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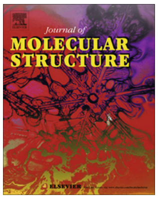

Synthesis and charge-transfer complex formations of 1,*n*-bis(3,6-diethylcarbazol-9-yl)alkanes with three π-acceptors

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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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ABSTRACT

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 $P2_1/n$, respectively. The methylene chain adopted an anti conformation in **2b** and a gauche-anti-gauche conformation in **2d**, enabling coplanar orientations of carbazole 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}.

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, ΔH_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 $-CH_2-$ 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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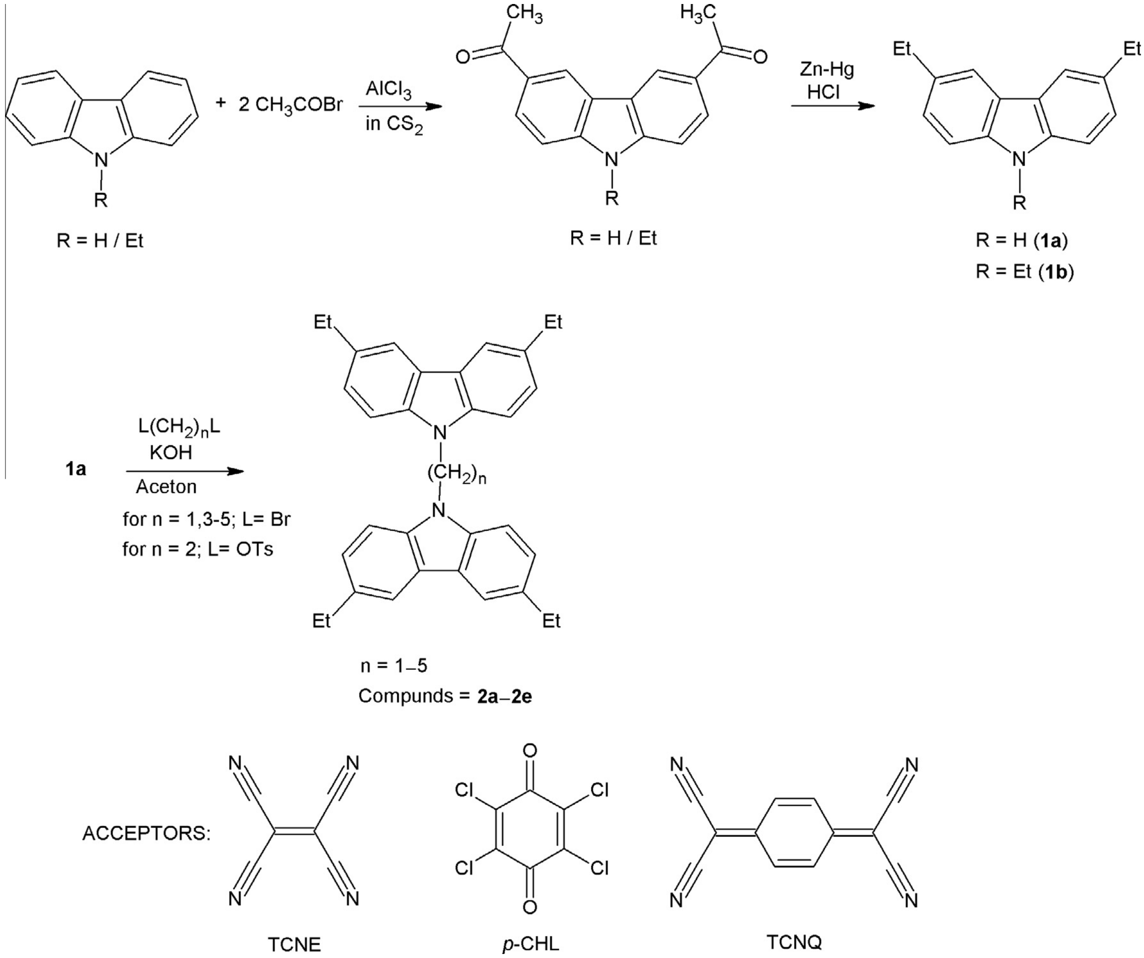

Scheme 1. Synthesis and structures of the title donor and acceptor compounds.

2. Experimental

2.1. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer using tetramethylsilane (TMS) as the internal reference and $CDCl_3$ 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) $AlCl_3$, and 150 ml of dry CS_2 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 $HgCl_2$ (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-3,6-diacetylcarbazole 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 Na_2SO_4 and evaporated under reduced pressure. The crude product was chromatographed over a silicagel column using hexane/CH_2Cl_2 (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**,