

Photochemical Nitration by Tetranitromethane. Part XXII.† Adducts as Precursors of Nitro Substitution Products from the Photolysis of 1-Methoxynaphthalene–Tetranitromethane, Dehydrodimer Formation and the Regiochemistry of Trinitromethanide Ion Attack on the Radical Cation of 1-Methoxynaphthalene

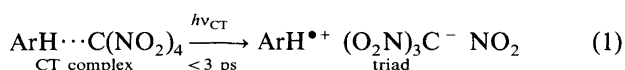
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The photolysis of 1-methoxynaphthalene with tetranitromethane in dichloromethane at 20°C gives mainly 1-methoxy-4-nitronaphthalene (**2**) and 1-methoxy-4-trinitromethylnaphthalene (**5**), together with smaller amounts of 1-methoxy-2-nitronaphthalene (**1**) and the two adducts, 4-methoxy-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene (**6**) and 4-methoxy-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (**7**). Photolysis in the presence of trifluoroacetic acid under otherwise identical conditions gives initially exclusively 4,4'-dimethoxy-1,1'-binaphthalene (**10**) as the product, trinitromethanide ion being eliminated as a reactant by protonation to give nitroform. EPR spectral and cyclic voltammetric data indicate that the radical cation **10**^{•+} is present in this reaction. Evidence is presented that, in the absence of trifluoroacetic acid, the reaction products **1**, **2** and **5** all arise by decomposition of highly labile nitro-trinitromethyl or nitro-trinitromethyl adducts **11**, **12** and **14**. The regiochemistry of attack of trinitromethanide ion on the radical cation of 1-methoxynaphthalene is discussed, and it is proposed that this step is reversible, the regiochemistry of attack being determined by the relative energies of the carbon radicals formed in the process. X-Ray crystal structures are reported for 1-methoxy-4-trinitromethylnaphthalene (**5**) and 4,4'-dimethoxy-1,1'-binaphthalene (**10**).

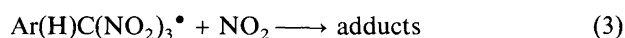
The photochemical addition of tetranitromethane to aromatic compounds (ArH) by excitation of the ArH–tetranitromethane charge-transfer (CT) complex by light matching the wavelength of the CT band has been shown^{1–3} to occur by recombination of a triad consisting of ArH^{•+}, trinitromethanide ion, and nitrogen dioxide [eqn. (1)].⁴



† Part XXI, see Ref. 6.

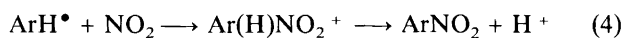
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The first chemical step which occurs, leading to the formation of adducts, is reaction between ArH^{•+} and trinitromethanide ion [eqn. (2)] to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)].^{1–3}



The ArH^{•+}–trinitromethanide reaction can be blocked by conducting the photolysis in the presence of trifluoroacetic acid (TFA), thus rendering trinitromethanide ion

unreactive by protonation and favouring slower reactions, such as coupling between $\text{ArH}^{\bullet+}$ and NO_2 [eqn. (4)]. Preparatively, this was shown by a significant change in

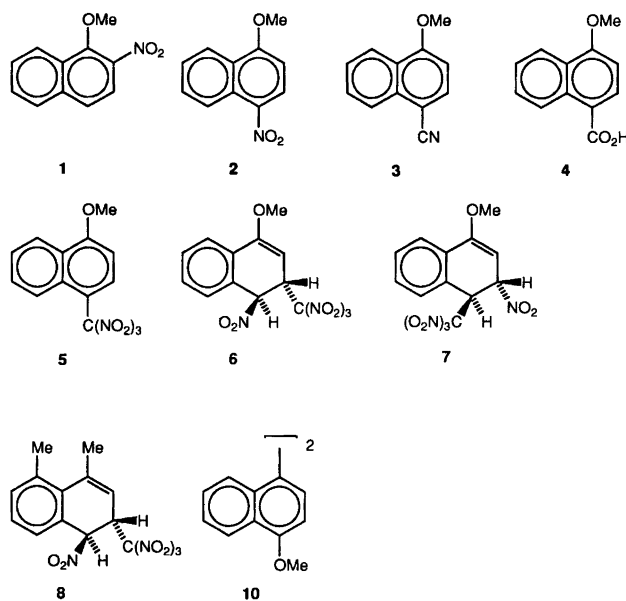


product distribution, for example in the case of naphthalene a switch in adduct/nitro substitution product ratio from 7.8 to 0.23 upon addition of 1.0 mol dm^{-3} TFA. A semiquantitative EPR spectral method was also developed to demonstrate the appearance of $\text{ArH}^{\bullet+}$ once the trinitromethanide ion had been suppressed by protonation.¹⁻³

For naphthalene⁵ and a series of methyl-substituted naphthalenes^{6,7} the attack of the trinitromethanide ion on the radical cation of the aromatic substrate [eqn. (2)] appears to occur preferentially at those ring positions in the radical cation favoured by their atomic charges; this effect is sometimes moderated by steric effects between the attacking trinitromethanide ion and methyl substituents on β or *peri* ring positions. For the above substrates, the point of attack of the trinitromethanide anion on the radical cation [eqn. (2)] could be demonstrated unequivocally by the isolation of high yields of the adducts formed by radical coupling of nitrogen dioxide with the delocalized carbon radical [eqn. (3)].

In contrast, the photolysis of charge-transfer complexes of substituted anisoles and tetranitromethane in dichloromethane give high yields (60–95%) of products of apparent aromatic substitution, the trinitromethylanisoles.⁸ The photolysis of these charge-transfer complexes in acetonitrile were reported to give predominantly nitro substitution products.⁸ Although adducts were detected^{8b} among the products from the photolyses of 4-chloro- and 4-methylanisoles, and characterized spectroscopically in more detail for 4-chloroanisole,⁹ the chemical-photocatalytic properties of these adducts were such that only a small proportion of the nitro or trinitromethyl substitution products could be safely accounted for by addition-elimination mechanisms.⁸

In a study of the photolysis of 1-methoxynaphthalene-tetranitromethane charge-transfer complexes in dichloromethane, with product analysis by GLC, a high yield of a mixture of the 2-nitro- and 4-nitro-1-methoxynaphthalenes, **1** and **2**, was detected with minor amounts (1–6%) of 4-methoxy-1-naphthonitrile (**3**).¹⁰ Further, from these reactions 4-methoxy-1-naphthoic acid (**4**) precipitated during or after photolysis; in the presence of a variety of alcohols the corresponding esters of **4** were instead formed in yields of up to 47%. The formation of 4-methoxy-1-naphthoic acid (**4**) or its esters, and the detection of 4-methoxy-1-naphthonitrile (**3**) on GLC analysis, were seen as evidence that 1-methoxy-4-trinitromethylnaphthalene (**5**) was present in the reaction mixture and underwent hydrolysis to the carboxylic acid or ester formation in the prevailing acidic conditions of the reaction medium, or pyrolysis in the GLC inlet system to give 4-methoxy-1-naphthonitrile (**3**).¹⁰ Although no direct evidence of



the formation of nitro-trinitromethyl adducts was obtained, such adducts were suggested as labile intermediates in the formation of the postulated 1-methoxy-4-trinitromethylnaphthalene (**5**) precursor and also at least partially in the formation of the nitro products **1** and **2**.¹⁰ Other nitration mechanisms of *thermal* nature, such as nitration by photochemically generated NO_2 (this species was shown to accumulate during photolysis), were also shown to intervene.

We now report a further study of the photolysis of the charge-transfer complex of 1-methoxynaphthalene with tetranitromethane. In addition to the isolation of 1-methoxy-4-trinitromethylnaphthalene (**5**), and the detection of two nitro-trinitromethyl adducts **6** and **7**, we present evidence that most of the products isolated, including 1-methoxy-4-nitronaphthalene (**2**), arise by the rapid decomposition of transient adducts. We also show that photolysis in the presence of TFA diverts the reaction along a third pathway, coupling of two $\text{ArH}^{\bullet+}$ to eventually give the dehydrodimer, 4,4'-dimethoxy-1,1'-binaphthalene, in almost quantitative yield.

Results

General. The photochemical experiments were performed with filtered light (cut-off $< 435 \text{ nm}$, 5 cm water IR filter, from a 300 W lamp) as described before,¹⁰ and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of $< 0^\circ\text{C}$.⁵ The crude product mixtures were stored at -20°C and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 1, 3 and 5) as soon as possible.

Photochemistry in dichloromethane at 20 °C and identification of the aromatic products. A solution of 1-methoxynaphthalene (0.4 mol dm⁻³) and tetranitromethane (0.8 mol dm⁻³) in dichloromethane was irradiated at 20 °C. The composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The solution after 1 h (conversion ~100%) after work-up contained 1-methoxy-2-nitronaphthalene (**1**) (5%), 1-methoxy-4-nitronaphthalene (**2**) (50%), 1-methoxy-4-trinitromethylnaphthalene (**5**) (35%) and the two unstable adducts **6** (6%) and **7** (3%). The aromatic compounds were separated by chromatography on a silica gel Chromatotron plate, and the nitro derivatives of 1-methoxynaphthalene **1** and **2** were identified by comparison with authentic material. The structure of 1-methoxy-4-trinitromethylnaphthalene (**5**), C₁₂H₉N₃O₇, m.p. 192–194 °C, was determined by single-crystal X-ray analysis; a perspective drawing is presented in Fig. 1, and the corresponding atomic coordinates are given in Table 2. The structure consists of two crystallographically independent molecules. Comparison of torsional angles for the two molecules reveals that for both molecules the methoxy group lies in the plane of the naphthalene ring system with the O(1)–C(9) and O(1')–C(9') bonds eclipsed with the C(1)–C(2) and C(1')–C(2') bonds, respectively. The differences between the two molecules lie in the orientation of the trinitromethyl groups relative to the ring system [e.g. torsional angles: C(4A)–C(4)–C(10)–N(3) 49.8(5)°, C(4A')–C(4')–C(10')–N(3') 56.2(6)°], and are presumably related to optimum pack-

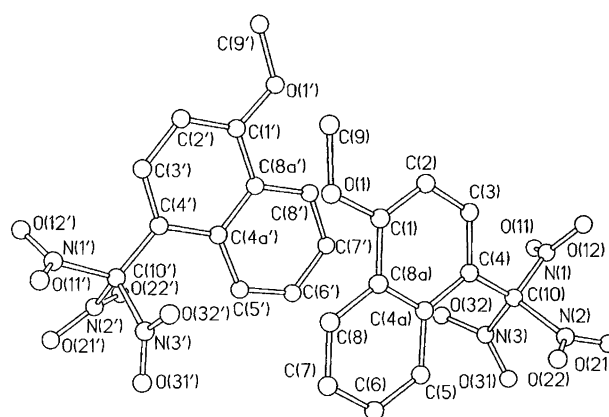


Fig. 1. Perspective drawing of compound **5**.

ing in the crystal lattice and have no chemical significance.

Neither of the unstable adducts **6** and **7** could be isolated from the Chromatotron plate, and their identification is based on consideration of NMR data derived from a product mixture for a reaction at –20 °C, below.

Extension of the reaction time for the photolysis reaction at 20 °C to 2 h (Table 1) resulted in a significant reduction in the yield of 1-methoxy-4-trinitromethylnaphthalene (**5**), and the precipitation of some 4-methoxy-1-naphthoic acid (**4**). This observation indicates clearly the origin in this reaction of the 4-methoxy-1-naphthoic acid (**4**) reported earlier.¹⁰

Table 1. Overview of yields of products from the photolysis of 1-methoxynaphthalene (0.4 mol dm⁻³) and tetranitromethane (0.8 mol dm⁻³) in dichloromethane.

| t/h | Conversion (%) | Yield (%) | | | | | | | |
|-----------|----------------|-----------|------|-----|------|------|------|------|---------|
| | | 1 | 2 | 4 | 5 | 6 | 7 | 10 | Unknown |
| At 20 °C | | | | | | | | | |
| 0.25 | 36.5 | 2.0 | 38.2 | – | 41.3 | 7.4 | 11.0 | – | – |
| 0.5 | 68.2 | 3.0 | 41.7 | – | 41.7 | 6.2 | 7.7 | – | – |
| 1 | ~100 | 5.2 | 50.4 | – | 34.6 | 6.3 | 3.3 | – | – |
| 2 | 100 | 7.3 | 57.4 | 4.8 | 24.1 | 6.5 | – | – | – |
| At –20 °C | | | | | | | | | |
| 0.5 | 53.8 | 2.0 | 42.2 | – | 40.7 | 6.3 | 8.6 | – | – |
| 1 | 92.6 | 3.1 | 47.4 | – | 34.3 | 7.2 | 8.0 | – | – |
| 2 | 100 | 5.1 | 61.4 | – | 21.4 | 10.2 | 2.0 | – | – |
| At –50 °C | | | | | | | | | |
| 0.5 | 40 | 2.0 | 42.6 | – | 40.0 | 5.8 | 12.0 | – | – |
| 1 | 60 | 3.7 | 55.4 | – | 30.1 | 6.3 | 4.7 | – | – |
| 2 | 90.5 | 4.3 | 70.2 | – | 17.3 | 6.4 | 1.7 | – | – |
| 4 | 100 | 5.5 | 89.3 | – | ~0 | 5.3 | ~0 | – | – |
| At –78 °C | | | | | | | | | |
| 0.25 | 38.9 | 5.0 | 24.3 | – | 42.7 | 4.2 | 9.7 | 11.3 | 2.7 |
| 0.5 | 77.5 | 4.7 | 37.0 | – | 36.5 | 2.9 | 6.8 | 7.8 | 4.2 |
| 1 | 85.0 | 4.7 | 37.0 | – | 11.5 | 2.9 | 2.4 | ~0 | 12.4 |

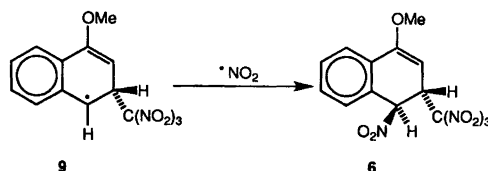
Table 2. Fractional coordinates for atoms in 1-methoxy-4-trinitromethylnaphthalene (**5**).

| Atom | $10^4 X/a$ | $10^4 Y/b$ | $10^4 Z/c$ | $10^3 U/\text{\AA}^2$ ^a |
|------------|------------|------------|------------|------------------------------------|
| Molecule 1 | | | | |
| O(1) | 5134(4) | 1138(2) | 2213(2) | 28(1) |
| O(11) | 7026(4) | 2230(2) | 5870(2) | 42(1) |
| O(12) | 6191(4) | 778(3) | 5756(2) | 40(1) |
| O(21) | 8745(4) | 139(2) | 5788(2) | 33(1) |
| O(22) | 8678(4) | -351(2) | 4655(2) | 30(1) |
| O(31) | 9913(4) | 1794(2) | 5214(2) | 30(1) |
| O(32) | 8560(4) | 2778(2) | 4665(2) | 39(1) |
| N(1) | 6931(5) | 1436(3) | 5577(2) | 29(1) |
| N(2) | 8471(4) | 231(3) | 5146(2) | 25(1) |
| N(3) | 8868(5) | 1997(3) | 4943(2) | 25(1) |
| C(1) | 5725(6) | 1144(3) | 2879(2) | 18(1) |
| C(2) | 5076(5) | 1163(3) | 3530(2) | 21(1) |
| C(3) | 5781(6) | 1180(3) | 4189(2) | 18(1) |
| C(4) | 7106(6) | 1181(3) | 4202(2) | 15(1) |
| C(4A) | 7809(6) | 1156(3) | 3524(2) | 17(1) |
| C(5) | 9190(6) | 1133(3) | 3468(2) | 26(2) |
| C(6) | 9791(6) | 1113(4) | 2799(3) | 29(1) |
| C(7) | 9089(7) | 1093(4) | 2145(3) | 29(2) |
| C(8) | 7762(7) | 1101(3) | 2177(2) | 27(2) |
| C(8A) | 7095(6) | 1127(3) | 2854(2) | 17(1) |
| C(9) | 3743(7) | 1143(4) | 2191(3) | 35(2) |
| C(10) | 7802(5) | 1203(3) | 4918(2) | 21(1) |
| Molecule 2 | | | | |
| O(1') | 3100(4) | 3618(2) | 2532(2) | 23(1) |
| O(11') | 6057(4) | 4516(2) | -565(2) | 32(1) |
| O(12') | 6782(4) | 3040(2) | -732(2) | 33(1) |
| O(21') | 7921(4) | 5276(2) | 925(2) | 32(1) |
| O(22') | 8632(4) | 4831(2) | -148(2) | 34(1) |
| O(31') | 7520(4) | 2125(2) | 544(2) | 33(1) |
| O(32') | 9222(5) | 3067(3) | 496(2) | 36(1) |
| N(1') | 6610(4) | 3771(3) | -368(2) | 24(1) |
| N(2') | 7979(4) | 4721(3) | 403(2) | 25(1) |
| N(3') | 8067(6) | 2912(3) | 493(2) | 24(1) |
| C(1') | 4032(6) | 3663(3) | 2001(2) | 16(1) |
| C(2') | 3772(5) | 3681(3) | 1266(2) | 19(1) |
| C(3') | 4806(5) | 3730(3) | 767(2) | 19(1) |
| C(4') | 6069(5) | 3762(3) | 982(2) | 17(1) |
| C(4A') | 6381(6) | 3717(3) | 1759(2) | 16(1) |
| C(5') | 7666(6) | 3713(4) | 2047(2) | 23(1) |
| C(6') | 7883(6) | 3677(3) | 2786(2) | 24(1) |
| C(7') | 6846(6) | 3650(3) | 3281(2) | 24(1) |
| C(8') | 5597(6) | 3642(3) | 3029(2) | 21(1) |
| C(9') | 1778(6) | 3590(4) | 2306(3) | 28(2) |
| C(10') | 7116(5) | 3795(3) | 422(2) | 20(1) |

^a The equivalent isotropic temperature factor in Tables 2 and 4 is defined as one-third of orthogonalized U_{ij} tensor (in \AA^2).

*Photochemistry in dichloromethane at -20°C and identification of the unstable adducts **6** and **7**.* Reaction of 1-methoxynaphthalene and tetranitromethane for 1 h, as above except at -20°C , gave a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of 1-methoxy-2-nitronaphthalene (**1**, 3%), 1-methoxy-4-nitronaphthalene (**2**, 47%), 1-methoxy-4-trinitromethylnaphthalene (**5**, 34%), and the two unstable adducts **6** (7%) and **7** (8%). The two adducts were labile in solution, with the less stable adduct **7** having a half-life of ca. 4.5 h in (^2H)-chloroform at 23°C . The structures of the two adducts

were assigned tentatively on the basis of NMR data. The more stable adduct (**6**) was assigned the 4-methoxy-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene structure. A nuclear Overhauser experiment allowed the location of H3 (δ 4.73) between the 4- OCH_3 (δ 3.79) and H2 (δ 5.50) substituents, leaving the signal at δ 5.79 to be assigned to H1 in the structure. The ^{13}C NMR spectrum for adduct **6** was partially assigned on the basis of reverse detected heteronuclear correlation spectra (HMQC). The crucial signal at δ 41.67 was assigned to C2, a chemical shift consistent with the $\text{H}-\text{C}-\text{C}(\text{NO}_2)_3$ structural feature. The assignment of the signal at δ 81.84 is as expected for the $\text{H}-\text{C}-\text{NO}_2$ structural feature at C1. Although no stereochemical information was obtainable from the spectroscopic data, the *r*-1-nitro-*t*-2-trinitromethyl stereochemistry is assigned by analogy with a similar structure **8** formed in the photolysis of 1,8-dimethylnaphthalene with tetranitromethane,⁷ and is consistent with the radical coupling of nitrogen dioxide with the carbon radical **9**, *trans* to the bulky trinitromethyl group (Scheme 1).^{5b,6,7}



Scheme 1.

For the less stable adduct (**7**), tentatively identified as 4-methoxy-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene, nuclear Overhauser experiments allowed the assignment of the signals arising from the methoxy protons (δ 3.75), H1 (δ 5.42), H2 (δ 5.22) and H3 (δ 4.48). Using reverse-detected heteronuclear correlation spectra (HMQC) only the signal due to C1 (δ 44.88) could be assigned with certainty, but this chemical shift allows the certain location of the trinitromethyl group at C1 and, given the ^1H NMR chemical shift of H2, by implication the attachment of the nitro function with the *trans* stereochemistry at C2.

*Photochemistry in dichloromethane in the presence of trifluoroacetic acid at 20°C and the identification of 4,4'-dimethoxy-1,1'-binaphthalene (**10**).* A solution of 1-methoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.8 mol dm^{-3}) was irradiated at 20°C . The composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 3). The solution after 15 min (conversion $\sim 27\%$) contained essentially a mixture of 4,4'-dimethoxy-1,1'-binaphthalene (**10**) and unreacted 1-methoxynaphthalene. The dehydromer **10** was isolated by crystallization from dichloromethane and its structure determined by single-crystal X-ray analysis. A perspective drawing of **10**, $\text{C}_{22}\text{H}_{18}\text{O}_2$, m.p. $264\text{--}266^\circ\text{C}$, is presented in Fig. 2, and

Table 3. Overview of yields of products from the photolysis of 1-methoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.8 mol dm^{-3}).

| t/h | Conversion (%) | Yield (%) | | |
|------------------------|----------------|-----------|-------|-------------|
| | | 2 | 10 | Nitrodimers |
| At 20°C | | | | |
| 0.08 | 14.9 | Trace | ~ 100 | — |
| 0.25 | 26.8 | Trace | ~ 100 | Trace |
| 0.5 | 59.2 | 14.5 | 85.5 | Trace |
| At -50°C | | | | |
| 0.08 | 38.3 | Trace | ~ 100 | Trace |
| 0.25 | 60.3 | Trace | 95 | 5 |
| 0.5 | 100 | Trace | 88.1 | 11.9 |

the corresponding atomic coordinates are given in Table 4. In this structure **10** the O(1)–C(11) and C(1)–C(2) bonds are eclipsed and the displacement of the two naphthalene ring systems from coplanarity is indicated by the torsional angle: C(3)–C(4)–C(4a)–C(3a) $61.5(7)^\circ$.

At longer reaction times, significant amounts of 1-methoxy-4-nitronaphthalene (**2**) (15%) were formed in addition to the dehydromer **10**. For the corresponding reaction at -50°C , the formation of 1-methoxy-4-nitronaphthalene was substantially suppressed and the products were the dehydromer **10** and what appeared to be a mixture of nitrated dehydromers which were not investigated further.

Photochemistry in dichloromethane at -78°C . A solution of 1-methoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane was irradiated at -78°C , as above, and the composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The notable feature of this reaction was the formation of 4,4'-dimethoxy-1,1'-

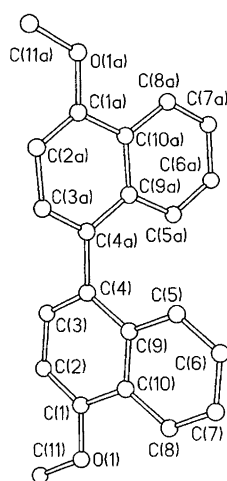


Fig. 2. Perspective drawing of compound **10**.

Table 4. Fractional coordinates for atoms in 4,4'-dimethoxy-1,1'-binaphthalene (**10**).

| Atom | $10^4 X/a$ | $10^4 Y/b$ | $10^4 Z/c$ | $10^3 U/\text{\AA}^2$ |
|-------|------------|------------|------------|-----------------------|
| O(1) | 1957(1) | 839(4) | 3115(3) | 23(1) |
| C(1) | 1408(1) | 836(6) | 2892(4) | 16(1) |
| C(2) | 1060(1) | -627(6) | 2117(4) | 20(1) |
| C(3) | 503(1) | -455(5) | 1972(4) | 20(1) |
| C(4) | 295(1) | 1110(5) | 2569(4) | 15(1) |
| C(5) | 479(1) | 4344(6) | 4047(4) | 18(1) |
| C(6) | 829(1) | 5824(6) | 4812(4) | 22(1) |
| C(7) | 1381(1) | 5691(6) | 4934(4) | 21(1) |
| C(8) | 1569(1) | 4100(6) | 4311(4) | 18(1) |
| C(9) | 655(1) | 2659(5) | 3369(4) | 15(1) |
| C(10) | 1218(1) | 2517(5) | 3523(4) | 15(1) |
| C(11) | 2166(1) | -818(6) | 2466(5) | 29(1) |

binaphthalene (**10**) among the products at relatively low conversion (39%) of starting material into products.

Photochemistry in acetonitrile. The charge-transfer complex of 1-methoxynaphthalene and tetranitromethane in acetonitrile was photolysed, as above, and the composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 5). The product compositions were similar to those obtained for dichloromethane solutions at the appropriate reaction temperatures, except that for the reaction in acetonitrile at -20°C adducts **6** and **7** were not detected among the products, and the formation of 1-methoxy-2-nitronaphthalene **1** became more significant.

Cyclic voltammetry of 1-methoxynaphthalene and 4,4'-dimethoxy-1,1'-binaphthalene. The behaviour of 1-methoxynaphthalene upon cyclic voltammetry in dichloromethane– Bu_4NPF_6 was briefly reported earlier.¹⁰ It was concluded that this compound exhibited quasi-reversible behaviour at scan rates $\geq 200 \text{ mV s}^{-1}$ (E_{pa} and E_{pc} 1.47 and 1.15 V vs. Ag/AgCl, respectively). In view of the facile anodic dehydromerization of alkoxyaromatics¹¹ and the quantitative formation of 4,4'-dimethoxy-1,1'-binaph-

Table 5. Overview of yields of products from the photolysis of 1-methoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in acetonitrile.

| t/h | Conversion (%) | Yield (%) | | | | |
|------------------------|----------------|-----------|------|------|-----|-----|
| | | 1 | 2 | 5 | 6 | 7 |
| At 20°C | | | | | | |
| 0.25 | 23.6 | 3.2 | 42.0 | 49.5 | 2.7 | 2.0 |
| 0.5 | 47.1 | 4.1 | 50.5 | 38.8 | 3.3 | 3.3 |
| 1 | 88.0 | 4.3 | 54.1 | 38.0 | 2.2 | 1.4 |
| 2 | 100 | 5.0 | 75.5 | 17.5 | 1.3 | 0.7 |
| At -20°C | | | | | | |
| 0.5 | 19.1 | 18.8 | 51.0 | 30.2 | — | — |
| 1 | 36.3 | 18.3 | 58.5 | 23.2 | — | — |
| 2 | 66.9 | 19.3 | 63.1 | 17.6 | — | — |

thalene by photolysis of 1-methoxynaphthalene-tetranitromethane-TFA, as demonstrated above, it was realized that the cathodic peak might originate from reduction of the dehydromer radical cation instead.

Repetition of the experiment (dichloromethane-Bu₄NPF₆, 100 mV s⁻¹) showed that the cathodic peak at 1.15 V upon repeated cycling built up to a reversible redox system (E_{pa} and E_{pc} 1.224 and 1.162 V vs. Ag/AgCl at 400 mV s⁻¹). Addition of authentic 4,4'-dimethoxy-1,1'-binaphthalene (**10**) matched exactly this redox couple. Cyclic voltammetry of **10** under the same conditions in the 0.5–1.4 V region displayed a reversible system with E_{pa} and E_{pc} 1.23 and 1.16 V vs. Ag/AgCl in the sweep range of 0.2–20 mV s⁻¹, i_{pc}/i_{pa} increasing from 0.16 to 0.76. Thus it appears that 1-methoxynaphthalene is oxidized at the first anodic wave to its radical cation which rapidly dimerizes to give the dehydromer radical cation. This is typical behaviour of radical cations of alkoxy- and aminoaromatics.¹¹

EPR spectroscopic detection of the radical cation of 10^{•+} under photochemical conditions. We have previously shown^{1–3} that the photolysis of solutions of ArH-tetranitromethane under standardized conditions (–60°C, dichloromethane, 6 min irradiation) does not generate any paramagnetic species in cases corresponding to reactive or moderately reactive ArH^{•+}. Thus the reactions between components of the triad of eqn. (1) must be fast [eqns. (2) and/or (4)]. On the other hand, similar solutions with added TFA (0.4 mol dm⁻³) in many cases exhibited EPR signals corresponding to ArH^{•+} or (ArH)₂^{•+}, showing that the ArH^{•+}–trinitromethanide reaction [eqn. (2)] had been strongly suppressed by protonation, and that the ArH^{•+}–NO₂ [eqn. (4)] step is not fast enough to prevent a significant radical cation concentration from building up. This phenomenon was semi-quantitatively described by the ratio (denoted ξ) of the EPR spectral intensities of the TFA containing solution and the one not containing TFA, respectively. For highly reactive radical cations ξ was ca. 1 [both eqns. (2) and (4) fast], for moderately reactive ones $1 < \xi < \text{up to ca. } 1000$ [eqn. (2) fast, eqn. (4) slow], whereas reasonably stable radical cations again showed ξ values around 1 [both eqns. (2) and (4) slow]. It was also predicted that, for one and the same ArH, ξ ought to follow a volcano-type relation over a sufficiently large range of temperature.

1-Methoxynaphthalene seemed to be a typical representative of a slow-reacting radical cation.^{2,3} Photolysis of 1-methoxynaphthalene-tetranitromethane in the temperature range between –60 and –80°C gave an intense, well resolved EPR spectrum identical to that obtained by DDQ oxidation of 1-methoxynaphthalene in dichloromethane-TFA. With TFA-tetranitromethane an intense, broad unresolved singlet was seen, and ξ was ≈ 1 , as calculated by using absolute intensities of the first derivative spectra, or ≈ 50 , as calculated by using absolute intensities obtained by double integration of equally

overmodulated first derivative signals. The latter technique is more adequate in this particular case since the shapes of spectra to be compared are so different; as would be expected,² the ξ values come out to be larger by this method. The variation of $\log \xi$ with temperature in the range of –70 to 0°C was as expected, with a shallow maximum of $\log \xi$ around the middle of the range (Fig. 3), irrespective of the computational method used.

However, in view of the propensity of alkoxyaromatics to undergo dehydromerization,¹¹ and a hint in the literature¹² that the oxidation of 1-methoxynaphthalene by Tl(III) trifluoroacetate in TFA at room temperature would produce the EPR spectrum of the dehydromer radical cation **10**, we took a closer look at the spectrum obtained by photolysis of 1-methoxynaphthalene-tetranitromethane at –60°C. A sample of authentic **10** under similar conditions gave a spectrum identical to that obtained from 1-methoxynaphthalene. 4-Deuterio-1-methoxynaphthalene also gave rise to an identical spectrum; since a deuterium atom in the 4-position would be expected to significantly affect the EPR spectrum of the 1-methoxynaphthalene radical cation, this result unambiguously establishes that the deuterium has been removed, most likely by loss from the dication which is an intermediate during dehydromerization (Fig. 4). Several other oxidation methods were tried [photo-oxidation in the presence of Hg(II) trifluoroacetate¹³ or DDQ,¹⁴ oxidation by SbCl₅ in SbCl₃,¹⁵ or Tl(III) trifluoroacetate]^{12,16} on these three compounds, and in all cases the

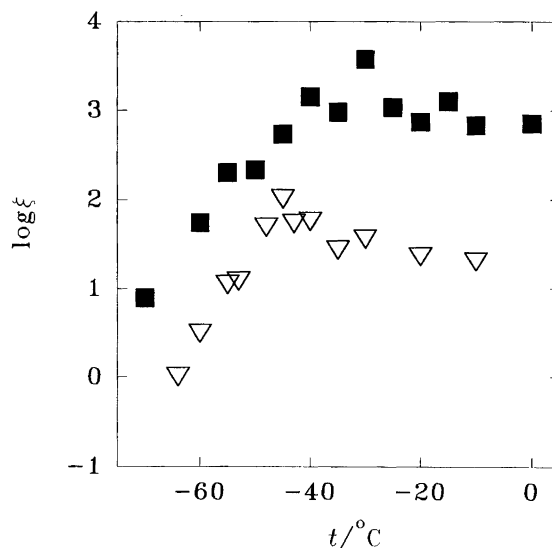


Fig. 3. Variation of $\log \xi$ with temperature, ξ being either calculated as the ratio between the absolute intensities of the first-derivative EPR spectra from the photolysis of a 1-methoxynaphthalene-tetranitromethane-TFA solution in dichloromethane and a 1-methoxynaphthalene-tetranitromethane solution in dichloromethane (triangles), or as the ratio between the absolute intensities of the doubly integrated first derivative spectra under the same conditions (squares). See Ref. 2.

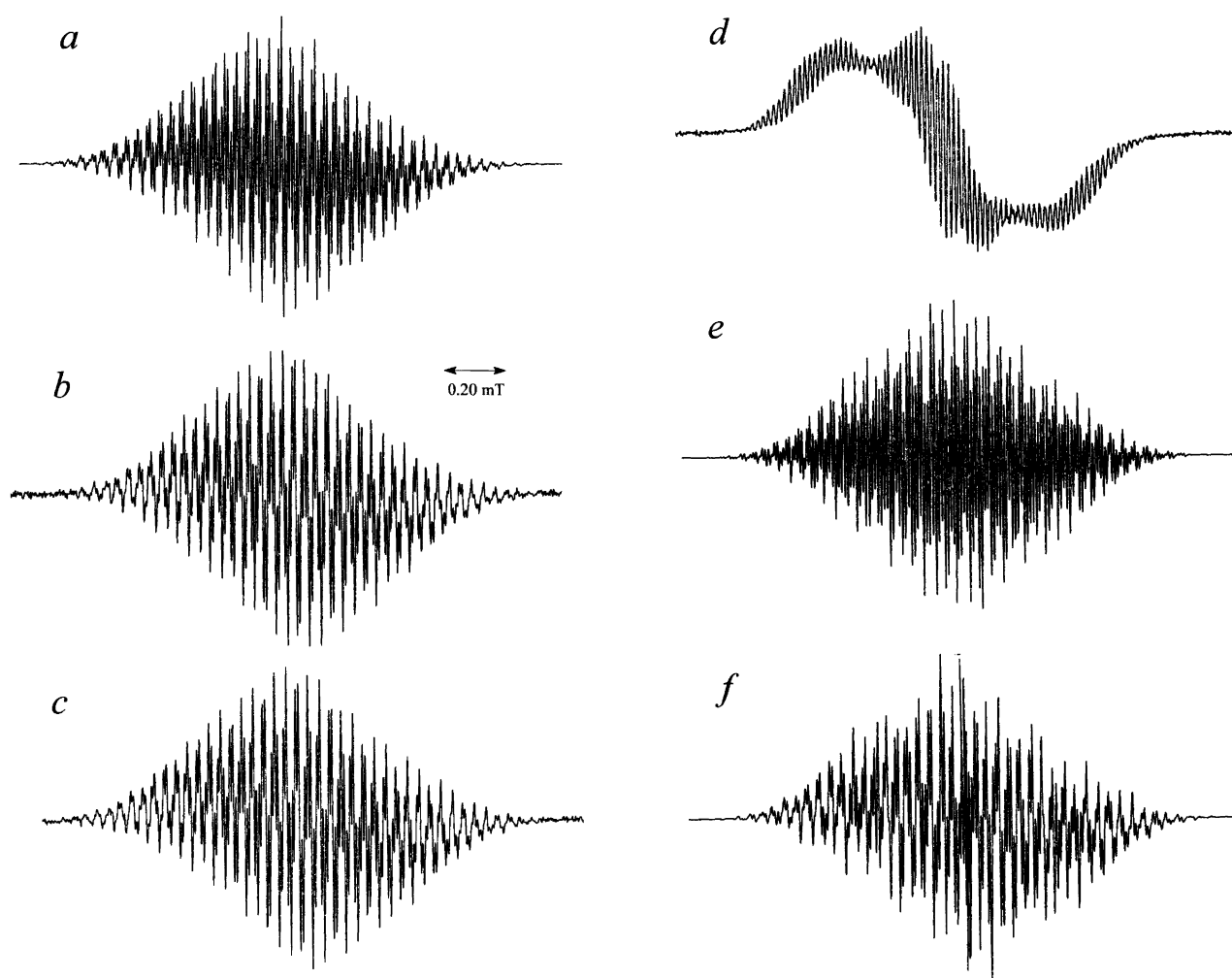


Fig. 4. Examples of EPR spectra of $10^{\bullet+}$, obtained by (a) Tl(III) trifluoroacetate oxidation of 1-methoxynaphthalene (80 mmol dm^{-3}) in dichloromethane–TFA (0.8 mol dm^{-3}) at -30°C , recorded at -60°C with a modulation amplitude of 0.005 mT ; (b) photolysis of 1-methoxynaphthalene (80 mmol dm^{-3})–tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at -70°C , recorded with a modulation amplitude of 0.008 mT ; (c) photolysis of 10 (3 mmol dm^{-3})–tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at -70°C , recorded with a modulation amplitude of 0.008 mT ; (d) photolysis of 1-(d_3 -methoxy)naphthalene (80 mmol dm^{-3}) and Hg(II) trifluoroacetate in dichloromethane–TFA (0.8 mol dm^{-3}) at -60°C , and simulations obtained by the parameters given in the text and a linewidth of (e) 0.010 mT and (f) 0.015 mT .

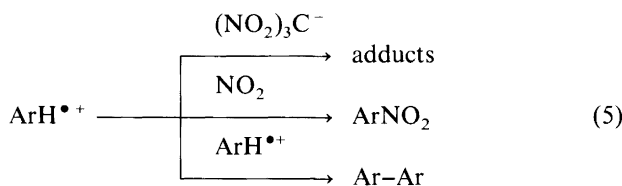
same spectrum as that from the photolysis of 1-methoxynaphthalene-tetranitromethane was obtained. No Hg couplings were visible in the spectra recorded from experiments with Hg(II) trifluoroacetate as the oxidant.¹⁷

Upon closer inspection (Fig. 4), the EPR spectrum of $10^{\bullet+}$ displayed 47 groups of lines with an average spacing of ca. 0.037 mT , and accumulation of spectra of the low-field outer wing indicated that the smallest resolvable coupling constant was 0.040 mT . Any smaller coupling constant would be $<0.003 \text{ mT}$. The EPR spectrum from Hg(II)- $h\nu$ oxidation of 1-(d_3 -methoxy)naphthalene was also recorded (Fig. 4e) and indicated that the coupling constant to the methoxy hydrogens would be 0.11 mT [as for the parent compound, any of the oxidation methods listed above gave the same EPR spectrum from 1-(d_3 -methoxy)naphthalene, as well as from its dehydodimer]. The EPR spectrum of $10^{\bullet+}$ could be simulated by

the following parameters: $a^{\text{OMe}}(6\text{H}) = 0.110$, $a^{\text{H}2} \approx 0$, $a^{\text{H}3} = 0.040$ (2H), $a^{\text{H}5} = 0.289$ (2H), $a^{\text{H}6} = 0.050$ (2H), $a^{\text{H}7} = 0.080$ (2H) and $a^{\text{H}8} = 0.070 \text{ mT}$ (2H) (Figs. 4e and 4f), the coupling constants being tentatively assigned on the basis of the spin density distribution calculated for $10^{\bullet+}$.

Discussion

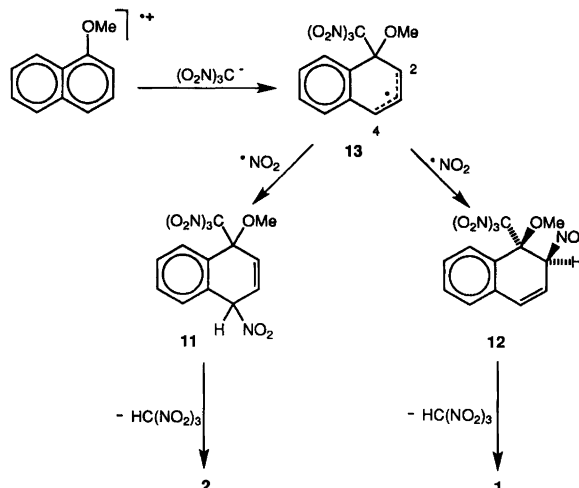
The mode of formation of the 1-methoxynitronaphthalenes **1** and **2**, 1-methoxy-4-trinitromethylnaphthalene (**5**), the adducts **6** and **7**, and 4,4'-dimethoxy-1,1'-binaphthalene (**10**) in the photolysis of the 1-methoxynaphthalene-tetranitromethane charge transfer complex. After formation of the triad [eqn. (1)] the radical cation $\text{ArH}^{\bullet+}$ has several competing pathways to reach products [eqn. (5)],



and as recently shown, the fastest step usually is reaction with the trinitromethanide ion.¹⁻³ When this step is blocked by protonation, $\text{ArH}^{\bullet+} - \text{NO}_2$ coupling usually takes over as the slower step, as shown both synthetically and by EPR spectroscopic observation. In the case of 1-methoxynaphthalene a third process, coupling between two $\text{ArH}^{\bullet+}$ to give the dehydrodimer **10**, becomes significant as a consequence of the known propensity of alkoxyaromatics to undergo fast oxidative dehydrodimerization.¹¹ Thus with TFA present, the $\text{ArH}^{\bullet+} - \text{NO}_2$ coupling step appears to be the slowest one, and the dehydrodimer is formed almost quantitatively at 20°C at low conversion (Table 3); at higher conversion 4-nitro-1-methoxynaphthalene (**2**) appears, presumably formed by thermal nitration by NO_2 , as indicated by the fact that only traces of **2** are detected at -50°C. The implication of this observation is that, certainly at 20 and -50°C but by inference also at -20°C, the nitro-substitution products **1** and **2** do not arise directly via radical coupling of the radical cation of 1-methoxynaphthalene and nitrogen dioxide.

What then is the mode of formation of these nitro compounds **1** and **2** at low photolytic conversion? Although it is recognized that the *thermal* nitration induced by NO_2 present in the reaction medium, generated photochemically and presumably also by the secondary decomposition of 1-methoxy-4-trinitromethylnaphthalene (**5**), is undoubtedly the source of some nitro compounds **1** and **2** at longer reaction times and at higher temperature, this reaction pathway will clearly not account for the extent of the formation of these nitro compounds at short reaction times and low temperature (Table 1). That reaction possibility which remains is the formation of highly labile adducts **11** and **12** as intermediates, which should decompose rapidly with loss of nitroform to give 1-methoxy-2-nitronaphthalene (**1**) and 1-methoxy-4-nitronaphthalene (**2**), respectively. The formation of adducts **11** and **12** would occur via attack of trinitromethanide ion *ipso* to the methoxy substituent in the radical cation of 1-methoxynaphthalene to give the delocalized carbon radical **13** (Scheme 2). In the subsequent radical coupling reaction between the delocalized carbon radical **13** and nitrogen dioxide it appears likely for steric reasons that the 1-methoxy-4-nitro-1-trinitromethyl adducts **11** would be formed in higher yield than the alternative 1-methoxy-2-nitro-1-trinitromethyl adduct **12** (Scheme 2); this argument is consistent with the observed 2-nitro-/4-nitro-product ratio of 10-20.

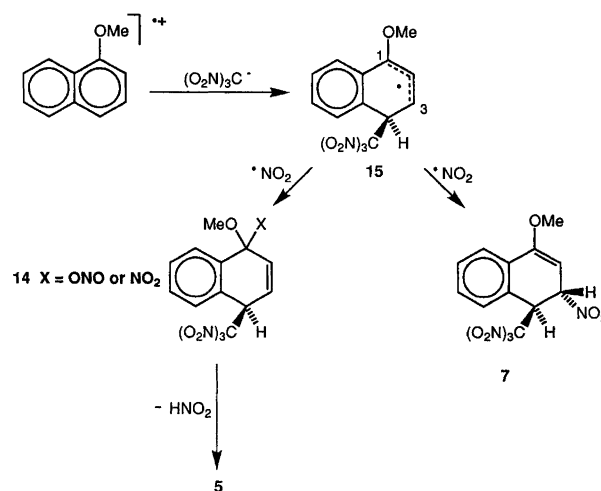
The precise mode of formation of the 1-methoxy-4-trinitromethylnaphthalene **5** is somewhat uncertain, but it seems likely that it arises by further reaction of inter-



Scheme 2.

mediate 1-methoxy-4-trinitromethyl-1-X-adduct(s) **14** (Scheme 3), where X may be either NO_2 or ONO . In either case, loss of nitrous acid from the 1,4-positions would give the apparent trinitromethyl substitution product **5**. In this context it is notable that the alternative radical reaction of nitrogen dioxide with the delocalized carbon radical **15** at C3 would lead to 1-methoxy-*r*-2-nitro-*t*-trinitromethyl-1,2-dihydronaphthalene (**7**) which has been identified as a labile reaction product. Unfortunately **7** could not be isolated, and the mixture in which it was obtained was too complex for meaningful decomposition experiments to be conducted.

The origin of the more stable, but still labile, adduct **6** appears certain. Reaction of trinitromethanide ion at C3 in the radical cation of 1-methoxynaphthalene would yield the carbon radical **9** (Scheme 1), which on radical coupling with nitrogen dioxide would give the *trans* adduct **6**.



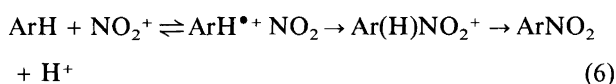
Scheme 3.

EPR spectroscopy as a tool for studying the photolysis of ArH-tetranitromethane reactions. The photolysis of 1-methoxynaphthalene-tetranitromethane in dichloromethane at -60°C gives rise to the EPR spectrum of the radical cation of the dehydrodimer of 1-methoxynaphthalene, $\mathbf{10}^{\bullet+}$, a species formed by further reactions of the 1-methoxynaphthalene radical cation. The fact that the latter is not seen even at a temperature as low as -80°C attests to its high reactivity toward dimerization. The photolysis experiment carried out at -78°C shows that the dimerization process can compete with even the $\text{ArH}^{\bullet+}$ -trinitromethanide reaction at this temperature, clearly due to the differing temperature coefficients of the reactions.

Thus the EPR experiments with 1-methoxynaphthalene-tetranitromethane at -60°C or lower are at least partially indicative of the dehydrodimerization chemistry observed (Table 1, -78°C), even if a dominant part of the reaction must proceed via $(1\text{-methoxynaphthalene})^{\bullet+}$. With TFA present, the preparative outcome is almost quantitatively dehydrodimerization. Unfortunately, the EPR signal in this case cannot be assigned to $\mathbf{10}^{\bullet+}$ with any certainty owing to lack of resolution. Only very early during runs with TFA present can one detect the visible ≈ 40 -line character of the spectrum, with only the ca. 0.04 mT splitting distinguishable.

However, there now appears a problem of quantitative nature with the diagnostic value of the EPR method, since the ξ value cannot reflect the competitive reactions of $\text{ArH}^{\bullet+}$. We observe the 'daughter ion' $\text{Ar}-\text{Ar}^{\bullet+}$, a more stable species than $\text{ArH}^{\bullet+}$, and then ξ will to an unknown degree be different from what actually ought to be found for $\text{ArH}^{\bullet+}$ itself. However, from a qualitative point of view, there is no problem; the finding that a daughter ion is formed upon suppression of eqn. (2) by protonation is in itself sufficient to show that the trinitromethanide-radical cation reaction has been blocked.

Implications of the 1-methoxynaphthalene photolysis results for the Perrin hypothesis. The Perrin hypothesis,^{18,19} that electrophilic nitration by nitronium ion proceeds with a radical pair as an intermediate [eqn. (6)],



has been refuted by the fact that the distribution of nitro substitution products is significantly different when NO_2^+ induced nitration of ArH is compared with $\text{ArH}^{\bullet+}$ - NO_2 coupling.³ However, as with isomer distributions from aromatic substitutions in general, the differences observed are quantitatively modest and their significance has been questioned.²⁰ The case of 1-methoxynaphthalene now adds a qualitative difference which is much more decisive, as outlined below.

The photolysis of 1-methoxynaphthalene-tetranitromethane-TFA in the first step generates the triad [eqn. (1)], of which trinitromethanide ion is immediately pro-

tonated, leaving behind $(1\text{-methoxynaphthalene})^{\bullet+}$ and NO_2 . Among the reactions which the radical cation can undergo, the $\text{ArH}^{\bullet+}$ - NO_2 step in this case is so slow that the coupling between two $\text{ArH}^{\bullet+}$ takes precedence (Table 3) and a new type of product is formed, the dehydrodimer $\mathbf{10}$. On the other hand, 1-methoxynaphthalene is mononitrated by NO_2^+ (Ref. 21), showing that the radical pair of eqn. (6) cannot be an intermediate.

The slowness of the $\text{ArH}^{\bullet+}$ - NO_2 step also shows that the predominant part of the nitro substitution products from the reaction with only tetranitromethane present cannot be formed in this way but instead must originate from intermediate adducts, as discussed above.

The regiochemistry of the attack of trinitromethanide ion on the radical cation of 1-methoxynaphthalene. On the basis of the product yields at low conversion of reactants given in Table 1, and the analysis above of the regiochemistry of trinitromethanide ion attack on the radical cation of 1-methoxynaphthalene giving rise to those products, the overall pattern of the regiochemistry of trinitromethanide ion attack can be determined; these data are presented in Table 6. Although the high incidence of trinitromethanide ion attack at C1 of the radical cation might be considered not surprising given the calculated (AM1)²² atomic charge at that ring carbon atom (Fig. 5), it is not possible to account for the observed relative levels of attack of trinitromethanide ion at C3 and C4 on this basis given the calculated atomic charges.

For the reaction of trinitromethanide ion with the radical cation of 1-methoxynaphthalene it is clear that a different rationale is required to account for the observed regiochemistry. It seems likely that for this substrate a determining factor in the choice of reaction pathway is the relative energies of the three products of ionic coupling of the trinitromethanide ion and the radical cation, i.e. the three carbon radicals $\mathbf{16}$, $\mathbf{17}$ and $\mathbf{18}$. Of these three radicals the carbon radical $\mathbf{17}$ arising by trinitromethanide ion attack at C3 would be expected to be higher in energy than the more extensively delocalized radicals $\mathbf{16}$ and $\mathbf{18}$. The implication of the foregoing is that the reaction between trinitromethanide ion and the radical cation of 1-methoxynaphthalene is reversible, a situation which has been established already for the reactions of the two rather stable radical cations, tris(4-bromophenyl)aminium ion and tris(4-chlorophenyl)-

Table 6. The regiochemistry of trinitromethanide ion attack on the radical cation of 1-methoxynaphthalene in dichloromethane solution.

| | Products arising from attack of $(\text{O}_2\text{N})_3\text{C}^-$ (%) | | |
|--------------------------|--|--------------|--------------|
| | Attack at C1 | Attack at C3 | Attack at C4 |
| At 20°C | 40 | 7 | 52 |
| At -20°C | 44 | 6 | 49 |
| At -50°C | 45 | 6 | 52 |
| At -78°C | 29 | 4 | 52 |

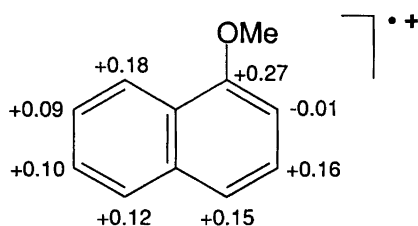
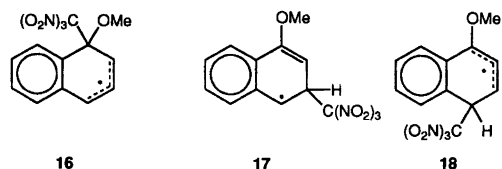


Fig. 5. Calculated (optimized; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties in the radical cation of 1-methoxynaphthalene.

aminium ion.²³ In this connection it is noteworthy that photolysis of the charge transfer complex of 1-methoxynaphthalene and tetranitromethane at -78°C in dichloromethane leads to some dehydrodimer (**10**) formation in addition to the normal products initiated by attack of trinitromethanide ion on the radical cation of 1-methoxynaphthalene.



The pattern of reactivity of nucleophiles with radical cations – a possible rationalization. It is now clear that for the reactions of trinitromethanide ion with the radical cations of naphthalene⁵ and the variety of methyl-substituted naphthalene derivatives,^{6,7} referred to in the Introduction to this article, the regiochemistry of attack is controlled by the relative atomic charges of the carbon atoms of the substrate, moderated on occasions by steric effects. These reactions of relatively unstable radical cations appear to be subject to kinetic control. In contrast, the evidence presented above for 1-methoxynaphthalene and earlier for the two rather stable radical cations, tris(4-bromophenyl)aminium and tris(4-chlorophenyl)aminium ions²³ indicates the operation of thermodynamic control in their reactions with trinitromethanide ion. It appears therefore that the reactivity of radical cations with nucleophiles will depend markedly on the relative energies of the radical cations and the carbon radicals derived by ionic coupling of the radical cation with the nucleophile. If this argument is accepted, it is to be expected that the radical cations of some substrates will exhibit reactivity with nucleophiles between the two extremes highlighted in this discussion. The importance of equilibrium control of reactions of relatively unreactive radical cations has been stressed earlier.^{11,24}

Experimental

Materials and methods. Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600

series FTIR spectrometer; ^1H NMR spectra were recorded on a Varian Unity 300 spectrometer with SiMe_4 as an internal standard. Tetranitromethane and 1-methoxynaphthalene were purchased from Aldrich. Antimony pentachloride (1 mol dm^{-3} in dichloromethane), antimony trichloride (analytical grade) and DDQ were from Merck. Thallium(III) trifluoroacetate was from Strem Chemicals and mercury(II) trifluoroacetate from Johnson Matthey. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and trifluoroacetic acid was from Merck. 4,4'-Dimethoxy-1,1'-binaphthalene (**10**),²⁵ 4-(^2H)-1-methoxynaphthalene,^{26a} 1-(d_3 -methoxy)naphthalene^{26a} and its dehydrodimer^{26b} were prepared according to literature methods.

EPR spectra were recorded² by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using the 50 W high-pressure Hg lamp from Bruker (ER 202) and a filter with cut-off at $<430\text{ nm}$ from Schott, Germany. The following methods were used to generate radical cations from 1-methoxynaphthalene, 4-(^2H)-1-methoxynaphthalene and 4,4'-dimethoxy-1,1'-binaphthalene (**10**): (i) photolysis of substrate ($8\text{--}80\text{ mmol dm}^{-3}$) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane, (ii) photolysis of substrate ($8\text{--}80\text{ mmol dm}^{-3}$), tetranitromethane (0.8 mol dm^{-3}) and TFA (0.4 mol dm^{-3}) in dichloromethane, (iii) photolysis of substrate ($4\text{--}80\text{ mmol dm}^{-3}$), mercury(II) trifluoroacetate (50 mmol dm^{-3}) and TFA ($0.4\text{--}1.2\text{ mol dm}^{-3}$), (iv) oxidation of the substrate ($0.5\text{--}50\text{ mmol dm}^{-3}$) by a solution of SbCl_5 ($\sim 10\text{ mmol dm}^{-3}$) in a 1:1 (v/v.) mixture of SbCl_3 and dichloromethane, (v) oxidation (sometimes photoinduced) of the substrate (5 mmol dm^{-3}) by DDQ ($2\text{--}3\text{ mmol dm}^{-3}$) in TFA or TFA–dichloromethane, and (vi) oxidation of the substrate ($1\text{--}5\text{ mmol dm}^{-3}$) by thallium(III) trifluoroacetate ($2\text{--}3\text{ mmol dm}^{-3}$) in TFA or TFA (0.8 mol dm^{-3} – dichloromethane). In general, the lower substrate concentrations refer to those of **10** or its deuterated form.

Cyclic voltammetry was performed in dichloromethane– Bu_4NPF_6 (0.2 mol dm^{-3}), using the BAS-100 instrument.⁹ Spin densities of **10** $^{\bullet+}$ were calculated by the HyperChem program.

Warning. While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.²⁷

General procedure for the photonitration of 1-methoxynaphthalene with tetranitromethane. A solution of 1-methoxynaphthalene (500 mg , 0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane or acetonitrile was irradiated at 20 , -20 , -50 or -78°C with filtered light ($\lambda_{\text{cut-off}} < 435\text{ nm}$). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pres-

sure at $\leq 0^\circ\text{C}$, and the product composition determined by NMR spectral analysis (Tables 1, 3 and 5).

Reaction in dichloromethane at 20°C and the identification of the aromatic products. Reaction of 1-methoxynaphthalene-tetranitromethane in dichloromethane at 20°C , as above, for 1 h gave a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of 1-methoxy-2-nitronaphthalene (**1**, 5%), 1-methoxy-4-nitronaphthalene (**2**, 50%), 1-methoxy-4-trinitromethylnaphthalene (**5**, 35%), 4-methoxy-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene (**6**, 6%), and 4-methoxy-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (**7**, 3%). The three aromatic compounds were separated by chromatography on a silica gel Chromatotron plate and gave in order of elution:

1-Methoxy-4-trinitromethylnaphthalene (**5**) m.p. $192\text{--}194^\circ\text{C}$ (decomp.) (X-ray crystal structure determined, below). IR: ν_{max} (KBr) 1619, 1588, 1574 cm^{-1} , ^1H NMR (CDCl_3) δ 4.11 (s, OMe), 6.87 (d, $J_{\text{H}_2,\text{H}_3} = 8.8\text{ Hz}$, H2), 7.28 (m, H5), 7.56 (d, $J_{\text{H}_3,\text{H}_2} = 8.8\text{ Hz}$, H3), 7.62 (m, H6, H7), 8.45 (m, H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.87 gave enhancements at δ 4.11 (1.8%) and at δ 7.56 (9.9%); irradiation at δ 8.45 gave enhancements at δ 4.11 (1.7%) and at δ 7.62 (1.3%).

1-Methoxy-2-nitronaphthalene (**1**), m.p. $78\text{--}80^\circ\text{C}$ (Lit.²⁸ m.p. 80°C), identical with authentic material.

1-Methoxy-4-nitronaphthalene (**2**), m.p. $83\text{--}84^\circ\text{C}$ (Lit.²⁸ $83\text{--}85^\circ\text{C}$), identical with authentic material.

Neither of the adducts **6** and **7** could be isolated from the Chromatotron plate.

Extension of the reaction time for the reaction above to 2 h resulted in the precipitation of some 4-methoxy-1-naphthoic acid **4**, identified by comparison with an authentic sample.

*Reaction in dichloromethane at -20°C and the identification of the nitrotrinitromethyl adducts **6** and **7**.* Reaction of 1-methoxynaphthalene-tetranitromethane in dichloromethane at -20°C , as above, for 1 h gave a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of 1-methoxy-2-nitronaphthalene (**1**, 3%), 1-methoxy-4-nitronaphthalene (**2**, 47%), 1-methoxy-4-trinitromethylnaphthalene (**5**, 34%), 4-methoxy-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene (**6**, 7%) and 4-methoxy-*r*-2-nitro-*t*-trinitromethyl-1,2-dihydronaphthalene (**7**, 8%). The two adducts **6** and **7** were labile in solution, the less stable adduct **7** having a half-life of ca. 4.5 h in (^2H)-chloroform at 23°C . Although this lability precluded their isolation, the stability of the adducts was sufficient to allow their characterization by NMR techniques:

4-Methoxy-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene (**6**), ^1H NMR (CDCl_3) δ 3.79 (s, OMe), 4.73 (dd, $J_{\text{H}_3,\text{H}_2} = 6.4\text{ Hz}$, $J_{\text{H}_3,\text{H}_1} = 1.5\text{ Hz}$, H3), 5.50 (d, $J_{\text{H}_2,\text{H}_3} = 6.4\text{ Hz}$, H2), 5.79 (br s, H1), the remainder of the spectrum was obscured by signals of the other compo-

nents of the mixture. Nuclear Overhauser experiments gave the following results: irradiation at δ 4.73 gave enhancements at δ 3.79 (2.1%) and at δ 5.50 (3.9%). ^{13}C NMR (CDCl_3) δ 41.67 (C2), 81.84 (C1), 82.36 (C3); the remainder of the spectrum was obscured by signals of the other components of the mixture. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

4-Methoxy-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (**7**), ^1H NMR (CDCl_3) δ 3.75 (s, OMe), 4.48 (dd, $J_{\text{H}_3,\text{H}_2} = 6.8\text{ Hz}$, $J_{\text{H}_3,\text{H}_1} = 1.0\text{ Hz}$, H3), 5.22 (d, $J_{\text{H}_2,\text{H}_3} = 6.8\text{ Hz}$, H2), 5.42 (br s, H1); the remainder of the spectrum was obscured by signals of the other components of the mixture. Nuclear Overhauser experiments gave the following results: irradiation at δ 4.48 gave enhancements at δ 3.75 (1.4%) and at δ 5.22 (3.8%); irradiation at δ 5.22 gave enhancements at δ 4.48 (5.0%) and at δ 5.42 (3.2%). ^{13}C NMR (CDCl_3) δ 44.88 (C1), the remainder of the spectrum was obscured by signals of the other components of the mixture. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

*Reaction in dichloromethane containing trifluoroacetic acid (0.8 mol dm^{-3}) at 20°C and the identification of 4,4'-dimethoxy-1,1'-binaphthalene (**10**).* Reaction of 1-methoxynaphthalene-tetranitromethane, as above, but in dichloromethane containing trifluoroacetic acid (0.8 mol dm^{-3}) at 20°C for 15 min gave a product shown (^1H NMR) to be essentially a mixture of 1-methoxynaphthalene (73%) and 4,4'-dimethoxy-1,1'-binaphthalene (**10**, 27%). The dehydrodimer **10** was isolated by crystallization (dichloromethane) to give 4,4'-dimethoxy-1,1'-binaphthalene, m.p. $264\text{--}266^\circ\text{C}$ (Lit.²⁹ $252\text{--}254^\circ\text{C}$) (X-ray crystal structure determined, below). IR: ν_{max} (KBr) 1264, 1239, 1084 cm^{-1} . ^1H NMR (CDCl_3) δ 4.09 (s, OMe), 6.92 (d, $J_{\text{H}_3,\text{H}_2} = 7.8\text{ Hz}$, H3), 7.30 (dd, $J_{\text{H}_7,\text{H}_8} = 7.4\text{ Hz}$, $J_{\text{H}_7,\text{H}_6} = 6.4\text{ Hz}$, H7), 7.38 (d, $J_{\text{H}_2,\text{H}_3} = 7.8\text{ Hz}$, H2), 7.38 (d, $J_{\text{H}_8,\text{H}_7} = 7.4\text{ Hz}$, H8), 7.46 (dd, $J_{\text{H}_6,\text{H}_5} = 8.3\text{ Hz}$, $J_{\text{H}_6,\text{H}_7} = 6.4\text{ Hz}$, H6), 8.36 (d, $J_{\text{H}_5,\text{H}_6} = 8.3\text{ Hz}$, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.09 gave an enhancement at δ 6.92 (3.9%); irradiation at δ 6.92 gave enhancements at δ 4.09 (0.6%) and at δ 7.38 (1.9%); irradiation at δ 8.36 gave enhancements at δ 4.09 (0.15%) and at δ 7.46 (0.5%).

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, $\lambda(\text{Mo } K\alpha) 0.71073\text{ \AA}$, from a crystal monochromator] are given below. The space group was, in each case, determined unambiguously as a result of the structure analyses reported below, but initially indicated by conditions limiting possible reflections, ω -Scans were used to collect reflection intensities out to a maximum Bragg angle θ , given below. The cell parameters were determined by least-squares refinements for which the set-

ting angles of 25 accurately centred high-angle reflections were used.

Crystal data. *1-Methoxy-4-trinitromethylnaphthalene* (**5**). $C_{12}H_9N_3O_7$, $M = 307.22$, orthorhombic, $P2_12_12_1$, $a = 10.245(2)$, $b = 13.647(2)$, $c = 18.168$ Å; $V = 2540.1(7)$ Å³, $D_c = 1.607$ g cm⁻³, $Z = 8$, $\mu(\text{Mo } K\alpha) = 1.35$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.60 \times 0.36 \times 0.26$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\Theta = 24.99^\circ$. The number of independent reflections measured was 2001, 1543 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0387$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.037, $wR_{(\text{all data})} = 0.078$.

4,4'-Dimethoxy-1,1'-binaphthalene (**10**). $C_{22}H_{18}O_2$, $M = 314.36$, monoclinic, $C2/c$, $a = 25.902(7)$, $b = 6.463(2)$, $c = 9.572(3)$ Å, $\beta = 107.91(2)^\circ$; $V = 1524.7(8)$ Å³, $D_c = 1.369$ g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 0.86$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.56 \times 0.20 \times 0.06$ mm. Data were collected at 132(2) K out to a maximum Bragg angle $\theta = 21.87^\circ$. The number of independent reflections measured was 820, 435 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0474$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.041, $wR_{(\text{all data})} = 0.093$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)³⁰ were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(\text{obs})}$, shown here as a comparison for the refinement based on F . Reflection weights $1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$, where $P = [F_o^2 + 2F_c^2]/3$, were used. All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl hydrogens were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

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