Formation of a 1,3-Dipolar Nitro Addition Product from the Photochemical Reaction of 1,2-Dimethylnaphthalene and Tetranitromethane

Craig P. Butts,[a] Jane L. Calvert,[a] Lennart Eberson,*[b] Michael P. Hartshorn*[a] and Ward T. Robinson[a]

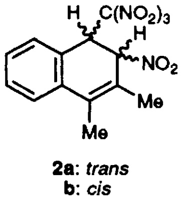
[a] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*
[b] *Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden*

The photochemical reaction between tetranitromethane and 1,2-dimethylnaphthalene gives, among other adducts, a product of internal 1,3-dipolar cycloaddition of a nitro group from the trinitromethyl group across the 1,2-double bond of the primary adduct, 1,2-dimethyl-*r*-3-nitro-4-trinitromethyl-3,4-dihydronaphthalene.

The photochemical addition of tetranitromethane (TNM) to aromatic compounds (ArH) is now a well established reaction, leading to nitro/trinitromethyl or nitrito/trinitromethyl addition across 1,2- or 1,4-bonds of ArH (anthracene and derivatives thereof,[1] 1,4-dimethylnaphthalene,[2,3] naphthalene,[4,5] fluoranthene,[6] 1,4,5,8-tetramethylnaphthalene,[7] benzene,[8] dibenzofuran,[9] 4-chloroanisole[10]). The adducts undergo further thermal reactions of heterolytic[3,4,6] or homolytic[3] nature and are in many cases precursors of nitro (shown conclusively[3,4,6,9]) and/or trinitromethyl (not shown but strongly implicated[10]) substitution products.

A second, possible reaction mode of the nitro group is 1,3-dipolar addition across a double bond, known to occur photochemically[11] for many kinds of olefins and thermally[12] either for strained olefins like *trans*-cyclooctene or for suitably activated nitro groups. We now show that a product of intramolecular 1,3-cycloaddition of a nitro group, originating from the trinitromethyl group of a nitro/trinitromethyl adduct, is produced during the photochemical reaction between TNM and 1,2-dimethylnaphthalene in dichloromethane, thus adding one further possibility to the rich spectrum of reactivity and complexity in these systems.

A solution of TNM (0.8 mol dm^{-3}) and 1,2-dimethylnaphthalene (0.4 mol dm^{-3}) in dichloromethane (8 ml) was irradiated for 3 h at 20 °C by filtered light (cutoff <435 nm). The volatile material was removed under reduced pressure at ≤0 °C and the product composition determined by NMR spectral analysis. The major products were adducts (>90%), from which the cycloaddition product **1** (24%), m.p. 208 °C (decomp.) was isolated by HPLC. Its structure was established by an X-ray crystallographic study (Fig. 1).†



2a: *trans*
b: *cis*

The isolation of **1** from the photolysis of TNM and 1,2-dimethylnaphthalene raises the problem of its possible mode of formation. Assuming initial 3,4-addition of nitro/trinitromethyl to 1,2-dimethylnaphthalene, an epimeric pair of adducts (**2a** and **2b**) is expected. Of these, **2a** is the precursor of **1** and could undergo this transformation either thermally or photochemically. Within the limits of experimental detection, no **2a** was seen in the reaction mixture. Since **2a** would be transparent in the range of wavelengths employed, we suggest that the thermal variety of the 1,3-dipolar addition of a nitro group to a double bond is involved. This is in line with previous findings that nitro groups activated by adjacent electron-withdrawing groups (fluorine, nitro) undergo the thermal reaction with ease.[12a,c] An alternative mechanism, which cannot be wholly excluded would be excitation of a charge transfer complex between **2a** and TNM, followed by

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† *Crystal data*: $C_{13}H_{12}N_4O_8$, $M = 352.27$, orthorhombic, space group $P2_12_12_1$, $a = 8.661(2)$, $b = 12.132(2)$, $c = 14.011(2)$ Å, $V = 1472.2$ Å^3, $Z = 4$, μ(Mo-Kα) 1.35 cm^{-1}, Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 123 K using a Siemens P4 4-circle diffractometer for a colourless crystal of dimensions 0.28 × 0.20 × 0.16 mm. All 1872 reflections were used in all calculations with SHELX92 for solution by direct methods and SHELXL92 for refinements using intensities [$wR2 = 0.1044$ for all data; $R1(I) > 2\sigma(I)$ 0.045]. Atomic coordinates, bond lengths, and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No 1.

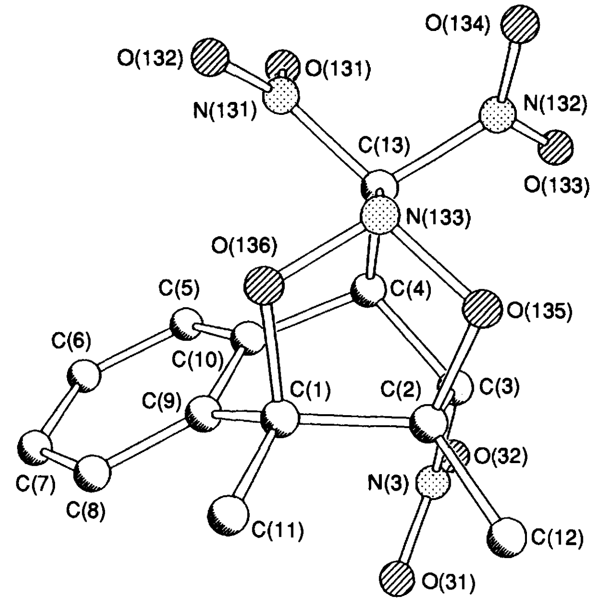

Fig. 1 Perspective view of the structure of **1**

internal cycloaddition within $\mathbf{2a}^{\cdot+}$ to give $\mathbf{1}^{\cdot+}$, followed by one-electron reduction of the latter by trinitromethanide ion.[13]

More generally, the detection of a compound involving bonding *via* oxygen from a trinitromethyl group raises new mechanistic possibilities for the thermal/photochemical interaction between tetranitromethane and ArH, which may be realistic alternatives or complements to the prevailing triad hypothesis.[14]

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