyl-4-nitronaphthalene and 4-acetoxy-1-methylnaphthalene, which were identified from their characteristic ^{1}H NMR, IR and mass spectra.[16] A small aliquot of the crude reaction mixture, taken prior to column chromatography, was subjected to GC–MS analysis to yield a mixture of mono-nitro derivatives including the 2-, 3-, 4-, 5- and 8-isomers in 25, 2, 44, 7 and 8% yields together with 4-acetoxy-1-methylnaphthalene in 14% yield. The nitration of 2-methylnaphthalene with nitric acid in acetic anhydride was similarly carried out at 0 °C to afford a complex mixture of four isomeric mono-nitro-1-methylnaphthalenes, as indicated by GC–MS analysis (see the Experimental section). Chromatographic separation of the crude reaction mixture on

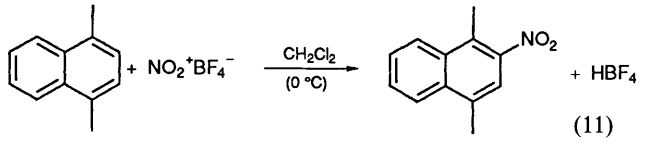
neutral alumina afforded a fraction consisting of pure 2-methyl-1-nitronaphthalene (60%), which was readily identified by its ^1H NMR, IR and mass spectra,[26a] together with a minor fraction consisting of at least three isomers.

The treatment of 1,4-dimethylnaphthalene (DMN) with $pyNO_2^+BF_4^-$ in acetonitrile at 0 °C resulted in a wine-red solution which persisted for 16 h, whereupon the analysis of the reaction mixture showed the DMN and $pyNO_2^+$ to be unchanged (by the inspection of the ^1H NMR spectrum). Accordingly, the mixture of dimethylnaphthalene and $pyNO_2^+BF_4^-$ was gently warmed to 50 °C for 3 h. Ether was then added to the pale yellow solution in order to precipitate the pyridinium tetrafluoroborate. Evaporation of the filtrate *in vacuo* afforded a mixture of the side-chain nitration product **2** (87%) and 1,4-dimethyl-2-nitronaphthalene (8%) by GC–MS analysis, eqn. (10).



(10)

The nitration of 1,4-dimethylnaphthalene was also directly effected with the nitronium salt. Thus the dropwise addition of dimethylnaphthalene (0.16 mmol) in dichloromethane (2 cm^3) to an ice-cold slurry of $NO_2^+BF_4^-$ (0.16 mmol) with 2 cm^3 of dichloromethane resulted in the development of a pale green colour, accompanied by the slow dissolution of the salt. Work-up of the reaction mixture with water yielded a single product 1,4-dimethyl-2-nitronaphthalene (75%) together with unchanged DMN (30%) by GC–MS analysis. Column chromatography on neutral alumina led to a pure sample of 1,4-dimethyl-2-nitronaphthalene in 50% yield, and the ^1H and ^{13}C NMR, IR and mass spectra coincided with those of an authentic sample.[24]



(11)

Discussion

Mechanistic studies of aromatic nitration have traditionally relied on product analysis to ascertain the competitive rates and isomer distributions that are pertinent to substrate and positional selectivity.[30–32] The recent reintroduction of the idea of a prior electron-transfer step,[33] originally suggested by Kenner and others, [34–37] has rekindled an interest in electrophilic aromatic nitration, and it has spawned a variety of associated 'non-conventional' nitration techniques, methodologies, and mechanistic probes—including electrochemical nitrations with NO_2,[14,17] gas-phase nitrations,[38] aromatic radical-cation nitrations,[16] NMR (CIDNP) techniques,[18] auto-oxidative nitrations with NO^+,[39] and photo-induced nitrations.[10,11] Foremost among the aromatic substrates are naphthalene and the various methylnaphthalenes as targets of extensive scrutiny since they represent the borderline cases–these electron-rich polynuclear hydrocarbons being susceptible to both electrophilic attack as well as oxidation.[40,41]

Direct Comparison of the Electrophilic and Charge-transfer Nitrations of the Naphthalenes.—The dichotomy between electrophilic and electron-transfer pathways for naphthalene nitration is represented in this study by the thermal and charge-transfer activation of $pyNO_2^+BF_4^-$ that was first introduced by Olah as the nitronium carrier in organic solvents.[42] Thus the nitration of naphthalene proceeds quantitatively with this reagent by both the thermal and charge-transfer pathways, as shown in Table 3 by the consistently high yields of the 1-nitro- and 2-nitronaphthalenes. The similarity in the isomeric product distribution (entries 2 and 4) is striking, the differences in temperature notwithstanding. Indeed the isomer distribution given as the α/β ratio has been reported to vary from *ca.* 10 to 60 for the nitration of naphthalene under a variety of conditions differing widely in the solvent, the temperature, as well as in the nitronium carrier.[3] [The exceptions are the gas-phase nitration with tetranitromethane and photolytic nitration with N_2O_4, both of which yield the statistical distribution of 1- and 2-nitronaphthalenes owing to the *homolytic* substitution *via* $NO_2^\bullet$ dissociation.[43]] However, it is important to emphasize that any small change (including experimental uncertainties) in the yield of the minor 2-isomer is strongly magnified in the magnitude of the α/β ratio. As such, we believe that the comparison of the absolute isomer yields, and not their ratios,[14,16] is a more useful diagnostic probe in any mechanistic differentiation for aromatic nitration. With this limitation in mind, we conclude from the data in Table 3 that there is little to distinguish the electrophilic from the charge-transfer pathway for the nitration of naphthalene, since the preponderant nitration at the 1-position is the consistent result.

The nitration of 1-methylnaphthalene presents an optimum opportunity to examine the effects of nitration on the product distribution owing to the formation of five isomeric products of nuclear substitution, as summarized in Table 4. The thermal and charge-transfer nitrations with $pyNO_2^+BF_4^-$ (entries 3 and 6) show a striking coincidence in the formation of the same isomeric mixture of nitration products. Moreover, only minor deviations are discernible with the other nitrating agents, including acetyl nitrate and tetranitromethane, in both thermal and charge-transfer nitrations.

The nitration of 1,4-dimethylnaphthalene (DMN) is known to be highly sensitive to the nature of the nitronium carrier, the temperature, the solvent, as well as to the presence of nucleophiles and excess of acid or base. For example, Robinson's report of the side-chain substitution of DMN leading only to **2** with nitric acid in acetic anhydride,[23] differs from Davies and Warren's claim of the 5-nitro isomer as the exclusive product.[44] The definitive study of this system at low temperatures by Fischer and Wilkinson.[24] established the *ipso* adduct **4** (where X = OAc, ONO_2) as the critical intermediate which subsequently affords the side-chain product **2** upon its decomposition at higher temperatures, eqns. (12a,b). The formation of the *ipso* adduct **4** as both the acetate and nitrate derivatives under these conditions is consistent with the nucleophilic trapping of the first-formed Wheland intermediate, eqn. (13).

The formation of the analogous adducts [*viz.*, **1** in eqn. (5) with X^- = pyridine and **3** in eqn. (7) with X^- = $C(NO_2)_3^-$] as the critical intermediates in the photo-induced nitration of 1,4-dimethylnaphthalene with the *N*-nitropyridinium and tetranitromethane acceptors, thus establishes the unity of the electrophilic and charge-transfer pathways. In both processes, the side-chain nitration product **2** is clearly associated with the subsequent (slower) decomposition of the metastable *ipso* adducts **1**, **3** and **4**. Thus the strong similarity in the formation of **2** and/or the *ipso* adduct as the ultimate product(s) of DMN nitration in Table 5 (columns 3 and 4) leads us to the

Table 3 Electrophilic and charge-transfer nitrations of naphthalene.

Method	Reagent	Solvent	T/°C	Nitronaphthalene (mol %) 1-NO_2	2-NO_2	α/β
Thermal	HNO_3	Ac_2O	0	94	6	16
Thermal	$pyNO_2^+BF_4^-$	MeCN	25	89	9	9.8
Thermal	HNO_3/NaN_3	Ac_2O	0	95	4	24
Charge-transfer	$pyNO_2^+BF_4^-$	MeCN	−40	83	15	5.5
Charge-transfer	$C(NO_2)_4$	MeCN	25	82	11	7.4

Table 4 Nitrations of 1-methylnaphthalene.

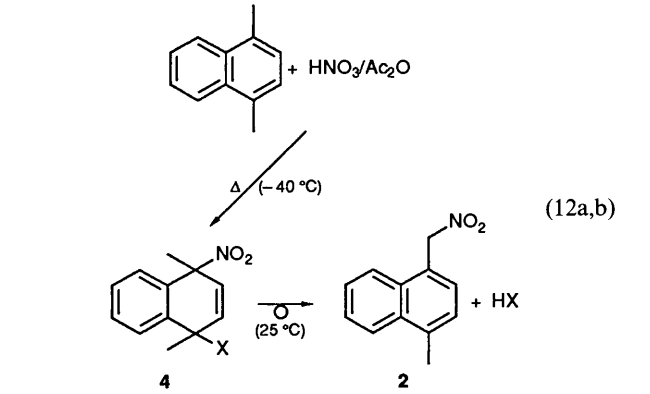
Method	Reagent	Solvent	T/°C	% Nitro-1-methylnaphthalene 2-NO_2	3-NO_2	4-NO_2	5-NO_2	8-NO_2
Thermal[a]	HNO_3	Ac_2O	25	23	6	43	10	18
Thermal	HNO_3	Ac_2O	0	25	2	44	7	8
Thermal	$pyNO_2^+BF_4^-$	MeCN	25	31	2	52	8	7
Thermal[b]	N_2O_4[c]	CH_2Cl_2	*e*	18	—	66	10	6
Thermal[b]	NO_2[d]	CH_2Cl_2	*e*	8	—	88	1	3
Charge-transfer	$pyNO_2^+BF_4^-$	MeCN	−40	30	2	52	8	8
Charge-transfer	$C(NO_2)_4$	MeCN	25	10	15	59	9	7

[a] From ref. 26. [b] From ref. 16. [c] With methanesulfonic acid added. [d] With 1,4-dimethylnaphthalene cation radical (see ref. 54). [e] Ambient temperatures.

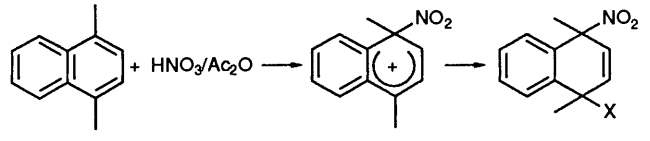
Table 5 Nitrations of 1,4-dimethylnaphthalene.

Method	Reagent	Solvent	T/°C	Nitronaphthalene (mol %) 2-NO_2[a]	Adduct[b]	Side chain[c]
Thermal[d]	HNO_3	Ac_2O	−40	(Minor)	>90	(Minor)
Thermal[e]	HNO_3	Ac_2O	25	(Minor)	0	100
Thermal	$NO_2^+BF_4^-$	CH_2Cl_2	0	100	0	0
Thermal	$pyNO_2^+BF_4^-$	MeCN	50	8	0	87
Charge-transfer	$pyNO_2^+BF_4^-$	MeCN	0	0	70	29
Charge-transfer	$C(NO_2)_4$	CH_2Cl_2	25	9	45	35
Charge-transfer	$C(NO_2)_4$	CD_3CN	−40	—	>90	(Trace)
Charge-transfer	$C(NO_2)_4$	MeCN	0	8	65	23
Charge-transfer	$C(NO_2)_4$	MeCN	25	9	43	40

[a] 1,4-Dimethyl-2-nitronaphthalene. [b] *ipso* adduct. [c] Side-chain nitration (1-nitromethyl-4-methylnaphthalene). [d] From ref. 24. [e] From ref. 23.

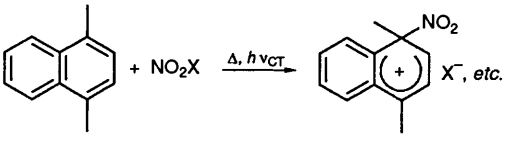


(12a,b)



where $X^- = OAc^-, ONO_2^-$ (13)

inescapable conclusion that the electrophilic and charge-transfer pathways are not distinguishable. In every case, the

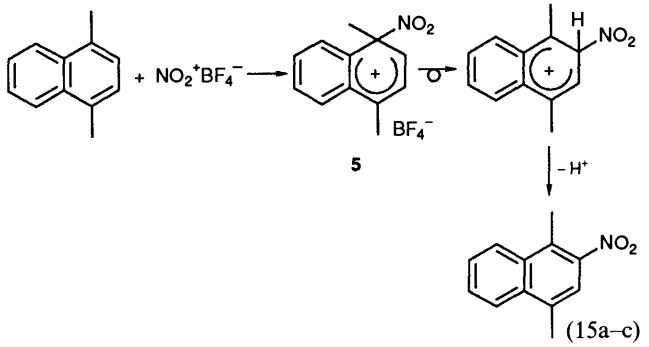


(14)

where X = py, OAc^-, $C(NO_2)_3^-$, *etc.*

Wheland intermediate **5** that is generated by *ipso* addition is the first-formed intermediate irrespective of an electrophilic or charge-transfer activation, eqn. (14). In the absence of a nucleophile, the *ipso* Wheland intermediate is subject to a 1,2-nitro shift[45–47] to an unsubstituted ring position, followed by a facile proton loss. Such a situation is presented with the nitronium salt $NO_2^+BF_4^-$, and the result is shown in Table 5 (entry 3) by the formation of 1,4-dimethyl-2-nitronaphthalene as the sole product, eqns. (15a–c).

The Cation-radical Pair [$ArH^{\bullet+}$, NO_2] *as the Reactive Intermediate in Charge-transfer Nitration.*—The charge-transfer nitration is induced by a vertical, non-adiabatic process involving as it does the direct photoexcitation of the charge-transfer complex.[11] Thus it has been demonstrated[48,49] that the actinic irradiation of the charge-transfer bands ($h\nu_{CT}$) of arene complexes with tetranitromethane leads spontaneously to the solvent-caged triad in eqn. (16). By analogy, the corresponding

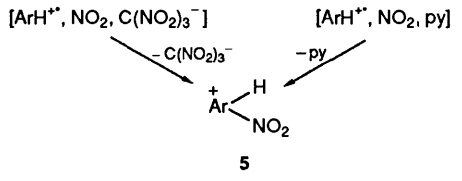


$$ArH + C(NO_2)_4 \rightleftharpoons [ArH, C(NO_2)_4] \xrightarrow{h\nu_{CT}} [ArH^{\bullet+}, NO_2, C(NO_2)_3^-] \quad (16)$$

charge-transfer complex with the *N*-nitropyridinium acceptor will lead to a similar triad, but containing a different (neutral) base, eqn. (17).[50]

$$ArH + pyNO_2^+ \rightleftharpoons [ArH, pyNO_2^+] \xrightarrow{h\nu_{CR}} [ArH^{\bullet+}, NO_2, py] \quad (17)$$

It is important to emphasize that any mechanism proposed for charge-transfer nitration must explicitly include the fate of these triads as the obligatory intermediates. For the charge-transfer nitration pertinent to this study, the naphthalene cation radical ($ArH^{\bullet+}$) and NO_2 are the critical components of both triads that lead to the Wheland intermediate, eqns. (18a,b).



(18a,b)

Time-resolved spectroscopy of the triad (to be described in a later paper) allows the kinetics of the cation-radical pair to be charted in some detail. Suffice it to mention here, the collapse of the cation-radical pair in eqn. (18) is a fast process, occurring as it does with little or no activation energy.[11] As such, the regioselectivity in the formation of the Wheland intermediate is expected to parallel the spin density on the aromatic cation radical.[37,51] Indeed, the spin densities on the cation radicals depicted in Fig. 3 show a strong correlation with the isomeric product distributions obtained in the nitration of naphthalene (Table 3), 1-/2-methylnaphthalene (Table 4) and 1,4-dimethylnaphthalene (Table 5). In particular, the preponderant formation of 1-nitronaphthalene accords with the high spin density on the α-carbon of naphthalene.[52] Similarly, the formation of the 4-nitro isomer as the major product from 1-methylnaphthalene also follows from the high spin density at the 4-position.[53] Moreover the product distribution observed in Table 4 generally follows the track of the spin densities at the various nuclear positions of the 1-methylnaphthalene cation radical in the order: 4 > 1 > 5 > 8 > 2 > 3.[53] The somewhat higher yield of the 2-nitro isomer than was expected from the spin densities may be due to the contribution from *ipso* attack at the 1-position followed by 1,2-NO_2 shift [compare eqn. 15(b)]. It is also noteworthy that 2-methylnaphthalene affords the 1-nitro derivative as the major isomer from both the thermal nitration with nitric acid in acetic anhydride[26] and the charge-transfer nitration with tetranitromethane, in accord with the large value of the spin density at the α-position of the 2-methylnaphthalene

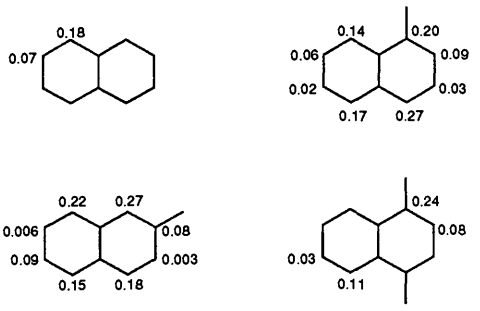


Fig. 3 UHF spin densities in the cation radicals of naphthalene, 1-/2-methylnaphthalene and 1,4-dimethylnaphthalene[52,53]

cation radical.[53] Most importantly, the high spin density at the 1-position of the 1,4-dimethylnaphthalene cation radical[53] predicts the predominant *ipso* attack, as in the formation of the adducts **1**, **3** and **4** in eqns. (5), (7) and (12), respectively. Moreover, the competitive formation 1,4-dimethyl-2-nitronaphthalene in eqn. (8) indicates that the collapse of the ion-radical pair at the 2-position is a minor pathway. In this regard, the direct exposure of NO_2 to the 1,4-dimethylnaphthalene cation radical salt,[54–56,*] as reported by Eberson and Radner,[16] also probably involves *ipso* attack as the primary process. If so, the 2-nitro isomer arises from a subsequent 1,2-NO_2 shift [eqn. (15b)] followed by proton loss in competition with a minor pathway involving the direct attack of NO_2 at the 2-position.

Comments on the Electrophilic Nitration of the Naphthalenes.—The uniform patterns of nitration products in Tables 3–5 are sufficient to establish the indistinguishability of electrophilic and charge-transfer nitration of naphthalene, 1-methylnaphthalene and 1,4-dimethylnaphthalene. Furthermore the unique behaviour of 1,4-dimethylnaphthalene to afford the *ipso* adducts **1**, **3** and **4** in common, points to the *ipso* Wheland intermediate **5** as the critical (high-energy) species in both electrophilic and charge-transfer activation [see eqn. (14)]. Such a reactive intermediate in electrophilic nitration is generally considered to be derived from the direct addition of the electrophile. The involvement of any other reactive species is experimentally difficult to establish in this type of thermal activation.[57] As an adiabatic process, the reactive intermediates are difficult to generate in sufficient concentrations for direct observation. Thus the rate of proton transfer from the Wheland intermediate, as established by the pioneering studies of the deuterium kinetic isotope effect by Melander,[58,59] is sufficiently fast to preclude its build-up (except in cases such as the *ipso* adducts **5** to the methylnaphthalenes). If proton loss is equally facile from each of the isomeric Wheland intermediates, the product distribution in naphthalene nitration is solely determined by the regiospecificity in the formation of the Wheland intermediates. Since the latter is defined in charge-transfer nitration during the cation-radical collapse in eqn. (18), it is reasonable to conclude from the common pattern of unique product distributions in Tables 3–5 that electrophilic nitrations of the naphthalenes arise *via* either the same or a deceptively analogous pathway.

Experimental

Materials.—Naphthalene (Matheson, Coleman & Bell) and 2-methylnaphthalene (Eastman) were recrystallized from ethanol followed by vacuum sublimation. 1-Methylnaphthalene

* Note that naphthalene cation-radical salts as isolated consist of π-dimers $(C_{10}H_8)_2^{+\bullet}$, as described by Fritz, Keller *et al.*[54–56]

(Aldrich) and 1,4-dimethylnaphthalene (Aldrich) were used as received. Tetranitromethane (TNM) was prepared and purified according to a literature procedure.[60] Acetonitrile (Fisher HPLC grade) and dichloromethane (Fisher) were first distilled from P_2O_5, then from calcium hydride and stored under an argon atmosphere. Reinecke salt and 2-nitronaphthalene from Aldrich were used as received. Nitric acid was purified by the distillation of fuming nitric acid (300 cm^3) from a mixture of urea (15 g) and sulphuric acid (500 cm^3) at ambient temperature at reduced pressures.[61] The purity of the colourless nitric acid thus obtained was checked by the titrimetric procedure reported by Elsenbauer[25] and found to be >99%. It was stored at −20 °C. Nitronium tetrafluoroborate was prepared from anhydrous nitric acid, anhydrous HF and BF_3 as described in the literature.[62] Recrystallization of the crude product from a mixture of acetonitrile and dichloromethane at −78 °C under an argon atmosphere yielded $NO_2^+BF_4^-$ as free-flowing colourless crystals. *N*-Nitropyridinium tetrafluoroborate was prepared from anhydrous pyridine and NO_2BF_4 in CH_3CN as described by Olah.[42] The pale yellow product was recrystallized from a mixture of acetonitrile and diethyl ether to yield colourless crystals of $pyNO_2^+BF_4^-$. Both nitronium tetrafluoroborate and *N*-nitropyridinium tetrafluoroborate were stored at −20 °C in a glove box under a dry nitrogen atmosphere. All subsequent manipulations of these reagents were carried out either in a glove box or in a Schlenk flask under a positive pressure of dry argon.

Instrumentation.—The electronic spectra were recorded on a Hewlett-Packard 8450A diode-array UV–VIS spectrometer. NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 90 MHz for ^1H and 22.5 MHz for ^{13}C. Proton chemical shifts are reported in ppm downfield from a $(CH_3)_4Si$ internal standard. Carbon-13 chemical shifts are reported in ppm, and the centre of the multiple resonance of $CDCl_3$ (δ 77) was taken as the reference. IR spectra were recorded on a Nicolet 10DX FT spectrometer. Melting points were determined on a Mel-Temp (Laboratory Devices) apparatus and are uncorrected. Routine GC analyses were performed on a Hewlett-Packard 5790A chromatograph equipped with a flame ionization detector, using a 12.5 M SE-30 (cross-linked methylsilicone) capillary column. For quantitative GC analysis of the reaction mixtures, tridecane (Aldrich) was added as a calibration standard. The GC–MS analysis were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP5970 mass spectrometer (EI, 70 eV).

Determination of the Formation Constant of EDA Complexes.—1,4-DMN–$pyNO_2BF_4$–CH_3CN. A 3 cm^3 aliquot of a stock acetonitrile solution of $pyNO_2^+BF_4^-$ (0.02 mol dm^{-3}) contained in a 1 cm quartz UV cuvette fitted with Teflon stopcock was cooled in an ice bath. 1,4-DMN was added with the aid of a microlitre syringe in increasing amounts, and the change in the absorbance of the CT band at 450 nm was noted after the cell had been equilibrated to 0 °C for 3 to 5 min. The concentration of 1,4-DMN was varied from 0.032 to 0.23 mol dm^{-3}. From the absorption data, the formation constant K and extinction coefficient ε were calculated using the Benesi–Hildebrand equation.[19] A plot of $[pyNO_2BF_4]/A_{CT}$ *versus* [1,4-DMN] was linear, where A_{CT} is the absorbance of the CT band at 450 nm. The plot consisted of seven points and the linear fit was obtained by the method of least squares with a correlation coefficient of at least 0.99. The value of the extinction coefficient and formation constant were evaluated from the intercept and slope, respectively, of the linear plot.

Methylnaphthalene–TNM: To a solution containing the methylnaphthalene (MN, 0.02 mol dm^{-3}; 3 cm^3) in dichloromethane, was added a known amount of tetranitromethane (TNM) with the aid of a microlitre syringe, and the CT absorbance at 450 nm was noted at 25 °C. The concentration of TNM was varied from 0.08 to 0.8 mol dm^{-3} for 1,4-DMN, 0.4 to 0.8 mol dm^{-3} for 1-MN and 0.17 to 1.2 mol dm^{-3} for 2 MN. Plots of $[MN]/A_{CT}$ *versus* [TNM] were linear as noted above.

General Procedure for the Thermal Nitration with HNO_3–Ac_2O.—The nitrating mixture was prepared by the addition of nitric acid (105 mm^3, 2.5 mmol) to acetic anhydride (5 cm^3) previously cooled to −20 °C in a solid CO_2–acetone bath. The mixture was warmed to 0 °C and stirred for 15 min. In another flask, a solution of the aromatic substrate (2 mmol) in acetic anhydride (5 cm^3) was cooled to 0 °C. The colourless nitrating mixture was added dropwise to the solution of the substrate at 0 °C. When the addition was complete, the mixture was stirred at 0 °C for an additional 1 h. The reaction mixture was cooled to −20 °C, and neutralized by the dropwise addition of aqueous ammonium hydroxide. The reaction mixture was extracted with ether, the ethereal extract was dried over anhydrous $MgSO_4$, and ether was subsequently removed *in vacuo* to afford the crude product.

Naphthalene. Nitration of naphthalene (256 mg, 2 mmol) yielded a yellow viscous oil. After addition of tridecane (200 mm^3, 0.80 mmol), the crude product was dissolved in CH_2Cl_2, and it was subjected to GC and GC–MS analysis. The products were identified as 1-nitro- and 2-nitro-naphthalene by the co-injection of an authentic sample of each. The correction (response) factor of 1- and 2-nitronaphthalenes with respect to tridecane was 1.82 and 1.94, respectively. From the GC analysis, the yield of 1-nitronaphthalene was determined to be 1.88 mmol (94%) and that of 2-nitronaphthalene was 0.12 mmol (6%). The reaction was repeated with a nitration mixture containing sodium azide (81 mg, 1.2 mmol). This reaction was complete to an extent of only 64%. The yield of 1-nitronaphthalene was determined by GC analysis to be 95% and that of 2-nitronaphthalene was 4%.

1-*Methylnaphthalene.* Nitration of 1-methylnaphthalene (280 mg, 1.9 mmol) yielded a yellow viscous oil. The crude product was chromatographed on neutral alumina. Elution with dichloromethane yielded a pale yellow solid which was identified as 1-methyl-4-nitronaphthalene after recrystallization from methanol: m.p. 71 °C (lit.,[26a] 71–72 °C); $\delta_H(CDCl_3)$ 8.64 (m, 1 H), 8.13 (m, 2 H), 7.68 (m, 2 H), 7.37 (m, 1 H) and 2.77 (s, 3 H); *m/z* (EI, 70 eV) 187 (M^+, 66), 159 (17), 157 (8), 141 (32), 140 (11), 139 (43), 130 (22), 129 (52), 128 (60), 127 (23), 116 (12) and 115 (100).

Further elution with dichloromethane yielded a small amount of a colourless viscous oil which was identified as 1-acetoxy-1-methylnaphthalene: ν_{max}(neat)/cm^{-1} 1754 (C=O), 1540, 1368, 1204, 1144, 1051, 898, 843, 767 and 750; $\delta_H(CDCl_3)$ 7.87 (m, 2 H), 7.53 (m, 2 H), 7.16 (m, 2 H), 2.61 (s, 3 H, 1-CH_3) and 2.39 (s, 3 H, $COCH_3$); *m/z* (EI, 70 eV) 200 (M^+, 35), 159 (41), 158 (99), 157 ($M^+ - OCOCH_3$, 100), 130 (26) 129 (65), 128 (88), 127 (40) and 115 (24).

Mass spectral data of nitro-1-methylnaphthalenes: *m/z* (EI, 70 eV) 2-NO_2: 187 (M^+, 28) 170 (46), 142 (34), 141 (18), 140 (13), 139 (28), 128 (14), 116 (12) and 115 (100); 5-NO_2: 187 (M^+, 60), 142 (14), 141 (26), 140 (12), 139 (42), 131 (11), 130 (44), 129 (30), 128 (46), 127 (21), 116 (21) and 115 (100); 8-NO_2: 187 (M^+, 27), 170 (71), 141 (18), 140 (23), 139 (37), 128 (17), 127 (16), 116 (12) and 115 (100); 3-NO_2: 187 (M^+, 100), 141 (65), 139 (30), 129 (32), 128 (14) and 115 (75).

The other isomeric nitro-1-methylnaphthalenes were not separated, and they were recovered from the column as a mixture. The original reaction mixture was also analysed by GC, and the products were identified by GC–MS analysis. The order of elution of the isomers was in the following order: 8-NO_2 (3.39 min), 2-NO_2 (4.01 min), 5-NO_2 (4.22 min), 4-NO_2

(4.51 min) and 3-NO_2 (4.84 min) at 175 °C (isothermal conditions). The same order of elution was reported by Alcorn and Wells[26] under different GC conditions. The mass spectral fragmentation pattern of the various isomers of nitronaphthalenes was reported previously.[16] Based on the GC peak integration, (and assuming a constant response of the nitro-1-methylnaphthalene isomers), the relative isomer distribution was calculated to be 2-NO_2 (25%), 3-NO_2 (2%), 4-NO_2 (44%), 5-NO_2 (7%) and 8-NO_2 (8%).

2-Methylnaphthalene. Nitration of 2-methylnaphthalene (284 mg, 2 mmol) yielded a yellow solid. Chromatographic separation of the crude product on neutral alumina with dichloromethane yielded 2-methyl-1-nitronaphthalene: m.p. 80 °C (lit.,[26a] 81 °C); $\delta_H(CDCl_3)$ 7.86 (d, 2 H, J = 8.6 Hz), 7.58 (m, 2 H), 7.33 (d, 2 H, J = 8.6 Hz) and 2.49 (s, 3 H); *m/z* (EI, 70 eV) 187 (M^+, 62), 170 (11), 142 (33), 141 (28), 140 (14), 139 (38), 130 (23), 129 (33), 128 (45), 127 (23), 116 (22) and 115 (100). The yield of 2-methyl-1-nitronaphthalene was 61%. The other isomers were not separated by either column chromatography on alumina or by capillary column GC.

Thermal Nitration with $pyNO_2^+BF_4^-$ *in* CH_3CN.—*Naphthalene.* To a stirred colourless solution of *N*-nitropyridinium tetrafluoroborate (64 mg, 0.3 mmol) in dry acetonitrile (3 cm^3) under argon, was added naphthalene (19 mg, 0.15 mmol) at room temperature. Initially a very bright yellow colour appeared which faded within an hour to give a very pale yellow solution. Upon addition of 10 cm^3 of ether, a white solid precipitated which was identified as pyridinium tetrafluoroborate by comparison of its ^1H NMR spectrum with that of an authentic sample. The product mixture contained 1-nitronaphthalene (89%) and 2-nitronaphthalene (9%) by GC analysis.

1-Methylnaphthalene. Nitration of 1-methylnaphthalene (20 mm^3; 0.15 mmol) with *N*-nitropyridinium tetrafluoroborate (0.3 mmol) in acetonitrile (as described above) yielded a mixture of mono-nitrated products according to GC–MS analysis. The isomer distribution based on GC peak integration was: 8-NO_2 (7%), 2-NO_2 (31%), 5-NO_2 (8%), 4-NO_2 (52%) and 3-NO_2 (2%).

1,4-Dimethylnaphthalene. A mixture of 1,4-dimethylnaphthalene (46 mm^3, 0.3 mmol) and *N*-nitropyridinium tetrafluoroborate (63 mg, 0.3 mmol) in acetonitrile (5 cm^3) was stirred for 3 h at 50 °C (water bath). Addition of ether (20 cm^3) yielded a colourless precipitate, which was identified as pyridinium tetrafluoroborate. The solution was evaporated to dryness, and then analysed by ^1H NMR spectroscopy and GC. The major product was identified as 4-methyl-1-nitromethylnaphthalene by comparison of the ^1H NMR spectrum and GC retention time with those of an authentic sample [kindly donated by L. Eberson]. $\delta_H(CDCl_3)$ 8.00 (m, 2 H), 7.44 (m, 4 H), 5.86 (s, 2 H, CH_2NO_2), 2.71 (s, 3 H) ppm. *m/z* (EI, 70 eV) 201 (M^+, 2), 156 (13), 155 ($M^+ - NO_2$, 100), 153 (18), 152 (13) and 128 (14). The minor product was identified as 1,4-dimethyl-2-nitronaphthalene by spectral and GC comparison with the product obtained from the nitration of 1,4-dimethylnaphthalene with $NO_2^+BF_4^-$, as described below. The yields of 4-methyl-1-nitromethylnaphthalene (87%) and 1,4-dimethyl-2-nitronaphthalene (8%), were ascertained from the integration of the methyl and methylene resonances in the ^1H NMR spectrum with nitromethane as the internal standard.

Nitration of 1,4-*DMN with* NO_2BF_4.—To a stirred ice-cold slurry of nitronium tetrafluoroborate (22 mg, 0.16 mmol) in dichloromethane (2 cm^3) under an argon atmosphere, was added dropwise a solution of 1,4-dimethylnaphthalene (25 mm^3, 0.16 mmol) in dichloromethane (2 cm^3). The solution immediately turned pale green with the simultaneous dissolution of nitronium tetrafluoroborate. After being stirred for an hour, the reaction was quenched with water. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed *in vacuo*. Analysis of the crude product by ^1H NMR spectroscopy and GC indicated the presence of unchanged starting material (0.05 mmol, 30%) and a single product with methyl resonances at 2.69 and 2.79 ppm (0.12 mmol, 75%). A preparative-scale reaction was carried out as described above using 2.5 cm^3 of 1,4-dimethylnaphthalene (0.016 mol) and 2.19 g of nitronium tetrafluoroborate (0.016 mol) in dichloromethane (60 cm^3) at 0 °C. The pure product was isolated (1.61 g, 50% yield) after column chromatography on neutral alumina and identified as 1,4-dimethyl-2-nitronaphthalene. It was recrystallized from methanol. M.p. 69–70 °C (lit.,[24] 67–68 °C); ν_{max}(KBr)/cm^{-1} 3082, 2980, 2930, 1589, 1521, 1507, 1415, 1385, 1341, 1166, 1032, 887, 883, 807, and 756; $\delta_H(CDCl_3)$ 8.14 (m, 3 H), 7.63 (m, 2 H), 2.79 (s, 3 H) and 2.69 (s, 3 H); $\delta_C(CDCl_3)$ 147.4, 144.7, 134.3, 133.8, 132.5, 128.1, 127.3, 126.3, 124.8, 120.4, 19.2 and 14.2; *m/z* (EI, 70 eV) 201 (M^+, 52), 184 (65), 156 (74), 155 (19), 154 (28), 153 (65), 152 (52), 151 (18), 141 (11), 139 (19), 129 (100), 128 (77), 127 (38) and 115 (50).

Charge-transfer Nitration

General Procedure.—Photolysis of the charge-transfer complexes was carried out in a 1 cm quartz cuvette fitted with a Teflon stopcock, and the reaction mixture was constantly stirred magnetically. The cuvette was immersed in water contained in a transparent Pyrex Dewar. Photolysis at −40 °C was carried out by immersion of the cuvette in a solid CO_2–acetone bath contained in a Pyrex Dewar. A continuous stream of dry nitrogen minimized the condensation of moisture on the window of the Dewar. The reactions were generally followed by observing the disappearance of the CT band by UV–VIS spectroscopy. The output from either a 450 W xenon lamp (Osram XBO 450 W OFR) or a 500 W mercury lamp (Osram HBO 500 W 2L2) was first passed through an IR water filter, then a Corning sharp cut-off filter, and finally focussed onto the cuvette. Corning cut-off filters CS-3-72 (λ < 425 nm) and CS-3-73 (λ < 415 nm) were used to irradiate specifically the charge-transfer bands of the complexes.

Charge-transfer Nitration with $pyNO_2^+BF_4^-$.—*Naphthalene.* A solution containing *N*-nitropyridinium tetrafluoroborate (0.125 g, 0.6 mmol) in acetonitrile (3 cm^3) was cooled to −40 °C in a solid CO_2–acetone bath. Naphthalene (0.038 g, 0.3 mmol) was added, and the mixture was stirred at −40 °C until all the naphthalene dissolved. A 3 cm^3 aliquot of this mixture was transferred to a 1 cm quartz cuvette maintained at −40 °C, and the solution was photolysed at λ > 425 nm for 3 h. The residual solution was left in the dark at −40 °C for 3 h. Both the photolysed and the control (dark) solutions were worked-up as follows. Water was added at −40 °C and the frozen mixture was warmed to room temperature. The mixture was extracted with ether, the ether extract dried over anhydrous $MgSO_4$, and the solvent was removed on the rotary evaporator. GC analysis of the photolysed solution indicated the presence of naphthalene (0.054 mmol, 36%), 1-nitronaphthalene (0.08 mmol, 53%) and 2-nitronaphthalene (0.014 mmol, 9.3%). GC analysis of the control (dark) solution indicated the presence of only unchanged naphthalene.

1-Methylnaphthalene. Charge-transfer nitration of 1-methylnaphthalene (0.045 g, 0.3 mmol) as described for naphthalene yielded a mixture of nitro-1-methylnaphthalenes together with unchanged 1-methylnaphthalene (50%) after 3 h. The products were identified by GC analysis in comparison with the thermal nitration products. Based on the integraion of the GC peaks, the isomer distribution was: 8-NO_2 (8%), 2-NO_2 (30%), 3-NO_2 (2%), 5-NO_2 (8%), 4-NO_2 (52%). GC analysis of the control

(dark) solution indicated the presence of only 1-methylnaphthalene.

1,4-*Dimethylnaphthalene.* Charge-transfer irradiation was carried out at 0 °C in an ice bath. Thus a red solution containing 1,4-dimethylnaphthalene (50 mm^3, 0.3 mmol) and *N*-nitropyridinium tetrafluoroborate (64 mg, 0.3 mmol) in acetonitrile (3 cm^3) was irradiated at $\lambda > 425$ nm. Bleaching of the red solution was observed, and after 3 h of irradiation, the yellow solution was diluted with ether. The colourless crystals of **1** upon ^1H NMR analysis (in $CDCl_3$) showed singlet resonances at 2.29, 2.24, 2.21 and 2.06 ppm in the methyl region and resonances at 6.45 and 6.42 ppm in the alkene region. The solution of **1** also showed resonances due to the pyridinium moiety at 8.75 and 8.10 ppm. Based on the similarity of the ^1H NMR spectrum with those of the *ipso* adducts **3** and **4**,[24] it was assigned to *N*-(1,4-dimethyl-4-nitro-1,4-dihydronaphthyl)-pyridinium tetrafluoroborate. The yield of this adduct **1** was 70%. The crude product also contained 4-methyl-1-nitromethylnaphthalene (29%). When the photolysate was allowed to stand at room temperature overnight the pyridinium adduct **1** decomposed to yield only 4-methyl-1-nitromethylnaphthalene and pyridinium tetrafluoroborate. A control (dark) reaction carried out 0 °C for 16 h did not afford any products, and the starting materials were recovered intact.

Charge-transfer Nitration with Tetranitromethane.—Naphthalene. A reddish brown solution containing naphthalene (20 mg, 0.15 mmol) and an excess of tetranitromethane (300 mm^3, 2.5 mmol) in acetonitrile was irradiated at $\lambda > 425$ nm for 17 h at ambient temperature. During the photolysis, bleaching of the CT band was observed, and the solution turned yellow finally. After removal of solvent and the excess of TNM, the reaction mixture was diluted with dichloromethane, and the mixture was repeatedly extracted with water to remove the nitroform. The yield of nitroform was estimated by spectrophotometry at λ = 350 nm (ε = 14 000 $dm^3\ mol^{-1}\ cm^{-1}$) to be 57% (0.085 mmol). The organic layer was analysed by GC, and it contained unchanged naphthalene (0.06 mmol), 1-nitronaphthalene (0.074 mmol) and 2-nitrophthalene (0.01 mmol).

1-*Methylnaphthalene.* A reddish brown solution containing 1-methylnaphthalene (42.6 mg, 0.3 mmol) and an excess of TNM (300 mm^3, 2.5 mmol) in acetonitrile (3 cm^3) was irradiated at $\lambda > 425$ nm for 14 h. Work-up yielded nitroform 32% (0.09 mmol), and the ^1H NMR spectrum of the crude product showed resonances at 2.83 and 2.77 due to the methyl group in 2- and 4-nitro-1-methylnaphthalene, respectively, as major products. Additional singlet resonances at 2.07 and 2.02 and multiple resonances between 5 and 7 ppm were assigned to a mixture of *ipso* adducts. GC analysis of the crude product indicated the presence of five isomeric mono-nitro-1-methylnaphthalenes as follows: 8-NO_2 (7%), 2-NO_2 (10%), 5-NO_2 (9%), 4-NO_2 (59%) and 3-NO_2 (15%).

2-*Methylnaphthalene.* A reddish brown solution containing 2-methylnaphthalene (43 mg, 0.3 mmol) and TNM (250 mm^3, 2 mmol) was irradiated at $\lambda > 425$ nm for 16 h. After the usual work-up, the ^1H NMR spectrum of the crude product showed methyl resonances at 2.49, 2.54 and 2.57 ppm due to the isomeric nitro-2-methylnaphthalenes. It did not exhibit resonances in the alkene region 5-7 ppm. GC and GC–MS analysis indicated 2-methyl-1-nitronaphthalene to be the major product. The other isomers were not separated by capillary GC.

1,4-*Dimethylnaphthalene.* (*a*) *In* CH_2Cl_2. A dark red solution containing 1,4-dimethylnaphthalene (1 cm^3, 6.5 mmol) and TNM (2 cm^3, 16.7 mmol) in dichloromethane (10 cm^3) was irradiated at λ = 425 nm at 0 °C for 8 h. Upon the removal of the solvent and the excess of TNM, the reddish brown slurry was dissolved in ether (10 cm^3) and left at −20 °C overnight. The pale yellow solid was identified as 4-methyl-1-nitromethylnaphthalene (0.158 mg). The solvent was removed from the mother liquor, and the resulting red solid was recrystallized twice from a mixture of ether and hexane (1:1 v/v) to yield a colourless solid **3a** identified as 1,4-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene. $\delta_H(CDCl_3)$ 7.75 (m, 4 H), 6.67 (d, 1 H, J = 10.7 Hz), 6.24 (d, 1 H, J = 10.7 Hz), 2.20 (s, 3 H), 2.10 (s, 3 H); $\delta_C(CDCl_3)$ 133.9, 131.5, 131.2, 130.6, 130.1, 128.2, 127.0, 126.3, 86.7, 49.2, 26.8 and 26.3. The stereochemistry of this adduct was found to be *trans* by X-ray crystallography (*vide infra*). Careful examination of the ^1H NMR spectrum of the crude product indicated the presence of a minor, presumably the *cis*, isomer with methyl resonances at 2.06 and 1.96 ppm and alkene resonances at 6.62 and 6.41 ppm. The minor isomer was not isolated. The ratio of the *cis*/*trans* isomers was 1:4, by the integration of the methyl resonances in the ^1H NMR spectrum. The yield of the various products from this reaction were 4-methyl-1-nitromethylnaphthalene (35%), 1,4-dimethyl-2-nitronaphthalene (9%) and the mixture of the *cis*- and *trans*-adducts (45%).

Single crystals of **3a** suitable for the X-ray crystallographic analysis were obtained by the slow diffusion of hexane into a saturated solution of the adduct in ether at room temperature. Thus a small tube containing 100 mg of the adduct in 2 cm^3 of ether was suspended in a large round-bottomed flask containing hexane. The round-bottomed flask was stoppered and left undisturbed overnight at room temperature. A colourless single crystal of the adduct was immediately subjected to an X-ray crystallographic analysis (*vide infra*).

(*b*) *In* CH_3CN. A reddish brown solution containing 1,4-dimethylnaphthalene (46 mm^3, 0.3 mmol) and TNM (100 mm^3, 0.84 mmol) in acetonitrile (3 cm^3) was photolysed at 0 °C at $\lambda > 425$ nm, and the reaction was visually monitored by the bleaching of the CT band. After 3 h, the acetonitrile and excess of TNM were removed, and the crude product was analysed by ^1H NMR spectroscopy using CH_3NO_2 as the internal standard. The product mixture consisted of a mixture of *cis*- and *trans*-adducts (65%) in a 1:3 ratio, 4-methyl-1-nitromethylnaphthalene (23%) and 1,4-dimethyl-2-nitronaphthalene (8%). When the same photolysis was carried out at ambient temperatures, the product mixture consisted of a mixture of *cis*- and *trans*-adducts (43%), 4-methyl-1-nitromethylnaphthalene (40%) and 1,4-dimethyl-2-nitronaphthalene (9%). In another experiment, a solution containing 1,4-dimethylnaphthalene (23 mm^3, 0.15 mmol) and TNM (100 mm^3, 0.84 mmol) in CD_3CN (1.5 cm^3) was irradiated directly in the NMR probe at −30 °C. The output from a 500 W Hg lamp, filtered through a Corning cut-off filter ($\lambda < 425$ nm), was sent through a quartz light guide directly into the sample. After irradiation for 2 h, all the starting material disappeared, and only the resonances of the adduct were observed in the alkene region 5–7 ppm. Under these conditions, only a small amount of the side-chain nitration product was noted.

Determination of the Quantum Yield of CT Photonitration.—The quantum efficiency of charge-transfer nitration of 1,4-dimethylnaphthalene with TNM was determined in CH_2Cl_2 and CH_3CN. The output from a 1 kW mercury–xenon lamp was passed through an IR water filter, an interference filter (λ = 505 ± 5 nm FWHM, Edmund Scientific), and then focussed onto the sample. The lamp output was calibrated with a potassium Reineckate actinometer.[63] The photon flux of the lamp was 2.5 ± 0.1 × 10^{-7} einstein min^{-1}. The absorbance of the solutions irradiated was always maintained at >2 (at 505 nm) to ensure the complete absorption of light. Corrections were made for any transmitted light (<5%). The actinometry solutions contained 1,4-dimethylnaphthalene (23 mm^3, 0.15 mmol) and TNM (500 mm^3, 4.2 mmol) in 3 cm^3 of the solvent. The extent of the reaction was monitored by the bleaching of the

Table 6 Bond Distances.

Atom 1	Atom 2	d/Å[a]	Atom 1	Atom 2	d/Å	Atom 1	Atom 2	d/Å
O(1)	N(1)	1.224(3)	N(2)	C(11)	1.517(3)	C(4)	C(5)	1.532(3)
O(2)	N(1)	1.216(3)	N(3)	C(11)	1.556(3)	C(4)	C(13)	1.509(3)
O(3)	N(2)	1.214(2)	N(4)	C(11)	1.539(3)	C(5)	C(6)	1.390(3)
O(4)	N(2)	1.210(3)	C(1)	C(2)	1.583(3)	C(5)	C(10)	1.402(3)
O(5)	N(3)	1.190(3)	C(1)	C(10)	1.524(3)	C(6)	C(7)	1.377(4)
O(6)	N(3)	1.223(3)	C(1)	C(11)	1.578(3)	C(7)	C(8)	1.377(4)
O(7)	N(4)	1.217(3)	C(1)	C(12)	1.531(3)	C(8)	C(9)	1.367(3)
O(8)	N(4)	1.209(3)	C(2)	C(3)	1.312(3)	C(9)	C(10)	1.405(3)
N(1)	C(4)	1.584(3)	C(3)	C(4)	1.471(3)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 7 Bond angles.

Atom 1	Atom 2	Atom 3	Angle/°[a]	Atom 1	Atom 2	Atom 3	Angle/°	Atom 1	Atom 2	Atom 3	Angle/°
O(1)	N(1)	O(2)	125.7(3)	C(2)	C(1)	C(12)	108.5(2)	C(6)	C(5)	C(10)	119.7(2)
O(1)	N(1)	C(4)	116.9(3)	C(10)	C(1)	C(11)	110.9(2)	C(5)	C(6)	C(7)	121.8(3)
O(2)	N(1)	C(4)	117.4(2)	C(10)	C(1)	C(12)	109.7(2)	C(6)	C(7)	C(8)	118.8(3)
O(3)	N(2)	O(4)	126.0(3)	C(11)	C(1)	C(12)	112.1(2)	C(7)	C(8)	C(9)	120.5(3)
O(3)	N(2)	C(11)	116.9(2)	C(1)	C(2)	C(3)	124.2(2)	C(8)	C(9)	C(10)	122.1(3)
O(4)	N(2)	C(11)	116.9(2)	C(2)	C(3)	C(4)	125.9(2)	C(1)	C(10)	C(5)	122.8(2)
O(5)	N(3)	O(6)	128.6(3)	N(1)	C(4)	C(3)	104(9(2)	C(1)	C(10)	C(9)	119.9(2)
O(5)	N(3)	C(11)	119.2(2)	N(1)	C(4)	C(5)	105.6(2)	C(5)	C(10)	C(9)	117.1(2)
O(6)	N(3)	C(11)	112.1(2)	N(1)	C(4)	C(13)	107.6(2)	N(2)	C(11)	N(3)	107.4(2)
O(7)	N(4)	O(8)	126.1(2)	C(3)	C(4)	C(5)	113.1(2)	N(2)	C(11)	N(4)	105.1(2)
O(7)	N(4)	C(11)	114.9(2)	C(3)	C(4)	C(13)	111.7(2)	N(2)	C(11)	C(1)	110.4(2)
O(8)	N(4)	C(11)	119.0(2)	C(5)	C(4)	C(13)	113.2(2)	N(3)	C(11)	N(4)	102.2(2)
C(2)	C(1)	C(10)	111.8(2)	C(4)	C(5)	C(6)	118.4(2)	N(3)	C(11)	C(1)	113.8(2)
C(2)	C(1)	C(11)	103.7(2)	C(4)	C(5)	C(10)	121.9(2)	N(4)	C(11)	C(1)	117.1(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 8 Positional parameters and their estimated standard deviations.

Atom	x	y	z
O(1)	0.121 8(3)	0.859 1(4)	0.663 2(4)
O(2)	0.145 2(2)	0.818 4(4)	0.449 2(3)
O(3)	0.366 7(2)	0.356 0(4)	0.766 0(3)
O(4)	0.495 1(3)	0.372 8(5)	0.720 0(3)
O(5)	0.333 6(3)	0.071 8(4)	0.678 8(3)
O(6)	0.294 3(3)	0.065 4(4)	0.492 4(3)
O(7)	0.484 2(2)	0.154 6(4)	0.549 2(3)
O(8)	0.445 2(2)	0.363 1(4)	0.452 9(3)
N(1)	0.160 1(3)	0.794 3(5)	0.601 1(4)
N(2)	0.412 4(3)	0.342 1(4)	0.699 9(3)
N(3)	0.325 7(3)	0.124 8(4)	0.586 9(3)
N(4)	0.436 1(3)	0.268 2(5)	0.520 0(3)
C(1)	0.276 9(3)	0.404 7(5)	0.520 4(4)
C(2)	0.325 6(3)	0.560 2(5)	0.537 4(4)
C(3)	0.304 6(3)	0.672 0(5)	0.596 0(4)
C(4)	0.234 8(3)	0.666 6(5)	0.658 6(4)
C(5)	0.179 0(3)	0.517 6(5)	0.640 5(4)
C(6)	0.105 6(3)	0.504 1(6)	0.687 5(4)
C(7)	0.051 3(3)	0.374 5(7)	0.673 7(5)
C(8)	0.069 8(3)	0.256 6(6)	0.610 0(5)
C(9)	0.141 3(3)	0.267 8(6)	0.562 2(4)
C(10)	0.199 5(3)	0.396 7(5)	0.577 5(4)
C(11)	0.359 5(3)	0.290 5(5)	0.578 8(4)
C(12)	0.234 4(4)	0.375 4(6)	0.391 4(4)
C(13)	0.278 2(4)	0.707 6(6)	0.783 5(4)

CT band between 500 and 580 nm, and the reaction was allowed to proceed to 10–15% conversion. The quantum yield for the CT photonitration of 1,4-dimethylnaphthalene was found to be 0.29 and 0.50 in acetonitrile and dichloromethane, respectively.

X-*Ray Crystallography of the* ipso *Adduct* **3**.—A large, clear, fragment of approximate dimensions 0.40 × 0.40 × 0.25 mm was cut from a very large plate and mounted on a glass fibre in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo-Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement were: temperature 22 °C; space group $P2_1/c$, monoclinic; cell constants a = 14.890(6), b = 8.802(5), c = 12.247(7) Å, β = 108.05(4)°; V = 1526 Å^3; molecular formula $C_{13}H_{12}N_4O_8$; formula weight 352.26; formula units per cell z = 4; density ρ = 1.53 g cm^{-3}; absorption coefficient μ = 1.22 cm^{-1}; radiation (Mo-Kα) λ = 0.710 73 Å; collection range for unit-cell determination 15 ⩽ 2θ ⩽ 30°; number of reflections 25; collection range 4 ⩽ 2θ ⩽ 52°; scan width Δθ = (1.10 + 0.35 tanθ)°; maximum scan time 90 s; scan speed range 0.7–5.0° min^{-1}; total data collected 3158; independent data $I > 3\sigma(I)$ 1441; $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ 0.057; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ 0.051; weights: $w = \sigma(F)^{-2}$. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was unambiguously shown to be $P2_1/c$. Intensities were measured using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a verification of the crystal stability and electronic reliability, and these did not vary significantly. In reducing the data, Lorentz and polarization factors were applied, however no correction for absorption was made due to the small absorption coefficient. The structure was solved by MULTAN,[64] which revealed the position of all 25 non-hydrogen atoms in the asymmetric unit. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and held fixed. Hydrogen isotropic temperature factors were fixed on the thermal motion of the associated carbons. After all shift/esd

ratios were less than 0.1, convergence was reached at the agreement factors listed above. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement, and the final difference density map showed no peaks greater than 0.20 e $Å^{-3}$. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. Bond distances, bond angles and non-hydrogen positional parameters are given in Tables 6–8. Isotropic and anisotropic refinements and temperature factors have been deposited at the Cambridge Crystallographic Data Centre.*

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