

9-Ethyl-3-(9*H*-9-ethylcarbazol-3-yl)-4-nitro-9*H*-carbazoleErol Asker^{a*} and John Masnovi^b^aBalikesir University, Necatibey Faculty of Education, 10100 Balikesir, Turkey, and^bDepartment of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

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In the molecule of the title compound, C₂₈H₂₃N₃O₂, the nitro group is almost perpendicular to the carbazole ring to which it is attached. The crystal packing is determined by C—H···O and π – π interactions, where the nitrated carbazole ring of one molecule associates in a shifted parallel planar orientation with the centrosymmetrically related non-nitrated carbazole ring of a neighbouring molecule.

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean σ (C—C) = 0.007 Å

R factor = 0.038

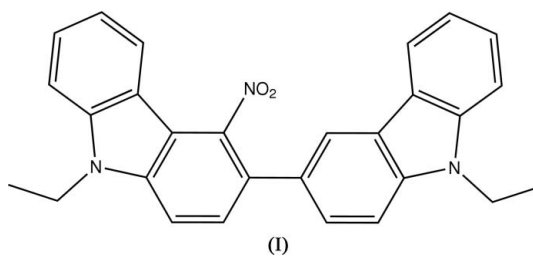
wR factor = 0.106

Data-to-parameter ratio = 6.6

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

Comment

Nitrocarbazoles serve as precursors for the synthesis of aminocarbazoles, which are of interest due to their pharmaceutical and photoconduction properties (Shufen *et al.*, 1995). Photochemical nitration of carbazoles using tetranitromethane (TNM) can be used as an alternative route to the conventional methods which require the use of nitric acid. Photochemical reactions between carbazoles and TNM take place through an electron-transfer process upon irradiation of their donor–acceptor (EDA) complexes (Iles & Ledwith, 1969; Masnovi *et al.*, 1990). Photonitration products of carbazoles vary depending on the nature of the substituents on the carbazole rings. While unsubstituted carbazoles lead to 3-nitro derivatives, 3-alkyl-substituted carbazoles give rise to 1- and 6-nitro derivatives. In the case of 9,9'-diethyl-3,3'-dicarbazolyl, nitration takes place mainly at the C4 centre. This can be explained by the stabilization of the positive charge of the cation intermediate by the resonance structures involving the N atoms of both carbazole rings. The higher reactivity of the carbazole C4 centre suppresses the possible nitration at C3. Hence, only a minimum quantity of the 6-nitro product was isolated. Due to the conjugation of carbazole ringring systems with each other, the electron-withdrawing nitro group of one ring system reduces the reactivity of the second ring system, making the introduction of another nitro group more difficult. We report here the X-ray crystal structure of the title compound, (I) (Fig. 1).



The essential features of the structures of the nitrated and non-nitrated carbazole groups of (I), such as bond lengths and angles (Table 1), are not unusual (Asker & Masnovi, 2004;

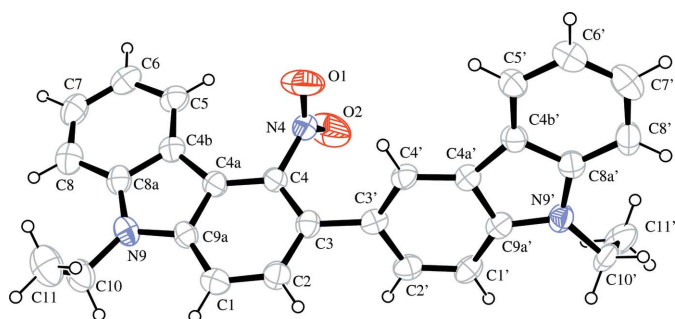


Figure 1

A drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

Chen *et al.*, 1992). The only notable distinction is that the C3–C4–C4a internal bond angle of $123.1(4)^\circ$ (where the nitro group is attached) is about 2.7° larger than that of the corresponding C3'–C4'–C4a' angle [$120.4(4)^\circ$]. The C3–C4 bond [$1.402(6) \text{ \AA}$] is also somewhat longer than the corresponding C3'–C4' bond [$1.373(6) \text{ \AA}$].

The dihedral angle between the planes of the carbazole ring systems is $62.76(5)^\circ$. The plane of the nitro group is nearly perpendicular [$83.10(25)^\circ$] to the plane of the carbazole group to which it is attached. The interference of the second carbazole group in the molecule is thought to be responsible for a favourable parallel planar geometry. The torsion angles C9a–N9–C10–C11 [$88.4(6)^\circ$] and C9a'–N9'–C10'–C11' [$87.1(6)^\circ$] indicate that the *N*-ethyl substituents are almost perpendicular to the planes of the corresponding carbazole ring systems.

The molecular packing is determined by C–H...O and π – π interactions (Fig. 2 and Table 2). In the crystal structure, the nitrated carbazole group of one molecule associates in a shifted parallel planar orientation with the centrosymmetrically related non-nitrated carbazole ring of a neighbouring molecule. Thus, the dihedral angle between the planes of the pyrrole rings of two neighbouring carbazole groups at $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ is $2.0(3)^\circ$, with a ring-centroid separation of $3.634(3) \text{ \AA}$ and an interplanar spacing of *ca.* 3.49 \AA , corresponding to a ring-centroid offset of *ca.* 1.03 \AA .

Experimental

The title compound was synthesized through the photolysis of donor–acceptor complexes of 9,9'-diethyl-3,3'-dicarbazolyl with tetranitromethane (TNM) 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 9,9'-diethyl-3,3'-dicarbazolyl (100 mg, 0.26 mmol) and TNM (500 mg, 2.5 mmol) in dichloromethane (5 ml). 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 35 min of irradiation time, the reaction mixture was extracted with water, the solvent was removed under reduced pressure, and the remaining yellow solid was treated by column chromatography using basic alumina (80–200 mesh, activity III) with dichloromethane–hexane as the eluting solvents. The solvents were removed using a rotary

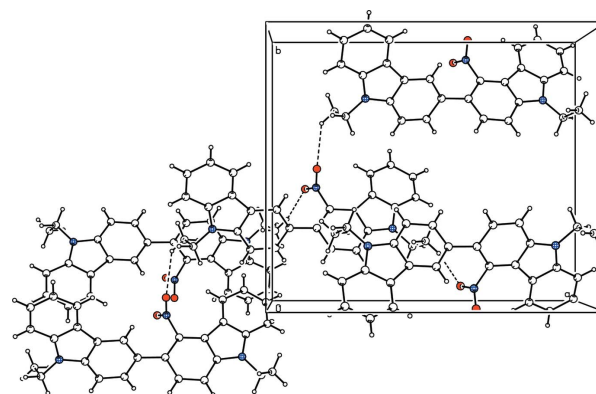


Figure 2

The molecular packing of (I), viewed down the *c* axis. Dashed lines indicate C–H...O hydrogen bonds.

evaporation system to give 86 mg (77%) of the title compound, in addition to 7 mg (6%) of 9-ethyl-3-(9-ethylcarbazol-3-yl)-6-nitrocarbazole (m.p. 465–467 K, yellow powder). Single crystals of (I) suitable for X-ray diffraction analysis were obtained from a solution in CH_2Cl_2 by slow evaporation at ambient conditions (m.p. 429 K).

Crystal data

$\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_2$
 $M_r = 433.49$
 Monoclinic, *Cc*
 $a = 16.2810(13) \text{ \AA}$
 $b = 13.8472(8) \text{ \AA}$
 $c = 9.9233(9) \text{ \AA}$
 $\beta = 90.721(7)^\circ$
 $V = 2237.0(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.287 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 5.7\text{--}18.4^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Slab, yellow
 $0.51 \times 0.27 \times 0.17 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: none
 2071 measured reflections
 1975 independent reflections
 1466 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.010$

$\theta_{\text{max}} = 25.0^\circ$
 $h = -19 \rightarrow 19$
 $k = -16 \rightarrow 16$
 $l = 0 \rightarrow 11$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.107$
 $S = 1.03$
 1975 reflections
 299 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.1062P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}} = 0.017$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

C3–C4	1.402 (6)	C3'–C4'	1.373 (6)
C4a–C4–C3	123.1 (4)	C3'–C4'–C4a'	120.4 (4)
C9a–N9–C10–C11	88.4 (6)	C9a'–N9'–C10'–C11'	87.1 (6)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11—H11A \cdots O2 ⁱ	0.96	2.52	3.379 (7)	149
C11'—H11D \cdots O1 ⁱⁱ	0.96	2.59	3.290 (6)	130

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$.

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C})$ for the rest. There were no Friedel opposites in the data set; in the absence of significant anomalous scattering, these would not be independent.

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*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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