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Charge-Transfer Complexations of Oxidative Coupling Products of Carbazole with TCNE and P-Chloranil

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Abstract

Charge-transfer (CT) complexations of 9H-carbazole (Cz), 9,9'-dicarbazyl (DCz), 3,9';9,9''-tricarbazyl (TCz), and polycarbazyl (PCz) with π–acceptors tetracyanoethylene (TCNE) and p–chloranil (p-CHL) were investigated spectroscopically. The relative stabilities, thermodynamic properties and stoichiometries of the CT complexes were discussed based on the molecular structure of the donor molecules and relative electron affinities of the acceptor molecules. It is concluded that DCz, TCz, and PCz form less stable complexes with TCNE and p-CHL than their monomeric analogues Cz.

Keywords: *CT-complexes, carbazoles; TCNE; p-chloranil.*

Karbazolun Yükseltgenmeli Kenetlenme Ürünlerinin TCNE ve P-Kloranil ile Yük-Transfer Kompleksleşmeleri

Özet

Karbazol (Cz), 9,9'-dikarbazil (DCz), 3,9';9,9''-trikarbazil (TCz) ve policarbazilin (PCz) tetrasiyanoetilen (TCNE) ve p-kloranil (p-CHL) π–akseptörleriyle yük-transfer (CT) kompleksleşmeleri spektroskopik olarak incelenmiştir. CT komplekslerinin bağıl kararlılıkları, termodinamik özellikleri ve stökiyometrileri donör moleküllerin moleküler yapılarını ve akseptör moleküllerin bağıl elektron ilgilerini temel alarak tartışılmıştır. Çalışma sonucunda DCz, TCz, ve PCz nin TCNE ve p-CHL ile monomerik analoğu olan Cz ye göre daha kararsız kompleks oluşturdukları sonucuna varılmıştır.

Anahtar kelimeler: *CT-compleksleri, karbazollar, TCNE, p-kloranil.*

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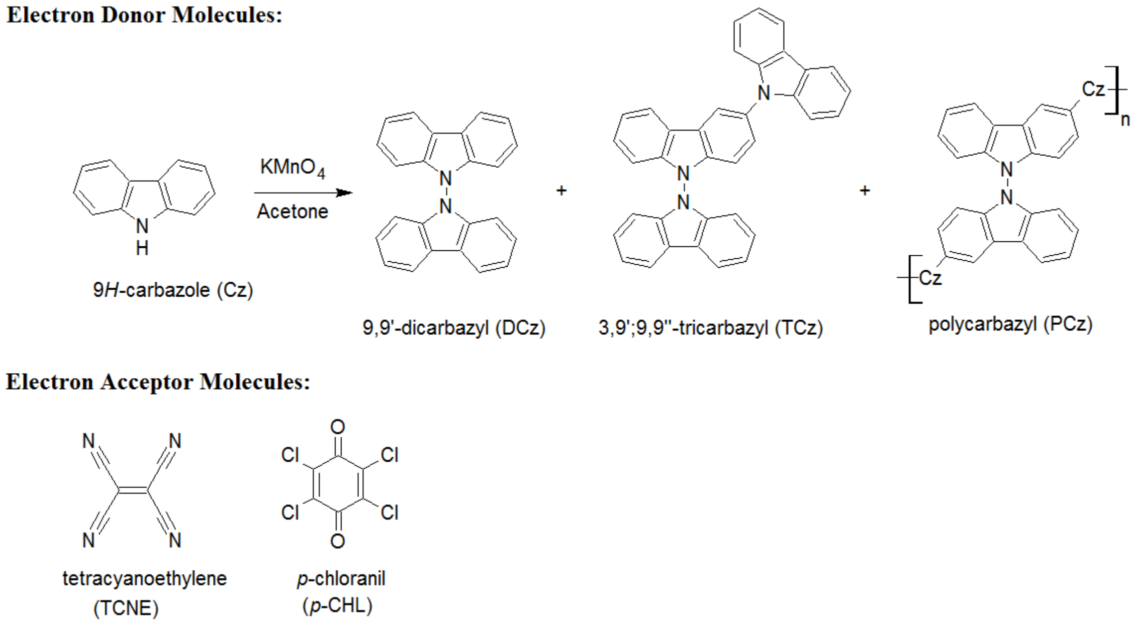
1. Introduction

Carbazole, a naturally occurring N-containing heterocyclic aromatic compound with 14-π electrons, is one of the main components of shale oil, crude oil, petroleum products and coal tar [1, 2]. Derivatives of carbazole have drawn much attention due to their applications as dyes [3,4], drugs [5], and low and high molecular weight amorphous materials [6-10]. Oxidation of carbazole with potassium permanganate in hot acetone gives mainly three products one of which was first identified by Perkin and Tucker (1921) as 9,9’-dicarbazyl (m.p. 221 °C) [11], and the second was identified by Robinson (1966) as 3,9’;9,9’’-tricarbazyl (m.p. 267 °C) [12]. The third amorphous product has not been identified yet but predicted to be polycarbazyl, which grew out of DCz [12]. Studies indicate that hole transporting properties of carbazoles are greatly enhanced when they form charge transfer (CT) complexes with certain electron acceptors such as tetracyanoethylene (TCNE), 2,4,7-trinitrofluorene-9-one (TNF), and *p*-chloranil (*p*-CHL) [13,14]. Therefore, it is helpful to understand CT complexation properties of this type of compounds. Here we present the results of a study based on the spectroscopic determination of the properties of CT complexes of carbazole (Cz), 9,9’-dicarbazyl (DCz), 3,9’;9,9’’-tricarbazyl (TCz) and polycarbazyl (PCz) with the π-acceptors TCNE and *p*-CHL (Scheme 1).



Scheme 1. Structural formulas of electron donor and acceptor molecules.

2. Experimental

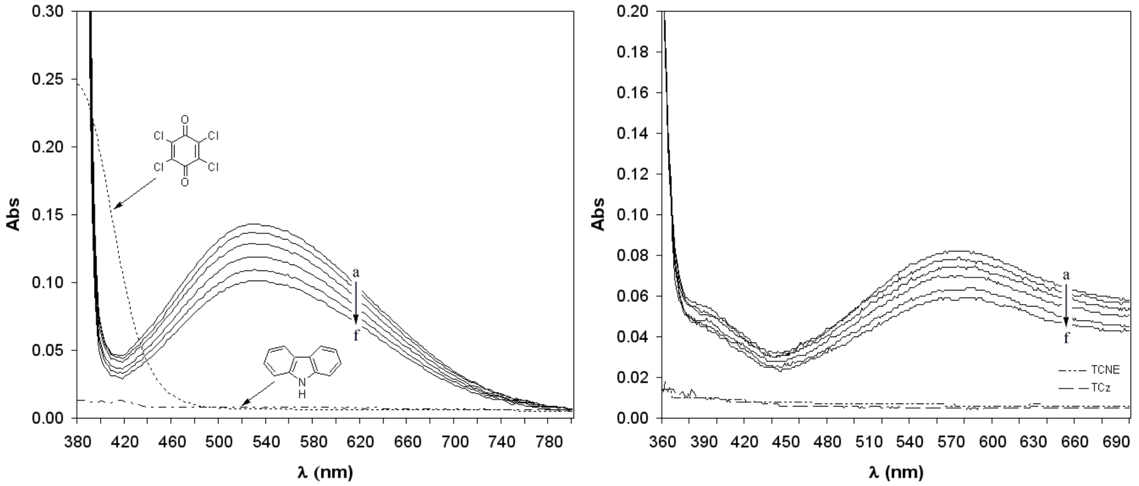
2.1. Instrumentation and materials

All absorbance measurements were recorded on a PG Instruments T70 double beam UV-Visible spectrophotometer in optical quartz cells with 1.0 cm path length using dichloromethane and chloroform as the solvents.

Carbazole (Cz) (Aldrich) was purified by silica gel column chromatography using hexane/acetone (4:1, v/v) as an eluent and by recrystallization from acetone. DCz, TCz, and PCz were synthesized via the oxidation of Cz with $KMnO_4$ in boiling acetone as described in the literature [11] (Scheme 1) and purified by silica gel column chromatography using hexane/dichloromethane as an eluent and recrystallization from dichloromethane. TCNE (Aldrich) and *p*-CHL (Alfa Aesar) were purified by sublimation. The solvents were high pure grade and were used without further purification.

2.2. Absorption measurements

The Benesi-Hildebrand technique was used for the determination of the CT molar extinction coefficients (ε) and equilibrium constants (K) for the formation of electron donor-acceptor (EDA) complexes of Cz, DCz, TCz, and PCz with TCNE and *p*-CHL [15]. For the CT absorbance measurements, in a 1.0 cm UV cuvette 2.0 ml solution containing 80 mM TCNE and 1.0 mM carbazole unit was placed. This was diluted 10 times by addition of 100 µl increments of the initially prepared 1.0 mM carbazole solutions. The TCNE–carbazole concentration ratios were varied from 80:1 to 53:1 through a series of 10 dilutions. In the carbazole–*p*-CHL complexation experiments the donor concentrations were kept high (15 mM carbazole unit vs. 1 mM *p*-CHL) due to the low solubility of the acceptor. The donor concentrations were changed from 50:1 to 37:1 by diluting via 5 times 100 µl and 5 times 150 µl addition of the donor solution. Absorbance changes were monitored after each dilution from their electronic spectra at λ_{CT} maxima. Electronic absorption spectra of TCz–TCNE CT-complex at varying concentrations of TCNE and of Cz–*p*-CHL CT-complex at varying *p*-CHL concentrations are given in Figure 1.



a) b)

Figure 1. Electronic absorption spectra of **a)** Cz–*p*-CHL CT-complex in $CHCl_3$; constant [*p*-CHL] = 1.0 mM, changing [Cz] = a) 50 mM, b) 45.5 mM, c) 42 mM, d) 38 mM, e) 34 mM, and f) 31 mM. and **b)** TCz–TCNE CT-complex in CH_2Cl_2; constant [TCz] = 0.33 mM, changing [TCNE] = a) 80 mM, b) 69 mM, c) 61.5 mM, d) 55 mM, e) 50 mM, and f) 46 mM.

Cz, DCz, TCz and PCz form blue complexes with TCNE and yellow to violet complexes with *p*-CHL in solution according to the following hypothetical equation:

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

The equation for the equilibrium constant K for the above reaction can be written as:

$$K = \frac{[\mathrm{D,A}]}{([\mathrm{A}]_0 - [\mathrm{D,A}])([\mathrm{D}]_0 - [\mathrm{D,A}])} \qquad (1)$$

The equilibrium constants (K) for EDA complex formation are related to the maximum absorption (A) of the CT-complex, the molar extinction coefficient (ε), and the initial concentrations of donor ($[\mathrm{D}]_0$) and acceptor ($[\mathrm{A}]_0$). Replacing the equilibrium constant of the DA complex, [D,A], with (A/ε) from Beer-Lambert law and ignoring [D,A] concentration in ($[\mathrm{A}]_0$ – [D,A]) when $[\mathrm{A}]_0 >> [\mathrm{D}]_0$, and ($[\mathrm{D}]_0$ – [D,A]) when $[\mathrm{D}]_0 >> [\mathrm{A}]_0$ eq. 1 yields the Benesi-Hildebrand equation (eq. 2a and 2b).

$$\frac{[\mathrm{D}]_0}{A} = \frac{1}{K\varepsilon}\frac{1}{[\mathrm{A}]_0} + \frac{1}{\varepsilon} \qquad \text{where } [\mathrm{A}]_0 >> [\mathrm{D}]_0 \qquad (2a)$$

$$\frac{[\mathrm{A}]_0}{A} = \frac{1}{K\varepsilon}\frac{1}{[\mathrm{D}]_0} + \frac{1}{\varepsilon} \qquad \text{where } [\mathrm{D}]_0 >> [\mathrm{A}]_0 \qquad (2b)$$

Plotting $[\mathrm{D}]_0/A$ vs. $1/[\mathrm{A}]_0$ in eq. 2a or $[\mathrm{A}]_0/A$ vs. $1/[\mathrm{D}]_0$ in eq. 2b yields $1/K\varepsilon$ as the slope and $1/\varepsilon$ as the intercept, where $[\mathrm{D}]_0$ represent the initial concentration of the carbazole group in the donor molecule. Benesi-Hildebrand plots of complexes of Cz, DCz, TCz and PCz with TCNE and *p*-CHL are given in Figure 2.

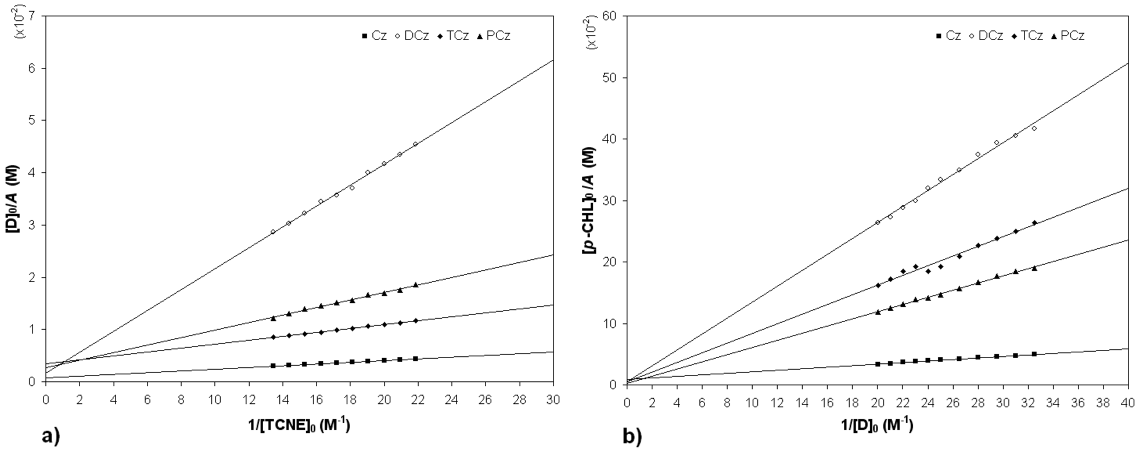


Figure 2. Benesi–Hildebrand plots of **a)** CT-complexes of Cz, DCz, TCz, and PCz with TCNE and **b)** CT-complexes of Cz, DCz, TCz, and PCz with *p*-CHL.

The stoichiometries of the complexation of carbazoles with TCNE were determined using the Job method of continuous variation [16]. Equal concentrations of donor group and acceptor molecules were prepared separately. The donor and acceptor solutions were mixed in 2.0 mL volumetric flasks in which the mole fraction of the components differed from 0.1 to 0.9. Then the absorbances were recorded at the maximum CT wavelength on each dilution. Job plots of Cz, DCz, TCz, and PCz with TCNE and *p*-CHL complexes are given in Figure 3.

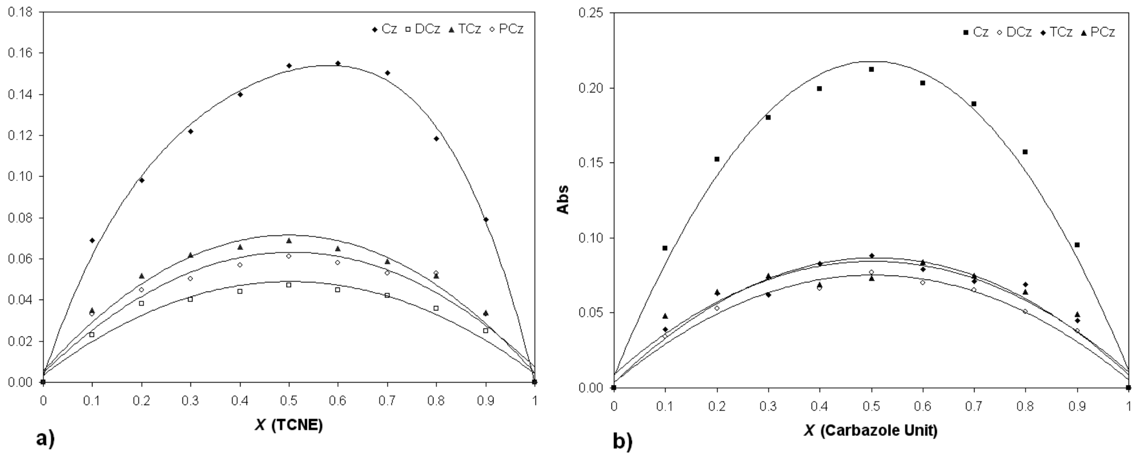


Figure 3. Job plots of **a)** CT-complexes of Cz, DCz, TCz, and PCz with TCNE and **b)** CT-complexes of Cz, DCz, TCz, and PCz with p-CHL.

Thermodynamic properties of EDA complexes were determined using the van't Hoff equation and Beer-Lambert law by measuring absorption spectra of the complexes at different temperatures at λ_{CT} for each complexation. The volume changes were measured for these temperatures and concentration changes were taken into account in calculating the thermodynamic constants, accordingly. The integrated form of the van't Hoff equation used in the calculations is:

$$-\left(\frac{\Delta H}{R}\right)\frac{1}{T}+\frac{\Delta S}{R}=\ln\left(\frac{A/\varepsilon}{([\mathrm{A}]_0-A/\varepsilon)([\mathrm{D}]_0-A/\varepsilon)}\right) \qquad (3)$$

A plot of ln$K$ (the whole term on the right side of the equation) vs. $1/T$ in eq. 3 yielded $-\Delta H/R$ as the slope and $\Delta S/R$ as the intercept. The van't Hoff plots of Cz, DCz, TCz and PCz with TCNE and *p*-CHL are given in Figure 4.

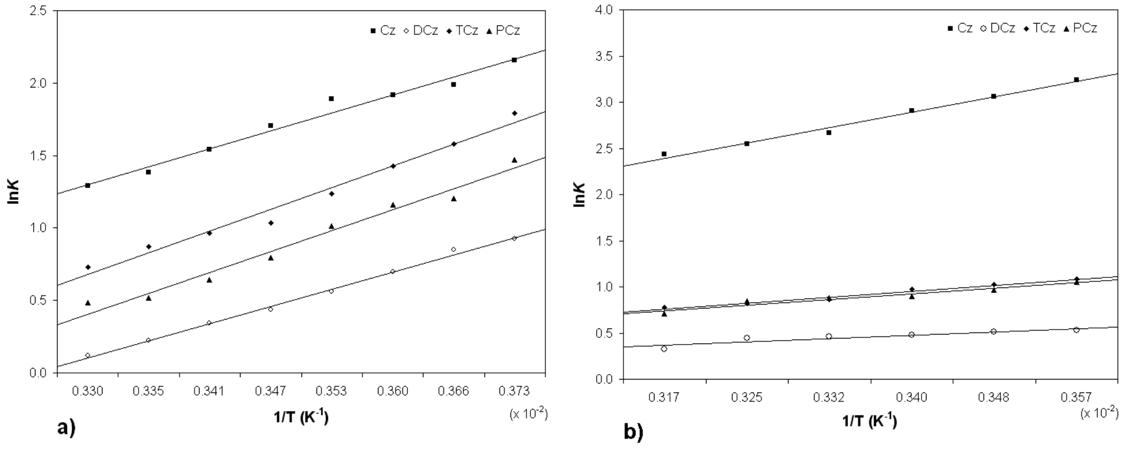


Figure 4. Van't Hoff plots of **a)** CT-complexes of Cz, DCz, TCz, and PCz with TCNE (10 mM carbazole group, 10 mM TCNE in CH_2Cl_2) and **b)** CT-complexes of Cz, DCz, TCz, and PCz with p-CHL (10 mM carbazole group, 10 mM p-CHL in $CHCl_3$).

3. Results and Discussion

Non-bonded intermolecular association of an electron donor with an electron acceptor usually results in a DA complex. Dark blue colored DA complexes of carbazoles with TCNE is a clear indication of association among their respective molecular orbitals. The greater the electron affinity of the acceptor (or the ionization potential of the donor), the smaller the energy of the CT absorption maximum, ($h\nu_{CT}$) becomes. Relatively high ionization potential (*IP*) of carbazoles around 7.6-8.0 eV make them strong π-donors [17,18], while electron affinity (*EA*) of TCNE, 3.17 eV, makes it a good π-acceptor [19]. Relatively lower *EA* of *p*-CHL around 2.46-2.59 eV makes it somewhat worse π-acceptor than TCNE [20]. According to Mulliken [21] the energy of CT transition is given by $h\nu_{CT} \cong IP_D - EA_A - \omega$, where ω is a term mainly coming from coulombic attraction between positively charged donor and negatively charged acceptor ion pair, $[D^{\bullet +}, A^{\bullet -}]$, in the excited state. Charge transfer absorption occurs when one electron from one of the highest occupied molecular orbitals (HOMO’s) of the donor is promoted to the lowest unoccupied molecular orbital (LUMO) of the acceptor. Selected HOMO’s of carbazole and LUMO’s of TCNE and *p*-CHL calculated by AM1 semi-empirical method [22] implemented in the HyperChem 8.02 molecular modeling software [23] are given in Figure 5. Electron donor-acceptor CT transition of carbazoles with TCNE requires lower energies than with *p*-CHL. Considering the donor molecules the energies of CT bands with both acceptors were in the order of Cz < TCz ≅ PCz < DCz. The lower energy of the CT transition band of Cz donor with both TCNE and *p*-CHL could be attributed to the delocalization of N-H σ-electrons by induction. The complexes investigated in this study were stable, i.e. did not go under dissociative electron transfer. Instead, the components were preserved via the back electron transfer process from the $D^{+\bullet}$, $A^{-\bullet}$ ion pair.

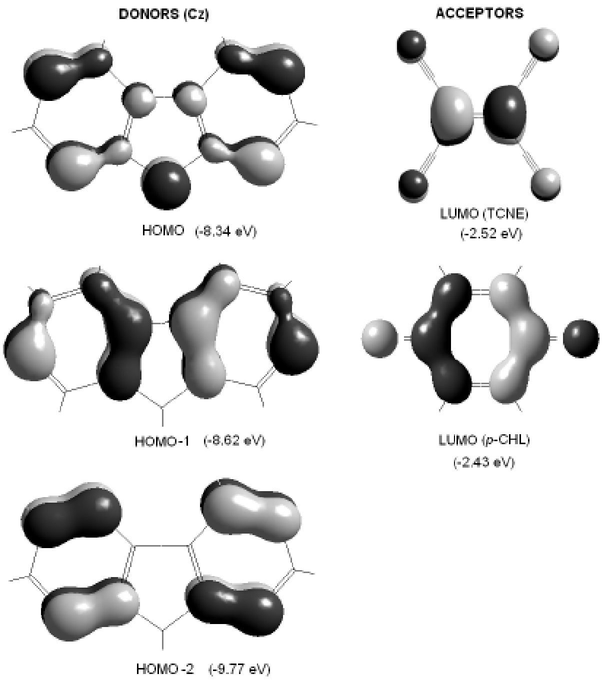


Figure 5. Selected HOMO’s of carbazole and LUMO’s of TCNE and p-CHL calculated by semi-empirical AM1 method.

The values of ε's and K's for the CT complexes of Cz, DCz, TCz, and PCz are calculated from their Benesi–Hildebrand plots and the results are given in Table 1.

Table 1. Properties of CT complexes of Cz, DCz, TCz, and PCz with acceptors TCNE and *p*–CHL.

TCNE	λ^{a}	λ_{CT}^{b}	$K\varepsilon_{CT}^{c}$ (M^{-2} cm^{-1})	K^{d} (M^{-1})	ΔH (kcal/mol)	ΔS (eu)
Cz	329	601	5909 ± 90	4.69	–3.98 ± 0.28	–10.53 ± 0.99
DCz	331	541	500 ± 38	0.40	–3.82 ± 0.09	–12.38 ± 0.32
TCz	342	574	2678 ± 10	2.13	–4.85 ± 0.22	–14.62 ± 0.78
PCz	342	574	1392 ± 38	1.10	–8.35 ± 0.98	–14.53 ± 0.96
p-CHL	λ^{a}	λ_{CT}^{b}	$K\varepsilon_{CT}^{e}$ (M^{-2} cm^{-1})	K^{f} (M^{-1})	ΔH (kcal/mol)	ΔS (eu)
Cz	329	532	786±11.9	3.57	–4.174 ± 0.18	–8.46 ± 0.62
DCz	331	502	77±2.3	0.35	–0.88 ± 0.21	–2.07 ± 0.69
TCz	342	520	127±6.7	0.58	–1.61 ± 0.11	–3.58 ± 0.37
PCz	342	520	172±3.4	0.78	1.51 ± 0.20	–3.31 ± 0.66

[a] Lowest energy absorption maximum of uncomplexed carbazole (nm). [b] Lowest energy CT maximum (nm). [c] Acceptor in excess. [d] Donor in excess. [e] $\varepsilon = 1260\ M^{-1}\ cm^{-1}$ at 21 ± 1 °C. [f] $\varepsilon = 220\ M^{-1}\ cm^{-1}$ at 21 ± 1 °C.

Extinction coefficient of the CT absorption of the complexes of donor molecules with the same chromophore unit is determined from their molar concentrations in solution [24]. Since the carbazole group is the only chromophore unit in all four compounds, their ε values expected to be proportional to their molar carbazole group contents per mole of the compounds. In the previous studies conducted on the complexes of alkyl substituted carbazoles with TCNE, the ε values were calculated as around 1260 $M^{-1}cm^{-1}$ and also accepted in this study for consistency [25,26]. The average extinction coefficient of the CT complexes of the donor molecules with *p*-CHL is determined as 220 $M^{-1}cm^{-1}$ in this study. The values of equilibrium constant, K, ranged between 0.40-4.69 M^{-1} for the complexes of carbazoles with TCNE and between 0.35-3.57 M^{-1} with *p*-CHL. These values indicate that, considering both TCNE and *p*-CHL, complex formation was favored the most with Cz and the least with DCz. The higher K values for Cz complexes can be attributed to the relatively higher ionization potential and steric openness of Cz. The lower K values for complexes of DCz with both acceptors can be explained by lower ionization potential due to the removal of the hydrogen atoms at the interconnecting nitrogen atoms and to the steric hindrance of the central pyrrolic rings due to the scissor-like geometry [27]. From the calculated structures of DCz and TCz (Figure 6) it can be seen that planes of the carbazole rings in DCz are perpendicular and the H-atoms at C1 and C8 might sterically hinder the positioning of the acceptor molecules on both sides of the central five-membered pyrrolic ring. The third carbazole group in TCz is more open with a calculated dihedral angle of 25.10°. TCz and PCz exhibited similar complex formation behavior, having close $h\nu_{CT}$ bands and K values because of their structural resemblance.

Thermodynamic properties of complexations were determined by calculating their enthalpies and entropies of formation using eq. 3. The negative enthalpies of carbazoles with TCNE and *p*-CHL show the formation of weakly associated complexes. The negative values of both enthalpy and entropy changes indicate that complexation is favored at lower temperatures. However, relatively lower enthalpies of complex formation of DCz, TCz and PCz with *p*-CHL compared to that of *p*-CHL-Cz complexation suggest that the former three donor molecules associate more loosely with the acceptor.

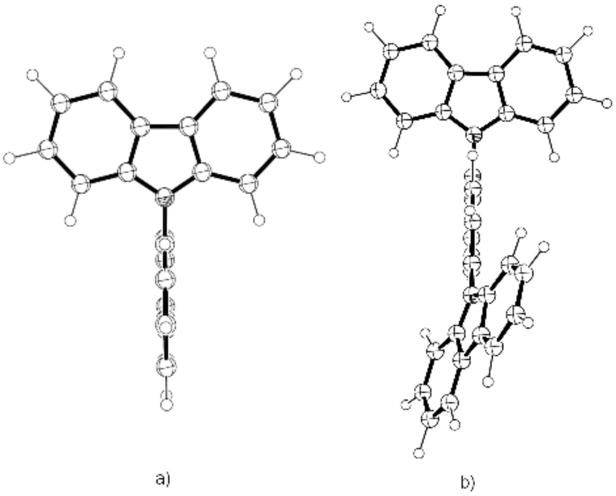


Figure 6. Calculated structures of DCz and TCz representing geometrical alignments of carbazole groups.

This is, again, attributable to their relatively lower ionization potentials. The mean of the enthalpies and the mean of the entropies of formation for the complexes of donors with TCNE were found to be more negative than those for the complexes with *p*-CHL. This result shows the higher temperature dependency of the complexes of TCNE than *p*-CHL, which could be explained by the higher electron affinity of TCNE than *p*-CHL.

The Job method of continuous variation enables one to determine the molecularity of the predominant complex. All the donors except Cz form complexes in the ratio of 1:1 at the chosen concentrations (Figure 6 & 7). The stoichiometry of the complexation between Cz and TCNE was in the form of [DA_2]. Higher absorbance values measured at higher mole fractions of acceptors indicate that other donors also formed [DA_2] type complexes, but complexes of [DA] type remained predominant.

4. Conclusion

The electron donor molecules Cz, DCz, TCz and PCz form weakly associated CT complexes with the electron acceptors TCNE and *p*-CHL in solution. From the equilibrium constants of complexation it can be concluded that stability of the complexes with both acceptors were in the order of Cz > TCz ≅ PCz > DCz. Thermodynamic constants of the complexation show the temperature dependencies of the complexation remained in the same order. In all four donor molecules, electron donor ability of carbazole was the best, TCz and PCz were the second best and DCz was the worst. The perpendicular alignment of the two carbazole rings in DCz is blamed for the worst electron donor property. The stoichiometries of complexation were found to be mainly 1:1 D-A ratio (except 1:2 ratio in Cz-TCNE complex). However, at higher mole fractions of TCNE and *p*-CHL, existence of 1:2 complexes in addition to predominant 1:1 complexes was determined.

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