

9-Ethyl-3-methyl-1,6-dinitrocarbazole

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The title compound, C₁₅H₁₃N₃O₄, crystallizes in the triclinic space group *P* $\bar{1}$. The 6-nitro and methyl groups are essentially planar with the carbazole moiety, while the 1-nitro group is twisted out of the carbazole plane. Two neighboring molecules are associated with each other through one benzene ring, indicating a weak π - π interaction.

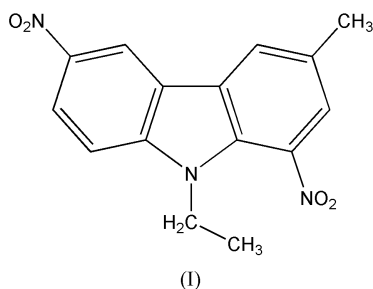
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ (C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.116
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Comment

Aminocarbazoles are widely used as intermediates for the preparation of carbazole-based synthetic dyes, agrochemicals, pharmaceuticals, light-sensitive materials, surfactants, and polymers (Shufen *et al.*, 1995). Aminocarbazoles can easily be prepared by the reduction of nitrocarbazoles, while photochemical nitration of carbazoles proceeds readily through an electron-transfer process between the electron donor-acceptor (EDA) complexes of carbazoles with tetranitromethane (TNM) (Iles & Ledwith, 1969). Nitration on the unsubstituted benzene rings of carbazoles proceeds *via* the introduction of the first nitro group mainly at the C3 position. Introduction of the second nitro group at the C6 position on the second benzene ring proceeds more slowly at the same conditions due to the reduced electron density of the π -system due to the presence of the first nitro group. It came to our attention (Asker, 2001) that the existence of an alkyl group at the C3 position on any of the benzene rings significantly activates the C1 position on the same ring. In our attempts to elucidate the nature of the nitration process, we have prepared the title compound, (I), and undertaken a single-crystal X-ray structure determination.



The title compound, (I) (Fig. 1), crystallizes in the space group *P* $\bar{1}$. Bond distances and angles are in agreement with those for related compounds (Baker *et al.*, 1991; Chen *et al.*, 1992). However, compared to unnitrated carbazole rings, the C1–C9A [1.404 (3) Å] and C6–C7 [1.396 (3) Å] bonds at the attachment centers of the nitro groups are found to be slightly longer. Similarly, the C1–C2–C3 [122. (2)°] and C5–C6–C7 [124 (2)°] interior angles are also found to be slightly greater (Table 1).

The 1-nitrated benzene ring of one molecule associates with the 3-nitrated benzene ring of a second molecule in a way that their nitro groups are pointing to the opposite directions indicating a weak π - π interaction while forming C—H...O interactions with a third molecule (Fig. 2).

The 6-nitro substituent is coplanar with the carbazole ring system with the a dihedral angle between the two planes of 5.27 (15)°, while steric interaction with the ethyl group result in the plane of the 1-nitro group twisting out of the carbazolyl plane with a dihedral angle between the two planes of 37.24 (9)°. Atoms N1, N6, C10 and C12 deviate from the carbazole best least-squares plane by 0.1750 (24), -0.0950 (25), -0.279 (3) and -0.027 (3) Å, respectively.

Experimental

Nitration of 9-ethyl-3-methylcarbazole was performed through a photochemical reaction using TNM as the nitrating agent in dichloromethane. A Westinghouse sun lamp (275 W) was used as the light source. The reaction was carried out in a 25 ml test tube dissolving 100 mg (0.5 mmol) of 9-ethyl-3-methylcarbazole and 500 mg (2.5 mmol) of TNM in 5 ml of dichloromethane. The light source was placed at a distance of approximately 15 cm from the reaction tube and a Corning sharp cutoff UV filter was placed between the light source and the test tube. After 3 h of irradiation, the reaction mixture was extracted with water, the solvent was removed under reduced pressure, and the remaining yellow solid was column chromatographed using basic alumina (80–200 mesh, activity III) and dichloromethane/hexane as the eluting solvents. The title compound, (I), was obtained after recrystallization from CH₂Cl₂ as yellow needles (m.p. 429 K). ¹H NMR (300 MHz, CDCl₃, p.p.m.): 8.99 (*d*, 2.17 Hz, 1H), 8.45 (*d* of *d*, 8.96 and 2.19 Hz, 1H), 8.20 (*s*, 1H), 7.88 (*s*, 1H), 7.54 (*d*, 9.14 Hz, 1H), 4.42 (*q*, 7.04 Hz, 2H), 2.61 (*s*, 3H), 1.43 (*t*, 7.13 Hz, 3H).

Crystal data

C ₁₅ H ₁₃ N ₃ O ₄	<i>Z</i> = 2
<i>M_r</i> = 299.28	<i>D_x</i> = 1.442 Mg m ⁻³
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 6.7094 (4) Å	Cell parameters from 25
<i>b</i> = 8.8147 (6) Å	reflections
<i>c</i> = 12.2004 (9) Å	θ = 6.1–14.0°
α = 72.908 (6)°	μ = 0.11 mm ⁻¹
β = 87.720 (6)°	<i>T</i> = 293 (2) K
γ = 88.718 (6)°	Slab, yellow
<i>V</i> = 689.09 (8) Å ³	0.51 × 0.20 × 0.12 mm

Data collection

Nonius CAD-4 diffractometer	θ_{\max} = 25.0°
ω scans	<i>h</i> = -7 → 7
Absorption correction: none	<i>k</i> = 0 → 10
2698 measured reflections	<i>l</i> = -13 → 14
2442 independent reflections	3 standard reflections
1692 reflections with <i>I</i> _{net} > 2σ(<i>I</i> _{net})	frequency: 120 min
<i>R</i> _{int} = 0.007	intensity decay: 1.2%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.1899P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.02	$\Delta\rho_{\max} = 0.14 \text{ e } \text{Å}^{-3}$
2442 reflections	$\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
200 parameters	
H-atom parameters constrained	

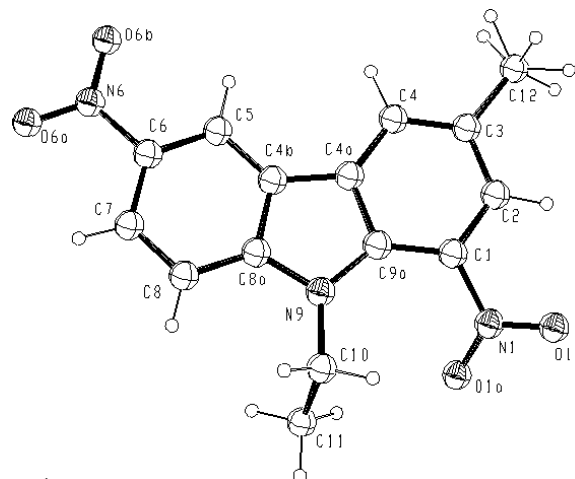


Figure 1
ORTEP (Johnson, 1976) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms are represented by small spheres.

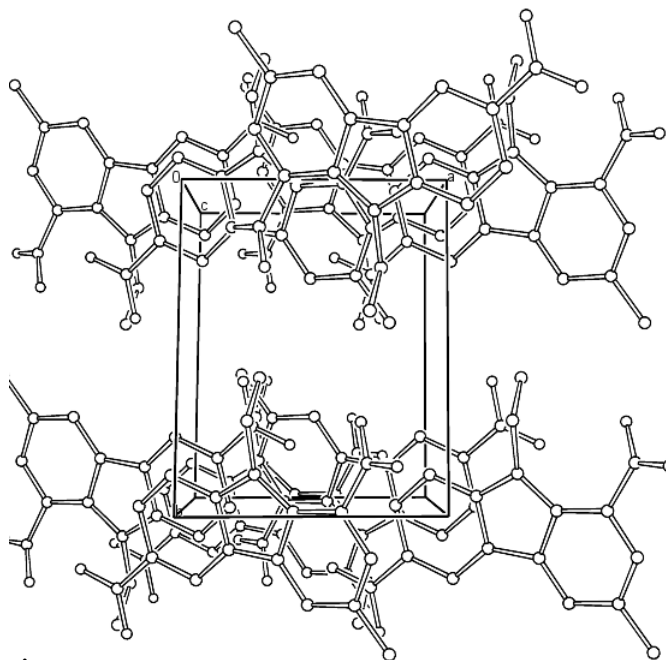


Figure 2
The molecular packing of (I). H atoms have been omitted for clarity.

Table 1

Selected geometric parameters (Å, °).

C1—C2	1.384 (3)	C4B—C5	1.382 (3)
C1—C9A	1.404 (3)	C4B—C8A	1.411 (3)
C2—C3	1.385 (3)	C5—C6	1.374 (3)
C3—C4	1.389 (3)	C6—C7	1.396 (3)
C4—C4A	1.383 (3)	C7—C8	1.374 (3)
C4A—C9A	1.414 (3)	C8—C8A	1.395 (3)
C4A—C4B	1.444 (3)	C10—C11	1.505 (3)
C2—C1—C9A	120.07 (19)	C6—C5—C4B	117.50 (19)
C1—C2—C3	122.4 (2)	C5—C6—C7	123.19 (19)
C2—C3—C4	118.3 (2)	C8—C7—C6	119.64 (19)
C4A—C4—C3	120.1 (2)	C7—C8—C8A	118.28 (19)
C4—C4A—C9A	122.05 (19)	C8—C8A—C4B	121.21 (19)
C5—C4B—C8A	120.16 (18)	C1—C9A—C4A	117.00 (19)

H atoms were located by difference Fourier techniques and allowed to ride on their parent atoms at distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene H atoms, respectively, with $U_{\text{iso}}(\text{H}) = 0.001 \text{ \AA}^2 + U_{\text{eq}}(\text{C})$ of the parent atom. The methyl group shows disorder of the H atoms; it was treated as an idealized disordered methyl group with the site-occupation factors fixed at 0.5.

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: *NRCVAX SOLVER*; program(s) used to refine structure: *NRCVAX LSTSQ* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *SHELXL97*.

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