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Kinetics of Isomerization via Photoinduced Electron Transfer. I. Spectral Analysis and Structural Reorganization of Hexamethyl Dewar Benzene Exciplexes

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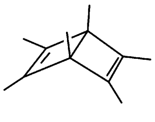
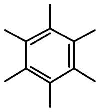
It is well recognized that emission spectra from the reactions of excited-state electron acceptors (A*) with hexamethyl Dewar benzene (D) are typically dominated by fluorescence from exciplexes of its valence isomerization product hexamethylbenzene (B) (i.e., $A^{\bullet -}B^{\bullet +}$). We were able to obtain well-defined emission spectra of the $A^{\bullet -}D^{\bullet +}$ exciplexes with several cyanonaphthalenes as the excited-state electron acceptors by subtraction of the dominant $A^{\bullet -}B^{\bullet +}$ fluorescence from the total emission. Interestingly, a comparison of band shapes and maxima between the exciplexes of D and B reveals that the reorganization energy for return electron transfer in $A^{\bullet -}D^{\bullet +}$ is much larger than in $A^{\bullet -}B^{\bullet +}$ (∼1.2 vs 0.57 eV). Furthermore, a comparison between exciplexes of D and of 1,2-dimethylcyclobutene as a model compound showed that a greater reorganization energy is associated with return electron transfer from the $A^{\bullet -}D^{\bullet +}$ exciplexes. DFT calculations identified much of the "excess" reorganization energy in $A^{\bullet -}D^{\bullet +}$ with a change in the dihedral angle (flap angle) between the two cyclobutene moieties, which is ∼12° smaller in $D^{\bullet +}$ than in D. Approximately one-fourth of the total reorganization energy of ∼1.2 eV for the D exciplexes is due to this angle deformation. Spectra of the exciplexes of B and of model olefins were analyzed by using a familiar two-mode model whereas those of D required a three-mode model to account for the intermediate frequency (491 cm^{-1}) mode associated with the flap angle deformation. Remarkably, although the driving forces for return electron transfer are nearly identical for the exciplexes of D and B with the same acceptor, the rate constants for nonradiative return electron transfer are predicted to be 4 to 5 orders of magnitude greater for the $A^{\bullet -}D^{\bullet +}$ exciplexes because of their larger reorganization energies.

Introduction

An attractive feature of photoinduced electron-transfer reactions and, in particular, isomerization reactions is the potential for chemical amplification via subsequent chain reactions.[1] An early example of such "quantum amplification" is the valence isomerization of hexamethyl Dewar benzene (D) to hexamethylbenzene (B) (Scheme 1).[2] In polar media, D reacts with an excited electron acceptor A to produce separated radical ions ($A^{\bullet -}$ and $D^{\bullet +}$), and the radical cation $D^{\bullet +}$ isomerizes to $B^{\bullet +}$, which then oxidizes another D to generate another $D^{\bullet +}$. The resulting chain reaction can lead to quantum yields (amplification factors) in excess of 100.[2a]



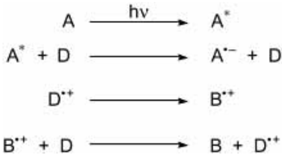
D



B

Because of complicated kinetics caused by the chain reaction in polar solvents, the rate constant for isomerization ($D^{\bullet +}$ → $B^{\bullet +}$) should be easier to study in less polar solvents, where the primary geminate pair does not dissociate into free radical ions.

SCHEME 1: Electron-Transfer-Induced Isomerization of D to B via a Chain Mechanism in Polar Solvents



Moreover, the reactions in such solvents have additional spectroscopic features that can be used to investigate the kinetics.

The geminate pair, the primary intermediate in these photoinduced electron transfer reactions, is an exciplex with largely ionic character (see below) admixed with some contribution from the locally excited state of the acceptor (i.e., $A^{\bullet -}D^{\bullet +} \leftrightarrow A^{*}D$). For brevity, the exciplexes of D and B will be denoted simply as $A^{\bullet -}D^{\bullet +}$ and $A^{\bullet -}B^{\bullet +}$.

In less polar media, three reactions of $A^{\bullet -}D^{\bullet +}$ have been identified by previous investigators (Scheme 2).[3] These reactions are decays to A + D (return electron transfer), an unusual isomerization-coupled return electron transfer leading directly to A + B, and the so-called "adiabatic" isomerization leading to the geminate pair $A^{\bullet -}B^{\bullet +}$. The last reaction is indicated by the similarity of the exciplex emission spectra resulting from reactions of $^{1}A^{*}$ with D and of $^{1}A^{*}$ with B.[3] This conversion of $A^{\bullet -}D^{\bullet +}$ to $A^{\bullet -}B^{\bullet +}$ is presumably analogous to the conversion of free $D^{\bullet +}$ to $B^{\bullet +}$ in polar solvents.

Although the exciplex emission from reactions of $^{1}A^{*}$ with D is usually dominated by $A^{\bullet -}B^{\bullet +}$ fluorescence, there are

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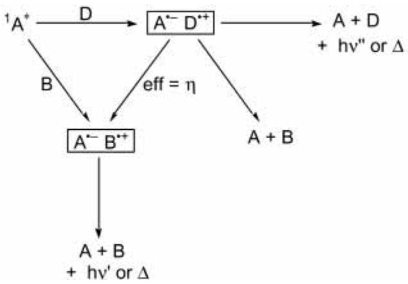
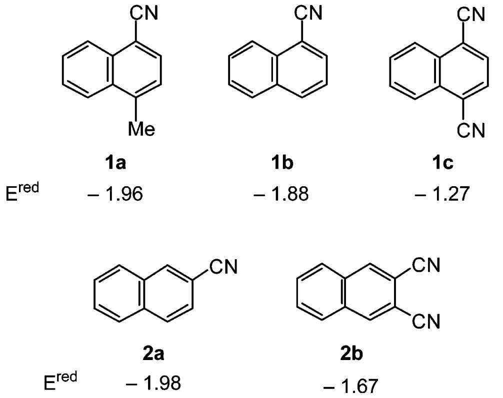
SCHEME 2: Simplified Scheme for the Photoinduced Isomerization of D to B in Low-Polarity Solvents[a]



[a] The two highlighted contact radical-ion pairs (exciplexes) are the key intermediates.

SCHEME 3: α- and β-Substituted Cyanonaphthalene Electron Acceptors (1a−c and 2a and b)[a]



[a] The reduction potentials, measured in acetonitrile, are in V vs SCE.

indications of an additional, very weak emission thought to be from the $A^{\bullet-}D^{\bullet+}$ exciplex.[3a,e] In connection with a detailed study of the kinetics and the parameters controlling the reactions of $A^{\bullet-}D^{\bullet+}$, it was important to identify and analyze the weak emission from this intermediate for several reasons. First, an analysis of the spectral band shape can provide information about the reorganization energy for return electron transfer.[4,5] Second, from the radiative rate constant (k_f), the electron-transfer matrix element (V) can be evaluated.[5a−c] Third, from the reorganization energies and the matrix element, the rate constant for nonradiative return electron transfer (k_{-et}) can be predicted. Finally, the kinetics of the reactions in Scheme 2, which remains largely unexplored, can be investigated by analyzing fluorescence decay data.

Results and Discussion

As the first part of a study of these reactions, we have examined the $A^{\bullet-}B^{\bullet+}$ and $A^{\bullet-}B^{\bullet+}$ exciplex emissions with several cyanonaphthalene derivatives as the acceptors (Scheme 3) in diethyl ether. The reduction potentials span a range of ~0.7 V. In these systems, the efficiency of radical ion isomerization (η) (Scheme 2) is in the range of 0.2 to 0.5.

1. $A^{\bullet-}D^{\bullet+}$ Exciplex Emission. After subtracting residual $^1A^*$ fluorescence from the total emission, the normalized exciplex emission spectra for the same $^1A^*$ reacting with D and B were compared. The latter represents the authentic $A^{\bullet-}B^{\bullet+}$ exciplex. On the long-wavelength edge, the spectra with D showed a higher intensity than those with B, and subtracting an appropriate fraction of the authentic $A^{\bullet-}B^{\bullet+}$ spectrum yielded a well-defined spectrum for the $A^{\bullet-}D^{\bullet+}$ exciplex (Figure 1).[6] Despite the relatively small contribution of $A^{\bullet-}D^{\bullet+}$ emission relative to that of $A^{\bullet-}B^{\bullet+}$, it was possible to extract reliable spectra of $A^{\bullet-}D^{\bullet+}$ because of the large displacement (~80 nm) between the two spectra. As evident from Figure 1, most of the low-energy half of the $A^{\bullet-}D^{\bullet+}$ spectrum is well-defined because of the low contribution from $A^{\bullet-}B^{\bullet+}$ in this region. To enhance the reliability of the high-energy half of the $A^{\bullet-}D^{\bullet+}$ spectrum, conditions were chosen to maximize the contribution from this component. For more details, see Experimental Section.

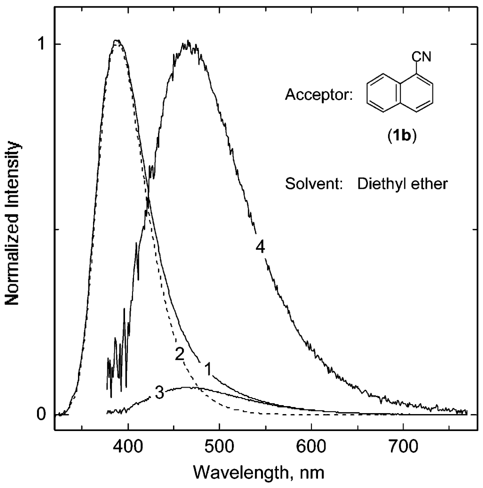


Figure 1. Spectrum 1: emission of a solution of **1b** and 0.41 M hexamethyl Dewar benzene (D) in aerated diethyl ether from which the residual fluorescence of excited **1b** was subtracted. Spectrum 2: analogous emission of a solution of **1b** and 0.08 M hexamethylbenzene (B). Spectrum 3: spectrum 1 minus spectrum 2. Spectrum 4: spectrum 3 multiplied by 13.4.

The $A^{\bullet-}D^{\bullet+}$ spectrum is structureless, typical of an exciplex, but much broader than that of the $A^{\bullet-}B^{\bullet+}$ exciplex. Examples of the spectra, in reduced form and normalized to unity, are shown in Figure 2. A reduced spectrum is proportional to $I_\lambda \nu^{-3}$, where I_λ is the measured emission intensity in photons/(nm s) and ν is the wavenumber.[7] A factor of ν^{-2} converts I_λ to a spectrum in photons/(cm^{-1} s). An additional factor of ν^{-1} reduces that spectrum to a Franck−Condon weighted density of states, FCWD, the form most suitable for spectral comparisons.[8]

Listed in Table 1 are the maxima, ν^r_{max}, and the average wavenumbers (first moments), ν^r_{av}, of the reduced spectra. The ν^r_{av} are uniformly smaller than the corresponding ν^r_{max} by 480 ± 30 cm^{-1}, a reflection of the asymmetry (and degree of deviation from a Gaussian line shape) of the spectra. Both the maxima and the average wavenumbers of the reduced spectra of the $A^{\bullet-}D^{\bullet+}$ exciplexes are at lower energies than those of the corresponding $A^{\bullet-}B^{\bullet+}$ exciplexes by 4700 to 5800 cm^{-1} (0.58 to 0.72 eV) (Table 1). For each acceptor, the two exciplexes ($A^{\bullet-}D^{\bullet+}$ and $A^{\bullet-}B^{\bullet+}$) should have nearly equal free energies (ΔG) relative to that of the neutral ground state because the oxidation potentials of B and D are nearly identical.[9] The shift of ~0.6−0.7 eV in ν^r_{max} corresponds, therefore, to the *difference* in reorganization energies for return electron transfer between $A^{\bullet-}D^{\bullet+}$ and $A^{\bullet-}B^{\bullet+}$.

As shown in Figure 2, the spectra of the D exciplexes are significantly broader than those of B (by ~1300−2000 cm^{-1}, Table 1), again in agreement with a much larger reorganization energy for $A^{\bullet-}D^{\bullet+}$ than for $A^{\bullet-}B^{\bullet+}$. In addition, whereas the spectra for exciplexes of B all have very similar band shapes (fwhm ≈ 4400 cm^{-1}), the spectra for exciplexes of D seem to fall into two groups. The spectra of D with all α-substituted cyanonaphthalenes (**1a−c**) have virtually identical band shapes (fwhm = 5700 cm^{-1}), and so do those with β-cyanonaphthalenes

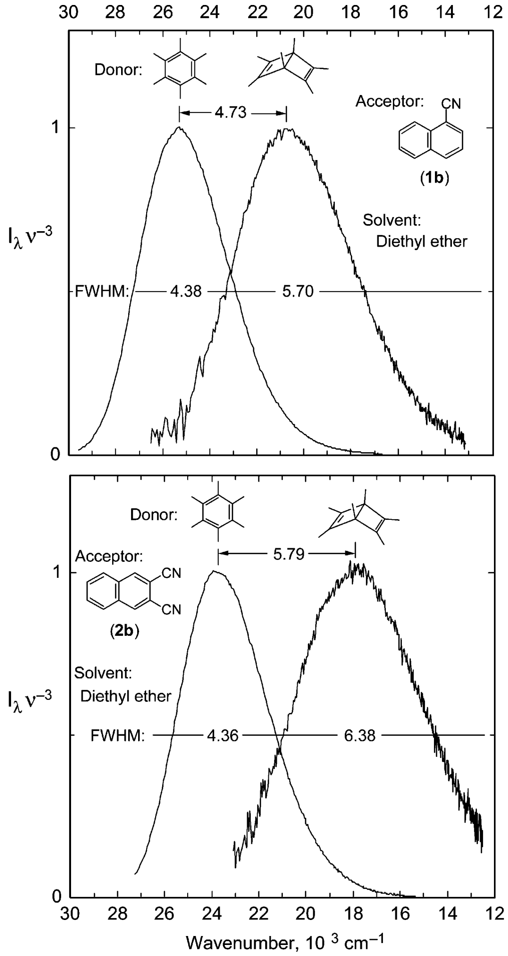


Figure 2. Normalized, reduced emission spectra in diethyl ether of the exciplexes of **1b** and of **2b** with hexamethylbenzene (B) and with hexamethyl Dewar benzene (D) vs wavenumber. The spectral shift between the B and D exciplexes of **1b** (4.73×10^3 cm^{-1}) is accompanied by an increase in fwhm (1.32×10^3 cm^{-1}). The larger spectral shift for the exciplexes of **2b** (5.79×10^3 cm^{-1}) is also accompanied by a larger increase in fwhm (2.02×10^3 cm^{-1}), consistent with a further increase in reorganization energy; see text.

TABLE 1: Full Width at Half Maximum (fwhm), Wavenumber at Maximum (ν^r_{max}), and Average Wavenumber (ν^r_{av}) of the Reduced Spectra of Cyanonaphthalene Exciplexes with Hexamethylbenzene (B) and with Hexamethyl Dewar Benzene (D) in Diethyl Ether[a]

	$A^{\bullet-}B^{\bullet+}$			$A^{\bullet-}D^{\bullet+}$		
A	fwhm	ν^r_{max}	ν^r_{av}	fwhm	ν^r_{max}	ν^r_{av}
2a	4.46	26.53	26.01	6.38	21.69	21.17
1a	4.39	25.77	25.26	5.70	21.01	20.58
1b	4.38	25.38	24.85	5.70	20.65	20.17
2b	4.36	23.74	23.21	6.38	17.95	17.48
1c	4.50	20.88	20.37	5.70	15.72	15.28

[a] All values are in 1000 cm^{-1}.

(**2a**, **b**) (fwhm = 6380 cm^{-1}) (Table 1). The different bandwidths suggest that these two sets also have somewhat different reorganization energies.

2. Exciplexes of Model Donors. The fact that the D exciplexes have much larger reorganization energies than the B exciplexes in a low-polarity solvent indicates that the difference in geometry between the radical cation and the neutral donor is greater for the pair $D^{\bullet+}/D$ than for the pair $B^{\bullet+}/B$. One obvious difference is the greater degree of charge/spin localization in $D^{\bullet+}$ than in $B^{\bullet+}$; another is the greater flexibility with respect to bending distortions in D and $D^{\bullet+}$. To investigate the structural effects in more detail, one cyclic and one simple olefin were studied as model donors, 1,2-dimethycyclobutene (DMCB) and 2,3-dimethyl-2-butene (DMB). Their radical cations are even more localized than $D^{\bullet+}$, but they lack the somewhat flexible bridging structure of $D^{\bullet+}$ and D. The exciplex spectra of DMCB and DMB with **1b** are considerably broader (fwhm = 5600 and 5400 cm^{-1}, respectively) than that of the B exciplex (4400 cm^{-1}). Although one of these exciplexes, $\mathbf{1b}^{\bullet-}\mathrm{DMCB}^{\bullet+}$, has almost the same fwhm as does $\mathbf{1b}^{\bullet-}D^{\bullet+}$, the spectra differ in more subtle ways, indicating that the reorganization energies are different (see below).

3. Theoretical Fitting of Spectra (Two-Mode Model). Exciplex energies (ΔG) and reorganization energies can be evaluated by fitting emission spectra to a theoretical model. In the simplest realistic model, the familiar two-mode model[4,5,10] given by eqs 1−3, the total reorganization energy, is represented by contributions of one low-frequency (mostly solvent and librational motion, λ_s) and one high-frequency (skeletal vibrations, λ_v) mode with a frequency (ν_v) typical of a carbon−carbon stretch. The emission is characterized by a vibronic progression (stick spectrum) in the ν_v mode, with Franck−Condon factors F_{0j} representing transitions from the lowest vibrational sublevel of the exciplex to the jth vibrational sublevel of the neutral ground state. Each spectral line is given a Gaussian line shape with a rms width (σ) corresponding to the value of λ_s. The resulting FCWD, for a general energy argument g, is FC(g). The reduced spectrum, $I_\lambda \nu^{-3}$, is proportional to the FCWD as a function of photon energy relative to the free energy of the exciplex, FC($h\nu - \Delta G$). The other quantities in eqs 1−3, (h, k_B, T) have their usual meanings.

$$I_\lambda \nu^{-3} \propto \mathrm{FC}(h\nu - \Delta G) \qquad (1)$$

$$\mathrm{FC}(g) = \sum_{j=0}^{\infty} F_{0j}(\sigma\sqrt{2\pi})^{-1} \exp\left(-\frac{(g + \lambda_s + jh\nu_v)^2}{2\sigma^2}\right) \qquad (2)$$

$$\sigma = (2\lambda_s k_B T)^{1/2} \qquad F_{0j} = \frac{e^{-S}S^j}{j!} \qquad S = \frac{\lambda_v}{h\nu_v} \qquad (3)$$

An exact formula for the total reorganization energy,[5c] ($\lambda_s + \lambda_v$), and an approximate formula[4] for the fwhm are given in eqs 4 and 5. Within the model, the total reorganization energy is exactly equal to $\Delta G - h\nu^r_{av}$, and reliable conclusions about the relative values of ($\lambda_s + \lambda_v$) can be drawn from comparisons of the displacement of $h\nu^r_{av}$ relative to ΔG. However, because λ_v and λ_s contribute to fwhm^2 with different weights ($h\nu_v$ and $2k_B$T), the width of a spectrum is not a simple measure of the total reorganization energy.

$$\lambda_s + \lambda_v = \Delta G - h\nu^r_{av} \qquad (4)$$

$$\mathrm{fwhm}^2 \approx (8 \ln 2)\,(h\nu_v\lambda_v + 2k_B T\lambda_s) \qquad (5)$$

As mentioned above, the reduced spectra of all B exciplexes have very similar spectral distributions, which implies similar reorganization energies. Assuming a typical value of 1400 cm^{-1} for ν_v, a least-squares fitting of the spectra gave values for λ_s of 0.33 ± 0.02 eV and for λ_v of 0.24 ± 0.01 eV (Figure 3 and Table 2). The charge-transfer character of these exciplexes undoubtedly changes with the reduction potential of the acceptors. Nevertheless, the spectral distribution and hence the reorganization energy for the exciplexes with higher energy and

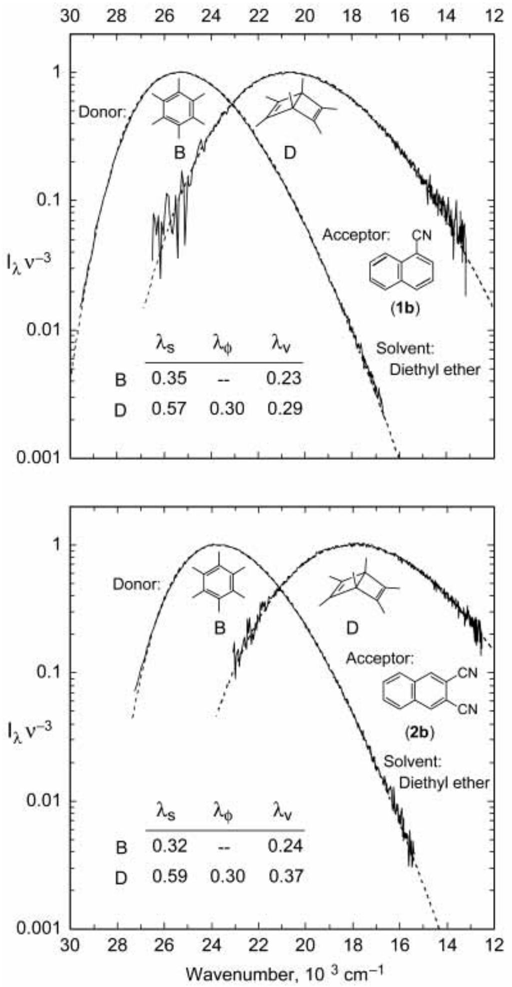


Figure 3. Normalized, reduced emission spectra of the exciplexes of **1b** and of **2b** with hexamethylbenzene (B) and with hexamethyl Dewar benzene (D) in diethyl ether plotted semilogarithmically vs wavenumber, solid curves. The dashed curves are spectra calculated using parameters obtained from Tables 2 (for the B exciplexes) and 4 (for the D exciplexes).

TABLE 2: Reduction Potentials of the Cyanonaphththalene Acceptors (in V vs SCE) and Parameters Obtained from Fitting the Spectra of Their Exciplexes with B (in eV) According to a Two-Mode Model (Equations 1−3) Assuming ν_v = 1400 cm^{-1}

		$A^{\bullet-}B^{\bullet+}$				
A	$-E^{red}_A$	ΔG	λ_s	λ_v	λ_{total}	Δ^a
2a	1.98	3.795	0.33	0.24	0.57	0.225
1a	1.96	3.702	0.34	0.23	0.57	0.152
1b	1.88	3.658	0.35	0.23	0.58	0.191
2b	1.67	3.437	0.32	0.24	0.56	0.177
1c	1.27	3.085	0.31	0.25	0.56	0.225

[a] $\Delta = \Delta G - (E^{ox}_B - E^{red}_A)$, where E^{ox}_B = 1.59 V vs SCE.

more locally excited character appear to be the same as for the exciplex with lowest energy and with charge-transfer character approaching unity. Evidently, all of these exciplexes have high enough charge-transfer character to justify the application of electron-transfer theory.

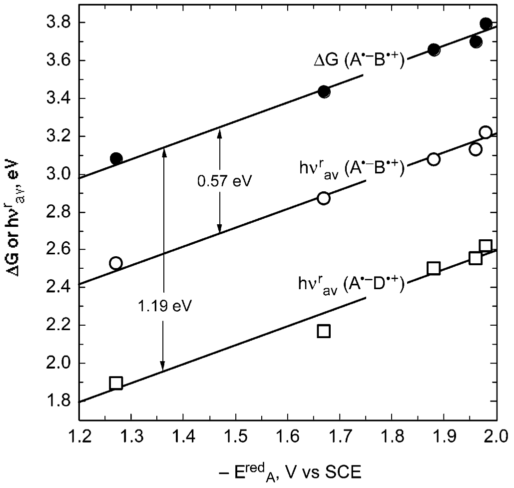


Figure 4. Energy (Δ*G*) of the exciplexes ($A^{\bullet-}B^{\bullet+}$) of cyanonaphthalene acceptors (A, Scheme 3) with hexamethylbenzene (B) in diethyl ether plotted vs the reduction potential of the acceptor (E^{red}_A). Also included are plots of the average emission wavenumber ($h\nu^r_{av}$) for $A^{\bullet-}B^{\bullet+}$ fluorescence and the corresponding $h\nu^r_{av}$ for the hexamethyl Dewar benzene analogues ($A^{\bullet-}D^{\bullet+}$) vs E^{red}_A. The lines are the best fits with a slope of unity. The displacements between the Δ*G* and the $h\nu^r_{av}$ lines (0.57 and 1.19 eV, respectively) correspond to the total reorganization energies for return electron transfer.

Values for Δ*G* obtained from the fitting show a linear dependence, with a slope of unity, on the reduction potential of the acceptor (E^{red}_A) (Figure 4). The values of Δ*G* are larger than the difference between redox potentials in polar solvents, $E^{redox} = (E^{ox}_B - E^{red}_A)$, by an increment Δ of 0.19 ± 0.04 eV (Table 2). This energy increment, $\Delta = \Delta G - E^{redox}$, is in reasonable agreement with the value expected from a correlation of Δ with the dielectric constant (ϵ) of the solvent (0.14 eV for diethyl ether, $\epsilon = 4.2$).[11] This correlation was derived empirically from a combination of absorption spectra of several charge-transfer complexes and emission spectra from the corresponding contact radical-ion pairs.[11] The approximate slopes of unity for the correlations shown in Figure 4 again indicate that these exciplexes are of high ionic charcater.

Figure 4 also shows the values of $h\nu^r_{av}$ for the B and D exciplexes, again as functions of E^{red}_A. The approximately uniform differences between Δ*G* and $h\nu^r_{av}$ for the B exciplexes reflect the nearly constant value of the total reorganization energy for $A^{\bullet-}B^{\bullet+}$ (~0.57 eV). The $h\nu^r_{av}$ values for the D exciplexes are displaced from the corresponding Δ*G* plot by ~1.19 eV, indicating a total reorganization energy of this magnitude for $A^{\bullet-}D^{\bullet+}$, which is approximately double that for the B exciplexes.

Shown in Figure 5 are theoretical spectra for the model olefin exciplexes with Δ*G*, λ_s, and λ_v evaluated by spectral fitting, again with ν_v assumed to equal 1400 cm^{-1} (Table 3). The value for λ_v, ~0.4 eV, for both model donors is larger than that for B (0.24 eV), supporting the notion that λ_v is linked to the degree of localization in the radical cation. The reorganization energies associated with low-frequency modes (λ_s) for the DMCB and DMB exciplexes (0.45 and 0.33 eV, respectively) are slightly larger or comparable to those for the B exciplexes (~0.33 eV). Although the spectrum of $\mathbf{1b}^{\bullet-}$DMB$^{\bullet+}$ is significantly different from that of $\mathbf{1b}^{\bullet-}B^{\bullet+}$ (ν^r_{max} of 24.29 and 25.38 × 10^3 cm^{-1}, fwhm of 5.4 and 4.4 × 10^3 cm^{-1}, respectively), the fitting procedure (Figures 3 and 5) gave nearly identical Δ*G* values for both exciplexes (Tables 2 and 3). Similar values of Δ*G* are to be expected if the exciplexes are indeed highly ionic because the acceptor is the same and the donors have similar oxidation potentials.[12] The similarity of the Δ*G* values thus supports the validity of the two-mode electron-transfer model for fitting and interpreting the spectra.

On the basis of the relative degrees of charge/spin localization in the radical cations, one would expect D to have a total reorganization energy that is intermediate between that of B

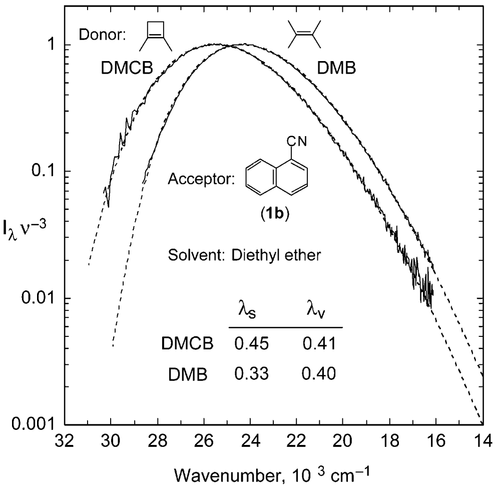
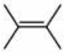


Figure 5. Normalized, reduced emission spectra of the exciplexes of **1b** with 1,2-dimethylcyclobutene (DMCB) and with 2,3-dimethyl-2-butene (DMB) in diethyl ether plotted semilogarithmically vs wavenumber, solid curves. The dashed curves are spectra calculated using parameters from Table 3.

TABLE 3: Parameters (in eV) Obtained from Fitting Spectra of 1-Cyanonaphthalene (1b) Exciplexes with Olefins in Diethyl Ether According to a Two-Mode Model (Equations 1−3) Asuming ν_v = 1400 cm^{-1}

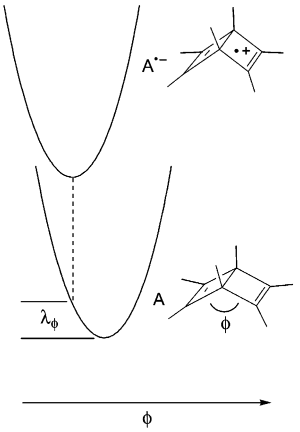
donor	ΔG	λ_s	λ_v	λ_{total}
 (DMCB)	3.955	0.45	0.41	0.86
 (DMB)	3.675	0.33	0.40	0.73

and those of the model donors DMCB and DMB. In fact, however, the total reorganization energy of the exciplexes of D (~1.19 eV) is much larger than those of B (0.57 eV) and of DMCB and DMB (0.86 and 0.73 eV respectively). In particular, it exceeds the total reorganization energy of the closest analogue (DMCB) by ~0.3 eV.

To identify the origin of the large reorganization energy, the spectra of the D exciplexes were fit to the standard two-mode model. Although the resulting values of λ_v (0.3 to 0.4 eV) were unremarkable, the required values of λ_s (~0.8 eV) were surprisingly large. This suggests that the distinguishing feature of D and its radical cation is a large reorganization (normal-coordinate change and reorganization energy) in a low-frequency mode that is unique to this molecule. A likely hypothesis is that the large reorganization energy of the D exciplexes is associated with a "low-frequency" angular distortion of the bridging structure connecting the two olefinic moieties.

4. DFT Calculation of Angle Deformation Energy. Quantum mechanical calculations predict that the dihedral angle between the cyclobutene rings in D (ϕ, Scheme 4) decreases significantly upon one-electron oxidation. At the B3LYP/6-311+G** level of theory, ϕ changes from 116.0° in D to 104.2° in $D^{\bullet+}$. This bending distortion (reorganization) is presumably a consequence of removing an electron from a HOMO that is antibonding between the formally nonbonded carbons belonging to the two ethylenic bonds.[13] The reorganization energy associated with this mode-specific reorganization (λ_ϕ) was estimated from the energy difference between the fully optimized D structure and a hypothetical D structure in which ϕ was fixed at 104.2° while all other geometrical parameters were the same as in the fully optimized structure. The resulting value of λ_ϕ is ~0.3 eV. The totally symmetric (a_1) bending frequency associated with this mode was calculated to be 492 cm^{-1},[14] very similar to the measured[15] value of 491 cm^{-1}.

SCHEME 4: Additional Reorganization Energy, λ_ϕ, Associated with the Decrease in the Dihedral (Flap) Angle, ϕ, in the Radical Cation Moiety of $A^{\bullet-}D^{\bullet+}$ Relative to the Neutral State



5. Theoretical Fitting of $A^{\bullet-}D^{\bullet+}$ Spectra (Three-Mode Model). A frequency of 491 cm^{-1} is too high ($\gg k_BT$) to justify simply lumping the ϕ bending mode with other "classical" low-frequency motions that contribute to the low-frequency reorganization energy in the two-mode model.[16] Instead, for any detailed analysis, this mode should be accommodated explicitly in the FCWD (eqs 6−8, three-mode model). Given the relatively small spacing between the energy levels of the ϕ mode, excited states of this mode will be initially populated to some degree. For symmetry, thermal occupation of the residual high-frequency (ν_v) mode is also accommodated. Hence, eq 6 includes Boltzmann factors for the two modes, P_i and $P'_{i'}$ (eqs 7 and 8). The initial and final quantum numbers for the ν_v mode are i and j, respectively, and the corresponding Franck−Condon factors are F_{ij}. The corresponding quantities for the ν_ϕ mode are i', j', and $F'_{i'j'}$. The reduced spectrum is still proportional to FC($h\nu - \Delta G$) (eq 1), and the Gaussian individual line width σ is still given by eq 3. It can be shown that the total reorganization energy is still given by $\Delta G - h\nu^{\mathrm{r}}_{\mathrm{av}}$.

$$\mathrm{FC}(g) = \sum_{i,i'=0}^{\infty} P_i P'_{i'} \sum_{j,j'=0}^{\infty} F_{ij} F'_{i'j'} (\sigma\sqrt{2\pi})^{-1} \times \exp\left(-\frac{[g + \lambda_s + (j-i)h\nu_v + (j'-i')h\nu_\phi]^2}{2\sigma^2}\right) \quad (6)$$

$$P_i = \left[1 - \exp\left(-\frac{h\nu_v}{k_BT}\right)\right] \exp\left(-\frac{ih\nu_v}{k_BT}\right) \quad (7)$$

$$P'_{i'} = \left[1 - \exp\left(-\frac{h\nu_\phi}{k_BT}\right)\right] \exp\left(-\frac{i'h\nu_\phi}{k_BT}\right) \quad (8)$$

Equations for computing the Franck−Condon factors were taken from the literature.[17]

Equation 6 is written in a form that highlights its relationship to eq 2, but a more compact equivalent[18] was used for the actual computations.

The spectra of the D exciplexes were analyzed according to this three-mode model to evaluate λ_s and λ_v, holding λ_ϕ at the

TABLE 4: Parameters (in eV) Obtained from Fitting Exciplex Spectra of Cyanonaphthalene Acceptors with D According to a Three-Mode Model (Equations 6−8) Asuming $\nu_\phi = 491$ cm^{-1} and $\nu_v = 1400$ cm^{-1}[a]

	$A^{\bullet-}D^{\bullet+}$			
A	λ_s	λ_ϕ	λ_v	λ_{total}
2a	0.48	0.3	0.38	1.16
1a	0.56	0.3	0.29	1.15
1b	0.57	0.3	0.29	1.16
2b	0.59	0.3	0.37	1.26
1c	(0.60)[b]	0.3	(0.29)[b]	1.19

[a] Fixed values for ΔG, equal to those for the corresponding $A^{\bullet-}B^{\bullet+}$ exciplexes (Table 2), and fixed values for λ_ϕ were used in the fitting. [b] These values are less accurate because a larger portion of the spectrum extends beyond the detection limit of 800 nm.

computed value of 0.3 eV and ν_ϕ at the experimental value of 491 cm^{-1}. The exciplex energies, ΔG, were taken to be the same for $A^{\bullet-}D^{\bullet+}$ as those determined for $A^{\bullet-}B^{\bullet+}$ (Table 2) because in this case the limited range of accurate spectra does not allow a reliable determination of all three parameters. The reorganization energies obtained from the fitting procedure are given in Table 4. Examples of the theoretical spectra calculated with these parameters are shown in Figure 3. The fact that the theoretical model can account for the position, width, and non-Gaussian shape of each spectrum indicates that the breadth of these spectra is indeed due to large reorganization energies rather than, for example, overlapping emissions from more than one exciplex species.

With the exception of **2a**, which gives a slightly smaller value than the other acceptors, λ_s values for the D exciplexes are ∼0.58 ± 0.02 eV as compared with 0.33 ± 0.02 for the B exciplexes.[19] The high-frequency reorganization energies λ_v for the D exciplexes with the α- and β-substituted acceptors are 0.29 and 0.37 eV, respectively, as compared with ∼0.24 eV for all exciplexes of B. Thus, the large difference of ∼0.6−0.7 eV in the total reorganization energy for the D exciplexes relative to those of the B exciplexes is mostly due to the additional angle-bending mode λ_ϕ (calculated to be 0.3 eV) and to a difference in λ_s (0.25 eV). The difference in λ_v is relatively small (0.05 for the α- and 0.13 eV for the β-acceptors).

The largest difference between the exciplexes of D and that of the closest analogue, **1b**/DMCB, is the additional λ_ϕ (0.3 eV), present only in the D exciplexes. D exciplexes with α-acceptors also have somewhat larger λ_s values (∼0.58 vs 0.45 eV), probably representing additional unique modes of distortion in D/$D^{\bullet+}$, but they have smaller λ_v values (0.29 vs 0.41 eV), probably because of the higher degree of delocalization in $D^{\bullet+}$. The fact that the D exciplexes with α- and β-acceptors have significantly different values of λ_v (0.29 vs 0.37 eV) suggests, surprisingly, that the skeletal geometry of the radical cation in the exciplex is influenced somewhat by the nature of the radical anion or vice versa.

As mentioned above, relative values of the fwhm do not necessarily reflect the relative values of the total reorganization energy. The exciplex spectra of D with the α-acceptors and that of DMCB with **1b** have similar fwhm values (5700 and 5600 cm^{-1}, respectively), but the total reorganization energies are very different (∼1.17 and 0.86 eV). In this case, the nearly equal fwhm is accidental. The effects of the additional λ_ϕ (0.3 eV) and a λ_s that is larger by 0.13 eV are nearly compensated by a λ_v that is 0.12 eV smaller. The reason for this compensation is that the fwhm depends much more strongly on λ_v than on the reorganization energies for lower-frequency modes, as indicated by the different weighting factors for λ_v and λ_s in eq 5 for the two-mode case. In the example of the DMCB exciplex, for which the two-mode formulation is applicable, λ_v is weighted ∼3.4 times more heavily than λ_s ($h\nu_v = 1400$ cm^{-1}; $2k_BT = 410$ cm^{-1}).

6. Matrix Elements and Return Electron-Transfer Rate Constants. Rate constants for nonradiative return electron transfer in the B and D exciplexes, $(k_{-et})_B$ and $(k_{-et})_D$, can be estimated from the energy parameters (ΔG, λ_s, λ_ϕ, and λ_v) together with the electron-transfer matrix element V coupling the exciplex (charge-transfer) state with the neutral ground state (eq 9).[4,5,16b,20] The matrix element V can be determined from the corresponding radiative rate constant k_f, which is proportional to V^2, ν^r_{av}, and $|\Delta\mu|^2$, where $\Delta\mu$ is the difference in the permanent dipole moment between the two states.[5b,c] In work to be reported separately, the ratio of k_f values for the two donors with the same acceptor, $(k_f)_D/(k_f)_B$, was found to be nearly the same (0.28 ± 0.01) for all five acceptors used in this work. The values of ν^r_{av} for the two exciplexes with a given acceptor differ by only ∼20%. The dipole-moment factors, $|\Delta\mu|^2$, are presumably comparable. Hence, the ratio of V^2 for the two exciplexes, V^2_D/V^2_B, is ∼0.35. From this ratio and the parameters given in Tables 2 and 4, it is predicted that the nonradiative decay rate constants for the D exciplexes $(k_{-et})_D$ are 4−5 orders of magnitude higher than those of the corresponding B exciplexes $(k_{-et})_B$ even though the D and B exciplexes have equal energies relative to their neutral ground states.

$$k_{-\mathrm{et}} = \frac{4\pi^2}{h} V^2\, \mathrm{FC}(-\Delta G) \qquad (9)$$

A huge difference in k_{-et} values can already be predicted from a comparison of the reduced emission spectra, which are proportional to FC($h\nu - \Delta G$) (eq 1). For a given acceptor, $(k_{-et})_D/(k_{-et})_B$ is the product of two factors, V^2_D/V^2_B and $\mathrm{FC}_D(-\Delta G)/\mathrm{FC}_B(-\Delta G)$. The first factor, as mentioned above, is relatively modest, ∼0.35. The second factor is approximately the ratio of the reduced emission spectra, extrapolated to zero frequency (Figure 3). Although the D curve should be multiplied by a factor of ∼0.25 for proper comparison with the B curve,[21] it is clear that this extrapolation will yield vastly different values for the two exciplexes and a vastly larger value for k_{-et} for the D exciplexes. Both the shift and the greater breadth of the $A^{\bullet-}D^{\bullet+}$ spectrum contribute to this result, and both are consequences of much larger reorganization energies for $A^{\bullet-}D^{\bullet+}$ than for $A^{\bullet-}B^{\bullet+}$. It is a dramatic illustration of the influence of the reorganization energies that, for pairs of exciplexes with *equal* driving force for return electron transfer, the predicted rate constants differ by *many* orders of magnitude.

Exciplexes involving cyanoaromatic acceptors and methylbenzene donors typically have V values of ∼0.1 eV.[5] Assuming a similar V for the $A^{\bullet-}B^{\bullet+}$ exciplexes, then even the lowest-energy B exciplex **1c**$^{\bullet-}B^{\bullet+}$ (i.e., the one with the fastest return electron transfer) is predicted to have k_{-et} in the range of only 10^4 s^{-1}. This value is well below the total rate constant for all decay processes of this exciplex, ∼1.1×10^7 s^{-1} (lifetime ≈ 90 ns), and thus is predicted not to contribute measurably to the decay rate for this or the other B exciplexes. More importantly, in the context of the radical-ion isomerization reaction, k_{-et} values in the 10^8 s^{-1} range are predicted for the lowest-energy D exciplex, **1c**$^{\bullet-}D^{\bullet+}$.[20c] Such a large k_{-et} is expected to be competitive with other decay processes of the D exciplexes, for which preliminary results indicate lifetimes in the nanosecond range. Indeed, the lifetime of **1c**$^{\bullet-}D^{\bullet+}$ seems to be noticeably shorter than those of the other D exciplexes, probably because nonradiative return electron transfer should be fastest for this pair. Thus, at least in this case, it appears that the large reorganization energy governing return electron transfer in the $A^{\bullet-}D^{\bullet+}$ exciplex leads to a reduction in efficiency of the isomerization of $D^{\bullet+}$ to $B^{\bullet+}$.

The complete reaction kinetics of isomerization in these exciplexes is currently under investigation using a combination of steady-state and time-resolved experiments and taking advantage of the distinct emission spectra of the two exciplexes, $A^{\bullet-}B^{\bullet+}$ and $A^{\bullet-}D^{\bullet+}$. The overall kinetic analysis of the reactions in Scheme 2, including additional processes omitted here for simplicity, will be reported in subsequent publications.

Experimental Section

Materials. Hexamethylbenzene (Aldrich) was recrystallized twice from ethanol. Hexamethyl Dewar benzene, D, (Aldrich) was freshly distilled over lithium aluminum hydride under a nitrogen atmosphere at 17 mmHg (bp 38−39 °C). Repeated fractional distillation of D as well as low-temperature sublimation gave the same fluorescence results, providing evidence that the emissions are not due to impurities. 1-Cyanonaphthalene (**1b**) (Aldrich) and 2-cyanonaphthalene (**2a**) (Kodak) were purified by sublimation under vacuum, and 2,3-dicyanonaphthalene (**2b**) (Aldrich) was recrystallized from acetonitrile. 1-Cyano-4-methylnaphthalene **(1a)** was prepared according to a literature procedure[22] and further purified by sublimation (120 °C, 0.7 mmHg) and recrystallization from ethanol/water. 1,4-Dicyanonaphthalene (**1c**) was prepared from the dibromo analogue according to a literature procedure[23] and purified by recrystallization first from toluene/charcoal and then twice from methanol/charcoal to give colorless crystals (mp 209−212 °C, literature value[23] 210 °C). 2,3-Dimethyl-2-butene, DMB, (Aldrich, 99+%) was used as received. 1,2-Dimethylcyclobutene, DMCB, was prepared from 3,4-dimethyl-1,3-butadiene according to a literature procedure.[24] The distilled product was heated (65 °C) with maleic anhydride to remove traces of the starting diene and then purified by preparative gas chromatography (5% SP-1200/1.75% Bentone 34 on 100/120 mesh Suppelcoport; 50 °C oven temperature). Ether (anhydrous, EM Science) was freshly distilled over sodium under nitrogen.

Fluorescence. A Spex Fluorolog 212 spectrometer was used to measure the fluorescence spectra using 1-cm quartz cells. Corrected spectra were obtained using a calibrated quartz lamp.

To increase the reliability of the spectral subtraction, the measurements were performed at high concentrations of D (~0.4 M) in aerated solution. With increasing [D], the ratio of the $A^{\bullet-}D^{\bullet+}$ component increases relative to that of $A^{\bullet-}B^{\bullet+}$ because of the known[3] quenching of $A^{\bullet-}B^{\bullet+}$ by D. The $A^{\bullet-}D^{\bullet+}/A^{\bullet-}B^{\bullet+}$ fluorescence ratio is further enhanced in aerated solutions relative to that in degassed solutions. This is because the $A^{\bullet-}B^{\bullet+}$ exciplex has a longer lifetime and is, therefore, more susceptible to quenching by oxygen, as will be discussed in detail with other kinetic data in a separate publication. Although the spectra were obtained at high concentrations of D, the possibility of contamination by emission from 2:1 complexes was ruled out by comparison with the weaker spectra obtained at a much lower concentration (0.02 M).

For the spectra shown in Figures 2 and 3 and reported in Tables 1 and 4, the peak intensities of the $A^{\bullet-}B^{\bullet+}$ and $A^{\bullet-}D^{\bullet+}$ components (cf. Figure 1) were in the following ratios: 11−15 for **1a**, **1b**, and **2b**. The corresponding ratio for **1c**, which gives the lowest-energy exciplex, was 42. For **2a**, where the exciplex exists in equilibrium with free A*, the ratio was 1.2.

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(6) In one case (**2a**), the two exciplex emissions are comparably weak. The rather complicated kinetic reasons for this exceptional behavior will be discussed in a future paper.

(7) The symbol ν is used for both frequency and wavenumber. It will be clear from the context which one is meant.

(8) The familiar factor of ν^{-3} is applicable when the transition moment is constant. It is replaced by ν^{-1} here because the square of the transition moment of the exciplex itself is proportional to ν^{-2}. (See ref 5c.)

(9) On the basis of electrochemical measurements, B and D were reported to have equal oxidation potentials.[2a] The highly irreversible oxidation of D makes this comparison inconclusive. The near equality of these oxidation potentials has been established, however, from cases (**2a** and **1b**) where the exciplexes equilibrate with uncomplexed A*, with equilibrium constants for the two donors differing only by a factor ~2, which corresponds to a difference of less than 20 mV. In general, equilibration experiments are much more sensitive to differences in redox potentials than other techniques. Details of these experiments will be presented in a separate publication.

(10) In ref 5c, the equivalent of eq 1 is expressed in terms of the free energy for return electron transfer, $\Delta G_{-\text{et}} = -\Delta G$.

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(13) The ground state of $D^{\bullet+}$ is assumed to be of $^2B_2$ symmetry, corresponding to an assignment of the HOMO of D to a π orbital of b_2 symmetry rather than an a_2 π orbital of similar energy. EPR data[13a−c] and a prior ab initio calculation (MP2/6-31G)[13d] indicate that the ground state is $^2B_2$, as does an ab initio calculation on the parent Dewar benzene radical cation.[2b] Our density functional [B3LYP/6-311+G**, QCISD//B3LYP/6-31G*, and B3LYP/6-31G*] and ab initio [MP4(SDQ)/6-31G//HF/3-21G* and MP2/6-31G*] calculations also indicate a b_2 HOMO. As further support of this symmetry assignment, we note that at the B3LYP/6-311+G** level of theory the energy gap between the HOMO and HOMO-1 for D is calculated to be 0.43 eV, in good agreement with results from photoelectron spectroscopy (0.4−0.5 eV).[13e,f] On the basis of semiempirical calculations (CNDO), however, the HOMO and HOMO-1 of D were previously assigned to π orbitals of a_1 and b_2 symmetry, respectively.[13e] This "inverted" order of the π orbitals was attributed to significant $\pi-\sigma$ through-bond interactions in D. We ascribe the difference from our results to the well-known tendency of CNDO to exaggerate through-bond interactions.[13g] A later report[13f] also assigned an "inverted" order to the π orbitals of D on the basis of two qualitative molecular orbital arguments. First, it was argued that the $\pi-\pi$ through-space interaction in D should be significantly less than in the parent molecule—Dewar benzene—which had been securely assigned a "normal" π-orbital ordering because of the larger flap (ϕ bending) angle reported for D (124.5°) versus that for Dewar benzene (117.3°). However, the large flap angle for D, as well as some of its other experimentally derived structural parameters, have recently been questioned.[13h] Our calculations (B3LYP/6-311+G**) predict a flap angle of 116.0°, which is quite similar to that of Dewar benzene. Second, it was expected that replacing the two bridgehead C−H σ orbitals of Dewar benzene with the two $C-CH_3$ σ

orbitals of D would lead to increased $\pi-\sigma$ through-bond interactions in D. Our calculations reveal, however, that the $\pi-\pi$ through-bond interaction of the $a_1-\pi$ orbital of D occurs principally with the bridgehead−bridgehead C−C σ orbital, not the bridgehead $C-CH_3$ σ orbitals, and therefore should be quite similar to that in Dewar benzene. (a) Qin, X.-Z.; Werst, D. W.; Trifunac, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 2026. (b) Arnold, A.; Gerson, F. *J. Am. Chem. Soc.* **1990**, *112*, 2027. (c) Williams, F.; Guo, Q.-X.; Nelsen, S. F. *J. Am. Chem. Soc.* **1990**, *112*, 2028. (d) Salhi-Benachenhou, N.; Eriksson, L. A.; Lunell, S. *Acta Chem. Scand.* **1997**, *51*, 636. (e) Bougeard, D.; Schrader, B.; Bleckmann, P.; Plesser, T. *Liebigs Ann. Chem.* **1974**, 137. (f) Bieri, G.; Heilbronner, E.; Kobayashi, T.; Schmelzer, A.; Goldstein, M. J.; Leight, R. S.; Lipton, M. S. *Helv. Chim. Acta* **1976**, *59*, 2657. (g) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. (h) Brown, A. B.; Kiprof, P.; McKay, S. E.; Beros, I. *Internet J. Chem.* **1998**, *1*, 18.

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(19) The values of λ_s for the D exciplexes may not be as reliable as for the B exciplexes because fixed values of ΔG were used in the fitting. A small difference between the actual value of ΔG and the assumed value would result in an equal, small error in the value of λ_s.

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(21) A factor of ∼0.35 is due to a difference in the values of V^2. An additional factor of ∼0.7, arising from the greater width of the reduced spectrum for the D exciplexes, is required because the normalized spectra should have equal integrals, eqs 2 and 6, rather than equal maximum values.

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