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Electron-transfer absorption of sterically bulky donor–acceptor pairs: electron donor–acceptor complexes or random pairs?

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Abstract

Electron-transfer absorption of substituted benzene donors with tetracyanoethene (TCNE) is studied in dichloromethane and at several temperatures. For quantitative comparison of the intensities of electron-transfer absorbance, *A* of different electron donor/acceptor (D/A) pairs at various free donor and acceptor molar concentrations (C_D and C_A) an absorption coefficient $\kappa = A/(C_D C_A)$ is introduced. The results indicate that κ values of sterically bulky alkyl substituted D/A pairs are several orders of magnitude lower than those of the corresponding sterically unhindered pairs with similar structures and electron transfer properties. For a series of comparable sterically bulky and unhindered donors, when strong donors are compared to weak donors, a more than 10-fold increase in κ values is observed for the sterically unhindered donors, while the change is less than two-fold for sterically bulky donors. This supports the view that the electron transfer absorption of the sterically bulky D/A pairs originates from unassociated random pairs. Further evidence comes from the fact that κ values of sterically bulky D/A pairs show very weak or no temperature dependence. By fitting the absorption spectra of the CT bands of the electron D/A complexes formed between TCNE and sterically unhindered donors, electronic coupling elements and reorganization parameters are obtained. Based on these parameters, the electron transfer absorption spectra of the random pairs discussed earlier are simulated and compared with experiments.

Keywords: Electron transfer absorption; Random pair; Tetracyanoethene; Electron D/A

1. Introduction

For non-adiabatic electron transfer, rate constants are usually expressed as the product of an electronic coupling matrix element, H_{ab}, and a Franck–Condon weighted density of states [1–3]. Electron donor–acceptor (EDA) complexes are weakly associated neutral D/A pairs in which photo-induced electron transfer can occur directly by excitation in a charge transfer (CT) absorption band [4,5]. Parameters needed to define the Franck–Condon weighted density of states can be obtained by fitting the CT absorption band profiles [6,7]. The electronic coupling matrix element, H_{ab}, can be calculated by the Mulliken–Hush equation if the molar absorptivity (ε_{max}), transition energy (E_{abs}), bandwidth ($\Delta\nu_{1/2}$) and electron separation distance (r) are known [8,9]. Weak interaction between donor and acceptor in their ground states in solution makes the EDA association loose and reversible. EDA pairs with different separation distances and orientations might contribute to the absorption of the CT band. We show that for EDA complexes formed by weakly complexed D/A pairs, the contributions of distantly separated pairs contribute an important part to the total absorption. Apart from the EDA complexes, free D/A molecules are present in the solution as random pairs with statistical separation distances from a fraction of a nanometer to infinity. We propose that these random pairs are likely to make a significant contribution to the CT band. So far no detailed analysis has been given for the relative contribution of such EDA pairs at different separation distances to the total absorption. The Benesi–Hildebrand method provides a measure of the total equilibrium constant of all the EDA complexes with various separation distances, while the obtained ε corresponds to a weighted average molar absorptivity.

In recent work, we found that, when in moderately polar solvents, an EDA complex is excited in its CT band; the free ion yields exhibit strong wavelength dependence [10]. We proposed that weak absorption by long-distance, unassociated or “random” D/A pairs is mainly responsible for the free radical ion yield [10,11]. In this work, we measured the absorption spectra of solutions of the electron acceptor, tetracyanoethene (TCNE) with a series of comparable sterically bulky and unhindered donors. In some cases, formation of EDA complexes was prevented by using donors

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with large steric bulk. However, bulky donors like 1,3,5-tri-*tert*-butylbenzene (TBB), hexaethylbenzene (HEB) and 1,2,4,5-tetra-*iso*-propylbenzene (TIPB) still give weak CT absorption spectra in solution with TCNE. A random D/A pair model can satisfactorily explain these spectra. The photoexcitation of the CT absorption of these weakly interacted but non-complexed donor and acceptor pairs will directly result in the formation of long distance EDA ion pairs. A large portion of these ion pairs are actually solvent separated ion pairs which are important in producing free ions by further separation. To probe the interaction strength of different D/A pairs, temperature dependence experiments are conducted. Finally, the profiles and intensities of electron transfer absorption spectra of the random pairs discussed earlier are simulated and compared with the experimental results.

2. Experiments

The acceptor used in the experiment was tetracyanoethene (TCNE, Acros, 98%), which is a strong electron acceptor [12]. Donors used were 1,3,5-trimethylbenzene (TMB, Aldrich, 99%), 1,3,5-triethylbenzene (TEB, Aldrich, 98%), 1,3,5-tri-*tert*-butylbenzene (TBB, Aldrich, 97%), 1,3,5-tri-*iso*-propylbenzene (TriIPB, Acros, 97%), durene (DUR, Aldrich, 99%), 1,2,4,5-tetra-*iso*-propylbenzene (TIPB, Aldrich, 96%), hexamethylbenzene (HMB, Aldrich, >99%) and hexaethylbenzene (HEB, Aldrich). Solvents used were dichloromethane. TCNE was recrystallized from dichloromethane before use. All other reagents were used as received. For all the experiments, the concentration of TCNE was 0.04 M. The donor concentration was $2\times10^{-4} \sim 0.2$ M.

Absorption spectra were recorded in 1 cm cells using a Perkin-Elmer Lambda 9 spectrometer. The cell temperature was controlled by using Brinkmann RM6 circulation system. Moisture is removed from the cavity by blowing N_2 gas.

3. Results and discussion

3.1. Introduction of the concept of “random pairs”

For a homogeneous solution of donor and acceptor, the molar absorptivity ($\epsilon(\nu,r)$) of D/A pairs at separation distance r_{DA} is related to the electronic coupling matrix element ($H_{\mathrm{ab}}(r)$), the Frank–Condon factor (FC(g)) and electron transfer distance (r_{DA}) by Eq. (1) and (2) [6].

$$\varepsilon(\nu, r) = \frac{8N_0\pi^3\,\mathrm{e}^2\,D_{\mathrm{OP}}[H_{\mathrm{ab}}(r)]^2 r_{\mathrm{DA}}^2}{3000h^2c\nu\ln 10}\mathrm{FC}(g) \tag{1}$$

$$\mathrm{FC}(g) = \sum_{j=0}^{\infty} F_j(4\pi\lambda_{\mathrm{S}}k_{\mathrm{B}}T)^{-1/2}\,\mathrm{e}^{-(jh\nu_{\mathrm{V}}+g+\lambda_{\mathrm{S}})^2/4\lambda_{\mathrm{S}}k_{\mathrm{B}}T} \tag{2}$$

$$F_j = \frac{\mathrm{e}^{-S}\,S^j}{j} \qquad S = \frac{\lambda_{\mathrm{V}}}{h\nu_{\mathrm{V}}} \qquad g = \Delta G^0 - h\nu$$

FC(g) is the Franck–Condon weighted density of states. This term is a function of ΔG^0, the standard state free energy change associated with the electron transfer reaction. FC(g) is also a function of several other factors, the reorganization energy λ_{s}, associated with solvent and other low-frequency modes, and the reorganization energy λ_{V}, associated with a single averaged high frequency mode of frequency ν_{V}, j is the number of quanta of the ν_{V} mode.

The Benesi–Hildebrand method cannot provide information about the relative contribution at each separation distance in the total absorption [5]. The dependence of absorption on distance is calculated with following assumptions. The concentrations of both EDA complex and random pairs with separation distance r are proportional to the product of free donor and acceptor concentration. At given free donor and acceptor concentrations, the EDA complex concentration is controlled by its formation constant, K, while the concentration of random pairs at each separation r (Å) is directly related to the statistical distribution of free donor and acceptor molecules in bulk solution. CT absorption is the sum of that from EDA complexes and random pairs at different separation distances (Eq. (3)).

$$\begin{aligned} A &= A_{\mathrm{EDA}} + A_{\mathrm{random}} = \int_{r_0}^{r_{\mathrm{m}}} \mathrm{d}A(r_i) + \int_{r_{\mathrm{m}}}^{\infty} \mathrm{d}A_{\mathrm{random}}(r) \\ &= \int_{r_0}^{r_{\mathrm{m}}} \varepsilon(r)\,\mathrm{d}C_{\mathrm{EDA}}(r) + \int_{r_{\mathrm{m}}}^{\infty} \varepsilon(r)\,\mathrm{d}C_{\mathrm{D},\ldots,\mathrm{A}}^{\mathrm{random}}(r) \\ &= \int_{r_0}^{r_{\mathrm{m}}} \varepsilon(r)C_{\mathrm{D}}C_{\mathrm{A}}\,\mathrm{d}K(r) \\ &\quad + \int_{r_{\mathrm{m}}}^{\infty} 4\pi \times 10^{-27} N_0 r^2 \varepsilon(r) C_{\mathrm{D}}C_{\mathrm{A}}\,\mathrm{d}r \end{aligned} \tag{3}$$

where N_0 is Avogadro’s constant, r_{m} can be understood as a critical separation distance beyond which specific EDA interaction decays to zero. From Eq. (3), it is clear that absorption intensities of both EDA complexes and random pairs are proportional to the product of free donor and acceptor concentrations.

For a quantitative comparison of the intensities of electron-transfer absorptions, A, of different electron D/A pairs at various free donor and acceptor molar concentrations, C_{D} and C_{A}, a concentration-independent parameter κ is introduced:

$$\kappa = \frac{A}{C_{\mathrm{D}}C_{\mathrm{A}}} \tag{4}$$

Thus Eq. (3) can be written as

$$\begin{aligned} \kappa &= \kappa_{\mathrm{EDA}} + \kappa_{\text{random pair}} \\ &= \int_{r_0}^{r_{\mathrm{m}}} \varepsilon(r)\,\mathrm{d}K(r) + \int_{r_{\mathrm{m}}}^{\infty} 4\pi \times 10^{-27} N_0 r^2 \varepsilon(r)\,\mathrm{d}r \end{aligned} \tag{5}$$

The κ value depends on both the molar absorptivity $\varepsilon(r)$ and the formation equilibrium constant at each individual separation distance. The formation equilibrium constant at each

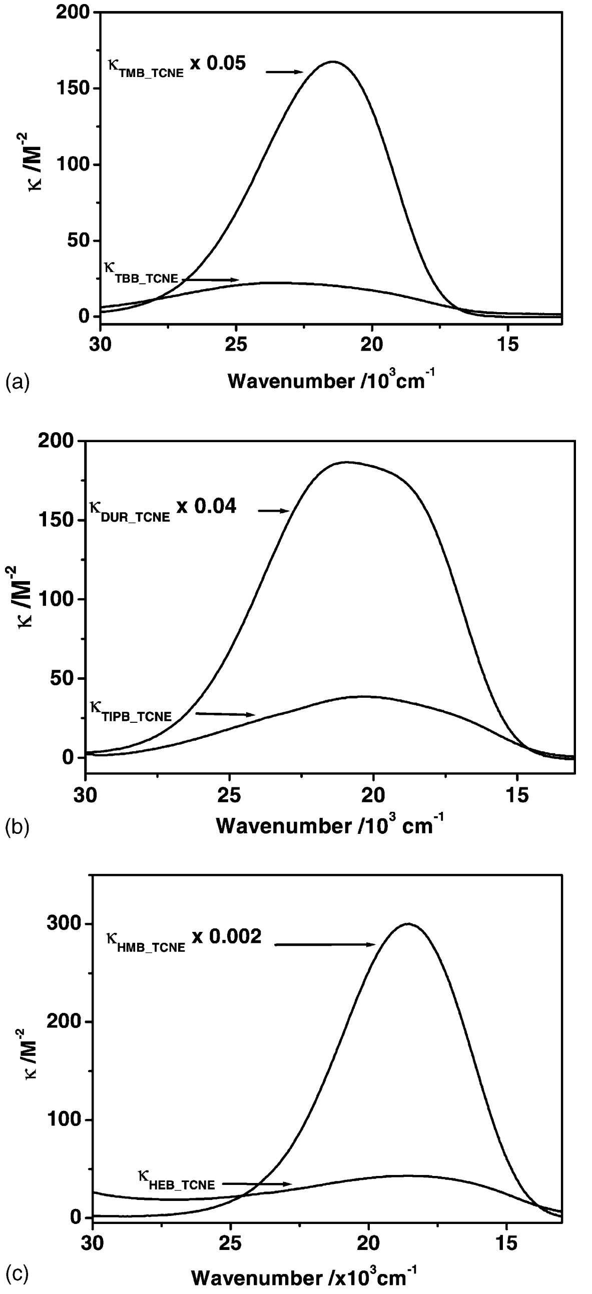


Fig. 1. The absorption spectra of electron acceptor, TCNE with three pairs of electron donors in DCM. (a) TMB vs. TBB; (b) DUR vs. TIPB; (c) HMB vs. HEB.

individual separation distance is directly related to the separation distribution of *D*/*A* pairs. For a quantitative description of CT absorption in EDA systems, detailed information about the separation distance distribution of EDA complexes and random pairs is needed. To probe such a separation distance distribution, the CT absorption of TCNE and a series of donors with similar structures and electronic properties but with different steric hindrance are compared (Fig. 1 and Scheme 1).

The oxidation potentials for unhindered donor TMB and bulky donor TBB are 2.11 [13] and 2.10, [14], respectively. There is no significant change in their electron donation properties. Space-fill molecular models indicate that the face-to-face contact separation distances for TCNE with TMB and TBB are 3.5 and 4.8 Å, respectively. Fig. 2 shows the κ profiles of TCNE with similar donors like TMB, TEB, TriIPB and TBB in dichloromethane. The κ values for TCNE with these donors decrease as the donor becomes bulkier, from 3620 to 1150, 100 and 22. This means that the κ values exhibit strong dependence on the contact separation distance. Assuming that separation distance distribution for the above D/A pairs at long distances are similar and steric hindrance affects only the short distance distribution, the more than three-fold decrease in κ value from TMB to TEB indicates that more than 70% of the absorption in TCNE–TMB is caused by D/A pairs with separation distances between 3.5 and 3.8 Å. Similarly, the more than 30-fold decrease in κ value from TMB to TriIPB shows that about 97% of the absorption in TCNE–TMB is caused by D/A pairs with separation distances from 3.6 to 4.1 Å. The extremely weak absorption of TCNE–TBB ($\kappa = 22$) compared with that of TCNE–TMB shows that absorption by D/A pairs with large separation distances (>4.8 Å) contributes only 0.4% to the total absorption of TCNE–TMB. Control experiment indicates that the weak absorption is not caused by impurities like *tert*-butylbenzene and di-*tert*-butylbenzene. For stronger electron donors, an even larger decrease in κ values induced by steric hindrance can be expected. For example, as the donor is changed from sterically unhindered HMB to sterically bulky HEB, the corresponding κ value decreases from 87 800 to 43. A more than 2000-fold decrease is observed.

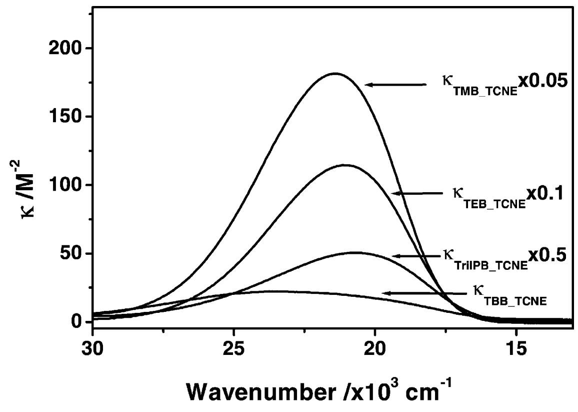
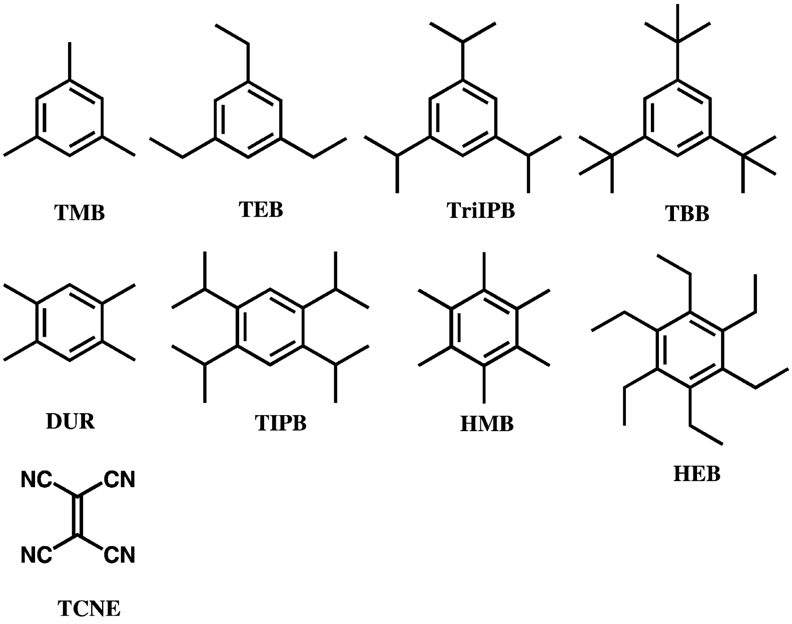


Fig. 2. Steric effect of a complete set of donors on κ values.

In Eq. (3), absorption caused by D/A pairs at a given separation distance is determined by molar absorptivity, $\epsilon(r)$, and D/A pair concentration at that separation distance. As we will discuss later, the molar absorptivity shows only a relatively weak distance dependence at separation from 3.5 to 4.8 Å, which means that the main reason for the weak absorption at long separation comes from the low D/A pair concentration. Such a low concentration can only be possible when there is no interaction between a donor and an acceptor molecule. In another word, they are statistically distributed.



Scheme 1. Structures of donor and the acceptor molecules and their abbreviations.

For these long distance D/A pairs from TCNE with sterically bulky donors, if there is no specific EDA interaction (>$k_B T$) between donor and acceptor molecules, we call them random pairs. For these random pairs, Eq. (5) can be simplified to

$$\kappa(\nu) = \frac{\text{Absorbance}}{C_\text{D} C_\text{A}} = \int_{r_\text{m}}^{\infty} 4\pi \times 10^{-27} N_0 r^2 \varepsilon(r)\,\mathrm{d}r \qquad (6)$$

3.2. *Influences of driving force and bulkiness on EDA system absorption*

The κ values for TCNE with various sterically unhindered donors are collected in Table 1. It is clear that κ values exhibit strong dependence on both electron donation and the steric bulk of the donors.

As can be seen from Table 1, the change in electron donation properties from TBB to TIPB to HEB is almost the same as that of unhindered donors from TMB to DUR to HMB. As discussed earlier, κ values of TCNE with stronger donors exhibit larger decreases when bulky substituents are introduced. From TMB to HMB, a more than 20-fold increase in κ value is observed. However, for the sterically bulky donors TBB, TIPB and HEB, only less than two-fold increase in κ value can be seen. The smaller changes in κ values for TCNE with sterically bulky donors having different electronic donation properties imply that the separation distance distribution for these D/A pairs is similar. This can be understood from our view that the electron transfer absorption of the sterically bulky D/A pairs originates from random pairs.

Apart from the weakness of electron transfer absorption of TCNE with sterical bulkiness, another feature of the absorption is that they should exhibit clear blue shifts compared with absorptions of TCNE with sterically unhindered donors of similar electronic donation properties. As we have discussed before, the transition energy at maximum $\nu_\text{max}(r)$ for electron transfer absorption at a given D/A separation

Table 1
The effect of bulky substituent groups on κ values of EDA pairs of TCNE with different donors

Donors	r_D (Å)	κ ($\text{M}^{-2}\,\text{cm}^{-1}$)	Maximum ($\times 10^3\,\text{cm}^{-1}$)	$\Delta\nu_{1/2}$ ($\times 10^3\,\text{cm}^{-1}$)	$E_{1/2}(D^+/D)$ (V vs. SCE)
TMB	3.5	3620	21.5	5.6	2.11
TEB	3.8	1150	21.1	5.6	
TriIPB	4.1	100	20.6	6.4	
TBB	4.7	22	23.8	9.9	2.10
DUR	3.5	8440	20.9	7.4	1.78
TIPB	4.7	38	20.4[a]	7.8	1.77
HMB	3.5	87800	18.6	5.3	1.59
HEB	4.6	43	18.5[a]	10.3	1.61

[a] We could not see an obvious blue shift in TIPB/TCNE and HEB/TCNE spectra. This may be the result of the limited precision in determining the maximum of a weak absorption spectrum.

distance can be written as [15]

$$\nu_{\max}(r) = \lambda_S(r) + \lambda_V + \Delta G^0(r) \tag{7}$$

$\lambda_S(r)$ and λ_V are the solvent and intramolecular reorganization energies, respectively. $\Delta G^0(r)$ is the standard free energy change of the electron transfer transition. Under the Marcus two-sphere assumption, $\lambda_S(r)$ (eV) can be written as

$$\lambda_S(r) = \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r}\right)\left(\frac{1}{D_{OP}} - \frac{1}{D_S}\right) \tag{8}$$

where r_D and r_A are radii of donor and acceptor molecules, D_{OP} and D_S are optical and static dielectric constants of the medium. $\Delta G^0(r)$ (eV) can be written as

$$\Delta G^0(r) = \left[E_{1/2}\left(\frac{D^+}{D}\right) - E_{1/2}\left(\frac{A}{A^-}\right)\right] - \frac{1}{D_S r} \tag{9}$$

where $E_{1/2}(D^+/D)$ and $E_{1/2}(A/A^-)$ are the redox potentials of donor and acceptor, respectively. Introducing Eqs. (8) and (9) into (7), we have

$$\begin{aligned}\nu_{\max}(r) &= \lambda_V + \left[E_{1/2}\left(\frac{D^+}{D}\right) - E_{1/2}\left(\frac{A}{A^-}\right)\right] \\ &\quad + \left(\frac{1}{2r_D} + \frac{1}{2r_A}\right)\left(\frac{1}{D_{OP}} - \frac{1}{D_S}\right) - \frac{1}{D_{OP} r}\end{aligned} \tag{10}$$

From Eq. (10), it is obvious that an increased separation distance between donor and acceptor will result in increases in transition energy or blue shifts in the CT absorption band.

It is generally believed that there exists a weak π–π interaction between donor and acceptor molecules in EDA complexes. The strength of such interactions in EDA complexes can be evaluated directly by measuring the formation enthalpy of the complexes. For TCNE with sterically unhindered donors, if the electron transfer absorption is caused by random D/A pairs, we can expect that the formation enthalpy will be zero or negligible.

To obtain formation enthalpy, ΔH^0, a modified method based on the conventional Van't Hoff equation is used. By combining the Benesi–Hildebrand method [5] and the Beer–Lambert law, we have

$$K = \frac{A}{(C_D^0 - C_{DA})(C_A^0 - C_{DA})\varepsilon b} \tag{11}$$

where A is the absorbance, C_D^0 and C_A^0 are the initial concentrations of the donor and acceptor, respectively, and C_{DA} is the concentration of the EDA complex. Under the condition that $C_D^0 \gg C_A^0$ and the assumption that $C_A^0 - C_{DA}$ and molar absorptivity are temperature independent, the following relationship can be deduced:

$$\frac{d(\ln\kappa)}{d(1/T)} = \frac{d(\ln\varepsilon K)}{d(1/T)} = \frac{d(\ln K)}{d(1/T)} \approx \frac{d(\ln A)}{d(1/T)} \tag{12}$$

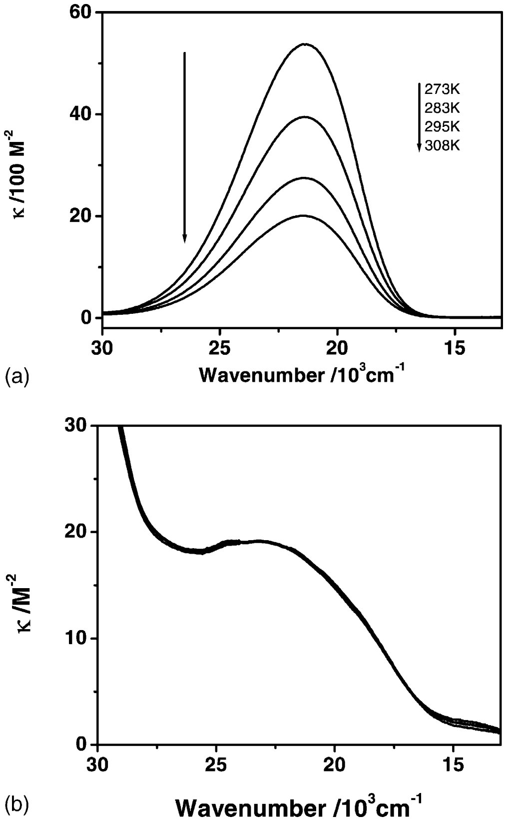


Fig. 3. (a) Absorption spectra of TMB/TCNE at different temperatures; (b) absorption spectra of TBB–TCNE at different temperatures.

The formation enthalpy, ΔH^0, for different D/A pairs can be obtained from the slope of the plot of $\ln A$ versus $1/T$. Fig. 3a shows the absorption spectra of 0.02 M TCNE with 0.15 M TMB in DCM at different temperatures. The absorption intensity is very sensitive to the change in temperature. As temperature increases from 273 to 308 K, maximum κ values decrease from ca. 5300 to 2000 M^{-2}. From the linear dependence of $\ln A$ on $1/T$ the formation enthalpy, ΔH^0, of the EDA complex between TCNE and TMB is -20.7 ± 1.2 kJ/mol. ΔH^0 of EDA complexes of TCNE with other sterically unhindered donors are determined similarly. They are listed in Table 2. As expected, $|\Delta H^0|$ increases as methyl substitution of the donor molecule increases.

By definition, we consider random pairs to be EDA pairs with no interactions, that is, the formation enthalpies are zero. No temperature dependence should be observed for pure random pair absorption spectrum. Fig. 3b shows the absorption spectra of 0.05 M TCNE with 0.2 M TBB in DCM at different temperatures. As discussed earlier, TBB is a sterically bulky donor with almost the same electron donation

Table 2
The formation enthalpy, ΔH^0 of EDA complexes of TCNE with TMB, DUR and HMB

Donor	ΔH^0 (kJ/mol)
TMB	-20.7 ± 1.2
DUR	-27.1 ± 2.8
HMB	-30.2 ± 0.8

properties as that of TMB. In comparison to TCNE with TMB, no detectable temperature dependence is observed. This proved that there is no specific interaction between donor and acceptor molecules in the solution. It is evident that the CT absorption band is from random pairs between TCNE and TBB. For solutions of TCNE with sterically bulky donors TIPB and HEB, the CT absorption intensities exhibit non-zero but very weak temperature dependence. We believe that the intensity arises from EDA random pairs also. The extremely weak temperature dependence can be understood as non-pure random pair parts of the system, since they are less bulky than TBB.

3.3. Theoretical consideration of κ in random pair absorptions

To perform an accurate calculation of profile and strength of random pair absorption, the impact of structures and orientations of donors and acceptor molecules on separation distance distribution and electronic coupling needs to be addressed. The solvent structure and its implication in controlling the donor/acceptor separation distance distribution also need to be taken into consideration. The development of such a precise model that covers all these factors in the calculation is beyond the purpose of this work. The present calculation will be based on the framework of electron transfer theory under two-spherical assumption with a dielectric continuum model for solvent. The result will provide us a simple estimation of the delectability of absorption caused by random pair under the donor and acceptor concentrations. Under the earlier assumptions, $\kappa(\nu)$ of random pairs can be calculated by Eq. (6) if the molar absorptivity, $\epsilon(r,\nu)$, at different separation distances is known. To calculate $\epsilon(r,\nu)$ by using Eq. (1), $H_{\mathrm{ab}}(r)$, $\lambda_{\mathrm{s}}(r)$, λ_{V}, $\Delta G^0(r)$ are needed. The electronic coupling between donor and acceptor molecules is assumed to decay exponentially as the separation distance r increases and can be calculated by Eq. (13) [9,16] if the electronic coupling at separation r_0 is known.

$$H_{\mathrm{ab}}(r) = H^0_{\mathrm{ab}}(r_0)\,\mathrm{e}^{-\beta(r-r_0)/2} \tag{13}$$

Based on Eqs. (8) and (9), the solvent reorganization energy, $\lambda_{\mathrm{s}}(r)$ and free energy, $\Delta G^0(r)$, at separation r can be calculated by Eqs. (14) and (15) [1]

$$\lambda_{\mathrm{S}}(r) = \lambda_{\mathrm{S}}(r_0) + \left(\frac{1}{r_0} - \frac{1}{r}\right)\left(\frac{1}{D_{\mathrm{OP}}} - \frac{1}{D_{\mathrm{S}}}\right) \tag{14}$$

$$\Delta G^0(r) = \Delta G^0(r_0) - \left(\frac{1}{r} - \frac{1}{r_0}\right)\frac{1}{D_{\mathrm{S}}} \tag{15}$$

where $\lambda_{\mathrm{s}}(r_0)$ and $\Delta G^0(r_0)$ are the solvent reorganization energy and standard free energy change at the separation r_0. Values of $H^0_{\mathrm{ab}}(r_0)$, $\lambda_{\mathrm{s}}(r_0)$ and $\Delta G^0(r_0)$ at the separation r_0 can be obtained by fitting the absorption spectra of EDA complexes of TCNE with TMB and HMB.

As discussed in Section 3.1, the interaction between donor and acceptor is very sensitive to changes in separation distance. Because of the strong interaction between D/A molecules at short distance, most of the CT absorption for TCNE with sterically unhindered donors such as TMB and HMB comes from EDA complexes which are close to contact in separation. The separation distance distribution and contributions of random pairs to the absorption can be ignored in these systems. The EDA complexes can then be described as single specie with a contact separation distance. For these systems, Eq. (4) can be simplified as

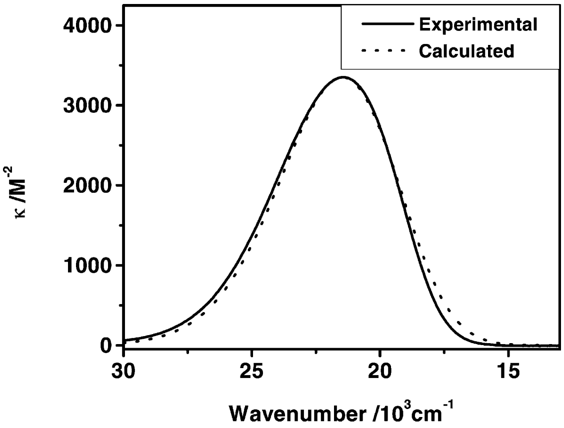


Fig. 4. Experimental absorption spectrum of TMB–TCNE in DCM at room temperature and theoretical fitting by Eqs. (1), (2) and (16) using $\kappa = 1.56$, $H^0_{\mathrm{ab}} = 1400\,\mathrm{cm}^{-1}$, $\lambda_{\mathrm{v}} = 2400\,\mathrm{cm}^{-1}$, $\lambda_{\mathrm{s}} = 5800\,\mathrm{cm}^{-1}$, $\nu_{\mathrm{v}} = 1400\,\mathrm{cm}^{-1}$ and $\Delta G(r_0) = 13\,940\,\mathrm{cm}^{-1}$.

$$\kappa(r_0, \nu) = \varepsilon(r_0, \nu)K \tag{16}$$

Fig. 4 exhibits the theoretical and experimental $\kappa(\nu)$ profile of the CT absorption of TCNE–TMB complex in DCM. To fit the $\kappa(\nu)$ profile by Eq. (1), Eq. (16) is introduced into Eq. (1) and a K value of 1.56 is used according to literature [12]. The other parameter used in the fitting is $\nu_{\mathrm{v}} = 1400\,\mathrm{cm}^{-1}$, which is a typical value for a skeletal stretching mode of the ring system involved [6,7]. The shape of the spectrum is found to be very sensitive to the parameters. As can be seen, the fit to experiment is good. From the fitting of CT absorption to the $\kappa(\nu)$ profile of TCNE–TMB in DCM, we obtained reorganization energies, $\lambda_{\mathrm{V}} = 2400\,\mathrm{cm}^{-1}$, $\lambda_{\mathrm{S}} = 5800\,\mathrm{cm}^{-1}$, $\Delta G^0(r_0) = 13\,940\,\mathrm{cm}^{-1}$, and the electronic coupling factor $H^0_{\mathrm{ab}} = 1481\,\mathrm{cm}^{-1}$. Results of HMB/TCNE are also shown in Table 3.

For the calculation of the $\kappa(\nu)$ profile of random pairs, spherical models are used and the solvent is considered a structureless dielectric continuum. The radii of both donor and acceptor spheres are calculated from their molecular

Table 3
Parameters obtained from fitting absorption spectra of EDA complexes of TCNE with TMB and HMB

Donors	λ_{V} (cm^{-1})	λ_{S} (cm^{-1})	ΔG^0 (r_0) (cm^{-1})	H^0_{ab} (cm^{-1})
TMB	2400	5800	13940	1400
HMB	2200	6300	10780	1800

volumes, respectively. The limit and error involved in the dielectric continuum solvent model is discussed later. $E_{1/2}(D^+/D)$ values (versus SCE) for TMB, TBB, HMB and HEB are 2.11 [13], 2.10 [14], 1.61 [13] and 1.59 [14], respectively. The steric hindrance has almost no effect on $E_{1/2}(D^+/D)$. From Eq. (9), we expect that, at the same separation r, the standard free energy change, $\Delta G^0(r)$ of the CT absorption of TCNE with a sterically unhindered donor equals that of TCNE with a comparable sterically bulky donor. The $\Delta G^0(r_\mathbf{0})$ which is obtained by fitting the CT absorption of EDA complexes and corresponds to the free energy change at contact separation r_0 between TCNE and sterically unhindered donors can be used to calculate $\Delta G^0(r)$ of random pairs between TCNE and sterically bulky donors by using Eq. (15). Similarly, $H_{\mathrm{ab}}(r)$ and $\lambda_{\mathrm{S}}(r)$ can be calculated from Eq. (13) and (14) by using $H^0_{\mathrm{ab}}(r_0)$ and $\lambda_{\mathrm{S}}(r_0)$ values obtained from fitting the CT absorption of TCNE with sterically unhindered donors. Other parameters used in the calculation are the same as for TMB except that here the contact separation distance of 7.2 Å between TCNE and TBB is chosen as r_{m}. Both TBB and TCNE are planar molecules, with face-to-face contact separation of ca. 4.8 Å and edge-to-edge contact separation of ca. 9.5 Å. We expect that a space-fill model for acceptor and donor molecules provides an adequate approximation that allows calculation of the $\kappa(\nu)$ profile of random pairs at long separation. The contact separation of 7.2 Å arising from a spherical model for both donor and acceptor should be regarded as a statistical average of contact separations for different orientations from 4.8 (face-to-face) to 9.5 Å (edge-to-edge). Such EDA pairs may be regarded as random pairs. A more sophisticated model will be needed if accurate calculations of probabilities for random pairs at different separation distances is expected at small separation ($r < 10$ Å) (see, for example [17]). Another factor that should be taken into consideration in any detailed modeling is that the orientation distribution depends on the separation distance when the separation distance is smaller than the edge-to-edge contact separation. At a separation of 4.8 Å, the EDA pair must be face to face. As the separation distance increases, other configurations are permitted. This will have an important effect on the evaluation of H_{ab} at different separation. $H^0_{\mathrm{ab}}(r_{\mathrm{m}})$ is calculated to be 232 cm^{-1} from Eq. (13) by using $H^0_{\mathrm{ab}}(r_0) = 1481\,\mathrm{cm}^{-1}$ at $r_0 = 3.5$ Å and $\beta = 1.0$ Å^{-1} ([18,19] as discussed in Section 3.1, the EDA complex between TCNE and TMB can be described by a single species with a sandwich structure that has a face-to-face separation of 3.5 Å. Because of EDA complex formation, the separation distance distribution does not play a significant role in the CT absorption of TMB and TCNE. Instead of using the separation distance of 6.7 Å based on a spherical model as r_0, a more realistic r_0 of 3.5 Å is used together with $H^0_{\mathrm{ab}}(r_0)$ of 1481 cm^{-1} obtained from a spectral fit of the CT band to calculate the $H^0_{\mathrm{ab}}(r_{\mathrm{m}})$ of the random pairs of TCNE with TBB. A β-value of 1.0 Å^{-1} should work well (see references [18,19]) in the calculation of decay of H_{ab} of EDA pairs with similar orientation or orientation distribution at each separation as the separation distance increases. Most of EDA complex between TMB and TCNE are in face-to-face configuration which favors strong electronic coupling between the donor and acceptor molecules. However, the orientation of EDA pairs between TCNE and TBB is random. When a β-value of 1.0 Å^{-1} is used to calculate $H^0_{\mathrm{ab}}(r_{\mathrm{m}})$ of TBB–TCNE from $H^0_{\mathrm{ab}}(r_0)$ of TMB–TCNE, differences in the orientation distribution between the two systems are ignored. This will result in a large $H^0_{\mathrm{ab}}(r_{\mathrm{m}})$ value. At this stage, the effect of orientation factor can not be addressed quantitatively. An estimate of the relative strength of random pair absorption is sketched in Fig. 5. Intensities of $\varepsilon_{\max}(r)$ probability of finding a donor at distance r ($P(r)$) and $\kappa(r)$ are calculated from Eqs. (1), (3) and (6). The spherical model for estimating random pair absorption uses contact distances for donor and acceptor spheres that are larger than the real contact pair when EDA complex is formed. Rather than the spherical contact separation distance, a more realistic r_0 value of 3.5 Å is used in spectral fitting when EDA complex is formed.

From the Fig. 5b it is clear that $\varepsilon_{\max}(r)$ decays almost exponentially with increasing separation distance, but the κ value decays more slowly. The increasing probability and decreasing molar absorptivity at longer separation distance are largely compromised in the calculation of $\kappa(r)$. The relative absorption strength of random pairs at a separation

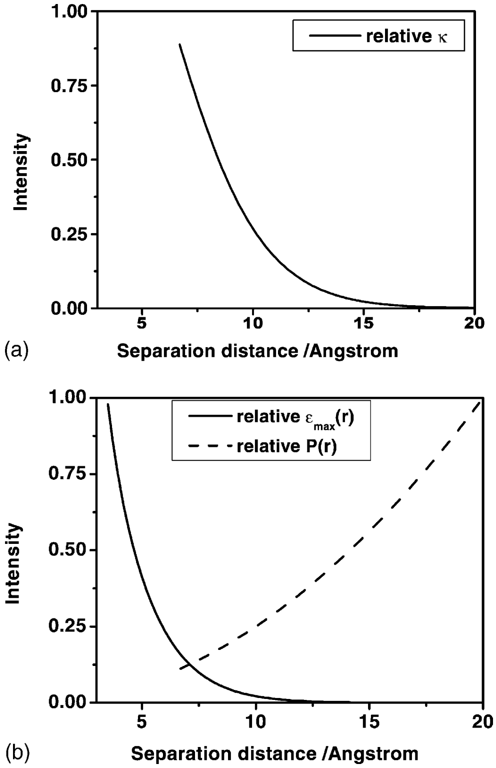


Fig. 5. (a) Variation of relative values of κ for random pairs at $\lambda_{\max}$ against separation distance r; (b) variations of relative values of molar absorptivity (ϵ) at $\lambda_{\max}$ and radius distribution for random pairs against separation distance r. For details of the calculations, see text.

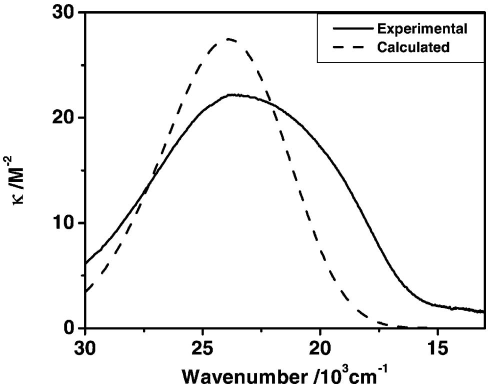


Fig. 6. Experimental and calculated κ profiles of TBB–TCNE random pairs.

distance of 10 Å is ca. 20% of that at the contact separation. For the systems concerned, the separation distance between donor and acceptor with one layer of solvent molecules is ca. 10 Å. This means that a large portion of EDA excitation results in the direct formation of solvent separated EDA ion pairs. As we have proved in previous work, these solvent separated EDA ion pairs are main source that produce free ions in moderately or weakly polar solvents. It is worthwhile to mention that in Fig. 5, calculation of ε is performed from 3.5 to 20 Å, while calculations of $P(r)$ and κ are from 6.7 to 20 Å.

Although theories allow a good fit to the EDA complex absorption (see Fig. 4), the calculation of random pair absorption is only partially satisfactory. For example, the experimental and calculated spectra of TMB–TCNE are compared in Fig. 6. The experimental width is 9770 cm^{-1}, the calculated width is 6510 cm^{-1}. Similar results are obtained for HEB–TCNE random pair. We think the following two reasons contribute to the disagreement. First, as said earlier, the actual molecular shape is not spherical. All the donors and acceptors used in the experiments are planar or near planar molecules. Anisotropy effects could be large when the donor and acceptor are close to each other. Second, a continuum solvent model is assumed, in which the solvent molecules have neither shape nor size and the solvent is structureless. This means the donor and acceptor molecules can move continuously and have a uniform distribution at any separation distance. The relative probability of finding a donor around an acceptor is monotonously increasing as separation distance increases. If we take the structure of the solvent molecules into consideration, it is reasonable to believe that there is a very small chance for a donor to find an acceptor between contact pairs and single-layer-separated-pairs. The result of relative κ at short separation distance is definitely over-calculated. Although there is no quantitative adjustment available here, we can see the maximum of random electron transfer should be at donor–solvent–acceptor pairs. To summarize in a sentence, the separation distance distribution becomes rather complicated with many factors contributing to the absorption strength and positions. Ignoring this effect will cause discrepancies between theory and experiment. Further work on such effects will be conducted.

4. Conclusions

Electron-transfer absorption of substituted benzene donors with TCNE is studied in dichloromathane at different temperatures. Evidence is provided to show the existence of random pairs in sterically bulky D/A systems. First, absorbance of different electron D/A pairs at various free donor and acceptor molar concentrations is investigated. It is found that absorption strength of sterically bulky D/A pairs are several orders of magnitude smaller than those of the corresponding sterically unhindered pairs with similar structures and electron transfer properties. When donors are changed from weak to strong, a more than 10-fold increase in κ value is observed for sterically unhindered donors, while the change in κ value is less than two-fold for sterically bulky donors. This supports the view that the electron transfer absorption of the sterically bulky D/A pairs originates from random pairs rather than from bound pairs. Further evidence comes from the fact that κ values of sterically bulky D/A pairs show very weak or no temperature dependence, which indicates a zero formation enthalpy for D/A pairs that give CT absorption. The absorption spectrum by such random pairs is predicted. By fitting the absorption spectra of the CT band of the EDA complexes formed between TCNE and sterically unhindered donors, electronic coupling elements and reorganization parameters are obtained. Based on these parameters, the electron transfer absorption spectra of the random pairs discussed earlier are simulated and compared with experimental results.

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