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Synthesis and charge-transfer complex formations of 1,n-bis(3,6-diethylcarbazol-9-yl)alkanes with three π -acceptors

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HIGHLIGHTS

- ▶ 1,*n*-Bis(3,6-diethylcarbazol-9-yl)alkanes (n = 1-5) as the π -donors were prepared.
- ▶ They formed charge-transfer (CT) complexes with three π -acceptors were observed.
- ▶ Thermodynamic properties of the complexes were determined.
- ▶ Single crystal X-ray structures of the two of the donor molecules were determined.

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$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

Dimeric 1,*n*-bis(3,6-diethylcarbazol-9-yl)alkanes (where *n* = 1–5) were synthesized and their structures were characterized via spectroscopic techniques. Structures of two of the dimers, 1,2-bis(3,6-diethylcarbazol-9-yl)ethane (**2b**) and 1,4-bis(3,6-diethylcarbazol-9-yl)butane (**2d**), were investigated by single crystal X-ray crystallographic techniques. The crystal structures of **2b** and **2d** were solved in the monoclinic space groups C2/*c* and *P*2₁/*n*, respectively. The methylene chain adopted an anti conformation in **2b** and a gauche-anti-gauche conformation in **2d**, enabling coplanar orientations of carbazoler rings in both structures. The molecular packing in both structures was stabilized by intermolecular π - π stacking. Charge transfer complexations of **2a-2e** with the π -acceptors *p*-chloranil, tetracyanoethylene, and tetracyanoquinodimethane in solution were investigated by determining their stoichiometries, molar absorptivities, equilibrium constants, enthalpies, and entropies. All the dimers formed weakly associated complexes with each of the acceptors having equilibrium constants between 1.32–8.94 M⁻¹ in 1,2-dichloroethane. Complexations were driven by the slightly negative formation enthalpies between -2.00 and -4.24 kcal mol⁻¹.

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1. Introduction

Derivatives of naturally occurring carbazole are of interest for two main reasons: one is due to their pharmacological activities such as antibacterial, antifungal [1,2], anti-HIV, and anticancer activities [3,4] and the other is their uses in industry and material sciences due to their photoconducting properties [5–8]. Charge transfer (CT) complexations of carbazole donors with certain electron acceptors gratefully enhance their photoconduction properties. In fact, the first industrially used organic photoconductor is a CT complex between poly-9-vinylcarbazole (PVK) and trinitrofluorenone (TNF) [9]. There are numerous studies conducted on the CT complexations of PVK with various electron acceptor molecules [10–15]. Studying CT complexations of polymeric systems has its drawbacks due to their low solubility. To overcome this limitation researchers have used their dimeric model compounds to attain information about their complexations. For this purpose, studies on CT complexations of dianthrylalkanes and dicarbazolylalkanes had been conducted and their results had been published [16-19]. In our previous works we have reported the results of the studies on CT complexations of 1,n-di(9-ethylcarbazol-3-yl)alkanes [20] and 1,n-di(3-methylcarbazol-9-yl)alkanes [21]. We propose that electron donor alkyl groups would increase the electron affinity (E_a) of carbazole chromophore and result in higher equilibrium constants, K, and lower enthalpies of formation, $\Delta H_{\rm f}$. In this contribution we extend our work to the syntheses and CT complexations of 1,*n*-bis(3,6-diethylcarbazol-9-yl)alkanes, in which each carbazole groups are separated with 1-5 -CH₂- groups and carry two ethyl groups on the C3 and C6 positions. We have included two monomeric analogues, 9-ethylcarbazole (1a) and 3,6,9-triethylcarbazole (1b) for comparisons. As the electron acceptors, tetracyanoethylene, (TCNE), para-chloranil, (p-CHL), and tetracyanoquinodimethane (TCNQ) were selected. Structures of the donor and acceptor molecules discussed in the present study are given in Scheme 1.





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Scheme 1. Synthesis and structures of the title donor and acceptor compounds.

2. Experimental

2.1. Instrumentation

¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer using tetramethylsilane (TMS) as the internal reference and CDCl₃ as the solvent. IR spectra were taken on a Perkin Elmer Spectrum 100 FT-IR spectrometer using attenuated total reflection (ATR) sampling. Electronic absorption measurements were recorded on a PG Instruments T80 + double beam UV–Visible spectrophotometer in 3.5 ml, 1.0 cm path length optical quartz cells with polytetrafluoroethylene (PTFE) stopper. The instrument was equipped with a PTC-2 peltier temperature controller to perform temperature studies.

2.2. Synthesis

2.2.1. Synthesis of 3,6,9-triethylcarbazole (1b)

Commercially available 9-ethylcarbazole (**1a**) was diacetylated according to the general procedure described in the literature [22]. To a mixture of 9.75 g (50 mmol) of **1a**, 16.0 g of (~0.12 mol) AlCl₃, and 150 ml of dry CS₂ was added 15.0 g of acetyl bromide (~0.12 mol) drop-wise under an anhydrous atmosphere in an ice bath. After refluxing for 3 h, the solvent was evaporated off and the residue was treated with ice-dilute HCl, filtered and washed with distilled water. 9-Ethyl-3,6-diacetylcarbazole was obtained as pale yellow crystals (7.2 g) after recrystallization from acetone (m.p. 184–186 °C; lit. [22] 184–190 °C). 9-Ethyl-3,6-diacetylcarbazole was reduced via Clemmensen reduction reaction [23].

A mixture of HgCl₂ (500 mg), Zn powder (10.0 g), concentrated HCl (2.5 ml, %36) and water (50 ml) was stirred at ambient temperature for 15 min to amalgamate pulverized zinc. Then, the liquid phase was decanted and the zinc amalgam was washed three times with 25 ml of water. To this, conc. HCl (50 ml) and 9-Ethyl-3,6diacetylcarbazole were added and the mixture was stirred for 2 h. Toluene (50 ml) was added and the mixture was refluxed for 12 h, during which time three times 10 ml of conc. HCl was added to the flask. Then, the content of the flask was cooled to room temperature and the resultant phases were separated, the aqueous phase was washed with benzene and the organic phases were combined, washed with water, dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was chromatographed over a silicagel column using hexane/CH₂Cl₂ (10:1) as eluent and recrystallized from methanol to give **2b** as colorless crystals (47% yield, m.p. 84 °C; lit. [24] 84-86 °C).

2.2. Syntheses of 1,n-bis(3,6-diethylcarbazol-9-yl)alkanes (2a-2e)

Carbazole, recrystallized from aceton, (16.7 g) was diacetylated according to the same procedure described above to yield 3,6-diacetylcarbazole (15.6 g; 62.2%; m.p. 234, lit. [25] 235–237 °C). Clemmensen reduction of 3,6-diacetylcarbazole (12.5 g) yielded 5.8 g (63.0%; m.p. 119 °C) of 3,6-diethylcarbazole as colorless crystals after column chromatography (silica gel, 10:1 v/v hexane/acetone as eluent) and recrystallization from aceton.

Syntheses of **2a**, **2c–2e** were achieved via nucleophilic substitution reactions between 3,6-diethylcarbazol-9-ide nucleophile and corresponding 1,*n*-dibromoalkane substrates. In the case of **2b**,

bromides had to be replaced with *p*-toluenesulfonate (-OTs) due to very slow reaction rate. Procedure for the synthesis of **2c** is given here as an example. KOH (0.5 g) was added to a stirred solution of 1.0 g (4.48 mmol) of 3,6-diethylcarbazole in 25 ml of acetone at RT. To this 0.39 g (2.24 mmol) of CH_2Br_2 was added and the resulting mixture was refluxed for 2 h; then the content of the flask was poured onto crushed ice, filtered, washed with water and air dried. The crude product was purified by column chromatography (silica gel) using 20:1 v/v hexane/CH₂Cl₂ as eluent and recrystallized from CH₂Cl₂ to give **2a** as colorless, fine needles.

Bis(3,6-diethylcarbazol-9-yl)methane (**2a**): 72%, m.p. 254 °C; FTIR (ATR) \bar{u} (cm⁻¹): 3052, 3025, 2970. 2953, 2864, 1610, 1492, 1493, 1463, 1367, 1309, 1229, 1216, 1156, 1053, 872, 806, 752, 677; ¹H NMR (300 MHz, CDCl₃), δ: 7.89 (s, 4H), 7.36 (d, *J* = 8.50 Hz, 4H), 7.22 (d, *J* = 8.50 Hz, 4H), 6.53 (s, 2H), 2.80 (q, *J* = 7.61 Hz, 8H), 1.32 (t, *J* = 7.61 Hz, 12H); ¹³C NMR: (75 MHz, CDCl₃) δ: 139.1, 135.9, 126.5, 123.9, 119.4, 109.3, 53.0, 29.1, 16.7; UV–Vis, (1,2dichloroethane), λ_{max}/nm ($\varepsilon \times 10^{-3} 1 mol^{-1} cm^{-1}$): 264 (31.6), 298 (36.3), 332 (9.1), 346 (9.7).

1,2-Bis(3,6-diethylcarbazol-9-yl)ethane (**2b**): 54%, m.p. 178 °C; FTIR (ATR) \bar{u} (cm⁻¹): 3054, 3025, 2960, 2924, 2859, 1609, 1489, 1475, 1453, 1361, 1307, 1258, 1197, 1142, 1055, 883. 796, 740, 657; ¹H NMR (300 MHz, CDCl₃), δ : 7.89 (s, 4H), 7.35 (d, J = 8.44 Hz, 4H), 7.21 (d, J = 8.48 Hz, 4H), 4.58 (s, 4H), 2.85 (q, J = 7.61 Hz, 8H), 1.35 (t, J = 7.61 Hz, 12H); ¹³C NMR: (75 MHz, CDCl₃) δ : 139.1, 135.4, 126.3, 123.5, 119.5, 108.0, 41.3, 29.2, 16.9; UV–Vis, (1,2-dichloroethane), λ_{max}/nm ($\varepsilon \times 10^{-3} 1 \text{ mol}^{-1} \text{ cm}^{-1}$): 266 (43.8), 300 (40.1), 340 (9.6), 354 (10.7).

1,3-Bis(3,6-diethylcarbazol-9-yl)propane (**2c**): 67%, m.p. 61 °C; FTIR (ATR) \bar{u} (cm⁻¹): 3047, 3014, 2959, 2927, 2869, 1609, 1492, 1472, 1453, 1376, 1345, 1323, 1262, 1247, 1219, 1192, 1148, 1056, 993, 875, 803, 748, 722; ¹H NMR (300 MHz, CDCl₃), δ : 7.89 (s, 4H), 7.25 (d, *J* = 8.42 Hz, 4H), 7.16 (d, *J* = 8.51 Hz, 4H), 4.24 (t, *J* = 7.64 Hz, 4H), 2.82 (q, *J* = 7.64 Hz, 8H), 2.39 (quintet, *J* = 7.63 Hz, 2H), 1.32 (t, *J* = 7.63 Hz, 12H); ¹³C NMR: (75 MHz, CDCl₃) δ : 139.2, 135.1, 126.1, 123.3, 119.4, 108.4, 41.0, 29.2, 28.3, 16.9; UV–Vis, (1,2-dichloroethane), λ_{max}/mm ($\varepsilon \times 10^{-3} 1 mol^{-1} - cm^{-1}$): 266 (43.2), 300 (38.6), 340 (9.1), 354 (8.4).

1,4-Bis(3,6-diethylcarbazol-9-yl)butane (**2d**): 67%, m.p. 141 °C; FTIR (ATR) \bar{u} (cm⁻¹): 3048, 3014, 2957, 2925, 2861, 1609, 1576, 1491, 1476, 1450, 1350, 1325, 1307, 1256, 1215, 1179, 1147, 1056. 884, 798, 755, 735; ¹H NMR (300 MHz, CDCl₃), δ : 7.89 (s, 4H), 7.24 (d, *J* = 8.49 Hz, 4H), 7.16 (d, *J* = 7.49 Hz, 4H), 4.12 (s, 4H), 2.82 (q, *J* = 7.62 Hz, 8H), 1.90 (s, 4H), 1.35 (t, *J* = 7.62 Hz, 12H); ¹³C NMR: (75 MHz, CDCl₃) δ : 139.3, 134.9, 126.0, 123.1, 119.3, 108.6, 43.0, 29.2, 27.2, 16.8; UV–Vis, (1,2-dichloroethane), λ_{max}/nm ($\epsilon \times 10^{-3} 1 \text{ mol}^{-1} \text{ cm}^{-1}$): 268 (37.6), 300 (31.4), 342 (7.1), 356 (7.9).

1,5-Bis(3,6-diethylcarbazol-9-yl)pentane (**2e**): 78%, m.p. 99 °C; FTIR (ATR) \bar{u} (cm⁻¹): 3048, 3014, 2960, 2933, 2965, 1608, 1575, 1491, 1475, 1456, 1351, 1326, 1268, 1251, 1234, 1203, 1172, 1150, 1057, 882, 803, 752, 724; ¹H NMR (300 MHz, CDCl₃), δ : 7.92 (s, 4H), 7.29 (d, *J* = 7.76 Hz, 4H), 7.25 (d, *J* = 7.76 Hz, 4H), 4.20 (t, *J* = 7.04 Hz, 4H), 2.86 (q, *J* = 7.32 Hz, 8H), 1.88 (quintet, *J* = 7.62 Hz, 4H), 1.46 (quintet, *J* = 6.61 Hz, 2H), 1.37 (t, *J* = 7.32 Hz, 12H); ¹³C NMR: (75 MHz, CDCl₃) δ : 139.3, 134.8, 126.0, 123.0, 119.3, 108.5, 43.1, 29.2, 25.3, 16.8; UV–Vis, (1,2-dichloroethane), λ_{max}/nm ($\epsilon \times 10^{-3}1 \text{ mol}^{-1} \text{ cm}^{-1}$): 268 (45.3), 300 (35.7), 342 (8.7), 356 (8.7).

2.3. Single-crystal X-ray diffraction measurements

The single crystals were grown from 1:1 dichloromethane/hexane solution. X-ray diffraction measurements of the compounds **2b** and **2d** were carried out at ambient temperature on a Rigaku RAX-IS-RAPID S diffractometer equipped with CCD detector, using Mo Kα radiation [26]. The program used for data collection and cell refinement: CrystalStructure [27]; data reduction: SORTAV [28]; structure solution: SIR92 [29]; structure refinement with direct methods: SHELXL97 [30]; molecular graphics: ORTEP-3 for Windows [31] and Mercury CSD 2.0 [32]; preparation of materials for publication: WinGX [33]. All non-hydrogen atoms were found from E-map and refined anisotropically; the hydrogen atoms were positioned geometrically from the difference Fourier map and allowed to ride on their corresponding parent atoms with C-H distances of 0.93 Å (aromatic), 0.96 Å (methyl), and 0.97 Å (methylene) with Uiso(H) = 1.5Ueq(C) of the parent atom for the methyl group and 1.2Ueq(C) for the rest. The crystal data and details of the data collection and refinement for the compounds are given in Table 1. CCDC numbers 915656 (2b) and 915657 (2d) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

2.4. Absorption measurements

2.4.1. Determination of complexation stoichiometries

The stoichiometries of the complexations of the donor molecules with the three π -acceptors were determined using Job's plots (method of continuous variation) [34]. In 10 ml volumetric flasks, 10 mM of carbazole donor unit (i.e. 5 mM dicarbazoles) and 10 mM of acceptor molecules in 1,2-dichloroethane were prepared separately. These solutions were mixed in 2.0 ml volumetric flasks where the total concentration of the components held constant while their mole fractions differed from 0.1 to 0.9. Acceptor solu-

Table 1

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Summary of general and crystal data with data collection and structure refinement of **2b** and **2d**.

Compound	2b	2d
Empirical formula	C34H36N2	C ₃₆ H ₄₀ N ₂
Formula weight	472.65 g/mol	500.70 g/mol
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
Unit cell dimensions		
Α	22.9058(9)Å	12.4306(7) Å
В	7.0733(2) Å	9.0721(4) Å
С	17.0765(8)Å	13.6954(3) Å
В	97.7671(23)°	109.598(27)°
Volume	2741.34(18) Å ³	1454.98(14) Å ³
Ζ	4	2
Calculated density	1.145 g/cm ³	1.143 g/cm ³
Absorption coefficient	0.066 mm^{-1}	0.066 mm^{-1}
F(000)	1016	540
Crystal size	$0.7\times0.5\times0.2~mm$	$0.6\times0.5\times0.3~mm$
θ Range for data	3.02-30.03°	2.71-25.14°
collection		
Limiting indices		
	$-32 \leqslant h \leqslant 31$	$-14 \leqslant h \leqslant 14$
	$0 \leqslant k \leqslant 10$	$0 \leqslant k \leqslant 10$
	$0 \leqslant l \leqslant 24$	$0 \leqslant l \leqslant 16$
Reflections collected/	39953/3997	28160/2578
unique	[R(int) < 0.0341]	[R(int) < 0.001]
Refinement method	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²
Data/restraints/	3997/0/73	2578/0/77
Goodness-of-fit on F^2	2 637	2 405
Final R indices	$R_1 = 0.2044$	$R_1 = 0.1494$
$[I > 2\sigma(I)]$	$wR_2 = 0.6061$	$wR_2 = 0.5325$
R indices (all data)	$R_1 = 0.2075.$	$R_1 = 0.1529.$
it malees (an autu)	$wR_2 = 0.6087$	$wR_2 = 0.5367$
Largest diff neak and	0.113 and -0.421 e Å ⁻³	$0.075 \text{ and } -0.487 \text{ e} ^{\text{A}-3}$
hole	0,115 and -0,421 c A	5.575 and -0.467 CM



Fig. 1. ORTEP drawings of 2b and 2d with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Table 2	
Selected bond lengths (Å), bond and torsion	angles (°) for the compounds $\mathbf{2b}$ and $\mathbf{2d}$.

2b		2d	
C1-C9a	1.386 (5)	C1-C9a	1.390 (7)
C3-C11	1.502 (7)	C3-C12	1.526 (9)
C4A-C4a	1.462 (4)	C4a-C4b	1.426 (6)
C6-C13	1.507 (7)	C6-C14	1.503 (8)
N9-C10	1.435 (5)	N9-C10	1.466 (6)
C10-C10 ⁱ	1.535 (7)	C11-C11 ⁱ	1.501 (9)
C9A-C1-C2	116.5 (4)	C2-C1-C9a	115.9 (5)
C1-C2-C3	123.9 (4)	C1-C2-C3	123.8 (6)
C2-C3-C4	118.0 (4)	C2-C3-C4	119.2 (5)
C8a-C4b-C4a	105.6 (3)	C8a-C4b-C4a	106.4 (4)
C6-C7-C8	122.8 (4)	C8a-C6-C7	123.0 (5)
C7-C8-C8a	116.6 (4)	C8a-C8-C7	117.8 (5)
N9-C8a-C4b	109.6 (3)	N9-C8a-C4b	108.4 (4)
C9a-N9-C8a	108.1 (3)	C9a-N9-C8a	109.2 (4)
C9a-N9-C10-C10 ⁱ	93.1 (5)	C9a-N9-C10-C11	-83.1 (6)
C8a-N9-C10-C10 ⁱ	-89.2 (5)	C8a-N9-C10-C11	101.8 (5)
C2-C3-C11-C12	90.4 (6)	C2-C3-C12-C13	67.8 (9)
C4-C3-C11-C12	-86.8(6)	C4-C3-C12-C13	-108.0(8)
C5-C6-C13-C14	89.8 (7)	C5-C6-C14-C15	-103.6 (7)
C7-C6-C13-C14	-82.9 (7)	C7-C6-C14-C15	74.7 (7)

Symmetry code: (i) -x + 3/2, -y - 1/2, -z. Symmetry code: (i) -x + 1, -y, -z + 2.

tions of the same concentration, as they were in the complex solution, were used as the blank to eliminate the absorption due to the acceptor. The average absorptions of three scans at λ_{max} of the CT complexes were used in the plots.

2.4.2. Determination of molar absorptivities and complexation constants

For the determination of molar absorptivity, ε , and equilibrium constant, *K*, values of CT complexations, Benesi–Hildebrand technique was used [35]. Stock solutions of 0.6 mM of carbazole unit (i.e. 0.6 mM monomers and 0.3 mM dimmers) were prepared in 25 ml flasks. Another solution containing 0.6 mM carbazole unit and 60 mM TCNE was prepared in a 2 ml flask and 1 ml of this was transferred into a quartz UV cell using a 250 µl syringe. This solution was diluted with 250 µl, 0.6 mM donor solution 10 times. After each dilution absorbances at three data points around λ_{CT} were recorded in three scans. In the complexations where *p*-CHL and TCNQ were acceptors, due to their low solubilities, the concen-



Fig. 2. Diagrams showing π - π overlaps in the structures of **2b** and **2d**.

trations of the donor molecules were kept high and diluted with 0.6 mM acceptor solutions.

2.4.3. Determination of enthalpy and entropy changes of complexations

The enthalpy and entropy changes (ΔH and ΔS) of complex formations were determined using the van't Hoff equation. In 2.0 ml volumetric flasks, solutions containing 5 mM acceptor and 5 mM carbazole unit at 25.0 °C in 1,2-dichloroethane were prepared. Absorbances of the complexes at 10–45 °C (±0.1 °C) in 5 °C intervals, at three data points around λ_{CT} were recorded at three independent scans. When the solvent was dichloromethane



Fig. 3. Molecular packing diagrams of 2b and 2d. Color changes represent the halves generated by symmetry operations. H atoms have been omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Representation of CT process between HOMO's of an electron donor and LUMO of an electron acceptor molecule.

absorbances were recorded at temperatures ranging between 7 and 32 °C (±0.1 °C) in 5 °C intervals. Concentration changes due to the expansion/contraction of the solvents [36] at changing temperatures were taken into account in calculating the thermodynamic constants.

3. Results and discussion

3.1. Synthesis of the donor compounds

For the diacetylation of carbazole, which exhibits the chemical behaviors of secondary aromatic amines, was achieved via Friedel–Crafts method. Nagai and Huang [24] proved that using acetyl bromide instead of acetyl chloride gives much higher yield of 3,6-diacetylcarbazole compared to monoacetylated derivative in CS₂. This is considered due to the weaker C–Br bond in acetyl bromide than C–Cl bond in acetyl chloride and stabilization of acylium ion by the polar solvent. 3,6-Diacetylcarbazole was easily reduced to 3,6-diethylcarbazole via Clemmensen reduction reaction. Synthesis of bis(3,6-diethylcarbazol-9-yl)alkanes were achieved via nucleophilic substitution reaction of 3,6-diethylcarbazole with



Fig. 4. Electronic spectra of (A) **2c** $(3 \times 10^{-5} \text{ M})$, *p*-CHL, TCNE, and TCNQ $(6 \times 10^{-5} \text{ M})$ and (B) complexes of 2c with the acceptors *p*-CHL, TCNE, and TCNQ in 1,2-dichloroethane at 25 °C.

Table 3
Thermodynamic properties of CT complexes of the donor compounds with the acceptors <i>p</i> -CHL, TCNE, and TCNQ.

	λ ^c	λ_{CT}^{d}	$K \epsilon_{\rm CT}^{\rm e} ({\rm M}^{-2} {\rm cm}^{-1})$	$K^{g}(M^{-1})$	ΔH (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)
TCNE ^a						
M1	347	596	3705 ± 42	2.94	-2.00 ± 0.06	-2.63 ± 0.20
M2	356	635	11260 ± 225	8.94	-2.69 ± 0.19	-3.62 ± 0.65
D1	346	612	2800 ± 28	2.22	-2.03 ± 0.09	-1.80 ± 0.30
D2	354	625	6990 ± 141	5.55	-2.29 ± 0.17	-1.55 ± 0.57
D3	354	626	7250 ± 138	5.75	-2.31 ± 0.09	-1.51 ± 0.29
D4	356	627	8265 ± 152	6.56	-2.20 ± 0.08	-1.02 ± 0.29
D5	356	628	8285 ± 129 ^e	6.58 ^g	-2.56 ± 0.13	-2.04 ± 0.42
TCNE ^b						
M1	347	596	7861 ± 100	6.24	-2.29 ± 0.09	-7.60 ± 0.30
M2	356	635	19886 ± 363	15.78	-3.13 ± 0.14	-8.79 ± 0.49
D1	346	612	6441 ± 99	5.11	-1.82 ± 0.10	-5.08 ± 0.33
D2	354	625	12640 ± 315	10.03	-2.89 ± 0.05	-7.35 ± 0.17
D3	354	626	12911 ± 361	10.25	-2.91 ± 0.10	-7.31 ± 0.34
D4	356	627	13534 ± 271	10.74	-3.37 ± 0.03	-8.69 ± 0.09
D5	356	628	15370 ± 245^{f}	12.20 ^h	-3.49 ± 0.02	-8.81 ± 0.07
p-CHL ^a						
M1	347	527	2645 ± 23	2.91	-2.26 ± 0.15	-5.05 ± 0.49
M2	356	559	3480 ± 44	3.83	-2.78 ± 0.19	-6.09 ± 0.60
D1	346	550	2850 ± 32	3.13	-2.09 ± 0.15	-2.74 ± 0.52
D2	354	553	3180 ± 59	3.50	-2.55 ± 0.22	-3.95 ± 0.72
D3	354	553	3280 ± 48	3.60	-2.58 ± 0.11	-4.02 ± 0.37
D4	356	554	3560 ± 84	3.91	-2.71 ± 0.07	-4.50 ± 0.23
D5	356	554	$3915 \pm 62^{\rm f}$	4.30 ⁱ	-2.87 ± 0.09	-4.72 ± 0.29
<i>TCNQ</i> ^a						
M1	347	590	7965 ± 194	3.21	-3.56 ± 0.12	-7.16 ± 0.38
M2	356	625	10915 ± 221	4.40	-4.03 ± 0.16	-7.85 ± 0.53
D1	346	608	3260 ± 26	1.32	-2.32 ± 0.07	-2.47 ± 0.22
D2	354	621	6235 ± 78	2.51	-3.93 ± 0.16	-7.22 ± 0.53
D3	354	621	7475 ± 68	3.01	-3.82 ± 0.08	-6.16 ± 0.26
D4	356	623	9545 ± 89	3.85	-4.14 ± 0.09	-7.00 ± 0.31
D5	356	624	9075 ± 179	3.66	-4.24 ± 0.10	-7.07 ± 0.33

^a Experiments performed in 1,2-dichloroethane.

^b Experiments performed in dichloromethane.

^c Lowest energy absorption maximum (nm) of the donor molecule.

^d Lowest energy CT maximum (nm).

^e Acceptor in excess.

^f Donor in excess.

 $^{\rm g}~\epsilon$ = 910 $M^{-1}~cm^{-1}$ at 25 ± 0.1 °C.

 $^{\rm h}~\varepsilon$ = 1260 $M^{-1}~cm^{-1}$ at 25 ± 0.1 °C.

ⁱ ε = 2480 M⁻¹ cm⁻¹ at 25 ± 0.1 °C.

corresponding 1,*n*-dibromoalkanes (for n = 1, 3-5) and ethylene ditosylate (for n = 2). As the nucleophile 3,6-diethylcarbazolide anion was formed by abstracting the proton attached to carbazole nitrogen by hydroxide ion in acetone. The much lower reaction rate when 1,2-dibromoethane was used is due to lower partial positive charge on the α -carbon to the nucleophile because of the existence of the second electronegative atom on the neighboring carbon atom. The use of -OTs as a better leaving group increased the reaction rate considerably.

3.2. Crystal structures

The crystal structures of the compounds **2b** and **2d** were solved in the monoclinic space groups C2/c and $P2_1/n$, respectively. In the structures of the both compounds, the asymmetric unit contains half a molecule. The other halves of the molecules are generated from the first ones by the crystallographic inversion centers, which were lying between the central C–C bonds of the alkylene separators. The atom numbering scheme of the compounds **2b** and **2d** are shown in Fig. 1. The selected bond lengths, bond and torsion angles are listed in Table 2. Bond lengths and angles are comparable to those of related compounds reported in the literature [37]. In both structures C1–C9a bond is somewhat shorter and C4a–C4b bond is longer than the other C–C bonds in the carbazole rings.

In the structure of **2b** the conformation of the C–C connector is anti while in **2d** the C–C–C–C chain is arranged in a gauche-antigauche conformation. These conformations allowed the carbazole moieties position themselves in parallel planar geometries. The ethyl groups on C3 and C6 positions point the same direction in 2b, whereas they point opposite directions in 2d. The molecular packings in both structures were mainly determined by π - π interactions between carbazole moieties. The dihedral angle of 0.44(14)° between the mean planes of central pyrollic rings of the neighboring **2b** molecules at (x, y, z) and (1 - x, 1 - y, -z) with a ring-centroid separation of 3.525(2) Å and interplanar spacings of ca. 3.3.331 Å corresponding to a ring-centroid ofset of ca. 1.153 Å indicates this partial overlap. A similar overlap was observed in the structure of **2d** having a dihedral angle between the mean planes of pyrrolic rings of the molecules at (x, y, z) and (1 - x, y)1 - y, -z) is $0.18(18)^{\circ}$ with a ring centroid separation of 3.580(4) Å and interplanar spacings of ca. 3.492 Å corresponding to a ring-centroid ofset of ca. 0.789 Å. These interactions account for semiconducting properties and charge transfer complexations of carbazole derivatives with π -acceptors. Intermolecular π - π interactions and molecular packing of 2b and 2d are shown in Figs. 2 and 3, respectively.

3.3. Charge-transfer complexations

Charge transfer bands in the electronic spectra of EDA complexes are observed in solutions due to absorbed photon energies to transfer electrons from higher energy, occupied molecular



Scheme 3. Representation of three of the ground state HOMO's of carbazole donors and LUMO's of the acceptor molecules.

orbitals of the donor molecules to the lowest lying molecular orbital of the acceptors (Scheme 2). Carbazole donors studied in this work gave maximum absorbances of the light with $\lambda = 527$ – 635 nm depending on the acceptor. Color changes upon mixing donor and acceptor solutions are clear indication of CT complexation. As a representative, the CT spectra of the complexes formed between the donor **2c** and the acceptors *p*-CHL, TCNE, and TCNQ are shown in Fig. 4.

Absorbances due to CT formation are outside the region where the individual donor or acceptor molecules absorb light. Hence, the absorbances around 527–635 nm could be related to the concentration of the CT complex. Lowest energy λ_{max} and λ_{CT} are listed in Table 3.

The energy associated with charge-transfer is related to electron affinity (E_a) of the acceptor and ionization potential (I_p) of the donor molecules and electrostatic attraction between the donor and acceptor molecules according to the equation, $\Delta E = E_a$ - $-I_p + J$. Measured E_a values for TCNE, TCNQ and p-CHL found in the literature are 3.17 ± 0.2 [38], 2.8 ± 0.2 [39,40] and $1.37 \pm 0.1 \text{ eV}$ [41], respectively. Measured I_p values are around 7.6-8.0 [42,43] for carbazole and 7.41 eV [44] for ethylcarbazole. The 0.37 eV difference between the E_a values of TCNE and p-CHL is also supported by the 72 nm mean difference between their respective λ_{CT} values. However, according to λ_{CT} values TCNQ should have an E_a value close to 3.05 eV, assuming these three acceptors exhibit similar or very close I values related to electrostatic attractions with the donors. Introduction of alkyl subtituents on carbazole rings reduces I_p values up to 0.3 eV [45]. There are two λ_{CT} bands observed from the spectra of the CT complexes of the donor compounds with TCNE around 416 nm and 630 nm. The peak around 416 nm is assigned to the transition from donors' HOMO-3 to TCNE's LUMO (Scheme 3) [46]. In the CT spectra of the carbazole donors with p-CHL and TCNQ are not resolvable due to



Fig. 5. Job plots of CT complexes of the donor compounds with (A) *p*-CHL, (B) TCNE, and (C) TCNQ in 1,2-dichloroethane. *X* is the mole fraction of the carbazole unit in the solution.

the absorptions of uncomplexed acceptors at these λ_{CT} values. The transition bands due to HOMO-2 and HOMO-1 of carbazoles and LUMO of acceptors appear as two overlapping peaks resulting in a broad shoulder having λ_{CT} values around 550 (*p*-CHL), 620 (TCNQ), and 625 nm (TCNE).

Carbazoles form donor–acceptor complexes with the electron acceptors according to following equation:

$$D + A \Leftrightarrow DA$$
 (1)

Equilibrium constant, K of the CT complex formation is a function of concentration of D, A and DA species at equilibrium (Eq. (2)).

$$K = [\mathsf{D}\mathsf{A}]/([\mathsf{D}][\mathsf{A}]) \tag{2}$$

In photometric studies the concentration of DA could be related to its absorbance by Beer's law and used to deduce the concentration of D and A using Benesi Hildebrand equation (Eqs. (3a) and (3b)). This method requires initial concentration of one of the components to be very high and changing compared to the low and fixed concentration of the other component.

$$([D]_0 l)/A = (K\varepsilon)^{-1}(1/[A]_0) + \varepsilon^{-1} \text{ when } [A]_0 \gg [D]_0$$
 (3a)

and

$$([A]_0 l)/A = (K\varepsilon)^{-1}(1/[D]_0) + \varepsilon^{-1} \text{ when } [D]_0 \gg [A]_0$$
 (3b)

where *A* is the absorbance at λ_{CT} , ε is the molar absorption coefficient of the complex, *l* is the optical path length (1.0 cm), [A]₀ is the initial concentration of the acceptor and [D]₀ is the initial concentration of the donor. From the linear Eqs. (3a) and (3b), ($K\varepsilon$)⁻¹ is obtained as the slope and (ε)⁻¹ as the intercept. When the donor compounds are dimers acting as two individually behaving monomers Eqs. (3a) and (3b) becomes

$$([D]_0 l)/A = (2K\varepsilon)^{-1}(1/[A]_0) + (2\varepsilon)^{-1}$$
 when $[A]_0 \gg [D]_0$ (4a)

$$([A]_0 l)/A = (2K\varepsilon)^{-1}(1/[D]_0) + \varepsilon^{-1} \text{ when } [A]_0 \gg [D]_0$$
 (4b)

A plot of $[D]_0 I/A$ vs. $(1/[A]_0)$ in Eq. (4a) would yield $(2K\varepsilon)^{-1}$ as the slope and $(2\varepsilon)^{-1}$ as the intercept, whereas a plot of $[A]_0 I/A$ vs. $(1/[D]_0)$ in Eq. (4a) would yield $(2K\varepsilon)^{-1}$ as the slope and $(\varepsilon)^{-1}$ as the intercept. Note that, since these equations are in linear forms, they are usable only when donors and acceptors form complexes in 1:1 M ratio. Therefore, the stoichiometries of the complexations should be determined beforehand and should be proved that Benesi-Hildebrand (B–H) technique is applicable. Job plots (Fig. 5) show that all monomers and dimers gave the highest absorbances when they are mixed in 1:1 donor unit–acceptor molar ratio. These experiments also show that the dimers behave like two individual monomers which form complexes independent from each other. The B–H plots are given in Fig. 6 and results of the calculations of ε and K values are given in Table 3.

Instead of calculating ε values for each of the donor-acceptor complexes, we have used their average and assigned the same value to all complexes to minimize experimental errors. This allowed us calculate more reliable *K* values from their slopes. The average ε values were determined as 1380 (195) M⁻¹ cm⁻¹ for carbazole-TCNE, 830 (99) M^{-1} cm⁻¹ for carbazole-*p*-CHL, and 2520 (324) M⁻¹ cm⁻¹ for carbazole–TCNQ complexes in 1,2-dichloroethane. The numbers in the parentheses are the mean error of standard deviations (e.s.d.'s) of ε values determined by the regression analyses. Same experiments were done in dichloromethane for carbazole–TCNE complexations and the average ε value was determined as 1350 (102) M^{-1} cm⁻¹. The average ε values determined in this study are close and in the range of e.s.d.'s to the values determined in the previous studies [20,46]. Because the molar absorptivity is an intrinsic property determined by the size of the molecule and the probability that electronic transition will take place [47], all the donors should have the same molar absorptivity values for their complexes with the same acceptors. This assumption is reasonable because the absorbances around 600 nm are only due to π - π ^{*} electronic transitions from the carbazole rings to the acceptor molecules. Hence, to be consistent and to compare our results with the earlier studies same ε values reported are also used here. Among the acceptors, TCNE formed complexes with the highest equilibrium constants. The formation constants of complexes with p-CHL and TCNQ have similar values. Comparing the donor molecules, as the length of the methylene chain increases the dimers exhibit similar complexation behaviors to their monomeric analogue, 1b. Interference of one carbazole ring on the complexation of the other was observed the most in **2a** as its K values suggest. This effect was decreased as the carbazole rings are separated farther apart in 2c-2e. In CT complexations inert solvents that are not interacting with either of the components need to be used. The solvents used in this study obey this criteria but complexation in CH₂Cl₂ is more favored compared to CH₂ClCH₂Cl. Although they have similar dipole moments [36] the size of CH₂-ClCH₂Cl seems prevented close approach of the donor acceptor molecules. The *K* values obtained in CH₂Cl₂ were found roughly twice those determined in CH₂ClCH₂Cl. The effect of number of alkyl substituents present on the carbazole rings on complexation is attained by comparing the results of this study with our previous works [20,21]. 3,6,9-Trialkylcarbazoles form complexes with TCNE in CH₂Cl₂ with 5.8 and 2.8 M⁻¹ higher *K* values compared to 9-alkyl- and 3,9-dialkylcarbazoles. Apparently, lowered I_p 's of carbazole rings by the electron donating alkyl groups played a notable effect on the complexation.



Fig. 6. Benesi-Hildebrand plots of the complexes of carbazole donors with (A) p-CHL, (B) TCNE, and (C) TCNQ in 1,2-dichloroethane at 25 °C.



Fig. 7. The van't Hoff plots of the complexes of carbazole donors with (A) p-CHL, (B) TCNE, and (C) TCNQ in 1,2-dichloroethane.

3.4. Determination of the thermodynamic constants

The van't Hoff equation combined with Beer's law is used for the determination of enthalpy and entropy changes of CT complexations (Eqs. (5) and (6)).

$$-RT\ln K = \Delta H - T\Delta S \tag{5}$$

$$\ln(A/\varepsilon) - \ln([D]_0 - (A/\varepsilon)) - \ln([A]_0 - (A/\varepsilon))$$

= -(\Delta H/R)(1/T) + (\Delta S/R) (6)

A plot of $\ln K$ (the whole term on the left in Eq. (6)) vs. 1/T would yield $-\Delta H/R$ as the slope and $\Delta S/R$ as the intercept. The van't Hoff plots of carbazoles with *p*-CHL, TCNE and TCNQ are given in Fig. 7, respectively and the thermodynamic constants are summarized in Table 3.

The enthalpies of complex formation found between -1.82 and -4.24 kcal/mol indicate that the process is slightly exothermic. They also suggest that the interactions between donor and acceptor molecules are weak, which is a common feature of complex formation. Comparing their ΔH values, **1b** formed more strongly associated complexes than 1a. Among the dimeric donor compounds 2a has the least negative ΔH values because of the steric interference of the second carbazole group on the same sp³-hybridized carbon. As the length of the $-CH_2$ - chain increased ΔH values became more negative, indicating that carbazole groups of the dimers behave like two individual monomers. Among the acceptor molecules TCNQ formed more strongly associated complexes than TCNE and *p*-CHL. This is attributed to the size and the nodal properties of LUMO of TCNQ and HOMO-2 of carbazole ring. More negative ΔH values of complex formation between carbazoles and TCNE were determined in dichloromethane compared to 1.2-dichloroethane.

The negative ΔS values of complex formations show that complexations are entropically disfavored and the process is driven by the formation enthalpies. The ΔS values increase and get closer to those of monomeric analogues as the $-CH_2$ - chain length increases. More negative ΔS values for **1b** compared to **1a** indicate that ethyl groups on the carbazole ring increased the strength of the intermolecular association and caused decrease in the randomness of the complexes. The ΔS for the carbazole–TCNE complexations in dichloromethane were found to be more negative than in 1,2dichloroethane. The *K*, ΔS , and ΔS values suggest that the more strongly the donor and acceptor compounds associate the more temperature dependency they exhibit. Hence the complexations at high temperatures are less favored and will cause less negative ΔG and lower *K* values.

4. Conclusion

1,n-Bis(3,6-diethylcarbazol-9-yl)alkanes as the dimeric model compounds of poly-9-vinylcarbazoles were prepared and crystal structures of two of them, 2b and 2d, were solved. The crystal packing and intermolecular associations show that these two dimers adopted conformations along the methylene chains so that π - π interactions between carbazole ring systems would be possible. From the results of the complexation studies it is concluded that 1,n-bis(3,6-diethylcarbazol-9-yl)alkanes formed stable intermolecular CT complexes with the π acceptors *p*-CHL, TCNE, and TCNQ in 1,2-dichloroethane. The stoichiometries of complexation determined as one donor unit to one acceptor molecule. The equilibrium constants, K, of the complexations were determined by the linear Benesi-Hildebrand method. It was observed that value of K increases as the chain length separating the two carbazole groups increases. Higher K values of complexations were determined when dichloromethane was used as the solvent. The enthalpies and entropies of complex formations were calculated using the van't Hoff equation. Slightly more negative ΔH and ΔS values of complex formations between the donor compounds and TCNQ were obtained compared to TCNE and *p*-CHL. These results imply that complexes with TCNQ show more temperature dependency. When comparing the solvents, more strongly associated complexes with higher temperature dependency are formed in dichloromethane than 1,2-dichloroethane. Comparing the monomers, 3,6,9-triethylcarbazole formed complexes with higher K and more negative ΔH and ΔS values than 9-ethylcarbazole. Electron donor ethyl groups caused increase in K values and temperature dependencies of the complexations.

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