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Photochemical Nitration by Tetranitromethane. Part XLI.† Addition *Ipso* to a Methoxy Group and the Effect of Methanol in the Photochemical Reaction between 1,4-Dimethoxynaphthalene and Tetranitromethane

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The photolysis of the charge transfer complex between 1,4-dimethoxynaphthalene and tetranitromethane in dichloromethane gives mainly 1,4-dimethoxy-2-nitronaphthalene (**1**), 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**) and 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**) together with smaller amounts of the labile adducts 1,4-dimethoxy-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**4**), 1,4-dimethoxy-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (**5**) and 1,4-dimethoxy-1-nitro-2-trinitromethyl-1,2-dihydronaphthalene (**6**). Photolysis in acetonitrile gives higher yields of adducts **4** and **5**. Photolysis in dichloromethane containing methanol gives mainly 1,1,4-trimethoxy-2-trinitromethyl-1,2-dihydronaphthalene (**7**) and 1,1,4-trimethoxy-2-nitro-1,2-dihydronaphthalene (**8**). Photolysis in acetonitrile containing methanol gives high yields of **8** and 4,4-dimethoxy-3-nitro-3,4-dihydro-1(2*H*)-naphthalenone (**9**). The formation of adducts via attack of trinitromethanide ion or nitrogen dioxide *ipso* to a methoxy group during the photolysis of 1,4-dimethoxynaphthalene and tetranitromethane is discussed, and arguments are presented that such adducts give compounds **2** and **3** via rearrangement and/or elimination reactions. The effect of methanol and the mode of formation of compounds **7**–**9** via nucleophilic addition or nucleophilic displacement are discussed.

X-Ray crystallographic structures are reported for 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**) and 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**).

The photochemical addition of tetranitromethane to aromatic compounds (ArH) by excitation of the ArH···tetranitromethane charge-transfer (CT) complex by light matching the absorption band of the CT complex has been shown[2,3] to occur by recombination of a triad consisting of the radical cation of the aromatic compound ($ArH^{\cdot+}$), trinitromethanide ion and nitrogen dioxide [eqn. (1)].[4] The fast step is the reaction between $ArH^{\cdot+}$ and trinitromethanide ion, giving a neutral carbon radical [eqn. (2)], which then reacts with nitrogen dioxide to give nitro-trinitromethyl and/or nitrito-trinitromethyl adducts [eqn. (3)]. The addition takes place 1,2- and/or 1,4-to the aromatic system.

$$\underset{\text{CT complex}}{ArH\cdots C(NO_2)_4} \xrightarrow{h\nu_{CT}} \underset{\text{triad}}{ArH^{\cdot+}(O_2N)_3C^-NO_2} \quad (1)$$

$$ArH^{\cdot+} + (O_2N)_3C^- \rightarrow Ar(H)C(NO_2)_3^{\cdot} \quad (2)$$

$$Ar(H)C(NO_2)_3^{\cdot} + NO_2 \rightarrow \text{adducts} \quad (3)$$

By adding a protic acid such as trifluoroacetic acid (TFA),[2,3] or by using 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) as the solvent,[5,6] the reactivity of trinitromethanide ion can be strongly decreased. TFA is an acid strong enough to protonate trinitromethanide ion in dichloromethane, giving the much less nucleophilic nitro-

† Part XL, see Ref. 1.
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form, while HFP has a powerful ability to deactivate nucleophiles, especially hard ones, via hydrogen-bond donation.[7] This leaves behind only the slow coupling between $ArH^{\cdot+}$ and NO_2 and/or the self-coupling of two $ArH^{\cdot+}$ which eventually gives the dehydrodimer (Ar–Ar), or its radical cation.[8,9] Thus it is possible to induce a build-up of the concentration of $ArH^{\cdot+}$ (or $Ar\text{–}Ar^{\cdot+}$) accessible for EPR spectroscopic studies. The coupling of $ArH^{\cdot+}$ and NO_2 has been shown[10] to yield a different isomer ratio compared with the reaction between ArH and NO_2^+, an observation that contradicts the Perrin hypothesis[11] which suggests that electrophilic aromatic nitration by NO_2^+ is the result of the coupling of $ArH^{\cdot+}$ and NO_2 produced via an initial electron transfer between ArH and NO_2^+.

The adducts formed are more or less labile and undergo subsequent photochemical or thermal reactions. Elimination of nitroform gives $ArNO_2$, while elimination of nitrous acid gives $ArC(NO_2)_3$ [eqn. (4)].

$$Ar(H)(NO_2)C(NO_2)_3 \rightarrow \begin{cases} ArNO_2 + HC(NO_2)_3 \\ ArC(NO_2)_3 + HNO_2 \end{cases} \quad (4)$$

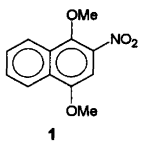
In some cases heterocyclic cage structures are formed,[12] either via slow intramolecular 1,3-dipolar cycloaddition of one nitro group in the trinitromethyl group to the alkene function in *vicinal* adducts, or from a nitro-denitro cyclization reaction which gives nitronic esters. The nitrito-trinitromethyl adducts are readily hydrolyzed, either during the photolysis or work-up, to give hydroxy-trinitromethyl adducts [eqn. (5)].

$$Ar(H)(ONO)C(NO_2)_3 + H_2O \rightarrow Ar(H)(OH)C(NO_2)_3 + HNO_2 \quad (5)$$

As part of a continuing study of the photolysis reactions of aromatic compounds with tetranitromethane, the reactions of 1,4-dimethoxynaphthalene have been studied. The possibility of addition of trinitromethanide ion or nitrogen dioxide *ipso* to a methoxy group has been suggested before,[8,13,14] but no adducts arising directly from this regiochemistry of attack were stable enough to be detected. In the following, it will be shown that during the photolysis of 1,4-dimethoxynaphthalene and tetranitromethane, adducts are formed via addition of trinitromethanide ion or nitrogen dioxide *ipso* to a methoxy group, and that these adducts are precursors to some of the stable products isolated. It will also be shown that when methanol is present new methoxylated products are obtained. Whether these are formed via nucleophilic displacement of trinitromethanide ion by methanol or via competition between trinitromethanide ion and methanol in the attack of the radical cation of 1,4-dimethoxynaphthalene is discussed.

Results

Photolysis in dichloromethane at 0 and −20 °C. A solution of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane was irradiated at 0 or −20 °C. The composition of the reaction mixtures was monitored by withdrawing samples for NMR spectral analyses (Table 1). The solution after 1.5 h irradiation (83% conversion) at 0 °C contained 1,4-dimethoxy-2-nitronaphthalene (**1**) (38%), 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**) (10%), 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**) (24%) and two labile adducts 1,4-dimethoxy-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**4**) (7%) and 1,4-dimethoxy-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (**5**) (2%).



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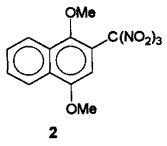

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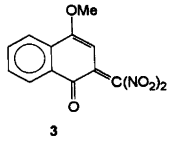

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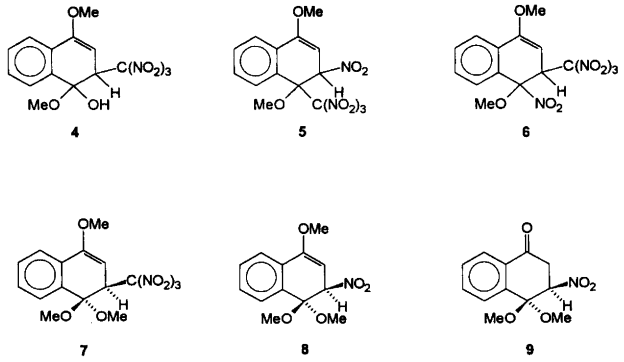
Table 1. Overview of yields of products from the photolysis of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at 0 and −20 °C.

		Yield (%)						
t/h	Conversion (%)	**1**	**2**	**3**	**4**	**5**	**6**	Unknown
At 0 °C								
0.5	29.5	13.2	4.4	3.5	7.1	1.3	—	—
1.0	58.8	26.3	10.6	10.0	10.0	1.9	—	—
1.5	82.7	38.3	9.8	23.5	7.4	2.5	—	1.2
At −20 °C[a]								
0.5	41.3	15.3	6.6	4.4	10.4	4.9	4.1	—
1	70.7	23.9	13.9	13.1	11.9	5.0	2.9	—
1.5	92.9	33.2	17.7	16.5	13.8	6.4	3.3	1.9
2	100	41.6	22.6	25.3	5.3	2.2	1.1	2.0

[a]A new lamp was used.



After 1.5 h irradiation (93% conversion) at −20 °C the reaction mixture contained **1** (33%), **2** (18%), **3** (16%), **4** (14%), **5** (6%) and a third adduct, 1,4-dimethoxy-1-nitro-2-trinitromethyl-1,2-dihydronaphthalene (**6**) (3%), not detected when the photolysis was carried out at 0 °C. The yield of **2** was higher when the photolysis was carried out at −20 °C. Prolonged irradiation caused the yields of adducts to decrease. The apparently strange result that the reaction was faster at −20 °C arose from the use of a new lamp in this experiment.

Compounds **1** and **2** were isolated by separation on a silica gel Chromatotron plate, while **3** was separated from the reaction mixtures by recrystallisation from chloroform. The trinitromethylarene **2** showed a tendency to decompose during the separation process but was stable in $CDCl_3$ at room temperature for at least 2 weeks. Compound **1** was identified by NMR spectroscopy, while the structures of **2** and **3** were determined by single-crystal X-ray analyses. A perspective drawing of 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**), $C_{13}H_{11}N_3O_8$, is presented in Fig. 1, and the corresponding atomic coordinates are given in Table 2. Similar information for 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**), $C_{12}H_8N_2O_6$, is presented in Fig. 2 and Table 3. In the solid state the dimethoxytrinitromethyl compound **2** exists in a conformation in which the C4-methoxy group lies close to the plane of the naphthalene ring system, but the C1-methoxy group is significantly displaced from that plane [torsional angles: C(3)–C(4)–O(4)–C(11) 5.9(3)°, C(8A)–C(1)–O(1)–C(9) 67.9(2)°]; the orientation of the trinitromethyl group is indicated by the near-eclipsing of the C(10)–N(1) and (C2)–C(3) bonds [torsional angle: C(3)–C(2)–C(10)–N(1) 8.1(3)°]. The conformation of the naphthalenone **3** is such that, with the exception of the N(91)-nitro group [torsional angle: C(2)–C(9)–N(91)–O(912) 98.2°], the remainder of the molecule is essentially planar. The extended conjugation in the system is evident in the UV spectrum (λ_{max} 230, 292, 510 nm). The other spectroscopic data for compounds **2** and **3** were consistent with the established structures.

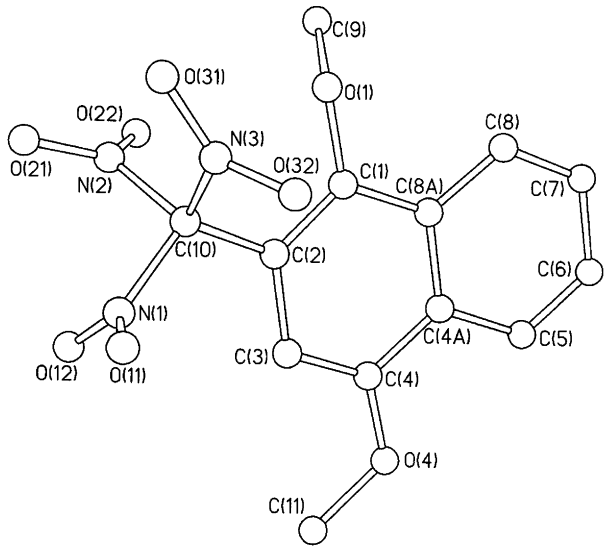


Fig. 1. Perspective drawing of compound **2**.

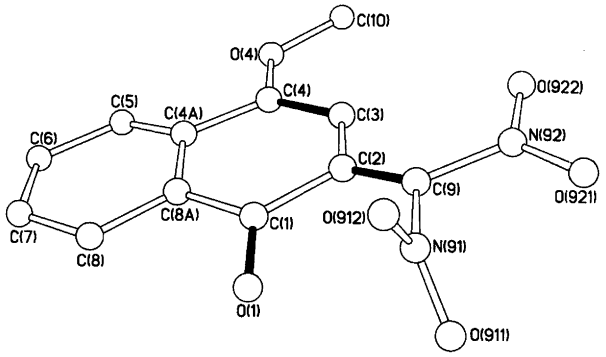


Fig. 2. Perspective drawing of compound **3**. Double bonds are shown in black.

Since none of the adducts **4**–**6** could be isolated, their structures were determined from the NMR spectra of product mixtures and comparison with analogous compounds, together with studies of the decomposition of the adducts. The crucial structural element of the adducts is the connectivity at C1 and C2 of the non-aromatic ring, but stereochemical assignments were not possible. Adducts **4** and **6** were both shown to have the trinitromethyl group attached to C2 by reverse-detected heteronuclear correlation spectroscopy (HMQC). Since **6** was shown to yield **2** during decomposition, it appears certain that **6** is a 1-nitro-2-trinitromethyl adduct. The decomposition of **4** yields **3**, and it is therefore logical to suggest that **4** has the structure of a 1-hydroxy-2-trinitromethyl adduct. Adduct **5** was shown by HMQC to have a nitro group at C2, and during its decomposition **3** is formed. Thus the trinitromethyl function must be present, and this leaves no alternative but a 1-trinitromethyl-2-nitro adduct.

Photolysis in acetonitrile at 0 °C. A solution of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in acetonitrile was irradiated at 0 °C. The composition of the reaction mixtures was monitored by withdrawing samples for NMR spectral

Table 2. Fractional coordinates for atoms in 1,4-dimethoxy-2-trinitromethynaphthalene (**2**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^{2a}$
O(1)	529(2)	3772(1)	8898(1)	22(1)
O(11)	6039(2)	615(2)	7434(2)	55(1)
O(12)	4076(3)	−94(2)	6343(2)	54(1)
O(21)	1738(2)	−513(2)	8881(2)	40(1)
O(22)	−178(2)	1076(2)	8015(2)	33(1)
O(31)	2921(2)	1341(2)	10252(1)	40(1)
O(32)	4506(2)	2924(2)	8984(2)	24(1)
O(4)	3816(2)	4533(1)	3413(1)	24(1)
N(1)	4518(3)	610(2)	7161(2)	39(1)
N(2)	1324(3)	638(2)	8302(2)	28(1)
N(3)	3493(2)	1983(2)	9173(2)	28(1)
C(1)	1325(2)	3975(2)	7532(2)	19(1)
C(2)	2508(3)	2896(2)	6942(2)	20(1)
C(3)	3388(3)	3034(2)	5535(2)	21(1)
C(4)	3081(2)	4285(2)	4769(2)	18(1)
C(4a)	1983(2)	5462(2)	5376(2)	19(1)
C(5)	1790(3)	6800(2)	4631(2)	22(1)
C(6)	789(3)	7930(2)	5248(2)	26(1)
C(7)	−77(3)	7786(2)	6641(2)	25(1)
C(8)	58(2)	6507(2)	7388(2)	21(1)
C(8a)	1085(2)	5310(2)	6775(2)	19(1)
C(9)	−1495(3)	3835(2)	9221(2)	25(1)
C(10)	2912(3)	1603(2)	7854(2)	24(1)
C(11)	4839(3)	3379(2)	2704(2)	26(1)

[a]The equivalent isotropic temperature factor is defined as one-third of orthogonalized U_{ij} tensor (Å^2).

Table 3. Fractional coordinates for atoms in 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**).

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
O(1)	2864(2)	5995(5)	−1110(10)	24(1)
O(4)	583(2)	8555(4)	1552(11)	23(1)
O(911)	3580(3)	5478(5)	3405(11)	36(2)
O(912)	4049(2)	7019(5)	1458(12)	36(2)
O(921)	3737(2)	7958(5)	6212(11)	31(1)
O(922)	2672(2)	8665(5)	6363(11)	27(1)
N(91)	3578(3)	6537(7)	2636(11)	26(2)
N(92)	3142(3)	8043(6)	5429(11)	21(2)
C(1)	2336(4)	6478(6)	−319(13)	16(2)
C(2)	2359(4)	7310(6)	1952(13)	18(2)
C(3)	1763(4)	8042(7)	2477(14)	17(2)
C(4)	1163(3)	7908(6)	1137(15)	18(2)
C(4a)	1083(3)	7014(6)	−853(14)	18(2)
C(5)	451(4)	6872(7)	−2103(13)	23(2)
C(6)	406(4)	6013(7)	−4013(14)	26(2)
C(7)	974(4)	5311(7)	−4713(14)	27(2)
C(8)	1607(3)	5461(6)	−3485(15)	19(2)
C(8a)	1659(4)	6307(6)	−1549(14)	19(2)
C(9)	2970(4)	7315(6)	3264(14)	18(2)
C(10)	576(4)	9493(7)	3447(15)	26(2)

studies (Table 4). The solution after 3 h irradiation (85% conversion) contained **1** (13%), **3** (29%) **4** (18%), **5** (22%) and 1,1,4-trimethoxy-2-nitro-1,2-dihydronaphthalene (**8**) (1%). Compared with the photochemical reaction in dichloromethane, the main differences were a slower reaction rate and that compound **2** was not detected in the reaction mixture, while the yield of **1** had decreased and the yields of **3** and adducts **4** and **5** had increased.

Photolysis at 0 °C in dichloromethane containing methanol (2.2 mol dm^{-3}), and identification of adducts 7–9. Reaction conditions were as above, except that methanol (2.2 mol dm^{-3}) was added. After 5 h irradiation (79% conversion) the photolysis product contained a mixture (Table 5) of **1** (1%), **3** (4%), 1,1,4-trimethoxy-2-trinitromethyl-1,2-dihydronaphthalene (**7**) (28%), **8** (32%) and 4,4-dimethoxy-3-nitro-3,4-dihydro-1(2*H*)-naphthalenone

Table 4. Overview of yields of products from the photolysis of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in acetonitrile at 0 °C.

		Yield (%)					
t/h	Conversion (%)	**1**	**3**	**4**	**5**	**8**	Unknown
0.5	20.0	1.9	3.4	3.4	11.2	—	—
1	39.7	4.0	11.5	8.6	15.5	—	—
2	68.3	11.5	20.2	16.6	20.4	0.7	—
3	85.4	13.1	29.3	18.3	22.2	1.0	—

Table 5. Overview of yields of products from the photolysis of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane or acetonitrile containing methanol (2.2 mol dm^{-3}) at 0 °C.

		Yield (%)					
t/h	Conversion (%)	**1**	**3**	**7**	**8**	**9**	Unknown
Dichloromethane							
1	36.9	6.4	8.9	7.8	10.4	—	3.4
2	48.1	6.2	11.5	11.5	14.4	—	4.5
3	61.2	4.5	8.9	20.0	22.1	1.6	6.1
4	69.8	2.2	7.0	23.1	27.1	2.8	7.6
5	78.9	1.3	4.2	27.9	31.6	5.1	8.8
Acetonitrile							
1	20.0	0.9	1.0	—	15.4	1.2	1.7
2	41.5	4.3	9.5	0.7	20.1	4.5	2.5
3	53.7	3.7	10.2	1.0	25.2	9.9	3.7
4	64.0	2.4	7.1	1.4	31.4	16.8	4.9
5	74.3	3.0	7.6	1.6	34.8	22.4	5.5

(**9**) (5%). Compounds **7**–**9** were isolated by HPLC on a cyanopropyl column, using mixtures of dichloromethane–pentane as the eluent. Their structures were determined from their NMR data, and in the case of **7** also from mass spectrometry.

Photolysis at 0 °C in acetonitrile containing methanol (2.2 mol dm^{-3}). Reaction conditions were as above, except that methanol (2.2 mol dm^{-3}) was added. After 5 h irradiation (74% conversion) the photolysis product contained a mixture (Table 5) of **1** (3%), **3** (8%), **7** (2%), **8** (35%) and **9** (22%).

Studies of the thermal decomposition of adducts 4–6 in deuteriochloroform. The thermal decomposition of adducts **4**–**6** in a sample containing **1** (25%), **2** (6%), **3** (7%), **4** (4.5%), **5** (7%) and **6** (7%), (the remainder consisted of unreacted 1,4-dimethoxynaphthalene), in deuteriochloroform were monitored by ^{1}H NMR spectroscopy (Table 6 and Fig. 3). Since none of the adducts could be isolated, these studies were performed with samples containing mixtures of the adducts and the other photolysis products. The rates of decay respectively formation were fitted to first-order rate equations. Adducts **4** and **5** both yielded the naphthalenone compound **3** and methanol during decomposition. The rate of decay of adduct **4** was $5.2(4) \times 10^{-3}$ min^{-1}, while adduct **5** decomposed with $k = 4.7(1) \times 10^{-2}$ min^{-1}. The formation of **3** had a rate of $3.8(1) \times 10^{-2}$ min^{-1}. The most labile adduct **6** had a rate of decay of $9.5(2) \times 10^{-2}$ min^{-1}, and formed compound **2** [$k = 1.0(1) \times 10^{-1}$ min^{-1}] during decomposition. A small increase of the yield of **1** was also detected [$k = 8(1) \times 10^{-2}$ min^{-1}], possibly due to a slow transformation of **2** into **1** or via elimination of nitrous acid from **5** in a minor pathway.

A similar experiment was performed in deuteriochloroform containing 2.2 mol dm^{-3} methanol in order to test if compounds **7**–**9** might be formed from adducts **4**–**6** via a nucleophilic displacement of trinitromethanide ion by methanol. However, during the decomposition of the adducts, no formation of compounds **7**–**9** was detected.

EPR spectroscopic detection of the radical cation of 1,4-dimethoxynaphthalene under photochemical conditions. Since the attack of trinitromethanide on radical cations ion is a fast reaction, this species must be deactivated to allow EPR spectroscopic studies to be made. This can be achieved by the addition of an acid strong enough to protonate trinitromethanide ion in dichloromethane, such as trifluoroacetic acid. However, this technique does not always give well resolved spectra, and the acidic and/or nucleophilic properties of TFA are strong enough to cause unwanted transformations in sensitive systems.[15,16] Another and much milder method is to use 1,1,1,3,3,3-hexafluoropropan-2-ol as the solvent (the pK_a

Table 6. Time dependence of the product distribution during the decomposition of adducts **4**, **5** and **6** in deuteriochloroform at room temperature.

	Yield (%)					
t/min	**1**	**2**	**3**	**4**	**5**	**6**
0	24.6	6.1	6.8	4.5	6.9	6.9
3	25.3	7.1	7.7	4.5	6.1	5.3
8	25.9	8.3	9.2	4.5	4.8	3.3
12	26.3	9.1	10.2	4.2	4.0	2.2
19	26.7	9.8	11.7	4.0	2.8	1.1
41	27.0	10.4	14.1	3.7	1.0	—
87	27.4	10.0	15.8	2.9	—	—

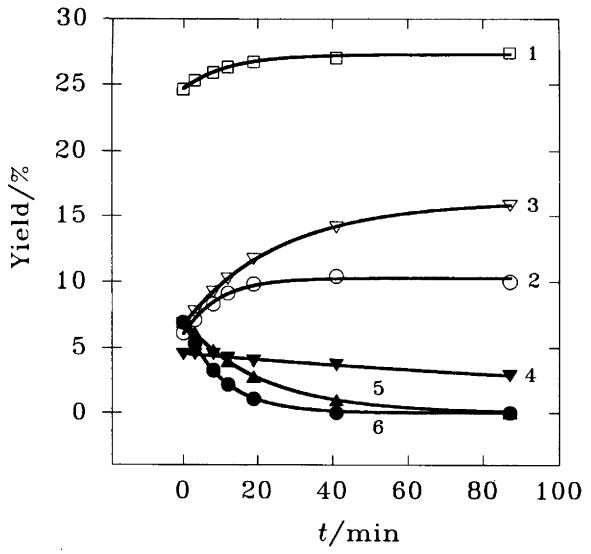


Fig. 3. Time dependence of the yields of 1,4-dimethoxy-2-nitronaphthalene (**1**) (empty squares), 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**) (empty circles) and 4-methoxy-2-(dinitromethylene)-1(2*H*)-napthalenone (**3**) (empty triangles) during the decomposition of adduct **4** (filled triangles down), **5** (filled triangles up) and **6** (filled circles) in $CDCl_3$ at room temperature. The curves represent the best fits to first-order rate equations with $k = 8(1) \times 10^{-2}$, $1.0(1) \times 10^{-1}$, $3.8(1) \times 10^{-2}$, $5.2(4) \times 10^{-3}$, $4.7(1) \times 10^{-2}$ and $9.5(2) \times 10^{-2}$ min^{-1}, respectively.

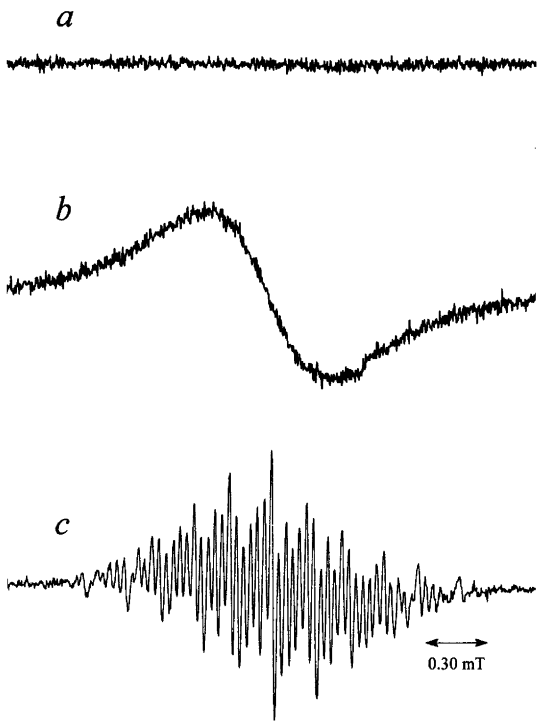


Fig. 4. EPR spectra recorded during photolysis ($\lambda > 430$ nm) of a solution of 1,4-dimethoxynaphthalene and tetranitromethane in (*a*) dichloromethane, (*b*) dichloromethane containing trifluoroacetic acid (0.2 mmol dm^{-3}) and (*c*) 1,1,1,3,3,3-hexafluoropropan-2-ol.

of HFP is 9.3). This non-nucleophilic solvent has a powerful ability to suppress the reactivity of trinitromethanide ion and other nucleophiles via hydrogen-bond donation. The use of HFP as the solvent for EPR studies of radical cations has been shown[8,17] to be superior to the so far preferred solvent, TFA. The EPR spectroscopic activity of a solution of 1,4-dimethoxynaphthalene and tetranitromethane in dichloromethane, in dichloromethane containing trifluoroacetic acid or in HFP under photochemical conditions was investigated (Fig. 4). The dichloromethane solution was EPR silent, while the addition of trifluoroacetic gave a poorly resolved spectrum. Exchanging the solvent for HFP gave a resolved spectrum, which could be simulated with the following HFS values: 0.375 (2 H), 0.202 (6 H), 0.170 (2 H) and 0.067 (2 H) mT, and with a linewidth of 0.01 mT. (Lit.[18] 0.335, 0.219, 0.146, 0.070 mT.)

Discussion

Photolysis of the 1,4-dimethoxynaphthalene–tetranitromethane CT complex in dichloromethane. The mode of formation of 1–6. After formation of the triad [eqn. (1)], the fast step is the nucleophilic attack of trinitromethanide ion upon $ArH^{\cdot+}$. A MINDO/3 calculation gives an estimate of the charge distribution of the radical cation of 1,4-dimethoxynaphthalene (Fig. 5). Based on this criterion only, the most likely position for the nucleophilic attack is at C1, i.e. *ipso* to a methoxy group.

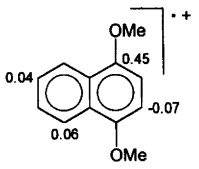
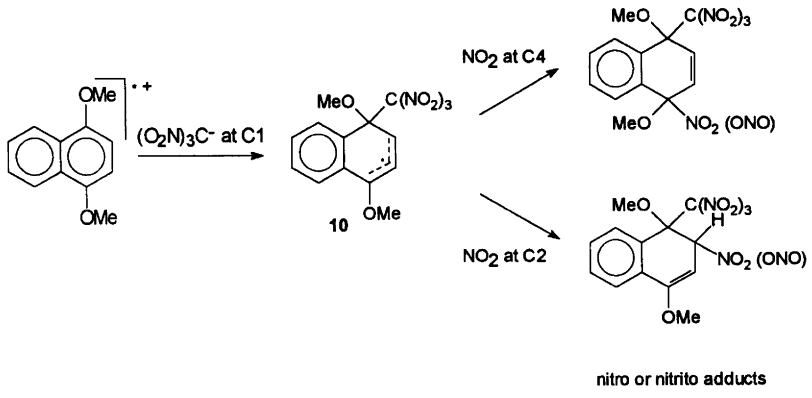


Fig. 5. Calculated (optimized; MINDO/3; UHF method; HyperChem® programme) atomic charge distribution in the radical cation of 1,4-dimethoxynaphthalene.

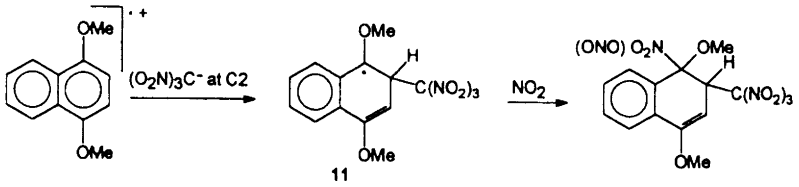
In the subsequent radical coupling reaction between the delocalized carbon radical **10** and nitrogen dioxide, there are several possible pathways (Scheme 1). Nitrogen dioxide can couple either at C2 or C4, and depending on whether the bond formation takes place between carbon and nitrogen, or carbon and oxygen, either nitro or nitrito adducts are formed. However, not only electronic factors should be considered when discussing the regiochemistry of the nucleophilic attack. Also spatial demands play an important role, and in **10** the steric compression caused by the *geminal* methoxy and trinitromethyl group is evident. The alternative position for trinitromethanide ion to attack the radical cation of 1,4-dimethoxynaphthalene is at C2 (Scheme 2). This would relieve some of the strain compared to **10**, and even if the stabilization through delocalization in **11** should be somewhat less, it can be compared with a benzylic radical with a stabilizing methoxy group. An alternative mode of formation of the adducts with a C2 connected trinitromethyl group is via allylic rearrangement of the trinitromethyl group in highly strained 1-nitro-4-trinitromethyl adducts, but we deem this pathway less likely.

The main reaction leading to the formation of 1,4-dimethoxy-2-nitronaphthalene (**1**) is believed to be the coupling of the radical cation of 1,4-dimethoxynaphthalene with the NO_2 formed during photolysis. Another possible source is a 1-trinitromethyl-2-nitro adduct that after elimination of nitroform would give **1**. However, since none of the adducts detected gave any significant amount of **1** during decomposition this could not be verified. The photochemical decomposition of **2** might also augment the yield of **1**, especially after prolonged photolysis.[19]

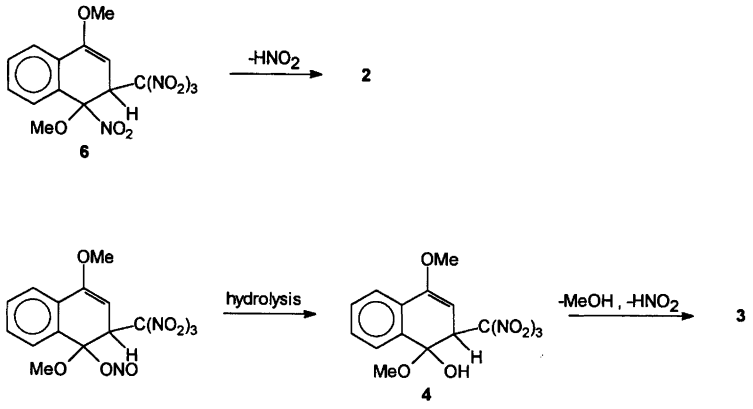
The formation of the trinitromethylarene **2** and the naphthalenone compound **3** from adducts **6** and **4**, respectively, seems certain (Scheme 3). The decay of the 1-nitro-2-trinitromethyl adduct **6**, was shown to be coupled with the formation of **2**. Thus it can be concluded that **2** was formed from **6** via elimination of nitrous acid. The precursor of **3** is probably a 1-nitrito-2-trinitromethyl adduct which after hydrolysis yields a 1-*hydroxy*-2-trinitromethyl adduct. The relatively high percentage of nitrito addition might be due to this mode of coupling being sterically favoured. A nitrito group *ipso* to a methoxy group would have less spatial demands than a nitro group at the same position. The question is then whether the detected species **4** is the nitrito or the hydroxy derivative. Since nitrito adducts are easily hydrolyzed and no intermediate compound could be detected when **4** decomposed to give **3**, we favour the second alternative. The hydroxy compound might also be stabilized via hydrogen bonding between the hydroxy group and one of the nitro groups in the trinitromethyl function. Elimination of methanol and nitrous acid then completes the reaction. The introduction of the unexpected *gem*-dinitromethylene function has been reported in some other reactions involving tetranitromethane. Thus 3-methylindole[20] and 1,1-disubstituted hydrazines[21] have been shown to yield products with this structure element.



Scheme 1.



Scheme 2.

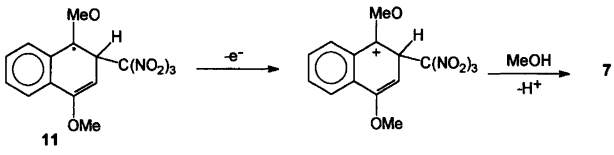


Scheme 3.

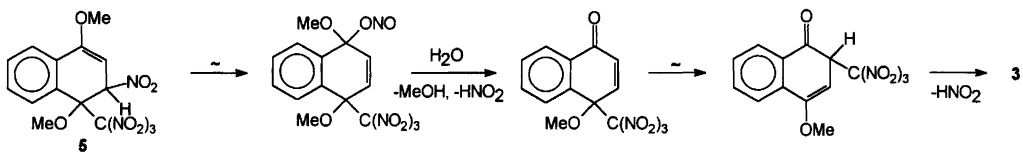
The decomposition studies of adduct **5** showed that this compound,like **4**, is a precursor of **3**. From analyses of NMR spectral data it could be concluded that **5** has a nitro group at C2, while **3** instead has a function derived from a trinitromethyl group at the same position. Therefore the reaction pathway leading to **3** must involve two rearrangements (Scheme 4). An allylic rearrangement of NO_2, with subsequent C–O bond formation, gives a 1,4-nitrito-trinitromethyl adduct. Hydrolysis and elimination of methanol and nitrous acid gives an enone, which then undergoes a second allylic rearrangement of the trinitromethyl group. The driving force for this double rearrangement must be a progressive release of steric compression. Elimination of methanol and nitrous acid then yields **3** with its extended conjugation. Another possible pathway where **5** yields **3** with adduct **4** as an intermediate was ruled out from the decomposition study. When adduct **5** decomposes there is a concomitant increase of the yield of **3** while the amount of **4** is unchanged. Had **5** formed **4**, an increase of the yield of **4** had been noticed due to the different half-lives of the two adducts.

Photolysis of the 1,4-dimethoxynaphthalene–tetranitromethane CT complex in acetonitrile. The higher polarity of this solvent decreases the reactivity of trinitromethanide ion so that the rate of reaction is lower than in dichloromethane. The yield of **1** is decreased, while the yields of **3** and its precursors **4** and **5** are higher compared to photolysis in dichloromethane. An interesting feature is that the adducts **4** and **5** appear to be more stable in acetonitrile than in dichloromethane, in contrast to earlier observations.[22]

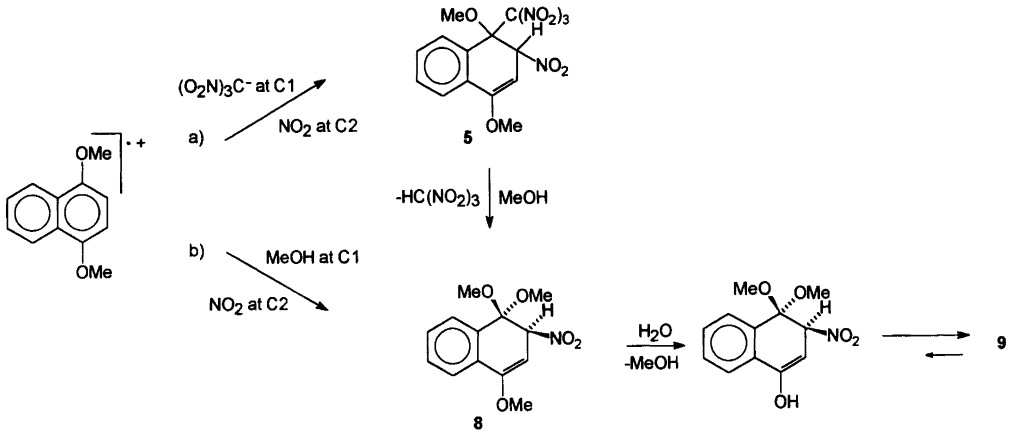
Photolysis in dichloromethane containing methanol, and the mode of formation of adducts 8–10. When the photolysis of 1,4-dimethoxynaphthalene and tetranitromethane was carried out in dichloromethane containing methanol, high yields of the methoxy-trinitromethyl adduct **7** and the methoxy-nitro adduct **8** were obtained. This means that methanol plays an active role as a reagent during the photolysis. The crucial step leading to the formation of **7** is believed to be the oxidation of the radical **11**, followed by nucleophilic attack of methanol (Scheme 5). Carbon centered radicals with an adjacent oxygen function have been reported to have low oxidation potentials.[23] The formation of **8** is less straightforward. Either methanol is able to compete with trinitromethanide ion in the attack on the radical cation of 1,4-dimethoxynaphthalene, or the third methoxy group is incorporated via a nucleophilic displacement of trinitromethanide ion (Scheme 6). The control experiment where methanol was added to a mixture of adducts **4–6** in deuteriochloroform showed no formation of **7–9**. This result favours pathway b in Scheme 6, but since the conditions during the photochemical experiments and the NMR studies of the compounds are not identical, the nucleophilic displacement reaction outlined in pathway a cannot be completely excluded. Methanol is a



Scheme 5.



Scheme 4.



Scheme 6.

weaker nucleophile than trinitromethanide ion, but the relative concentration of methanol is high. The addition of methanol may also suppress the reactivity of trinitromethanide ion via hydrogen bonding. This effect has been seen before when photolyses of mixtures of alkoxyarenes and tetranitromethane were carried out with ethanol present.[24] Since no products with C2 connected methoxy groups were detected in the reaction mixtures, and accepting pathway b in Scheme 6, it is concluded that methanol attacks the radical cation of 1,4-dimethoxynaphthalene at C1, *ipso* to a methoxy group. The steric compression in this case should be significantly less than when the attacking species is trinitromethanide ion, and thus the important factor of the regiochemical outcome is the charge distribution in the radical cation of 1,4-dimethoxynaphthalene. The nucleophilic attack of methanol at C1 gives a carbon radical which then combines with NO_2, giving the enol ether **8**, a compound which after hydrolysis gives **9** (Scheme 6).

This new method to produce ketals was tested in the preparation of 9,9-dimethoxy-10(9*H*)-anthracenone.[25] This compound has been reported[26] to be of importance as an intermediate in the synthesis of A_1 adenosine receptor ligands, but its preparation suffered from the low yield (15% in a two-step reaction starting with anthracene). By using tetranitromethane as a mild oxidant and running the reaction in the presence of methanol the yield could be much improved (60% in a two-step reaction starting with anthraquinone).

Photolysis in acetonitrile containing methanol. The yield of the methoxy-trinitromethyl adduct **7** is much lower when the photolysis is carried out in acetonitrile containing methanol compared to the corresponding experiment in dichloromethane. As discussed above there are two mechanistic alternatives. Either the selectivity of the deactivated trinitromethanide ion is changed so that the dominant position for the attack is at C1, followed by nucleophilic displacement of trinitromethanide ion by methanol, or the reactivity of trinitromethanide ion is so low that the fast reaction is instead the attack of methanol on the radical cation of 1,4-dimethoxynaphthalene. Since no substitution of the trinitromethyl group was detected when methanol was added to a solution of adducts **4**–**6** in deuteriochloroform, we favour the second alternative.

Experimental

Materials and methods. Melting points are uncorrected. The NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer, and the mass spectra were recorded on a JEOL JMS SX-102 instrument. Tetranitromethane was purchased from Aldrich. 1,4-Dimethoxynaphthalene was prepared according to a literature method.[27] Dichloromethane (SupraSolv), acetonitrile (Uvasol), trifluoroacetic acid (Uvasol), 1,1,1,3,3,3-hexafluoropropan-2-ol (Uvasol) and methanol (*p.a.*) were from Merck. HPLC separations were made with a Varian 5000 liquid chromatograph on a Supelco cyanopropyl column and with a Pye Unicam LC-UV detector, using hexane–dichloromethane mixtures as the eluent.

EPR spectra were recorded by the Upgrade version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR) using a 50 W high-pressure Hg lamp (Bruker, ER 202) and a filter with cut-off at 430 nm (Schott).

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.[28]

General procedure for the photochemical reactions. A more detailed description of the equipment used for the photolyses has been given before.[29] A solution of 1,4-dimethoxynaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane or acetonitrile was irradiated at −20, 0 or 20 °C with filtered light (cut-off at 435 nm). Aliquots were withdrawn at

appropriate time intervals, the volatile material was removed under reduced pressure at $\leqslant 0\,^{\circ}C$, and the product composition was determined as soon as possible by NMR spectral analyses.

Photolysis in dichloromethane and identification of the stable products and adduct ***6***. Reaction conditions were as above. Upon mixing, 1,4-dimethoxynaphthalene and tetranitromethane gave a dark red CT complex. After 1.5 h irradiation (83% conversion) at 0 °C, the photolysis product was shown to be a mixture (Table 1) of 1,4-dimethoxy-2-nitronaphthalene (**1**) (38%), 1,4-dimethoxy-2-trinitromethylnaphthalene (**2**) (10%), 4-methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone (**3**) (24%), and two labile adducts, 1,4-dimethoxy-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**4**) (7%) and 1,4-dimethoxy-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (**5**) (2%). After 1.5 h irradiation (93% conversion) at −20 °C the reaction mixture contained **1** (33%), **2** (18%), **3** (16%), **4** (14%), **5** (6%) and a third adduct, 1,4-dimethoxy-1-nitro-2-trinitromethyl-1,2-dihydronaphthalene (**6**) (3%), not detected when the photolysis was carried out at 0 °C. Compounds **1** and **2** were isolated by separation on a silica gel Chromatotron plate using hexane as the eluent. The trinitromethylarene **2**, proved to be rather sensitive to the separation method used, but small amounts of high purity could be obtained. It should also be noted that the pure compound was stable in deuteriochloroform at room temperature. No change was noticeable after 2 weeks. Compound **3** was isolated by recrystallisation from chloroform. None of the adducts **4**–**6** was stable enough to be isolated, so their structure assignments were determined from NMR spectra obtained from the reaction mixtures together with studies of their decompositions.

1,4-Dimethoxy-2-nitronaphthalene (**1**) m.p. 95–96 °C (Lit.[30] 97–98 °C). NMR data were as reported in the literature.[30]

1,4-Dimethoxy-2-trinitromethylnaphthalene (**2**) m.p. 115–116 °C. (X-ray crystal structure determined, see below.) ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 1-OMe), 3.98 (s, 4-OMe) 6.52 (s, H3), 7.70 (m, 2 H, H6 and H7), 8.07 (m, H5), 8.35 (m, H8). ^{13}C NMR ($CDCl_3$): δ 56.10 (4-OMe), 62.72 (1-OMe), 99.31 (C3), 123.27 (C8), 124.28 (C5), 128.30 (C6 or C7), 129.31 (C6 or C7); the remainder of the spectrum could not be detected. The assignments above were confirmed by HMQC and HMBC spectra.

*4-Methoxy-2-(dinitromethylene)-1(2*H*)-naphthalenone* (**3**) m.p. 177–178 °C. (X-ray crystal structure determined, see below.) The UV spectrum in dichloromethane gave λ_{max} (log ε): 230 (4.36), 292 (4.52), 510 (4.43). (X-ray crystal structure determined, see below.) ^{1}H NMR (CD_3CN): δ 4.16 (s, OMe), 7.26 (s, H3), 7.55 (ddd, $J_{H7,H6}$ 7.6 Hz, $J_{H7,H8}$ 7.6 Hz, $J_{H7,H5}$ 1.2 Hz, H7), 7.69 (ddd, $J_{H6,H5}$ 7.6 Hz, $J_{H6,H7}$ 7.6 Hz, $J_{H6,H8}$ 1.4 Hz, H6), 7.82 (ddd, $J_{H5,H6}$ 7.6 Hz, $J_{H5,H7}$ 1.2 Hz, $J_{H5,H8}$ 0.4 Hz, H5), 7.98 (ddd, $J_{H8,H7}$ 7.6 Hz, $J_{H8,H6}$ 1.4 Hz, $J_{H8,H5}$ 0.4 Hz, H8). ^{13}C NMR (CD_3CN): δ 57.71 (OMe), 94.01 (C3), 124.64 (C5), 128.99 (C8), 131.41 (C2), 132.51 (C7), 136.02 (C6), 167.13 (C4), 182.49 (C1); the remainder of the spectrum could not be detected. The assignments above were confirmed by HMQC, HMBC and NOESY.

1,4-Dimethoxy-1-nitro-2-trinitromethyl-1,2-dihydronaphthalene (**6**). ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 1-OMe), 3.78 (s, 4-OMe), 4.91 (d, $J_{H2,H3}$ 5.9 Hz, H3), 5.81 (d, $J_{H3,H2}$ 5.9 Hz, H2), the remainder of the spectrum was obscured by signals of the other components in the mixture. ^{13}C NMR ($CDCl_3$): δ 46.0 (C2), 88.8 (C3); the remainder of the spectrum was obscured by signals of the other components in the mixture. The above assignments were confirmed by HMQC spectra. The correlation between H2 and the ^{13}C NMR resonance at 46.0 ppm is consistent with the H–**C**–$C(NO_2)_3$ structure element.[8]

Photolysis in acetonitrile at 0 °C and identification of adducts ***4*** *and* ***5***. Reaction conditions were as above. After 3 h irradiation (85% conversion) the photolysis product was shown to be a mixture (Table 4) of **1** (13%), **3** (29%), **4** (18%), **5** (22%) and 1,1,4-trimethoxy-2-nitro-1,2-dihydronaphthalene (**8**) (1%).

1,4-Dimethoxy-2-trinitromethyl-1,2-dihydronaphthalen-1-ol (**4**). ^{1}H NMR ($CDCl_3$): δ 3.39 (s, 1-OMe), 3.76 (s, 4-OMe), 4.75 (d, $J_{H2,H3}$ 5.8 Hz, H2), 4.92 (d, $J_{H3,H2}$ 5.8 Hz, H3); the remainder of the spectrum was obscured by signals of the other components in the mixture. ^{13}C NMR ($CDCl_3$): δ 49.2 (C2), 87.7 (C3); the remainder of the spectrum was obscured by signals of the other components in the mixture. The above assignments were confirmed by HMQC spectra. The correlation between H2 and the ^{13}C NMR resonance at 49.2 ppm is consistent with the H–**C**–$C(NO_2)_3$ structure element.[8]

1,4-Dimethoxy-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (**5**). ^{1}H NMR ($CDCl_3$): δ 3.12 (s, 1-OMe), 3.84 (s, 4-OMe), 5.25 (d, $J_{H3,H2}$ 3.0 Hz, H3), 5.61 (d, $J_{H2,H3}$ 3.0 Hz, H2); the remainder of the spectrum was obscured by signals of the other components in the mixture. ^{13}C NMR ($CDCl_3$): δ 86.8 (C2), 89.3 (C3); the remainder of the spectrum was obscured by signals of the other components in the mixture. The above assignments were confirmed by HMQC spectra. The correlation between H2 and the ^{13}C NMR resonance at 86.8 ppm is consistent with the H–**C**–NO_2 structure element.[8]

Photolysis at 0 °C in dichloromethane containing methanol (2.2 mol dm^{-3}), and identification of adducts ***7***–***9***. Reaction conditions were as above, except that methanol (2.2 mol dm^{-3}) was added. After 5 h irradiation (79% conversion) the photolysis product was shown to be a mixture (Table 5) of **1** (1%), **3** (4%), 1,1,4-trimethoxy-2-trinitromethyl-1,2-dihydronaphthalene (**7**) (28%), **8** (32%) and 4,4-dimethoxy-3-nitro-3,4-dihydro-1(2*H*)-naphthalenone (**9**) (5%). Compounds **7**–**9** were isolated by HPLC chromatography on a cyanopropyl column, using mixtures of dichloromethane–pentane as the eluent.

1,1,4 - Trimethoxy - 2 - trinitromethyl - 1,2 - dihydro - naphthalene (**7**) m.p. 104–106 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 2.84 [s, 1-OMe, syn to the $C(NO_2)_3$ group], 3.36 [s, 1-OMe, anti to the $C(NO_2)_3$ group], 3.76 (s, 4-OMe), 4.70 (d, $J_{H2,H3}$ 6.6 Hz, H2), 5.05 (d, $J_{H3,H2}$ 6.6 Hz, H3), 7.43 (m, 2 H, H6 and H7), 7.61 (m, 2 H, H5 and H8). ^{13}C NMR ($CDCl_3$): δ 46.66 (C2), 51.55 [1-OMe anti to the $C(NO_2)_3$ group], 52.36 [1-OMe syn to the $C(NO_2)_3$ group], 55.82 (4-OMe), 87.87 (C3), 99.58 (C1), 123.63 (C5 or C8), 127.11 (C5 or C8), 129.53 (C4a or C8a), 129.79 (C6 or C7), 129.98 (C6 or C7), 132.63 (C4a or C8a), 156.93 (C4). The assignments above were confirmed by HMQC, HMBC and NOESY. *m/z* CI (CH_4): 370 (64%), 323 (100%), 293 (68%), 218 (92%). *m/z* EI: 323 (100%), 246 (61%), 188 (64%).

1,1,4-Trimethoxy-2-nitro-1,2-dihydronaphthalene (**8**) m.p. 117–119 °C. ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 1-OMe, anti to the NO_2 group), 3.57 (s, 1-OMe, syn to the NO_2 group), 3.81 (s, 4- OMe), 5.07 (d, $J_{H3,H2}$ 7.0 Hz, H3), 5.57 (d, $J_{H2,H3}$ 7.0 Hz, H2), 7.40 (ddd, $J_{H7,H6}$ 7.5 Hz, $J_{H7,H8}$ 7.5 Hz, $J_{H7,H5}$ 1.5 Hz, H7), 7.43(ddd, $J_{H6,H5}$ 7.5 Hz, $J_{H6,H7}$ 7.5 Hz, $J_{H6,H8}$ 1.6 Hz, H6), 7.67 (ddd, $J_{H8,H6}$ 7.5 Hz, $J_{H8,H7}$ 1.6 Hz, $J_{H8,H5}$ 0.5 Hz, H8), 7.74 (ddd, $J_{H5,H6}$ 7.5 Hz, $J_{H5,H7}$ 1.5 Hz, $J_{H5,H8}$ 0.5 Hz, H5). ^{13}C NMR ($CDCl_3$): δ 50.23 (1-OMe syn to the NO_2 group), 50.37 (1-OMe anti to the NO_2 group), 55.72 (4-OMe), 85.28 (C2), 88.48 (C3), 97.98 (C1), 123.82 (C5), 127.19 (C8), 129.02 (C7), 129.60 (C6), 130.31 (C4a), 132.52 (C8a), 158.76 (C3). The assignments above were confirmed by HMQC, HMBC and NOESY.

*4,4 -Dimethoxy-3-nitro-3,4-dihydro-1 (2*H*)-naphthalenone* (**9**) m.p. 132–134 °C. ^{1}H NMR ($CDCl_3$): δ 2.98 (s, 1-OMe, anti to the NO_2 group), 3.18 (dd, $J_{H2,H2}$ 18.6 Hz, $J_{H2,H3}$ 2.3 Hz, H2, syn to the NO_2 group), 3.26 (dd, $J_{H2,H2}$ 18.6 Hz, $J_{H2,H3}$ 4.5 Hz, H2, syn to the NO_2 group), 3.65 (s, 1-OMe, anti to the NO_2 group), 5.56 (dd, $J_{H3,H2}$ 4.5 Hz, $J_{H3,H2}$ 2.3 Hz, H3), 7.56 (ddd, $J_{H7,H8}$ 7.7 Hz, $J_{H7,H6}$ 7.5 Hz, $J_{H7,H5}$ 1.4 Hz, H7), 7.63 (ddd, $J_{H6,H5}$ 7.7 Hz, $J_{H6,H7}$ 7.5 Hz, $J_{H6,H8}$ 1.5 Hz, H6), 7.77 (ddd, $J_{H5,H6}$ 7.7 Hz, $J_{H5,H7}$ 1.4 Hz, $J_{H5,H8}$ 0.5 Hz, H5), 8.12 (ddd, $J_{H8,H7}$ 7.7 Hz, $J_{H8,H6}$ 1.5 Hz, $J_{H8,H5}$ 0.5 Hz, H8). ^{13}C NMR ($CDCl_3$): δ 38.94 (C2), 49.58 (1-OMe, syn to the NO_2 group), 50.19 (1-OMe, anti to the NO_2 group), 83.73 (C3), 97.44 (C4), 127.46 (C8), 127.89 (C5), 130.37 (C7), 130.57(C4a), 131.94 (C8a), 133.61 (C6), 192.30 (C1). The assignments above were confirmed by HMQC, HMBC and NOESY.

Photolysis at 0 °C in acetonitrile containing methanol (2.2 mol dm^{-3}). Reaction conditions were as above except that methanol (2.2 mol dm^{-3}) was added. After 5 h irradiation (74% conversion) the photolysis product was shown to be a mixture (Table 5) of **1** (3%), **3** (8%), **7** (2%), **8** (35%) and **9** (22%).

Studies of the thermal decomposition of adducts 4–6 in deuteriochloroform. The thermal decomposition of adducts **4**–**6** in a sample containing **1** (25%), **2** (6%), **3** (7%), **4** (4.5%), **5** (7%) and **6** (7%) (the remainder consisted of unreacted 1,4-dimethoxynaphthalene), in deuteriochloroform were monitored with ^{1}H NMR spectroscopy (Table 6 and Fig. 3). Since neither of the adducts could be isolated, these studies had to be performed with samples containing mixtures of the adducts and the other photolysis products. Adducts **4** and **5** both yielded the naphthalenone compound **3** and methanol during decomposition. Adduct **4** had a half-life of >90 min, while the half-life of adduct **5** was about 15 min. The most labile adduct **6**, had a half-life <10 min, and gave the trinitromethyl compound **2** during decomposition. A small increase of the yield of **1** was also detected.

A similar experiment was performed in deuteriochloroform containing methanol (2.2 mol dm^{-3}) in order to test if compounds **7**–**9** might be formed from adducts **4**–**6** via a nucleophilic displacement of trinitromethanide ion by methanol. However, during the decomposition of the adducts, no formation of compounds **7**–**9** was detected.

EPR spectroscopic detection of the radical cation of 1,4-dimethoxynaphthalene under photochemical conditions. A solution of 1,4-dimethoxynaphthalene and tetranitromethane (a) in dichloromethane, (b) in dichloromethane containing trifluoroacetic acid (0.2 mol dm^{-3}) or (c) in 1,1,1,3,3,3-hexafluoropropan-2-ol was irradiated and studied with EPR spectroscopy (Fig. 4) as described above. The concentrations used were in (a) and (b) 1,4-dimethoxynaphthalene (0.03 mol dm^{-3}) and tetranitromethane (0.4 mol dm^{-3}). In (c), due to poor solubility, a more dilute solution of 1,4-dimethoxynaphthalene (0.003 mol dm^{-3}) and tetranitromethane (0.1 mol dm^{-3}) was used.

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, λ(Mo *K*α) 0.710 73 Å, 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 setting angles of about 25 accurately centered high-angle reflections were used.

Crystal data.

1,4-Dimethoxy-2-trinitromethylnaphthalene (**2**), $C_{13}H_{11}N_3O_8$, *M* 337.25, triclinic, $P\bar{1}$, *a* 7.378(3), *b* 9.562(2), *c* 9.976(2) Å, α 83.74(1), β 78.33(3), γ 82.99°; *V* 681.5(3) Å^3, D_c 1.643 g cm^{-3}, *Z* 2, μ(Mo *K*α) 1.39 cm^{-1}. The crystal was orange and of approximate dimensions 0.78 × 0.34 × 0.30 mm. Data were collected at

158(2) K out to a maximum Bragg angle $\theta = 23.99°$. The number of independent reflections measured 2142, 1704 with $I > 2\sigma(I)$. Absorption corrections were not applied. g_1 0.0651, g_2 0.00, $R_{(obs)}$-factor 0.0383, $wR_{(all\ data)}$ 0.1048.

4-Methoxy-2-(dinitromethylene)-1(2H)-naphthalenone (**3**). $C_{12}H_8N_2O_6$, M 276.20, orthorhombic, $Pna2_1$, a 19.104(4), b 10.799(3), c 5.419(3) Å; V 1118.0(7) Å^3, D_c 1.641 g cm^{-3}, Z 4, μ(Mo $K\alpha$) 1.35 cm^{-1}. The crystal was dark red and of approximate dimensions $0.80 \times 0.20 \times 0.12$ mm. Data were collected at 158(2) K out to a maximum Bragg angle $\theta = 22.50°$. Number of independent reflections measured 824, 630 with $I > 2\sigma(I)$. Absorption corrections were not applied. g_1 0.0586, g_2 0.00, $R_{(obs)}$-factor 0.0462, $wR_{(all\ data)}$ 0.1150.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)[31] were employed. This program is based on intensities and uses all data. The observed threshold $I > 2\sigma(I)$ was used only for calculating $R_{(obs)}$, 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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