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9,9′-Diethyl-3,3′-di-9H-carbazolyl

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Key indicators
Single-crystal X-ray study
T = 295 K
Mean r(C–C) = 0.005 Å
R factor = 0.060
wR factor = 0.135
Data-to-parameter ratio = 13.6

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

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In the title compound, C28H24N2, the carbazole ring systems are essentially planar to within 0.076 (3) Å. The dihedral angle between the planes of the ring systems is 40.38 (4)°. The contribution of intermolecular π–π interactions to the molecular stacking is observed.

Comment
Dicarbazolylalkanes, as the dimeric model compounds of poly-N-vinylcarbazole (PVK) and poly-3-vinylcarbazole (P3VK), have attracted some interest in studies dealing with photophysical properties of the corresponding polymers (Schildcrout et al., 1991; Haderski et al., 2000; Tani et al., 2001). Crystal structures of some of the dicarbazolyl model compounds have already been reported (Baker et al., 1991; Asker & Masnovi, 2005). In this paper, we report the structure of 9,9’-diethyl-3,3’-dicarbazolyl, (I), which was synthesized according to a literature procedure via oxidation of 9-ethylcarbazole by ferric chloride (Sadaki et al., 1995).

The 13 atoms of each carbazole ring in (I) (Fig. 1) are essentially coplanar to within 0.076 (3) Å. Bond distances and angles in the carbazole rings (Table I) are in agreement with each other, as well as with those of related compounds reported in the literature (Baker et al., 1991; Asker & Masnovi, 2005). The torsion angles C9a—N—C10—C11 [93.1 (4)°] and C9a’—N’—C10’—C11’ [82.3 (4)°] show how the N-ethyl substituents are oriented out of the carbazole ring system planes. Examination of the packing (Fig. 2) reveals the existence of π–π stacking interactions in the structure of (I), where the two carbazole groups of one molecule associate centrosymmetrically with one carbazole group of each of two adjacent molecules in such an orientation that their dipoles and ethyl groups point in opposite directions.

Experimental
The title compound, (I), was prepared according to the literature procedure via oxidation of 9-ethylcarbazole by ferric chloride (Sadaki et al., 1995). To a solution of 9-ethylcarbazole (5.0 g, 0.026
mole) in dichloromethane (60 ml) in an oven-dried three-necked 250 ml flask. FeCl₃ (5.0 g, 0.031 mol) was added portionwise, with stirring, in an ice bath. The mixture was stirred for an additional hour at room temperature, during which time the solution became dark green. After 1 h, the reaction medium was carefully neutralized by dropwise addition of aqueous NaOH solution. After extraction of the mixture with additional dichloromethane (50 ml) and washing three times with water, the solvent was removed and the resulting solid was air-dried. Column chromatography of the crude product over basic alumina (80–200 mesh, activity III), using dichloromethane/hexane as eluant, yielded 2.2 g (43.7%) of colorless crystals [m.p. 464–465 K (Chen et al., 2000)]. ¹H NMR (300 MHz, CDCl₃): δ 7.31 Hz, 4H), 1.49 (m, 8H), 7.28 (m, 2H), 1.44 (q, 4H) 7.31 Hz, 6H).

Crystal data

C₂₈H₂₄N₂

Mᵣ = 388.49

Tetragonal, I₄₁/a

a = 22.6201 (8) Å
c = 16.3918 (12) Å

V = 8387.2 (7) Å³

Z = 16

Dₐ = 1.231 Mg m⁻³

Cell parameters from 25 standard reflections

θ = 5.7–18.4°

µ = 0.07 mm⁻¹

T = 295 (2) K

Prism, colorless

0.51 × 0.43 × 0.42 mm

Data collection

Enraf-Nonius CAD-4 diffractometer

omega scans

Absorption correction: none

3689 measured reflections

3689 independent reflections

1481 reflections with I > 2σ(I)

Refinement

Refinement on F²

R[F² > 2σ(F²)] = 0.060

wR(F²) = 0.135

S = 0.86

3689 reflections

271 parameters

H-atom parameters constrained

w = 1/[σ²(Fo)² + (0.24P)²]

where P = (Fo)² + 2Fo²/3

Table 1

Selected geometric parameters (Å, °).

| C₄a−C₄b | 1.444 (4) | C₁′−C₂′ | 1.378 (4) |
| C₃−C₂ | 1.400 (4) | C₁−C₂ | 1.378 (4) |
| C₃−C₃′ | 1.485 (4) | C₄a′−C₄b′ | 1.446 (4) |
| C₃′−C₂′ | 1.399 (4) |
| C₄−C₃−C₂ | 118.0 (3) | C₁−C₉a−C₄a | 122.1 (3) |
| N′−C₈a′−C₉a′ | 109.4 (3) | N−C₉a−C₄a | 109.2 (3) |
| C₁′−C₆′−C₄a′ | 112.0 (3) | C₂−C₁−C₅a | 117.4 (4) |
| C₄′−C₃′−C₂′ | 117.2 (3) | C₁−C₂−C₃ | 123.0 (4) |
| N′−C₈a′−C₉a′ | 108.7 (3) | C₁′−C₂′−C₃′ | 123.4 (3) |
| N−C₈a−C₄b | 108.7 (3) | C₇−C₆−C₅ | 120.9 (3) |
| C₂−C₁−C₉a′ | 117.8 (3) | C₇′−C₆′−C₅′ | 120.3 (4) |

C₉a′−N′−C₁₀′−C₁₁′ | 82.3 (4) | C₉a−N−C₁₀−C₁₁ | 93.1 (4)

H atoms were positioned geometrically 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 Uiso(H) = 1.5Ueq(C) of the parent atom for the methyl groups and 1.2Ueq(C) for the rest.

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References


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 (Spek, 2003); software used to prepare material for publication: WinGX publication routines (Farrugia, 1999).