9-15-2004

9-Ethyl-3-Methyl-1, 6-Dinitrocarbazole

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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 = 12.2

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

The title compound, C15H13N3O4, crystallizes in the triclinic space group P\textsuperscript{T}. 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.

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 tetrinitromethane (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\textsuperscript{T}. Bond distances and angles are in agreement with those for related compounds (Baker et al., 1991; Chen et al., 1992). However, compared to unnitratated carbazole rings, the C1–C9\textsuperscript{A} [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-nitratated benzene ring of one molecule associates with the 3-nitratated 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)°. 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**

Nitrations 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. 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**

C15H13N3O4
Mr = 299.28
Triclinic, Pt
a = 6.7094 (4) Å
b = 8.8147 (6) Å
c = 12.2004 (9) Å
α = 72.908 (6)°
β = 87.270 (6)°
γ = 88.718 (6)°
V = 688.99 (8) Å3
Z = 2

Dm = 1.442 Mg m−3
Mo Kα radiation

Cell parameters from 25 reflections
θ = 6.1–14.0°
μ = 0.11 mm−1
T = 293 (2) K

Absorption correction: none
Iσmax = 25.0°
h = −7 → 7
k = 0 → 10
l = −13 → 14
3 standard reflections
frequency: 120 min
intensity decay: 1.2%

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Deviation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C2</td>
<td>1.384 (3)</td>
<td>±0.027 (3)</td>
</tr>
<tr>
<td>C1–C9A</td>
<td>1.404 (3)</td>
<td>±0.037 (3)</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.385 (3)</td>
<td>±0.024 (3)</td>
</tr>
<tr>
<td>C3–C4</td>
<td>1.389 (3)</td>
<td>±0.025 (3)</td>
</tr>
<tr>
<td>C4–C4A</td>
<td>1.383 (3)</td>
<td>±0.025 (3)</td>
</tr>
<tr>
<td>C4–C9A</td>
<td>1.414 (3)</td>
<td>±0.030 (3)</td>
</tr>
<tr>
<td>C4A–C4B</td>
<td>1.444 (3)</td>
<td>±0.030 (3)</td>
</tr>
<tr>
<td>C2–C1–C9A</td>
<td>120.07 (19)</td>
<td>±0.027 (3)</td>
</tr>
<tr>
<td>C1–C2–C3</td>
<td>122.4 (2)</td>
<td>±0.030 (3)</td>
</tr>
<tr>
<td>C2–C3–C4</td>
<td>118.3 (2)</td>
<td>±0.029 (3)</td>
</tr>
<tr>
<td>C4–C4A–C9A</td>
<td>122.05 (19)</td>
<td>±0.025 (3)</td>
</tr>
<tr>
<td>C4A–C4B–C8A</td>
<td>120.16 (18)</td>
<td>±0.025 (3)</td>
</tr>
</tbody>
</table>

**Figure 1**

ORTEPII (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.
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 $U_{	ext{iso}}(H) = 0.001 \, \text{Å}^2 + U_{	ext{eq}}(C)$ 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.

References
Asker, E. (2001). PhD dissertation, Cleveland State University, USA.