

1,3-Bis(9-ethylcarbazol-3-yl)propane

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In the title compound, $C_{31}H_{30}N_2$, π - π overlap is absent in the region where carbazole groups of two adjacent molecules are inclined toward each other. The ethyl groups which protrude from the plane of the carbazole groups and the alkylene chain connecting the two carbazole groups are responsible for the poor molecular stacking.

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Key indicators

Single-crystal X-ray study

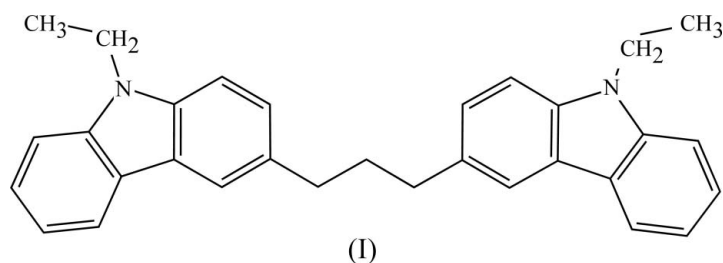
 $T = 293$ KMean $\sigma(C-C) = 0.008$ Å R factor = 0.052 wR factor = 0.129

Data-to-parameter ratio = 8.0

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

Comment

Poly(*N*-vinylcarbazole) (PVK) is among the most studied semiconducting polymers due to its commercial applications in electrophotography (Pielichowski & Sanetra, 1984; Loh *et al.*, 1991; Rocquin & Chevrot, 1997; Li *et al.*, 1998). Poly(3-vinylcarbazole) (P3VK), another carbazole-containing photoconducting polymer that has been applied to electrophotography, is a structural isomer of PVK (Sliva, 1978; Shiraishi *et al.*, 1995). In an effort to understand the photophysical and chemical properties of PVK, some of its dimeric model compounds have been prepared and their single-crystal X-ray studies have been reported (Chen *et al.*, 1992). We report here the crystal structure of the title compound, (I), as a model of P3VK.



The carbazole skeletons in (I) (Fig. 1) are essentially planar to within 0.056 (4) Å. The geometric parameters in (I) (Table 1) are very similar and do not vary from the standard values for the carbazole groups of related compounds (Baker *et al.*, 1991; Nesterov *et al.*, 2002; Aravindan *et al.*, 2003). The torsion angles $C8A-N-C10-C11$ [$84.1(7)^\circ$] and $C8A'-N'-C10'-C11'$ [$90.1(6)^\circ$] indicate that the orientations of both of the *N*-ethyl substituents are almost perpendicular to the carbazole planes. The carbazole groups exhibit a *gauche-anti* conformation along the $C12-C13-C12'$ methylene chain.

The crystal packing diagram (Fig. 2) indicates that only van der Waals forces contribute to the crystal packing. The *N*-alkyl groups and the methylene chain connecting the two carbazole groups are thought to be responsible for any possible π - π interaction which is essential for good photoconduction in polyvinylcarbazoles.

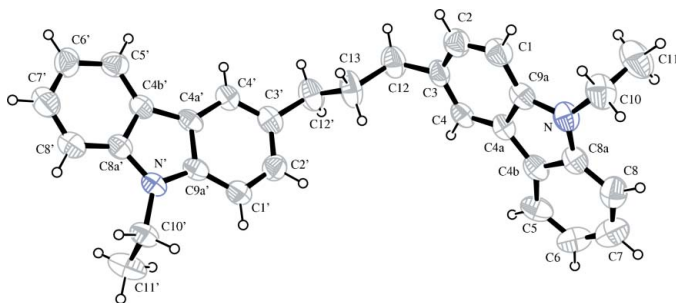


Figure 1
ORTEP3 (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

Experimental

Multistep synthesis of the title compound, (I), involves Friedel–Crafts acylation, aldol condensation, carbonyl reduction and catalytic hydrogenation reactions. 3-Acetyl-9-ethylcarbazole was prepared *via* Friedel–Crafts acylation of 9-ethylcarbazole with acetyl chloride, according to the literature procedure of Lopatinskii & Sirotkina (1964). C–C bond formation was achieved *via* a base-catalyzed aldol condensation of this ketone with 9-ethylcarbazole-3-carbaldehyde. A solution of 3-acetyl-9-ethylcarbazole (3.55 g, 0.015 mol) and 9-ethylcarbazole-3-carbaldehyde (3.35 g, 0.015 mol) in dry dimethylformamide (30 ml) was prepared in an oven-dried 100 ml three-necked flask. To this, finely powdered sodium methoxide was added portionwise in an ice bath under a nitrogen flow. The reaction mixture was stirred for 18 h at room temperature and was then diluted with methanol (50 ml) to give a yellow precipitate. The precipitate was separated from the reaction mixture by filtration and washed with water and air-dried. Column chromatography on basic alumina using dichloromethane/hexane as the eluting solvents gave 4.1 g (62% yield) of 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one as yellow needles after recrystallization from dichloromethane (m.p. 507 K).

1,3-Bis(9-ethylcarbazol-3-yl)propan-1-one was prepared *via* catalytic hydrogenation of 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one. In a 100 ml flask, 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one (2.0 g, 4.52 mmol) was dissolved in tetrahydrofuran (40 ml). To this, 10% Pd/C (200 mg) was added and stirred under an H₂ atmosphere until 100 ml of H₂ was consumed (about 2 h). The contents of the flask were filtered and the solvent was removed *in vacuo*. Column chromatography on basic alumina using dichloromethane/hexane as the eluting solvents gave 1.85 g (92.1%) of 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one as fine light-yellow crystals (m.p. 421–422 K).

In the final step, the carbonyl group of 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one was reduced with lithium aluminium hydride (LAH)/AlCl₃. In an oven-dried 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer bar and a reflux condenser was prepared a mixture of 1,3-bis(9-ethylcarbazol-3-yl)propan-1-one (1.5 g, 3.4 mmol), aluminium chloride (1.0 g), and anhydrous diethyl ether (30 ml). To this, LAH (0.20 g) was added portionwise over 30 min *via* an addition funnel at 273 K and under a nitrogen flow. After the addition was complete, the reaction mixture was heated under reflux for 2 h. The mixture was cooled to room temperature and the reaction was quenched carefully with dropwise addition of water (10 ml). The resulting mixture was extracted with diethyl ether (40 ml), the solvent was removed under reduced pressure, and the resultant beige solid was dried over calcium sulfate. The crude product was column chromatographed using alumina (80–200 mesh,

activity III) and dichloromethane/*n*-hexane as the eluting solvents to give 1.22 g (84.0%) of (I) as colorless prisms after recrystallization from CH₂Cl₂/*n*-hexane (m.p. 384–385 K). ¹H NMR (300 MHz, CDCl₃): δ 8.10 (*d*, 7.49 Hz, 2H), 7.95 (*s*, 2H), 7.51–7.15 (*m*, 10H), 4.37 (*q*, 7.31 Hz, 4H), 2.91 (*t*, 7.31 Hz, 4H), 2.18 (quintet, 7.31 Hz, 2H), 1.44 (*t*, 7.31 Hz, 6H).

Crystal data

C₃₁H₃₀N₂
M_r = 430.57
 Orthorhombic, *P*2₁*ca*
a = 8.1950 (9) Å
b = 11.1921 (8) Å
c = 26.931 (3) Å
V = 2470.1 (3) Å³
Z = 4
D_x = 1.158 Mg m^{−3}

Mo Kα radiation
 Cell parameters from 25 reflections
 θ = 4.0–14.0°
 μ = 0.07 mm^{−1}
T = 293 (2) K
 Block, colorless
 0.36 × 0.32 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: none
 3373 measured reflections
 2370 independent reflections
 1246 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

θ_{\max} = 25.1°
h = −9 → 9
k = −12 → 13
l = −31 → 32
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.0%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.129$
S = 0.96
 2370 reflections
 298 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.13 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.11 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.356 (7)	C4A'–C9A'	1.414 (6)
C3–C12	1.515 (7)	C4B'–C4A'	1.441 (6)
C3'–C2'	1.409 (7)	C4B'–C5'	1.400 (7)
C4A–C4B	1.433 (6)	C4B'–C8A'	1.408 (6)
C4A–C9A	1.408 (6)	C8A–C4B	1.412 (7)
N–C8A–C4B	108.0 (5)	C5'–C4B'–C8A'	119.7 (5)
N'–C8A'–C4B'	108.8 (4)	C5'–C6'–C7'	120.9 (6)
N–C9A–C4A	108.3 (5)	C6'–C5'–C4B'	118.1 (5)
N'–C9A'–C4A'	109.3 (4)	C6–C5–C4B	119.7 (6)
C1'–C2'–C3'	122.5 (5)	C6–C7–C8	122.1 (7)
C1–C2–C3	122.7 (6)	C7–C6–C5	120.3 (6)
C1'–C9A'–C4A'	120.3 (5)	C7'–C8'–C8A'	117.6 (5)
C1–C9A–C4A	120.5 (5)	C8'–C7'–C6'	122.3 (6)
C2'–C1'–C9A'	118.0 (5)	C8'–C8A'–C4B'	121.3 (5)
C2–C1–C9A	118.3 (5)	C8–C8A–C4B	122.2 (6)
C3'–C4'–C4A'	119.9 (5)	C8A'–C4B'–C4A'	106.7 (4)
C4–C3–C2	118.6 (5)	C8A–C4B–C4A	107.5 (4)
C4'–C3'–C2'	118.7 (5)	C8A–C8–C7	117.4 (6)
C4–C4A–C9A	119.0 (5)	C8A–N–C9A	109.1 (4)
C4'–C4A'–C9A'	120.5 (5)	C9A'–C4A'–C4B'	106.1 (4)
C4A–C4–C3	120.9 (5)	C9A–C4A–C4B	106.9 (4)
C5–C4B–C8A	118.2 (5)	C9A'–N'–C8A'	109.0 (4)

H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms at distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl, and methylene H atoms, respectively, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ of the parent atom for the methyl groups and $1.2U_{\text{eq}}(\text{C})$ for the remainder.

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: *ORTEP3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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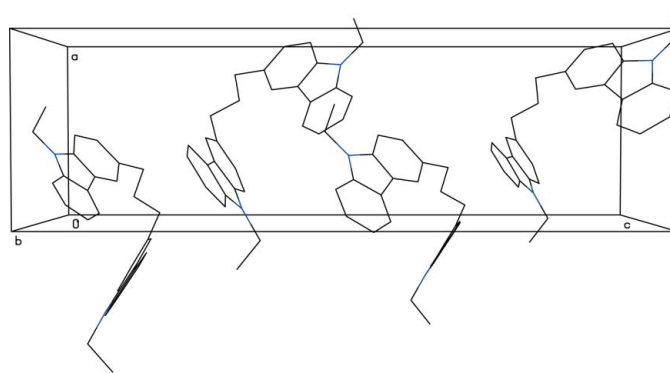


Figure 2

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

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