Exciplex Dipole Moments: Cyanoanthracene Acceptors and Methyl-Substituted Benzene Donors

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A transient dc photocurrent technique was used to measure the dipole moments of exciplexes formed between the electronically excited electron acceptors 9,10-dicyanoanthracene (DCA) or 2,6,9,10-tetracyanoanthracene (TCA) and methyl-substituted benzene (SB) donors. For either acceptor in benzene solution, exciplex dipole moments increase with decreasing donor oxidation potential until a maximum dipole moment of ca. 11 D is reached. A similar trend has been previously observed using other techniques, but the maximum dipole moments that we report are substantially less than is usually assumed for such systems. Mutual ion polarization is the likely cause of this difference, and a simple equation for estimating its effects is provided.

Introduction

Because of its important role in both photochemical reactions and biological processes, photoinduced electron transfer has been intensely studied for more than three decades. With the advent of ultrafast techniques, chemists have sought to understand the mechanisms involved in numerous excited-state electron transfers. The exciplex, a key intermediate in many such processes, remains elusive. Gaining a better description and understanding of these excited-state complexes has motivated this work.

Since their discovery, exciplexes have usually been studied using techniques based on optical spectroscopy. Often the main goal has been the description of exciplex electronic structure. For electron acceptors (A) with a low-lying excited singlet state like the cyanoanthracenes (CA) and relatively good electron donors (D) like the methyl-substituted benzenes (SB), the electronic structure of an exciplex can be approximated as a linear combination of locally excited (LE), $|A^*D\rangle$, and charge-transfer (CT), $|A^-D^+\rangle$, configurations:[1]

$$\psi_{\rm EX} = c_1|A^*D\rangle + c_2|A^-D^+\rangle \qquad (1)$$

The coefficients, c_1 and c_2, determine the extent of mixing between LE and CT configurations.

Several groups have used different experimental approaches to determine the extent of charge separation in exciplexes. Recently, Chow et al.[2] have studied emission of (dibenzoylmethanato)boron/SB exciplexes in various solvents and applied Lippert−Mataga[3] analysis to determine the variation in the extent of charge transfer within the series of exciplexes. They argue that, because of the small overlap, i.e. $\langle A^*D|A^-D^+\rangle \approx 0$, one can calculate the degree of charge separation, c_2^2, from measured dipole moments for exciplexes, $\mu_{\rm EX}$:

$$c_2^{\ 2} = \frac{\mu_{\rm EX}}{\mu_{\rm CRIP}} \qquad (2)$$

where $\mu_{\rm CRIP}$ is the dipole moment of a hypothetical contact radical ion pair (CRIP) with full electron transfer:[1,2]

$$\mu_{\rm CRIP} = er \qquad (3)$$

Here e is the unit charge and r is the center-to-center distance between the donor and acceptor molecules in the CRIP. According to the authors,[2] the largest values of $\mu_{\rm EX}$ that they observe in their sandwichlike exciplexes, namely 13.8 D, may be identified as $\mu_{\rm CRIP}$.

In another approach, Gould et al.[4] analyzed radiative rates of exciplex emission in various solvents for the same systems as used in this study, i.e., DCA or TCA as electron acceptors and SB as electron donors. They correlated the degree of fractional CT with exciplex emission rates and concluded that in these systems, depending on the redox properties of donor/acceptor pairs, the extent of charge separation varies and can reach almost 100%.[4] Using solvatochromic shifts for exciplexes with close to 100% CT character, they estimated $\mu_{\rm CRIP} = 13 \pm 2$ D, close to the values of Chow et al.[2] mentioned above for analogous systems.

Electrooptical experiments[5,6] allow a more direct measure of excited-state dipole moments because they do not require analysis of changes with solvent polarity but can be made in a single solvent. A disadvantage of both spectroscopic techniques is that they rely on the accuracy of estimates for solute cavity size. A general trend is that exciplex dipole moments from electrooptic measurements are somewhat smaller than those deduced from Lippert−Mataga analysis. For example, Groenen et al.[5] reported a 9.8 D dipole moment for dicyanoanthracene/hexamethylbenzene exciplexes in cyclohexane, lower than the 13 D of solvatochromic analysis.[2,4] Liptay[6] also lists dipole moments for a number of sandwichlike exciplexes in the range 9−12 D.

A more direct technique, transient microwave conductivity, has been used by Fessenden et al.[7] and Visser et al.[8] to measure excited-state dipole moments including those of some exciplexes. As in the case of the electrooptical technique, dipole moments tend to be lower than those estimated from solvatochromic shifts. The microwave conductivity technique, while more direct than either of the optical approaches, nevertheless depends on the accuracy of estimated rotational times and is limited to solvents of low polarity.

We have used the transient dc photocurrent technique to measure dipole moments of various excited species[9] including exciplexes.[10,11] This technique has almost no assumptions and

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allows *really direct* measurement of dipole moments.[9] In an earlier letter,[10] we reported the dipole moments of excited-state complexes formed between DCA or TCA and substituted benzene donors present as neat solvents. The observed dipolar species were assigned to 2:1 sandwich complexes (triplexes) between CA and two solvent molecules.[12] The present paper describes the study of CA/SB exciplexes at various donor concentrations (0.001−0.1 M) in benzene solutions. We confirm our previous conclusions and show that, at low donor concentrations, triplex formation can be avoided, and dipole moments of exciplexes, i.e. 1:1 complexes, can be measured.

Exciplexes measured in this study follow a previously established trend of dipole moment increase with decreasing donor oxidation potentials, but the maximum values level off at $\mu_{\mathrm{CRIP}} \approx 10.8$ D, much smaller than expected. Even for a minimum plausible value of $r = 3.0$ Å, this value would (see eqs 2 and 3) amount to only 75% contribution by the CT configuration of eq 1. We offer an alternative explanation in which the dipole moment for a CRIP in these systems is lowered because of mutual anion/cation polarization.

Experimental Section

Dipole Moment Measurements. The transient dc photocurrent method has been described previously.[9] In brief, the third harmonic (355 nm, fwhm <400 ps) of a Nd:YAG laser operating at 5 Hz was used to pump a H_2(g)-filled Raman shifter to produce a 416 nm pulse with a fwhm of ca. 20 ps (MPB Technologies Orion SE-R Laser). Transient dc photocurrent signals were measured with either a Tektronix P6245 active probe (1 MΩ, 1.5 GHz bandwidth), the so-called charge displacement mode, or with a standard 50 Ω cable, i.e. the displacement current mode.[9b] The unfocused laser light penetrated between the cell's two flat stainless steel electrodes separated by a 0.5 mm gap. Typical applied voltage was 1 kV. The signals were recorded with a Tektronix TDS 684A oscilloscope (1 GHz, 5 Gsamples/s). Data acquisition was controlled by a PC which also stored and averaged the signals. Depending on signal magnitude, the number of transients averaged varied in the range 1000−8000.

Dipole measurements require accurate determination of absorbed energy. All measurements were preceded and followed by a calibration in which incident and transmitted energies were measured with only solvent present between the electrodes. Absorbed energy was calculated from incident and transmitted energies measured during an experiment (i.e. with solution inside the cell). The two laser pulse energies were measured with Molectron J4-09 pyroelectric detectors. Reflection at the quartz−air interface was also taken into account. Typical absorbed energies ranged between 10 and 45 μJ, which corresponds to excitation of less than 10% of CA molecules inside the cell.

The conductivity cell is constructed so that a solution can be periodically refreshed during an experiment. Solutions were deoxygenated by bubbling with nitrogen while in a reservoir above the cell.

Fluorescence Measurements. Lifetimes of the TCA/benzene and DCA/benzene excited-state complexes (EX1) were measured by exciting either TCA or DCA in deoxygenated solutions and detecting fluorescence at a right angle to the direction of excitation using a fast photodiode (New Focus model 1437, 25 GHz). Fluorescence lifetimes of secondary exciplexes (EX2), which are formed by substitution of the benzene in EX1 by a SB, were measured similarly. Because of EX2's red-shift in fluorescence and the smaller quantum yields of that fluorescence,[4a,b] a more sensitive Thorlab's DET2-SI (rise time < 1 ns) photodiode was used.

Bimolecular quenching rate constants were determined by Stern−Volmer analysis of steady-state fluorescence quenching; fluorescence spectra were measured with a Perkin-Elmer LS 50 spectrofluorimeter. Excitation of DCA and TCA at 416 nm and use of low donor concentrations almost precluded ground-state CT complex excitation[4a] and minimized the effects of nonstationary quenching.

Materials. The solvent, benzene, and liquid donors toluene (TOL), *p*-xylene (p-XYL), and *m*-xylene (m-XYL), all Spectrograde, as well as 1,2,4-trimethylbenzene (124 TMB) and 1,3,5 trimethylbenzene (135 TMB), both 98% purity, were all from Aldrich and were used without further purification. The solid donors durene (DUR), 98% purity, pentamethylbenzene (PMB), 99+% purity, and hexamethylbenzene (HMB), 99+% purity, were all from Aldrich and used without further purification. TCA and DCA were generously supplied to us by S. Farid and I. Gould of Kodak. The TCA was purified by preparative thin-layer chromatography.

Results

As shown previously,[9−11] the photoresponse is a measure of the time-dependent voltage, v, across a load resistor, R, caused by the displacement current from newly formed rotating dipoles in a cell with voltage, V_0, applied across electrode gap d. In a simplified model, which assumes zero rotation time for dipoles, the time-dependent voltage, v, is given by

$$v + \tau_{\mathrm{RC}} \frac{\mathrm{d}v}{\mathrm{d}t} = \varphi(\epsilon,n) \frac{V_0 R}{\mathrm{d}^2} \sum_i \frac{\mu_i^{\,2}}{3k_{\mathrm{B}}T} \frac{\mathrm{d}N_i}{\mathrm{d}t} \tag{4}$$

where τ_{RC} is the RC time of the circuit and N_i is the number of species with dipole moment μ_i. In systems with concentrations of SB less than 0.1 M and bimolecular quenching rate constants not greater than 10^{10} M^{-1} s^{-1}, the formation of EX2 occurs on a substantially longer time scale than EX2 rotation, τ_{rot}. From fluorescence depolarization measurements, we estimated that $\tau_{\mathrm{rot}} \sim 0.1-0.3$ ns,[10] and therefore the implicit assumption that $\tau_{\mathrm{rot}} = 0$ made in eq 4 is appropriate for this study. The coefficient $\varphi(\epsilon,n)$ includes effects of the cavity field being different from the external one (cavity field factor) as well as an additional contribution from solvent molecules oriented by the solute.[9b] Both these effects depend on solvent dielectric constant, ϵ, refractive index, n, and the cavity *shape*, not size. In the case of a spherical cavity in a nonpolar solvent (i.e. $\epsilon = n^2$), relevant to our systems,

$$\varphi_{\mathrm{sphere}}^{\mathrm{nonpolar}}(\epsilon,n) = \left(\frac{3\epsilon}{2\epsilon + 1}\right)^2 \tag{5}$$

All dipole moments reported here will assume that the cavity is spherical. For the sandwichlike exciplexes between cyanoanthracenes and methyl-substituted benzenes, the cavity is roughly oblate-shaped.[9b] The result is that use of the spherical cavity approximation overestimates the exciplex dipole moments by approximately 3%.[10,13] For triplexes which, on the other hand, are roughly prolate-shaped, the spherical approximation underestimates dipole moments by ca. 1%.[13]

As mentioned above, because of the formation of triplexes in neat donor solvents,[11] it was necessary to use dilute solutions of donor molecules in order to measure exciplex, i.e. EX2, dipole moments. Benzene was chosen as the solvent because useful absorbances (∼0.3/cm at 416 nm) for TCA could be achieved therein. Scheme 1 illustrates the three-state model used to

TABLE 1: Dipole Moments and Lifetimes of Excited-State Complexes (from Dipole Signals, τ_1, and from Time-Resolved Fluorescence, τ_f) Formed between TCA or DCA in Neat Benzene Solutions (EX1)

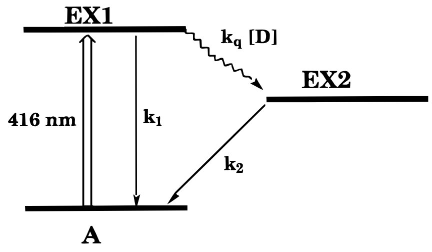
acceptor	μ_1 (D)	τ_1/τ_f (ns)
DCA	1.7	13.1/13.5
TCA	3.4	16.0/16.1

TABLE 2: Dipole Moments, Lifetimes, and Bimolecular Quenching Rate Constants of Cyanoanthracene/Substituted Benzene Exciplexes in Benzene

donor/ acceptor	I_{donor} (eV)[a]	$E_{ox} - E_{red}$ (V)[b]	μ_2 (D)[c]	τ_2/τ_f (ns)[d]	$k_q/10^9$ M^{-1} s^{-1} [e]
PMB/DCA	7.95	2.62	8.2	54/64	6.0
HMB/DCA	7.85	2.50	10.8	72/72	9.2
TOL/TCA	8.85	2.69	4.5	28/—[f]	0.02
m-XYL/TCA	8.59	2.58	8.4	36/36	2.1
p-XYL/TCA	8.44	2.50	9.5	63/70	4.8
135 TMB/TCA	8.39	2.55	10.0	61/65	4.6
124 TMB/TCA	8.27	2.36	10.5	50/59	6.0
DUR/TCA	8.02	2.22	10.9	38/36	9.3
PMB/TCA	7.95	2.15	10.4	19/22	14.0
HMB/TCA	7.85	2.03	10.8	11/11	15.0

[a] From ref 19. [b] In acetonitrile, from refs 2, 4, 19 where also E_{red} of DCA, −0.91 V, and TCA, −0.44 V, were used. [c] Dipole moments of exciplexes are accurate to within 10% of reported values. [d] τ_2 is the exciplex lifetime from the photocurrent signal, and τ_f is the lifetime from time-resolved fluorescence. [e] Bimolecular rate constants, k_q, are determined through Stern−Volmer analysis of steady-state fluorescence. [f] The TCA/toluene exciplex fluorescence was difficult to distinguish from that of TCA/benzene.

SCHEME 1: Kinetic Scheme Used in the Fitting Procedure[a]



[a] Upon photoexcitation of acceptor molecule, A, to its first excited singlet state formation of an excited-state complex, EX1, occurs between A* and benzene. Through diffusional quenching, EX2 is formed as donor molecule D (an SB) substitutes for benzene.

describe data. Excitation of either DCA or TCA in benzene leads to fast formation (<10 ps)[14] of the CA/benzene excited-state complex (EX1) with a small dipole moment.[11] It was shown earlier[4] that both EX1 and EX2 are formed with unit probability upon quenching of a neutral molecule or EX1, respectively. We also see that the rates of EX1 quenching and EX2 formation are identical, which confirms 100% efficiency of EX2 formation during quenching. The measured dipole moments and the lifetimes of these EX1 are listed in Table 1.

Substitution of the first donor (benzene) by the SB and formation of the exciplex EX2 was observed by both changes in fluorescence spectra and increase in the dipole signal. Table 2 includes bimolecular quenching rate constants, k_q, calculated from Stern−Volmer analysis of steady-state fluorescence quenching data and fluorescence lifetimes from Table 1. For either acceptor, these rate constants increase with decreasing donor oxidation potential. The rate constants are somewhat smaller than diffusion-controlled, which is in good agreement with previous studies in similar systems.[2,15] Steady-state fluorescence measurements indicate that at concentrations < 0.02 M donor molecules with oxidation potentials larger than that of PMB do not significantly quench ^{1}DCA* in benzene and no EX2 signal could be identified in such systems. In no system studied could we unambiguously identify fluorescence from triplex[16] species, A^-DD^+.

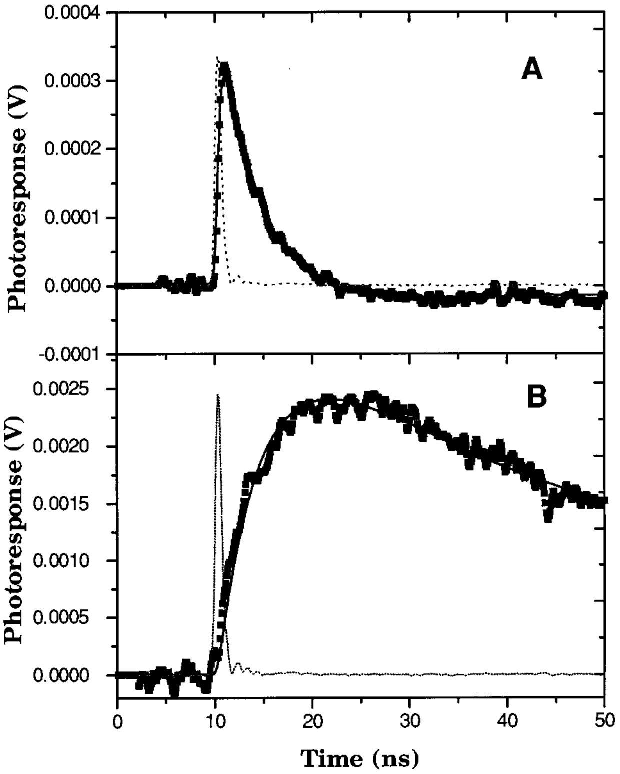


Figure 1. Photoresponse for a solution of DCA and 0.02 M HMB in benzene: (A) acquired in the displacement current mode (50 Ω); (B) acquired in the displacement charge mode (1 MΩ). The dashed lines in each case denote the laser pulse, the solid squares show the best fits, and the solid lines are the experimental signals. Absorbed energy in both cases is 30 μJ. Note that trace B has a different scale because its magnitude is almost 10 times greater.

The newly formed dipoles of EX2 are larger than those of EX1. Because the dipole signal is proportional to the square of the dipole moment (see eq 4), a larger portion of the dipole signal results from the dipole moment of EX2, μ_2, than from EX1. The formation of EX1 occurs faster than can be experimentally resolved; thus it is treated as instantaneous. The fast formation of EX1 means that there is no particular advantage in using the displacement charge mode versus the displacement current mode for measuring the EX1 signal. In the displacement current mode, where τ_{RC} (eq 4) is small, the signal, v, is primarily proportional to the *derivative of the dipole concentration*. Thus, if new dipolar species are formed gradually, their contribution to the dipole signal is small compared to the portion from EX1. In this case we choose to take advantage of the displacement charge mode, i.e. the condition where τ_{RC} (eq 4) is large. Then the signal is proportional to the *concentration of dipolar species* and not the change in concentration with time. For dipoles that are formed gradually, the displacement charge mode provides signals of greater amplitude than does the displacement current mode (see Figure 1), and what is more important, the signal is not biased toward faster formed species. So, using the displacement charge mode allows improved accuracy of dipole measurements for secondary exciplexes EX2.

As illustrated in Figure 2 for DCA/HMB in benzene, the signal magnitude increases with increasing donor concentration and the rise time shortens. These signals were fit according to eq 4 applied to Scheme 1 by minimizing χ^2 (an averaged squared

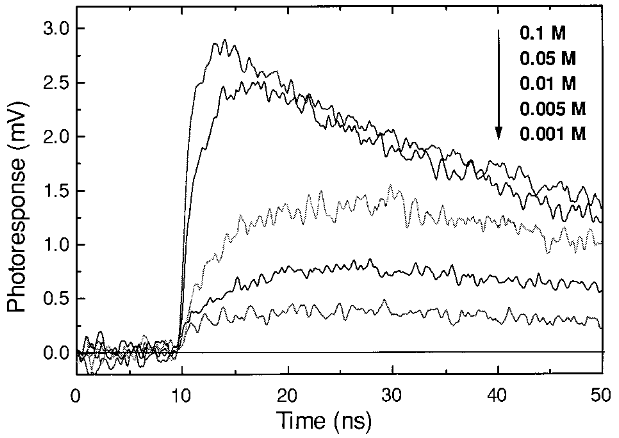


Figure 2. Photoresponses acquired for a series of DCA solutions in benzene with varying concentrations of HMB. Signals are normalized to the same absorbed laser energy, 18 μJ. Note the signal rise time shortening with increasing donor concentration.

difference between the experimental and calculated intensities) with only three parameters, μ_2 (primarily defines the signal magnitude), τ_2 (primarily defines the rise time), and τ_q (primarily defines the decay time), varied (see Appendix for details). Because the three parameters, τ_1, μ_1, (dipole lifetime and dipole moment of EX1), and τ_q ($\tau_q = 1/k_q[\mathrm{SB}]$), were measured independently, they can be held constant in the fitting and only μ_2 and τ_2 (dipole moment and dipole lifetime of EX2) varied. Actually, we vary not only μ_2 and τ_2 but τ_q as well. At low concentrations, τ_q is found to be within 10% of that estimated from Stern−Volmer analysis and usually a bit shorter.[17] Table 2 reports dipole moments at low donor concentration, μ_2. These dipole moments are reproducible to within ±10%. For comparison, exciplex lifetimes determined from time-resolved fluorescence, τ_f, and from dipole measurements, τ_2, are also reported in Table 2. There is generally good agreement between τ_2 and τ_f. Oxygen quenching of exciplexes is well-known[2,18] and is most likely to be the source of discrepancies. With donor concentration increase, when two additional processes—formation of triplexes and direct excitation of ground-state CT complexes—become important, the dipole signal kinetics can no longer be well described by Scheme 1 with only two dipolar states. Effective dipole moments can, however, still be determined from signal magnitudes in the displacement charge mode.

Figure 3 depicts dipole moments for the system TCA/135TMB in benzene as a function of 135TMB concentration. Note that at low SB concentrations, the dipole moment is independent of 135TMB concentration and may be identified as μ_2, the exciplex dipole moment. As donor concentration is increased beyond ~0.1 M (the concentration is system dependent), the signal magnitude increase is greater than would be expected for exciplex formation alone, causing the effective dipole moments to increase with SB concentration (see Figure 3). The increase is accompanied by a decrease in the dipole lifetime and poor quality fits to the two-state model of Scheme 1. This trend is consistent with our previous observation of a large dipole moment for CA excited-state complexes with neat donor solvents[10] and is explained by the formation of triplexes. As SB concentration is increased, the contribution to the signal from triplexes increases and the effective dipole moment increases (see Figure 3). The signal eventually reaches the magnitude of that observed in neat SB solvents. The fact that the triplexes are formed with less than diffusion-controlled rates[2,4,17] correlates well with previous observations that formation of cation dimers, D_2^+, via diffusional collisions of D^+ and D is slow.[19] Thus triplex formation competes effectively with exciplex relaxation to the ground state only at high concentrations. Even in neat donor solvents, triplexes are not necessarily formed with unit probability, as is seen in the differing effective dipole moment increases for various neat SB solvents[11] compared to those of corresponding exciplexes (see Table 2).

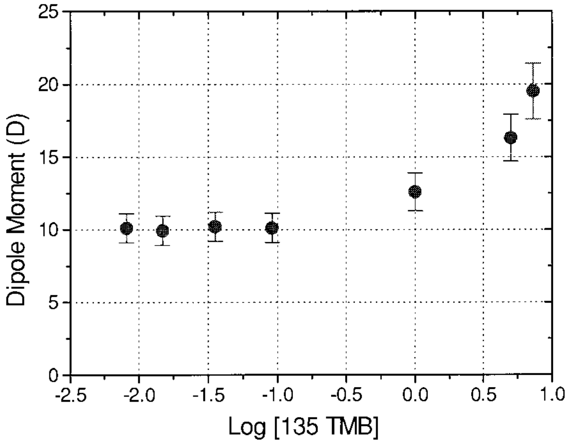


Figure 3. Excited-state dipole moment for TCA/135TMB solutions in benzene as a function of 135TMB concentration. The exciplex (AD) dipole moment remains constant over a wide range of donor (D) concentration until the rate of triplex (ADD) formation starts competing with exciplex relaxation to the ground state. Triplex formation contributes to the effective dipole moment at concentrations exceeding 0.1 M. The highest value (for 7.2 M) is measured in neat 135TMB solvent.[11]

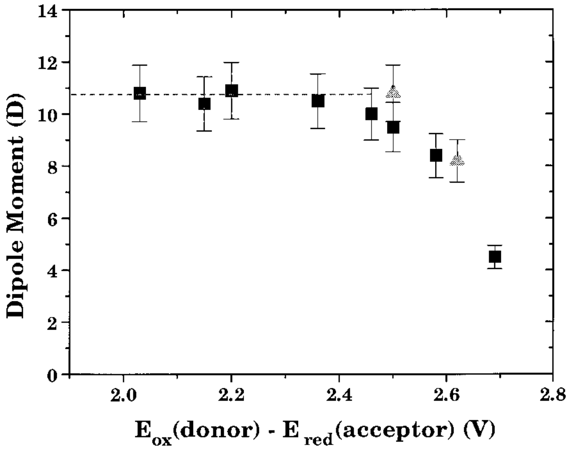


Figure 4. Dipole moments vs redox potential differences, $E_{ox}(D) - E_{red}(A)$, for dilute exciplexes EX2. Redox potentials are in acetonitrile. The solid squares are for the systems with TCA as acceptor, and the solid triangles are for systems with DCA as acceptor.

Figure 4 summarizes our values for the dipole moments, μ_2, of different CA/SB exciplexes. Data are presented in a commonly used form[2,4] as a function of the difference between donor oxidation (E_{ox}) and acceptor reduction (E_{red}) potentials in acetonitrile. The apparent decrease of μ_2 values with $E_{redox} = E_{ox} - E_{red}$ agrees well with previously reported optical studies in such systems,[2,4] but the maximum value for either acceptor of only ca. 10.7 ± 0.4 D is smaller than in those of earlier optical studies.[4]

The rate constants of CA/SB exciplex formation in benzene have different slopes in their dependence on redox potentials when DCA and TCA exciplexes are compared (see Figure 5). This, probably, reflects the differing energetics for substitution of benzene by SB in TCA and DCA-based complexes, EX1. The free energy difference for initial and final states of the substitution, $-\Delta G$, may be estimated from redox potentials of

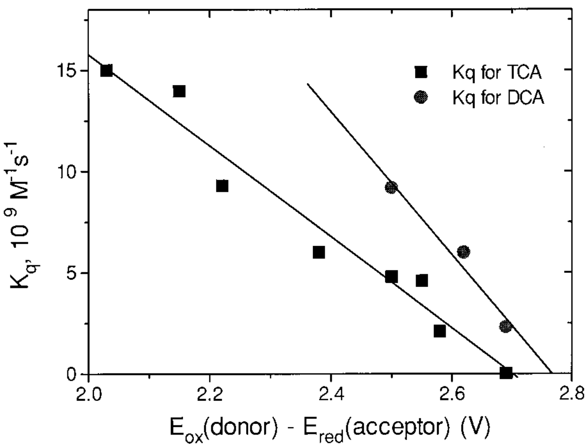


Figure 5. Quenching rate constants of TCA and DCA complexes (EX1) with benzene solvent by substituted benzenes (SB) as a function of redox potential difference, $E_{ox}(D) - E_{red}(A)$, for CA/SB exciplexes (EX2). Redox potentials are in acetonitrile (see Table 2).

the constituents.[4,15] E_{redox} of the TCA/benzene complex is smaller than that of the DCA/benzene complex,[4,20] making $|-\Delta G|$ for donor substitution reactions smaller in the case of the TCA complex. Consequently, TCA-based exciplexes EX2 will form more slowly (smaller driving force) than will DCA exciplexes with the same value of E_{redox} for EX2.

Discussion

The dipole moment increase with decrease in E_{redox} that is observed in this study agrees well with that from previous investigations of such systems.[2,4] The small maximum value of μ_2 was initially surprising to us because it should be the dipole moment of a contact radical ion pair, i.e., μ_{CRIP}. Thus, our value for μ_{CRIP}, ca. 11 D, is at the lower limit of spectroscopic estimates (13 ± 2 D). Other direct methods such as microwave conductivity and electrooptical techniques agree better with our smaller numbers.[6,7]

Unpolarizable ion pairs in contact would have dipole moments of from 14.4 to 16.8 D as the center-to-center separation distance varies from 3.0 to 3.5 Å. What explains the discrepancy with measured values? There are only two components in the definition of a dipole moment, the amount of charge transfer and the separation distance of the centers of positive and negative charge. The observed "saturation" in dipole moment values with E_{redox} decrease (see Figure 4) demonstrates that 11 D is the *maximum* value accessible in the CA/SB series. Small radiative decay rates for the systems with largest dipole moments[4] confirm a vanishing contribution of the $|A^*D\rangle$ configuration to the exciplex wave function, i.e. that c_1 in eq 1 approaches zero. Thus, since charge separation is close to complete, there is only one possibility left, namely, that the *center-to-center charge separation* in CRIPs is different from the frequently assumed value of ca. 3.5 Å. Yet, the *center-to-center molecule separation* in sandwichlike complexes cannot accommodate the necessary dipole moment reduction, because the corresponding distance, ca. 2.3 Å, would be too small. It is worth mentioning that the spectroscopically estimated larger dipole moments of 13−14 D[2,4] correspond to point charge separations of ca. 2.7−2.9 Å. Even those separations are smaller than the expected center-to-center molecule separations in exciplexes. Crystallographically measured donor/acceptor separations in charge-transfer crystals, even for systems with less steric hindrance than CA/SB, are not less than 3.1 Å.[21] One can argue that molecular arrangements in CT crystals are governed by a periodic crystal field which prevents molecules from reaching their minimum possible mutual separation, but on the other hand, methyl substituents in the SB molecules are bulky enough to push the donor molecule away from a CA even further than 3.5 Å. Ab initio calculations for a similar complex, HMB−tetracyanoethylene, with less steric hindrance than in SB/CA complexes resulted in a 3.5 Å interplanar distance.[22]

Our measured dipole moments emphasize that taking the *center-to-center molecular separation* in a complex to be the same as the *center-to-center charge separation* is a mistake. The two entities are not identical because the charge distribution on each ion need not be symmetrical about the molecular plane. It is known that out-of-plane polarizabilities, α_{zz}, for aromatic molecules are not negligibly small.[23] A number of experiments[23b−d] have yielded ground-state polarizabilities α_{zz} for anthracene in the range 12−16 Å^3. The polarizability of a CA$^-$ anion radical may be even larger, but because the negative charge on CA$^-$ is primarily localized on the cyano groups and because α_{zz} for anthracene changes little upon electronic excitation,[23a] a value of $\alpha_{zz} = 15$ Å^3 is a reasonable estimate for CA$^-$ anions. An estimate for the SB$^+$ cation's out-of-plane polarizability can be made by assuming that the cation radical's polarizability is not much different than that of a neutral benzene molecule;[23b] we estimate for methyl-substituted benzenes $\alpha_{zz} \approx 7.5$ Å^3. That gives a conservative estimate for the overall polarizability of the two ions in a CA/SB exciplex of $\alpha' \approx 22$ Å^3.

In the point dipole approximation, the dipole moment decrease, $\Delta\mu$, resulting from this out-of-plane polarizability, α', can be estimated using eq 6:

$$\Delta\mu = -\alpha' E_c = -\alpha' e/r^2 = -\mu_0(\alpha'/r^3) \qquad (6)$$

where $\mu_0 = er$, i.e. the value of μ_{CRIP} with unpolarizable ions, and $E_c = e/r^2$ is the Coulomb field of the counterion with its center of charge a distance r away. Because the exciplex is in a solvent, each ion experiences a reaction field, E_r, which tends to push the charges apart. After adding all these fields together, we arrive at eq 7 for the exciplex dipole moment with complete charge separation, but polarizable ions,

$$\mu_{CRIP} = \mu_0 + \alpha'(E_c + E_r) = \mu_0 + \alpha'(-e/r^2 + f\mu_{CRIP}/\rho^3) \quad (7)$$

Here ρ is the exciplex radius and $f = 2(\epsilon - 1)/(2\epsilon + 1)$ is the, so-called, reaction field factor,[6,9] which changes from 0 in a vacuum to 1 in highly polar solvents. Solving eq 7 for μ_{CRIP}, we obtain

$$\mu_{CRIP} = \frac{\mu_0(1 - \alpha'/r^3)}{\left(1 - \frac{\alpha'}{\rho^3}\frac{2(\epsilon - 1)}{2\epsilon + 1}\right)} \qquad (8)$$

We emphasize that, even when charge separation is complete, the exciplex dipole moment should depend on solvent polarity because of the mutual polarization of the ions in the ionic, $|A^-D^+\rangle$, configuration. Indeed, we obtained a value of 11.3 ± 1.1 D for the DCA/HMB exciplex dipole moment in the moderately polar solvent fluorobenzene ($\epsilon = 5.4$), which in accordance with eq 8 seems to be slightly larger than the value 10.8 ± 0.3 D, measured in benzene solution. However, further study of CA/SB exciplexes in solvents of increasing polarity is needed before firm conclusions can be reached regarding possible solvent polarity effects on exciplex dipole moments.

If nonlinear contributions to the polarizability can be ignored even up to the electric fields experienced by ions ca. 3 Å apart ($\sim 10^8$ V/cm), then we can use eq 8 to estimate μ_{CRIP}. Taking $\alpha' = 22$ Å^3, the exciplex radius $\rho = 5$ Å,[4b] and the charge separation, r, as for unpolarized ions, i.e. 3.5 Å, we calculate that in benzene ($\epsilon = 2.3$, $f = 0.46$) the dipole moment for an exciplex with complete charge separation is $\mu_{\mathrm{CRIP}} = 0.53\mu_0 =$ 8.9 D, a bit lower than we observe experimentally. Even in high-polarity solvents ($\epsilon \rightarrow \infty$, $f = 1$), the calculated $\mu_{\mathrm{CRIP}} =$ 9.9 D remains smaller than the observed value of ca. 11 D. However, it is clear from eq 8 that literature values of ion polarizabilities result in large reductions in calculated exciplex dipole moments that are in reasonable agreement with experiment, especially since the center-to-center intermolecular distance may be greater than 3.5 Å.[24]

The idea of mutual ion polarization in CT complexes is not new[25,26] but, to the best of our knowledge, has not been fully appreciated for sandwichlike complexes. This is surprising in light of the significance of that polarization. Equation 8 makes it understandable that discrepancies between calculated and experimental dipole moments in exciplexes and CT complexes diminish with increased ion separation distance. Indeed, we previously reported a 35 D dipole moment for the triplet exciplex of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD) and C_{60} molecules.[11] This is very close to the value of 34 D, calculated from er with r equal to 7.1 Å, the van der Waals estimate for the TMPD/C_{60} center-to-center distance. Also, the triplex between TCA and 135TMB has a dipole moment of 20 D,[10] which is 2 times, not 50%, larger than the corresponding exciplex dipole moment of 10 D (see Table 2). In both examples polarization effects are less important than for sandwich exciplexes because the greater separation between opposite charges reduces the mutual Coulomb field.

Conclusions

We have used the transient dc photocurrent method to measure the dipole moments of exciplexes formed between excited singlet cyanoanthracene electron acceptors and methyl-substituted benzene donors in benzene solutions. For both acceptors, the dipole moment increases with decreasing donor oxidation potential and saturates at ca. 11 D. This trend is in good agreement with spectroscopic estimates for similar systems,[2,4] but the maximum value measured here is substantially smaller. Based on previous spectroscopic arguments[4] and the dipole moment saturation observed for good donors, we conclude that the dipole moment of a contact radical ion pair, μ_{CRIP}, in these systems is ca. 11 D. We believe that the out-of-plane polarization of the exciplex ions is responsible for the small value of μ_{CRIP}. Literature polarizability values for neutral aromatics support this idea.

The donor concentration dependence of the measured dipole moments confirms our earlier conclusion regarding triplex[10] formation between cyanoanthracenes and neat methylbenzene solvents.

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Appendix

Use of eq 4 in the fitting of the dipole signals requires evaluation of the time-dependent concentrations, N_i, of the dipolar species involved. Neglecting nonstationary quenching (which should happen on a subnanosecond time scale), concentrations of EX1and EX2 (N_1 and N_2 respectively) can be found by solving the following differential equations:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -N_1\left(\frac{1}{\tau_1} + k_{\mathrm{q}}D\right) \qquad (\mathrm{A.1})$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \left(-\frac{N_2}{\tau_2} + k_{\mathrm{q}}DN_1\right) \qquad (\mathrm{A.2})$$

Here τ_1 and τ_2 are the lifetimes of EX1 and EX2 respectively, and k_{q} is the bimolecular rate constant for EX2 formation via "quenching" of EX1 by another donor molecule (D). In solving these equations we assume that EX1 is instantaneously produced after laser excitation with concentration N_0. Then after introducing quenching time $\tau_{\mathrm{q}} = 1/k_{\mathrm{q}}D$, we obtain

$$N_1 = N_0 \exp\left(-\frac{t}{\tau_1{}'}\right) \qquad (\mathrm{A.3})$$

$$N_2 = N_0 \frac{\tau_1{}'\tau_2}{\tau_{\mathrm{q}}\,(\tau_1{}' - \tau_2)}\left[\exp\left(-\frac{t}{\tau_1{}'}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right] \qquad (\mathrm{A.4})$$

where $\tau_1{}'$ is the shortened by the quenching lifetime of EX1:

$$\tau_1{}' = \frac{\tau_1\tau_{\mathrm{q}}}{\tau_{\mathrm{q}} + \tau_1} \qquad (\mathrm{A.5})$$

Obviously $\tau_1{}'$ is also the formation time of EX2. During fitting only τ_{q} and τ_2 were varied.

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(13) As was shown in ref 9b, the local field at a dipole depends on cavity shape through a "depolarizing factor" A_a and solvent dielectric constant, ϵ, and is described by a local field factor: $\varphi_i = \epsilon/[\epsilon + (1 - \epsilon)A_a]$. The default spherical approximation, with $A_a = 1/3$, can be appropriately adjusted by assuming a spheroidal cavity shape with dimensions a, parallel to the intermolecular axis, and b, perpendicular to it, as $A_a = b/(3a)$. Note that the actual axis lengths are not important, only their ratio, i.e. the cavity shape. Taking $b \approx 9$ Å for all species and $a \approx 7$ Å for exciplexes versus $a \approx 10$ Å for triplexes, we estimate $\varphi_c/(\varphi_c)_{\mathrm{spher}}$ to be ca. 1.066 and 0.98 for these species, respectively.

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