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

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(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 σ(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.

The title compound, $C_{16}H_{12}N_4O_8$, was prepared by the photochemical reaction of 9-methylanthracene and tetranitromethane in dichloromethane. Intermolecula face-to-face π–π 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; Lehnig & 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-methylanthracen/TNM charge-transfer (CT) complex leads to the formation of a triad consisting of a 9-methylanthraceneradical 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 hydranthryl radical, the trinitromethide addition to 9-methylanthracene occurs at the less hindered C10 site. Radical–radical coupling between nitrogen dioxide and the resulting hydranthryl radical takes place from the site opposite to the trinitromethyl group.
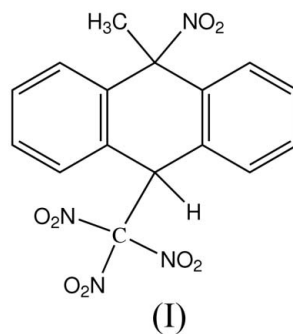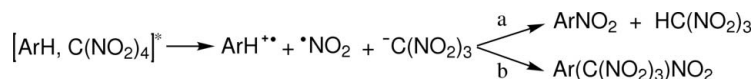
We report here the crystal structure of the title compound, (I), as the photoreaction product of 9-methylanthracene with TNM (Fig. 1). The bond lengths and angles of the tricyclic ring
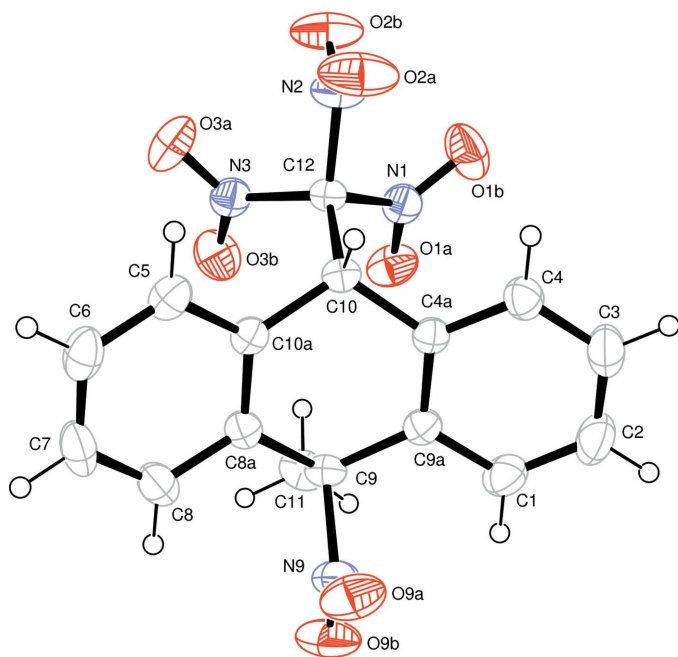
Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level.

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).
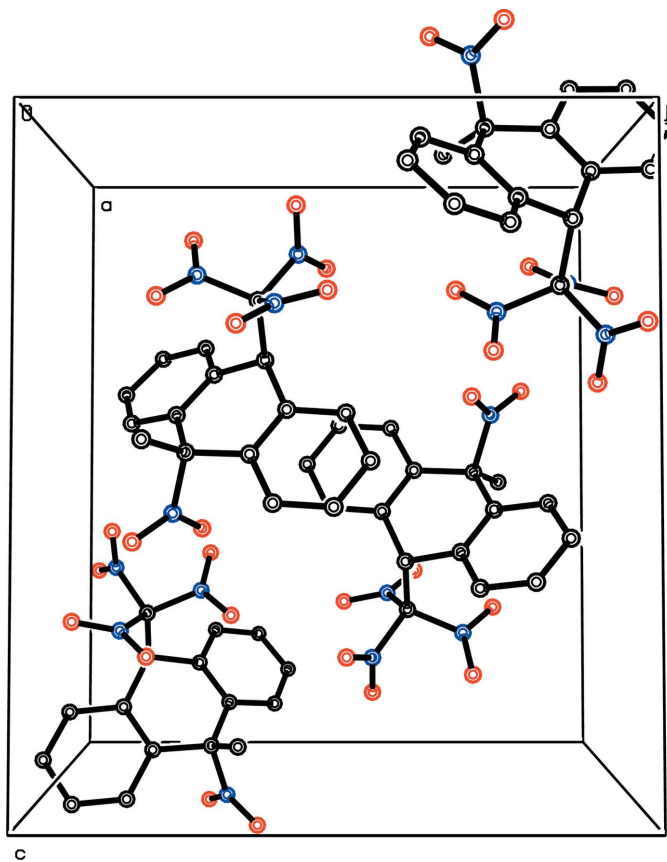

Figure 2
The molecular packing of (I), viewed down the *a* axis. H atoms have been omitted for clarity.

Crystal data

$C_{16}H_{12}N_4O_8$	$D_x = 1.552$ Mg m^{-3}
$M_r = 388.3$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 7.9797$ (6) Å	reflections
$b = 13.5449$ (10) Å	$\theta = 20$–25°
$c = 15.3793$ (9) Å	$\mu = 0.13$ mm^{-1}
$\beta = 91.816$ (6)°	$T = 295$ (2) K
$V = 1661.4$ (2) Å^3	Prism, colorless
$Z = 4$	$0.35 \times 0.35 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 25.1°$
diffractometer	$h = -9 \rightarrow 9$
ω scans	$k = 0 \rightarrow 16$
Absorption correction: none	$l = 0 \rightarrow 18$
2949 measured reflections	3 standard reflections
2949 independent reflections	frequency: 120 min
2311 reflections with $I > 2\sigma(I)$	intensity decay: 1.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1197P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 9.7917P]$
$wR(F^2) = 0.133$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.015$
2949 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N3—C12	1.526 (3)	N2—C12	1.540 (3)
N1—C12	1.531 (3)	C10—C12	1.582 (3)
N9—C9	1.563 (3)	C9—C11	1.523 (3)
C10a—C10—C4a	112.93 (17)	C9a—C9—C8a	112.98 (18)
C9a—C9—C11	113.44 (19)	C11—C9—C8a	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).

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