

Bis(9-ethylcarbazol-3-yl)methane

Erol Asker^{a*} and John Masnovi^b^aBalıkesir Üniversitesi, Necatibey Eğitim Fakültesi, 10100 Balıkesir, Turkey, and^bDepartment of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

Correspondence e-mail: asker@balikesir.edu.tr

Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.041

wR factor = 0.099

Data-to-parameter ratio = 6.7

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

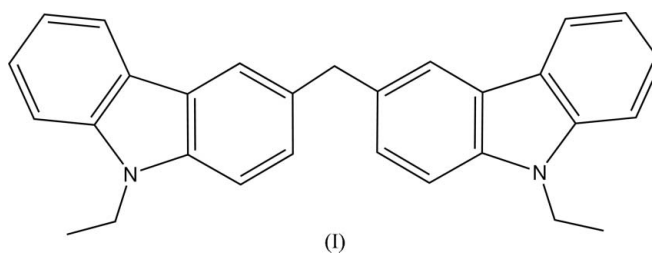
In the title compound, $\text{C}_{29}\text{H}_{26}\text{N}_2$, the carbazole ring systems are essentially planar. There is no indication of $\pi-\pi$ interactions in the crystal structure, adjacent carbazole groups being non-parallel.

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Comment

Poly(*N*-vinylcarbazole) (PVK), renowned as the first organic polymer, has found applications in electrophotography as a hole-transporting material and is among the most studied semi-conducting polymers (Loh *et al.*, 1991; Rocquin & Chevrot, 1997; Li *et al.*, 1998). It is believed that the orientation of the pendant carbazole groups along the polymer chain plays an important role in the photoconduction process (Turner & Pai, 1979). Time-resolved emission studies have been conducted on a number of bis(*N*-carbazolyl)alkanes and related compounds, the bichromophoric model compounds of PVK, to gain information about the photophysical properties of PVK (Klöpffer, 1969; Masuhara *et al.*, 1983; Cai & Edward, 1994). Single-crystal X-ray studies on several of these dimers have also been reported (Baker *et al.*, 1991). Recently, we have reported the crystal structure of 1,3-bis(9-ethylcarbazol-3-yl)propane as a model of poly(3-vinylcarbazole) (P3VK), a structural isomer of PVK (Asker & Masnovi, 2005). We report here the structure of the title compound, (I), another bichromophoric model compound of P3VK.



The carbazole ring systems in (I) (Fig. 1) are essentially planar, with r.m.s. deviations of 0.0158 (3) (primed ring) and 0.0292 (3) Å (unprimed ring). The dihedral angle between the planes of the carbazole ring systems is 85.12 (5)°. Bond distances and angles of the carbazole ring systems (Table 1) are in agreement with each other, as well as with those of related dicarbazoles reported in the literature (Baker *et al.*, 1991; Asker & Masnovi, 2005). The interior angles at the C3 [119.0 (3)°] and C3' [118.7 (3)°] centers attached to the methylene group are about 2° smaller than those at the C6 [121.0 (4)°] and C6' [121.4 (4)°] centers. The C2–C3 and C2'–C3' bonds are about 0.023 Å longer than the corresponding C6–C7 and C6'–C7' bonds. Similar differences were

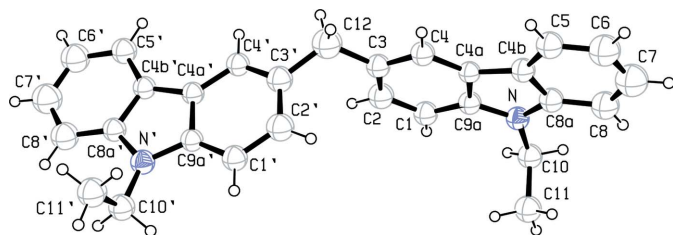


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level.

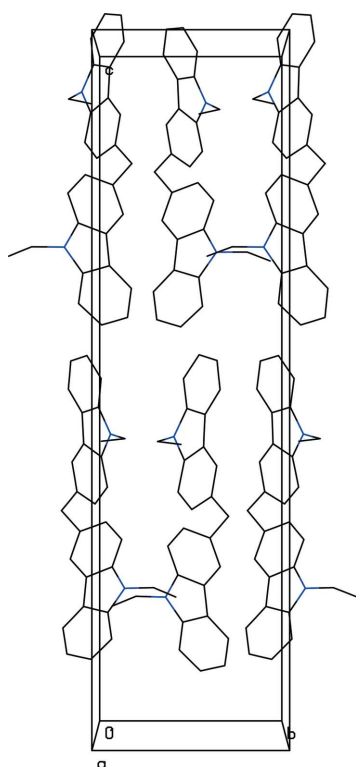


Figure 2
The molecular packing of (I), viewed down the *a* axis. H atoms have been omitted for clarity.

observed in the structure of 1,3-bis(9-ethylcarbazol-3-yl)propane (Asker & Masnovi, 2005). The torsion angles $C9a-N-C10-C11$ [$-83.1(4)^\circ$] and $C9a'-N'-C10'-C11'$ [$88.8(4)^\circ$] indicate that the *N*-ethyl substituents are almost perpendicular to the planes of the corresponding carbazole ring systems. The packing diagram (Fig. 2) shows no indication of π - π interactions, adjacent carbazole groups being non-parallel.

Experimental

The title compound, (I), was prepared *via* the acid-catalysed condensation of 9-ethylcarbazole with formaldehyde. In a 250 ml three-necked flask fitted with a magnetic stirrer bar, a solution was prepared from 9-ethylcarbazole (7.0 g, 0.036 mol), acetic acid (50 ml) and a catalytic amount of sulfuric acid (0.2 ml). Keeping this solution in an ice bath whilst stirring vigorously, formaldehyde (0.216 g,

0.0072 mol) dissolved in 3 ml of acetic acid was added dropwise using a dropping funnel over a 30 min period. The temperature was then raised to room temperature and the mixture was stirred for a further 5 min, during which time a beige precipitate formed. After filtration, washing with 0.5 l distilled water and drying, the crude product was column chromatographed using basic alumina (activity III, 80–200 mesh) as the stationary phase and dichloromethane–hexane (1:9 *v/v*) as the eluting solution. The title compound (1.23 g, 42.7% yield with respect to the amount of H_2CO used) was obtained as colorless blocks [m.p. 419–420 K from diethyl ether; literature m.p. 416–417 K (Bruck, 1970)], along with 0.70 g of polymer as white powder [m.p. around 463 K; literature 463–473 K (Bruck, 1970)]. 1H NMR (300 MHz, $CDCl_3$): δ 8.05 (*d*, 7.86 Hz, 2H), 7.98 (*s*, 2H), 7.47–7.30 (*m*, 8H), 7.18 (*t*, 6.76 Hz, 2H), 4.36 (*s*, 2H), 4.34 (*q*, 7.31 Hz, 4H), 1.41 (*t*, 7.31 Hz, 6H).

Crystal data

$C_{29}H_{26}N_2$
 $M_r = 402.52$
Orthorhombic, $Pna2_1$
 $a = 8.2889(6) \text{ \AA}$
 $b = 8.5229(8) \text{ \AA}$
 $c = 31.158(3) \text{ \AA}$
 $V = 2201.2(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.215 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 8.6\text{--}12.6^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
Block, colorless
 $0.40 \times 0.35 \times 0.28 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
Absorption correction: none
1884 measured reflections
1884 independent reflections
1432 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 25.1^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 36$
3 standard reflections
frequency: 120 min
intensity decay: 0.7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.099$
 $S = 1.03$
1884 reflections
280 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0628P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Table 1

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

$C4a-C4b$	1.441 (4)	$C3'-C2'$	1.407 (6)
$C4a'-C4b'$	1.430 (5)	$C1'-C2'$	1.381 (5)
$C2-C1$	1.373 (5)	$C7-C6$	1.384 (6)
$C2-C3$	1.409 (5)	$C7'-C6'$	1.384 (7)
$C1'-C9a'-C4a'$	121.1 (3)	$C1-C9a-C4a$	121.3 (3)
$N'-C9a'-C4a'$	108.6 (3)	$C9a'-C1'-C2'$	117.7 (3)
$N'-C8a'-C4b'$	108.9 (3)	$C4-C3-C2$	119.0 (3)
$C1-C2-C3$	122.1 (4)	$C1'-C2'-C3'$	122.5 (4)
$C4'-C3'-C2'$	118.7 (3)	$C2-C1-C9a$	118.1 (3)
$N-C8a-C4b$	109.5 (3)	$C5-C6-C7$	121.0 (4)
$N-C9a-C4a$	109.5 (3)	$C7'-C6'-C5'$	121.4 (4)
$C9a-N-C10-C11$	$-83.1(4)$	$C9a'-N'-C10'-C11'$	$88.8(4)$

H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms at distances of 0.93, 0.96 and 0.97 \AA for aromatic, methyl and methylene H atoms, respectively, with U_{iso}

(H) = $1.5U_{\text{eq}}(\text{C})$ for the parent atom for the methyl groups and $1.2U_{\text{eq}}(\text{C})$ for the others.

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).

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