Crystal structure of (*E*)-1,2-*bis*(9-hexyl-9*H*-carbazol-3-yl)ethene, $C_{38}H_{42}N_2$

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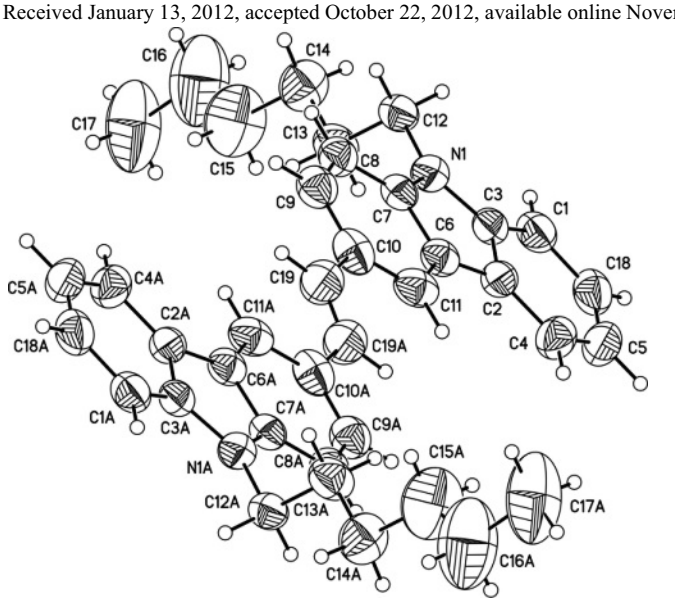

Abstract

$C_{38}H_{42}N_2$, monoclinic, $P2_1/c$ (no. 14), a = 5.1381(4) Å, b = 14.238(1) Å, c = 21.372(2) Å, β = 92.359(4)°, V = 1562.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.0863, $wR_{ref}(F^2)$ = 0.2868, T = 130(2) K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.35×0.42×0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.64 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13960, 3584
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2188
$N(param)_{refined}$:	183
Programs:	SHELX [13], WinGX [14]

Source of material

9-hexyl-9*H*-carbazole-3-carbaldehyde (2): Phosphorous oxide chloride ($POCl_3$) (1.17 ml, 12.55 mmol) was added dropwise to dimethylformamide (DMF) (1.13 ml, 14.60 mmol) at 0°C under an argon atmosphere. Then, the solution of hexylcarbazole (3.145 g, 12.50 mmol) in dry $CHCl_3$ (7.5ml) was added to the reaction flask, and the reaction mixture was refluxed for 16h and cooled to room temperature. The reaction mixture was then poured into ice water and neutralized with sodium bicarbonate to pH 8. The aqueous solution was extracted with chloroform several times. The chloroform solution was washed with water, and dried with anhydrous sodium sulfate. After filtration, the solvent was removed. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 24/1, *v*/*v*) to give compound **2** (2.551 g, 73.0%).

^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 10.10 (s, 1H; CHO), 8.62 (d, J=1.5 Hz, 1H; Ar-H), 8.16 (d, J = 7.8 Hz, 1H; Ar-H), 8.01 (dd, J = 8.6 Hz, 1H; Ar-H), 7.57-7.44 (m, 3H; Ar-H), 7.33 (m, 1H; Ar-H), 4.34 (t, J = 7.2 Hz, 2H; Hexyl-H), 1.90 (m, 2H), 1.38-1.25 (m, 6H; Hexyl-H), 0.87 ppm (t, J = 7.1 Hz, 3H; Hexyl-H); **^{13}C NMR** (75 MHz, $CDCl_3$, 25°C, TMS): δ = 191.22, 143.58, 140.68, 128.02, 126.63, 126.18, 123.46, 122.57, 122.51, 120.22, 119.77, 108.87, 108.42, 42.93, 30.99, 28.38, 26.40, 21.99, 13.44 ppm; **FTIR**: $\tilde{\nu}$ = 1688 cm^{-1};

elemental analysis: calcd (%) for $C_{19}H_{21}NO$: C 81.68, H 7.58, N 5.01; found: C 81.66, H 7.63, N 4.94.

(*E*)-1,2-*bis*(9-hexyl-9*H*-carbazol-3-yl)ethene (1): To a suspension of the Zn powder (5.182 g, 79.2 mmol) in dry THF (200 ml), $TiCl_4$ (4.42 ml, 40.21 mmol) was added by syringe at 0°C under an argon atmosphere. After addition of pyridine (3.2 ml), the suspension was refluxed at 80°C for 2h. A solution of compound **2** (1.120 g, 4.01 mmol) in dry THF (100ml) was then added dropwise over 1.5h to the gently refluxing suspension. The resulting mixture was refluxed continuously with stirring for 24h, and after cooling to room temperature, the saturated aqueous $NaHCO_3$ (200ml) was added. The reaction mixture was filtered, and the filtrate was extracted with CH_2Cl_2 several times. Then, the CH_2Cl_2 solution was washed with water, dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/CH_2Cl_2, 1/2, *v*/*v*) on silica gel to give compound **1** (0.655 g, 62.0%). **m.p.** 191°C; **^{1}H NMR** (300 MHz, $CDCl_3$, 25°C, TMS): δ = 8.27 (d, J = 1.2 Hz, 2H; Ar-H), 8.15 (d, J = 7.5 Hz, 2H; Ar-H), 7.72 (dd, J = 8.6 Hz, 2H; Ar-H), 7.50-7.44 (m, 2H; Ar-H), 7.39 (t, J = 7.8 Hz, 6H; Ar-H), 7.28-7.22 (m, 2H; Ar-H), 4.30 (t, J = 7.4 Hz, 4H; Hexyl-H), 1.88 (m, 4H; Hexyl-H), 1.41-1.29 (m, 12H; Hexyl-H), 0.87 ppm (t, J = 7.1 Hz, 6H; Hexyl-H); **^{13}C NMR** (75 MHz, $CDCl_3$, 25°C, TMS): δ = 140.86, 139.97, 129.22, 127.06, 125.66, 124.23, 123.00, 120.41, 118.85, 118.22, 116.93, 108.83, 108.12, 43.22, 31.59, 28.99, 26.98, 22.54, 13.99 ppm; **FTIR**: $\tilde{\nu}$ = 3017, 1677 cm^{-1}; **HRMS** (MALDI-TOF): *m*/*z*: calcd for $C_{38}H_{42}N_2$: 526.33; found: 526.13;

elemental analysis calcd (%) for $C_{38}H_{42}N_2$: C 86.65, H 8.04, N 5.32; found: C 86.57, H 8.05, N 5.26. The crystal was obtained by Crystallization of compound **1** from the dichloromethane and *n*-hexane mixed solution.

Discussion

In recent years, carbazole-based oligomers and polymers, characterized by good molecular planarity, versatility in functionalization and chemical and environmental stability, have been intensively investigated in the fields such as organic field-effect transistors (OFETs), organic light-emitting diodes

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(OLEDs), and photovoltaic devices [1-7]. With the increase of the conjugated system, these materials exhibit enhanced carrier mobilities and adjusted luminescences as well. Unfortunately, the problem of poor solubility occurs subsequently, which gravely hinders the processibilites. *N*-alkyl substituted carbazole-based host materials are a promising class due to satisfactory solubilites. Moreover, it was reported that the suitable length of alkyl chains greatly improved the mobilties of the target materials [8-9]. In this paper, (*E*)-1,2-*bis*(9-hexyl-9*H*-carbazol-3-yl)ethene (**1**) was synthesized by McMurry reaction. The rigidity and conjugated system of carbazole was enhanced by the vinyl connection. At the same time, the introduction of the hexyl group increased the solubility as well as the capacity of self-assembling. All these might improve performance of the target compound to certain extent. Obviously, knowledge of the structural parameters and the intra- and intermolecular interactions is inevitable to a better understanding of structure-properties relationships that contribute to explore strategies for novel materials with excellent performances more conveniently. The title compound (*E*)-1,2-*bis*(9-hexyl-9*H*-carbazol-3-yl)ethene (**1**), crystallizes in the monoclinic centrosymmetric space group $P2_1/c$. There are two molecules in the unit cell with a half of **1** per asymmetric unit. Each carbazole skeleton is nearly planar with a slight distortion. The mean deviation of framework atoms from the plane for both carbazoles is 0.0065 Å. The planes of the two carbazole rings are parallel with a dihedral angle of 0.0°. **1** adopts an *anti* conformation with respect to the C19–C19A bond. Bond lengths and angles in **1** accord with those of related dicarbazoles reported in the literature [10-12]. The structure is stabilized by vander Waals forces and weak C–H···D interactions. Classic C–H···D interactions are C5–H5···Cg1(i) = 3.36 Å and C8–H8···Cg2(ii) = 3.42 Å, where Cg1 and Cg2 are centroids of benzene rings containing C6, C7, C8, C9, C10, C11, and C1, C2, C3, C4, C5, C18, respectively [symmetry code: (i) 1-x,½+y,½-z; (ii) -x,-½+y,½-z]. No classic intermolecular D–D interactions are found between the carbazole groups.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9)	4*e*	0.011	0.4318	0.4148	0.104
H(11)	4*e*	0.5634	0.6282	0.4092	0.102
H(1)	4*e*	0.1229	0.7322	0.146	0.102
H(8)	4*e*	–0.1537	0.474	0.3186	0.097
H(4)	4*e*	0.6988	0.7716	0.3192	0.11
H(5)	4*e*	0.7337	0.8629	0.2315	0.122
H(12A)	4*e*	–0.2229	0.6282	0.1762	0.094
H(12B)	4*e*	–0.293	0.5506	0.2248	0.094
H(13A)	4*e*	0.0972	0.5291	0.1371	0.119
H(13B)	4*e*	0.0217	0.4514	0.1849	0.119
H(14A)	4*e*	–0.3006	0.5146	0.0848	0.141
H(14B)	4*e*	–0.392	0.442	0.1346	0.141
H(17A)	4*e*	0.0425	0.2893	–0.0199	0.353
H(17B)	4*e*	–0.2204	0.236	–0.0341	0.353
H(17C)	4*e*	–0.057	0.2154	0.028	0.353
H(15A)	4*e*	0.0268	0.4082	0.0553	0.233
H(15B)	4*e*	–0.0669	0.3361	0.1043	0.233
H(16A)	4*e*	–0.3186	0.3872	0.0011	0.314
H(16B)	4*e*	–0.4103	0.314	0.0501	0.314
H(19)	4*e*	0.3057	0.4388	0.5032	0.122
H(18)	4*e*	0.4535	0.8439	0.1455	0.118

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(7)	4*e*	0.1071(5)	0.5778(2)	0.3043(1)	0.063(1)	0.069(2)	0.074(2)	0.012(1)	0.008(1)	–0.002(1)
C(2)	4*e*	0.3913(5)	0.6961(2)	0.2859(1)	0.066(2)	0.068(2)	0.085(2)	0.002(1)	0.011(1)	–0.014(1)
C(3)	4*e*	0.2184(5)	0.6854(2)	0.2337(1)	0.066(1)	0.064(1)	0.085(2)	0.008(1)	0.012(1)	0.003(1)
C(6)	4*e*	0.3212(5)	0.6260(2)	0.3311(1)	0.070(2)	0.074(2)	0.070(2)	0.011(1)	0.011(1)	–0.011(1)
C(10)	4*e*	0.3017(7)	0.5238(2)	0.4215(1)	0.106(2)	0.086(2)	0.065(2)	0.025(2)	0.024(2)	0.006(1)
C(9)	4*e*	0.0900(6)	0.4804(2)	0.3935(2)	0.090(2)	0.084(2)	0.087(2)	0.010(2)	0.015(2)	0.004(2)
C(11)	4*e*	0.4200(6)	0.5977(2)	0.3906(1)	0.075(2)	0.101(2)	0.078(2)	0.016(2)	0.001(1)	–0.025(2)
C(1)	4*e*	0.2376(6)	0.7399(2)	0.1805(2)	0.083(2)	0.081(2)	0.093(2)	0.015(2)	0.008(2)	0.013(2)
C(8)	4*e*	–0.0095(6)	0.5051(2)	0.3363(1)	0.079(2)	0.076(2)	0.088(2)	0.006(1)	0.013(2)	0.002(1)
C(4)	4*e*	0.5841(6)	0.7632(2)	0.2848(2)	0.091(2)	0.083(2)	0.102(2)	–0.010(2)	0.018(2)	–0.018(2)
C(5)	4*e*	0.6038(7)	0.8175(2)	0.2324(2)	0.096(2)	0.077(2)	0.133(3)	–0.016(2)	0.029(2)	–0.015(2)
N(1)	4*e*	0.0456(4)	0.6141(2)	0.2456(1)	0.068(1)	0.074(1)	0.080(1)	0.002(1)	–0.000(1)	0.004(1)
C(12)	4*e*	–0.1520(5)	0.5771(2)	0.2016(1)	0.067(2)	0.080(2)	0.087(2)	0.008(1)	–0.004(1)	–0.001(1)
C(13)	4*e*	–0.0465(7)	0.5027(3)	0.1593(2)	0.091(2)	0.103(2)	0.102(2)	0.017(2)	0.000(2)	–0.019(2)
C(14)	4*e*	–0.2422(8)	0.4647(3)	0.1129(2)	0.131(3)	0.120(3)	0.102(3)	–0.009(2)	0.003(2)	–0.022(2)
C(17)	4*e*	–0.109(2)	0.2631(5)	–0.0017(3)	0.42(1)	0.150(5)	0.141(5)	–0.013(6)	0.093(6)	–0.046(4)
C(15)	4*e*	–0.127(2)	0.3835(5)	0.0744(3)	0.259(8)	0.192(6)	0.130(4)	–0.018(5)	–0.007(4)	–0.072(4)
C(16)	4*e*	–0.258(2)	0.3414(6)	0.0320(4)	0.42(2)	0.177(7)	0.194(7)	–0.022(9)	0.048(8)	–0.035(6)
C(19)	4*e*	0.4018(6)	0.4863(3)	0.4853(2)	0.098(2)	0.096(2)	0.112(3)	–0.005(2)	0.032(2)	–0.021(2)
C(18)	4*e*	0.4344(7)	0.8063(2)	0.1806(2)	0.105(2)	0.074(2)	0.120(3)	0.011(2)	0.037(2)	0.017(2)

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