(E)-9,10-Dihydro-9-methyl-9-nitro-10-(trinitromethyl)anthracene

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Key indicators
Single-crystal X-ray study
T = 295 K
Mean r(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.133
Data-to-parameter ratio = 11.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, C_{16}H_{12}N_{4}O_{8}, was prepared by the photochemical reaction of 9-methylanthracene and tetranitromethane in dichloromethane. Intermolecular face-to-face \( \pi - \pi \) stacking interactions are present along the \( a \) axis.

Comment
Photonitration of various aromatic compounds using tetranitromethane (TNM) has attracted some attention as an alternative to the conventional nitration processes which require the use of concentrated nitric and sulfuric acids (Kochi, 1991; Butts et al., 1996; Cox, 1998; Lehning & Schürmann, 1998). There are two possible photonitration products depending on the nature of the aromatic compound. In general, unsubstituted non-heteroaromatic compounds result in nitration, while alkyl substituted ones, such as 9-methylanthracene, lead to the addition of both trinitromethyl and nitro groups. Owing to the dissociative fragmentation of TNM, irradiation of the 9-methylanthracene/TNM charge-transfer (CT) complex leads to the formation of a triad consisting of a 9-methylanthracen radical cation, a nitrogen dioxide radical and a trinitromethide anion. The subsequent addition reactions occur at the C9 and C10 positions of the anthracene central ring. The larger trinitromethyl group adds first through an ion-pair collapse and reorders pseudoaxially at the C10 position of the central dihydroanthracene ring. In order to form a more stable hydanthryl radical, the trinitromethide addition to 9-methylanthracene occurs at the less hindered C10 site. Radical–radical coupling between nitrogen dioxide and the resulting hydanthryl radical takes place from the site opposite to the trinitromethyl group.

\[
\text{[ArH, C(NO_{2})_{4}]} \xrightarrow{a} \text{ArH}^{\text{••}} + \text{NO_{2}^{•} + C(NO_{2})_{3}} \xrightarrow{b} \text{Ar(C(NO_{2})_{3})NO_{2}}
\]

We report here the crystal structure of the title compound, (I), as the photoreaction product of 9-methylanthracene with TNM (Fig. 1). The bond lengths and angles of the tricyclic ring...
system are in agreement with those of alkyl-substituted 9,10-dihydroanthracenes (Brinkmann et al., 1970; Rabideau, 1978; Dalling et al., 1981). The larger trinitromethyl group is attached pseudoaxially at the C10 position of the meso ring, which adopts a boat conformation. Pseudoaxial positioning of the bulkier groups in other 9,10-dihydroanthracene derivatives is also known (Cam & Bock, 1978; Dalling et al., 1981).

The trinitromethyl and nitro groups prefer to have a trans configuration. The dihedral angle between the two benzene ring planes is 28.93 (9)°. The bond distance between C9 and the methyl atom C11 [1.523 (3) Å] is shorter than that between C10 and the trinitromethyl atom C12 [1.582 (3) Å] owing to the high functionalities of the nitro groups. The bond distance between C9 and N9 [1.563 (3) Å] is 0.033 Å longer than the average length of the other C12—N bonds. In addition to van der Waals forces, π–π interactions between one benzene ring of two neighboring molecules contribute to the stacking along the a axis (Fig. 2).

**Experimental**

The title compound was synthesized by irradiation of a solution containing 9-methylanthracene (100 mg, 0.52 mmol) and tetranitromethane (325 mg, 1.67 mmol) in pentane (49 ml) and CCl₄ (1 ml). A 500 nm cut-off filter was used to ensure that only the CT complex was excited, not the uncomplexed initial components present in the solution. The solution was purged with argon before and during the irradiation (30 min). After the irradiation, the solvents were removed and (I) (55 mg, 27.2%) was isolated by fractional crystallization from dichloromethane as colorless prisms (m.p. 421–422 K). ¹H NMR (300 MHz, CDCl₃, p.p.m.): δ 7.59–7.41 (m, 8H), 6.405 (s, 1H), 2.48 (s, 3H).

**Crystal data**

- Chemical formula: C₁₆H₁₂N₄O₈
- Molecular weight: 388.3
- Space group: P2₁/n
- Crystal system: Monoclinic
- Unit cell:
  - a = 7.9797 (6) Å
  - b = 13.5449 (10) Å
  - c = 15.3793 (9) Å
  - β = 91.816 (6)°
- Volume: 1661.4 (2) Å³
- Z = 4
- Density: 1.552 Mg m⁻³
- Radiation: Mo Kα (λ = 0.71073 Å)
- Temperature: 295 (2) K
- Orientation: Prism, colorless
- Dimensions: 0.35 x 0.35 x 0.18 mm

**Data collection**

- Instrument: Enraf–Nonius CAD-4 diffractometer
- Scans: ω scans
- Absorption correction: none
- 2949 measured reflections
- 2311 independent reflections
- 3 standard reflections
- Frequency: 120 min
- Intensity decay: 1.1%

**Refinement**

- Method: Refinement on F²
- Goodness-of-fit on F²: 0.040
- R(F²) = 0.133
- wR(F²) = 0.105
- 2949 reflections
- 253 parameters
- H-atoms constrained

**Figure 1**

ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level.

**Figure 2**

The molecular packing of (I), viewed down the a axis. H atoms have been omitted for clarity.
Table 1
Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3—C12</td>
<td>1.526 (3)</td>
<td>N2—C12</td>
<td>1.540 (3)</td>
</tr>
<tr>
<td>N1—C12</td>
<td>1.531 (3)</td>
<td>C10—C12</td>
<td>1.582 (3)</td>
</tr>
<tr>
<td>N9—C9</td>
<td>1.563 (3)</td>
<td>C9—C11</td>
<td>1.523 (3)</td>
</tr>
</tbody>
</table>

C10α—C10—C4α  112.93 (17)
C9α—C9—C8α  112.98 (18)
C11—C9—C8α  112.5 (2)

H atoms were positioned geometrically and allowed to ride on their parent atoms with C—H = 0.93, 0.96 and 0.98 Å for aromatic, methyl and methine H atoms, respectively, with $U_{iso}(H) = 1.5U_{eq}(C)$ of the parent atom for the methyl groups and $1.2U_{eq}(C)$ for the rest.

Data collection: CAD-4-PC Software (Enraf–Nonius, 1993); cell refinement: CAD-4-PC Software; data reduction: DATRD2 in NRCVAX (Gabe et al., 1989); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON/PLUTON (Spek, 2003); software used to prepare material for publication: WinGX (Farrugia, 1999).

References