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Effects of methyl substituent on the charge-transfer complexations of dicarbazolylalkanes with *p*-chloranil, tetracyanoethylene and tetracyanoquinodimethane

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ABSTRACT

Series of 1,*n*-dicarbazolylalkanes and 1,*n*-di(3-methylcarbazolyl)alkanes (where $n = 1–5$) were synthesized and the molar extinction coefficients, equilibrium constants, enthalpies, and entropies of their charge-transfer (CT) complexes with the π-acceptors *p*-chloranil, tetracyanoethylene, and tetracyanoquinodimethane were investigated. 1,*n*-Di(3-methylcarbazolyl)alkanes formed CT complexes with higher equilibrium constants, more negative enthalpies and entropies than 1,*n*-dicarbazolylalkanes. Vibrational spectra of CT complexes of one of the donor molecules (1,4-dicarbazolylbutane) with all three acceptors were compared.

1. Introduction

Electron donor–acceptor (EDA) or charge-transfer (CT) complexes have long been known. Their properties have first been described by Mulliken on the CT basis [1]. Recent interest about CT complexes of organic donor acceptor molecules arises from their photoconductive properties and potential industrial applications [2]. CT complexations of polymeric and lower weight molecular carbazoles have also been studied extensively due to their potential practical applications as, for example, high efficiency nonlinear optical materials, color displays, organic light emitting diodes (OLEDs), organic semiconductor lasers, solar cells [3–5].

Findings on the complexation properties of dimeric model compounds of carbazoles enable researchers interpret the behaviors of their polymeric analogues. For this basis, studies on the CT complexations of a series of dicarbazolyl alkanes with the acceptors tetranitromethane (TNM), tetracyanoethylene (TCNE) [6], and *p*-chloranil (*p*-CHL) [7] had been done. We have previously investigated the CT complexation properties of 1,*n*-di(9-ethylcarbazol-3-yl)alkanes ($n = 0–5$) with the acceptors TNM and TCNE [8]. These studies prove that the electron donating ability of a donor molecule is gratefully enhanced by the alkyl substituents on the benzene rings of carbazole. For the present study, we have prepared 1,*n*-dicarbazolylalkanes (D1a–D5a) and their methyl substituted analogues, 1,*n*-di(3-methylcarbazolyl)alkanes, (D1b–D5b) to investigate and compare their equilibrium (K_{eq}) and thermodynamic constants, enthalpy (ΔH) and entropy changes (ΔS), of CT formation with the electron acceptors TCNE, *p*-CHL and tetracyanoquinodimethane (TCNQ). To the donors, we have added 9-ethylcarbazole (Ma) and 9-ethyl-3-methylcarbazole (Mb) monomers for comparison. Structures of the donor and acceptor molecules discussed in the present study are given in Scheme 1.

2. Experimental

2.1. Instrumentation

Melting points were determined using a Stuart SMP10 melting point apparatus and were uncorrected. All absorbance measurements were recorded on a PG Instruments T80+ double beam UV–vis spectrophotometer in 3.5 ml, 1.0 cm path length optical quartz cells with polytetrafluoroethylene (PTFE) stoppers using dichloromethane as the solvent. In the thermodynamic experiments a PTC-2 peltier temperature controller unit was attached to the UV–vis spectrophotometer with a $\pm 0.1\,^{\circ}C$ uncertainty of temperature. IR spectra were taken on a Perkin Elmer Spectrum 100 FT-IR spectrometer using attenuated total reflection (ATR) sampling. NMR spectra were recorded on a Varian Mercury 300 MHz

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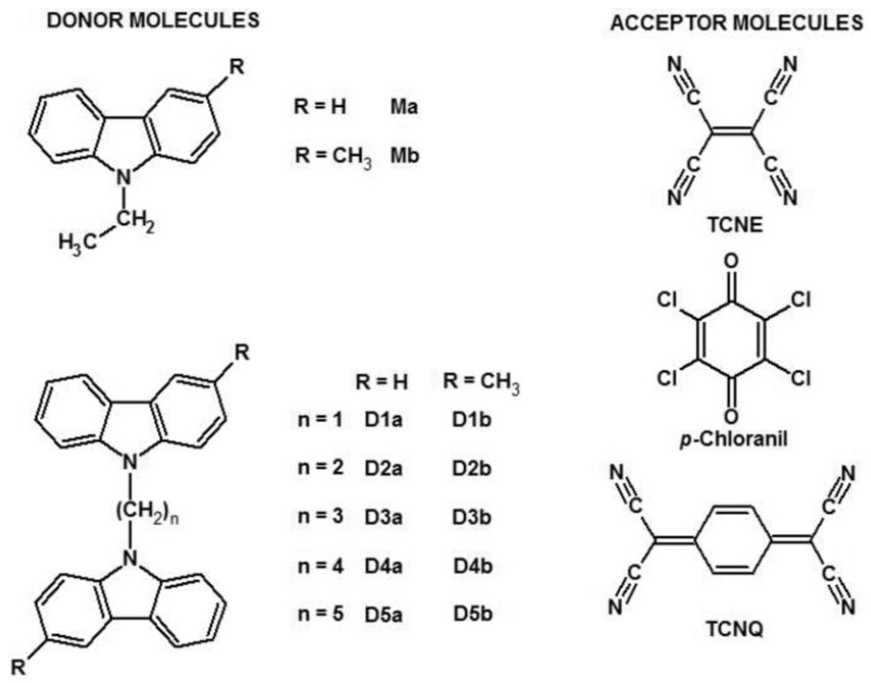

Scheme 1. Molecular structures of the donor and acceptor compounds discussed in this paper.

NMR spectrometer using tetramethylsilane (TMS) as the internal reference and $CDCl_3$ as the solvent.

2.2. Materials

The acceptors TCNE (Aldrich) and *p*-CHL (Alfa Aesar) were purified by sublimation and TCNQ (Alfa Aesar) by recrystallization from dichloromethane. The solvents used in the syntheses and absorption experiments were purified via the general methods explained in the literature [9]. Carbazole (Alfa Aesar) was purified by recrystallization from acetone prior to use for the syntheses. The monomer Ma (Aldrich) was purified by column chromatography (80–200 mesh silica gel) eluting fractionally with hexane/dichloromethane (9:1, v/v) and by recrystallization from ethanol, whereas Mb was prepared via Clemmensen reduction of 9-ethylcarbazole-3-carboxaldehyde (Aldrich) and purified by passing through a silica gel column and recrystallization from ethanol. The dimeric donors D1a, D3a–D5a, were prepared according to the literature method via S_N2 reactions between carbazolide anion and corresponding 1,*n*-dibromoalkane substrates [10]. Synthesis of D2a was achieved using ethylene glycol bis-p-toluenesulfonate as the substrate instead of 1,2-dibromoethane. The methyl substituted analogues of these dimers were synthesized via, firstly, diformylation using Vilsmeier–Haack method and then reduction of the formyl groups to methyl via Clemmensen reduction reaction. Due to the low solubilities of the formyl derivatives of D1a and D2a in toluene D1b and D2b were obtained in lower yields compared to D3b–D5b. The general procedure for the formylation of dicarbazolylalkanes is as follows. To a flame-dried 250 ml round-bottom flask, $POCl_3$ (4.0 ml; ~50 mmol) was added dropwise to vigorously stirred 50 ml of dimethyl formamide (DMF) at 0 °C in an ice bath during a 30 min time-period under N_2 atmosphere. Then, the temperature was raised to about 35 °C and 10 mmol of dicarbazolylalkane was added to the stirred mixture. After stirring the mixture for 12 h at 60–70 °C, a brown precipitate was formed as the product, which was then poured onto 500 ml of water at 45 °C and stirred to remove unreacted DMF–$POCl_3$ complex. The product was then filtered, washed well with water and air-dried.

The formylation products of dicarbazolylalkanes were not treated further and used for the synthesis of D1b–D5b via Clemmensen reduction as described in the literature [11]. The general procedure for the syntheses of D1b–D5b is as follows. A mixture of $HgCl_2$ (500 mg), Zn powder, concentrated HCl (2.5 ml, %36) and water (50 ml) was stirred at ambient temperature for 15 min to amalgamate the zinc metal. Then, the liquid phase was decanted and the zinc amalgam was washed three times with 25 ml of water. To this, concentrated HCl (50 ml) and aldehyde were added and the mixture was stirred for 2 h. Toluene (50 ml) was added and the mixture was refluxed for 48 h. 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 residue was passed through a silica gel column with CH_2Cl_2/hexane eluting solution. D1b–D5b were obtained after recrystallization from CH_2Cl_2/hexane solution via slow evaporation. Spectroscopic evidences regarding elucidation of their structures are given.

Di(3-methylcarbazol-9-yl)methane (D1b): m.p. 215–6 °C; FTIR (ATR) frequency ν: 3048, 2917, 2861, 1599, 1493, 1466, 1457, 1335, 1220, 1151 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ = 7.99 (d, J = 8.05 Hz, 2H), 7.82 (s, 2H), 7.08–7.40 (m, 10H), 6.60 (s, 2H), 2.48 (s, 6H); UV–vis, nm (ε) = 290 (16,200), 335 (4900), 351 (4400).

1,2-Di(3-methylcarbazol-9-yl)ethane (D2b): m.p. 222–3 °C; FTIR (ATR) frequency ν: 3048, 2919, 2858, 1603, 1458, 1359, 1302, 1257, 1197, 1145 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ = 7.96 (d, J = 7.03 Hz, 2H), 7.81 (s, 2H), 7.08–7.35 (m, 10H), 4.53 (t, J = 9.67 Hz, 4H), 2,45 (s, 6H); UV–vis, nm (ε) = 292 (15,700), 320 (3250), 335 (4100), 351 (3550).

1,3-Di(3-methylcarbazol-9-yl)propane (D3b): m.p. 153–4 °C; FTIR (ATR) frequency ν: 3047, 2917, 2861, 1601, 1490, 1466, 1456, 1334, 1220, 1151 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ = 8.01 (d, J = 7.15 Hz, 2H), 7.83 (s, 2H), 7.05–7.38 (m, 10H), 4.28 (t, J = 7.32 Hz, 4H), 2,47 (s. 6H), 2.36 (quintet, J = 7.62 Hz, 2H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ = 140.6, 138.7, 128.6, 127.3, 125.8, 123.3, 123.1, 120.7, 120.6, 119.1, 108.6, 108.4, 40.8, 28.2, 21.6; UV–vis, nm ($\varepsilon \times 10^{-3}$) = 296 (19.2), 320 (4.3), 335 (5.7), 351 (4.75).

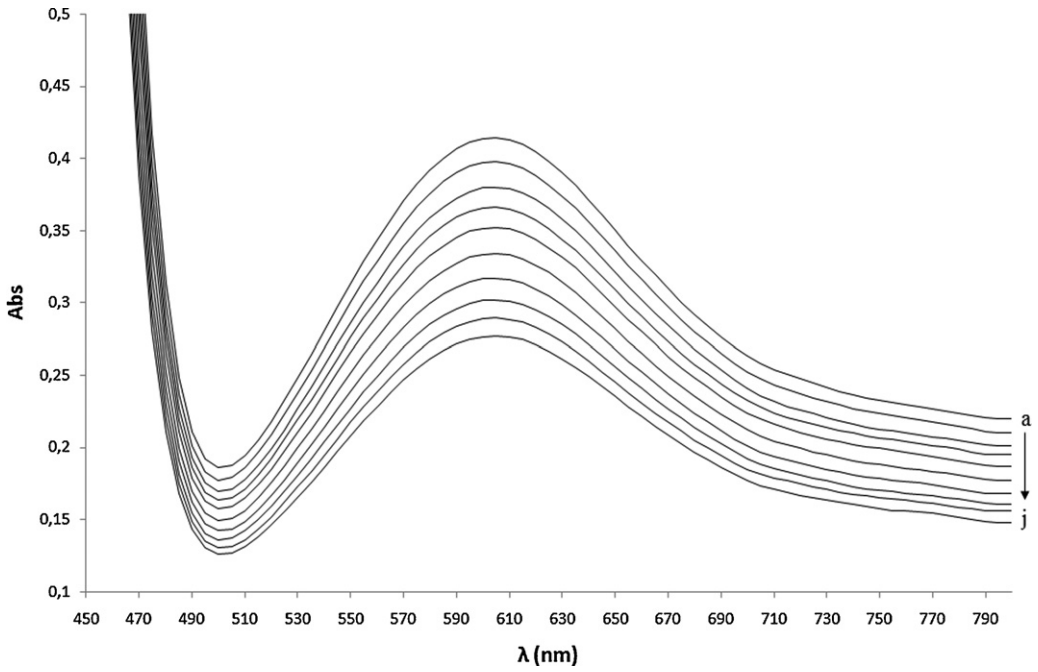

Fig. 1. Electronic spectra of D3b–TCNQ CT complex with changing D3b concentrations [TCNQ] = 5×10^{-4} M, [D3b] = *a* 2.5 to *j* 1.54×10^{-2} M at 25 °C.

1,4-Di(3-methylcarbazol-9-yl)butane (D4b): m.p. 1855–6 °C; FTIR (ATR) frequency ν: 3048, 2918, 2854, 1601, 1484, 1460, 1345, 1331, 1243, 1179, 1143 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ = 7.97 (d, J = 8.49 Hz, 2H), 7.81 (s, 2H), 7.10–7.39 (m, 10H), 4.11 (t, J = 7.35 Hz, 4H), 2,46 (s. 6H), 1.88 (quintet, J = 7.67 Hz, 4H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ = 140.7, 138.8, 128.4, 127.2, 125.7, 123.1, 122.8, 120.6, 119.1, 118.8, 108.7, 108.5, 43.0, 27.1, 21.6; UV–vis, nm ($\varepsilon \times 10^{-3}$) = 292 (18.9), 320 (5.3), 335 (6.7), 351 (6.5).

1,5-Di(3-methylcarbazol-9-yl)pentane (D5b): m.p. 125–6 °C; FTIR (ATR) frequency ν: 3045, 2917, 2856, 1601, 1489, 1465, 1453, 1348, 1330, 1320, 1292, 1228, 1150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ = 8.06 (d, J = 7.3 Hz, 2H), 7.90 (s, 2H), 7.18–7.46 (m, 10H), 4.21 (t, J = 7.18 Hz, 4H), 2.56 (s. 6H), 1.86 (quintet, J = 7.65 Hz, 4H); 1.44 (quintet, J = 7.33 Hz, 2H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ = 140.8, 138.9, 128.3, 127.2, 125.7, 123.2, 120.6, 120.5, 118.8, 108.7, 108.5, 43.1, 29.1, 25.5, 21.6; UV–vis, nm ($\varepsilon \times 10^{-3}$) = 292 (18.9), 320 (5.3), 335 (6.7), 351 (6.5).

2.3. Absorption measurements

The stoichiometries of the complexations of mono and dicarbazoles with TCNE, *p*-CHL and TCNQ were determined using Job's plots (method of continuous variation) [12]. In 10 ml volumetric flasks, 10 mM of carbazole donor and 10 mM of acceptor molecules in dichloromethane were prepared separately by directly weighing the respective components. These solutions were mixed in 2.0 ml volumetric flasks in which the mole fractions of the components differed from 0.1 to 0.9. Acceptor solutions 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 five different scans of the CT complexes on each dilution were recorded at the maximum CT wavelengths.

The equilibrium constants, K_{eq}, and molar absorptivities, ε, of CT complexations were determined utilizing the Benesi–Hildebrand technique [13]. For the TCNE–carbazole CT measurements, in a 1.0-cm quartz UV cuvette a solution consisted of 2.0 ml of 50 mM TCNE and 1 mM carbazole unit was placed. This was diluted 5 times by the addition of increments of 100 μl and 5 times by the addition of increments of 150 μl of the 1 mM carbazole solutions, to make total of 10 dilutions. During the dilutions TCNE–carbazole concentration ratios varied from about 50:1 to about 30:1. In this respect, the donor concentration was kept constant whereas the acceptor concentration decreased throughout the experiment. For the *p*-CHL–carbazole and TCNQ–carbazole CT measurements, concentration of the carbazole unit was kept high due to the lower solubility of these two acceptors. The low solubility of D1a prevented us from taking trustworthy measurements from their complexations with *p*-CHL and TCNQ. A 25–0.5 mM carbazole unit:acceptor ratio had to be used in the experiments involving D2a. Absorbance changes were monitored after each dilution at of the interest. Average of three runs of three data points near λ_{CT} was taken to minimize the experimental errors.

Thermodynamic properties of the CT complexations were determined using van't Hoff equation and Beer–Lambert law by measuring absorption spectra of the complexes at six different temperatures, 10 °C, 15 °C, 20 °C, 25 °C, 30 °C, and 35 °C (±0.1 °C), at λ_{CT}. In a 2.0-ml volumetric flask, a solution containing 10 mM acceptor and 10 mM carbazole unit at 25.0 °C was prepared. Then, the solution was transferred into an airtight capped quartz UV cell with l = 1 cm and equilibrated at the desired temperature (*ca.* 10 min.) using a peltier temperature controller system. 5 mM Acceptor and 5 mM carbazole unit concentrations were used when forming complexes between D2a and D4a with TCNQ due to the rapid precipitation of the EDA complexes at higher concentrations. Concentration changes due to the expansion/contraction of CH_2Cl_2 [14] at changing temperatures were taken into account in calculating the thermodynamic constants.

3. Results and discussion

3.1. Charge-transfer absorption bands

The color changes observed upon the mixture of carbazole compounds with various electron acceptors are indication of the formation of CT complexes. According to Mulliken, the formation of such color is due to CT excitation of DA complex [1]. The colors of CT complexes of the carbazole compounds with TCNE, TCNQ and *p*-CHL are, blue, bluish green and brownish purple, respectively. As a

Table 1
Thermodynamic properties of EDA complexes of carbazole donors with *p*-CHL, TCNE, and TCNQ in CH_2Cl_2.

p-CHL	λ[a] (nm)	λ_{CT}[b]	$K\varepsilon_{CT}$[c] ($M^{-2}\,cm^{-1}$)	r^2	K[e] (M^{-1})	ΔH (kcal mol^{-1})	ΔS (kcal $mol^{-1}\,K^{-1}$)
M1a	347	532	2665 ± 51	0.997	2.93	−2.51 ± 0.22	−4.92 ± 0.74
D1a	336	517	–	–	–	−1.87 ± 0.09	−3.05 ± 0.27
D2a	344	523	1470 ± 37	0.994	1.62	−2.62 ± 0.09	−4.45 ± 0.32
D3a	345	527	2520 ± 31	0.999	2.77	−2.52 ± 0.05	−4.16 ± 0.16
D4a	346	532	2590 ± 74	0.992	2.85	−2.65 ± 0.03	−4.18 ± 0.10
D5a	347	532	3200 ± 48	0.998	3.51	−3.00 ± 0.03	−5.42 ± 0.10
M1b	352	544	3880 ± 62	0.998	4.26	−3.49 ± 0.05	−7.14 ± 0.17
D1b	341	530	2520 ± 35	0.998	2.77	−3.17 ± 0.02	−5.30 ± 0.05
D2b	350	541	3250 ± 33	0.999	3.57	−3.12 ± 0.03	−5.17 ± 0.11
D3b	351	541	3290 ± 35	0.999	3.62	−3.23 ± 0.01	−5.72 ± 0.03
D4b	348	537	3500 ± 67	0.997	3.84	−3.10 ± 0.04	−5.12 ± 0.13
D5b	352	543	3490 ± 68	0.997	3.84	−3.86 ± 0.02	−7.07 ± 0.06
TCNE	λ[a] (nm)	λ_{CT}[b]	$K\varepsilon_{CT}$[d] ($M^{-2}\,cm^{-1}$)	r^2	K[f] (M^{-1})	ΔH (kcal mol^{-1})	ΔS (eu)
M1a	347	596	6430 ± 183	0.994	5.11	−2.43 ± 0.21	−5.35 ± 0.71
D1a	336	578	2860 ± 30	0.999	2.27	−1.83 ± 0.09	−3.60 ± 0.29
D2a	344	586	5770 ± 148	0.994	4.58	−2.53 ± 0.09	−4.83 ± 0.31
D3a	345	588	6460 ± 50	0.998	5.13	−2.43 ± 0.04	−4.56 ± 0.15
D4a	346	590	6910 ± 38	0.999	5.49	−2.54 ± 0.03	−4.52 ± 0.09
D5a	347	592	8420 ± 43	0.999	6.68	−2.87 ± 0.03	−5.71 ± 0.09
M1b	352	610	12,731 ± 139	0.998	10.10	−3.31 ± 0.04	−7.29 ± 0.15
D1b	341	598	7710 ± 108	0.999	6.12	−2.99 ± 0.01	−5.46 ± 0.04
D2b	350	606	9570 ± 160	0.997	7.59	−2.94 ± 0.03	−5.34 ± 0.11
D3b	351	606	8330 ± 80	0.998	6.61	−3.06 ± 0.01	−5.90 ± 0.04
D4b	348	604	9150 ± 330	0.993	7.26	−2.92 ± 0.04	−5.29 ± 0.14
D5b	352	609	9945 ± 119	0.998	7.89	−3.58 ± 0.02	−6.94 ± 0.05
TCNQ	λ[a] (nm)	λ_{CT}[b]	$K\varepsilon_{CT}$[c] ($M^{-2}\,cm^{-1}$)	r^2	K[g] (M^{-1})	ΔH (kcal mol^{-1})	ΔS (eu)
M1a	347	590	8060 ± 210	0.994	3.25	−3.72 ± 0.06	−10.16 ± 0.20
D1a	336	572	–	–	–	−1.90 ± 0.04	−4.30 ± 0.14
D2a	344	585	5270 ± 94	0.992	2.12	−2.03 ± 0.23	−3.15 ± 0.79
D3a	345	585	7490 ± 43	0.997	3.02	−4.13 ± 0.34	−10.93 ± 1.16
D4a	346	587	7860 ± 202	0.994	3.17	−2.86 ± 0.09	−5.63 ± 0.30
D5a	347	590	11,480 ± 414	0.987	4.63	−3.80 ± 0.08	−9.33 ± 0.26
M1b	352	604	14,070 ± 367	0.994	5.67	−3.80 ± 0.15	−9.36 ± 0.52
D1b	341	591	7160 ± 103	0.958	2.89	−3.98 ± 0.07	−9.12 ± 0.22
D2b	350	602	8980 ± 104	0.999	3.62	−3.32 ± 0.07	−9.84 ± 0.25
D3b	351	602	9980 ± 225	0.995	4.03	−3.93 ± 0.05	−9.10 ± 0.17
D4b	348	598	11,670 ± 110	0.999	4.70	−4.04 ± 0.05	−9.59 ± 0.19
D5b	352	604	14,990 ± 151	0.999	6.04	−4.26 ± 0.10	−9.66 ± 0.33

[a] Lowest energy absorption maximum (nm) of the donor molecule.
[b] Lowest energy CT maximum (nm).
[c] Donor in excess.
[d] Acceptor in excess.
[e] $\varepsilon = 910\,M^{-1}\,cm^{-1}$ at 25 ± 0.1 °C.
[f] $\varepsilon = 1260\,M^{-1}\,cm^{-1}$ at 25 ± 0.1 °C.
[g] $\varepsilon = 2480\,M^{-1}\,cm^{-1}$ at 25 ± 0.1 °C.

representative, the CT spectra of the EDA complex formed between the donor D3a and the acceptor TCNQ at various concentrations are shown in Fig. 1.

Dichloromethane solutions of the carbazole derivatives listed in Table 1 exhibit sharp absorbance cutoffs at ~360 nm. Their complexes have λ_{CT} bands at around 517–610 nm. Electron affinities (E_a) of TCNE, TCNQ and *p*-CHL are measured as 3.17 ± 0.2 [15], 2.8 ± 0.2 [16,17] and 1.37 ± 0.1 eV [18], respectively. This trend was observed in the λ_{CT} bands of the CT complexes of these acceptors with the carbazole series. Measured ionization potentials (I_p) of carbazole are around 7.6–8.0 [19,20] and ethylcarbazole is 7.41 eV [21]. Methyl substituent decreases the ionization potential of aromatic compounds by a factor of 0.1–0.3 eV, depending on the existence of other functional groups on the ring, and the position of the attachment [22]. Computed photoelectron spectroscopy (PES) bands of carbazole referring to the first three of the highest occupied molecular orbitals (HOMOs) with the I_p values of 7.68, 8.08 and 9.09 eV are used for elucidating the absorption bands of its CT complex with TCNE (Fig. 2). Carbazoles are expected to give three absorption maxima due to the CT transitions between HOMO-1, HOMO-2, and HOMO-3 of the donors and lowest unoccupied molecular orbitals (LUMOs) of the acceptors (Fig. 2). The transition bands due to HOMO-3 of the carbazole donors and LUMO of TCNE appear at about 385 nm [6]. The transition bands due to HOMO-2 and HOMO-1 appear as two overlapping peaks resulting in a broad shoulder having a λ_{max} around 600 nm. Similar absorption bands are observed in the CT spectra of carbazole derivatives with all three acceptors discussed in this study.

3.2. Determination of the equilibrium constants of CT complexes

The absorbance values at λ_{CT} of the complexes obtained experimentally were used for the determination of the molar extinction coefficients (ε), and the equilibrium constants (K_{eq}) using the Benesi–Hildebrand equation. This method gives credible results for the determination of ε and K_{eq} only when it generates linear plots for 1:1 donor–acceptor complexations. In other donor–acceptor ratios it gives more scattered plots leading to inaccurate results. Therefore, prior to calculating ε and K_{eq}, stoichiometries of complexations should be sorted out. The stoi-

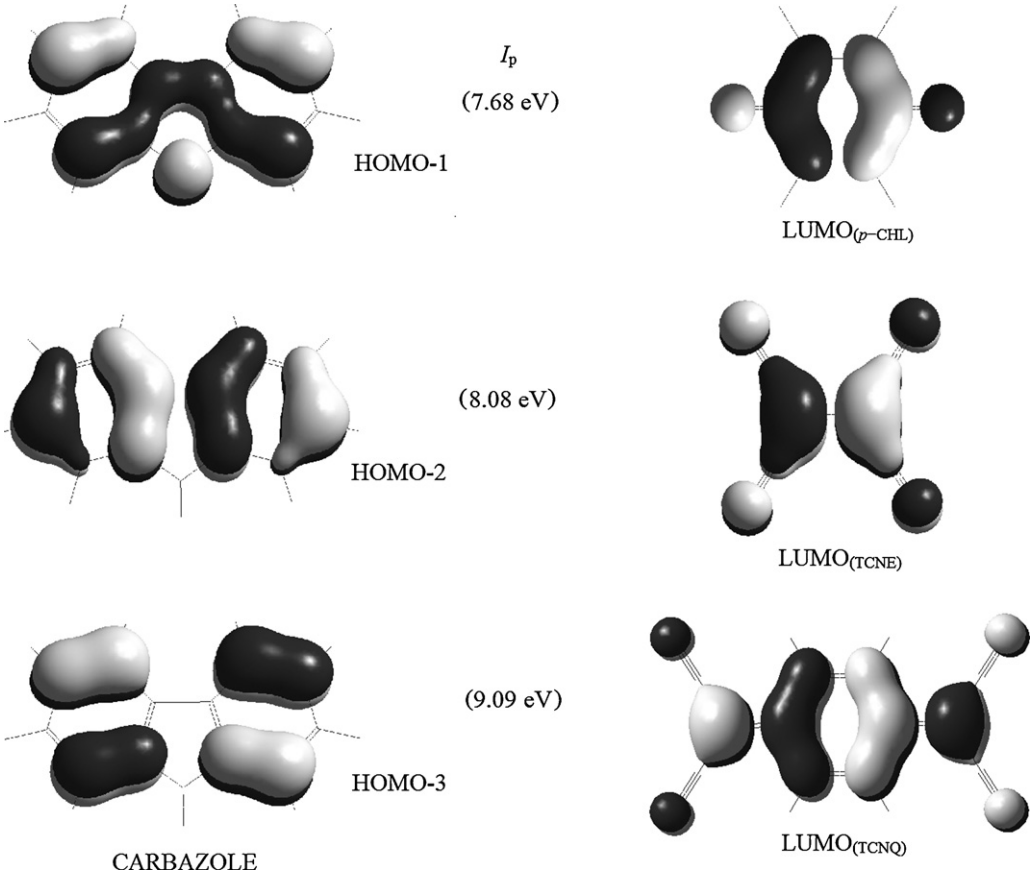

Fig. 2. Highest occupied donor orbitals of carbazole group and lowest unoccupied acceptor orbitals of *p*-CHL, TCNE, and TCNQ.

chiometries of the complexations were determined from the Job's plots [12]. Experimental results show that one carbazole unit associate with one acceptor molecule giving the highest absorbance at 1:1 mixture of the components. As representatives, Job's plots of D3b with TCNE, TCNQ and *p*-CHL are given in Fig. 3.

Carbazole donor molecules formed EDA complexes with the acceptors TCNE, TCNQ and *p*-CHL in dichloromethane according to the following hypothetical equation.

$$D + A \overset{K}{\rightleftharpoons} D, A$$

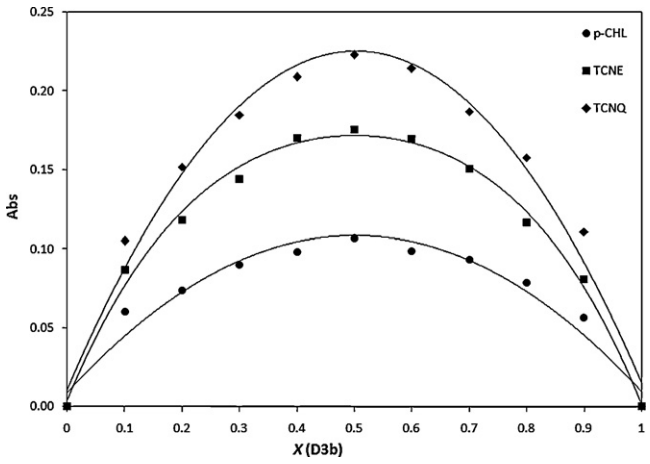

Fig. 3. Job's plots of the complexes of D3b with *p*-CHL, TCNE, and TCNQ.

The equilibrium constant K_{eq} for the above reaction can be written as:

$$K_{eq} = \frac{[D, A]}{([D]_0 - [D, A])([A]_0 - [D, A])} \quad (1)$$

The value of K_{eq} is related to A and ε of the complex at λ_{CT}, and the initial concentrations of the donor ($[D]_0$) and acceptor ($[A]_0$) molecules. Replacing [D,A] with (A/ε) from the Beer–Lambert law and ignoring [D,A] concentration in ($[A]_0 - [D,A]$) term when $[A]_0 \gg [D]_0$ and in ($[D]_0 - [D,A]$) term when $[D]_0 \gg [A]_0$ Eq. (1) yields Eqs. (2a) and (2b) as the Benesi–Hildebrand equations.

$$\frac{[D]_0}{A} = (K\varepsilon)^{-1}\left(\frac{1}{[A]_0}\right) + (\varepsilon)^{-1} \quad \text{when} \quad [A]_0 \gg [D]_0 \quad (2a)$$

$$\frac{[A]_0}{A} = (K\varepsilon)^{-1}\left(\frac{1}{[D]_0}\right) + (\varepsilon)^{-1} \quad \text{when} \quad [D]_0 \gg [A]_0 \quad (2b)$$

A Plot of $[D]_0/A$ vs. $(1/[A]_0)$ in Eq. (2a) or $[A]_0/A$ vs. $(1/[D]_0)$ in Eq. (2b) would yield $(K\varepsilon)^{-1}$ as the slope and $(\varepsilon)^{-1}$ as the intercept. In the case of dicarbazolylalkanes each dimer molecule can be accepted as two independently behaving monomers assuming that each chromophoric group associates with only one acceptor molecule. Therefore, $[D]_0$ should be multiplied with 2 in Eqs. (2a) and (2b) to yield Eqs. (3a) and (3b).

$$\frac{[D]_0}{A} = (2K\varepsilon)^{-1}\left(\frac{1}{[A]_0}\right) + (2\varepsilon)^{-1} \quad \text{when} \quad [A]_0 \gg [D]_0 \quad (3a)$$

$$\frac{[A]_0}{A} = (2K\varepsilon)^{-1}\left(\frac{1}{[D]_0}\right) + (\varepsilon)^{-1} \quad \text{when} \quad [D]_0 \gg [A]_0 \quad (3b)$$

For the dimer molecules a plot of $[D]_0/A$ vs. $(1/[A]_0)$ would yield $(2K\varepsilon)^{-1}$ as the slope and $(2\varepsilon)^{-1}$ as the intercept in Eq. (3a), whereas a

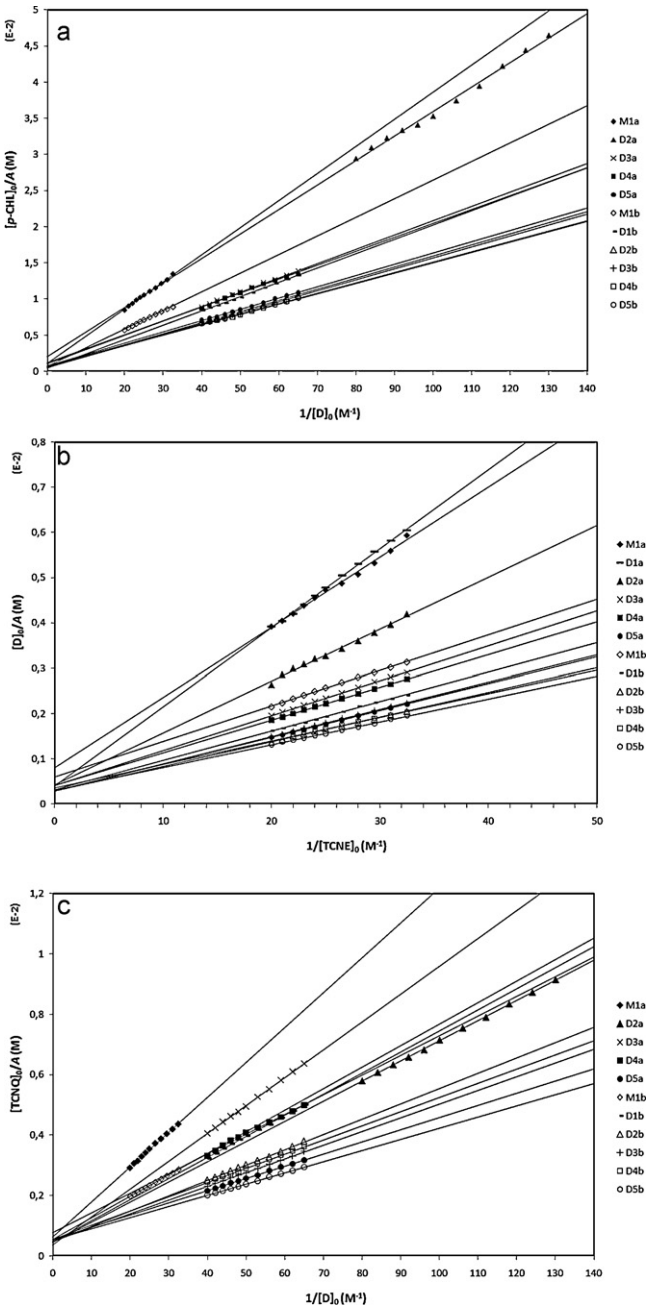

Fig. 4. Benesi–Hildebrand plots of the complexes of carbazole donors with (a) *p*-CHL, (b) TCNE, and (c) TCNQ at 25 °C.

plot of $[A]_0/A$ vs. $(1/[D]_0)$ would yield $(2K\varepsilon)^{-1}$ as the slope and $(\varepsilon)^{-1}$ as the intercept in Eq. (3b). Benesi–Hildebrand plots regarding the complexes of the carbazole donors with TCNE, *p*-CHL, and TCNQ are given in Fig. 4a–c and the results of the calculations regarding ε and K_{eq} values are given in Table 1.

From their BH plots the average ε values were determined to be $1310\,M^{-1}\,cm^{-1}$ for carbazole–TCNE, $910\,M^{-1}\,cm^{-1}$ for carbazole–*p*-CHL, and $2480\,M^{-1}\,cm^{-1}$ for carbazole–TCNQ complexes. To be consistent with the earlier studies [6,8] the value of $1260\,M^{-1}\,cm^{-1}$ for carbazole–TCNE complexes was accepted. Among the acceptors used in this study, *p*-CHL formed the most weakly bound complexes with the carbazole donors, having K_{eq} values between 1.62 and $4.26\,M^{-1}$. Presumably, D1a would have the lowest K_{eq} value, but the low solubility of this dimer in CH_2Cl_2 did not allow us to make reliable measurements. The calculated values of K_{eq} are between 2.27 and $10.10\,M^{-1}$ for carbazole–TCNE and between 2.12 and $6.04\,M^{-1}$ for carbazole–TCNQ complexes. Methyl substituted mono- and dicarbazoles formed complexes with much higher K_{eq} values compared to unsubstituted counterparts. This result could be attributed to the electron donor ability of the methyl substituent, which would result in a decrease in the I_p value of the carbazole moiety. The tetrahedral structure of the methyl substituent is thought to prevent donor–donor associations in solution enabling the carbazole groups to be more open to interactions with the acceptor molecules. Considering the effect of the length of the alkylene bridge on K_{eq} values, the dimers in which carbazole groups separated with 4 or 5 methylene groups ($n \geq 4$), behaved as if they were two independent monomers, having the K_{eq} values similar to those of related monomers, M1a and M1b.

Table 2
ANOVA summary for ΔH and ΔS based on the type of the acceptor molecules.

Source of variance	Sum of squares	*df*	Mean Square	*F*	*p*
ΔH					
Between groups	3.309	2	1.655	4.414	0.020
Within groups	12.369	33	0.375		
Total	15.678	35			
ΔS					
Between groups	74.825	2	37.412	12.825	<0.001
Within groups	96.269	33	2.917		
Total	171.094	35			

3.3. Determination of the thermodynamic constants

Thermodynamic properties of the CT complexations were determined according to the van't Hoff equation combined with the Beer–Lambert's law (Eq. (4)).

$$-\left(\frac{\Delta H}{R}\right)T^{-1} + \left(\frac{\Delta S}{R}\right) = \ln\left[\frac{A/\varepsilon}{([D]_0 - (A/\varepsilon))([A]_0 - (A/\varepsilon))}\right] \quad (4)$$

A plot of $\ln K$ vs. $1/T$ in Eq. (4) would yield $-\Delta H/R$ as the slope and $\Delta S/R$ as the intercept. The van't Hoff plots of carbazoles with TCNE, *p*-CHL and TCNQ are given in Fig. 5a–c, respectively.

The enthalpies and entropies of complex formation calculated using Eq. (4) are summarized in Table 1. Our results of ΔH calculations regarding the complex formation between *p*-CHL and the donors M1a, D1a–D5a are close to those found by Arslan et al. [7] except that for D1a. They found a more negative formation enthalpy ($-2.92\,kcal\,mol^{-1}$). The enthalpies of complexations between the donors M1a, D1a–D5a and the acceptor TCNE were found to be slightly less negative in this study compared to the results of Haderski et al. [6]. To evaluate the effect of the electron acceptor on the ΔH values a one-way analysis of variance (ANOVA) was performed on the calculated data (Table 2). The results show that there is a statistically significant difference in the ΔH values of the *p*-CHL, TCNE, and TCNQ ($F = 4.414$, $p < 0.05$). To find out the source of the difference Tukey's HSD post hoc analysis was performed (Table 3).

Table 3
Summary of Tukey's HSD comparison test for ΔH and ΔS.

Acceptor (*I*)	Acceptor (*J*)	Mean difference (*I*–*J*)	SE	*p*
ΔH				
p-CHL	TCNE	−0.1208	0.2499	0.880
p-CHL	TCNQ	0.5742	0.2499	0.070
TCNE	TCNQ	0.6950*	0.2499	0.024
ΔS				
p-CHL	TCNE	0.2092	0.2499	0.952
p-CHL	TCNQ	3.1575**	0.2499	<0.001
TCNE	TCNQ	2.9483**	0.2499	0.001

* The mean difference is significant at the 0.05 level.
** The mean difference is significant at the 0.01 level.

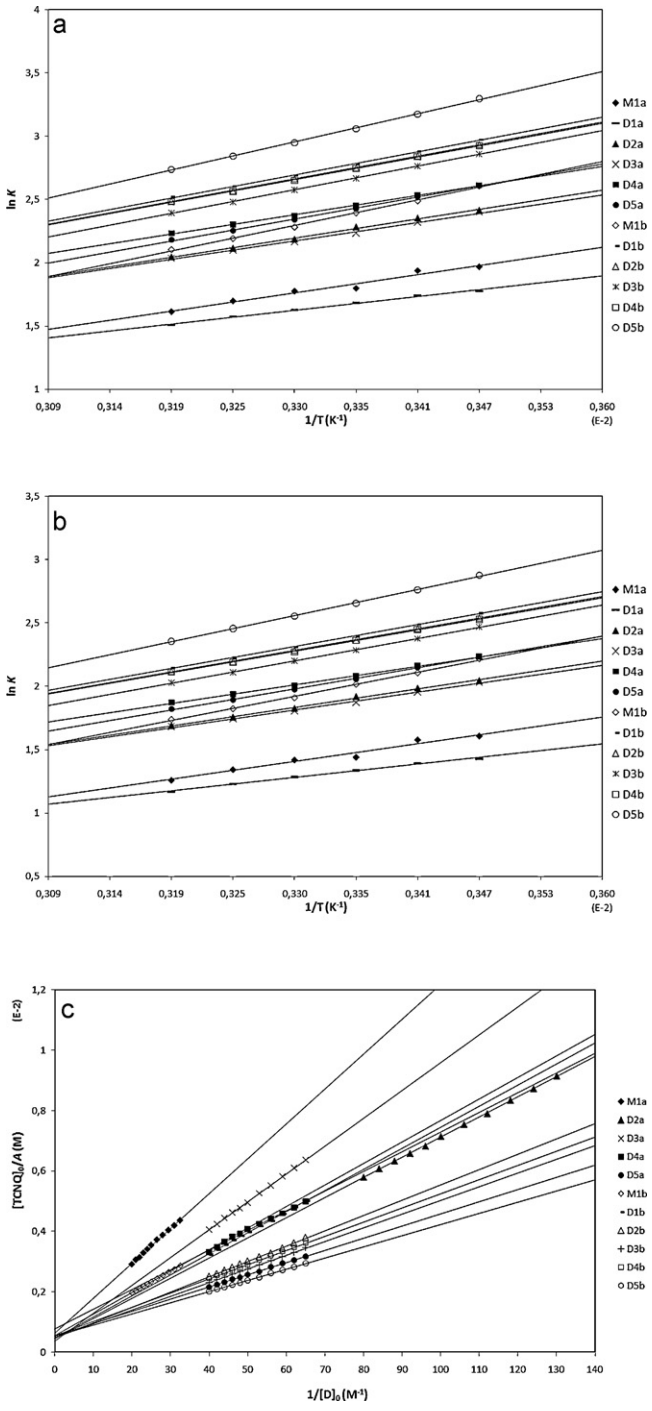

Fig. 5. Van't Hoff plots of the complexes of carbazole donors with (a) *p*-CHL, (b) TCNE, and (c) TCNQ.

From the results it is seen that there is not a significant difference between the mean ΔH values of the *p*-CHL and TCNE complexes while there are differences when compared the mean ΔH values of *p*-CHL with TCNQ and TCNE with TCNQ complexes. TCNQ formed more strongly bound complexes with the carbazole donors. When compared the E_a values of TCNQ with TCNE, this result seems to be surprising. Though, the geometries of the all three acceptors are planar, their sizes seem to affect the enthalpies of complexation. The LUMO of the larger TCNQ molecule had a better chance to overlap with the HOMO's of the carbazoles. This is true for the complexes of *p*-CHL, although it has a lower electron affinity than TCNE

Table 4
Summary of *t*-test for the comparison of ΔH and ΔS values of the donor groups.

Variable	Group	*N*	Mean	*SD*	*df*	*t*	*p*
ΔH	DH	18	−2.676	0.654	34	4.143	<0.01
	DCH_3	18	−3.440	0.430			
ΔS	DH	18	−5.482	2.294	34	2.401	0.022
	DCH_3	18	−7.142	1.828			

(1.37 ± 0.2 vs. 3.17 ± 0.1 eV), the difference between the average ΔH values of their complexes are statistically not significant.

The effect of the alkyl substituent on the ΔH values of complex formation was evaluated via performing a *t*-test to compare the ΔH values of M1a, D1a–D5a complexes with those of M1b, D1b–D5b (Table 4). The difference between the ΔH values of the donor groups (−3.44 for M1b, D1b–D5b, −2.68 for M1a, D1a–D5a), found to be statistically significant at the 0.01 confidence level. Electron donating ability of the methyl group through hyperconjugation enhanced the electron density of the π-system, resulting in more favorable formation enthalpies.

The calculated entropies of formation (Table 1) show that there is no correlation between the alkylene chain length and the entropy values. In general, the ΔS values regarding the TCNQ complexes are more negative, i.e. less favorable. It seems that the size of the acceptor was the determining factor in this case. The ΔS values for the complexation of D2a and D4a with TCNQ are considerably less negative than the other dimers. As noted earlier, TCNQ associates so strongly with these two dimers that at the concentrations used in thermodynamic studies at 25 °C, precipitation of dark green fine crystals of EDA complex were observed. This result was attributed to the even numbered methylene units forming the alkylene chain, which do not interfere with the π–π overlap between the donor and acceptor molecules. Likewise the enthalpies, the entropies of formation were also affected with the presence of the methyl group in M1b, D1b–D5b. According to the *t*-test results there is a statistically significant difference between the mean ΔS values of methyl substituted dimers and the other mono and dicarbazoles. The average of the entropies of methyl substituted dimers was found to be more negative by a factor of -1.66 kcal mol^{-1} K^{-1} than the others.

3.4. Vibrational spectroscopy

Vibrational techniques are used to study the nature of EDA associations in the crystalline state [23]. We were able to isolate the crystals of the EDA complexes of D4a with all three acceptors. This enabled us to determine the effects of the acceptors on the characteristic vibrational frequencies of D4a. The vibrational spectra of the complexes do not show much more differences than those of the parent donor and acceptor molecules. This is a common feature observed in the complexes formed with the weak π–π interactions [23–25]. Moderate shifts are observed in the C–H stretching and out-of-plane bending vibrations of the donor molecule. In general, a decrease in the electron density of the donor molecule results in a blue-shift, while an increase in the electron density of the acceptor causes a red-shift. This trend was observed in all three complexes. The C≡N stretching vibration of individual TCNE acceptors, appeared at ~2250 cm^{-1}, exhibited an 11 cm^{-1} red-shift, which indicates that the electron density is mainly accepted by the –CN groups. However, not a significant change in the υ (C≡N) band of TCNQ was observed, possibly due to delocalization of the accepted electron density over the aromatic π-system. The υ (C=O) band of *p*-CHL appeared at 1689 cm^{-1} shifted to a lower frequency ($\Delta\upsilon = 4$ cm^{-1}). The parent donor molecule, D4a, showed a υ (Ar–H) stretching band at 3051 cm^{-}1 and two out-of-plane bending bands at 741 and 717 cm^{-1}. Shifts to higher frequencies by about 5, 13 and 14 cm^{-1} at these bands were observed in the complexes of *p*-

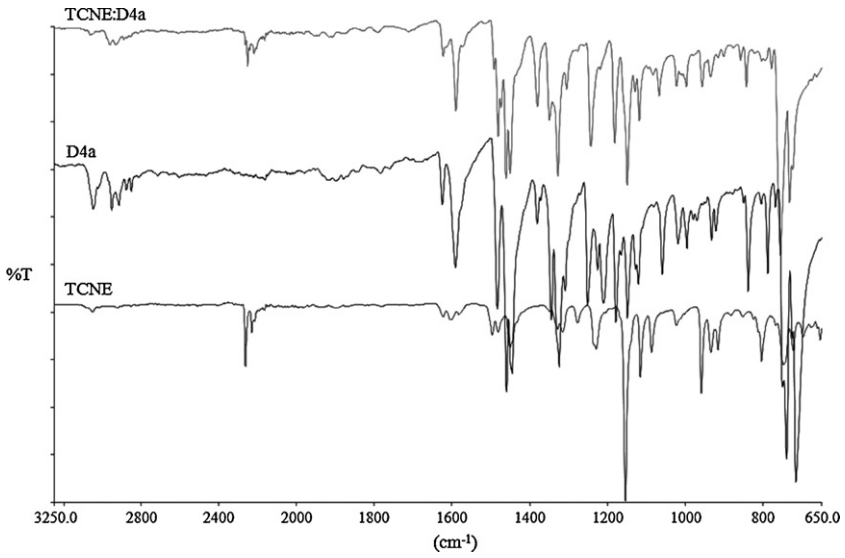

Fig. 6. FT-IR spectra of TCNE, D4a, and TCNE–D4a complex.

CHL, TCNQ and TCNE. These differences in the $\Delta\upsilon$ (Ar–H) values were attributed to the differences in the I_p values of the acceptor molecules. The IR spectra of D4a, TCNE, and D4a:TCNE complex are given in Fig. 6, as a representative.

4. Conclusion

1,*n*-Dicarbazolylalkanes (D1a–D5a), 1,*n*-di(3-methylcarbazolyl)alkanes (D1b–D5b), and their corresponding monomeric analogues (M1a and M1b) formed stable intermolecular CT complexes with the electron acceptors *p*-CHL, TCNE, and TCNQ in CH_2Cl_2. The stoichiometries of complexation determined by Job's method show that association was in 1:1 molecular ratio. The equilibrium constants, K_{eq}, of the complexations were determined by the linear Benesi–Hildebrand method. Among the dimeric donor molecules in both series, D1a and D1b have the smallest K_{eq} values. Increases in the K_{eq} values were observed as the chain length separating the two carbazole groups increased. The enthalpies and entropies of complex formations calculated utilizing van't Hoff equation suggest that there are not significant differences between the thermodynamic constants of the *p*-CHL and TCNE. However, the enthalpies of complexations involving TCNQ were slightly more negative and the entropies were greatly more negative, suggesting that complex formations are favored at low temperatures. With the all three acceptors methyl substituted mono and dicarbazole series formed EDA complexes with higher K_{eq} values, more negative enthalpies and entropies of formation. Moderate changes in the vibrational frequencies of the donor D4a and the acceptor molecules in their complexes in the solid state were observed. Further studies to determine the effect of mono- and diethyl substituents on the complexations are in progress.

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