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Photochemical Nitration by Tetranitromethane. Part XXI.† The Regiochemistry of Nitrito–Trinitromethyl and Nitro–Trinitromethyl Addition to 2,6-Dimethylnaphthalene

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The photonitration of 2,6-dimethylnaphthalene with tetranitromethane in dichloromethane at + 20 °C gives mainly the adducts *trans*-3,7-dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene **7**, the epimeric 2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes **8** and **10**, the epimeric 3,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes **9** and **12**, the epimeric 2,6-dimethyl-4-trinitromethyl-1,4-dihydronaphthalen-1-ols **11** and **16**, *trans*-3,7-dimethyl-1-trinitromethyl-1,2-dihydronaphthalen-2-ol **15**, the two regioisomeric nitro cycloadducts **13** and **14**, and the hydroxy cycloadduct **17**. *trans*-3,7-Dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene **7** and *trans*-3,7-dimethyl-1-trinitromethyl-1,2-dihydronaphthalen-2-ol **15** undergo thermal alkene–nitro cycloaddition to give the nitro cycloadduct **14** and the hydroxy cycloadduct **17**, respectively. The mode of formation of these products are discussed. X-ray crystal structures are reported for adducts **8**, **10**, **14** and **17**.

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[1,2] to occur by recombination of a triad consisting of $ArH^{\bullet+}$, trinitromethanide ion, and nitrogen dioxide [eqn. (1)].[3]

$$ArH\cdots C(NO_2)_4 \xrightarrow[<3\ ps]{h\nu_{CT}} ArH^{\bullet+}\ (O_2N)_3C^-\ NO_2 \quad (1)$$
triad

The first chemical step which occurs, leading to the formation of adducts, is reaction between $ArH^{\bullet+}$ and trinitromethanide ion [eqn. (2)] to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)].[1,2] In the photonitration of naphthalene[4] with

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

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

tetranitromethane the initial bond formation between trinitromethanide ion and $ArH^{\bullet+}$ occurs at the favourable 1-position, as judged by the calculated[5] (AM1)[6] atomic charges on the respective ring carbon atoms (Fig. 1). The subsequent coupling of the delocalized carbon radical **1**

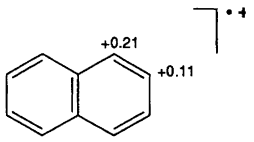

Fig. 1. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties in the radical cation of naphthalene.

with nitrogen dioxide then yields the nitro–trinitromethyl adducts **2**, **3** and **4**, and the labile nitrito–trinitromethyl adduct **5** which is hydrolysed during the reaction or the work-up procedure to give the hydroxy–trinitromethyl adduct **6** (Scheme 1).

For a series of methyl-substituted naphthalenes similar photoreactions with tetranitromethane yield adducts

† Parts XIX and XX, see Refs. 10 and 13, respectively.
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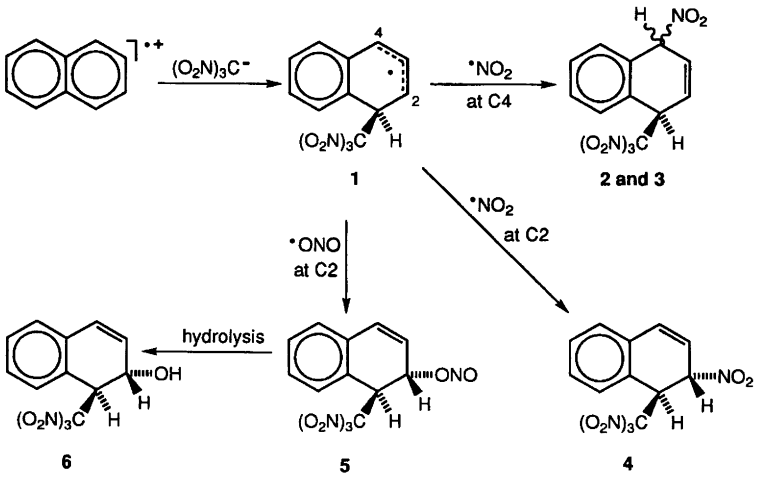


Scheme 1.

formed by attack of trinitromethanide ion at the ring carbon atoms indicated on the respective radical cation structures (Fig. 2). For the radical cations derived from 1,2-dimethylnaphthalene[7] and 1,8-dimethylnaphthalene,[8] trinitromethanide ion attack leading to adduct formation is in keeping with the calculated charges on the ring carbon atoms (Fig. 2). For the 1-methylnaphthalene radical cation adduct formation results predominantly from trinitromethanide attack at C4, the position favoured by the charge at that centre, but also to some extent by attack at C5.[9] The absence of adducts derived from attack of trinitromethanide ion at C8 in the 1-methylnaphthalene radical cation, apparently favoured by the charge distribution, was rationalized in terms of the steric hindrance arising from the *peri* interaction between the bulky attacking trinitromethanide ion at C8 and the 1-methyl group. Although the calculated charge distribution in the 2,3-dimethylnaphthalene radical cation appeared to suggest that trinitromethanide ion should attack with some

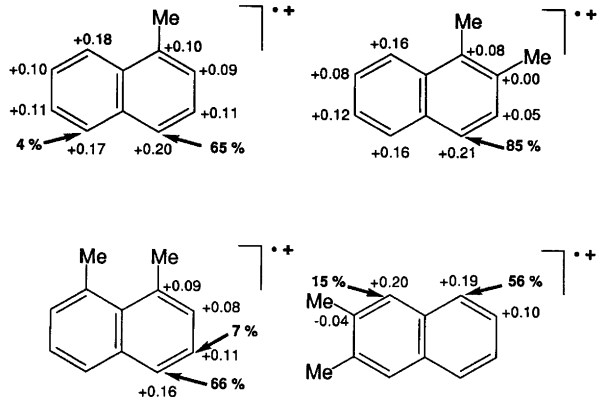


Fig. 2. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties in the radical cations of 1-methylnaphthalene, 1,2-dimethylnaphthalene, 1,8-dimethylnaphthalene, and 2,3-dimethylnaphthalene, and the position and amount of trinitromethanide ion attack leading to the formation of adducts.

preference at C1(C4), the predominant attack occurred at C5(8).[10] For this substrate it appears that the attack of trinitromethanide ion at C1(4) is hindered by the steric interaction between the attacking trinitromethanide ion and the buttressed methyl groups at C2(3).

The calculated[5] atomic charges on the ring carbon atoms of the radical cation of 2,6-dimethylnaphthalene are given in Fig. 3. On this basis it appeared that attack of trinitromethanide ion might occur at either C1(5) or C4(8) of the 2,6-dimethylnaphthalene radical cation, with consequent overall addition of tetranitromethane to the ring. It was recognised at the outset that the charge distribution in this radical cation might lead to a preference for attack of trinitromethanide at C4(8), and that this trend for attack would be favoured further by the steric interaction between the attacking trinitromethanide ion and the *vicinal* methyl group in the alternative attack at C1(5). In the event, these expectations appear justified, trinitromethanide ion attack occurring substantially, but not exclusively, at C4(8). We now report the results of this study.

Results

General. The photochemical experiments were performed with filtered light (cut-off < 435 nm, 5 cm water IR-filter, from a 300 W lamp) as described before,[11] and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent

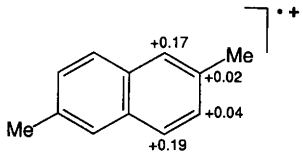
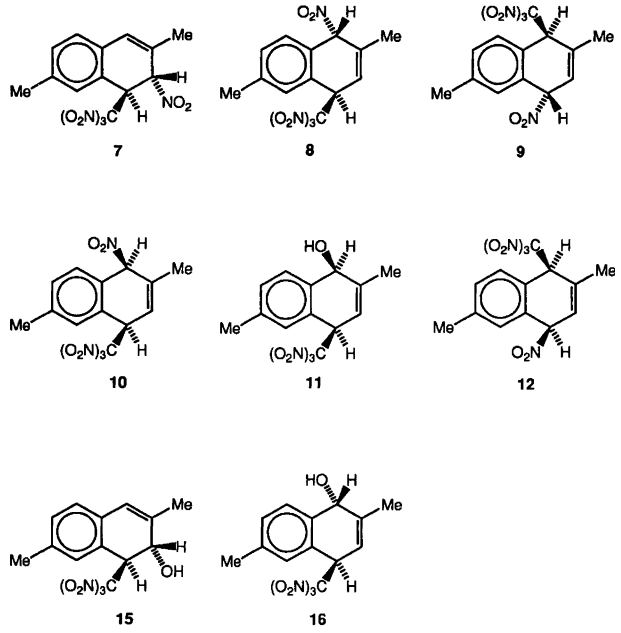


Fig. 3. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties in the radical cation of 2,6-dimethylnaphthalene.

and excess tetranitromethane, was conducted at a temperature $\leq 0°C$. The crude product mixtures were stored at $-20°C$ and were analysed (^1H NMR spectroscopy, see the Experimental section; Tables 1 and 6) as soon as possible.

Photochemistry in dichloromethane at +20°C and identification of adducts. A solution of 2,6-dimethylnaphthalene (0.4 mol dm^{-3}) and TNM (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 final solution (after 2 h, conversion $\approx 95\%$) after work-up contained the adducts **7** (15%), **8** (14%), **9** (11%), **10** (16%),



11 (5%), **12** (3%), **13** (1%), **14** (1%), **15** (7%), **16** (4%), **17** (1%), 3,7-dimethyl-1-trinitromethylnaphthalene **18** (trace), 2,6-dimethyl-1-nitronaphthalene **19** (16%), and 3,7-dimethyl-1-nitronaphthalene **20** (3%). The adducts were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents. For the convenience of the ensuing discussion the identification of the adducts will be described for groups of compounds, rather than in the order of elution given in the Experimental section.

Adducts **7** *and* **14**. Although *trans*-3,7-dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene **7** could be isolated only in admixture with adduct **8**, below, the product **14** of the intramolecular nitro–alkene cycloaddition of compound **7** was isolated in a pure state. On storage of a solution of the impure nitro–trinitromethyl adduct **7** in (^2H)chloroform in the dark at 22°C it was slowly converted into the nitro cycloadduct **14** with a half-life of 96 h. The structure of **14** was determined by single crystal X-ray analysis. A perspective drawing of **14**, $C_{13}H_{12}N_4O_8$, m.p. 169°C (decomp.) is presented in Fig. 4, and corresponding atomic coordinates are given in Table 2. The heterocyclic cage structure evident in Fig. 4 is formed from the nitro–trinitromethyl adduct **7** by thermal cycloaddition of a nitro group of the trinitromethyl function with the alkene system (cf. Refs. 7–10, 12). In **14**, N(1) is clearly trigonal pyramidal and bond length differences [C(11)–N(1) 1.485(3) Å, C(11)–N(2) 1.520(3) Å, C(11)–N(3) 1.534(3) Å] are similar to those observed earlier[7–10,12,13] for analogous heterocyclic cage structures. In the context of confirming the structure of the nitro–trinitromethyl adduct **7**, the C(4)–C(11) bond in **14** is close to *anti* to the C(3)–N(4) bond, pointing to a *trans*-2-nitro-1-trinitromethyl stereochemistry for adduct **7** [torsional angle: N(4)–C(3)–C(4)–C(11) $-173.0(2)°$]. The spectroscopic data for the nitro–trinitromethyl adduct **7** and its derived nitro cycloadduct **14** were in accord with the assigned and determined structures, respectively.

Adducts **15** *and* **17**. While the hydroxy cycloadduct **17** could be isolated in a pure state its precursor, hydroxy–trinitromethyl adduct **15** obtained from HPLC, always contained significant amounts of **17**, presumably the result of the cycloaddition of the hydroxy–trinitromethyl adduct **15** in the HPLC solvents after the separation and prior to their removal under reduced pressure. Storage of

Table 1. Overview of yields of products from the photolysis of 2,6-dimethylnaphthalene (0.4 mol dm^{-3}) in tetranitromethane (0.8 mol dm^{-3}) in dichloromethane.

		Yield (%)																
t/h	Conversion (%)	7	8	9	10	11	12	13	14	15	16	17	Unknown	Total adducts	18	19	20	Unknown aromatics
At +20°C																		
1	75	9.9	10.2	8.7	12.5	3.5	1.6	0.4	0.4	5.3	2.4	0.5	1.1	56.5	1.8	16.4	3.3	22.0
2	95	14.5	13.6	11.1	16.0	4.6	3.1	1.2	1.1	6.9	3.7	1.1	1.7	78.6	trace	16.0	2.8	2.6
At −20°C																		
1	30	1.2	2.2	0.9	2.1	0.9	0.6	–	–	1.0	0.7	0.1	0.2	9.9	3.8	41.8	6.1	38.4
2	71	1.5	3.1	1.6	2.9	1.2	1.0	0.1	–	1.3	0.7	0.1	0.4	13.9	3.1	63.3	8.6	11.1
3	100	1.8	3.3	1.9	3.2	1.1	1.0	0.3	–	1.3	0.7	–	0.5	15.1	2.4	54.7	7.9	19.9

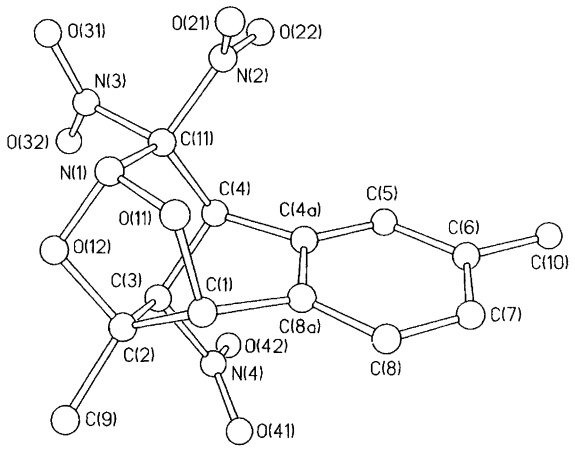
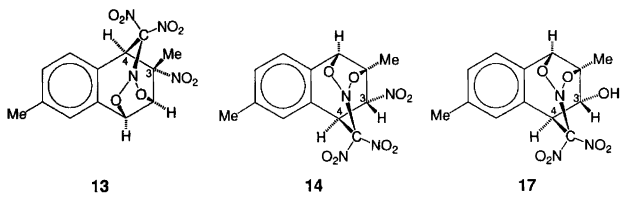


Fig. 4. Perspective drawing of compound **14**.

Table 2. Fractional coordinates for atoms in nitro cycloadduct **14**. The equivalent isotropic temperature factor in Tables 2–5 is defined as one-third of the orthogonalized U_{ij} tensor (Å^2).

Atom	$10^4Y/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
O(11)	7633(1)	1813(1)	7944(2)	23(1)
O(12)	6166(1)	1463(1)	6932(2)	19(1)
O(21)	8477(1)	1082(2)	5588(2)	41(1)
O(22)	8175(1)	−713(2)	5051(2)	45(1)
O(31)	6482(2)	794(2)	3348(2)	50(1)
O(32)	5783(1)	−486(1)	4401(2)	32(1)
O(41)	6540(1)	−912(2)	10724(2)	36(1)
O(42)	6203(2)	−2226(2)	8900(3)	54(1)
N(1)	6998(1)	1505(2)	6492(2)	21(1)
N(2)	8015(1)	231(2)	5512(2)	29(1)
N(3)	6400(1)	174(2)	4441(2)	27(1)
N(4)	6349(1)	−1237(2)	9320(3)	29(1)
C(1)	7376(2)	1219(2)	9277(3)	20(1)
C(2)	6372(1)	870(2)	8501(3)	18(1)
C(3)	6301(2)	−384(2)	7977(3)	18(1)
C(4)	7108(1)	−646(2)	7257(3)	18(1)
C(4A)	7951(1)	−653(2)	8669(3)	18(1)
C(5)	8571(2)	−1540(2)	8994(3)	22(1)
C(6)	9285(2)	−1533(2)	10397(3)	26(1)
C(7)	9248(2)	−633(2)	11480(3)	28(1)
C(8)	8723(2)	254(2)	11177(3)	26(1)
C(8A)	8033(2)	250(2)	9772(3)	20(1)
C(9)	5677(2)	1294(2)	9331(3)	24(1)
C(10)	9970(2)	−2488(2)	10749(3)	35(1)
C (11)	7139(2)	302(2)	6044(3)	21(1)



the impure hydroxy–trinitromethyl adduct **15**, containing ca. 20% of **17**, in (^{2}H)chloroform in the dark at 22°C resulted in its complete conversion into **17** with a half-life of ca. 13 h; the estimation of the half-life for this cycloaddition was complicated by the precipitation of **17** during the period of the observations.

The structure of **17**, $C_{13}H_{13}N_3O_7$, m.p. 183–184°C, was determined by single crystal X-ray analysis. A perspective drawing **17** is presented in Fig. 5, and the corresponding atomic coordinates are given in Table 3. The structure is closely similar to that of the nitro cycloadduct, including even the conformations of the geminal nitro groups. Again the bond length of the C(11)–N(1) bond [1.477(7) Å] is significantly shorter than the C(11)–N(2) [1.526(7) Å] and the C(11)–N(3) [1.543(7) Å] bond lengths, reflecting the structure of the heterocyclic cage. The C(4)–C(11) bond in the hydroxy cycloadduct **17** is close to *anti* to the C(3)–O(4) bond [torsional angle: O(4)–C(3)–C(4)–C(11) −169.0(4)°], thus indicating the *trans*-2-hydroxy-1-trinitromethyl structure for the hydroxy–trinitromethyl adduct **15**. The spectroscopic data for the hydroxy–trinitromethyl adduct **15** and its derived hydroxy cycloadduct **17** were in accord with the assigned and determined structures, respectively.

Adducts **8**, **10**, **11** *and* **16**. The epimeric 2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes **8** and **10** were separated by HPLC and the structures of both were determined by single crystal X-ray analysis. A perspective drawing of the *trans*-1-nitro-4-trinitromethyl epimer **8**, $C_{13}H_{12}N_4O_8$, m.p. 104°C (decomp.), is presented in Fig. 6, and corresponding atomic coordinates are presented in Table 4; similar information is presented for the *cis*-1-nitro-4-trinitromethyl epimer **10**, $C_{13}H_{12}N_4O_8$, m.p. 134–136°C in Fig. 7 and Table 5. The two structures exist in closely similar ring conformations with the alicyclic ring in somewhat distorted boat conformations [torsional angles: for **8** C(2)–C(1)–C(8A)–C(4A) 21.7(3)°, C(3)–C(4)–C(4A)–C(8A) −15.6(3)°; for **10** C(2)–C(1)–C(8A)–C(4A) 14.0(4)°, C(3)–C(4)–C(4A)–C(8A) −17.0(4)°], the nature of which indicates clearly that the trinitromethyl group in both structures adopts an orientation such that the C(4)–C(11) bond is close to perpendicular to the plane of the aromatic ring [torsional

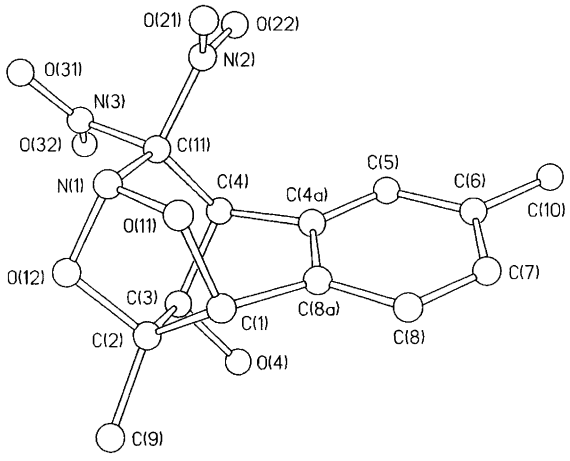


Fig. 5. Perspective drawing of compound **17**.

Table 3. Fractional coordinates for atoms in hydroxy cycloadduct **17**

Atom	$10^4X/A$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å$
O(11)	878(2)	3994(3)	1734(2)	17(1)
O(12)	47(2)	3338(4)	2740(2)	18(1)
O(21)	−36(3)	3502(4)	352(2)	25(1)
O(22)	−348(3)	1524(4)	277(3)	29(1)
O(31)	−1633(3)	2846(4)	1612(3)	27(1)
O(32)	−1265(3)	995(4)	2008(3)	28(1)
O(4)	1359(3)	532(4)	2903(2)	22(1)
N(1)	13(3)	3568(5)	1904(3)	18(1)
N(2)	−172(3)	2487(6)	639(3)	20(1)
N(3)	−1101(3)	2014(5)	1739(3)	19(1)
C(1)	1503(3)	3266(6)	2232(3)	17(1)
C(2)	890(4)	2679(6)	2869(4)	17(1)
C(3)	661(4)	1333(6)	2680(3)	18(2)
C(4)	500(4)	1275(6)	1775(3)	14(1)
C(4A)	1411(4)	1406(5)	1388(3)	13(1)
C(5)	1729(4)	594(6)	823(3)	17(2)
C(6)	2601(4)	686(6)	554(3)	20(2)
C(7)	3139(4)	1601(6)	885(3)	19(2)
C(8)	2817(4)	2449(6)	1439(4)	17(1)
C(8A)	1945(4)	2351(5)	1687(3)	14(1)
C(9)	1166(4)	2908(6)	3721(3)	24(1)
C(10)	2951(4)	−221(6)	−59(4)	31(2)
C(11)	−123(4)	2325(5)	1542(3)	13(1)

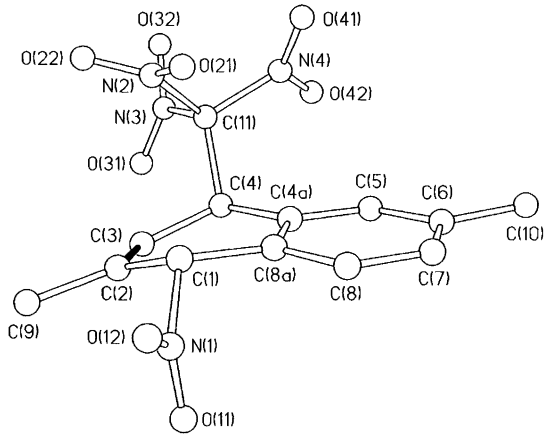


Fig. 6. Perspective drawing of compound **8**. The double bond is shown in black.

Table 4. Fractional coordinates for atoms in *trans*-2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **8**.

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
O(11)	6045(2)	4669(2)	2415(2)	29(1)
O(12)	4521(2)	3290(2)	−202(2)	33(1)
O(21)	8793(2)	1109(2)	469(2)	25(1)
O(22)	8845(2)	−537(2)	1702(2)	29(1)
O(31)	11569(2)	1432(2)	5695(2)	29(1)
O(32)	12247(2)	298(2)	4097(2)	33(1)
O(41)	12140(2)	2307(2)	1635(2)	30(1)
O(42)	13761(2)	3369(2)	4326(2)	26(1)
N(1)	5776(2)	3732(2)	1194(2)	21(1)
N(2)	9404(2)	700(2)	1646(2)	20(1)
N(3)	11647(2)	1153(3)	4475(2)	22(1)
N(4)	12404(2)	2586(2)	3017(2)	19(1)
C(1)	7097(3)	3051(2)	1422(2)	19(1)
C(2)	7291(3)	2295(2)	2674(2)	19(1)
C(3)	8818(3)	2402(2)	3802(2)	19(1)
C(4)	10436(2)	3197(2)	3895(2)	16(1)
C(4A)	10307(2)	4321(2)	2999(2)	15(1)
C(5)	11785(2)	5447(2)	3360(2)	18(1)
C(6)	11727(3)	6512(2)	2587(2)	19(1)
C(7)	10130(3)	6463(2)	1477(2)	21(1)
C(8)	8657(3)	5375(2)	1130(2)	20(1)
C(8A)	8717(2)	4283(2)	1867(2)	17(1)
C(9)	5692(3)	1369(3)	2537(3)	27(1)
C(10)	13339(3)	7662(2)	2926(3)	24(1)
C(11)	10948(2)	1951(2)	3254(2)	17(1)

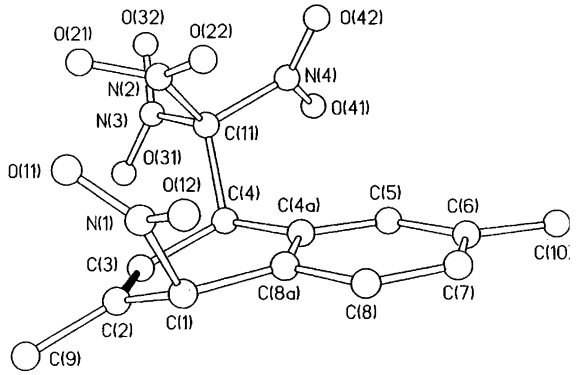


Fig. 7. Perspective drawing of compound **10**. The double bond is shown in black.

angles: for **8** C(5)–C(4A)–C(4)–C(11) −75.5(2)°; for **10** C(5)–C(4A)–C(4)–C(11) −76.8°]. Correspondingly, the orientation of the C(1)–N(1) bond differs significantly between the two structures [torsional angles: for **8** N(1)–C(1)–C(8A)–C(8) −38.3(2)°; for **10** N(1)–C(1)–C(8A)–C(8) 73.1(3)°]. The spectroscopic data for compounds **8** and **10** were in accord with the established structures. It is of interest to note that the elution order on HPLC of compounds **8** and **10** is consistent with the pattern observed earlier, i.e., *trans*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes are eluted ahead of the corresponding *cis*-1-nitro-4-trinitromethyl epimer.[8–10]

Neither of the compounds tentatively identified as the 2,6-dimethyl-4-trinitromethyl-1,4-dihydronaphthalen-1-ols **11** and **16** could be induced to give crystals of adequate quality for single crystal X-ray analysis. The spectroscopic data for these compounds are consistent with their structural assignments. In particular, the upfield chemical shifts of the aromatic protons H5 (**11**, δ 6.95; **16** δ 7.02) on the 2,6-dimethylnaphthalene skeleton were characteristic of compounds with a 4-trinitromethyl function, and the chemical shifts for protons at C1 (**11**, δ 4.79; δ 4.96) pointed to the presence of the C1-hydroxy groups in the two compounds. The relatively early elution of the *cis*-1-hydroxy-4-trinitromethyl compound **11** is of interest in the context of the more usual elution order (see above) for analogous 1-nitro-4-trinitromethyl adducts. This unusual elution order for the 1-hydroxy-4-trinitromethyl adducts is ascribed to the inherently more hindered environment of the hydroxy group in the *cis*-1-hydroxy-4-trinitromethyl compound **11** compared with that of the *trans*-1-hydroxy-

Table 5. Fractional coordinates for atoms in *cis*-2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **10**.

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	$10^3U/Å^2$
O(11)	4501(4)	2910(3)	1646(2)	31(1)
O(12)	6416(4)	1439(3)	2806(2)	31(1)
O(21)	828(3)	6534(3)	1279(2)	35(1)
O(22)	1940(4)	5417(3)	2645(2)	33(1)
O(31)	2100(4)	10422(3)	744(2)	35(1)
O(32)	−833(4)	10178(3)	1342(2)	36(1)
O(41)	1516(3)	10628(3)	2897(2)	30(1)
O(42)	427(4)	8241(3)	3432(2)	34(1)
N(1)	5884(4)	2746(3)	2208(2)	21(1)
N(2)	1557(4)	6616(3)	1998(2)	23(1)
N(3)	1066(4)	9779(3)	1306(2)	25(1)
N(4)	1280(4)	9110(3)	2889(2)	22(1)
C(1)	7095(5)	4228(4)	2162(2)	17(1)
C(2)	6570(4)	5525(4)	1303(2)	16(1)
C(3)	5479(4)	7222(4)	1282(2)	17(1)
C(4)	4626(4)	8009(4)	2087(2)	16(1)
C(4A)	5662(4)	6864(4)	2958(2)	16(1)
C(5)	5619(4)	7638(4)	3724(2)	17(1)
C(6)	6594(4)	6665(4)	4523(2)	18(1)
C(7)	7656(5)	4867(4)	4542(2)	21(1)
C(8)	7788(4)	4098(4)	3789(2)	20(1)
C(8A)	6793(4)	5072(4)	2988(2)	16(1)
C(9)	7457(5)	4820(5)	486(2)	26(1)
C(10)	6578(5)	7558(4)	5325(2)	28(1)
C(11)	2220(5)	8330(4)	2076(2)	18(1)

4-trinitromethyl epimer **16**. Given the apparent conformational control exerted by the trinitromethyl group in the 1-nitro-4-trinitromethyl adducts **8** and **10**, it is reasonable to assume that the conformation of the *cis*-1-hydroxy-4-trinitromethyl adduct would be similar to that found for the *cis*-1-nitro-4-trinitromethyl adduct **10** (Fig. 7) except for the obvious replacement of the nitro by a hydroxy group. In such a conformation the hydroxy group in the *cis*-1-hydroxy-4-trinitromethyl epimer **11** would be significantly more hindered than that for the *trans*-1-hydroxy-4-trinitromethyl epimer **16**, which would resemble the *trans*-1-nitro-4-trinitromethyl adduct **8** (Fig. 6) in conformation. The hydroxy group in the *trans*-1-hydroxy-4-trinitromethyl adduct **16** would therefore be more exposed for adsorption to a chromatographic substrate leading to a longer retention time on HPLC.

Adducts **9**, **12** *and* **14**. Of these adducts only the *trans*-3,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **9** could be isolated in a pure state, but gave crystals of inadequate quality for single crystal X-ray analysis. Isolated only in small quantities, and not exhibiting a parent ion in the mass spectrum, the structure of this compound rests largely on its spectroscopic data. The connectivity was established by a combination of nuclear Overhauser enhancement experiments and by long range reverse detected heteronuclear correlation spectra (HMBC). The *trans*-1-nitro-4-trinitromethyl stereochemistry was assigned to adduct **9** on the basis of its elution earlier than its *cis*-1-nitro-4-trinitromethyl stereoisomer **12**, and the known HPLC elution order for such pairs of stereoisomers (Refs. 8–10, and above).

The *cis*-3,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene stereoisomer **12** was isolated in low yield as an impure oil. The signal assigned to H5 appeared as a doublet ($J_{H5,H6}$ 7.9 Hz) at δ 7.07, pointing to the presence of the trinitromethyl group at C4, on the 3,7-dimethylnaphthalene skeleton. The somewhat larger coupling constant ($J_{H1,H2}$ 6.3 Hz) for adduct **12**, compared with similar *cis*-1-nitro-4-trinitromethyl adducts lacking the 3-methyl-4-trinitromethyl structural feature, e.g., adduct **10** above ($J_{H1,H2}$ 4.9 Hz), is presumably due to conformational changes in adduct **12** induced by steric interactions between the 4-trinitromethyl group and the adjacent 3-methyl group; these would be expected to lead to a more extreme boat conformation in adduct **12** leading to some reduction in the H1–C1–C2–H2 torsional angle, and a somewhat larger coupling constant.

Finally, the nitro cycloadduct **13** was isolated in small quantities and then only in admixture with its structurally isomeric nitro cycloadduct **14**, the structure of which has been determined above by single crystal X-ray analysis. The connectivity in nitro cycloadduct **13** was established by a combination of nuclear Overhauser enhancement experiments and by long-range reverse detected heteronuclear correlation spectra (HMBC). A comparison of the assignment of the ^1H NMR spectrum for adduct **13** with that of a closely analogous structure **21**[10] is given in Fig. 8. The chemical shift of the 3-methyl group (δ 1.94) is consistent with the presence of the *ipso* nitro group and the stereochemistry of the nitro cycloadduct **13** is assigned on the basis of its likely mode of formation. Its stereochemistry would follow automatically from knowledge of the stereochemistry of its precursor **22** (Scheme 2). Leading to the formation of the precursor **22**, reaction of trinitromethanide ion at C1 in the radical cation of 2,6-dimethylnaphthalene **23** would give the delocalized carbon radical **24**. Radical coupling of nitrogen dioxide, *ipso* to the adjacent methyl group would be expected to occur *anti* to the extremely bulky trinitromethyl group, to yield the precursor **22**. Cycloaddition of precursors such as structure **22** to give cycloadducts such as nitro cycloadduct **13** is now well established.[7–10,12,13]

Photochemistry in dichloromethane at −20°C and identification of some of the nitroaromatic products. A solution of 2,6-dimethylnaphthalene (0.4 mol dm^{-3}) and TNM (0.8 mol dm^{-3}) in dichloromethane was irradiated at −20°C for 3 h to give a mixture of adducts (total 15%),

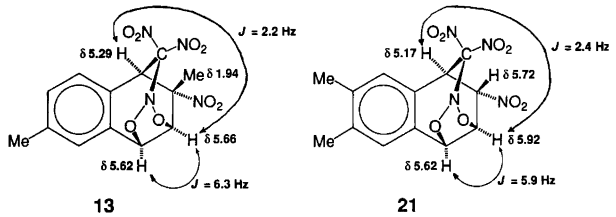
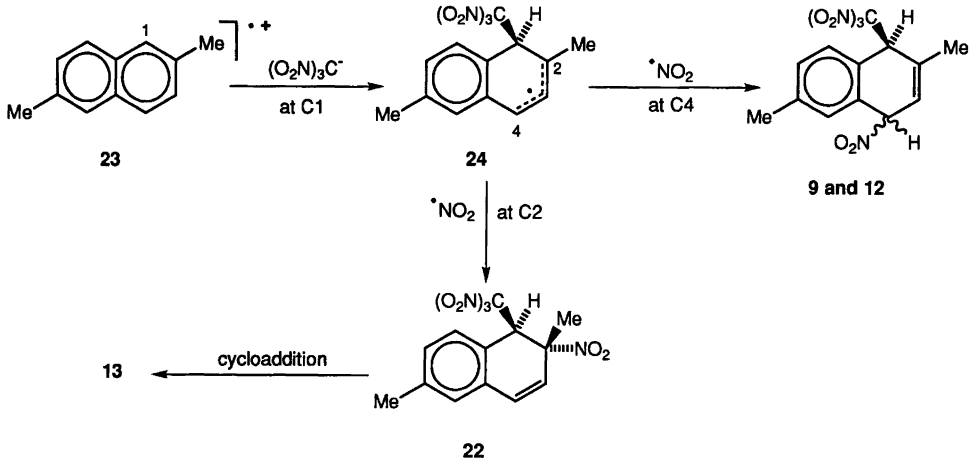
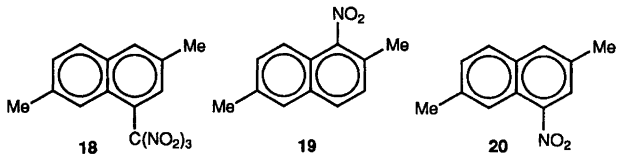


Fig. 8. ^1H NMR spectroscopic data for nitro cycloadducts **13** and **21**.



Scheme 2.

3,7-dimethyl-1-trinitromethylnaphthalene **18** (2%), 2,6-dimethyl-1-nitronaphthalene **19** (55%), 3,7-dimethyl-1-nitronaphthalene **20** (8%), and a mixture of other unidentified nitroaromatic products (total 20%). Chromatography of this mixture on a silica gel Chromatotron plate gave pure samples of the compounds **18–20**. The trinitromethyl compound **18** was identified from its spec-



troscopic data and its mass spectrum. The two nitronaphthalenes **19** and **20** were identified from their spectroscopic data and literature melting point data.

Cyclic voltammetry. Cyclic voltammetry of a solution of 2,6-dimethylnaphthalene in dichloromethane–tetrabutylammonium hexafluorophosphate (0.2 M) at a Pt button anode indicated irreversible oxidation at least up to the scan limit of the instrument (50 V s^{-1}). At a scan rate of 0.1 V s^{-1}, E_{pa} was 1.69 V (Ag/AgCl).

EPR spectroscopy. A solution of 2,6-dimethylnaphthalene (0.060 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at −60 °C was irradiated with filtered light ($\lambda > 430$ nm) in order to excite the CT complex between the two components.[3] After the accumulation of 30 spectra for a total period of 6 min, no paramagnetic species was detectable (absolute intensity ≈ 10 per spectrum, equal to the noise level). A sample of the same composition, but with [TFA] = 0.4 mol dm^{-3}, upon the same treatment gave an EPR signal with an absolute intensity of 170 per spectrum. This established an intensity ratio between the two solutions, previously[2] denoted ξ, of 17 and showed that protonation of trinitromethanide ion had blocked its reaction with the 2,6-dimethylnaphthalene radical cation, thus allowing for the latter to build up a significant concentration. A check experiment with only TFA present (0.4 mol dm^{-3}) but otherwise under the same conditions showed very low paramagnetic activity, insignificant compared with that obtained with tetranitromethane–TFA.

The EPR spectrum of (2,6-dimethylnaphthalene)$^{\bullet+}$ obtained above consisted of 13–15 lines with spacing ≈ 0.25 mT and no further resolution detectable. A less well resolved spectrum with identical spacing between the lines was obtained by irradiation of a DDQ–2,6-dimethylnaphthalene solution in dichloromethane at −60 °C. To the best of our knowledge, this EPR spectrum has only been characterized by its g value before (in SO_2–$AlCl_3$ at −60 °C).[14]

Discussion

From the results of the EPR spectroscopic experiments it is clear that the initial reaction step in the recombination of the components of the triad to form adducts involves attack of trinitromethanide ion on the 2,6-dimethylnaphthalene radical cation,[1,2] since removal of trinitromethanide ion by protonation leads to the development of the EPR spectrum of the radical cation. In terms of the adducts which have been identified (77%) for the reaction at +20 °C in dichloromethane (Table 1), there is a clear preference (ca. 4:1) for trinitromethanide ion attack at C4 compared with reaction at C1 of the 2,6-dimethylnaphthalene radical cation. This trend is in keeping with the relative atomic charges at C1 and C4 in the radical cation (Fig. 3); additionally it seems likely that the steric hindrance to trinitromethanide ion attack at C1 due to interaction with the 2-methyl group may be a contributing factor to the regioselectivity.[10] At −20 °C in dichloromethane the total yield of adducts is much reduced (to 15%) and there is a corresponding increase in the yield of nitroaromatic compounds, particularly of 2,6-dimethyl-1-nitronaphthalene **19**. In acetonitrile at +20 °C

(Table 6) the photolysis yields adducts (total 46%) and mainly the 1-nitro compound **19** (42%) among the remaining products. In connection with the formation of the 2,6-dimethyl-1-nitronaphthalene **19** it is notable that C1(5) is the centre with the highest calculated unpaired electron spin density (+0.45) in the 2,6-dimethylnaphthalene radical cation,[5] and it appears likely that much of the 2,6-dimethyl-1-nitronaphthalene **19** is formed by direct coupling of the radical cation with nitrogen dioxide.

The formation of the nitro cycloadduct **13** has been accounted for above (Scheme 2) in terms of the nitroalkene cycloaddition of the *trans*-2,6-dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene **22**, itself formed by radical coupling of nitrogen dioxide at C2 of the delocalized carbon radical **24**. The isolation of the stereoisomeric 3,7-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalenes **9** and **12** is consistent with that proposal as these compounds, **9** and **12**, would be formed by radical coupling of nitrogen dioxide at the alternative reactive centre in the delocalized carbon radical **24** (Scheme 2).

The formation of the adducts arising from trinitromethanide ion attack at C4 in the 2,6-dimethylnaphthalene radical cation may be rationalized in an analogous manner (Scheme 3). Radical coupling of nitrogen dioxide with the delocalized carbon radical **25** at C1 with C–N bond formation would give directly the epimeric nitro–trinitromethyl adducts **8** and **10**; the alternative mode of coupling with C–O bond formation would give first the nitrito–trinitromethyl adducts **11a** and **16a** which would be expected to be hydrolysed rapidly to the hydroxy–trinitromethyl adducts **11** and **16** under the prevailing acidic conditions of the reaction and work-up procedure. Similar radical coupling of nitrogen dioxide at C3 in the delocalized carbon radical **25** would occur *trans* to the bulky trinitromethyl group at C4, giving the nitro–trinitromethyl adduct **7** by C–N bond formation and the nitrito–trinitromethyl adduct **15a** by C–O bond formation; the hydroxy/trinitromethyl adduct **15** would then be formed on hydrolysis.

Although the precursor of the nitro cycloadduct **13** was neither isolated nor detected in the crude product of the photonitration of 2,6-dimethylnaphthalene, the cycloaddition precursors **7** and **15** were isolable, albeit in admixture with other adducts. Nonetheless, it was therefore possible to demonstrate the thermal alkene–nitro cycloaddition[7–10,12,13] in these compounds, **7** and **15**, to give the corresponding nitro cycloadduct **14** and hydroxy cycloadduct **17**.

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 Series FTIR spectrometer; ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer with $SiMe_4$ as an internal standard. HPLC separations were carried out on a Varian 5000 liquid chromatograph equipped with an Alltech cyanopropyl column, and by using a Varian UV-50 ultraviolet spectroscopic detector and hexane–dichloromethane as solvent mixtures. Tetranitromethane was purchased from Aldrich and 2,6-dimethylnaphthalene from L. Light & Co. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH.

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.[15]

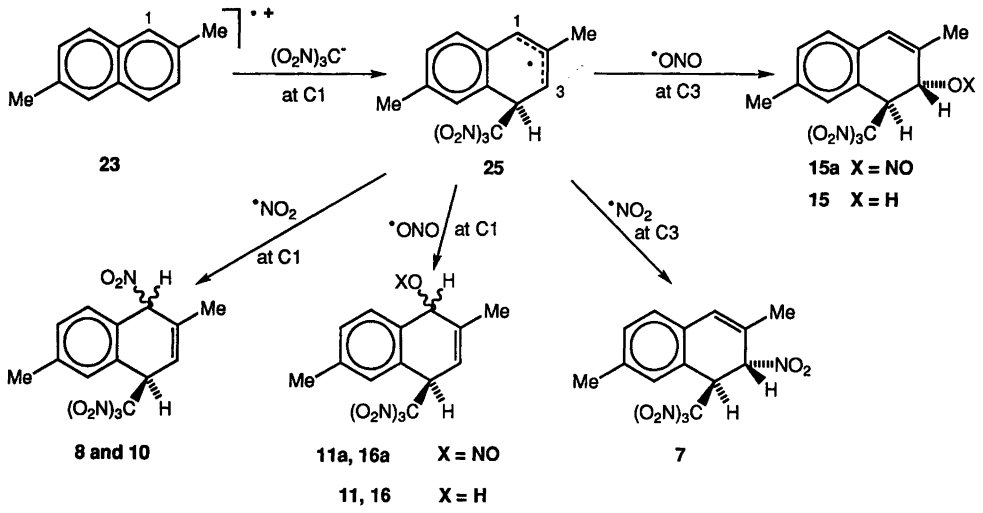
General procedure for the photonitration of 2,6-dimethylnaphthalene with tetranitromethane. A solution of 2,6-dimethylnaphthalene (500 mg, 0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane or acetonitrile was irradiated at +20 or −20°C with filtered light ($\lambda_{cut\text{-}off} < 435$ nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0°C, and the product composition determined by NMR spectral analysis (Tables 1 and 6).

Reaction in dichloromethane at +20°C and the identification of the products. Reaction of 2,6-dimethylnaphthalene–tetranitromethane in dichloromethane at +20°C, as above, for 2 h gave a product which was shown by ^{1}H NMR spectroscopy to be a mixture (Table 1) of adducts (total 79%), 2,6-dimethyl-1-nitronaphthalene (**19**) (16%) and other minor nitroaromatic compounds (total 3%). The adducts were partially separated by HPLC and gave in elution order:

Table 6. Overview of yields of products from the photolysis of 2,6-dimethylnaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in acetonitrile at +20°C[a]

		Yield (%)																
t/h	Conversion (%)	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	Unknown	Total adducts	**18**	**19**	**20**	Unknown aromatics
0.5	19	2.0	2.8	1.4	3.6	1.0	0.4	–	–	1.6	0.6	0.2	0.8	14.4	1.0	51.8	9.0	23.8
1	50	4.4	6.1	2.6	7.8	1.6	1.0	0.2	–	3.1	1.6	0.7	1.1	30.2	4.1	41.0	9.0	15.7
2	74	6.8	8.8	3.6	10.0	2.3	1.6	0.3	0.4	3.6	2.2	1.4	1.1	42.1	2.7	45.4	9.8	–
3	84	6.9	9.3	4.5	12.0	1.5	1.9	0.7	0.8	3.5	1.3	2.0	1.9	46.3	3.6	42.0	8.1	–

[a]Because of its limited solubility in acetonitrile, the 2,6-dimethylnaphthalene dissolved totally only after ca. 1.5 h.



Scheme 3.

trans-*3,7-Dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (7).* Isolated only in admixture with adduct **8** below. ^{1}H NMR ($CDCl_3$): δ 2.05 (d, $J_{Me,H4}$ 1.5 Hz, 3-Me), 2.32 (s, 7-Me), 5.41 (d, $J_{H2,H1}$ 1.4 Hz, H2), 5.67 (s, H1), 6.53 (d, $J_{H4,Me}$ 1.5 Hz, H4), 6.95 (br s, H8), 7.05 (d, $J_{H5,H6}$ 7.8 Hz, H5), 7.21 (br d, $J_{H6,H5}$ 7.8 Hz, H6). The structure and stereochemistry of this adduct is confirmed by its conversion into the nitro cycloadduct, the structure of which is determined below by X-ray crystallography.

trans-*2,6-Dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (8).* M.p. 104°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1620, 1592, 1568 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.97 (d, $J_{Me,H3}$ 1.5 Hz, 2-Me), 2.36 (s, 6-Me), 5.35 (br s, H4), 6.13 (br s, H1), 6.29 (dq, $J_{H3,H4}$ 3.0 Hz, $J_{H3,Me}$ 1.5 Hz, H3), 7.11 (br s, H5), 7.30–7.31 (m, H7, H8). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 1.97 gave enhancements at δ 6.13 (3.4%) and at δ 6.29 (4.5%); irradiation at δ 5.35 gave enhancements at δ 6.29 (5.1%) and at δ 7.11 (3.7%); irradiation at δ 6.29 gave enhancements at δ 1.97 (1.1%) and at δ 5.35 (3.4%). ^{13}C NMR ($CDCl_3$): δ 20.1 (2-Me), 21.2 (6-Me), 45.4 (C4), 87.0 (C1), 119.2 (C3), 124.2 (C4a), 126.9 (C8), 128.4 (C5), 129.1 (C8a), 131.5 (C7), 138.1 (C2), 140.9 (C6), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by HMBC spectroscopy.

trans-*3,7-Dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (9).* M.p. 185°C (decomp.) (crystals of inadequate quality for single crystal X-ray analysis; insufficient for elemental analysis; parent ion not visible in mass spectrum). IR: ν_{max} (KBr) 1620, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.11 (m, 3-Me), 2.37 (s, 7-Me), 5.33 (br s, H4), 6.18 (m, H1), 6.29 (m, H2), 7.21–7.22 (m, H5, H6, H8). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 2.11 gave enhancements at δ 5.33 (4.1%) and at δ 6.29 (5.1%); irradiation at δ 5.33 gave enhancements at δ 2.11 (0.7%) and at δ 7.21 (1.6%); irradiation at δ 6.29 gave enhancements at δ 2.11 (0.7%) and at δ 6.18 (1.6%). ^{13}C NMR ($CDCl_3$): δ 21.2 (7-Me), 23.8 (3-Me), 49.5 (C4), 83.6 (C1), 122.4 (C4a), 126.6 (C6), 128.7 (C2), 129.1 (C5), 131.0 (C8), 131.2 (C8a), 132.1 (C3), 141.0 (C7), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by HMBC spectroscopy.

cis-*2,6-Dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (10).* M.p. 134–136°C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1647, 1599, 1578, 1554 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.08 (br s, 2-Me), 2.37 (s, 6-Me), 5.30 (br s, H4), 5.78 (d, $J_{H1,H4}$ 2.4 Hz, H1), 6.47 (dq, $J_{H3,H4}$ 4.9 Hz, $J_{H3,Me}$ 1.5 Hz, H3), 6.97 (br s, H5), 7.34 (br d, $J_{H7,H8}$ 7.8 Hz, H7), 7.70 (d, $J_{H8,H7}$ 7.8 Hz, H8). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 2.08 gave enhancements at δ 5.78 (4.3%) and at δ 6.47 (5.5%); irradiation at δ 5.30 gave enhancements at δ 6.47 (3.7%) and at δ 6.97 (3.4%); irradiation at δ 5.78 gave enhancements at δ 2.08 (0.7%) and at δ 7.70 (3.1%); irradiation at δ 6.47 gave enhancements at δ 2.08 (0.6%) and at δ 5.30 (2.9%). ^{13}C NMR ($CDCl_3$): δ 21.4 (6-Me), 22.5 (2-Me), 44.9 (C4), 85.3 (C1), 121.4 (C3), 126.2 (C8a), 127.4 (C4a), 128.0 (C7), 131.0 (C5), 131.5 (C8), 137.2 (C2), 141.2 (C6), resonance for $C(NO_2)_3$ not observed. The above assignments were confirmed by HMBC spectroscopy.

cis-*2,6-Dimethyl-4-trinitromethyl-1,4-dihydronaphthalen-1-ol (11).* M.p. 108–110°C (crystals of inadequate quality for single crystal X-ray analysis; insufficient for elemental analysis; parent ion not visible in mass spectrum). IR: ν_{max} (KBr) 3416, 1618, 1598 (sh) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.02 (br s, 2-Me), 2.34 (s, 6-Me), 4.79 (br d, $J_{H1,OH}$ 9.7 Hz, H1), 5.16 (br s, H4), 6.02 (dq, $J_{H3,H4}$

4.4 Hz, $J_{H3,Me}$ 1.5 Hz, H3), 6.95 (br s, H5), 7.29 (br d, $J_{H7,H8}$ 7.8 Hz, H7), 7.48 (d, $J_{H8,H7}$ 7.8 Hz, H8).

cis-*3,7-Dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene* (**12**). An impure oil isolated only in small quantity. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3-Me), 2.43 (s, 7-Me), 5.40 (br s, H4), 5.82 (d, $J_{H1,H2}$ 6.3 Hz, H1), 6.48 (dq, $J_{H2,H1}$ 6.3 Hz, $J_{H2,Me}$ 1.5 Hz, H2), 7.07 (d, $J_{H5,H6}$ 7.9 Hz, H5), 7.24 (br d, $J_{H6,H5}$ 7.9 Hz, H6), 7.46 (br s, H8).

Nitro cycloadduct (**13**). Isolated only in small quantity and in admixture with the major nitro cycloadduct (**14**). ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 3-Me), 2.33 (s, 7-Me), 5.29 (d, $J_{H4,H2}$ 2.0 Hz, H4), 5.62 (d, $J_{H1,H2}$ 6.3 Hz, H1), 5.66 (dd, $J_{H2,H1}$ 6.3 Hz, $J_{H2,H4}$ 2.4 Hz, H2), 7.07 (br s, H8), 7.17 (br d, $J_{H6,H5}$ 7.8 Hz, H6), 7.25 (d, $J_{H5,H6}$ 7.8 Hz, H5). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 1.94 gave enhancements at δ 5.29 (5.6%) and at δ 5.66 (2.1%); irradiation at δ 2.33 gave enhancements at δ 7.07 (3.8%) and at 7.25 (2.5%); irradiation at δ 5.64 gave enhancements at δ 1.94 (1.3%) and at δ 7.07 (3.9%). ^{13}C NMR ($CDCl_3$): δ 21.3 (7-Me), 23.5 (3-Me), 48.1 (C4), 79.1 (C2), 82.3 (C1), 87.1 (C3), 127.9 (C8a), 128.5 (C8), 131.41, 131.44 (C5, C6), 133.3 (C4a), 141.0 (C7), resonance for $C(NO_2)_2$ not observed. The above assignments were confirmed by HMBC spectroscopy.

Nitro cycloadduct (**14**). M.p. 169°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1588, 1556 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 2-Me), 2.33 (s, 6-Me), 5.17 (d, $J_{H4,H3}$ 4.0 Hz, H4), 5.19 (s, H1), 5.64 (d, $J_{H3,H4}$ 4.0 Hz, H3), 7.06 (br s, H5), 7.19 (br d, $J_{H7,H8}$ 7.8 Hz, H7), 7.22 (d, $J_{H8,H7}$ 7.8 Hz, H8). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 2.07 gave enhancements at δ 5.19 (5.4%) and at δ 5.64 (3.8%); irradiation at δ 2.33 gave enhancements at δ 7.06 (4.0%) and at δ 7.19 (1.9%); irradiation at δ 5.18 gave enhancements at δ 2.07 (1.6%), at δ 5.64 (5.3%), at δ 7.06 (4.6%), and at δ 7.22 (2.6%); irradiation at δ 5.64 gave enhancements at δ 2.07 (1.1%) and at δ 5.17 (2.8%). ^{13}C NMR ($CDCl_3$): δ 19.3 (2-Me), 21.3 (6-Me), 46.2 (C4), 84.1 (C3), 85.7 (C1), 86.3 (C2), 125.9 (C8a), 127.9 (C8), 131.61 (C5), 131.64 (C7), 132.5 (C4a), 141.6 (C6), resonance for $C(NO_2)_2$ not observed. The above assignments were confirmed by HMBC spectroscopy.

trans-*3,7-Dimethyl-1-trinitromethyl-1,2-dihydronaphthalen-2-ol* (**15**). An oil isolated only in admixture with the hydroxy cycloadduct (**11**), below. ^{1}H NMR ($CDCl_3$): δ 1.91 (d, $J_{Me,H4}$ 1.5 Hz, 3-Me), 2.31 (s, 7-Me), 4.58 (br s, H1), 4.78 (br s, H2), 6.23 (d, $J_{H4,Me}$ 1.5 Hz, H4), 6.94 (br s, H8), 7.02 (d, $J_{H5,H6}$ 7.8 Hz, H5), 7.19 (br d, $J_{H6,H5}$ 7.8 Hz, H6).

trans-*2,6-Dimethyl-4-trinitromethyl-1,4-dihydronaphthalen-1-ol* (**16**). M.p. 75°C (decomp.), isolated in small quantity with crystals of inadequate quality for single crystal X-ray analysis, parent ion not visible in mass spectrum. IR: ν_{max}(KBr) 3452, 1599 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.04 (m, 2-Me), 2.34 (s, 6-Me), 4.96 (br s, H1), 5.19 (br s, H4), 6.00 (dq, $J_{H3,H4}$ 4.9 Hz, $J_{H3,Me}$ 1.0 Hz, H3), 7.02 (br s, H5), 7.30 (br d, $J_{H7,H8}$ 7.8 Hz, H7), 7.68 (d, $J_{H8,H7}$ 7.8 Hz, H8).

Hydroxy cycloadduct (**17**). M.p. 183–184°C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 3415, 1618, 1580 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 2-Me), 2.38 (s, 6-Me), 4.73 (s, H4), 4.75 (d, $J_{H3,OH}$ 3.9 Hz, H3), 4.93 (s, H1), 7.18 (br s, H5), 7.21–7.26 (m, H7, H8). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 1.75 gave enhancements at δ 4.75 (2.3%) and at δ 4.93 (6.7%); irradiation at δ 2.38 gave enhancements at δ 7.18 (3.7%) and at δ 7.21 (2.7%); irradiation at δ 4.93 gave enhancements at δ 1.75 (0.9%) and at δ 7.23 (2.9%). ^{13}C NMR ($CDCl_3$): δ 16.9 (2-Me), 21.4 (6-Me), 48.8 (C4), 70.6 (C3), 84.7 (C1), 87.7 (C2), 127.9 (C8), 128.5 (C8a), 130.6 (C5), 132.2 (C4a), 132.7 (C7), 141.2 (C6), resonance for $C(NO_2)_2$ not observed. The above assignments were confirmed by HMBC spectroscopy.

Reaction in dichloromethane at −20°C and the identification of some of the nitroaromatic products. Reaction of 2,6-dimethylnaphthalene–tetranitromethane in dichloromethane at −20°C, as above, for 3 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 1) of adducts (total 15%), 3,7-dimethyl-1-trinitromethylnaphthalene (**18**) (2%), 2,6-dimethyl-1-nitronaphthalene (**19**) (55%), 3,7-dimethyl-1-nitronaphthalene (**20**) (8%), and other unidentified nitroaromatic compounds (20%). Chromatography of this mixture on a silica gel Chromatotron plate gave, in order of elution:

3,7-Dimethyl-1-trinitromethylnaphthalene (**18**). (Eluted by pentane), m.p. 108°C (decomp.) (Found: $M^{+\bullet}$, 305.0652. $C_{13}H_{11}N_3O_6$ requires 305.0648; insufficient for elemental analysis). IR: ν_{max} (KBr) 1617, 1593, 1576 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 7-Me), 2.54 (s, 3-Me), 7.02 (br s, H8), 7.36 (d, $J_{H2,H4}$ 1.5 Hz, H2), 7.42 (dd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H8}$ 1.5 Hz, H6), 7.80 (d, $J_{H5,H6}$ 8.3 Hz, H5), 7.93 (br s, H4). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 2.47 gave enhancements at δ 7.02 (4.7%) and at δ 7.42 (4.0%); irradiation at δ 2.54 gave enhancements at δ 7.36 (4.8%) and at δ 7.93 (2.4%); irradiation at δ 7.02 gave an enhancement at δ 2.47 (0.5%); irradiation at δ 7.39 gave enhancements at δ 2.47 (0.5%), at δ 2.54 (0.5%) and at δ 7.80 (5.3%); irradiation at δ 7.80 gave enhancements at δ 7.42 (5.9%) and at δ 7.93 (3.3%); irradiation at δ 7.93 gave enhancements at δ 2.54 (0.5%) and at δ 7.80 (2.5%).

2,6-Dimethyl-1-nitronaphthalene (**19**). (Eluted by pentane), m.p. 66.5–67°C (lit.[16] 67–67.5°C). IR: ν_{max} (KBr) 1612,

1518 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.47 (s, 2-Me), 2.50 (s, 6-Me), 7.29 (d, $J_{H3,H4}$ 8.3 Hz, H3), 7.41 (dd, $J_{H7,H8}$ 8.8 Hz, $J_{H7,H5}$ 2.0 Hz, H7), 7.61 (br s, H5), 7.61 (d, $J_{H8,H7}$ 8.8 Hz, H8), 7.76 (d, $J_{H4,H3}$ 8.3 Hz, H4). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 7.29 gave enhancements at δ 7.76 (5.4%) and at δ 2.47 (0.7%); irradiation at δ 7.41 gave enhancements at δ 7.61 (4.6%) and at δ 2.50 (0.5%); irradiation at δ 7.61 gave enhancements at δ 7.76 (1.8%), at δ 7.41 (7.9%), and at δ 2.50 (0.8%); irradiation at δ 7.76 gave enhancements at δ 7.61 (1.5%) and at δ 7.29 (7.0%).

*3,7-Dimethyl-1-nitronaphthalene (***20***).* Eluted by ether–pentane (1:49), m.p. 80–81°C (Lit.[16] 83–84°C). IR: ν_{max} (KBr) 1615, 1518 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.55 (s, 3-Me), 2.56 (s, 7-Me), 7.41 (dd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H8}$ 1.4 Hz, H6), 7.75 (d, $J_{H5,H6}$ 8.3 Hz, H5), 7.84 (br s, H4), 8.05 (d, $J_{H8,H6}$ 1.4 Hz, H8), 8.29 (d, $J_{H4,H2}$ 1.0 Hz, H2). Nuclear Overhauser enhancement experiments gave the following results: irradiation at δ 7.41 gave enhancements at δ 7.75 (3.9%) and at δ 2.56 (0.2%); irradiation at δ 7.75 gave enhancements at δ 7.84 (1.6%) and at δ 7.41 (5.1%); irradiation at δ 7.84 gave enhancements at δ 7.75 (1.5%), and at δ 2.55 (0.1%); irradiation at δ 8.05 gave an enhancement at δ 2.56 (0.1%); irradiation at δ 8.29 gave an enhancement at δ 2.55 (0.2%).

Thermal cycloaddition of trans*-3,7-dimethyl-2-nitro-1-trinitromethyl-1,2-dihydronaphthalene (***7***) in (^2H)chloroform.* A solution of a mixture of the nitro–trinitromethyl adduct (**7**; 29%) and *trans*-2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (**8**; 71%) in (^2H)chloroform was stored at 22°C in the dark and the ^1H NMR spectrum monitored at appropriate time intervals. The nitro–trinitromethyl adduct **7** was slowly transformed (half-life 96 h) into the nitro cycloadduct **14**. The 2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene **8** was unchanged during the duration of the experiment. The nitro cycloadduct **14**, isolated by HPLC, was identical with an authentic sample, see above.

Thermal cycloaddition of trans*-3,7-dimethyl-1-trinitromethyl-1,2-dihydronaphthalen-2-ol (***15***) in (^2H)chloroform.* A solution of a mixture of the hydroxy–trinitromethyl adduct (**15**; 80%) and the hydroxy cycloadduct (**17**; 20%) in (^2H)chloroform was stored at 22°C in the dark and the ^1H NMR spectrum monitored at appropriate time intervals. The hydroxy–trinitromethyl adduct **15** was transformed into the hydroxy cycloadduct **17** with a half-life estimated to be ca. 13 h, the measurements being complicated by the precipitation of **17** during the period of the observations. After 170 h the ^1H NMR spectrum obtained was essentially that of pure **17**, above.

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, (μMo Kα) 0.71069 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 25 accurately centred high-angle reflections were used.

Crystal data: trans*-2,6-dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (***8***).* $C_{13}H_{12}N_4O_8$, $M = 352.27$, triclinic, space group $P\bar{1}$, $a = 9.621(2)$, $b = 9.708(2)$, $c = 9.720(2)$ Å; $\alpha = 101.03(3)$, $\beta = 117.60(3)$, $\gamma = 105.00(3)°$; $V = 723.9(3)$ Å^3, $D_c = 1.616$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 1.37 cm^{-1}. The crystal was colourless and of approximate dimensions $0.52 \times 0.40 \times 0.16$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 22.5°$. The number of independent reflections measured was 2346, 2016 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0480, g_2 0.5841; $R_{(obs)}$-factor 0.037, $wR_{(all\ data)}$ 0.099.

cis*-2,6-Dimethyl-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene (***10***).* $C_{13}H_{12}N_4O_8$, $M = 352.27$, triclinic, space group $P\bar{1}$, $a = 6.580(1)$, $b = 7.700(2)$, $c = 15.225(3)$ Å; $\alpha = 80.44(3)$, $\beta = 89.95(3)$, $\gamma = 75.96(3)°$; $V = 737.3(3)$ Å^3, $D_c = 1.587$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 1.34 cm^{-1}. The crystal was colourless and of approximate dimensions $0.55 \times 0.50 \times 0.42$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 22.88°$. The number of independent reflections measured was 1931, 1542 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0578, g_2 0.7244; $R_{(obs)}$-factor 0.045, $wR_{(all\ data)}$ 0.118.

*Nitro cycloadduct (***14***).* $C_{13}H_{12}N_4O_8$, $M = 352.27$, monoclinic, space group $P2_1/c$, $a = 15.234(3)$, $b = 11.663(2)$, $c = 8.531(2)$ Å; $\beta = 105.23(3)°$; $V = 1462.5(5)$ Å^3, $D_c = 1.600$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 1.35 cm^{-1}. The crystal was colourless and of approximate dimensions $0.80 \times 0.44 \times 0.38$ mm. Data were collected at 132(2) K out to a maximum Bragg angle $\theta = 22.5°$. The number of independent reflections measured was 2532, 1895 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0571, g_2 0.2816; $R_{(obs)}$-factor 0.0425, $wR_{(all\ data)}$ 0.108.

*Hydroxy cycloadduct (***17***).* $C_{13}H_{13}N_3O_7$, $M = 323.26$, orthorhombic, space group *Pbca*, $a = 15.028(3)$, $b = 10.710(2)$, $c = 16.779(3)$ Å; $V = 2700.6(9)$ Å^3, $D_c = 1.590$ g cm^{-3}, $Z = 8$, μ(Mo Kα) = 1.32 cm^{-1}. The crystal was colourless and of approximate dimensions $0.42 \times 0.40 \times 0.10$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 22.5°$. The number of independent reflections measured was 2372, 1060 with $I > 2\sigma(I)$. Absorption corrections were not applied; g_1 0.0498, g_2 0.0000; $R_{(obs)}$-factor 0.073, $wR_{(all\ data)}$ 0.166.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)[17] 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 refinements 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 hydrogen atoms 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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