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Solvent Effects on Photoinduced Electron Transfer in Rigid, Bichromophoric Systems

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Abstract: Intramolecular, photoinduced electron transfer is found to occur between a methoxybenzene donor moiety and electron-acceptor moieties separated from it by two different, paraffinic spacers, which maintain a minimum donor-acceptor separation of 3.8 or 5.8 Å, respectively. With a 1,1-dicyanoethylene acceptor moiety the electron transfer occurs extremely fast ($>10^{11}$ s⁻¹) irrespective of solvent polarity or donor-acceptor distance. With the weaker 1-carboalkoxyethylene acceptor moiety, however, long-range electron transfer occurs much more slowly even in solvents which are sufficiently polar to make it at least as exoergic as the fast electron transfer occurring with the stronger acceptor in apolar media. Solvent reorganization is concluded to provide a significant barrier for long-range electron transfer from the donor to the weaker but not to the stronger acceptor.

One-electron transfer between ground-state or electronically excited electron-donor (D) and -acceptor (A) species constitutes a topic of continuing interest. Many rate influencing factors have been identified or proposed.¹⁻⁸ These include the distance and relative orientation of D and A, the Gibbs free-energy change (ΔG) between the initial (DA) and final state (D⁺A⁻), as well as so-called reorganization factors related to geometrical and structural changes of the D and A species and to concomitant changes in the orientation/polarization of the solvent medium accompanying electron transfer.

It has been stipulated⁹⁻¹⁷ that rigid bichromophoric DA mol-

ecules, in which the separation and relative orientation of D and A chromophores are fixed by a saturated spacer, may provide discriminative information regarding the relative importance and interdependence of the factors influencing electron-transfer rates.

As part of our studies^{9,10} in this field, we recently reported¹⁷ the remarkable long-range, photoinduced electron transfer in compounds **1a** and **1b** (cf. Figure 1). Upon excitation of the aromatic donor chromophore, electron transfer to the 1,1-dicyanoethylene acceptor chromophore in **1b** occurs at a rate ($>10^{11}$ s⁻¹) exceeding experimental detection limits irrespective of solvent polarity. In the geometrically fully equivalent compound **1a**, which contains the less powerful carboethoxy ethylene acceptor chromophore, no photoinduced electron transfer could be detected in apolar media, but in the polar solvents acetonitrile and methanol electron transfer occurs with a rate of 6.6×10^7 and 11×10^7 s⁻¹, respectively.

Qualitatively these results satisfy the general trend for increased rate of electron transfer upon increasing stabilization of the final state (i.e., D⁺-A⁻) with respect to the initial state (i.e., ¹D*-A). Quantitatively, however, the situation seems more complicated. From previous studies^{9,18} the electron affinities of the acceptors incorporated in **1a** and **1b** are known to differ by 0.45 ± 0.05 eV. In view of the very large dipole moment inherent to the D⁺-A⁻ state of rigid bichromophoric molecules like **1a** and **1b**, it seemed likely¹⁹ that transfer from an apolar solvent like *n*-hexane to a polar solvent like acetonitrile stabilizes this state by more than 0.5 eV. This would make electron transfer for **1a** in acetonitrile more exothermic but, nevertheless, much slower than for **1b** in

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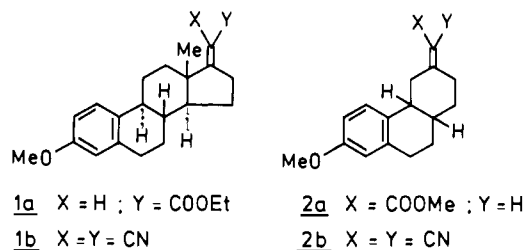


Figure 1. Bichromophoric electron donor-acceptor systems (**1a**, **1b**, **2a**, **2b**) and donor model compound (**3**), discussed in this study.

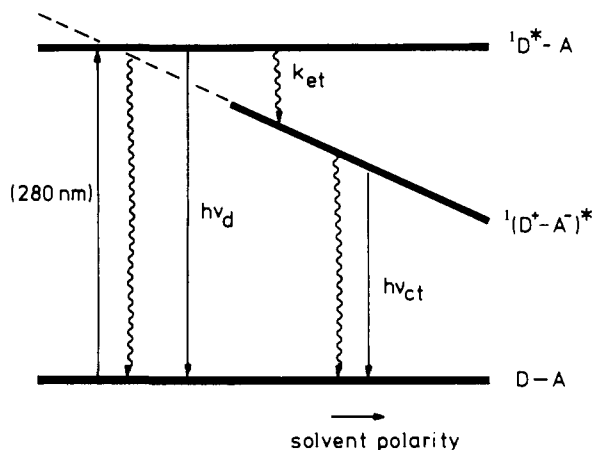


Figure 2. Generalized energy level diagram for bichromophoric donor-acceptor systems **1** and **2**. Upon decreasing solvent polarity the separation of the ground state ($D-A$) and the lowest locally excited state (${}^1D^*-A$) remains essentially unchanged while that between the ground state and the CT excited state (${}^1(D^+-A^-)^*$) increases resulting in an eventual level crossing at low polarity. (No differentiation between Franck-Condon states and relaxed states is made in this highly simplified sketch! Refer to Figure 5 for a more complete diagram.)

n-hexane. The ambiguity^{14,19} involved in calculation of the solvent stabilization of the D^+-A^- state of molecules like **1a** and **1b**, however, precluded a quantitative confirmation of this interesting phenomenon.

In the present communication the behavior of **1a** and **1b** is compared with that of **2a** and **2b** (cf. Figure 1), which contain comparable D/A pairs but held at a shorter distance. In contrast to **1a** and **1b**, the molecules **2a** and **2b** show charge-transfer (CT) fluorescence ($D^+-A^- \rightarrow D-A + h\nu_{ct}$) in a variety of solvents. The solvatochromism of this fluorescence provides *direct* information regarding the stabilization of the emissive D^+-A^- state as a function of solvent polarity for **2a** and **2b** and *mutatis mutandis* also for **1a** and **1b**.

Results and Discussion

Determination of Electron-Transfer Rates and Excited-State Solvation Energies via Emission Spectroscopy. Figure 2 provides a generalized energy-level diagram for the lowest singlet states of D-A systems like **1** and **2**. It should be emphasized that both **1** and **2** may be considered²⁰ to be rigid on the time scale of the photophysical events discussed. Any substantial change of the intramolecular D/A distance or orientation requires conversion of one or more of the interconnecting saturated rings between two chair conformations or from the preferred chair conformation into a boat-like conformation. The rate of such a process does not

Table I. Donor Fluorescence and Charge-Transfer Fluorescence Maxima ($\bar{\nu}_d$ and $\bar{\nu}_{ct} \times 10^{-3}, \text{cm}^{-1}$) and Corresponding Quantum Yields (ϕ_d, ϕ_{ct}) Observed for **1a** and **1b**^a

solvent Δf	1a		1b	
	$\bar{\nu}_d$	ϕ_d	$\bar{\nu}_{ct}$	ϕ_{ct}
<i>n</i> -hexane (0.092)	31.25	0.26		
diethyl ether (0.251)	31.25	0.26	23.53 ^b	5×10^{-3}
acetonitrile (0.392)	31.25	0.19		
methanol (0.393)	31.25	0.16		

^a see ref 17. ^b Fluorescence lifetime $\tau_{ct} = 19$ ns.

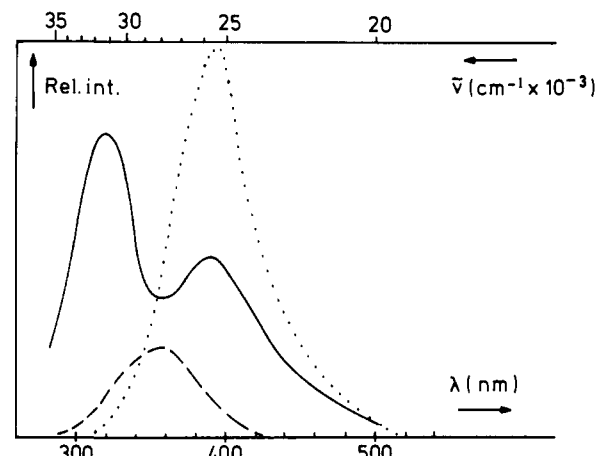


Figure 3. Fluorescence spectrum (solid line) of **2a** in 2-methyltetrahydrofuran, showing the simultaneous appearance (cf. Table II) of donor fluorescence ($\bar{\nu}_d = 31.250 \text{ cm}^{-1}$) and charge-transfer fluorescence ($\bar{\nu}_{ct} = 25.770 \text{ cm}^{-1}$). For comparison the fluorescence spectrum of **2b**, which displays charge-transfer fluorescence only, is shown in the solvents *n*-hexane (dashed line) and di-*n*-butyl ether (dotted line).

exceed $5 \times 10^6 \text{ s}^{-1}$ at 20 °C even for the most flexible system studied (i.e., **2**) as evidenced by recent investigations^{20a} on the photochemical cycloaddition between an aromatic group and a double bond, connected by this skeleton.

As indicated in Figure 2 the lowest locally excited singlet state in **1** and **2** is provided by the aromatic donor chromophore. The 1L_b absorption of this chromophore is found at λ_{max} 287 nm in **1** and **2** as well as in the model system **3**. The molar extinction is equal for **1a**, **1b**, **2a**, and **3** ($\epsilon_{\text{max}} 2000 \text{ L mol}^{-1} \text{ cm}^{-1}$) but significantly enhanced⁹ in **2b** ($\epsilon_{\text{max}} 4000 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **2b**) as a result of through-bond interaction^{9,10,18} with the acceptor chromophore. The latter shows no absorption above 250 nm. Excitation of the donor chromophore in **3** leads to rather intense fluorescence. The lifetime, quantum yield, and position of this fluorescence are unchanged by solvent²¹ polarity ($\tau_3 = 5.6$ ns, $\phi_3 = 0.26$, $\nu_3 = 31.250 \text{ cm}^{-1}$).

As evident from the data collected in Tables I and II, extensive or even complete quenching of the donor fluorescence occurs in **1a/1b** and in **2a/2b**. Intramolecular electron transfer is assumed to provide the additional decay channel responsible for this quenching. The rate constant of this process (k_{et}) may then be expressed^{15,17} in terms of the donor fluorescence quantum yield of **3** (ϕ_3) and the bichromophoric system under study (ϕ_d) via:

$$k_{et} = (\phi_3 - \phi_d) / \tau_3 \phi_d \quad (1)$$

The k_{et} values thus calculated are compiled in Table III.

For **2b** quenching of the donor, fluorescence is virtually complete²² ($\phi_d < 5 \times 10^{-4}$) in all solvents (cf. Table II) from which $k_{et} > 10^{11} \text{ s}^{-1}$ is calculated. The occurrence of intramolecular electron transfer as a quenching mechanism in **2b** is unequivocally testified⁹ by the appearance of a weak long-wavelength fluorescence attributable to radiative deactivation of the charge-transfer state populated upon electron transfer (see Figure 3).

(21) Polyhalogenated solvents strongly quench the fluorescence of **3**.

(22) The limit of detection was conservatively taken as $\phi_d \leq 5 \times 10^{-4}$, but in most cases it is probably $\leq 10^{-4}$.

Table II. Donor Fluorescence, Charge-Transfer Fluorescence Maxima ($\bar{\nu}_d$ and $\bar{\nu}_{ct} \times 10^{-3}$, cm^{-1}), and Corresponding Quantum Yields (ϕ_d , ϕ_{ct}) Observed for **2a** and **2b**, As Well As $\bar{\nu}_d$ and ϕ_d Values for the Reference System **3**

solvent (Δf)	2a				2b		3	
	$\bar{\nu}_d$	ϕ_d	$\bar{\nu}_{ct}$	ϕ_{ct}	$\bar{\nu}_{ct}$	ϕ_{ct}	$\bar{\nu}_d$	ϕ_d
<i>n</i> -hexane (0.092)	31.25	1.7×10^{-2}			27.78	0.4×10^{-3}	31.25	0.26
di- <i>n</i> -butyl ether (0.194)	31.25	<i>a</i>			25.44	2.2×10^{-3}	31.25	0.26
diethyl ether (0.251)	31.25	<i>a</i>			23.53	4.9×10^{-3}	31.25	0.26
2-methyltetrahydrofuran (0.305)	31.25	$(5.5 \times 10^{-4})^c$	25.77	$(10^{-3})^c$	21.74	20×10^{-3}	31.25	0.26
1,2-dichloroethane (0.326)			24.15	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>
acetonitrile (0.392)			22.72	<i>a</i>	18.69	0.1×10^{-3}	31.25	0.26

^aNot determined. ^bStrongly quenched in polyhalogenated solvents. ^cEstimated by deconvolution of the overlapping emission bands (see Figure 3).

Table III. Rate Constants for Photoinduced Intramolecular Electron Transfer (k_{et} in s^{-1}) in Bichromophoric Compounds As Calculated in Solvents of Various Polarity According to Eq 1

solvent	compound			
	1a	2a	1b	2b
<i>n</i> -hexane	$<2 \times 10^7$	2.6×10^9	$>10^{11}$	$>10^{11}$
diethyl ether	$<2 \times 10^7$	<i>a</i>	$>10^{11}$	$>10^{11}$
2-methyltetrahydrofuran	<i>a</i>	8.4×10^{10}	<i>a</i>	$>10^{11}$
acetonitrile	6.6×10^7	$>10^{11}$	$>10^{11}$	$>10^{11}$
methanol	11×10^7	<i>a</i>	$>10^{11}$	<i>a</i>

^aNot determined.

The position ($\bar{\nu}_{ct}$) of this fluorescence varies strongly with solvent polarity. This obviously results from the large dipole moment (μ_{ct}) of the $D^+ - A^-$ state. The solvation (free) energy (E_{solv}) of this state in a solvent with dielectric constant ϵ can be expressed²³ by:

$$E_{\text{solv}} = \frac{-\mu_{ct}^2}{\rho^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) = -\mu_{ct}^2 f / \rho^3 \quad (2)$$

neglecting dispersion contributions. In (2) ρ denotes the radius of the solvent cavity surrounding the molecule. If this cavity has a pronounced ellipsoidal shape, ρ is usually taken to equal 40% of its long axis.

The solvation energy can be factorized in two parts.²⁴ The first (E_p) describes the effect of electronic polarization of the solvent by the dipole of the solute and is given by (3) in which n denotes the optical refractive index of the solvent. The second describes the effect resulting from reorganization of the solvent dipoles around the solute, the so-called orientation polarization (E_{op}) and is given by (4):

$$E_p = \frac{-\mu_{ct}^2}{\rho^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) = -\mu_{ct}^2 f' / \rho^3 \quad (3)$$

$$E_{op} = -\mu_{ct}^2 (f - f') / \rho^3 \quad (4)$$

During fluorescence the electronic polarization of the solvent is lost but the orientation polarization is retained, thereby destabilizing the Franck-Condon ground state for CT fluorescence with E_{op} if the dipole moment of the ground state is negligible relative to that of the CT state. The overall solvent effect on the position of the CT fluorescence may then be expressed²⁵ by (5) in which $\bar{\nu}_{ct}(0)$ denotes the gas-phase value of $\bar{\nu}_{ct}$ and Δf the solvent polarity parameter given by $\Delta f = f - 1/2f'$.

$$\bar{\nu}_{ct} = \bar{\nu}_{ct}(0) - 2\mu_{ct}^2 \Delta f / \rho^3 hc \quad (5)$$

Formula 5 has been used successfully to correlate^{10,25} solvent polarity with the solvatochromism of CT-type fluorescences. Its applicability to the present system is testified by the excellent correlation (6) obtained for **2b** (see Figure 4):

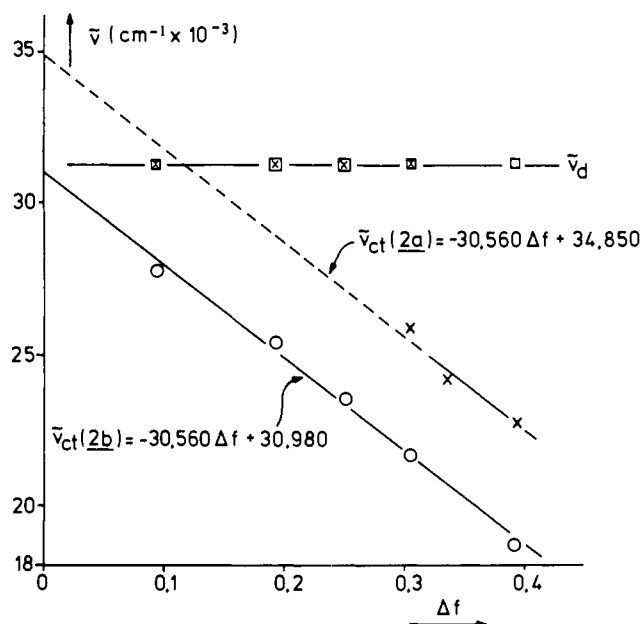
$$\bar{\nu}_{ct}(\mathbf{2b}) = 30980 - 30560 \Delta f \text{ (cm}^{-1}\text{)} \quad (\text{corr coeff } r = 0.995) \quad (6)$$

According to (5) the slope of (6) should correspond to $2\mu_{ct}^2 / \rho^3 hc$.

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**Figure 4.** Fluorescence maxima of compounds **2a** (x), **2b** (o) and the reference compound **3** (□) as a function of the solvent polarity parameter Δf .

In the theoretical derivation of (5), however, μ_{ct} is assumed²³ to be a point-dipole at the center of a spherical cavity, and therefore the slope found for an actual molecule can only be expected to yield an effective value of the μ_{ct}^2 / ρ^3 ratio. Using the reasonable value $\rho(\mathbf{2b}) = 5.6 \text{ \AA}$ (measured^{24,25} as 40% of the long axis of the ellipsoidal cavity in which the molecule fits), an effective value $\mu_{ct}(\mathbf{2b}) = 23 \text{ D}$ is calculated by combination of (5) and (6). This corresponds to a charge separation of 4.8 \AA which lies between the shortest atom-to-atom distance (3.8 \AA) and the center-to-center distance (5.8 \AA) of the donor and acceptor chromophores.

The behavior of **2a** is somewhat more complex than that of **2b**. In apolar solvents only fluorescence attributable to the donor chromophore is observed. In these solvents the occurrence of electron transfer can only be inferred from the strongly diminished value of ϕ_d as compared to that of the reference system **3** (see Table II). While the CT state of **2a** thus appears to be nonemissive in apolar solvents, a typical CT fluorescence ($\bar{\nu}_{ct}$) appears in several more polar solvents (see Table II and Figure 3). If the solvent dependence of $\bar{\nu}_{ct}$ for **2a** is assumed to parallel that of **2b**, the dashed line in Figure 4 is obtained which obeys the equation:

$$\bar{\nu}_{ct}(\mathbf{2a}) = 34850 - 30560 \Delta f \text{ (cm}^{-1}\text{)} \quad (7)$$

The extrapolation in Figure 4 suggests that, whereas electron transfer in **2b** is nearly thermoneutral in the gas phase, it requires substantial solvent stabilization for **2a** where electron transfer becomes thermodynamically feasible at $\Delta f > 0.1$. The $\bar{\nu}_{ct}(0)$ values of **2a** and **2b** differ by 3870 cm^{-1} (0.48 eV) which corresponds to the difference in electron affinity between the acceptor systems estimated earlier^{10,18} ($0.45 \pm 0.05 \text{ eV}$). As reported earlier,¹⁷ no CT fluorescence is observed for **1a**, while **1b** shows weak CT fluorescence in diethyl ether only (cf. Table I) at the same frequency where the CT fluorescence of **2b** (cf. Table II) occurs.

Analysis of the Electron-Transfer Rates. The data presented above allow an interesting discrimination of various factors influencing k_{et} . This is especially so because of the rigidity of the present bichromophoric systems, which allows individual variation of the parameters: donor-acceptor distance (i.e., **1** \rightarrow **2**), acceptor electron affinity (i.e., **1a** \rightarrow **1b** and **2a** \rightarrow **2b**), and solvent polarity.

Although the extremely fast electron transfer in **1b** and **2b** makes it impossible to detect any effect of the different donor-acceptor distances in these compounds, such an effect is clearly discernible upon comparison of **1a** and **2a**. A roughly exponential decrease of k_{et} with the donor-acceptor separation (r_{da}) has been inferred from experiments in solid matrix⁸ as well as in organized monolayer assemblies.^{26,27} The closest atom-to-atom distance of the D and A chromophores amounts to 5.8 Å in **1a** and 3.8 Å in **2a**. The shorter distance in **2a** therefore undoubtedly constitutes the main cause for the much larger k_{et} values in **2a** as compared to **1a** under identical solvent conditions (cf. Table III).

The change in Gibbs free energy (ΔG) is a crucial parameter in all discussions¹⁻⁸ concerning electron-transfer rates. Comparison of the k_{et} values (Table III) calculated for **1a** or **2a** with those for **1b** or **2b** clearly shows that k_{et} is dramatically enhanced if ΔG is made more negative by about 0.48 eV (i.e., the difference in electron affinity between the two acceptor systems employed) at constant donor-acceptor orientation and at constant medium polarity.

As indicated by the strong solvatochromism of $\tilde{\nu}_{ct}$, stabilization of the D^+-A^- state and thereby a more negative ΔG can also be achieved by increasing the solvent polarity. Qualitatively the k_{et} values for **1a** and **2a** (Table III) demonstrate the expected increase of k_{et} with solvent polarity. A most interesting effect is, however, found upon closer analysis of the data. As discussed above the solvent stabilization of the D^+-A^- state (E_{solv}) is given by (2) while the solvent shift of $\tilde{\nu}_{ct}$ for **2b** is given by (6) from which the effective value $2\mu_{ct}^2/\rho^3hc = 30560 \text{ cm}^{-1}$ is derived by application of (5). Substitution of this value in (2) gives:

$$E_{solv}(2) = -1.89 \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) = -1.89f \text{ (eV)} \quad (8)$$

The lack of CT fluorescence for **1a** and **1b** (except for **1b** in diethyl ether; see Table I) prohibits direct experimental determination of the effective μ^2/ρ^3 ratio for these molecules. The observations made for **2** suggest that a reasonable estimate of this ratio for **1** may be achieved by assuming the charge-separation distance to equal the average of the center-to-center (7.7 Å) and closest atom-to-atom (5.8 Å) distances of the D and A chromophores and by taking $\rho = 6.4 \text{ Å}$ which corresponds to 40% of the long axis of an ellipsoidal cavity in which **1** fits. Substitution of these numbers in (2) yields:

$$E_{solv}(1) \approx -2.48f \text{ (eV)} \quad (9)$$

Application of (8) and (9) for *n*-hexane ($\epsilon = 1.88$) and acetonitrile ($\epsilon = 37.50$) reveals that E_{solv} is more negative in the latter solvent by 0.56 eV for **2** and 0.73 eV for **1**. This implies that ΔG is more negative for **1a** or **2a** in acetonitrile than for **1b** or **2b** in *n*-hexane since the difference in solvation energy overcompensates the difference between the electron affinities of the two acceptor systems.

For both **2a** in acetonitrile and **2b** in *n*-hexane k_{et} exceeds the experimental detection limit, which prohibits meaningful comparison. For **1b**, however, k_{et} in *n*-hexane exceeds that of **1a** in polar solvents by several orders of magnitude notwithstanding the equally or even more negative ΔG calculated for latter!

In a recent review⁷ reorganization factors were called "the crux of the electron-transfer problem...". We propose that solvent reorientation effects in particular are responsible for the relatively slow electron transfer in **1a** even in polar solvents. The present systems **1a/1b** provide a unique opportunity to reveal these effects

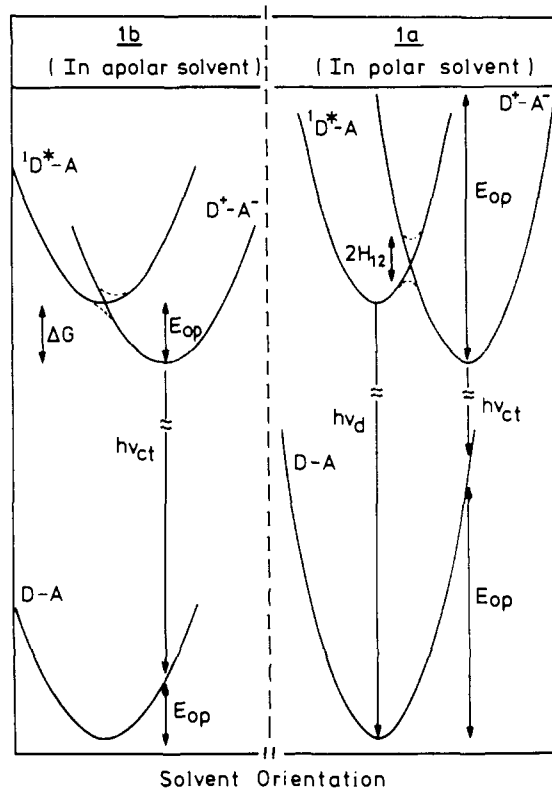


Figure 5. Schematic plot of the potential energy of the D-A, ${}^1D^*-A$, and D^+-A^- configurations of rigid bichromophoric systems **1a** and **1b** as a function of solvent reorientation. The situation sketched refers to low solvent polarity for **1b** and high solvent polarity for **1a** leading to isoergonic electron transfer conditions ($\Delta G(1a) = \Delta G(1b)$).

since manipulation of solvent polarity allows the comparison of isoergonic ($\Delta G(1a) = \Delta G(1b)$) electron transfer from a single donor to two structurally related acceptors of widely different electron affinity but held rigidly at the same orientation and separation to that donor.

The electron transfer in **1b** is nearly thermoneutral in the gas phase and slightly exothermic in nondipolar solvents where $E_{solv} = E_p$. For **1a** exothermicity can only be achieved by virtue of the large E_{solv} values provided by the orientation polarization (E_{op}) of dipolar solvents. The latter requires dipole rotations and therefore cannot change during the transformation of the system from the initial electronic configuration (${}^1D^*-A$) to the final electronic configuration (D^+-A^-) which is thought¹⁻⁸ to be a Franck-Condon-type process. Figure 5 gives a schematic representation of the energy of the D-A, ${}^1D^*-A$, and D^+-A^- electronic configurations of **1a** and **1b** as a function of the orientation of the solvent molecules around these systems. For **1b** the situation depicted corresponds to that in a solvent of low polarity providing a small amount of orientation polarization (E_{op}), while for **1a** the solvent polarity is increased to make electron transfer isoergonic with that in **1b** ($\Delta G(1a) = \Delta G(1b)$).

Although Figure 5, representing only a single section through the multidimensional potential energy surfaces, is much too simplified to allow quantitative conclusions, it serves to rationalize the different rates of electron transfer in **1a** and **1b** under isoergonic conditions. Since the electron jump occurs at the intersection of the ${}^1D^*-A$ and D^+-A^- potential energy surfaces, this requires a substantial amount of thermal activation to reorganize the solvent for **1a** but not for **1b**. This difference, however, is bound to disappear if the electronic coupling matrix element $H_{12} = \langle \Psi_{D^*A} | H | \Psi_{D^+A^-} \rangle$, which leads to a level splitting^{1-4,7} of $2H_{12}$ at the intersection (cf. Figure 5), becomes larger than the barrier separating the zero level of the ${}^1D^*-A$ state from the intersection. The latter situation probably prevails in systems (including **2**) where the donor-acceptor separation is small. In conclusion, medium (e.g., solvent) effects are of vital importance in long-range

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electron transfer where H_{12} is very small. Under these conditions electron transfer is slowed down^{28,29} by medium inertia for systems (e.g., **1a**) that require medium reorganization to make the process exothermic, but not for systems (e.g., **1b**) that possess sufficient "intrinsic" driving force to make electron transfer thermodynamically feasible without medium reorganization. In view of the present results as well as those obtained theoretically and experimentally by others,^{1-8,12} it may thus be concluded that rapid long-range electron transfer requires a situation where the overall exothermicity ($-\Delta G$) at least equals the total reorganization energy. Recently extensive studies by Miller et al.^{8,11,12} on long-range electron transfer between radical anions and neutral acceptors not only provided convincing evidence for the correctness of this conclusion but, furthermore, gave a clear indication that, as predicted theoretically^{1-4,7} from consideration of the Franck-Condon factors, k_{et} also slows down in the more strongly exothermic region, where $-\Delta G$ significantly exceeds the reorganization energy. A decrease of k_{et} in this so-called "inverted region" is now also evident from the relatively slow decay of the CT excited state (D^+-A^-) of **1b** observed under conditions where the energy gap separating it from the ground state ($D-A$) amounts to ≥ 3 eV ($1/\tau_{ct} = 5.3 \times 10^{-7}$ s⁻¹ in diethyl ether, where $h\nu_{ct} \approx 3$ eV; cf. Table I).³⁰

It seems quite probable that a fine tuning of energies plays a crucial role in determining the very efficient long-range electron transfer that occurs in many native and modified biological redox systems,³¹⁻³⁶ in particular in the primary chain of electron-transfer processes of the photosynthetic unit.³¹

Experimental Section

Measurements and Materials. Absorption and emission spectra were measured with Cary 17D and SPEX Fluorolog instruments, respectively. The emission spectra were measured from deoxygenated dilute (10^{-4} – 10^{-5} mol L⁻¹) solutions and corrected to reproduce relative intensity in units of quanta per wavelength interval. Quantum yields were determined using quinine sulfate in 1 N H₂SO₄ ($\phi = 0.55$) as a reference. Solvents used were of the purest grade commercially available. Fluorescence lifetimes were determined by the time-correlated single-photon counting

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technique with the equipment described earlier.¹⁰

Synthesis. The synthesis of the bichromophoric systems **1a** and **1b** has been described previously.^{17,37} The reference compound **3** was obtained commercially from Aldrich.

Compounds **2a** and **2b** were prepared from *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthren-3-one (**4**), which was obtained as described by Fahrenholtz et al.³⁸

Methyl (3Z)-cis-7-Methoxy-1,2,3,4,4a,9,10,10a-octahydro-3-phenanthrylideneacetate (2a). To a mechanically stirred suspension of 120 mmol of NaH in 200 mL of dry dimethoxyethane was added dropwise 180 mmol of triphenylphosphonoacetate in 100 mL of dry dimethoxyethane under an atmosphere of N₂. The mixture was stirred until no more H₂ evolution occurred. A solution of ketone **4** (40 mmol in 100 mL of dry dimethoxyethane) was added dropwise, and the reaction mixture was stirred for an additional 18 h, poured into 400 mL of H₂O, and extracted with pentane. From the dried (Na₂SO₄) pentane extract a crude mixture (ca 1:1) of the 3*E* and 3*Z* isomers were obtained (total yield ca. 60%).

The ¹H NMR spectra of these isomers differ significantly. The most characteristic difference occurs in the region where the equatorial, allylic hydrogens at C(2) and C(4) resonate. One of these protons resonates below 3 ppm, where it overlaps with other ring proton signals, while the other is strongly shifted downfield owing to the magnetic anisotropy of the nearby carbomethoxy group. For the *E* isomer the resonance of this low-field proton (H(2, eq)) appears at 3.50 ppm as a doublet of triplets due to coupling with H(2, ax) (²*J* ≈ 12 Hz) and with C(1)H₂ (³*J* ≈ 2 Hz), while for the *Z* isomer (**2a**) the low-field proton (H(4, eq)) is found at 3.64 ppm as a doublet of doublets due to coupling with H(4 ax) (²*J* ≈ 12 Hz) and with C(4a)H (³*J* ≈ 2 Hz). Fractional crystallization from ethanol yielded the pure *Z* isomer **2a**, as a white crystalline solid: mp 79–81 °C; IR (KBr) 1705, 1635 cm⁻¹; ¹H NMR (100 MHz, CDCl₃) δ 7.20 (d, 1 H, H(5)), 6.70 (d of d, 1 H, H(6)), 6.64 (d, 1 H, H(8)), 5.67 (s, 1 H, CHCOOMe), 3.75 (s, 3 H, ArOCH₃), 3.70 (s, 3 H, COOCH₃), 3.64 (d of d, 1 H, H(4, eq)), 3.0–1.5 (m, 10 H); MS, *m/z* 286 (C₁₈H₂₂O₃).

cis-7-Methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrylidene-3-malononitrile (2b). The ketone **4** (10 mmol), malononitrile (11 mmol), acetic acid (1.8 mL), and ammonium acetate (770 mg) were dissolved in 10 mL of benzene and refluxed at a Dean-Stark apparatus until water separation was complete. After workup the product was recrystallized from ethyl acetate, which yielded **2b** as a white solid (80%): mp 160–162 °C. Anal. Calcd for C₁₈H₁₈N₂O: C, 77.67; H, 6.52; N, 10.07. Found: C, 77.61; H, 6.47; N, 10.1 IR (KBr) 2200 cm⁻¹.

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Registry No. **1a**, 68352-07-8; **1b**, 68352-17-0; (*E*)-**2a**, 97997-87-0; (*Z*)-**2a**, 97997-88-1; **2b**, 68752-10-3; **3**, 1730-48-9; **4**, 24904-87-8; CH₂(CN)₂, 109-77-3; triphenylphosphonoacetate, 83037-86-9.

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