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# Distance Dependence of Singlet and Triplet Charge Recombination Pathways in a Series of Rigid Bichromophoric Systems

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The recombination process of the charge-separated state in a series of rigid donor−bridge−acceptor compounds **1**[*n*] follows two pathways, viz. recombination to the singlet ground state and recombination to the local triplet donor state. The rates of both these processes are shown to depend exponentially on distance, but with a significantly different damping factor. Thus at short distances singlet recombination is dominant, while at longer distances the triplet pathway eventually becomes the major process.

## Introduction

The distance dependence of electron transfer reactions has been studied extensively during the last decade using systems of the type donor−bridge−acceptor, in which a nonconjugated bridge connects the electron donor and acceptor.[1] A major concern in these studies is that the bridge should maintain a strictly defined relative orientation and distance between D and A and that the latter can be varied in well-defined increments. The series of bichromophoric compounds **1**[*n*] (Scheme 1) satisfies these demands to a high extent since not only the distance is fully defined, but at the same time the relative orientation of the dimethoxynaphthalene (DMN) donor, D, and the dicyanonovinyl acceptor, A, is fixed in each member of the series and rather constant across the series. It has been shown that photoinduced charge separation ($k_{cs}$) occurs, following local excitation of the DMN donor, for all members of the series (see Scheme 2).

This has allowed the study of the photoinduced charge separation ($k_{cs}$) as well as the consecutive charge recombination ($k_{cr}$) as a function of the bridge length. The latter may be expressed either in terms of the number of $\sigma$ bonds, *n*, separating D and A or as the center−to−center distance between D and A ($R_c$) in angstroms. In studies on charge recombination within rigidly linked systems published until now, this process was described with a single, distance dependent rate. In the systems **1**[*n*], however, recombination can occur either to the ground state ($k^1_{cr}$) or to a local DMN triplet state ($k^3_{cr}$), a situation that is typical for many other donor−acceptor systems as well.[2−12] We now present a study in which the distance dependence of $k^1_{cr}$ and $k^3_{cr}$ are separately determined for **1**[*n*],

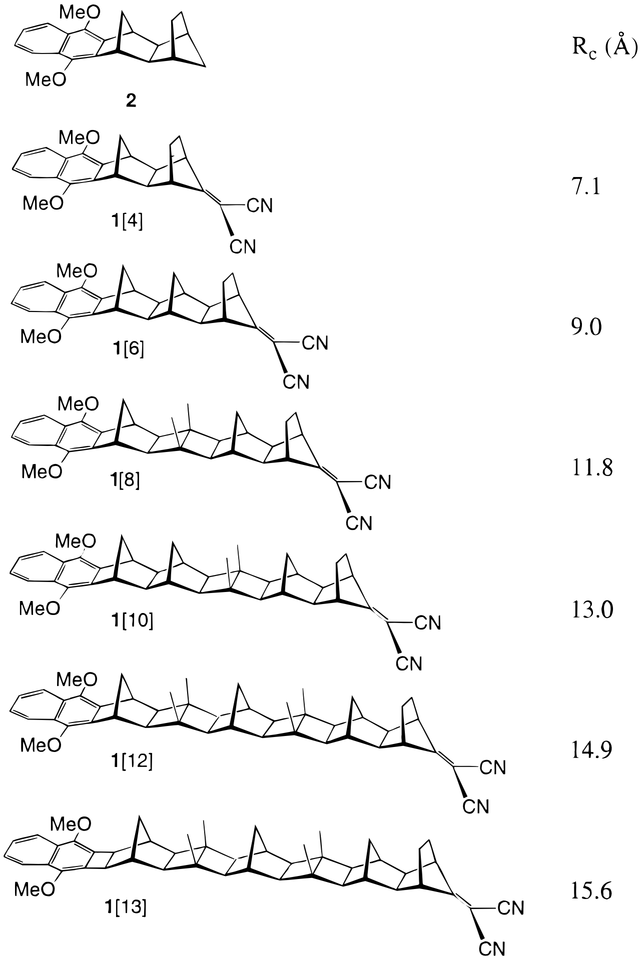
$$k_{et} = \frac{4\pi^2}{h}V^2\text{FCWD} \qquad (1)$$

$$V = V_0\cdot\exp(-\alpha R) \qquad (2)$$

$$k_{et} = k_{0,et}\cdot\exp(-\beta R) \qquad (3)$$

For weak coupling, which appears a reasonable assumption in most members of series **1**[*n*], the rate of electron transfer can be described by eq 1, in which *V* is the electronic coupling between the reactant and product states and FCWD is the Franck Condon weighed density of states. A major problem in interpreting the distance dependence of electron transfer rates is that both *V* and FCWD are in principle distance dependent, and it is not a simple task to separate these factors quantitatively. It has been argued, however, that the distance dependence of the electronic coupling plays a dominant role because this is expected to decrease exponentially with distance (eq 2). When FCWD is assumed to be virtually independent of distance, the

**SCHEME 1: Bichromophoric Compounds 1[*n*] and Donor Model Compound 2, Together with the Center to Center Distance (*R*c) in Angstroms between the Chromophores**



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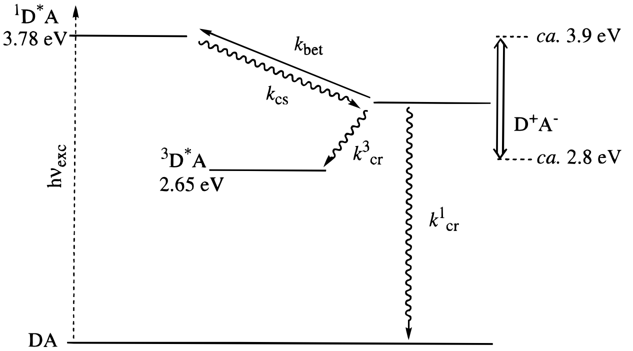
**SCHEME 2: Charge Separation and Recombination Processes in 1[*n*][a]**



[a] Note that the energy of the charge separated state varies as a function of *n* and solvent from slightly above $^1$D*A (*i.e.* for $n = 12$ in saturated hydrocarbon solvents) to about 1 eV below (*i.e.* in highly polar solvents). Under all circumstances the local donor triplet ($^3$D*A) is significantly below the CT state.

rate of electron transfer should thus also decrease exponentially with distance with a damping factor $\beta = 2\alpha$ (eq 3). An exponential distance dependence was indeed found for both $k_{\rm cs}$ and $k_{\rm cr}$ in **1**[*n*].[1a−g,13−17]

As already noted above, however, for $k_{\rm cr}$ the situation is complicated. In fact charge recombination can occur *via* three distinctly different pathways. Thus, as indicated in Scheme 2, under certain conditions the CT state is high enough in energy to allow thermally activated repopulation of the locally excited singlet state. This "back electron transfer" ($k_{\rm bet}$) occurs only for $n \geq 8$ in low-polarity solvents, as revealed by the delayed donor fluorescence emerging from it.[15,16] While conditions can be chosen to avoid a contribution of $k_{\rm bet}$ to $k_{\rm cr}$, still two discrete recombination pathways are always accessible, leading either to the ground state ($k^1_{\rm cr}$) or to the local triplet state of the DMN donor ($k^3_{\rm cr}$), which is always significantly lower in energy than the CT state (see Scheme 2). This implies that the $k_{\rm cr}$ values determined previously are in fact the sum of $k^1_{\rm cr}$ and $k^3_{\rm cr}$ and that the $\beta_{\rm cr}$ values represent a weighed average of that for singlet and triplet recombination ($\beta^1_{\rm cr}$ and $\beta^3_{\rm cr}$). The main purpose of the present study is to separate the singlet and triplet pathways, while no effort has yet been made to separate the influence of electronic coupling and FCWD for either of these pathways.

To separate the rates of the triplet and singlet recombination processes in **1**[*n*], we now determined quantum yields for the formation of $^3$D*A in the compounds **1**[*n*] in benzene and dioxane with transient absorption (TA) spectroscopy. As the charge separation in these compounds is complete in these solvents, except for **1**[12], and $k_{\rm bet}$ is negligible, except for **1**[12] in benzene, the yield of all $^3$D*A must stem from recombination of the CT state. Benzene and 1,4-dioxane were chosen as solvents because the overall recombination rates in these solvents are known from previous studies.[16]

## Results and Discussion

The overall rate of charge recombination in systems **1**[*n*] has been studied quite extensively.[1b−g,15−17] The main technique employed has been time-resolved microwave conductivity (TRMC), which allows direct detection of the decay of the dipolar CT state. In addition, the decay of the weak CT fluorescence emerging from this state has been measured in these cases where it was sufficiently strong. Consistent results for the decay rates were obtained with both techniques as tabulated in Table 1. From these data it is immediately clear that, in contrast to $k_{\rm cs}$,[1a,13] $k_{\rm cr}$ displays a very strong solvent dependence and increases dramatically upon increasing solvent polarity.

**TABLE 1: Rates of Charge Recombination $k_{\rm cr}$ ($\times 10^6$ s$^{-1}$) Obtained Earlier for 1[*n*] in Various Solvents[a]**

| | *trans*-decalin[b] | benzene[b] | di-*n*-butyl ether[c] | 1,4-dioxane[d] |
|---|---|---|---|---|
| **1**[4] | 125 | 1000 | 500 | *d* |
| **1**[6] | 22.2 | 167 | 100 | 2000 |
| **1**[8] | (17.2) | 31.3 | 20 | 400 |
| **1**[10] | (83.3) | 2.78 | 2.94 | 23.3 |
| **1**[12] | (90.9) | (1.35) | *f* | 3.37 |
| **1**[13] | *e* | (1.92) | *f* | 0.95 |

[a] Data in brackets refer to situations in which back electron transfer ($k_{\rm bet}$) to the locally excited state has been shown to contribute significantly. [b] Data obtained by TRMC from ref 16. [c] Data obtained from CT fluorescence from ref 1c. [d] Recombination too fast to be measured. [e] Not measured. [f] No CT emission observed.

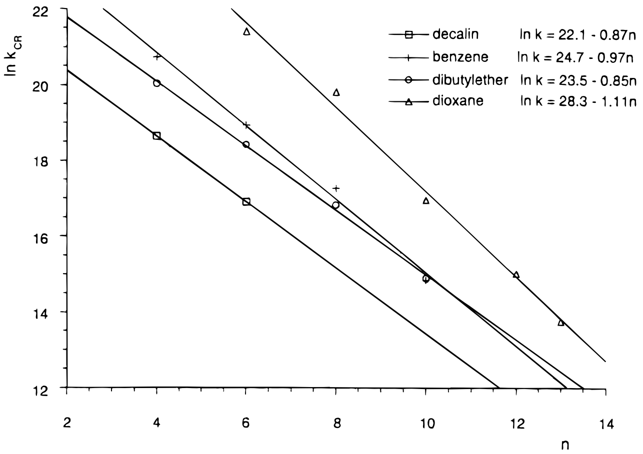


**Figure 1.** Semilogarithmic plot of the recombination rate in the series **1**[*n*] *vs* the number of $\sigma$ bonds (*n*) in the intervening bridge in *trans*-decalin, benzene, di-*n*-butyl ether and 1,4-dioxane.

Qualitatively this can be understood from the decrease of the energy gap separating the CT state from the ground state. Since recombination to the singlet ground state ($k^1_{\rm cr}$) occurs under "inverted region" conditions where the driving force is much larger than the reorganization energy ($-\Delta G^1_{\rm cr} \gg \lambda_{\rm cr}$) this implies that upon decreasing the driving force, the FCWD for this process should increase (see eq 4). It should, however, be noted that under such conditions eq 4 can only give a qualitatively correct picture of this effect. In fact the FCWD is much larger than predicted by eq 4 because nuclear tunneling becomes dominant,[18] as *e.g.* shown by the small temperature dependence of $k_{\rm cr}$ in systems **1**[*n*].[15,17]

The data compiled in Table 1 have been plotted in Figure 1. As noted earlier $k_{\rm cr}$ appears to decrease exponentially with distance, and even though the rates are very strongly solvent dependent, the damping factor $\beta_{\rm cr}$ appears rather solvent independent with an average value of 0.95 ± 0.10 per $\sigma$ bond ($\beta_{\rm cr} = 0.83$ Å$^{-1}$).

$$\mathrm{FCWD} = \frac{1}{\sqrt{4\pi\lambda k_{\rm B}T}} \exp\left[\frac{-(\Delta G + \lambda)^2}{4\lambda k_{\rm B}T}\right] \tag{4}$$

In order to determine the contributions of $k^1_{\rm cr}$ and $k^3_{\rm cr}$ to $k_{\rm cr}$, yields of formation of the $^3$D*A species were now determined from the TA spectrum of the compounds **1**[*n*] in dioxane and benzene. To obtain the exact amounts of triplet, the molar extinction of the $T_1 \rightarrow T_n$ absorption had to be determined. Attempts to obtain this value by complete triplet energy transfer from benzophenone (BP) to donor model **2** did not succeed due

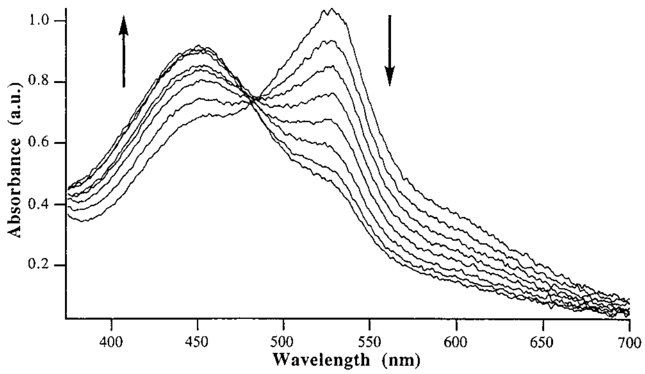


**Figure 2.** Transient absorption spectra of the sample containing benzophenone and an excess of **2** in benzene ($\lambda_{exc} = 355$ nm). Spectra shown were taken with an interval of 200 ns. Note that the full time window is short relative to the triplet lifetimes of both species taken separately.

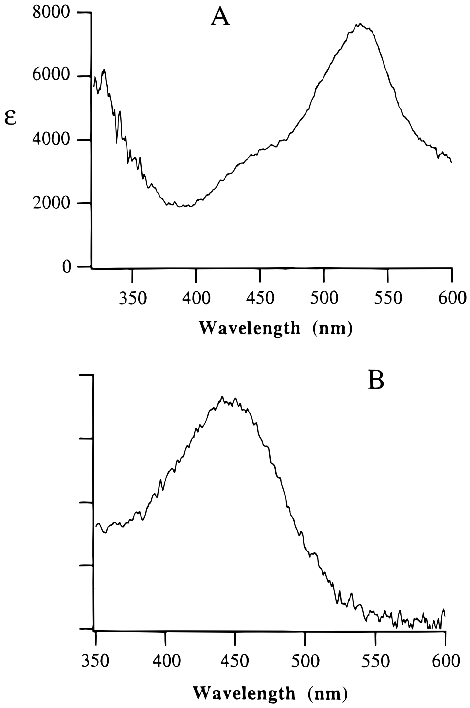


**Figure 3.** $T_1 \rightarrow T_n$ absorption spectra of (A) benzophenone and (B) **2** in benzene.

to incomplete quenching of the triplet of benzophenone, even at high **2** concentration, in a time window over which the decay of that triplet is negligible in the absence of **2**. However, during such a time window the TA spectra (see Figure 2) show an isosbestic point at 483 nm. At this point the molar extinctions of both triplet species have to be equal. From the known spectrum for the $T_1 \rightarrow T_n$ absorption of BP given in Figure 3A ($\epsilon_{max} = 7630$ M$^{-1}$ cm$^{-1}$ at 530 nm)[20,21] the molar extinction at the isosbestic point (5100 M$^{-1}$ cm$^{-1}$) can therefore be determined. The spectrum for the $T_1 \rightarrow T_n$ absorption of **2** was scaled to this value (Figure 3B) which yielded a molar extinction of 7000 M$^{-1}$ cm$^{-1}$ at 450 nm.

From the transient spectra of the compounds **1**[*n*], with $n =$ 4, 6, 8, 10 or 12, the triplet quantum yields were determined (see Experimental Section) and are given in Table 2 together with the lifetimes of the CT state as previously obtained with TRMC.[16] In the 12-bond compound the yield of charge separation is 0.81 in benzene and dioxane, in contrast to the shorter homologues where the charge separation is quantitative. The quantum yield for triplet formation in the donor model **2** is 0.67, so in the 12-bond bichromophore the yield of direct formation of the local triplet from the local singlet excited state amounts to 0.13. After correction is made for this contribution, the rates of recombination from the charge-separated state to the singlet ground state ($k^1_{cr}$) and to the $^3$D*A state ($k^3_{cr}$) were calculated under the assumption that $\Phi^1_{cr} + \Phi^3_{cr} = 1$ (Table 3). For **1**[12] in benzene this assumption is not valid, because repopulation of the local singlet state ($k_{bet}$) occurs, as was discussed previously.[15,16] Therefore the data for **1**[12] in benzene will be omitted from the following analysis.

**TABLE 2: Quantum Yields of Formation of the Local Donor Triplet ($\Phi_T$) Determined with Transient Absorption and Lifetime ($\tau_{CT}$) of the Charge-Separated State (As Determined Earlier with TRMC)[16] in the Compounds 1[*n*] in Benzene and Dioxane**

| | benzene | | 1,4-dioxane | |
|---|---|---|---|---|
| compound | $\Phi_T$ | $\tau_{CT}$ (ns) | $\Phi_T$ | $\tau_{CT}$ (ns) |
| **2** | 0.67[a] | | 0.67[a] | |
| **1**[4] | *b* | 0.8 | *b* | 0.08[c] |
| **1**[6] | 0.01 | 6 | 0.03 | 0.5 |
| **1**[8] | 0.03 | 40 | 0.09 | 2.5 |
| **1**[10] | 0.14 | 410[d] | 0.37 | 43 |
| **1**[12] | 0.37 | 740[d] | 0.64 | 297[d] |

[a] Value from ref 13. [b] Yield too low to be determined. [c] Value extrapolated from TRMC experiments on longer homologues. [d] Values corrected for self-quenching.

**TABLE 3: Rates of Charge Recombination to the Singlet Ground State ($k^1_{cr}$) and to the $^3$D*A State ($k^3_{cr}$) for the Compounds 1[*n*] in Benzene and 1,4-Dioxane**

| | benzene | | 1,4-dioxane | |
|---|---|---|---|---|
| *n* | $k^1_{cr}$ ($\times 10^5$ s$^{-1}$) | $k^3_{cr}$ ($\times 10^5$ s$^{-1}$) | $k^1_{cr}$ ($\times 10^5$ s$^{-1}$) | $k^3_{cr}$ ($\times 10^5$ s$^{-1}$) |
| 4 | 12000[a] | | 125000[a] | |
| 6 | 1650 | 20 | 19400 | 640 |
| 8 | 242 | 8.5 | 3660 | 340 |
| 10 | 21 | 3.4 | 146 | 87.0 |
| 12 | *b* | *b* | 7.3 | 26.4 |

[a] Value calculated from TRMC lifetimes under assumption of $\Phi_T = 0$. [b] Determination prevented by contribution of $k_{bet}$.

From the data in Table 3 it can be seen that both $k^1_{cr}$ and $k^3_{cr}$ increase sharply in dioxane as compared to benzene. More importantly, the data also show that while $k^1_{cr}$ exceeds $k^3_{cr}$ by several orders of magnitude at shorter charge separation distances, it becomes comparable or even smaller for larger separation distances. Thus the contribution of the triplet pathway ($\Phi_T$) increases strongly with the bridge length (see Table 2). Also $\Phi_T$ is always somewhat larger in the slightly more polar dioxane than in benzene. The latter appears in contradiction with polarity dependence results reported for a related rigid D−bridge−A system,[12] but in that case the polarity was only changed within a series of saturated hydrocarbon solvents. Most importantly the results now obtained show that $k^1_{cr}$ and $k^3_{cr}$ strongly differ in distance dependence. Logarithmic plots versus the number of $\sigma$ bonds (*n*) separating donor and acceptor are shown in Figure 4. Their near linearity[22] implies that for both $k^1_{cr}$ and $k^3_{cr}$ the distance dependence is close to exponential but with a significantly smaller damping constant for $k^3_{cr}$.

Because for most systems $k^1_{cr} \gg k^3_{cr}$, the overall damping factors (see below) are close to those now found for $k^1_{cr}$, *i.e.* $\beta^1_{cr} = 1.04$ per bond (0.91 Å$^{-1}$) in benzene and $\beta^1_{cr} = 1.22$ per bond (1.06 Å$^{-1}$) in dioxane. The damping factor for triplet recombination is dramatically smaller, viz. $\beta^3_{cr} = 0.45$ per bond (0.38 Å$^{-1}$) and 0.56 per bond (0.48 Å$^{-1}$) in benzene and dioxane, respectively.

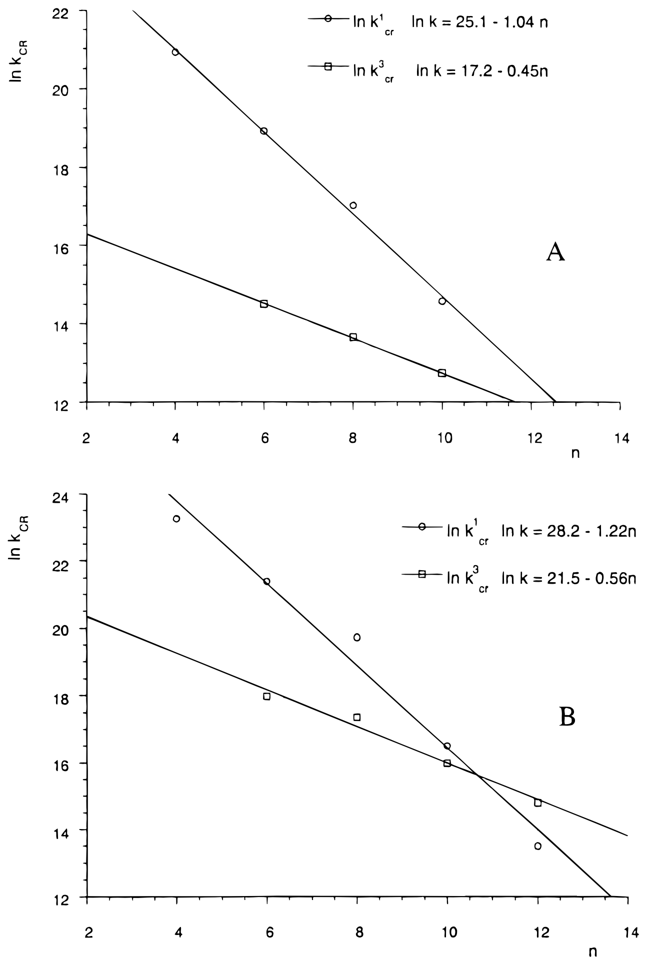


**Figure 4.** Plots of the logarithms of the recombination rates from the CT state to the ground state ($k^1_{cr}$) and to the local triplet state ($k^3_{cr}$) *vs* the number of sigma bonds in the intervening bridge ($n$) in the solvents benzene (A) and 1,4-dioxane (B). N.B.: the data point for $n = 12$ in benzene is omitted from the fit.

It should be noted that in Scheme 2 the spin character of the CT state is intentionally omitted. It is clear, however, that the charge separation process from $^1D^*$ initially prepares it with pure singlet character ($^1(D^+A^-)$). Thus an important question is the rate at which the CT state is going to acquire sufficient triplet character to produce $^3(D^*A)$ upon charge recombination. For short bridges this is apparently not a very competitive process, which can be attributed to at least two factors. First of all the rate of singlet recombination ($k^1_{cr}$) is high, but furthermore it should be noted that for short bridges the exchange interaction is expected to be quite large[9, 10, 23] making $^1(D^+A^-)$ and $^3(D^+A^-)$ distinct species, and the intersystem crossing between these ($k_{isc}$) requires spin−orbit coupling and may be quite slow in comparison to the singlet recombination.

For longer bridges, however, not only does the rate of the latter process decrease exponentially with increasing bridge length, but so does the exchange interaction, thereby leading to a strong attenuation of the singlet/triplet energy gap in the CT state. Under such conditions it is mainly hyperfine interaction which drives the intersystem crossing and allows the CT state to oscillate between singlet and triplet character ($^1(D^+A^-) \leftrightarrow {}^3(D^+A^-)$) with a frequency ($\omega_{isc}$) that may actually exceed the rate of singlet recombination. For $\omega_{isc} \gg k^1_{cr}$ the ratio of the singlet and triplet recombination yields closely reflects, apart from spin statistics, the ratio of the FCWD·$V^2$ factors for $^1(D^+A^-) \rightarrow DA$ and $^3(D^+A^-) \rightarrow {}^3DA$. Since the energy gap in the latter process is significantly smaller (in view of the large energy gap involved, charge recombination to the ground state in fact always remains deep in the inverted region), it is not unlikely that triplet recombination becomes the dominant pathway at larger bridge length just because it has a more favorable FCWD and as is actually observed here for **1**[12] in dioxane.

Thus the fact that $k^3_{cr}$ exceeds $k^1_{cr}$ at longer distances can qualitatively be explained from the increased triplet character of the CT state at larger distances and the more favorable FCWD for the triplet recombination pathway.

## Concluding Remarks

The electronic coupling ($V$) is often assumed to be the most important factor responsible for the distance dependence of electron transfer rates, and differences in "damping factor" between systems involving different media interposed between D and A are generally discussed in terms of structural effects of these media on $V$. The main result of the present study is that charge recombination pathways to the ground state and the $^3D^*A$ state in the bichromophoric compounds **1**[$n$] have very different damping factors. In both solvents studied, the rate of charge recombination to the $^3D^*A$ state is much less distance dependent than that for charge recombination to the ground state, and as a result the contribution of the triplet pathway tends to become dominant for larger separation distances. This implies that the overall distance dependence of charge recombination cannot be described adequately by a single set of distance dependent $V$ and FCWD factors but that in fact the distance dependence of two such sets should be taken into consideration as well as the distance dependence of the rate with which the CT state, prepared with singlet character, acquires triplet character.

## Experimental Section

Transient absorption spectra were obtained using a Lumonics EX700 XeCl excimer laser (308 nm) as the excitation source and a 450 W high-pressure Xe-arc in right angle geometry as probe light, pulsed with a Müller Elektronik MSP05 pulser to enhance its brightness during the observation time gate of the detector. The probe light, after passing through the sample cell, was collected by an optical fiber and fed into a Jarrel-Ash monospec 27 model 1234 spectrograph in which the light was dispersed by a grating (150 grooves/mm) onto an MCP intensified diode array detector (EG&G 1421G, 25 mm, 1024 diodes). With this setup a spectral range of about 600 nm was covered with a bandwidth of 7 nm (250 $\mu$m slit). The detector was gated at 100 ns by an EG&G FPG05 fast pulse generator, and the start of the time window was delayed in 100 ns increments relative to the laser pulse to obtain subsequent spectra across the total decay time of the transients studied. The timing of the laser, the probe light and the optical multichannel analyzer (OMA) gate pulse were controlled by an EG&G OMA III Model 1460 console with a 1303 pulse delay generator and a digital delay generator (EG&G 9650). Spectra were averaged over 25 pulses for each delay to improve the signal to noise ratio.

To excite benzophenone in the triplet energy transfer experiment, the third harmonic of a Spectra Physics Quanta Ray GCR-3 Nd-YAG (355 nm) was used instead of the excimer laser. The sample was prepared by dissolving benzophenone in benzene to a concentration yielding $A^{355}_{1cm} = 1$ and adding of an excess of **2**. The sample was degassed by several freeze−pump−thaw cycles.

The samples for the transient spectra of the compounds **1**[$n$] were prepared by dissolving the respective compound in benzene (Merck Uvasol) or 1,4-dioxane (Merck Uvasol) to a concentra-

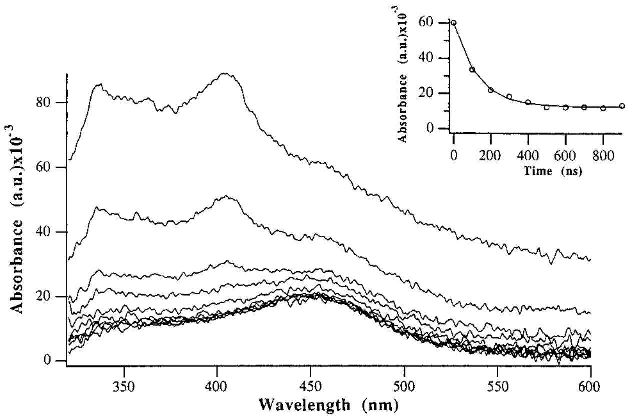


**Figure 5.** Transient absorption spectra of **1**[10] in benzene obtained with a gate width of 100 ns. The spectrum with the highest absorption values is taken just after the maximum of the laser pulse. Subsequent spectra were taken with incremental delays of 100 ns with respect to the laser pulse. The absorption of the DMN radical cation (strongest feature at 405 nm) decreases and a stable (over the time window shown) DMN triplet absorption centered around 450 nm remains. The inset shows the decay of the absorption at 450 nm.

tion yielding $A^{308}_{1\text{cm}} = 1-1.5$ and degassed by several freeze–pump–thaw cycles. The solutions were excited at 308 nm using the excimer laser. The absorbance of the dimethoxynaphthalene triplet was determined from the first spectrum in which the dimethoxynaphthalene radical cation absorption at 408 nm was absent (see Figure 5). At that delay time a dimethoxynaphthalene triplet absorption remains, which is constant in the time range used (${}^3\tau(\mathbf{2}) \approx 9\ \mu$s). After each experiment the laser power was determined by repeating the experiment with a benzophenone sample with an absorbance at 308 nm which equals the absorbance of the preceding sample. Quantum yields were determined by eq 5.

$$\Phi_{\text{isc}} = \frac{(A_{3\text{DMN}*})/\epsilon_{3\text{DMN}*}}{(A_{3\text{BP}*})/\epsilon_{3\text{BP}*}} \frac{A^{308}_{\text{BP}}}{A^{308}_{1[n]}} \qquad (5)$$

In this equation $A$ are the absorbances of the $T_1 \rightarrow T_n$ absorption of 1,4-dimethoxynaphthalene (DMN) at 450 nm and benzophenone (BP) at 530 nm respectively, $\epsilon$ are the molar extinction coefficients of these absorption bands ($\epsilon_{\text{max}}$(BP) = 7630 M$^{-1}$ cm$^{-1}$ at 530 nm[20,21] and $\epsilon_{\text{max}}$(DMN) = 7000 M$^{-1}$ cm$^{-1}$ at 450 nm), and A$^{308}$ are the absorbances at the excitation wavelength for both sample **1**[*n*] and reference BP.

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