

Photochemical Nitration by Tetranitromethane. Part XXIII.[†] Adduct Formation in the Photochemical Reaction of 1,3-Dimethylnaphthalene. Steric Effects and the Regiochemistry of Trinitromethanide Ion Attack on the Radical Cation of 1,3-Dimethylnaphthalene

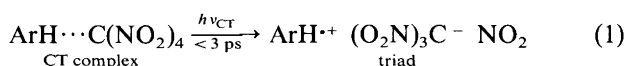
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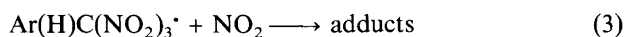
Ebersson, L., Hartshorn, M. P., Persson, O., Robinson, W. T. and Timmerman-Vaughan, D. J., 1995. Photochemical Nitration by Tetranitromethane. Part XXIII. Adduct Formation in the Photochemical Reaction of 1,3-Dimethylnaphthalene. Steric Effects and the Regiochemistry of Trinitromethanide Ion Attack on the Radical Cation of 1,3-Dimethylnaphthalene. – Acta Chem. Scand. 49: 482–494 © Acta Chemica Scandinavica 1995.

The photolysis of 1,3-dimethylnaphthalene with tetranitromethane in dichloromethane at 20°C gives adducts (total 50%) including 5,7-dimethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene **7**, 6,8-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene **8** and its epimer **10**, nitro cycloadduct **9**, 6,8-dimethyl-*t*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-1-ol **11**, hydroxy cycloadduct **12**, and 2,4-dimethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene **13**, and aromatic substitution products (total 50%) including 6,8-dimethyl-2-trinitromethylnaphthalene **14**, 5,7-dimethyl-1-trinitromethylnaphthalene **15** and 2,4-dimethyl-1-nitronaphthalene. The nitro-trinitromethyl adduct **7** undergoes slow nitro-alkene cycloaddition to give the second nitro cycloadduct **17**. The mode of formation of these products is discussed with particular reference to the regiochemistry of attack of trinitromethanide ion on the radical cation of 1,3-dimethylnaphthalene. Photolysis of 1,3-dimethylnaphthalene-tetranitromethane in dichloromethane containing trifluoroacetic acid gives 2,4-dimethyl-1-nitronaphthalene **16** and the dehydromer, 2,2',4,4'-tetramethylbinaphthalene **22**. X-Ray crystal structures are reported for adducts **8**–**10** and **17**.

The photochemical addition of tetranitromethane (TNM) to aromatic compounds (ArH) by excitation of the ArH–TNM 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^{•+}, the trinitromethanide ion and nitrogen dioxide [eqn. (1)]:³



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



In the photochemical reaction of naphthalene⁴ with tetranitromethane the initial bond formation between trinitromethanide ion and the naphthalene radical cation occurs at the favourable 1-position, as judged by the calculated⁵ (AMI)⁶ atomic charges on the respective ring carbon atoms (Fig. 1). The subsequent coupling of the delocalized carbon radical **1** with nitrogen dioxide then yields the nitro-trinitromethyl adducts **2**–**4**, and the labile nitro-trinitromethyl adduct **5**, which is hydrolysed during the reaction or the work-up procedure to give the hydroxy-trinitromethyl adduct **6** (Scheme 1).

Analogous reaction sequences occur in the photochemical reaction of 1-methylnaphthalene with tetranitromethane, nitro-trinitromethyl and hydroxy-trinitro-

[†] Part XXII, see Ref. 17.

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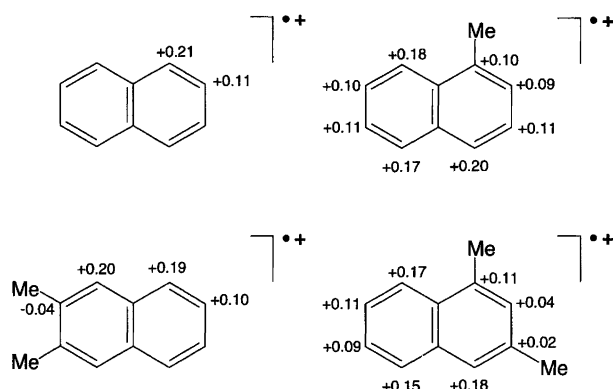


Fig. 1. Calculated (optimized AM1; UHF method) atomic charges on carbon atoms, including the overall charges for CH moieties in the radical cations of naphthalene, 1-methylnaphthalene, 2,3-dimethylnaphthalene, and 1,3-dimethylnaphthalene.

methyl adducts being formed in total yields of 69% (20 °C in dichloromethane), with the initial attack of trinitromethanide ion occurring at C4 (65%) and at C5 (4%).⁷ On the basis of the calculated atomic charges in the 1-methylnaphthalene radical cation (Fig. 1), attack of trinitromethanide ion might have been expected also at C8. The absence of adducts arising by trinitromethanide ion attack at C8 was ascribed to the *peri* interaction between the attacking trinitromethanide ion and the 1-methyl group.⁷ In the corresponding reaction of the 2,3-dimethylnaphthalene radical cation, steric hindrance to attack by trinitromethanide ion on the radical cation is again evident from the observed regiochemistry of the reaction.⁸ Although the calculated charge distribution in the 2,3-dimethylnaphthalene radical cation (Fig. 1) suggested that the trinitromethanide ion should attack with some preference at C1(C4), the predominant attack (ca. 4:1) occurred at C5(C8). Here it appears that the attack of the trinitromethanide ion at C1(C4) is hindered by the interaction between the attacking trinitromethanide ion and

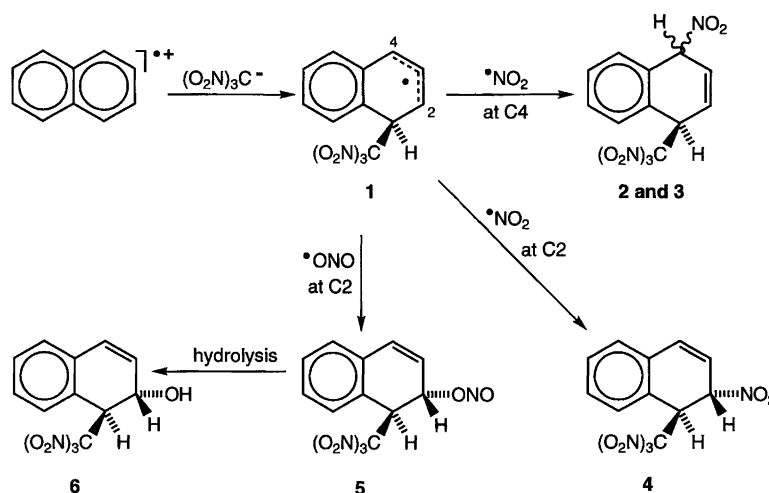
the buttressed methyl groups at C2(C3), adjacent to the C1(C4) ring positions.⁸

The calculated⁵ atomic charges on the ring carbon atoms of the radical cation of 1,3-dimethylnaphthalene are given in Fig. 1. On the basis of these calculated atomic charges it is apparent that the attack of trinitromethanide ion might occur at C4, C5 and C8, but it was recognised at the outset that attack at C4 might be limited by steric interaction between the attacking trinitromethanide ion and the *vicinal* 3-methyl group, and corresponding attack at C8 by steric interaction with the *peri* 1-methyl group. In the event, these expectations appear justified, with adduct formation in dichloromethane solution at 20 °C being initiated by trinitromethanide ion attack mainly at C5 (39%), but with some adduct formation from attack at C4 (12%) and even at C7 (4%). We now report the results of this study.

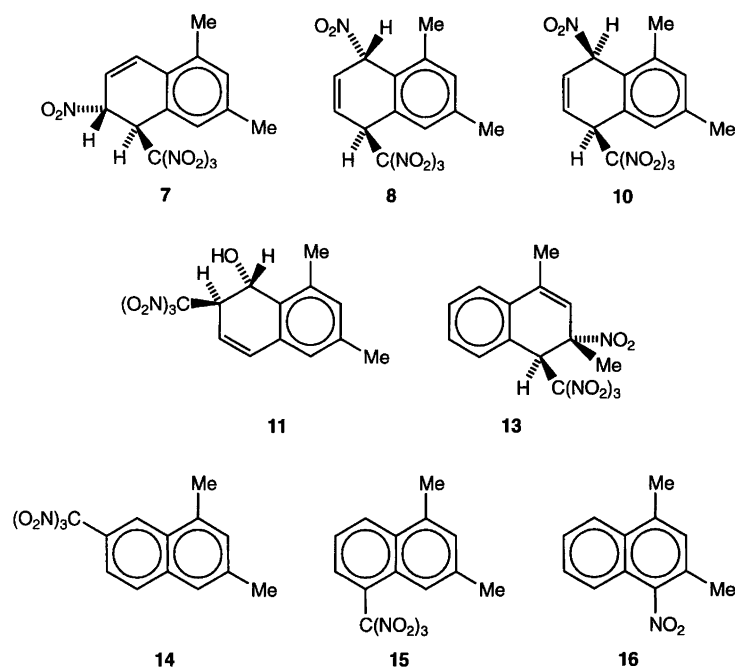
Results

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,⁹ and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature ≤ 0 °C. The crude product mixtures were stored at -20 °C and were analysed (¹H NMR spectroscopy, see Experimental section; Tables 1 and 2) as soon as possible.

Photochemistry in dichloromethane at 20 °C and identification of adducts. A solution of 1,3-dimethylnaphthalene (0.4 mol dm⁻³) and tetranitromethane (0.8 mol dm⁻³) in dichloromethane was irradiated at 20 °C. The composition of the reaction mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1). The final solution (after 2 h, conversion ca. 100%) after



Scheme 1.



work-up contained the adducts **7** (10%), **8** (8.5%), **9** (4.5%), **10** (10.5%), **11** (1%), **12** (2%), **13** (6%), 6,8-dimethyl-2-trinitromethylnaphthalene **14** (2.5%), 5,7-dimethyl-1-trinitromethylnaphthalene **5** (10%), and 2,4-dimethyl-1-nitronaphthalene **16** (38%). The adducts were separated partially by HPLC on a cyanopropyl column using hexane-dichloromethane mixtures as the eluting solvents.

The first adduct eluted was isolated only as an impure oil and was identified as 5,7-dimethyl-*r*-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene **7** on the basis of a consideration of its spectroscopic data and its slow

[$k = 0.0037(2) \text{ h}^{-1}$; $\tau_{1/2} = 186 \text{ h}$] conversion into the nitro cycloadduct **7** (see below). The ^1H NMR spectrum of adduct **7** was consistent only with its assignment as the product of nitro-trinitromethyl addition to the non-methylated ring in 1,3-dimethylnaphthalene, and the precise connectivity was defined by the results of nuclear Overhauser experiments and long-range reverse detected heteronuclear correlation spectra (HMBC). The stereochemistry of adduct **7** was assigned initially on the basis of its probable mode of formation. Attack of trinitromethanide ion at C5 of the radical cation of 1,3-dimethylnaphthalene would give the delocalized carbon radical

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

t/h	Conversion (%)	Yield (%)																			
		(7)	(8)	(10)	(11)	Adducts (7, 8, 10, 11)				(9)	(12)	(13)	Adducts (9, 12, 13)		Unknown adducts	Total adducts	(14)	(15)	(16)	Total aromatics	
At 20°C																					
1	80	8.6	7.6	11.7	1.6	29.5				1.8	1.6	5.9	9.3		6.9	45.7	2.7	3.4	48.2	54.3	
1.5	98	9.3	8.1	12.0	1.6	31.0				2.4	1.8	5.9	10.1		6.7	47.8	2.3	6.6	43.3	52.2	
2	100	10.1	8.5	10.5	1.4	30.5				4.5	1.8	5.6	11.9		7.3	49.7	2.5	9.9	37.9	50.3	
At 0°C																					
1	71	2.7	2.4	2.1	0.3	7.5				0.6	0.3	2.2	3.1		2.7	13.3	1.9	1.9	82.9	86.7	
1.5	90	3.0	2.5	2.4	0.3	8.2				1.3	0.2	2.6	4.1		3.0	15.3	1.6	2.2	80.9	84.7	
2	100	4.2	3.7	3.2	0.4	11.5				1.3	0.3	3.5	5.1		1.7	18.3	2.0	2.9	76.8	81.7	
At -20°C																					
1	42	1.4	0.6	0.1	—	2.1				trace	0.1	2.5	2.6		1.7	6.4	1.4	1.6	90.6	93.6	
1.5	68	1.2	1.1	1.4	—	3.7				0.3	0.2	2.6	3.1		1.5	8.0	0.8	0.9	90.0	91.7	
2	74	1.0	1.3	1.5	—	3.8				0.5	0.2	2.8	3.5		1.7	9.0	1.0	1.0	89.0	91.0	

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

t/h	Con- ver- sion (%)	Yield (%)															Total aro- matics	
		(7)	(8)	(10)	(11)	Adducts (7, 8, 10, 11)				Adducts (9, 12, 13)			Unknown adducts	Total adducts	(14)	(15)		(16)
At 20°C																		
1.5	89	3.2	3.5	3.3	0.9	10.9		0.6	0.2	3.7	4.5		3.7	19.1	3.7	4.1	73.1	80.9
2	100	2.8	3.2	2.4	0.5	8.9		1.0	0.2	2.7	3.9		3.2	16.0	3.3	4.5	76.2	84.0
At -20°C																		
1	57	1.4	1.7	1.5	—	4.6		—	0.1	3.0	3.1		1.9	9.6	1.9	1.4	87.1	90.4
2	89	1.3	1.5	1.6	—	4.4		—	0.1	3.2	3.3		2.5	10.2	1.1	0.7	88.0	89.8

18, which would then undergo radical coupling with nitrogen dioxide at C6 and *anti* to the bulky trinitromethyl group (Scheme 2). Subsequently, the structural and stereochemical assignment to adduct **7** was confirmed by the X-ray crystal structure determination for the related nitro cycloadduct **17** reported below.

The structure of the second adduct eluted from the HPLC column was determined by single crystal X-ray analysis. A perspective drawing of 6,8-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene **8**, $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_8$, m.p. $114.5\text{--}115.5^\circ\text{C}$, is presented in Fig. 2, and the corresponding atomic coordinates are given in Table 3. In the solid state the alicyclic ring exists in a slightly distorted boat conformation as indicated by the torsional angles: (3)–C(4)–C(4a)–C(8a) $17.5(3)^\circ$; C(2)–C(1)–C(8a)–C(4a) $-10.3(4)^\circ$. As in analogous structures reported earlier,^{4,7,10,11} the trinitromethyl group adopts an orientation such that the C(4)–C(9) bond is close to perpendicular to the plane of the aromatic ring [torsional angle: C(5)–C(4a)–C(4)–C(9) $74.9(3)^\circ$]. Finally, the orientation of the 1-nitro group is such that the protons of the 8-methyl group lie in its shielding zone, resulting in a somewhat upfield chemical shift for the 8-Me (δ 2.23). The remaining spectroscopic data were in accord with the established structure.

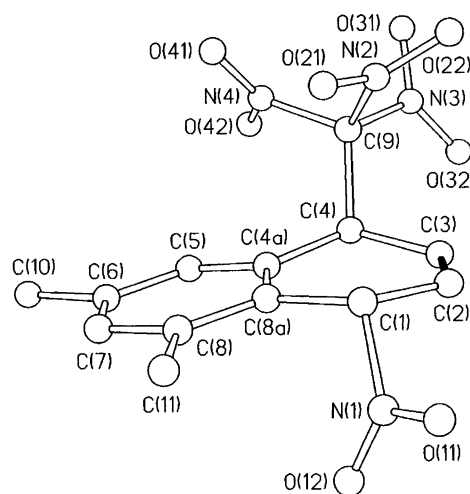
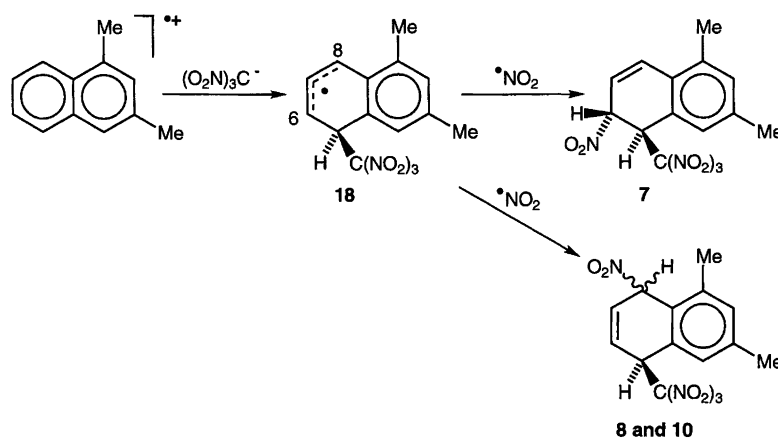


Fig. 2. Perspective drawing of compound **8**. Double bond is shown in black.

The structure of the third adduct eluted from the HPLC column was also determined by single-crystal X-ray analysis. A perspective drawing of the nitro cycloadduct **9**, $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_8$, m.p. $179.5\text{--}180.5^\circ\text{C}$, is presented in Fig. 3, and the corresponding atomic coordinates are given in Table 4. The heterocyclic cage structure



Scheme 2.

Table 3. Fractional coordinates for atoms in 6,8-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**8**). The equivalent isotropic temperature factor in Tables 3–6 is defined as one-third of orthogonalized U_{ij} tensor.

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$
O(11)	5679(3)	7006(3)	11590(2)	33(1)
O(12)	7770(3)	9265(2)	12039(2)	26(1)
O(21)	8187(3)	4510(2)	8640(2)	22(1)
O(22)	6270(3)	3462(2)	6157(2)	24(1)
O(31)	8052(3)	4760(2)	4694(2)	26(1)
O(32)	7138(3)	6461(2)	5025(2)	26(1)
O(41)	11068(3)	5570(2)	8285(2)	26(1)
O(42)	11330(3)	7383(2)	7319(2)	22(1)
N(1)	6934(4)	7805(3)	11469(3)	20(1)
N(2)	7627(3)	4515(3)	7341(3)	17(1)
N(3)	7875(3)	5737(3)	5484(3)	18(1)
N(4)	10536(3)	6337(3)	7659(2)	17(1)
C(1)	7429(4)	6889(3)	10453(3)	16(1)
C(2)	6256(4)	6648(3)	8829(3)	18(1)
C(3)	6809(4)	6960(3)	7845(3)	16(1)
C(4)	8678(4)	7480(3)	8218(3)	15(1)
C(4a)	9961(4)	8109(3)	9964(3)	12(1)
C(5)	11750(4)	9019(3)	10505(3)	14(1)
C(6)	13006(4)	9576(3)	12063(3)	16(1)
C(7)	12399(4)	9208(3)	13075(3)	19(1)
C(8)	10619(4)	8328(3)	12595(3)	16(1)
C(8a)	9373(4)	7791(3)	11013(3)	15(1)
C(9)	8687(4)	6056(3)	7231(3)	14(1)
C(10)	14937(4)	10481(4)	12598(3)	23(1)
C(11)	10102(4)	7976(4)	13790(3)	24(1)

in nitro cycloadduct **9** is presumably formed by thermal cycloaddition of a nitro group of the trinitromethyl function with the alkene system in a nitro-trinitromethyl precursor **13**. Unfortunately this precursor **13** could not be isolated from the product mixture. Nonetheless, there is an adequate precedent for the mode of formation of the nitro cycloadduct **9** (cf. Refs. 7, 8 and 10–12). In **9**, N(3) is clearly trigonal pyramidal, and bond length differences

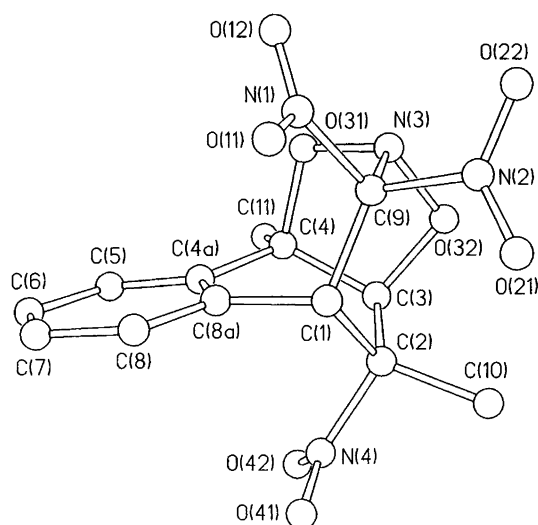


Fig. 3. Perspective drawing of compound **9**.

Table 4. Fractional coordinates for atoms in the nitro cycloadduct **9**.

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$
O(11)	3277(5)	3385(2)	590(4)	24(1)
O(12)	4378(5)	4225(2)	1267(4)	24(1)
O(21)	-1088(5)	3649(2)	147(4)	27(1)
O(22)	232(5)	4393(2)	-546(4)	29(1)
O(31)	3426(4)	4538(1)	4144(4)	18(1)
O(32)	417(4)	4587(1)	3554(4)	18(1)
O(41)	104(5)	2697(1)	5221(4)	22(1)
O(42)	731(4)	3360(1)	7108(4)	23(1)
N(1)	3284(5)	3848(2)	1231(5)	16(1)
N(2)	103(6)	4007(2)	392(5)	20(1)
N(3)	1891(5)	4527(2)	2761(5)	16(1)
N(4)	366(5)	3196(2)	5641(5)	18(1)
C(1)	1437(6)	3449(2)	3114(6)	15(1)
C(2)	158(6)	3634(2)	4246(6)	15(1)
C(3)	885(6)	4198(2)	4980(6)	16(1)
C(4)	2988(6)	4235(2)	5577(6)	16(1)
C(4a)	3938(6)	3672(2)	5650(6)	14(1)
C(5)	5497(6)	3526(2)	6853(6)	15(1)
C(6)	6368(6)	3019(2)	6738(6)	17(1)
C(7)	5676(6)	2655(2)	5424(6)	18(1)
C(8)	4093(6)	2790(2)	4219(6)	14(1)
C(8a)	3243(6)	3296(2)	4323(6)	15(1)
C(9)	1656(6)	3953(2)	2008(6)	13(1)
C(10)	-1908(6)	3642(2)	3442(6)	19(1)
C(11)	3633(7)	4610(2)	7104(6)	20(1)

[C(9)–N(1) 1.546(6) Å, C(9)–N(2) 1.538(6) Å, C(9)–N(3) 1.482(6) Å] are similar to those observed earlier^{7,8,10–14} for analogous heterocyclic cage structures. The nitro cycloadduct **9** differs from the nitro cycloadduct **19** only by the presence of the additional methyl group *ipso* to the C(2)–NO₂ group; the presence of this methyl group in the nitro cycloadduct **9**, which would be expected to interact sterically with the heterocyclic bridge system, leads to some conformational adjustment evident in the torsional angles: for **9**, C(9)–C(1)–C(2)–N(4) – 164.9(4)°; for **19** the corresponding torsional angle is – 172(2)°.⁷ The spectroscopic data for the nitro cycloadduct **9** were in accord with the established structure.

The fourth adduct eluted from the HPLC column was identified as the epimer of the nitro-trinitromethyl adduct **8** by single-crystal X-ray analysis. A perspective drawing of 6,8-dimethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene **10**, C₁₃H₁₂N₄O₈, m.p. 129°C (decomp.) is presented in Fig. 4, and corresponding atomic coordinates are given in Table 5. As with the structure of its epimer **8**, the alicyclic ring of the nitro-trinitromethyl adduct **10** exists in a boat conformation [torsional angles: C(2)–C(1)–C(8a)–C(4a) – 14.1(5)°; C(3)–C(4)–C(4a)–C(8a) 14.0(5)°] with the C(4)–C(9) bond close to perpendicular to the plane of the aromatic ring [torsional angle: C(5)–C(4a)–C(4)–C(9) 75.6(4)°]. The spectroscopic data for the nitro-trinitromethyl adduct **10** were consistent with its established structure.

The two adducts **11** and **12** eluted towards the end of the HPLC chromatogram were both isolated in low yield and as impure oils. Crystallization of the hydroxy cy-

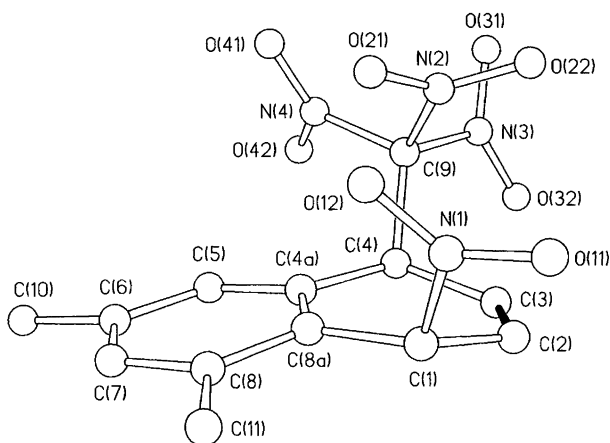
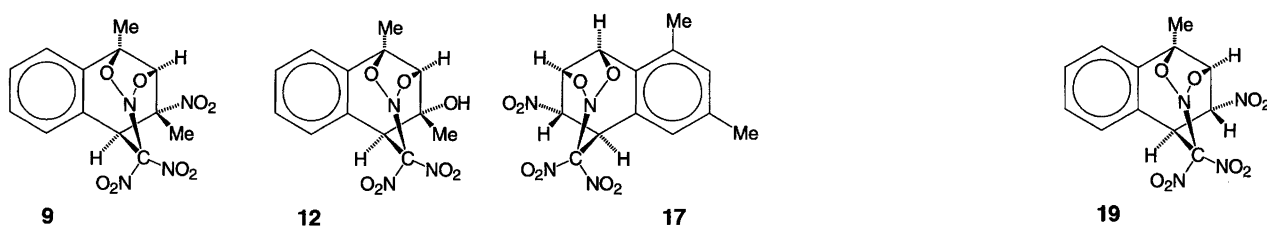


Fig. 4. Perspective drawing of compound **10**.

clodduct **12** gave crystals of poor quality and inadequate for single-crystal X-ray analysis. Notwithstanding these features of the two samples, the respective structural assignments seem certain. The structural assignment for the *r*-1-hydroxy-*t*-2-trinitromethyl adduct **11** is based on its ^1H NMR spectrum and nuclear Overhauser experiments, coupled with a comparison of these data (Fig. 5) with those of 4,8-dimethyl-*t*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-1-ol **20**;¹⁵ such minor differences in chemical shift which are observed are the result of the effects arising from the 6-methyl (**11**) or 4-methyl (**20**) groups. Consistent with the structural assignment to the *r*-1-hydroxy-*t*-2-trinitromethyl adduct **11** is the observation that the compound failed to undergo intramolecular cycloaddition on storage of a ^2H -chloroform solution at

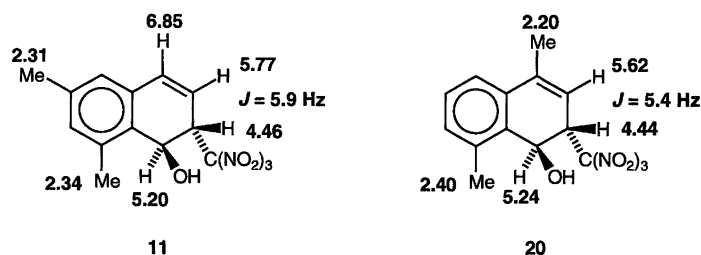


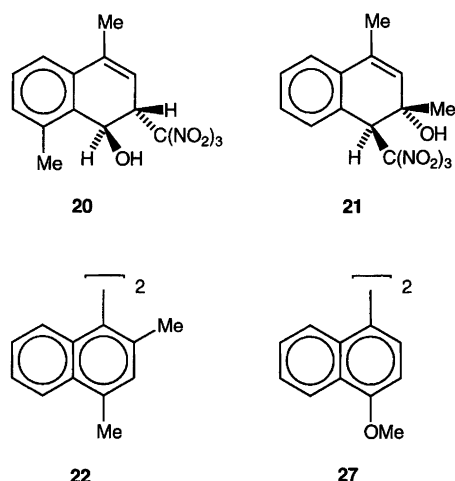
Fig. 5. ^1H NMR spectroscopic data for *t*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-ols **11** and **20**.

Table 5. Fractional coordinates for atoms in 6,8-dimethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydronaphthalene (**10**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{\AA}^2$
O(11)	9690(4)	6970(2)	5414(3)	41(1)
O(12)	8461(4)	7587(2)	3786(3)	31(1)
O(21)	5674(4)	6660(2)	2554(3)	39(1)
O(22)	5838(4)	5550(2)	3410(3)	33(1)
O(31)	2508(4)	5052(2)	2745(3)	36(1)
O(32)	2234(4)	5369(2)	4608(3)	34(1)
O(41)	1434(5)	6666(2)	1299(3)	60(1)
O(42)	553(4)	6560(2)	2464(3)	30(1)
N(1)	8494(4)	7334(2)	4816(3)	18(1)
N(2)	5103(4)	6134(2)	3066(3)	23(1)
N(3)	2644(4)	5486(2)	3616(3)	23(1)
N(4)	2011(5)	6531(2)	2272(3)	24(1)
C(1)	7006(5)	7520(2)	5475(3)	15(1)
C(2)	6442(5)	6797(2)	5997(3)	17(1)
C(3)	4909(5)	6496(2)	5589(3)	16(1)
C(4)	3572(5)	6813(2)	4523(3)	15(1)
C(4a)	3954(5)	7628(2)	4200(3)	13(1)
C(5)	2602(5)	8063(2)	3538(3)	14(1)
C(6)	2825(5)	8826(2)	3300(3)	16(1)
C(7)	4451(5)	9142(2)	3766(4)	18(1)
C(8)	5819(5)	8734(2)	4448(3)	16(1)
C(8a)	5577(5)	7955(2)	4662(3)	13(1)
C(9)	3366(5)	6276(2)	3397(4)	16(1)
C(10)	1327(5)	9297(2)	2620(4)	24(1)
C(11)	7515(5)	9126(2)	4963(4)	24(1)

22°C for 350 h; although *t*-1-trinitromethyl-1,2-dihydronaphthalen-*r*-2-ols undergo intramolecular cycloaddition readily (see below), *t*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-1-ols appear to be inert.¹⁵

The hydroxy cycloadduct **12** was identified in the first instance by a consideration of its NMR data, which



pointed to a structure which was the result of intramolecular cycloaddition of an intermediate *r*-2-hydroxy-*t*-1-trinitromethyl adduct **21** in the methyl-substituted ring. Comparison of the ^1H and ^{13}C NMR data for the hydroxy cycloadduct **12** and the nitro cycloadduct **9**, the structure of the latter which was established above by single-crystal X-ray analysis, supports this assignment (Fig. 6).

Finally, although the precursor of the nitro cycloadduct **9** could not be isolated by HPLC, 2,4-dimethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene **13** was detected in the ^1H NMR spectrum of product mixtures. It is significant that, while the nitro-trinitromethyl adduct **13** could be detected as a transient intermediate in the formation of nitro cycloadduct **9**, the corresponding hydroxy-trinitromethyl precursor **21** of the hydroxy cycloadduct **12** was never apparent in the ^1H NMR spectra of product mixtures. This is consistent with the earlier observation that hydroxy-trinitromethyl adducts such as compound **21** undergo cycloaddition more rapidly than the corresponding nitro-trinitromethyl adducts such as compound **13**.⁸

Photochemistry in dichloromethane at -20°C and identification of aromatic substitution products 14–16. A solution

of 1,3-dimethylnaphthalene (0.4 mol dm^{-3}) and tetra-nitromethane (0.8 mol dm^{-3}) in dichloromethane was irradiated at -20°C for 2 h to give a mixture of adducts (total 9%), 6,8-dimethyl-2-trinitromethylnaphthalene **14** (1%), 5,7-dimethyl-1-trinitromethylnaphthalene **15** (1%) and 2,4-dimethyl-1-nitronaphthalene **16** (89%). Chromatography of this mixture on a silica gel Chromatotron plate gave pure samples of the compounds **14**–**16**. The two trinitromethyl compounds **14** and **15**, which were isolated only in low yield, were identified from their spectroscopic data and mass spectra. The 2,4-dimethyl-1-nitronaphthalene **16** was identified from its spectroscopic data and literature melting point data.¹⁶

Photochemistry in dichloromethane at 0°C . This reaction was performed as before, giving products already known from the previous reactions (Table 1).

Photochemistry in acetonitrile at 20 or -20°C . These reactions were performed in the same way as in dichloromethane and the results are shown in Table 2.

*Thermal cycloaddition of 5,7-dimethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene **7** in ^2H -chloroform.* A solution of the impure nitro-trinitromethyl adduct **7** in ^2H -chloroform was stored at 22°C in the dark and the ^1H NMR spectrum of the solution monitored at appropriate time intervals. While the impurities were stable under these conditions, the nitro-trinitromethyl adduct **7** was slowly [$k = 0.0037(2) \text{ h}^{-1}$] converted into the nitro cycloadduct **17**. After 33 days the reaction was essentially complete (Fig. 7), and the nitro cycloadduct **17** was isolated by removal of the solvent under reduced pressure and crystallization from dichloromethane-hexane, and its structure determined by single-crystal X-ray analysis. A perspective drawing of the nitro cycloadduct **17**, $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_8$, m.p. 195°C (decomp.), is presented in Fig. 8, and corresponding atomic coordinates are given in Table 6. The structure of nitro cycloadduct **17** is essentially identical with that determined above for nitro cycloadduct **9**, except for the positions of attachment of the two methyl groups in the two structures. The spectroscopic data for nitro cycloadduct **17** were in accord with the established structure.

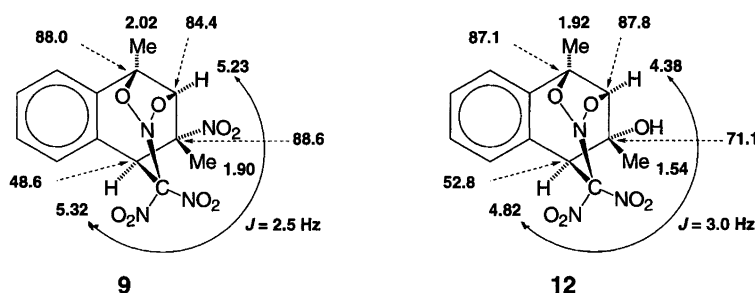


Fig. 6. ^1H NMR spectroscopic data for nitro cycloadducts **9** and **12**.

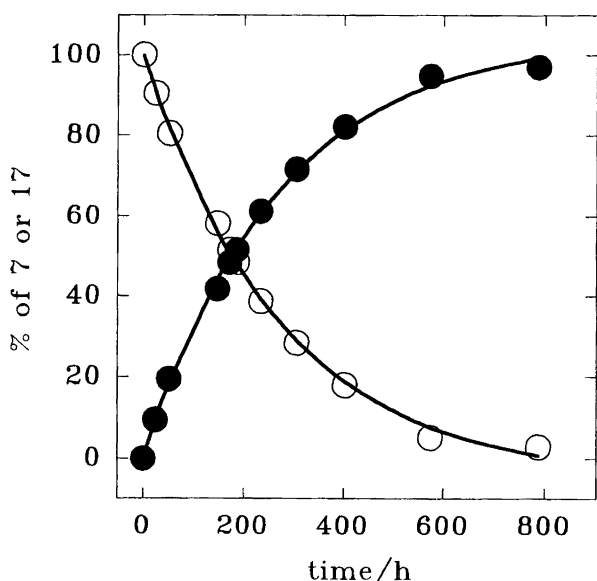


Fig. 7. Kinetics of cycloaddition **7**→**17** in [²H]-chloroform at 22°C. Empty circles, decay of **7**; filled circles, appearance of **17**. The solid lines correspond to exponentials with $k=0.0037\text{ h}^{-1}$.

Photochemistry in dichloromethane at 20°C in the presence of trifluoroacetic acid. A solution of 1,3-dimethylnaphthalene (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane containing trifluoroacetic acid (0.8 mol dm^{-3}) was irradiated at 20°C for 30 min to give a mixture of unreacted 1,3-dimethylnaphthalene (42% conversion), 2,4-dimethyl-1-nitronaphthalene **16** (34%), 2,2',4,4'-tetramethyl-1,1'-binaphthalene **22** (54%), and unidentified material (total 12%). Compounds **16** and **22** were identified by comparison with the ¹H NMR spectra of authentic materials.

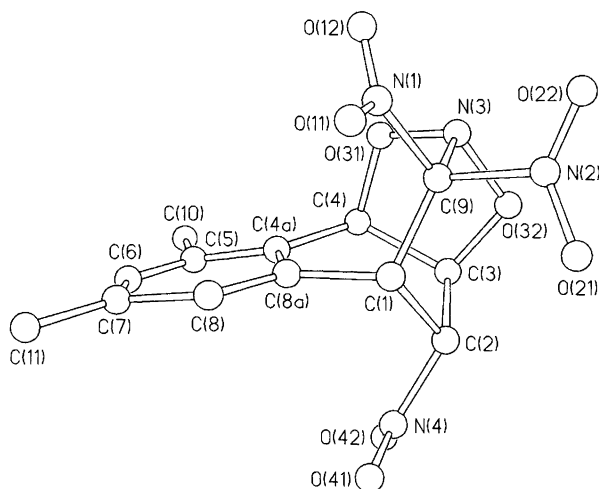


Fig. 8. Perspective drawing of compound **17**.

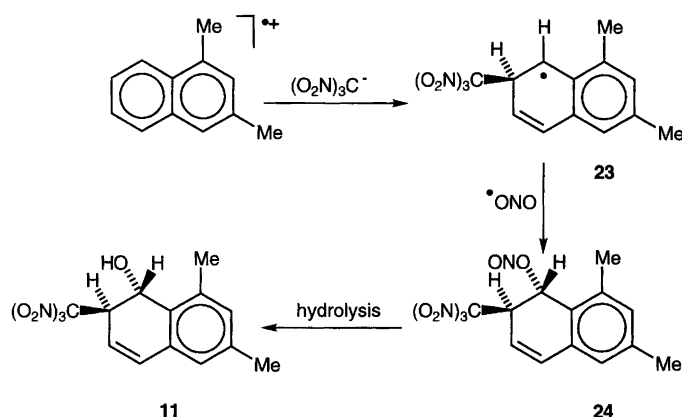
Table 6. Fractional coordinates for atoms in nitro cycloadduct (**17**).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U \text{ \AA}^2$
O(11)	5953(1)	-3899(3)	5791(1)	25(1)
O(12)	5945(1)	-4349(3)	6671(1)	24(1)
O(21)	7025(1)	180(3)	5778(1)	25(1)
O(22)	7490(1)	-1697(3)	6400(1)	27(1)
O(31)	5268(1)	-1278(3)	7167(1)	17(1)
O(32)	6111(1)	1014(3)	6966(1)	17(1)
O(41)	4577(1)	2416(3)	5397(1)	27(1)
O(42)	4242(1)	3640(3)	6177(1)	27(1)
N(1)	5973(2)	-3375(4)	6268(1)	19(1)
N(2)	6937(1)	-902(4)	6151(1)	18(1)
N(3)	6065(1)	-921(4)	6939(1)	17(1)
N(4)	4672(1)	2646(4)	5891(1)	20(1)
C(1)	5392(2)	-361(4)	5979(1)	12(1)
C(2)	5383(2)	1638(4)	6158(1)	14(1)
C(3)	5302(2)	1635(4)	6782(1)	15(1)
C(4)	4691(2)	176(4)	6994(1)	16(1)
C(4a)	4132(2)	-651(4)	6566(1)	13(1)
C(5)	3296(2)	-1098(4)	7758(1)	14(1)
C(6)	2885(2)	-2023(4)	6244(1)	19(1)
C(7)	3253(2)	-2518(5)	5754(1)	16(1)
C(8)	4086(2)	-2018(4)	5670(1)	16(1)
C(8a)	4511(2)	-1103(4)	6069(1)	11(1)
C(9)	6032(2)	-1327(4)	6338(1)	11(1)
C(10)	2851(2)	-648(4)	7186(1)	24(1)
C(11)	2784(2)	-3514(4)	5310(1)	25(1)

EPR spectral properties of the 1,3-dimethylnaphthalene-tetranitromethane system. Irradiation ($\lambda > 430\text{ nm}$) for 10 min of a solution of 1,3-dimethylnaphthalene (70 mmol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at -60°C failed to give an EPR signal, nor did it appear in an experiment where additionally TFA (0.4 or 0.8 mol dm^{-3}) had been added under otherwise identical conditions. This shows that the 1,3-dimethylnaphthalene radical cation, formed in the triad of eqn. (1), reacts fast with both trinitromethanide ion and NO_2 , as has been discussed earlier.² The EPR experiments will be reported elsewhere.¹⁷

Discussion

In terms of the adducts which have been identified (56%) for the reaction at 20°C in dichloromethane (Table 1), there is a clear preference (ca. 4:1) for trinitromethanide ion attack on the unsubstituted ring in the radical cation of 1,3-dimethylnaphthalene. The major point of attack is at C5 (39%), but with adduct **11** and 6,8-dimethyl-2-trinitromethylnaphthalene **14** (total 4%) being formed by initial attack of trinitromethanide ion at C7. Notably no adducts or 6,8-dimethyl-2-trinitromethylnaphthalene have been detected which might have been the result of trinitromethanide ion attack at C8; this outcome is clearly a reflection of the steric hindrance to attack by trinitromethanide ion at C8 exerted by the *peri* 1-methyl substituent, despite the atomic charge at C8 (Fig. 1) being apparently quite favourable for attack at that position.

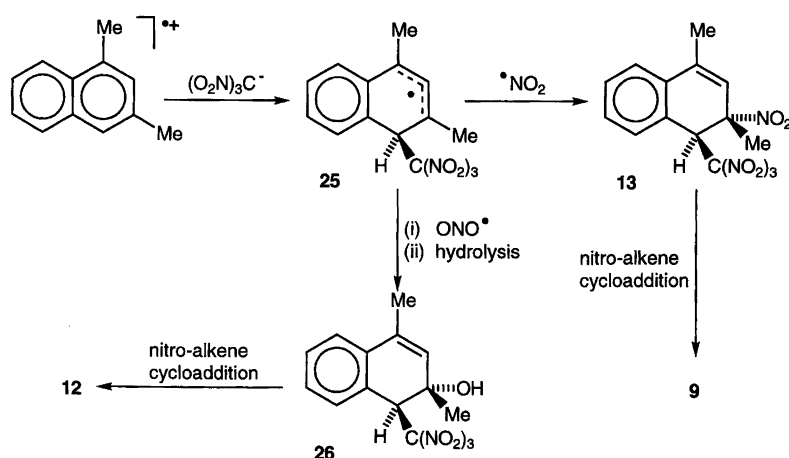


Scheme 3.

The modes of formation of the products arising from attack of trinitromethanide ion on the unsubstituted ring of the radical cation of 1,3-dimethylnaphthalene are given in Schemes 2 and 3. Attack of trinitromethanide ion at C5 would give the delocalized carbon radical **18** (Scheme 2); radical coupling with nitrogen dioxide at C6 in **18** would occur *anti* to the bulky trinitromethyl group to give the nitro-trinitromethyl adduct **7**, while coupling with nitrogen dioxide at C8 would be expected to be non-stereospecific and give the epimeric nitro-trinitromethyl adducts **8** and **10**. Attack of trinitromethanide ion at C7 of the radical cation of 1,3-dimethylnaphthalene would give the benzylic radical **23** (Scheme 3), which on radical coupling with nitrogen dioxide with C–O bond formation would yield the nitrito-trinitromethyl adduct **24**; this adduct **24** would be expected to be hydrolysed to give the hydroxy-trinitromethyl adduct **11** either under the prevailing acidic reaction conditions or during the work-up procedure. The precise mode of formation of 6,8-dimethyl-2-trinitromethylnaphthalene **14** from the benzylic radical **23** is uncertain, but one possibility is the loss of nitrous acid from the postulated intermediate, the nitro-trinitromethyl adduct **24**, in competition with hydrolysis to give the hydroxy-trinitromethyl adduct **11**.

In spite of the calculated atomic charge at C4 (Fig. 1), attack of trinitromethanide ion at C4 is limited by the steric interaction between the trinitromethanide ion and the methyl group at the adjacent C3 position. The mode of formation of adducts arising from trinitromethanide ion attack at C4 is given in Scheme 4. The delocalized carbon radical **25**, formed initially, undergoes radical coupling with nitrogen dioxide apparently exclusively at C3 with both C–N and C–O bond formation to give adducts **13** and **26**, the latter after hydrolysis of the corresponding nitrito-trinitromethyl adduct. While the nitro-trinitromethyl adduct **13** was detected among the reaction products, it was not isolated but yielded the nitro cycloadduct **9**, the product of nitroalkene cycloaddition. The hydroxy-trinitromethyl adduct **26** would be expected⁸ to undergo the nitroalkene cycloaddition reaction more readily than its nitro analogue **13**, and it is not surprising therefore that the precursor adduct **26** could not be detected among the products. No products were detected which could have been derived by coupling of nitrogen dioxide at C1 in the delocalized carbon radical **25**, but in this context it must be emphasized that of the total adduct yield (50%), some 7% remains unidentified.

The effect of the reaction temperature in dichloro-



Scheme 4.

methane on the relative yields of adducts and aromatic substitution products is marked; at 20 °C the adduct: aromatic ratio is ca 1:1, at 0 °C it is ca. 1:4, but at -20 °C the ratio is ca. 1:10 (Table 1). In acetonitrile this effect is less extreme, the adduct: aromatic ratio being ca. 1:5 (20 °C) and ca. 1:9 (-20 °C) (Table 2).

In the photolysis at 20 °C of 1,3-dimethylnaphthalene-tetranitromethane in dichloromethane containing trifluoroacetic acid the formation of adducts and the trinitromethyl aromatic derivatives **14** and **15** is suppressed by the protonation of trinitromethanide ion in the triad [eqn. (1)] of the 1,3-dimethylnaphthalene radical cation, the trinitromethanide ion and nitrogen dioxide. In the absence of the trinitromethanide ion, the 1,3-dimethylnaphthalene radical cation undergoes radical coupling with nitrogen dioxide to give 2,4-dimethyl-1-nitronaphthalene **16** and the dehydromer **22**. The formation of the dehydromer **22** in photolyses in the presence of trifluoroacetic acid parallels dehydromer **27** formation in a similar reaction of 1-methoxynaphthalene.¹⁸

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ¹H NMR spectra were recorded on a Varian Unity 300 spectrometer with SiMe₄ as an internal standard. Tetranitromethane was purchased from Aldrich and 1,3-dimethylnaphthalene from Janssen Chemical 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.¹⁹

General procedure for the photonitration of 1,3-dimethylnaphthalene with tetranitromethane. A solution of 1,3-dimethylnaphthalene (500 mg, 0.4 mol dm⁻³) and tetranitromethane (0.8 mol dm⁻³) in dichloromethane (at 20, 0 or -20 °C) or acetonitrile (20 or -20 °C) was irradiated with filtered light ($\lambda_{\text{cut-off}} < 435$ 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 2).

Reaction in dichloromethane at 20 °C and the identification of adducts (7–13). Reaction of 1,3-dimethylnaphthalene-tetranitromethane in dichloromethane at 20 °C, as above, for 2 h gave a product which was shown by ¹H NMR spectra to be a mixture (Table 1) of 5,7-dimethyl-*r*-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (**7**) (10%), 6,8-dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (**8**) (8.5%), the nitro cycloadduct (**9**) (4.5%), 6,8-dimethyl-*r*-1-nitro-*c*-4-trinitromethyl-1,4-dihydro-

naphthalene (**10**) (10.5%), and three further adducts (**11**) (1%), (**12**) (2%) and (**13**) (6%) which were identified tentatively from their ¹H NMR spectra, 6,8-dimethyl-2-trinitromethylnaphthalene (**14**) (2.5%), 5,7-dimethyl-1-trinitromethylnaphthalene (**15**) (10%), and 2,4-dimethyl-1-nitronaphthalene (**16**) (38%). The adducts were partially separated by HPLC and gave the following in elution order:

*5,7-Dimethyl-*r*-2-nitro-*t*-1-trinitromethyl-1,2-dihydronaphthalene (7)* as an impure oil. ¹H NMR (CDCl₃) δ 2.29 (s, 7-Me), 2.34 (s, 5-Me), 5.66 (dd, $J_{\text{H}_2, \text{H}_3}$ 6.8 Hz, $J_{\text{H}_2, \text{H}_4}$ 1.0 Hz, H2), 5.70 (br s, H1), 5.98 (ddd, $J_{\text{H}_3, \text{H}_4}$ 9.8 Hz, $J_{\text{H}_3, \text{H}_2}$ 6.8 Hz, $J_{\text{H}_3, \text{H}_1}$ 1.0 Hz, H3), 6.81 (br s, H8), 7.04 (d, $J_{\text{H}_4, \text{H}_3}$ 9.8 Hz), 7.08 (br s, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.29 gave enhancements at δ 6.81 (3.5%) and at δ 7.08 (3.7%); irradiation at δ 2.34 gave enhancements at δ 7.04 (8.0%) and at δ 7.08 (5.3%); irradiation at δ 5.66 gave enhancement at δ 5.98 (5.7%) and at δ 6.81 (4.7%); irradiation at δ 5.98 gave enhancements at δ 5.66 (5.4%) and at δ 7.04 (5.6%); irradiation at δ 6.81 gave enhancements at δ 2.29 (0.6%) and at δ 5.70 (4.5%). ¹³C NMR (CDCl₃) δ 18.8 (5-Me), 21.2 (7-Me), 43.8 (C1), 76.1 (C2), 114.9 (C3), 120.1 (C8a), 127.7 (C4a), 128.4 (C8), 131.6 (C4), 134.3 (C6), 136.0 (C5), 140.5 (C7), resonance for C(NO₂)₃ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC). The structure of the nitro-trinitromethyl adduct (**7**) was further confirmed by its thermal cycloaddition in [²H]-chloroform to give the nitro cycloadduct (**17**), the structure of which is established below.

*6,8-Dimethyl-*r*-1-nitro-*t*-4-trinitromethyl-1,4-dihydronaphthalene (8)*, m.p. 114.5–115.5 °C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1615, 1594, 1576, 1558 cm⁻¹. ¹H NMR (CDCl₃) δ 2.23 (s, 8-Me), 2.34 (s, 6-Me), 5.39 (br s, H4), 6.20 (br s, H1), 6.56 (m, H2 and H3), 6.98 (s, H5), 7.17 (s, H7). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.23 gave enhancements at δ 6.20 (7.2%) and δ 7.17 (6.6%); irradiation at δ 2.34 gave enhancements at δ 6.98 (5.3%) and at δ 7.17 (5.0%); irradiation at δ 5.39 gave enhancements at δ 6.56 (3.0%) and at δ 6.98 (4.8%); irradiation at δ 6.20 gave enhancements at δ 2.23 (1.5%) and at δ 6.57 (2.8%); irradiation at δ 6.98 gave enhancements at δ 2.34 (1.4%) and at δ 5.39 (4.7%). ¹³C NMR (CDCl₃) δ 19.2 (8-Me), 21.15 (6-Me), 44.7 (C4), 82.4 (C1), 124.5 (C2), 125.2 (C4a), 125.55 (C8a), 126.3 (C5), 131.1 (C3), 133.7 (C7), 138.9 (C8), 140.7 (C6), resonance for C(NO₂)₃ not observed. The above assignments were confirmed by long range reverse detected heteronuclear correlation spectra (HMBC).

Nitro cycloadduct (9), m.p. 179.5–180.5 °C (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1595, 1552 cm⁻¹. ¹H NMR (CDCl₃) δ 1.90 (s, 2-Me), 2.02 (s, 4-Me), 5.23 (d, $J_{\text{H}_3, \text{H}_1}$ 2.5 Hz, H3), 5.32 (d, $J_{\text{H}_1, \text{H}_3}$ 2.5 Hz, H1), 7.31–7.41 (m, H5–H8). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.90

gave enhancements at δ 5.23 (3.9%) and at δ 5.32 (4.9%); irradiation at δ 2.02 gave enhancements at δ 5.23 (7.5%) and at δ 7.35 (3.8%); irradiation at δ 5.23 gave enhancements at δ 1.90 (0.4%) and at δ 2.02 (0.5%); irradiation at δ 5.32 gave enhancements at δ 1.90 (0.4%) and at δ 7.37 (1.1%). ^{13}C NMR (CDCl_3) δ 20.7 (4-Me), 23.2 (2-Me), 48.6 (C1), 84.4 (C3), 88.0 (C4), 88.6 (C2), 129.3 (C8a), 136.9 (C4a), 124.05, 130.02, 130.5, 131.7 (C5, C6, C7, C8), resonance for $\text{C}(\text{NO}_2)_3$ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

6,8-Dimethyl-r-1-nitro-c-4-trinitromethyl-1,4-dihydronaphthalene (10), m.p. 129.0°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{max} (KBr) 1616, 1601, 1572, 1547 cm^{-1} . ^1H NMR (CDCl_3) δ 2.32 (s, 8-Me), 2.35 (s, 6-Me), 5.34 (br s, H4), 6.01 (dd, $J_{\text{H1,H2}}$ 5.9 Hz, $J_{\text{H1,H4}}$ 2.7 Hz, H1), 6.62 (ddd, $J_{\text{H3,H2}}$ 10.2 Hz, $J_{\text{H3,H4}}$ 4.8 Hz, $J_{\text{H3,H1}}$ 1.0 Hz, H3), 6.85 (ddd, $J_{\text{H2,H3}}$ 10.2 Hz, $J_{\text{H2,H1}}$ 5.9 Hz, $J_{\text{H2,H4}}$ 1.0 Hz, H2), 6.90 (s, H5), 7.23 (s, H7). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.33 gave enhancements at δ 6.01 (7.2%), at δ 6.90 (4.8%) and at δ 7.23 (8.7%); irradiation at δ 5.34 gave enhancements at δ 6.62 (4.7%) and at δ 6.90 (4.5%); irradiation at δ 6.01 gave enhancements at δ 2.32 (1.8%) and at δ 6.85 (4.6%); irradiation at δ 6.62 gave enhancements at δ 5.34 (4.4%) and at δ 6.85 (7.8%); irradiation at δ 7.23 gave enhancements at δ 2.32 (1.2%) and at δ 2.35 (0.9%). ^{13}C NMR (CDCl_3) δ 19.4 (8-Me), 21.2 (6-Me), 45.0 (C4), 79.1 (C1), 124.6 (C8a), 125.7 (C2), 126.8 (C5), 127.1 (C4a), 130.4 (C3), 133.6 (C7), 140.7 (C8), 141.2 (C6), resonance for $\text{C}(\text{NO}_2)_3$ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

6,8-Dimethyl-t-2-trinitromethyl-1,2-dihydronaphthalen-r-1-ol (11), isolated only in low yield as an impure oil. ^1H NMR (CDCl_3) δ 2.31 (s, 6-Me), 2.34 (s, 8-Me), 4.46 (d, $J_{\text{H2,H3}}$ 5.9 Hz, H2), 5.20 (br s, H1), 5.77 (ddd, $J_{\text{H3,H4}}$ 9.8 Hz, $J_{\text{H3,H2}}$ 5.9 Hz, $J_{\text{H3,H1}}$ 2.0 Hz, H3), 6.85 (dd, $J_{\text{H4,H3}}$ 9.8 Hz, $J_{\text{H4,H2}}$ 1.5 Hz, H4), 6.85 (s, H5), 7.02 (s, H7). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.46 gave enhancements at δ 5.20 (1.7%) and at δ 5.77 (1.9%); irradiation at δ 5.20 gave enhancements at δ 2.34 (1.3%) and at δ 4.46 (1.9%); irradiation at δ 5.77 gave enhancements at δ 4.46 (2.5%) and at δ 6.85 (2.0%); irradiation at δ 6.85 gave enhancements at δ 2.31 (0.8%) and at δ 5.77 (3.6%); irradiation at δ 7.02 gave enhancements at δ 2.31 (0.8%) and at δ 2.34 (0.8%).

Hydroxy cycloadduct (**12**), m.p. 151–153°C (insufficient for elemental analysis; parent ion not visible in mass spectrum; crystals were obtained by crystallization but were of inadequate quality for single-crystal X-ray analysis). IR: ν_{max} (KBr) 3565, 1603 cm^{-1} . ^1H NMR (CDCl_3) δ 1.54 (s, 2-Me), 1.92 (s, 4-Me), 4.38 (d, $J_{\text{H3,H1}}$ 3.0 Hz, H3), 4.82 (d, $J_{\text{H1,H3}}$ 3.0 Hz, H1), 7.40–7.49 (m, H5, H6, H7, H8). Nuclear Overhauser experiments gave the fol-

lowing results: irradiation at δ 1.54 gave enhancements at δ 4.38 (4.7%) and at δ 4.82 (5.7%); irradiation at δ 1.92 gave enhancements at δ 4.38 (7.9%) and at δ 7.43 (3.4%); irradiation at δ 4.38 gave enhancements at δ 1.54 (0.4%) and at δ 1.92 (0.6%); irradiation at δ 4.82 gave enhancements at δ 1.54 (0.6%) and at δ 7.46 (2.4%). ^{13}C NMR (CDCl_3) δ 21.1 (4-Me), 24.1 (2-Me), 52.85 (C1), 71.1 (C2), 87.1 (C4), 87.85 (C3), 123.9 (C7), 129.7 (C8), 130.0 (C6), 131.1 (C8a), 132.2 (C5), 137.5 (C4a), resonance for $\text{C}(\text{NO}_2)_3$ not observed. The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC).

Finally, although 2,4-dimethyl-r-2-nitro-t-1-trinitromethyl-1,2-dihydronaphthalene (**13**) could not be isolated, it was detected through its ^1H NMR spectrum in product mixtures. ^1H NMR (CDCl_3) δ 2.07 (d, $J_{4\text{-Me,H3}}$ 1.4 Hz, 4-Me), 2.09 (s, 2-Me), 5.55 (s, H1), 6.14 (d, $J_{\text{H3,4-Me}}$ 1.4 Hz, H3), the remainder of the spectrum was obscured by other signals of the reaction mixture.

Reaction in dichloromethane at -20°C and the identification of the aromatic products (14–16). Reaction of 1,3-dimethylnaphthalene-tetranitromethane in dichloromethane at -20°C , as above, for 2 h gave a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of adducts (**7**) (1%), (**8**) (1.3%), (**9**) (0.5%), (**10**) (1.5%), (**12**) (0.2%) and (**13**) (3%) together with the aromatic compounds 6,8-dimethyl-2-trinitromethylnaphthalene (**14**) (1%), 5,7-dimethyl-1-trinitromethylnaphthalene (**15**) (1%), and 2,4-dimethyl-1-nitronaphthalene (**16**) (89%). Chromatography of this mixture on a silica gel Chromatotron plate gave in elution order:

6,8-Dimethyl-2-trinitromethylnaphthalene (14), m.p. 73–74.5°C (insufficient for elemental analysis. Found: M^+ , 305.06478. $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_6$ requires 305.06478). IR: ν_{max} (KBr) 1602, 1587 cm^{-1} . ^1H NMR (CDCl_3) δ 2.53 (s, 6-Me), 2.68 (s, 8-Me), 7.34 (br s, H7), 7.50 (dd, $J_{\text{H3,H4}}$ 8.8 Hz, $J_{\text{H3,H1}}$ 1.9 Hz, H3), 7.56 (br s, H5), 7.92 (d, $J_{\text{H4,H3}}$ 8.8 Hz, H4), 8.26 (d, $J_{\text{H1,H3}}$ 1.9 Hz, H1). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.53 gave enhancements at δ 7.34 (3.5%) and at δ 7.56 (3.9%); irradiation at δ 2.68 gave enhancements at δ 7.34 (4.5%) and at δ 8.26 (8.4%); irradiation at δ 7.34 gave enhancements at δ 2.53 (0.3%) and at δ 2.68 (0.6%); irradiation at δ 7.53 gave enhancements at δ 2.53 (0.5%) and at δ 7.92 (9.5%); irradiation at δ 7.92 gave enhancements at δ 7.50 (7.0%) and at δ 7.56 (3.2%); irradiation at δ 8.26 gave an enhancement at δ 2.68 (1.0%).

5,7-Dimethyl-1-trinitromethylnaphthalene (15), m.p. 99.0°C (decomp.) (insufficient for elemental analysis. Found: M^+ , 305.06478. $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_6$ requires 305.06478). IR: ν_{max} (KBr) 1621, 1590 cm^{-1} . ^1H NMR (CDCl_3) δ 2.44 (s, 7-Me), 2.73 (s, 5-Me), 6.92 (br s, H8), 7.31 (br s, H6), 7.55 (dd, $J_{\text{H3,H2}}$ 7.0 Hz, $J_{\text{H3,H4}}$ 6.5 Hz, H3), 7.55 (dd, $J_{\text{H2,H3}}$ 7.0 Hz, $J_{\text{H2,H4}}$ 1.8 Hz, H2), 8.37 (dd, $J_{\text{H4,H3}}$ 6.5 Hz, $J_{\text{H4,H2}}$ 1.8 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation

at δ 2.44 gave enhancements at δ 6.92 (4.8%) and at δ 7.31 (3.4%); irradiation at δ 2.73 gave enhancements at δ 7.31 (4.6%) and at δ 8.37 (7.8%); irradiation at δ 6.92 gave an enhancement at δ 2.44 (0.6%); irradiation at δ 7.31 gave enhancements at δ 2.44 (0.5%) and at δ 2.73 (0.7%); irradiation at δ 7.55 gave an enhancement at δ 8.37 (4.0%); irradiation at δ 8.37 gave enhancements at δ 7.55 (2.9%) and at δ 2.73 (1.4%).

2,4-Dimethyl-1-nitronaphthalene (16), m.p. 84–85°C (Lit.¹⁶ 83–83.5°C). IR: ν_{\max} (KBr) 1513 cm^{-1} . ^1H NMR (CDCl_3) δ 2.47 (s, 2-Me), 2.70 (s, 4-Me), 7.21 (s, H3), 7.59 (m, H6,H7), 7.74 (m, H8), 8.00 (m, H5). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.47 gave an enhancement at δ 7.21 (2.8%); irradiation at δ 2.70 gave enhancements at δ 8.00 (5.1%) and at δ 7.21 (4.0%); irradiation at δ 7.21 gave enhancements at δ 2.47 (0.8%) and at δ 2.70 (0.7%); irradiation at δ 7.74 gave an enhancement at δ 7.59 (1.5%); irradiation at δ 8.00 gave enhancements at δ 7.59 (4.2%) and at δ 2.70 (1.1%).

Thermal cycloaddition of 5,7-dimethyl-r-nitro-t-1-trinitromethyl-1,2-dihydronaphthalene (7) in ^2H -chloroform. A solution of the nitro-trinitromethyl adduct (7) 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 186 h) into the nitro cycloadduct (17). Removal of the solvent under reduced pressure after 33 days and crystallization of the residue from dichloromethane–hexane gave:

Nitro cycloadduct (17), m.p. 195°C (decomp.) (X-ray crystal structure determined, see below). IR: ν_{\max} (KBr) 1600, 1560 cm^{-1} . ^1H NMR (CDCl_3) δ 2.28 (s, 7-Me), 2.36 (s, 5-Me), 5.16 (dd, $J_{\text{H}1,\text{H}2}$ 4.1 Hz, $J_{\text{H}1,\text{H}3}$ 2.4 Hz, H1), 5.70 (dd, $J_{\text{H}2,\text{H}1}$ 4.1 Hz, $J_{\text{H}2,\text{H}3}$ 2.0 Hz, H2), 5.91 (ddd, $J_{\text{H}3,\text{H}4}$ 6.1 Hz, $J_{\text{H}3,\text{H}1}$ 2.4 Hz, $J_{\text{H}3,\text{H}12}$ 2.0 Hz, H3), 5.96 (d, $J_{\text{H}4,\text{H}3}$ 6.1 Hz, H4), 6.91 (s, H8), 7.01 (s, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 2.28 gave enhancements at δ 6.91 (3.4%) and at δ 7.01 (3.3%); irradiation at δ 2.36 gave enhancements at δ 5.96 (5.0%) and at δ 7.01 (4.0%); irradiation at δ 5.16 gave enhancements at δ 5.70 (4.1%) and at δ 6.91 (3.7%); irradiation at δ 5.70 gave enhancements at δ 5.16 (2.4%) and at δ 5.91 (2.5%); irradiation at δ 6.91 gave enhancements at δ 2.28 (0.8%) and at δ 5.16 (4.1%); irradiation at δ 7.01 gave enhancements at δ 2.28 (0.4%) and at δ 2.36 (0.3%). ^{13}C NMR (CDCl_3) δ 17.9 (5-Me), 21.15 (7-Me), 45.4 (C1), 75.9 (C3), 77.2 (C4), 78.8 (C2), 127.1 (C8a), 128.9 (C5), 129.8 (C8), 133.6 (C6), 136.5 (C4a), 141.1 (C7), resonance for $\text{C}(\text{NO}_2)_3$ not observed. The above assignments were confirmed by long range reverse detected heteronuclear correlation spectra (HMBC and HMQC).

Photochemistry in dichloromethane at 20°C in the presence of trifluoroacetic acid. Reaction of 1,3-dimethylnaphthalene–tetranitromethane in dichloromethane at 20°C, as

above, for 30 min except for the addition of trifluoroacetic acid (0.8 mol dm^{-3}) gave a product which was shown by ^1H NMR spectra to be a mixture of unreacted 1,3-dimethylnaphthalene (42% conversion), 2,4-dimethyl-1-nitronaphthalene (16) (34%), 2,2',4,4'-tetramethyl-1,1'-binaphthalene (18) (54%), and unidentified material (total 12%). Compounds (16) and (18) were identified by comparison with the ^1H NMR spectra of authentic materials.

Preparation of 2,2',4,4'-tetramethyl-1,1'-binaphthalene (18). Thallium(III) trifluoroacetate (1.76 g, 3.2 mmol) was added to a solution of 1,3-dimethylnaphthalene (1.0 g, 6.4 mmol) in dry acetonitrile (15 ml) (cf. Ref. 20). The mixture was cooled to -60°C and boron trifluoride etherate (3.2 ml, 25 mmol) added dropwise. A white solid began to separate from the blue solution. When the addition of the boron trifluoride etherate was complete, the reaction mixture was allowed to warm to 20°C, the mixture stirred until a thallium(III) test was negative (ca. 1 h) and then poured into water (20 ml). The product was isolated by means of dichloromethane extraction, and after chromatography on silica gel gave the binaphthalene 18 (560 mg, 1.8 mmol) as a colourless powder, m.p. 176–177°C (Lit.²¹ 171.5–173°C). ^1H NMR (CDCl_3) δ 1.99 (s, 2-Me, 2'-Me), 2.77 (br s, 4-Me, 4'-Me), 7.08 (dd, $J_{\text{H}8,\text{H}7} = J_{\text{H}8',\text{H}7'} = 8.3$ Hz, $J_{\text{H}8,\text{H}6} = J_{\text{H}8',\text{H}6'} = 1.0$ Hz, H8/H8'), 7.19 (ddd, $J_{\text{H}7,\text{H}8} = J_{\text{H}7',\text{H}8'} = 8.3$ Hz, $J_{\text{H}7,\text{H}6} = J_{\text{H}7',\text{H}6'} = 6.8$ Hz, $J_{\text{H}7,\text{H}5} = J_{\text{H}7',\text{H}5'} = 1.0$ Hz, H7/H7'), 7.35 (s, H3/H3'), 7.41 (ddd, $J_{\text{H}6,\text{H}5} = J_{\text{H}6',\text{H}5'} = 8.3$ Hz, $J_{\text{H}6,\text{H}7} = J_{\text{H}6',\text{H}7'} = 6.8$ Hz, $J_{\text{H}6,\text{H}8} = J_{\text{H}6',\text{H}8'} = 1.5$ Hz, H6/H6'), 8.03 (d, $J_{\text{H}5,\text{H}6} = J_{\text{H}5',\text{H}6'} = 8.3$ Hz, H5/H5'). Nuclear Overhauser experiments gave the following results: irradiation at δ 1.99 gave enhancements at δ 7.08 (1.9%) and at δ 7.35 (7.2%); irradiation at δ 2.77 gave enhancements at δ 7.35 (8.2%) and at δ 8.03 (10.6%); irradiation at δ 7.08 gave enhancements at δ 1.99 (0.4%) and at δ 7.19 (6.6%); irradiation at δ 7.19 gave enhancements at δ 7.08 (14.3%) and at δ 7.41 (8.5%); irradiation at δ 7.39 gave enhancements at δ 1.99 (1.3%), at δ 2.77 (1.2%), at δ 7.19 (5.9%) and at δ 8.03 (6.9%); irradiation at δ 8.03 gave enhancements at δ 2.77 (1.7%) and at δ 7.41 (6.0%). ^{13}C NMR (CDCl_3) δ 19.4 (4-Me, 4'-Me), 20.0 (2-Me, 2'-Me), 124.1 (C5, C5'), 124.6 (C6, C6'), 125.7 (C7, C7'), 126.3 (C8, C8'), 129.6 (C3, C3'), 131.3 (C4a, C4a'), 133.0 (C8a, C8a'), 133.4 (C4, C4'), 133.5 (C2, C2'), 134.0 (C1, C1'). The above assignments were confirmed by long-range reverse detected heteronuclear correlation spectra (HMBC and HMQC).

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer 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 re-

finements for which the setting angles of 25 accurately centred high-angle reflections were used.

Crystal data

6,8-Dimethyl-r-1-nitro-t-4-trinitromethyl-1,4-dihydro-naphthalene (8), $C_{13}H_{12}N_4O_8$, $M = 352.27$, triclinic, space group $P\bar{1}$, $a = 9.423(2)$, $b = 9.830(2)$, $c = 10.039(2)$ Å, $\alpha = 101.61(3)$, $\beta = 112.01(3)$, $\gamma = 112.23(3)^\circ$; $V = 731.5(3)$ Å³, $D_c = 1.599$ g cm⁻³, $Z = 2$, copper X-radiation, $\mu(\text{Cu } K\alpha) = 1.54180$ Å, $\mu(\text{Cu } K\alpha) = 11.76$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.67 \times 0.58 \times 0.39$ mm. Data were collected at 120(2) K out to a maximum Bragg angle $\theta = 26.75^\circ$. The number of independent reflections measured was 1639, 1526 with $I > 2\sigma(I)$. Absorption corrections were not applied, $g_1 = 0.0582$, $g_2 = 0.01788$; $R_{(\text{obs})}$ -factor = 0.041, $wR_{(\text{all data})} = 0.108$.

Nitro cycloadduct (9), $C_{13}H_{12}N_4O_8$, $M = 352.27$, monoclinic, space group $P2_1/c$, $a = 7.594(2)$, $b = 23.672(5)$, $c = 8.179(2)$ Å, $\beta = 104.63(3)^\circ$; $V = 1422.6(6)$ Å³, $D_c = 1.645$ g cm⁻³, $Z = 4$, copper X-radiation, $\mu(\text{Cu } K\alpha) = 1.54180$ Å, $\mu(\text{Cu } K\alpha) = 12.09$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.80 \times 0.37 \times 0.28$ mm. Data were collected at 120(2) K out to a maximum Bragg angle $\theta = 26.75^\circ$. The number of independent reflections measured was 1677, 1410 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0706$, $g_2 = 2.4846$; $R_{(\text{obs})}$ -factor = 0.060, $wR_{(\text{all data})} = 0.161$.

6,8-Dimethyl-r-1-nitro-c-4-trinitromethyl-1,4-dihydro-naphthalene (10), $C_{13}H_{12}N_4O_8$, $M = 352.27$, monoclinic, space group $P2_1/c$, $a = 7.881(2)$, $b = 17.684(4)$, $c = 10.973(2)$ Å, $\beta = 102.29(3)^\circ$; $V = 1494.2(6)$ Å³, $D_c = 1.566$ g cm⁻³, $Z = 4$, copper X-radiation, $\mu(\text{Cu } K\alpha) = 1.54180$ Å, $\mu(\text{Cu } K\alpha) = 11.51$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.52 \times 0.50 \times 0.22$ mm. Data were collected at 130(2) K out to a maximum Bragg angle $\theta = 26.75^\circ$. The number of independent reflections measured was 1762, 1537 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0989$, $g_2 = 2.2498$; $R_{(\text{obs})}$ -factor = 0.059, $wR_{(\text{all data})} = 0.171$.

Nitro cycloadduct (17), $C_{13}H_{12}N_4O_8$, $M = 352.27$, orthorhombic, space group $Pbca$, $a = 7.361(2)$, $b = 16.023(4)$, $c = 24.491(6)$ Å; $V = 2889(1)$ Å³, $D_c = 1.620$ g cm⁻³, $Z = 8$, molybdenum X-radiation, $\mu(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 1.4$ cm⁻¹. The crystal was colourless and of approximate dimensions $0.49 \times 0.24 \times 0.13$ mm. Data were collected at 120(2) K out to a maximum Bragg angle $\theta = 24.99^\circ$. The number of independent reflections measured was 2533, 1022 with $I > 2\sigma(I)$. Absorption corrections were not applied; $g_1 = 0.0080$, $g_2 = 0.0000$; $R_{(\text{obs})}$ -factor = 0.035, $wR_{(\text{all data})} = 0.045$.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)²² were employed. This program is based on intensities and uses all data. The observed

threshold $I > 2\sigma(I)$ was used only for calculating $R_{(\text{obs})}$, shown here as a comparison for the refinement based on F . Reflection weights $1/[s^2(F_o^2) + (g_1P)^2 + g_2P]$, 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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