

# Photochemical Nitration by Tetranitromethane. XI.<sup>†</sup> Isolation and X-Ray Structural Analysis of an Anomalous *cis*-1-Nitro/2-trinitromethyl Adduct from 1,4,5,8-Tetramethylnaphthalene

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The photolysis of 1,4,5,8-tetramethylnaphthalene and tetranitromethane in dichloromethane or acetonitrile at  $-20^{\circ}\text{C}$  after long reaction times gave predominantly products of side-chain nitration, namely 4,5,8-trimethyl-1-nitromethylnaphthalene and 4,8-dimethyl-1,5-bis(nitromethyl)naphthalene, the latter a secondary photonitration product of the former. In addition, two stable adducts were formed resulting from nitro/trinitromethyl addition to 1,4,5,8-tetramethylnaphthalene. In the beginning of the reactions, labile 1,4-nitro/trinitromethyl adducts were detectable, but were transformed into the side-chain nitration product(s) during the course of the reactions.

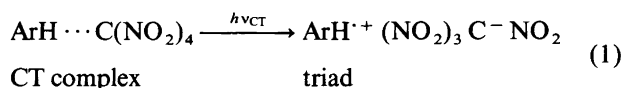
One of the stable adducts could be isolated in pure form and was subjected to X-ray crystallographic analysis. It was determined to be 1,4,5,8-tetramethyl-*r*-1-nitro-*c*-2-trinitromethyl-1,2-dihydronaphthalene, in which the addition mode with the attachment of trinitromethyl at the 2-position and nitro at the 1-position, differs from that of other systems studied. The second stable isomer was shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to be the corresponding *trans* isomer. The anomalous addition mode could be explained as a consequence of significantly different steric congestion in the transition states leading to C1 or C2 attack in the radical cation/trinitromethanide reaction.

The 1,4,5,8-tetramethylnaphthalene radical cation was shown to be fairly stable chemically under conditions resembling those prevailing during photolysis, and the system is therefore of interest in being kinetically slow in contrast with most other systems studied previously. All reactions must therefore occur between free, solvated species.

The intermediacy of nitro/trinitromethyl and/or nitro/trinitromethyl addition products in the photochemical reaction between tetranitromethane and aromatic compounds is now well established.<sup>2–9</sup> There is ample evidence that such adducts are partially, if not predominantly, precursors of nitro substitution products in the cases which have been fully analyzed from this point of view, and there is good reason to generalize this behavior to most other systems since even benzene<sup>7</sup> gives adducts in this reaction.

These findings are rationalized by a mechanism in which the  $\text{ArH}/\text{C}(\text{NO}_2)_4$  system is excited by light matching the wavelength of the charge-transfer (CT) band

arising from the interaction between  $\text{ArH}$  and  $\text{C}(\text{NO}_2)_4$ , thus forming a triad of  $\text{ArH}^{\cdot+}$ ,  $(\text{NO}_2)_3\text{C}^-$  and  $\text{NO}_2$  [eqn. (1)]. The trinitromethanide ion attacks the radical

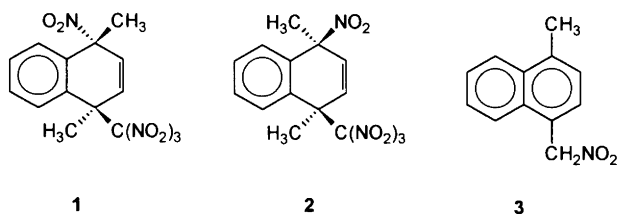


cation leading to a cyclohexadienyl-type radical which traps  $\text{NO}_2$  to give the adduct, in keeping with known behaviour of cyclohexadienyl radicals. A minor pathway involving coupling between the radical cation and  $\text{NO}_2$  can lead directly to a nitro substitution product.

From 1,4-dimethylnaphthalene,<sup>4</sup> the main products were the *cis*- and *trans*-1,4-nitro/trinitromethyl adducts (**1** and **2**, 90% yield) when the photolysis was carried out at low temperature ( $-50^{\circ}\text{C}$ ) in dichloromethane. In addition, the side-chain nitration product (**3**) was formed in

<sup>†</sup> Part X, see Ref. 1.

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7% yield. With increasing temperature the yield of **3** increased at the expense of **1** and **2**. Similar results, although with additional complications due to the formation of detectable amounts of 1,4-nitrito/trinitromethyl adducts, shown to be formed from **2** by a nitro/nitrito rearrangement, were obtained with acetonitrile as the solvent. In dichloromethane, no direct experimental evidence for the formation of nitrito/trinitromethyl adducts was obtained, but their presence in low concentrations was inferred from kinetic experiments. Most **3** formed was shown to originate from the decomposition of **1/2** with elimination of nitroform. It was also established that decomposition of **2** can occur via a homolytic pathway, presumably favored by the steric congestion in these adducts. This mechanism is initiated by  $\text{NO}_2$  cleaving off from adduct **2** and eventually leads to the formation of a product of nuclear nitro substitution, 1,4-dimethyl-2-nitronaphthalene, or reformation of 1,4-dimethylnaphthalene, depending on the reaction conditions. Thus the main feature of the 1,4-dimethylnaphthalene photonitration reaction is high complexity due to formation of adducts and their thermal decay to a simple mixture of nitro-substitution products.

1,4,5,8-Tetramethylnaphthalene has all four of the  $\alpha$ -positions blocked and we therefore anticipated that 1,4-adducts analogous to **1/2** would be even more reactive. Also, new addition modes might be induced by the higher level of steric congestion in transition states and/or intermediates formed after trinitromethanide attack upon the radical cation. Finally, previous work<sup>10,11</sup> indicates that the 1,4,5,8-tetramethylnaphthalene radical cation is a relatively stable species, being observable by EPR spectroscopy in dichloromethane–5% trifluoroacetic acid–trifluoroacetic anhydride ‘even at room temperature’. Thus reactions following the formation of the triad [eqn. (1)] are likely to be between free species.

We show below that these expectations were fulfilled, in that (i) labile 1,4-addition products were seen in the beginning of the reaction period and converted into  $\alpha$ -nitromethyl products during the run, and (ii) a new type of adduct was isolated, namely a 1-nitro-2-trinitromethyl addition product. This anomalous regiochemistry is, in all probability, determined by the steric properties of the system. Also, (iii) the 1,4,5,8-tetramethylnaphthalene radical cation was shown to possess relatively high chemical stability.

## Results

*Chemical stability of the 1,4,5,8-tetramethylnaphthalene radical cation.* A 5–10 mM solution of 1,4,5,8-tetra-

methylnaphthalene ( $\text{Me}_4\text{Naph}$ ) in trifluoroacetic acid (TFA) exhibited a very weak EPR signal originating from  $\text{Me}_4\text{Naph}^{+\cdot}$ , presumably formed by photooxidation of the hydrocarbon by diffuse daylight.<sup>12</sup> Addition of DDQ<sup>13</sup> produced a blue-green solution containing a high concentration of the radical cation, the EPR spectrum of which had hyperfine splittings constants agreeing well with published values [ $a^{\text{CH}_3} = 0.781$  mT and  $a^{\text{H}(\text{ring})} = 0.182$  mT, compared with 0.784(6) and 0.176(6) mT in dichloromethane/antimony pentachloride<sup>11</sup> at  $-70^\circ\text{C}$ ]. The EPR spectrum of  $\text{Me}_4\text{Naph}^{+\cdot}$  should, theoretically, possess 65 lines, all of which could be observed. With time, the radical cation decayed and the solution turned grey-brown.

These features are shown by an experiment illustrated in Fig. 1. A 2.3 mM solution of  $\text{Me}_4\text{Naph}$  in TFA was treated with DDQ and then monitored by UV spectroscopy. Curve 1, recorded immediately after mixing, has prominent maxima at 392 and 720 nm due to the radical cation which slowly decayed upon standing at room temperature (curves 2–9). The insert shows an EPR spectrum of the same solution, recorded 5 min after mixing. A first-order rate constant of  $0.018(1) \text{ min}^{-1}$  was estimated from the *Abs* values at 392 nm (due to the emerging maximum at about 665 nm, the 720 nm data were deemed less well suited for this estimate), corresponding to a half-life of  $\text{Me}_4\text{Naph}^{+\cdot}$  of  $\sim 40$  min under the prevailing conditions.

Experiments were then conducted on solutions of  $\text{Me}_4\text{Naph}$  (40–50 mM) and TNM ( $\sim 0.3$  M) in dichloromethane. The solutions were faintly red in color owing to the presence of the CT complex and were photolyzed in the EPR cavity with filtered light (cut-off at  $\lambda < 435$  nm). At room temperature no EPR signal was detectable, nor did any signal appear at  $-20^\circ\text{C}$ . In order to stabilize the radical cation the same experiments were repeated with 5% TFA added. At room temperature a broad EPR

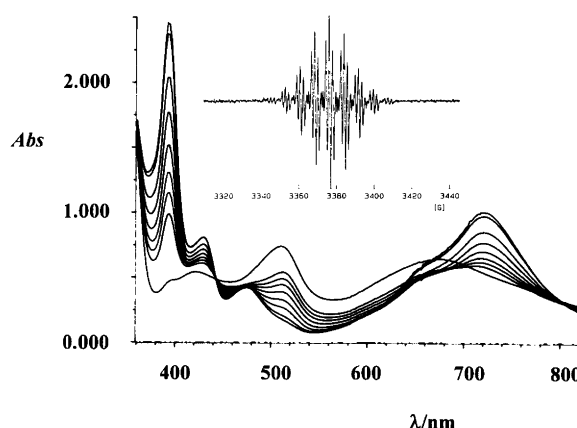


Fig. 1. Decay of  $\text{Me}_4\text{Naph}^{+\cdot}$ , formed by addition of DDQ to a 2.3 mM solution of  $\text{Me}_4\text{Naph}$  in TFA at room temperature. Curve 1 (with highest *Abs* at 720 nm) was taken immediately after mixing and curves 2–9 (in order of decreasing *Abs* at 720 nm) were recorded after 3, 13, 23, 33, 45, 55, 70, and 185 min. The insert shows the EPR spectrum of the same solution, recorded 5 min after mixing.

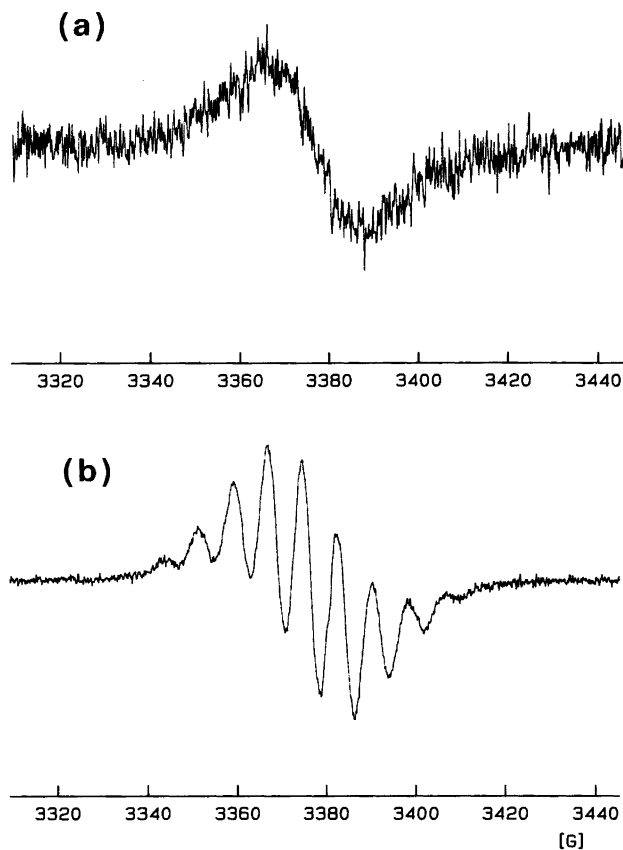


Fig. 2. Formation of radical species, in all probability  $\text{Me}_4\text{Naph}^{\bullet+}$ , in continuously photolyzed (light with cut-off < 435 nm) solutions of  $\text{Me}_4\text{Naph}$  (40–50 mM) and TNM (0.3 M) in dichloromethane at room temperature with (a) 5% TFA added and (b) 10% TFA added.

signal [Fig. 2(a)] was detected under constant irradiation; it disappeared immediately when irradiation was discontinued. With 10% TFA present, the EPR signal was stronger and showed fine-structure [Fig. 2(b)], corresponding to the larger hfs of the  $\text{Me}_4\text{Naph}^{\bullet+}$  EPR spectrum (average value 0.778 mT). It was separately shown that only a very weak spectrum appeared when TNM was left out. At  $-20^\circ\text{C}$ , the same features were observable in the presence of 5% TFA, and fully resolved spectra of  $\text{Me}_4\text{Naph}^{\bullet+}$  could be obtained.

The formation of  $\text{Me}_4\text{Naph}^{\bullet+}$  under photolytic reaction conditions was also monitored by UV spectroscopy (Fig. 3). A solution of 2.0 mM  $\text{Me}_4\text{Naph}$  and 0.14 M TNM in dichloromethane/TFA (90/10) was irradiated with filtered light (cut-off < 420 nm) from the spectrophotometer lamp. The band of the radical cation spectrum at  $\sim 720$  nm grows to a maximum (curves 1–13) and then begins to decay. At lower TFA concentration (5%), the same phenomena were observed, although the 720 nm band of the radical cation had its maximum *Abs* value after only 10 min. With no TFA present, no indication of the presence of  $\text{Me}_4\text{Naph}^{\bullet+}$  was obtained.

Cyclic voltammetry of  $\text{Me}_4\text{Naph}$  (2.3 mM) in dichloromethane/ $\text{Bu}_4\text{NPF}_6$  showed electrochemical

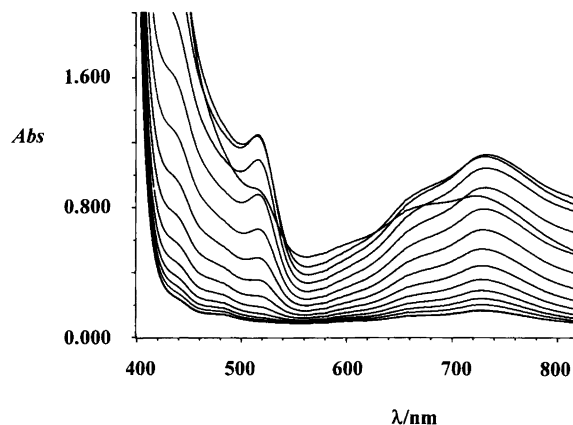
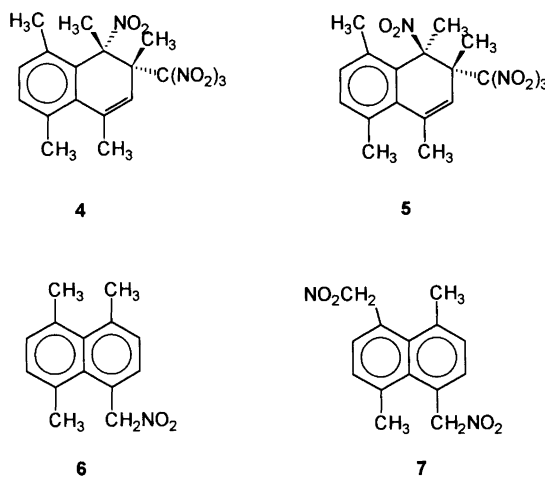


Fig. 3. Formation of  $\text{Me}_4\text{Naph}^{\bullet+}$  in a continuously photolyzed (spectrophotometer light with cut-off < 420 nm) solution of 2.0 mM  $\text{Me}_4\text{Naph}$  and 0.14 M TNM in dichloromethane/TFA (90/10) at room temperature. Curve 1 is the one with lowest *Abs* at 730 nm and curves 2–13 then follow in order of increasing *Abs* value at 730 nm. Curve 14 is the one running across the other curves. The interval between spectra is 3 min.

reversibility of the  $\text{Me}_4\text{Naph}^{\bullet+}/\text{Me}_4\text{Naph}$  couple at least down to a sweep rate of  $10\text{ mV s}^{-1}$  with  $(E_{\text{pa}} - E_{\text{pc}}) \sim 65\text{ mV}$  and  $(E_{\text{pa}} + E_{\text{pc}})/2 = 1.32\text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ ). The addition of one molar equivalent of tetrabutylammonium trinitromethanide induced irreversibility at this sweep rate; an increase to  $1000\text{--}2000\text{ mV s}^{-1}$  restored the cathodic current to about 50% of the anodic one, indicating a half-life of  $\text{Me}_4\text{Naph}^{\bullet+}$  in the range of 0.2–0.5 seconds under these conditions.

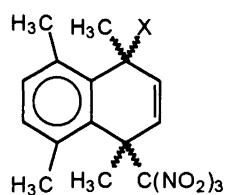
**Photochemistry in dichloromethane.** The photolysis of a solution of 1,4,5,8-tetramethylnaphthalene ( $0.34\text{ mol dm}^{-3}$ ) and TNM ( $0.68\text{ mol dm}^{-3}$ ) in dichloromethane was carried out with filtered light (cut-off at 435 nm) at  $-20^\circ\text{C}$  until the strongly red color of the CT band had been bleached. Work-up at  $0^\circ\text{C}$  gave a mixture of adducts **4** (20%) and **5** (10%),  $\alpha$  side-chain nitration products **6** (30%) and **7** (27%), and unidentified material ( $\sim 13\%$ ). The major adduct **4** was isolated by low-



temperature recrystallization of the crude product at  $-20^{\circ}\text{C}$  and shown by X-ray crystallography (see below) to be 1,4,5,8-tetramethyl-*r*-1-nitro-*c*-2-trinitromethyl-1,2-dihydronaphthalene. The minor adduct **5** could be separated in nearly pure form by HPLC and was shown by NMR spectral analysis to be the corresponding *trans* isomer, 1,4,5,8-tetramethyl-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene (**5**). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of adduct **4** were assigned from the long-range reverse detected  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear correlation spectra (HMBC). In particular, the  $^{13}\text{C}$  resonances of the Me-C(1)-NO<sub>2</sub> ( $\delta$  92.39), H-C(2)-C(NO<sub>2</sub>)<sub>3</sub> ( $\delta$  48.03), H-C(3)= ( $\delta$  114.14) and Me-C(4)= ( $\delta$  145.02) were assigned. For the other epimer **5**, HMBC spectra allowed the assignment of the following  $^{13}\text{C}$  resonances: C(1),  $\delta$  94.70; C(2),  $\delta$  47.02; C(3),  $\delta$  116.51; (C4)  $\delta$  143.78 which parallel closely those of adduct **4** above.

The two side-chain nitration products **6** and **7** were likewise isolated in pure form (silica gel TLC). The structure of the 1,5-bis(nitromethyl) derivative **7** was determined from its NMR spectra and nuclear Overhauser enhancement (nOe) experiments. In particular, the  $^1\text{H}$  resonances of H2 and H3, and H6 and H7, appeared as identical AB systems ( $\delta$  7.74 and 7.61,  $J_{\text{H,H}}$  9.8 Hz), and irradiation at  $\delta$  2.98 (4-Me, 8-Me gave enhancements of the signals due to H3/H7 ( $\delta$  7.61) and the 1- and 5-CH<sub>2</sub>NO<sub>2</sub> groups ( $\delta$  6.44); irradiation at  $\sigma$  6.44 gave enhancements of the signal due to 4-Me/8-Me ( $\delta$  2.98) and H2/H6 ( $\delta$  7.74).

When the reaction was monitored with time, two new adducts were detected during the first hour of the run and then disappeared during the next hour (Table 1, Fig. 4). They were assigned the structures of the two 1,4-nitro/trinitromethyl adducts **8** and **9** on the basis of  $^1\text{H}$  NMR spectral analysis (see below). Actually, **8** and **9** were not identified as such but as the corresponding hydroxy/trinitromethyl derivatives, **8a** and **9a**, as also found in the 1,4-dimethylnaphthalene system. These must be formed



**8, 9** epimers X = ONO

**8a, 9a** epimers X = OH

by hydrolysis of the nitrites during work-up. Nitrites are sensitive to acidic hydrolysis,<sup>14</sup> and during the normal course of the photonitration reactions acidity builds up slowly owing to formation of nitroform.<sup>3,4</sup> Apart from products **4**-**9**, the crude product mixtures at the end of the runs contained other compounds, believed to be products of further photonitration of the 1-nitromethyl derivative **6**.

**Table 1.** Overview of yield of products from the photolysis of 1,4,5,8-tetramethylnaphthalene ( $0.34 \text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.68 \text{ mol dm}^{-3}$ ) in dichloromethane at  $-20^{\circ}\text{C}$ .

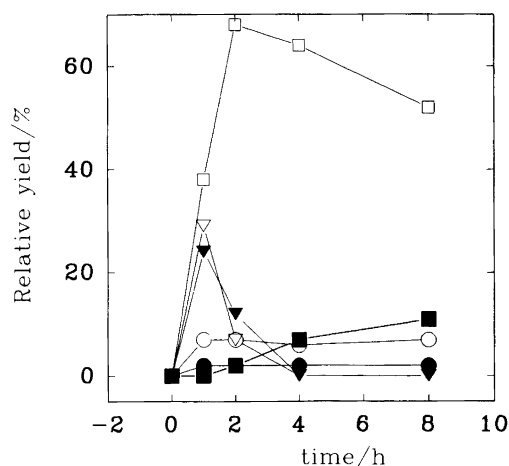
Reaction period/h	Relative yield (%)						Other <sup>a</sup>
	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	
0.5	21	8	58	—	8	5	—
1	24	9	58	—	4	3	—
2	24	10	27	11	—	—	24
8	16	8	24	11	—	—	41

<sup>a</sup>These are believed to be products of further photonitration of 4,5,8-trimethyl-1-nitromethylnaphthalene **6**.

The reaction was also carried out at  $-50^{\circ}\text{C}$  resulting in a similar product distribution, comprising **4** (24%), **5** (9%), **6** (51%), **7** (<5%) and others (16%). At this temperature, part of the substrate remained undissolved.

**Photochemistry in acetonitrile.** The photolysis of a solution of 1,4,5,8-tetramethylnaphthalene ( $0.34 \text{ mol dm}^{-3}$ ) and TNM ( $0.68 \text{ mol dm}^{-3}$ ) in acetonitrile was carried out with filtered light (cut-off at 435 nm) at  $-20^{\circ}\text{C}$  and monitored with time (Table 2, Fig. 5). At the end of the reaction the same end-products **4**-**7** as in dichloromethane were present, with more of **6** and **7** at the expense of adducts **4** and **5**. The labile adducts **8** and **9** were formed in totally about 35% relative yield after 1 h and disappeared during the next 2 h. 'Other' products of the same nature as in dichloromethane were also detected and again they were assumed to originate from further photonitration of **6**.

A run carried out at  $+20^{\circ}\text{C}$  gave the two nitromethyl derivatives **6** and **7** in 17 and 53% yield, respectively, none of the adducts **4** and **5** being detected. A check



**Fig. 4.** Product development from the photolysis of 1,4,5,8-tetramethylnaphthalene and tetranitromethane (Table 1) in dichloromethane at  $-20^{\circ}\text{C}$ :  $\circ$ , **4**;  $\bullet$ , **5**;  $\square$ , **6**;  $\blacksquare$ , **7**;  $\triangle$ , **8**;  $\blacktriangle$ , **9**. The lines are drawn to join the points of each species in order to improve readability.

**Table 2.** Overview of yield of products from the photolysis of 1,4,5,8-tetramethylnaphthalene ( $0.34 \text{ mol dm}^{-3}$ ) and tetranitromethane ( $0.68 \text{ mol dm}^{-3}$ ) in acetonitrile at  $-20^\circ\text{C}$ .

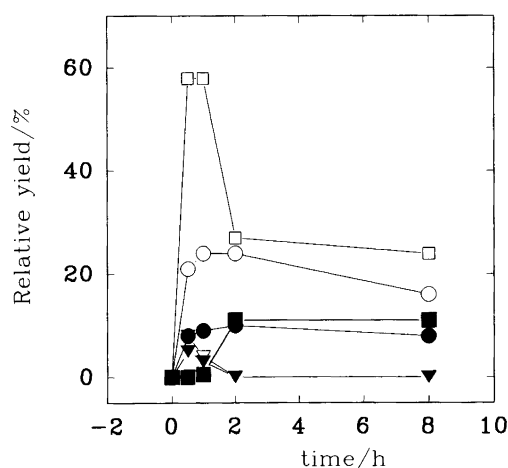
Reaction period/h	Relative yield (%)						
	4	5	6	7	8	9	Other <sup>a</sup>
1	7	2	38	—	29	24	—
2	7	2	68	2	7	12	2
4	6	2	64	7	—	—	21
8	7	2	52	11	—	—	28

<sup>a</sup>These are believed to be products of further photonitration of 4,5,8-trimethyl-1-nitromethylnaphthalene 6.

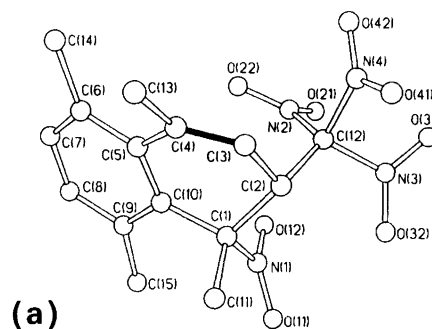
experiment showed that a solution of adduct 4 in acetonitrile- $d_3$  was unchanged after 48 h at  $+23^\circ\text{C}$ .

In order to trace the origin of the bis(nitromethyl) compound 7, 6 was subjected to photonitration by tetranitromethane in acetonitrile at  $+20^\circ\text{C}$ . After two hours the crude product contained 6 and 7 in a 1 : 1 ratio, together with considerable amounts of other, unidentified material, similar to that obtained in the photonitration of 1,4,5,8-tetramethylnaphthalene itself.

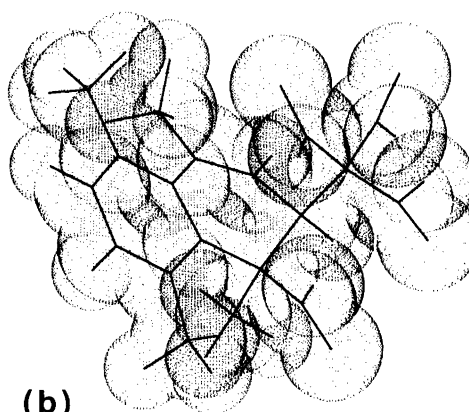
**X-Ray structure of adduct 4.** The structure of the major adduct 4 was determined by X-ray crystal analysis. A perspective drawing of 1,4,5,8-tetramethyl-*r*-1-nitro-*c*-2-trinitromethyl-1,2-dihydronaphthalene, 4,  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_8$ , m.p.  $128\text{--}135^\circ\text{C}$  (decomp.), is presented in Fig. 6 with the corresponding atomic coordinates in Table 3. In the solid state the aromatic ring is close to planar with the largest deviation being indicated by the torsional angle  $\text{C}(9)\text{--C}(10)\text{--C}(5)\text{--C}(6)$ ,  $-9.9^\circ$ . In contrast, the alicyclic ring, effectively a substituted cyclohexa-1,3-diene system, is considerably puckered. The relief of one of the *peri*



**Fig. 5.** Product development from the photolysis of 1,4,5,8-tetramethylnaphthalene and tetranitromethane (Table 1) in acetonitrile at  $-20^\circ\text{C}$ :  $\circ$ , 4;  $\bullet$ , 5;  $\square$ , 6;  $\blacksquare$ , 7;  $\triangle$ , 8;  $\blacktriangle$ , 9. The lines are drawn to join the points of each species in order to improve readability.



(a)



(b)

**Fig. 6.** (a) Perspective view of the experimental structure of 4 and (b) energy minimized ball-and-stick model of 4, as calculated by the MM<sup>+</sup> model (see also Table 4).

interactions is evident in the twisting of the 'diene' system, torsional angles being:  $\text{C}(3)\text{--C}(4)\text{--C}(5)\text{--C}(10)$   $25.8^\circ$ ,  $\text{C}(6)\text{--C}(5)\text{--C}(4)\text{--C}(13)$   $31.9^\circ$ . The second *peri* interaction present in 1,4,5,8-tetramethylnaphthalene is also relieved in adduct 4 by the change of C(1) into an  $\text{sp}^3$  carbon; the conformation adopted is revealed by the torsional angles:  $\text{C}(9)\text{--C}(10)\text{--C}(1)\text{--C}(11)$   $-85.3^\circ$ ,  $\text{C}(9)\text{--C}(10)\text{--C}(1)\text{--N}(1)$   $33.7^\circ$ . Bending of the  $\text{C}(5)\text{--C}(6)\text{--C}(14)$  and  $\text{C}(10)\text{--C}(9)\text{--C}(15)$  angles from  $120^\circ$  to  $124.9^\circ$  and  $125.7^\circ$ , respectively, indicate the strong non-bonded repulsions in the system, as does the elongation of the  $\text{C}(1)\text{--C}(2)$  bond, from ideally  $1.54$  to  $1.574 \text{ \AA}$ . The orientation of the trinitromethyl group relative to the ring systems is indicated by the torsional angle:  $\text{C}(11)\text{--C}(1)\text{--C}(2)\text{--C}(12)$   $155.8^\circ$ , the  $\text{C}(2)\text{--C}(12)$  bond being close to perpendicular to the mean plane of the carbon atoms of the bicyclic system.

The NMR spectroscopic data for adduct 4 are consistent with the established structure. In particular, the observed  $\text{H}(2)\text{--H}(3)$  coupling constant ( $J$   $7.9 \text{ Hz}$ ) corresponds closely to that derived from the Karplus equation and the torsional angle of  $\text{H}(2)\text{--C}(2)\text{--C}(3)\text{--H}(3)$ ,  $35.3^\circ$  ( $J$   $7.84 \text{ Hz}$ ).

Table 3. Fractional coordinates for atoms in 1,4,5,8-tetra-methyl-*r-r*-1-nitro-*c*-2-trinitromethyl-1,2-dihydronaphthalene (**4**).

Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U
O(11)	3592(3)	-66(2)	8702(1)	38(1)
O(12)	593(3)	766(2)	7995(1)	33(1)
O(21)	-1346(3)	1419(2)	6262(1)	49(1)
O(22)	-1393(3)	3585(2)	6640(1)	44(1)
O(31)	2408(3)	237(2)	5238(1)	49(1)
O(32)	3946(3)	-228(2)	6604(1)	37(1)
O(41)	4057(4)	2885(2)	4957(1)	50(1)
O(42)	587(4)	3542(2)	4780(1)	57(2)
N(1)	2283(3)	913(2)	8280(1)	26(1)
N(2)	-501(3)	2399(3)	6393(1)	35(1)
N(3)	2837(3)	913(2)	8280(1)	26(1)
N(4)	2192(4)	2953(2)	5220(2)	38(2)
C(1)	2762(4)	2419(2)	8061(2)	21(1)
C(2)	3217(4)	2648(2)	6949(2)	22(1)
C(3)	3309(4)	4211(3)	6725(2)	26(1)
C(4)	2112(4)	5292(3)	7186(2)	23(1)
C(5)	507(4)	5006(2)	7947(2)	20(1)
C(6)	-1294(4)	6102(2)	8200(2)	23(1)
C(7)	-2578(4)	5783(3)	8990(2)	26(1)
C(8)	-2082(4)	4469(3)	9531(2)	25(1)
C(9)	-369(4)	3336(2)	9272(2)	21(1)
C(10)	870(3)	3591(2)	8437(2)	19(1)
C(11)	4818(4)	2395(3)	8547(2)	30(1)
C(12)	1920(4)	2160(3)	6216(2)	26(1)
C(13)	2615(4)	6768(3)	7008(2)	35(2)
C(14)	-2015(4)	7575(3)	7642(2)	32(1)
C(15)	13(4)	1944(3)	9933(2)	31(2)

*Possible homolytic activity of 4.* We showed earlier<sup>1,4,5</sup> that nitro/trinitromethyl adducts display homolytic activity in acetonitrile and dichloromethane, especially if the trinitromethyl group is attached to a tertiary benzylic carbon, as in **1**. This type of reactivity manifests itself in the appearance of the trinitromethyl radical which can be trapped by a suitable spin trap, like  $\alpha$ -phenyl-*N*-tert-butyl nitron (PBN). However, with **4** and PBN as reactants, no spin adduct appeared in acetonitrile or dichloromethane solution over a period of 10 h.

## Discussion

*Structure of adducts 4 and 5.* The structural features of **4** pointed out above indicate that **4** is a strained molecule.

Table 4. Experimental and calculated (MM<sup>+</sup>) structural properties of **4** (numbering, see Fig. 3).

Bond or torsion angle	Bond	Experimental/ Å or deg	Calcd./ Å or deg
	C(1)-C(2)	1.574	1.55
C(5)-C(6)-C(14)		124.9	126
C(10)-C(9)-C(15)		125.7	126
C(9)-C(10)-C(5)-C(6)		-9.9	-11
C(3)-C(4)-C(5)-C(10)		25.8	17
C(6)-C(5)-C(4)-C(13)		31.9	18
C(9)-C(10)-C(1)-C(11)		-85.3	-83
C(9)-C(10)-C(1)-N(1)		33.7	36
C(11)-C(1)-C(2)-C(12)		155.8	169
H(2)-C(2)-C(3)-H(3)		35.3	33

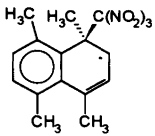
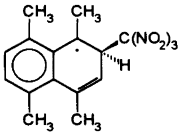
A molecular mechanics calculation (MM<sup>+</sup>) reproduced these quite well (Table 4), except that the puckering of the 1,3-diene system of the alicyclic ring did not come out as pronounced as in the crystal structure. It should be noted that the nitro group was built as a nitrogen bonded to two carbonyl oxygens, resulting in calculated N-O bond lengths of 1.18 Å compared with the experimental ones of 1.22 Å. Calculations employing the latter bond length did not, however, at all affect the geometry reflected in Table 4. The second conformer of **4**, with ax-NO<sub>2</sub>-eq-C(NO<sub>2</sub>)<sub>3</sub> geometry, was calculated (see Table 5) to be higher in energy by 5.3 kcal mol<sup>-1</sup>.

The *trans* adduct **4** in all probability is the ax-NO<sub>2</sub>-ax-C(NO<sub>2</sub>)<sub>3</sub> conformer. The calculated H(2)-C(2)-C(3)-H(3) dihedral angle in this case was 29° whereas that of the eq/eq conformer came out at 97°. Experimentally, the H(2)-H(3) coupling constant was 6.7 Hz, translated into a dihedral angle of 42° by the Karplus equation, somewhat larger than the calculated value. An angle of 97° would correspond to a coupling constant of ~0 Hz. Both *trans* conformers were of approximately the same energy (Table 5) and ~1.5 kcal mol<sup>-1</sup> above that of the low-energy conformer of **4**.

*Structure of the labile adducts 8 and 9.* The presence of adducts of 1,4-addition to a 1,4-dimethyl substituted naphthalene is readily recognized by the appearance of the characteristic coupling of ~10 Hz between two vinylic hydrogens.<sup>4</sup> Thus the 1,4-nitro/trinitromethyl adducts of 1,4-dimethylnaphthalene had resonances at: **1** (CDCl<sub>3</sub>),  $\delta$  6.26, 6.68, *J* 10.5 Hz, H<sub>2</sub>/H<sub>3</sub> and **2**,  $\delta$  6.49, 6.66, *J* 10.5 Hz, H<sub>2</sub>/H<sub>3</sub> and the corresponding 1,4-hydroxy/trinitromethyl adducts from 1,4-dimethylnaphthalene at  $\delta$  5.95, 6.36 (*J* 10.1 Hz) and 5.97, 6.29 (*J* 10.2 Hz). The NMR spectra of the latter also had singlets at  $\delta$  1.65 and 1.57, respectively, assigned to the C(OH)CH<sub>3</sub> group. The corresponding NMR features of **8** and **9** were in best agreement with those of the hydroxy/trinitromethyl adducts above [adduct **8**: (CDCl<sub>3</sub>)  $\delta$  5.79, 6.10, AB system, *J* 10.0 Hz, H<sub>2</sub>/H<sub>3</sub>. Adduct **9**: (CDCl<sub>3</sub>)  $\delta$  5.80, 6.14, AB system, *J* 9.8 Hz, H<sub>2</sub>/H<sub>3</sub>. In addition, singlets at  $\delta$  1.66 (**8**) and  $\delta$  1.59 (**9**) could be safely assigned to the C(OH)CH<sub>3</sub> hydrogens. Owing to the kinetic instability of **8** and **9** and the presence of the other products in the crude mixture, further verification of the assigned structures was not possible.

*Overview of the photochemical reaction.* As described above, the photoaddition of tetranitromethane to 1,4-dimethylnaphthalene has been shown<sup>4,8</sup> to give initially a mixture of nitro/trinitromethyl adducts **1** and **2**. A complex reaction sequence of thermal steps then leads from these labile adducts to the final mixture of substitution products. Complications arise from the formation of 1,4-nitrito/trinitromethyl adducts via a nitro/nitrito rearrangement of **2**, in itself formed by rearrangement of

**Table 5.** Relative energies of intermediates from the reaction between 1,4,5,8-tetramethylnaphthalene radical cation and trinitromethanide ion and their possible coupling products with NO<sub>2</sub> (attack via N) from molecular mechanics calculations. Energies are relative within each class of species.

Species	$E/\text{kcal mol}^{-1}$	$E_{\text{rel}}/\text{kcal mol}^{-1}$
	34.1	+5.4
	28.7	0
1,4,5,8-Tetramethyl- <i>r</i> -1-nitro- <i>c</i> -2-trinitromethyl-1,2-dihydronaphthalene ( <b>4</b> )		
eq-NO <sub>2</sub> -ax-C(NO <sub>2</sub> ) <sub>3</sub>	31.7	0
ax-NO <sub>2</sub> -eq-C(NO <sub>2</sub> ) <sub>3</sub>	37.0	+5.3
1,4,5,8-Tetramethyl- <i>r</i> -1-nitro- <i>t</i> -2-trinitromethyl-1,2-dihydronaphthalene ( <b>5</b> )		
eq-NO <sub>2</sub> -eq-C(NO <sub>2</sub> ) <sub>3</sub>	33.4	+1.7
ax-NO <sub>2</sub> -ax-C(NO <sub>2</sub> ) <sub>3</sub>	33.8	+2.1
1,4,5,8-Tetramethyl- <i>r</i> -1-trinitromethyl- <i>c</i> -2-nitro-1,2-dihydronaphthalene		
ax-C(NO <sub>2</sub> ) <sub>3</sub> -eq-NO <sub>2</sub>	41.7	+10.0
eq-C(NO <sub>2</sub> ) <sub>3</sub> -ax-NO <sub>2</sub>	45.2	+13.5
1,4,5,8-Tetramethyl- <i>r</i> -1-trinitromethyl- <i>t</i> -2-nitro-1,2-dihydronaphthalene		
ax-C(NO <sub>2</sub> ) <sub>3</sub> -ax-NO <sub>2</sub>	38.8	+7.1
eq-C(NO <sub>2</sub> ) <sub>3</sub> -eq-NO <sub>2</sub>	47.1	+15.4
1,4,5,8-Tetramethyl- <i>r</i> -1-trinitromethyl- <i>c</i> -4-nitro-1,4-dihydronaphthalene	37.0	+5.3
1,4,5,8-Tetramethyl- <i>r</i> -1-trinitromethyl- <i>t</i> -4-nitro-1,4-dihydronaphthalene	36.0	+4.3

1. Owing to technical difficulties, it was not possible to decide whether the nitro/trinitromethyl adducts were also formed directly in the photolysis step [via the triad of eqn. (1)].

Superficially, the events occurring in the system 1,4,5,8-tetramethylnaphthalene/tetranitromethane/ $h\nu$  look quite different. Adducts do appear, but are fairly stable and are of different regiochemistry, with the trinitromethyl group placed in the 2-position. No 1,4-nitro/trinitromethyl adducts are detectable, but instead labile 1,4-nitro/trinitromethyl adducts (**8** and **9**).

However, as detailed below, the 1,4,5,8-tetramethylnaphthalene reaction can best be viewed as being qualitatively analogous to that of 1,4-dimethylnaphthalene, yet with quantitatively significant differ-

ences. Thus 1,4-addition can still be a major pathway, although any initial 1,4-nitro/trinitromethyl adducts are now less stable than **1** and **2**. Essentially as formed, these are converted into either **6** or the unstable adducts **8** and **9**. Eventually, all primary products are converted into substitution products **6** and **7**, where **7** is a secondary product formed from **6** in a photochemical reaction. The new addition mode, formation of 2-trinitromethyl-1-nitro adducts **4** and **5** with different regiochemistry from all previous ones, is presumably dictated by the steric properties of Me<sub>4</sub>Naph.

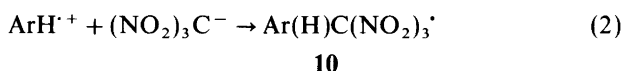
Yet it must be remembered that initial 1,4-nitro/trinitromethyl addition, followed by elimination of nitroform and rearrangement, is not the only pathway available to **6**. It has been shown that even in kinetically

fast systems, such as naphthalene, nitrogen dioxide leaks from the triad and builds up to significant concentrations during photolysis.<sup>2</sup> Thus plain nitration of Me<sub>4</sub>Naph by NO<sub>2</sub>, known<sup>15</sup> to give solely **6** under conditions resembling those prevailing during photolysis in dichloromethane at room temperature, may account at least for partial formation of **6** in runs at 20°C but almost certainly not at -50°C.

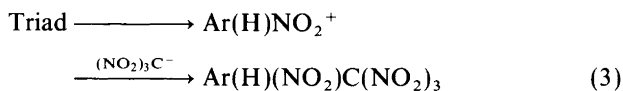
Another pathway open to **6** would be deprotonation of Me<sub>4</sub>Naph<sup>+</sup> at one methyl group,<sup>16</sup> followed by coupling of the benzylic radical with NO<sub>2</sub>. Again this is a chemical reaction which should be slowed down considerably at -50°C. However, the small change in product distribution, in fact the opposite of that expected for this process, on going from -20 to -50°C does not support this mechanism.

*The detailed mechanism.* The results summarized in Figs. 1–3 demonstrate that Me<sub>4</sub>Naph<sup>+</sup> is a fairly stable radical cation, on the verge of being EPR-active under the photolytic reaction conditions employed. It has a half-life of some 0.2 s in dichloromethane in the presence of 2.3 mM tetrabutylammonium trinitromethanide, indicating a second-order rate constant of ~1000–2000 M<sup>-1</sup> s<sup>-1</sup> for reaction between the radical cation and trinitromethanide ion. Thus it is safely concluded that reactions between the initially formed species [see eqn. (1)] take place between free, solvated species.

As before,<sup>3–7</sup> we picture the initial step as being attack of trinitromethanide upon the radical cation [eqn. (2)], assumed to occur along a trajectory perpendicular to the plane defined by the aromatic system, resulting in the formation of the neutral radical **10**. The latter is trapped by NO<sub>2</sub> to give adduct(s).



An alternative pathway from the triad of eqn. (1) would be initial coupling of the radical cation and NO<sub>2</sub>, followed by reaction between the Wheland intermediate and trinitromethanide ion [eqn. (3)].<sup>9</sup> We deem this

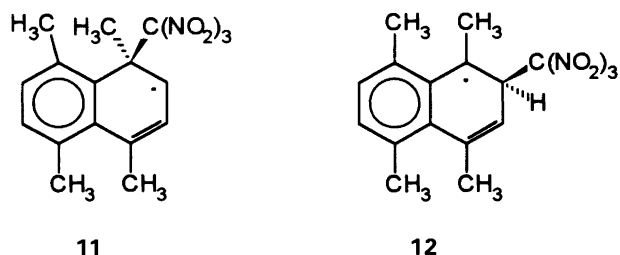


mechanism to be less likely, since it introduces unprecedented behavior of Ar(H)NO<sub>2</sub><sup>+</sup>, generally very prone to lose a proton to any base present, including those of much lower basicity than trinitromethanide ion, with formation of a nitro substitution product. A detailed analysis of the photoaddition of TNM to naphthalene<sup>3</sup> shows that this proposal would require a Naph<sup>+</sup>/NO<sub>2</sub> mode of attack of  $\alpha/\beta \sim 1.3$  whereas it is known that the actual ratio is  $\sim 50$ .<sup>17,18</sup>

Assuming that eqn. (2) is a correct representation of the initial step, we now must explain why trinitromethanide attack occurs both at the 1- and 2-positions, keeping in

mind that the 1-position should be strongly favored by the spin density distribution of the radical cation, as is indeed found for other naphthalene derivatives. Referring to our assumption above that all of **6** is formed as a secondary product from initially formed 1-trinitromethyl-4-nitro or nitrito adducts, it is readily seen that the ratio of C1/C2 attack is  $\sim 10$  in acetonitrile and  $\sim 2$  in dichloromethane, showing that C1 attack is also the major pathway in Me<sub>4</sub>Naph. The difference between the two solvents is explicable as an effect of solvation upon the reacting ions; both would be expected to be more strongly solvated in acetonitrile and hence higher selectivity is to be expected in this solvent. However, attack upon C2 is a significant pathway, and we suggest that the steric properties of Me<sub>4</sub>Naph<sup>+</sup> may account for this anomaly. The structure of Me<sub>4</sub>Naph has been determined by X-ray crystallography,<sup>19</sup> and the molecule was shown to be non-planar in the isolated state by MMPI calculations, owing to the strong *peri* methyl/methyl interactions.

The first step [eqn. (2)] will lead to arenyl intermediate **11** or **12**, of which **12** turned out to be 5.4 kcal mol<sup>-1</sup> more stable than **11** by MM<sup>+</sup> calculations



(Table 5). If this difference is reflected in the transition state leading to **11** or **12**, it is understandable that attack at C2 becomes significant for Me<sub>4</sub>Naph. From radical **12**, reaction with NO<sub>2</sub> will give **4**, which is most stable as the eq-NO<sub>2</sub>-ax-C(NO<sub>2</sub>)<sub>3</sub> conformer (Table 5), and **5**, the eq/eq and ax/ax conformers of which were estimated to be of approximately equal energy.

*Thermal stability of 4.* The usual tests of stability for adducts were applied and indicated that **4** is kinetically stable under conditions where other adducts were found to decompose more or less rapidly. Thus it was completely stable at room temperature in acetonitrile for 48 h, and showed no homolytic activity in dichloromethane or acetonitrile under similar conditions.

## Experimental

*Materials.* 1,4,5,8-Tetramethylnaphthalene was available from previous work.<sup>15</sup> Other chemicals, etc. were of the same origin as in Ref. 3(a).

**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.<sup>20</sup>



*Molecular mechanics calculations* were carried out by the MM<sup>+</sup> method, available in the HyperChem program (1992, Autodesk Inc.).

*General procedure for the photonitration of 1,4,5,8-tetramethylnaphthalene with tetranitromethane.* A solution of 1,4,5,8-tetramethylnaphthalene (0.34 mol dm<sup>-3</sup>) and tetranitromethane (0.68 mol dm<sup>-3</sup>) in dichloromethane at -20 or -50°C (at the latter temperature, the substrate remained partially undissolved during most of the run) or acetonitrile at -20 or +20°C was irradiated with filtered light (cut-off <435 nm).<sup>1</sup> Aliquots were withdrawn at appropriate time intervals, the volatile material was removed under reduced pressure at ≤0°C, and the product composition determined by NMR spectral analysis (Tables 2 and 3).

*Reaction in dichloromethane at -20°C and the identification of products.* Reaction of 1,4,5,8-tetramethylnaphthalene-tetranitromethane at -20°C, as above, gave, after bleaching of the CT band, a product which was shown by NMR spectroscopy to be a mixture of adducts **4** (20%) and **5** (10%), 4,5,8-trimethyl-1-nitromethylnaphthalene **6** (30%), 4,8-dimethyl-1,5-bis(nitromethyl)naphthalene **7** (27%) and unidentified material (~13%). The major adduct **4** was isolated by crystallization of the crude product from dichloromethane/pentane at -20°C to give *1,4,5,8-tetramethyl-r-1-nitro-c-2-trinitromethyl-1,2-dihydronaphthalene, 4* (20%), m.p. 128–135°C (decomp.). Anal. C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>8</sub>: C, H, N (X-ray crystal structure determined, see below). IR (KBr) 2919, arom. C–H stretch; 1599, C(NO<sub>2</sub>)<sub>3</sub>; 1552 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.11 (d, *J*<sub>H6,H7</sub> 7.9 Hz, H6), 7.00 (d, *J*<sub>H7,H6</sub> 7.9 Hz, H7), 5.76 (dq, *J*<sub>H3,H2</sub> 7.9 Hz, *J*<sub>H3,Me</sub> 1.5 Hz, H3), 4.38 (d, *J*<sub>H2,H3</sub> 7.9 Hz, H2), 2.45 (s, 5-Me), 2.22 (d, *J*<sub>Me,H3</sub> 1.5 Hz, 4-Me), 2.17 (s, 3 H, 1-Me), 2.05 (s, 3 H, 8-Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 145.0 (C4), 133.7 (C6), 133.6 (C10), 133.2 (C6), 132.9 (C7), 132.2 (C8), 132.1 (C9), 114.4 (C3), 92.4, (C1), 48.0 (C2), 25.6 (1-Me), 23.9 (4-Me), 23.2 (5-Me), 19.4 (8-Me). The above assignments were confirmed by long-range reverse detected <sup>1</sup>H–<sup>13</sup>C heteronuclear correlation spectra (HMBC).

The two nitromethylnaphthalene derivatives were isolated by chromatography on a silica gel Chromatotron plate (Harrison & Harrison) and gave:

*4,8-Dimethyl-1,5-bis(nitromethyl)naphthalene, 7*, m.p. 173–175°C (sublimed). Anal. C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, H, N. IR (KBr): 2950, arom. C–H stretch; 1597, arom. C=C, 1539 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 7.74 (d, *J*<sub>H2,H3</sub>, *J*<sub>H6,H7</sub> 9.8 Hz, 2 H, H2, H6), 7.61 (d, *J*<sub>H3,H2</sub>, *J*<sub>H7,H6</sub> 9.8 Hz, 2 H, H3, H7), 6.44 (s, 4 H, 1-CH<sub>2</sub>NO<sub>2</sub>, 5-CH<sub>2</sub>NO<sub>2</sub>), 2.98 (s, 6 H, 4-Me, 8-Me). NOE experiments gave the following results: irradiation at δ 6.44 gave enhancements at δ 2.98 (4%) and 7.74 (4%); irradiation at δ 2.98 gave enhancements at δ 6.44 (7%) and 7.61 (6%). <sup>13</sup>C NMR

(acetone-*d*<sub>6</sub>): δ 137.3 (C4), 134.6 (C9/C10), 134.2 (C2/C6), 130.5 (C3/C7), 126.6 (C1), 80.7 (4- and 8-CH<sub>2</sub>NO<sub>2</sub>), 24.5 (1-Me, 5-Me).

*4,5,8-Trimethyl-1-nitromethylnaphthalene, 6*, m.p. 101–103°C (lit.<sup>15</sup> 101–103°C). IR (KBr): 2924, arom. C–H stretch; 1616, arom. C=C; 1540 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 6.95–7.05 (m, 3 H, H3, H6, H7), 6.89 (d, *J*<sub>H2,H3</sub> 7.4 Hz, H2), 5.47 (s, 2 H, CH<sub>2</sub>NO<sub>2</sub>), 2.60 (s, 6 H, 4-Me, 5-Me), 2.51 (s, 3 H, 8-Me). NOE experiments gave the following results: irradiation at δ 5.47 gave enhancements at δ 6.89 (6%) and 2.51 (2%). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 139.7, 135.6, 134.9, 134.0, 133.2, 131.5, 130.8, 129.8, 128.6, 124.6, 80.9, CH<sub>2</sub>NO<sub>2</sub>, 26.8, 26.5, 25.0 methyl carbons.

HPLC separation of the crude mixture on a Varian 5000 liquid chromatograph equipped with an Alltech cyanopropyl column and a Varian UV-50 detector eluting with hexane/dichloromethane mixtures gave the nearly pure (~90% by <sup>1</sup>H NMR spectral analysis) minor adduct, assigned the structure 1,4,5,8-tetramethyl-*r*-1-nitro-*t*-2-trinitromethyl-1,2-dihydronaphthalene, **5** (10%). IR (Nujol) 1607, C(NO<sub>2</sub>)<sub>3</sub>; 1556 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.17 (d, *J*<sub>H6,H7</sub> 9.8 Hz, H6), 7.15 (d, *J*<sub>H7,H6</sub> 9.8 Hz, H7), 5.96 (dq, *J*<sub>H3,H2</sub> 6.7 Hz, *J*<sub>H3,Me</sub> 1.5 Hz, H3), 5.34 (d, *J*<sub>H2,H3</sub> 6.7 Hz, H2), 2.47 (s, 8-Me), 2.34 (s, 5-Me), 2.19 (s, 1-Me), 2.09 (d, *J*<sub>Me,H3</sub> 1.5 Hz, 4-Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.8 (C4), 136.0, 134.2, 134.1, 143.0 (C5, C6, C7, C10), 133.4 (C8), 133.1 (C9), 116.5 (C3), 94.7 (C1), 47.0 (C2), 24.3, 23.6, 22.8, 22.6 (methyl carbons). The above assignments were confirmed by long-range reverse detected <sup>1</sup>H–<sup>13</sup>C heteronuclear spectra (HMBC).

*Reactions in acetonitrile at +20°C.* Photolysis of 1,4,5,8-tetramethylnaphthalene-tetranitromethane in acetonitrile at +20°C, as above, gave, after bleaching of the CT band, a product which was shown by <sup>1</sup>H NMR spectral analysis to be a mixture of **6** (17%) and **7** (53%), together with unidentified material (30%). No trace of adducts **4** or **5** was detected, the limit of detection being 0.5%.

*Reactions in acetonitrile at -20°C.* Photolysis of 1,4,5,8-tetramethylnaphthalene-tetranitromethane in acetonitrile at -20°C, as above, gave after bleaching of the CT band a product which was shown by <sup>1</sup>H NMR spectral analysis to be a mixture of **4** (7%), **5** (2%), **6** (52%), together with unidentified material (28%).

*Photonitration of 6 with tetranitromethane in acetonitrile at +20°C.* Photolysis of **6** (10 mg) and tetranitromethane (17 mg) in acetonitrile (1 ml) at +20°C, as above, gave, after 2 h, a product which was shown by <sup>1</sup>H NMR spectroscopy to be a ~1:1 mixture of **6** and **7** together with about 65% of unidentified material, similar to that obtained in the photonitration of 1,4,5,8-tetramethylnaphthalene in acetonitrile at +20°C above.

**Stability of adduct 4 in acetonitrile.** The adduct **4** (5 mg) was dissolved in acetonitrile- $d_3$  (0.7 ml) and the solution stored at +23°C for 48 h, during which the  $^1\text{H}$  NMR spectrum was monitored at appropriate intervals. It remained unchanged during this period, indicating the high stability of **4** in acetonitrile.

**Crystallography.** Crystal data, established from precession photographs and measured accurately by means of a Siemens R3m/V four-circle diffractometer [Mo X-radiation,  $\lambda(\text{Mo K}\alpha)$  0.71069 Å from a crystal monochromator] are given below. The space group was determined unambiguously as a result of the structure analysis reported below, but initially indicated by conditions limiting possible reflections. 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 of 1,4,5,8-tetramethyl-r-1-nitro-c-2-trinitro-methyl-1,2-dihydronaphthalene (4).**  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_8$ ,  $M$  380.32, triclinic, space group  $P\bar{1}$ ,  $a$  6.4040(3),  $b$  9.553(5),  $c$  14.08(1) Å;  $\alpha$  83.74(5),  $\beta$  86.12(5),  $\gamma$  75.70(4)°;  $V$  829.1(8) Å<sup>3</sup>,  $D_c$  1.523 g cm<sup>-3</sup>,  $Z$  2,  $\mu(\text{Mo K}\alpha)$  1.26 cm<sup>-1</sup>. The crystal was pale yellow and of approximate dimensions 0.64 by 0.38 by 0.22 nm:  $\omega$  scan technique. Data were collected at 183 K out to a maximum Bragg angle  $\theta = 22.5^\circ$ . Number of independent reflections measured 2149, 575 with  $I > 2\sigma(I)$ . Absorption corrections were not applied;  $g_1$  0.0465;  $g_2$  0.3897;  $R_{(\text{obs})}$ -factor 0.037;  $wR_{(\text{all data})}$  0.085.

**Structure determination.** Full-matrix least-squares refinements (SHELXL-92) 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 refinements based on  $F$ . Reflection weights  $1/[\sigma^2(F_o^2) + (0.325P)^2 + 1.9595P]$ , 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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## References

1. Ebersson, L., Hartshorn, M. P. and Svensson, J. O. *Acta Chem. Scand.* 47 (1993) 925.
2. Ebersson, L. and Radner, F. *J. Am. Chem. Soc.* 113 (1991) 5825.
3. (a) Ebersson, L., Hartshorn, M. P., Radner, F. and Robinson, W. T. *J. Chem. Soc., Chem. Commun.* (1992) 566; (b) Ebersson, L., Hartshorn, M. P. and Radner, F. *J. Chem. Soc., Perkin Trans. 2* (1992) 1793.
4. Ebersson, L., Hartshorn, M. P. and Radner, F. *J. Chem. Soc., Perkin Trans. 2* (1992) 1799.
5. Ebersson, L., Hartshorn, M. P., Radner, F. and Robinson, W. T. *Acta Chem. Scand.* 47 (1993) 410.
6. Ebersson, L., Hartshorn, M. P., Radner, F., Merchán, M. and Roos, B. O. *Acta Chem. Scand.* 47 (1993) 176.
7. Ebersson, L. and Hartshorn, M. P. *J. Chem. Soc., Chem. Commun.* (1992) 1564.
8. Sankararaman, S. and Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* (1991) 1.
9. Kim, E. K., Bockman, M. and Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* (1992) 1879.
10. Terahara, A., Ohya-Nishiguchi, H., Hirota, N. and Oku, A. *J. Phys. Chem.* 90 (1986) 1564.
11. Howarth, O. W. and Fraenkel, G. K. *J. Chem. Phys.* 52 (1970) 6258.
12. Ebersson, L. and Radner, F. *Acta Chem. Scand.* 46 (1992) 630.
13. Handoo, K. L. and Gadru, K. *Curr. Sci.* 55 (1986) 920.
14. See, e.g., Oae, S., Asai, N. and Fujimori, K. *J. Chem. Soc., Perkin Trans. 2* (1978) 571; Doyle, M. P., Terpstra, J. W., Pickering, R. A. and LePoire, D. M. *J. Org. Chem.* 48 (1983) 3379; Igliesas, E., Garcia-Rio, L., Leis, R., Pena, M. E. and Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* (1992) 1673.
15. Ebersson, L. and Radner, F. *Acta Chem. Scand., Ser. B* 40 (1986) 71; *Acc. Chem. Res.* 20 (1987) 53.
16. For a review on radical cation chemistry, see: Hammerich, O. and Parker, V. D. *Adv. Phys. Org. Chem.* 20 (1984) 55.
17. Ebersson, L. and Radner, F. *Acta Chem. Scand., Ser. B* 34 (1980) 739.
18. Ross, D. S., Schmitt, R. J. and Malhotra, R. *Chem. Abstr.* 100 (1984) 155980b.
19. Imashiro, F., Takegoshi, K., Saika, A., Taira, Z. and Asahi, Y. *J. Am. Chem. Soc.* 107 (1985) 2341.
20. Tschinkel, J. G. *Ind. Eng. Chem.* 48 (1965) 732.

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