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Excited-State Conformational Dynamics of Flexibly and Semirigidly Bridged Electron Donor–Acceptor Systems in Solution. Influence of Temperature and Solvent Viscosity

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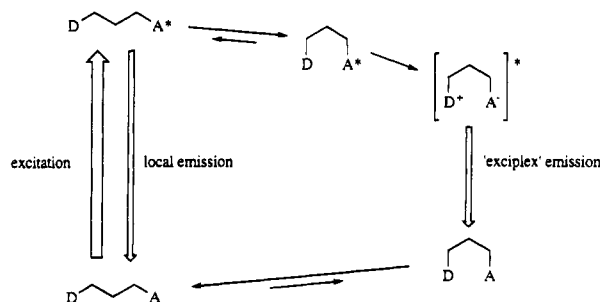
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The fluorescent behavior of a series of donor–bridge–acceptor systems was studied in nonpolar solvents of different viscosity as a function of temperature. The D/A units in these systems are held apart in the ground state by a saturated hydrocarbon bridge, which was either a flexible trimethylene chain or a semirigid piperidine ring. Photoexcitation of the semirigidly bridged systems containing a “strong” 4-cyanonaphthalene acceptor leads to long-range electron transfer forming an initial extended-charge-transfer (ECT) species which subsequently transforms into a folded dipolar species (compact-charge-transfer (CCT) state, similar to a tight polar exciplex) due to the Coulomb attraction (“harpooning mechanism”). From fluorescence decay rates of the ECT and CCT species folding rates were determined at different temperatures, which were analyzed in terms of activation energies needed for the conformational change. The activation energies for the piperidine bridged systems were typically 4–6 kcal/mol, consistent with the barrier for a chair to boat inversion of the piperidine ring (11–12 kcal/mol) being lowered considerably by the concomitant gain in Coulombic energy. No clear viscosity effect was found. In the flexibly bridged system with a “weak” naphthalene acceptor long-range electron transfer appears not to occur at least not in the low-polarity solvents employed and instead a conformational change precedes charge transfer. However, the flexibly bridged DA systems with a “strong” acceptor also appear to follow the “harpooning” mechanism. In this case low activation energies (2–4 kcal/mol) were found for the folding process, which were attributed to solvent viscosity only because the steric barrier imposed by the trimethylene chain is completely compensated by the gain in Coulombic energy accompanying the ECT → CCT folding process. The effect of viscosity on the activation energies found for the harpooning mechanism is discussed within the framework of Kramers’ theory.

Introduction

It is well-known that the thermodynamics and kinetics of intramolecular electron-transfer reactions in solution are strongly affected by structural and geometrical factors and by medium effects.¹ Important insight in especially the latter was gained from studies on donor–acceptor systems with rigidly extended bridges.² These conformationally well-defined systems allowed a careful examination of the dependence of the rate on the driving force and on donor–acceptor distance by systematic variation of donor, acceptor, and bridge length.^{3,4} Already in an early stage of our studies on electron transfer, we noted that rapid photoinduced long-range electron transfer, as demonstrated in these rigid systems, is occasionally followed by emissive charge recombination.^{5–8} Several other reports in the literature provided additional evidence that from extended charge separated states “exciplex-type” fluorescence can emerge.^{9–11} In the past two decades, much attention was paid to systems in which D and A groups are connected with a flexible polymethylene chain, which allows the formation of extended as well as folded or close-contact conformations. Many of these studies have been focused on the structural and geometrical aspects of exciplex formation on an experimental basis and have indeed provided valuable information on the photophysical dynamics. Although it was recognized that the steric requirements were not so restrictive in these polar exciplexes^{12,13} compared to intramolecular excimer formation, it was generally concluded that charge separation and especially the appearance of “exci-

SCHEME 1: Simplified Kinetic Scheme Commonly Assumed for Intramolecular Exciplex Formation



plex” fluorescence in these systems is restricted to conformations where the two chromophores are in close contact similar to intramolecular excimer formation (Scheme 1).

Scheme 1 has been used to analyze exciplex formation of intramolecular exciplexes in both nonpolar and polar media. However the general correctness of Scheme 1 in more polar solvents was already questioned as early as 1972 by Mataga and co-workers.¹⁴ Evidence was found in time-resolved absorption studies that in polar media a compact “sandwich” species if formed from an extended “loose” charge-separated species.^{14–17} The generality of this scheme was seriously questioned recently¹⁸ in light of the aforementioned long-range electron-transfer studies. These established that charge-transfer emission can occur from extended charge-separated states. Moreover, in a few reports in the literature on flexibly bridged systems containing strong D/A pairs capable of forming polar intramolecular exciplexes^{19–22} “anomalous” behavior has been reported upon lowering the temperature or increasing the viscosity. Often

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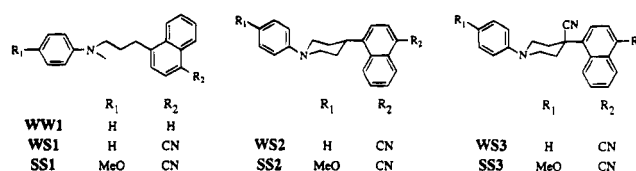
these changes abolished the intramolecular exciplex emission—as expected—but unexpectedly the quenching of the local fluorescence persisted or the quenching rate of the local fluorescence in these systems was viscosity independent, which also appears inconsistent with Scheme 1. Recently, we have directly compared as a function of solvent polarity, the emissive behavior of identical D/A pairs that are either semirigidly or flexibly bridged or not bridged at all.²³ It was concluded that the structure of emissive polar exciplexes formed between non-bridged or flexibly bridged D and A species may change considerably in response to solvent polarity, from a compact charge-transfer (CCT)-type structure in nonpolar to a more extended charge-transfer (ECT)-type structure in polar media. This confirmed the possibility of loose exciplexes in polar solvents, as considered explicitly by Mataga et al.^{14,15}

Despite the fact that these results demonstrated the inadequacy of Scheme 1 in polar solvents, it has in general been employed successfully in nonpolar and intermediately polar solvents in order to explain the observed rise time of the CCT species, ascribed to internal rotations around the methylene groups to bring D and A in close contact. Especially low-temperature studies have provided clear evidence for such conformational changes, as the intensity of the exciplex fluorescence normally decreases and displays a much longer rise time at low temperatures, while simultaneously the intensity of the local fluorescence increases.^{12,15,24–26} Also a clear viscosity effect has in general been noted (see, e.g., Mataga et al.¹⁵ and Yang et al.²⁷) in hydrocarbon solvents, where exciplex formation is retarded in more viscous solvents, which is in agreement with Scheme 1.

While the latter experiments seem to confirm the validity of Scheme 1 in not too polar media, we have shown recently that even in nonpolar solvents and in the gas phase several intramolecular donor–acceptor systems containing a semirigid bridge and a powerful D/A pair, undergo primarily rapid long-range electron transfer in an extended ground-state conformation upon photoexcitation, thereby creating an extended charge-transfer species (ECT).^{28–30} Due to the huge Coulombic attraction in such solvents, this initially formed species folds to a more compact charge-transfer (CCT) conformation. The spectacular change in molecular conformation due to a photo-generated Coulombic force was called the “harpooning” mechanism. Evidence for the occurrence of this harpooning mechanism was obtained by supersonic jet-studies,^{28,29} time-resolved fluorescence, and microwave conductivity studies,^{30–33} which established the change in dipole moment accompanying the large conformational change of the charge-separated species. While our earliest demonstrations of the harpooning mechanism referred to semirigidly bridged systems, more recently evidence for this mechanism was also found for a flexibly bridged donor–acceptor system (D–(CH₂)₃–A) in both the gas phase²⁹ and nonpolar solvents.^{23,30} Despite the low rotational barriers, we could observe a distinct rise time for the charge-transfer emission in a flexibly bridged system, having the same emission maximum as the analogous intermolecular system and thus indicating a compact charge-transfer (CCT) conformation.²³ The preceding extended CT emission could not be observed at room temperature. However, upon lowering the temperature in methylcyclohexane solution, the CCT emission diminished and the appearance of a new blue-shifted emission beside the quenched local emission unequivocally proved the existence of such an emissive ECT state for the first time for flexibly bridged donor–acceptor systems.

Detailed spectrotemporal analysis showed³⁰ that the two CT-emission bands (ECT and CCT) are kinetically related, and it

CHART 1: Donor–Bridge–Acceptor Systems Investigated



was shown that the shorter wavelength band decayed with a lifetime identical to the rise time of the red-shifted band of the CCT species.

Since the electrostatic forces depend strongly upon the dielectric constant of the surrounding solvent and the conformational changes are expected to depend also on solvent viscosity,³⁴ we decided to examine both the influence of dielectric constant and viscosity by variation of the hydrocarbon solvents as well as the temperature.

The D–bridge–A systems investigated in this paper differ both in the flexibility of the interconnecting bridge and in the D/A pair. Three types of bridges were investigated: a flexible trimethylene chain (1); a piperidine ring (2); a piperidine ring with a cyano group at the bridgehead carrying the acceptor (3). The sets of D–bridge–A systems depicted in Chart 1 consist of either *N,N*-dialkylaniline (“weak”) or *N,N*-dialkyl-4-methoxyaniline (“strong”) as electron donor, whereas the strong 4-cyanonaphthalene acceptor is used in all cases except for WW1, which has a naphthalene chromophore as a “weak” acceptor.

NMR studies confirm that the semirigidly bridged systems of Chart 1 adopt an extended ground-state conformation, due to the chair conformation of the six-membered piperidine ring and because both the phenyl and 4-cyano-1-naphthyl substituents occupy stereochemically preferred equatorial positions. The donor–acceptor distance (*r*_{DA}) was estimated to be 5.7 Å, measured from the amino nitrogen of the donor to the center of the aromatic acceptor ring attached to the bridge by using standard bond lengths and bond angles. The conversion to a conformation in which D and A are in close contact is hindered by the needed chair–boat interconversion of the piperidine ring. The ring interconversion imposes a steric barrier which is estimated to be at least 10 kcal/mol from dynamic NMR experiments.³⁵ As argued before, the energy needed to overcome this sterically imposed barrier can be provided by the Coulomb attraction force between the opposite charges created by electron transfer in the excited state. The presence of a solvent will express itself not only in decreased Coulomb attraction by dielectric shielding but also in the viscosity, which is expected to impose an additional barrier for the folding process as predicted by Kramers’ theory.³⁴

Methods

Experimental details and data analysis have been described in ref 30b. The synthesis and characterization of the compounds of Chart 1 will be described elsewhere. Here we present only some details relevant for the data analysis at different temperatures. Assuming an irreversible conversion of an ECT species to a CCT species, we attempted to analyze this behavior by three different methods.

(A) The first method is based on the ratio of the two emission bands, which is directly accessible from the steady-state spectra. The total fluorescence quantum yield (Φ_{tot}) provides information on both Φ_1 (fluorescence quantum yield of species 1) and Φ_2 (fluorescence quantum yield of species 2) and on the fractional yield Φ_{12} , which determines the ratio of the concentration of

component 2 formed from component 1, as $\Phi_{\text{tot}} = \Phi_1 + \Phi_{12}\Phi_2$. We define the fluorescence quantum yield of 1: $\Phi_1 = k_{f,1}/k_1$ with k_1 being the sum of all decay processes including radiative (k_f) and nonradiative (k_d) decay and folding k_{fold} (i.e., $k_1 = k_{f,1} + k_{d,1} + k_{\text{fold}}$) and the fluorescence quantum yield species 2 as $\Phi_2 = k_{f,2}/k_2$ with $k_2 = k_{f,2} + k_{d,2}$. In this it has been assumed that the electrostatic attraction is sufficient to make folding irreversible in the temperature region studied.

When we assume that the shape of the emission spectrum $\epsilon(\lambda)$ of each component is independent of temperature, we can decompose the steady-state spectra measured as a function of temperature with the help of a spectral parametrization,^{30b} where the concentrations c are a function of temperature T . Note that we can estimate only the shapes $c_i(T)$ (see also method C). From the ratio of the contributions to the steady-state spectra of the components we find

$$\frac{c_2(T) \int \epsilon_2(\lambda) d\lambda}{c_1(T) \int \epsilon_1(\lambda) d\lambda} = \frac{\Phi_{12}\Phi_2}{\Phi_1} = k_1 \Phi_{12} \frac{k_{f,2}}{k_{f,1}k_2} \quad (1)$$

Because of the assumed constant shapes $\epsilon_i(\lambda)$, the ratio $\int \epsilon_2(\lambda) d\lambda / \int \epsilon_1(\lambda) d\lambda$ is a constant (which is unknown).

Therefore only a relative measure of the folding rate constant k_{fold} can be found. We define

$$k_{\text{fold}} = \Phi_{12}k_1 \quad (2)$$

Assuming $k_{f,2}/(k_{f,1}k_2)$ is independent of temperature, we obtain an expression which allows the estimation of the activation energy E_a involved in the conformational change³⁶

$$\ln(k_{\text{fold,rel}}) = \ln(c_2(T)/c_1(T)) + \text{constant} \quad (3)$$

(B) A second method is to use only the decay rate of the ECT species as a function of temperature. The decay of the ECT species is determined by its charge recombination and conversion to the CCT species. When the conversion between the two species is very slow and thus k_{fold} is negligibly low or absent, k_1 can be regarded as an intrinsic decay rate constant $k_{1,\text{int}}$ of the ECT species. Assuming that the difference between k_1 and $k_{1,\text{int}}$ at other (higher) temperatures is related only to folding, eq 4 is obtained. The underlying assumption of eq 4

$$k_{\text{fold}} = k_1 - k_{1,\text{int}} \quad (4)$$

is that the sum of radiative and nonradiative rate constants $k_{1,\text{int}}$ does not change with temperature over the temperature range studied.

(C) The third approach is a combination of both time-resolved data and spectral shapes from steady-state spectra. An elaborate description of the theoretical methods used for this approach can be found in ref 30b. Here we present an extension relevant for the analysis of harpooning at different temperatures. When there is no apriori knowledge of the emission spectra, the fractional yield of harpooning Φ_{12} and the folding rate constant k_{fold} cannot be estimated from the data. We show that under a mild assumption on the emission spectra a relative measure can be derived. Specifically, the perfect, noise-free, time-resolved spectrum ψ is a superposition of the contributions of the n_{comp} different components:

$$\psi(t, \lambda) = \sum_{i=1}^{n_{\text{comp}}} c_i(t) \epsilon_i(\lambda) \quad (5)$$

where $c_i(t)$ and $\epsilon_i(\lambda)$ denote, respectively, the concentration and

emission spectrum of component i . Regarding eq 5, we note that the quantity which will be estimated is the product $c_i(t) \epsilon_i(\lambda)$ which in itself is insufficient for the determination of the absolute values of $c_i(t)$ and $\epsilon_i(\lambda)$. We now restrict ourselves to models with two components.

Suppose we have a model with two independent exponential decays $c_i^I(t) = e^{-k_i t} \otimes j(t)$ ($i = 1, 2$) (model I), where \otimes indicates convolution and $j(t)$ is the result of a convolution of the exciting laser pulse and the detector response, with accompanying decay-associated spectra (DAS)^{37,38} $\epsilon_i^I(\lambda)$. Then a model II where component 2 is formed from component 1 with fractional yield Φ_{12} is described by the linear combination:

$$c_1^I \epsilon_1^I + c_2^I \epsilon_2^I = c_1^I (\epsilon_1^I + \epsilon_2^I) + (c_2^I - c_1^I) \epsilon_2^I \quad (6)$$

Thus $c_1^I = c_1^I$, $\epsilon_1^I = \epsilon_1^I + \epsilon_2^I$, $c_2^I = \alpha(c_1^I - c_1^I)$ and $\epsilon_2^I = \epsilon_2^I/\alpha$, where $\alpha = \Phi_{12}k_1/(k_1 - k_2)$. In words, the differences between the two models are that the concentration of the formed component is proportional to the difference between the two decays, whereas the spectrum of the precursor is the sum of the two DAS. The other way around

$$\epsilon_1^I(\lambda) = \epsilon_1^II(\lambda) - \alpha \epsilon_2^II(\lambda) \quad (7)$$

thus the DAS of the precursor can contain negative amplitudes when the kinetics obey model II. It is well-known that negative amplitudes of a DAS indicate the presence of an (excited state) reaction,³⁸ like in model II. In general the fractional yield Φ_{12} is unknown and cannot be estimated from the data. However, since Φ_{12} determines the ratio of the real concentrations $\tilde{c}_2(t)$ and $\tilde{c}_1(t)$ (where the tilde indicates "real"), we can use a model function with $c_2^II(t)/\Phi_{12} \equiv \tilde{c}_2^II(t)$ (the circumflex indicates "estimated") and include the unknown Φ_{12} in the product $\Phi_{12} \epsilon_2^II(\lambda) \equiv \hat{\epsilon}_2^II(\lambda)$ which we can estimate. Now the information on Φ_{12} is not contained in the ratio of the estimated concentrations but instead in the ratio of the estimated spectra. This in turn is related to the ratio of the real emission spectra by

$$\frac{\hat{\epsilon}_2^II(\lambda)}{\hat{\epsilon}_1^II(\lambda')} = \frac{\Phi_{12} \tilde{\epsilon}_2^II(\lambda)}{\tilde{\epsilon}_1^II(\lambda')} \quad (8)$$

where λ' is an arbitrary wavelength which may be different from λ . From eq 8 we define the *relative* fractional yield $\Phi_{12,\text{rel}}$ as

$$\Phi_{12,\text{rel}} \equiv \frac{\Phi_{12} \mathcal{L}(\tilde{\epsilon}_2^II(\lambda))}{\mathcal{L}(\tilde{\epsilon}_1^II(\lambda'))} = \frac{\mathcal{L}(\hat{\epsilon}_2^II(\lambda))}{\mathcal{L}(\hat{\epsilon}_1^II(\lambda'))} \quad (9)$$

where $\mathcal{L}()$ denotes some linear operator. For example when we assume that the ratio of the areas under the real emission spectra is independent of temperature we take for this operator $\int \epsilon(\lambda) d\lambda$. When we assume that at a particular wavelength λ_0 the ratio of the emission spectra is constant, we have $\mathcal{L}(\epsilon(\lambda)) = \epsilon(\lambda_0)$.

The accompanying relative measure for the folding rate constant $k_{\text{fold,rel}}$ is given by eq 2.

Results and Discussion

Semirigidly Bridged Donor–Acceptor Systems. We will evaluate the effect of temperature in different solvents for the four different bridged systems, starting with system **WS3**. In Figure 1 the steady-state emission spectra of **WS3** in 2-methylbutane, methylcyclohexane, and *trans*-decalin are given. Excitation of the cyanonaphthalene chromophore does not lead

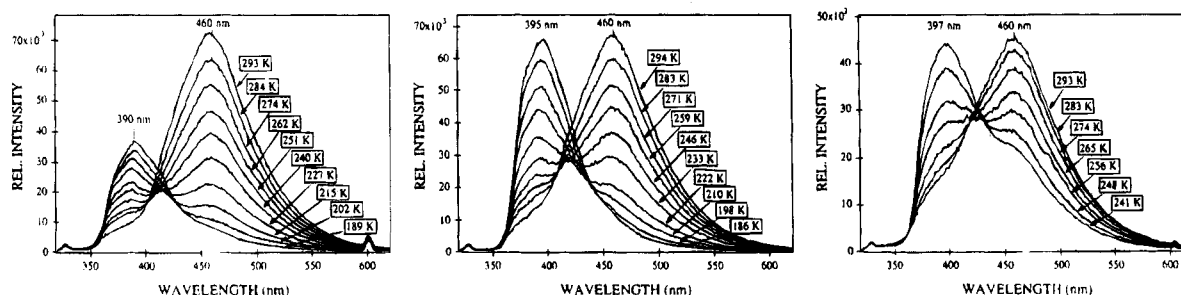


Figure 1. Steady-state spectra of compound **WS3** at different temperatures in three nonpolar solvents: (a) 2-methylbutane (left), (b) methylcyclohexane (middle), and (c) *trans*-decalin (right).

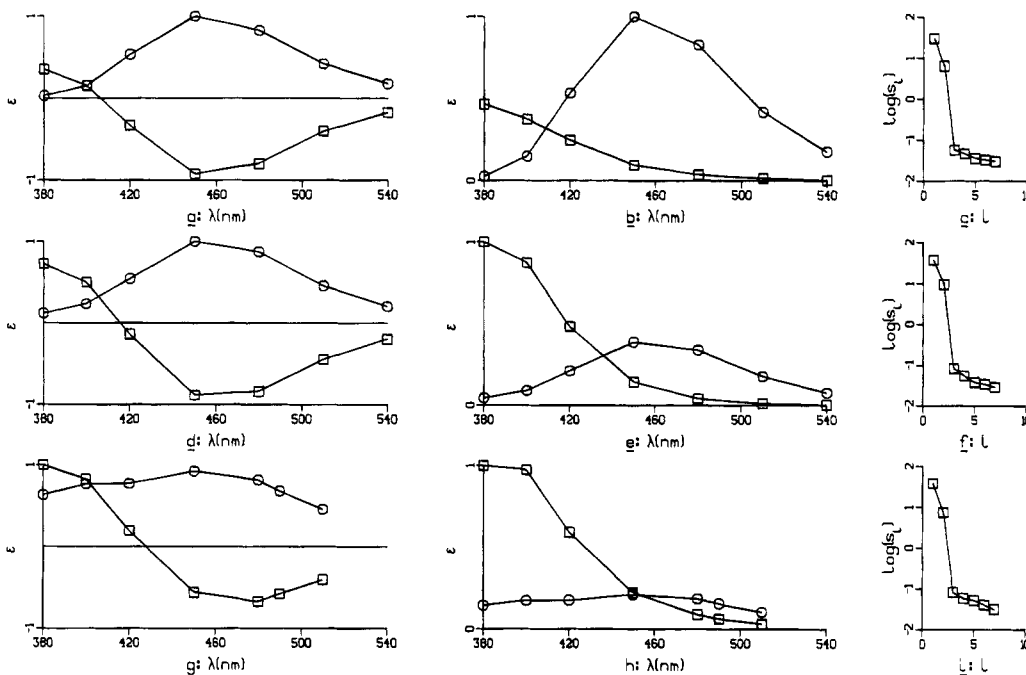


Figure 2. Decomposition of the trace data of **WS3** in 2-methylbutane at three temperatures using two kinetic models. Left: decay associated spectra of model I. No rescaling is done, so the amplitudes of the DAS represent the number of excited species at time zero after a hypothetical δ -pulse input. Middle: spectra of harpooning model II. The CCT spectrum (circles) is multiplied by the fractional yield of harpooning Φ_{12} . The ECT spectrum is indicated by squares. Right: logarithm of first 10 singular values as calculated from SVD of the emission decay data matrix. (a)–(c) $T = 290$ K, $k_1 = 0.109 \times 10^9 \text{ s}^{-1}$, decay rate of ECT (squares); $k_2 = 0.0207 \times 10^9 \text{ s}^{-1}$, decay rate of CCT (circles). (d)–(f) $T = 220$ K, $k_1 = 0.0262 \times 10^9 \text{ s}^{-1}$, $k_2 = 0.0177 \times 10^9 \text{ s}^{-1}$. (g)–(i) $T = 200$ K, $k_1 = 0.0240 \times 10^9 \text{ s}^{-1}$, $k_2 = 0.0150 \times 10^9 \text{ s}^{-1}$.

to significant local emission, which would be expected at 339 nm (cf. 1-methyl-4-cyanonaphthalene).^{30b} Instead the spectra consist of two overlapping broad emissions, bathochromically shifted with respect to the quenched local emission. At room temperature, the major structureless emission is centered at 460 nm in 2-methylbutane and is accompanied by a small short-wavelength shoulder. Upon cooling, the major emission diminishes and the short-wavelength emission at 390 nm increases. At ca. 235 K, both emissions have equal intensities and the 390 nm band even persists after complete solidification of the solvent (not shown), where the 460 nm band is hardly noticeable anymore. The temperature effects on the emission spectra were fully reversible. The excitation spectrum of the short-wavelength band is identical to that of the long-wavelength band and agrees very well with the absorption spectrum of **WS3**. According to our previous report,³⁰ the dynamic behavior observed is attributed to the transformation of an extended CT (ECT) species, emitting at 390 nm, to a more compact CT (CCT) species emitting at 460 nm, formed as a result of the electrostatic attraction force. As shown in Figure 1b,c, this interesting behavior of compound **WS3** is also observed in the other nonpolar solvents, methylcyclohexane, and *trans*-decalin, although the relative contributions of the bands are somewhat

different. In addition to the steady-state spectra, we have measured decay traces as a function of temperature for all D-bridge-A systems depicted in Chart 1. The traces which were collected at 7–11 wavelengths were globally analyzed and the decay rates are listed in Tables 2S–4S [supplementary material; see paragraph at end of paper].

From the decay traces we can deduce the conformational dynamics but can gain only limited spectral information. In Figure 2 we show the decomposition of the decay data of **WS3** in 2-methylbutane at temperatures of 290, 220, and 200 K. To estimate the rank of the matrix formed by concatenating the trace data collected at different wavelengths we performed a singular value decomposition (see methods in ref 30). There are two singular values clearly different from noise (Figure 2c) indicating that we are dealing with two spectrally and temporally different components. Figure 2a depicts the decay associated spectra, with the negative amplitudes of the fast decaying component (cf. eq 7, squares) which clearly represent the formation of the CCT state (circles) from the ECT state. The estimated spectra $\epsilon_1^H(\lambda)$ of model II are shown in Figure 2b, where the CCT spectrum there is multiplied by the fractional yield of harpooning Φ_{12} . At temperatures down to 220 K the spectral shapes remain almost the same (compare Figure 2d,e

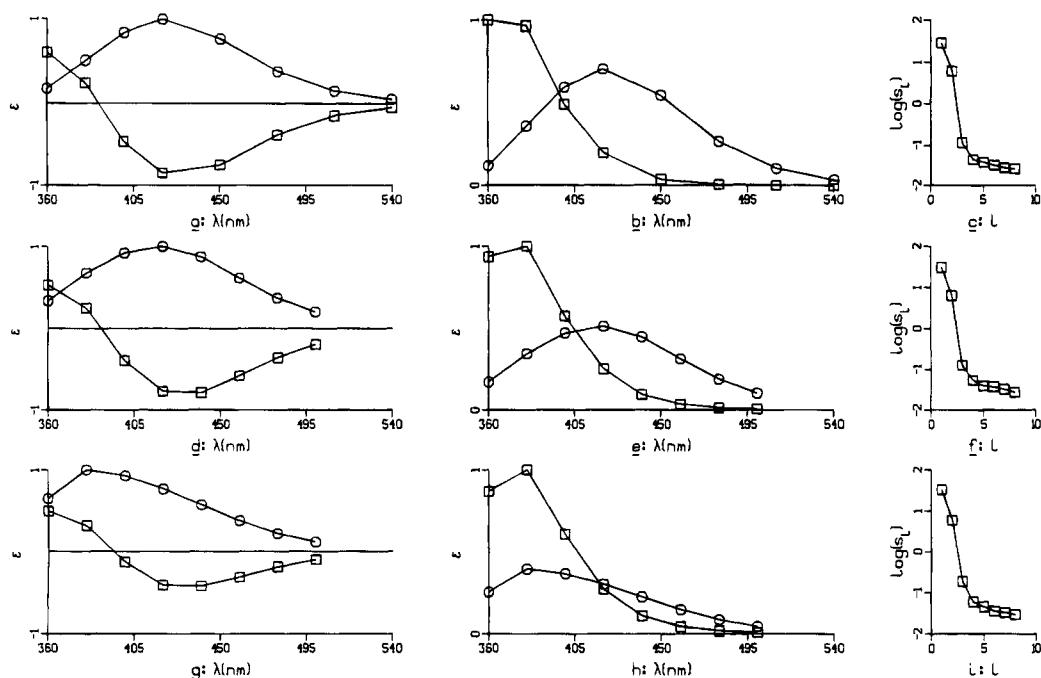


Figure 3. Decomposition of the trace data of **WS2** in 2-methylbutane at three temperatures using two kinetic models as in Figure 2. (a)–(c) $T = 290$ K, $k_1 = 0.130 \times 10^9 \text{ s}^{-1}$, decay rate of ECT (squares); $k_2 = 0.058 \times 10^9 \text{ s}^{-1}$, decay rate of CCT (circles). (d)–(f) $T = 270$ K, $k_1 = 0.099 \times 10^9 \text{ s}^{-1}$, $k_2 = 0.052 \times 10^9 \text{ s}^{-1}$. (g)–(i) $T = 250$ K, $k_1 = 0.088 \times 10^9 \text{ s}^{-1}$, $k_2 = 0.043 \times 10^9 \text{ s}^{-1}$.

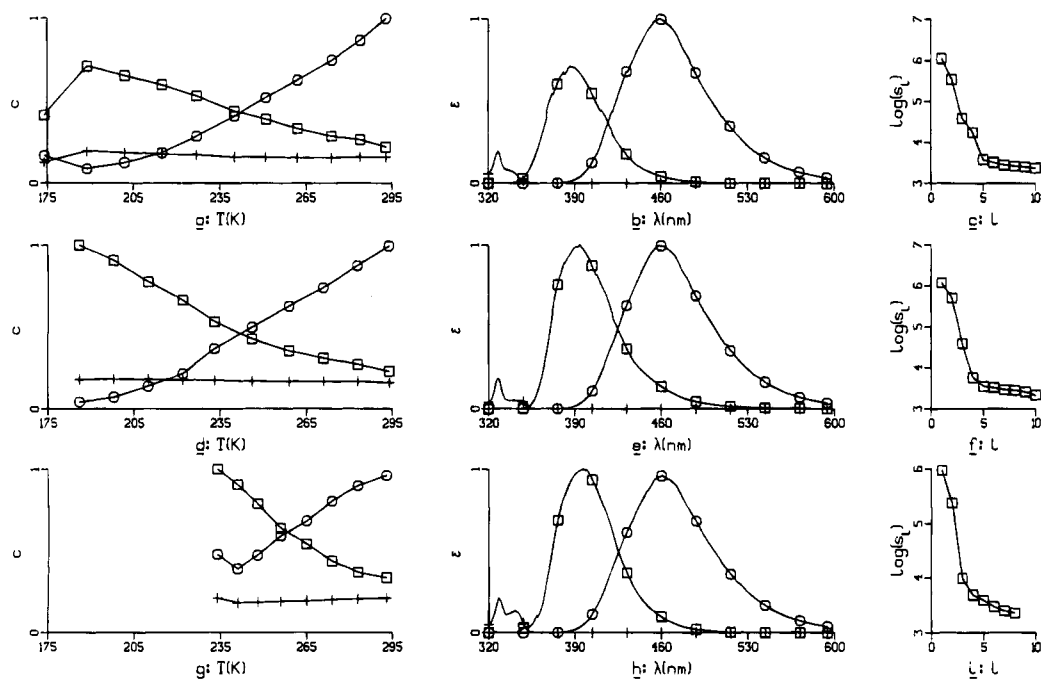


Figure 4. Decomposition of steady-state spectra of **WS3** at different temperatures using the spectral model. Squares, ECT; circles, CCT; plus signs, local fluorescence. At the left the amplitudes of the spectra in the middle part are shown, at the right the logarithm of the first 10 singular values as calculated from SVD of the steady-state data. (a)–(c) Solvent 2-methylbutane, (d)–(f) methylcyclohexane, (g)–(i) *trans*-decalin.

with Figure 2a,b). When we assume that the ratio of the real spectral amplitudes $\epsilon_2^{\text{II}}/\epsilon_1^{\text{II}}$ is temperature independent, we conclude from the reversal of the relative amplitudes in Figure 2b and Figure 2e that Φ_{12} decreases with temperature. When the temperature is lowered still further the shapes of the spectra change. There are still negative amplitudes in the DAS of the fast ECT decay (squares in Figure 2g) but the CCT spectrum is flattened (circles in Figure 2g,h). Analogously, in Figure 3 we depict the temperature dependence of harpooning in **WS2**. Note that already at 270 K a flattening of the CCT spectrum $\epsilon_2^{\text{II}}(\lambda)$ takes place (compare Figure 3b and 3e) and at 250 K its peak is buried under the ECT spectrum (Figure 3h). Thus there is a

qualitative change of, in particular, the CCT spectrum, which is more pronounced in **WS2** than in **WS3**.

Inspired by the temperature independence of the spectral shape in Figure 2b and 2e, we decomposed the steady state fluorescence spectra of **WS3** shown in Figure 1 with the help of a spectral model. The spectral model used describes the shapes of the steady state fluorescence spectra by a Gaussian model function in the energy domain with an extra “skewness” parameter.^{30b} These decompositions were again satisfactory. At the blue side of the ECT spectrum (circles in Figure 4b) some local fluorescence and Raman scattering (indicated by plus signs) is visible, which remains constant as a function of

TABLE 1: Activation Energies of Folding (in kcal/mol) As Determined from the Slope of the Fit $\ln(k_{\text{fold,rel}})$ versus $1000/T$ (between Parentheses the Standard Error in the Last Digit)

solvent	WS3 ^a	WS3 ^b	WS3 ^c	SS3 ^c	WS2 ^c	SS2 ^c	WS1 ^c	SS1 ^c
2-methylbutane	4.2(1)	4.4(5)	5.4(1)	5.6(5)	3.0(4)	5.1(5)	2.1(2)	<i>d</i>
methylcyclohexane	4.0(1)	3.7(5)	5.8(3)	5.4(5)	2.6(2)	5.7(5)	3.7(5)	3.7(1)
<i>trans</i> -decalin	5.2(1)	6(1)	5.6(3)	<i>d</i>	3.8(3)	6.2(5)	4.0(3)	<i>d</i>

^a Determined via method (A). ^b Determined via method (B). ^c Determined via method (C). ^d Not measured.

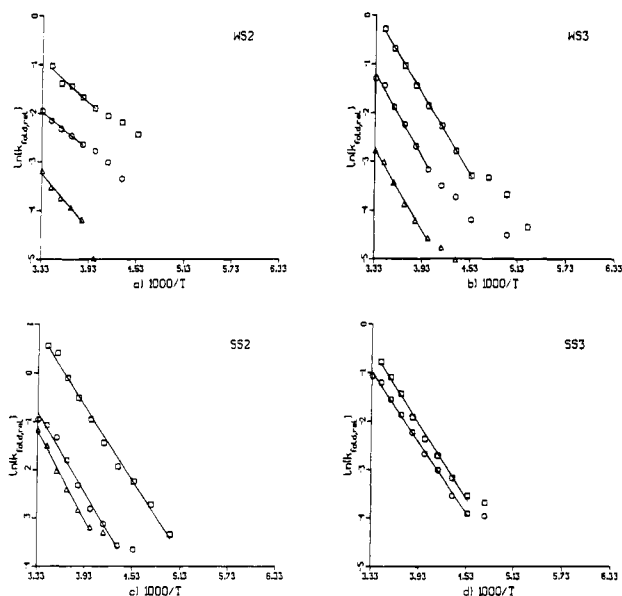


Figure 5. Plot of $\ln(k_{\text{fold,rel}})$ versus $1000/T$ (method C). Solvents: 2-methylbutane (squares), methylcyclohexane (circles), and *trans*-decalin (triangles): (a) WS2, (b) WS3, (c) SS2, and (d) SS3.

temperature (Figure 4a,d,g). The contributions of the CCT and ECT components behave complementarily, at lower temperature the ECT contribution increases at the expense of the CCT contribution. This picture is found in all three hydrocarbon solvents tested (Figure 4a,d,g).

We have plotted the logarithm of the relative measure of folding rate constant ($k_{\text{fold,rel}}$) against the inverse of temperature for WS3 for the three different methods described in the methods section. It was found that these plots allowed straight line fits for method A (not shown) and C (Figure 5b). From the slope values of the linear fits we find the activation energy, E_a . Method B appeared more complicated as a reliable value for the intrinsic decay rate constant of the ECT state (i.e., the decay rate constant of the ECT emission when no more folding takes place) was not directly accessible from the measurements at very low temperatures. Therefore the measured ECT decay rates (k_1) were fitted with an exponential activation energy E_a plus an intrinsic rate constant $k_{1,\text{int}}$ and the results are shown in Table 1. Inspection of Table 1 shows that methods A and B, which are based on stronger assumptions than method C, give somewhat lower activation energies. Most importantly, there is no clear solvent dependence of E_a regardless of the method used. It should be noted that especially E_a values obtained by method B were found to depend strongly on the k_1 values at low temperatures, which determine to a very large extent the estimated intrinsic decay rate $k_{1,\text{int}}$ of the ECT species. Therefore we restricted ourselves for the other systems only to the more precise method C. Also the activation energies of the other systems SS3, WS2, and SS2 tabulated in Table 1 were found to be virtually solvent independent. All activation energies are typically on the order of 4–6 kcal/mol, except for WS2. Most probably the assumption that $\epsilon(\epsilon_2^{\text{II}}(\lambda))/\epsilon(\epsilon_1^{\text{II}}(\lambda))$ (see eq 9) is temperature independent is not valid for WS2

(Figure 3) which can explain the low values as compared to the other three semirigidly bridged systems.

Using the rather simplified picture of the conformational change from an ECT into a CCT species with the assistance of the Coulomb attraction, the observed activation energy E_a equals the pure sterically imposed barrier of the piperidine ring (E_{ster}) reduced by the Coulombic energy (ΔE_C) which is gained by bringing D^+ and A^- together in the CCT species (eq 10). The steric barrier for the chair–boat interconversion of a neutral molecule is estimated to be about 10 kcal/mol³⁵ and is expected to be equal for solvents with different viscosity and dielectric constants:

$$E_a = E_{\text{ster}} - \Delta E_C \quad (10)$$

We have analyzed the gain in Coulomb energy (ΔE_C) in these nonpolar solvents by eq 11 assuming the same amount of folding of the piperidine ring and complete electron transfer in the transition state of the folding process:

$$\Delta E_C = \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s} \right) \left(\frac{1}{r_{\text{ECT}}} - \frac{1}{r_{\text{ts}}} \right) \quad (11)$$

The donor–acceptor distance in a folded boat conformation of the piperidine ring is calculated to be 3.6 Å, whereas the distance in the extended conformation is $r_{\text{ECT}} = 5.7$ Å.²⁹ Assuming that the transition state of the chair–boat inversion of the piperidine ring is a half-chair conformation, with the cyanonaphthalene ring rotated toward the anilino group, this yields a r_{ts} of about 4.7 Å. These values are not expected to differ much for the compounds studied here, as the positive charge will be rather localized at the nitrogen atom in the donor moiety and the negative charge in the cyanonaphthalene moiety. This is evidenced by the fact that the ECT states of these systems have identical dipole moments of ~ 28 D, as derived from the solvatochromic shift analysis^{30b} and TRMC measurements.³³ For the solvents studied here the Coulomb energy gain in the transition state is calculated to be -6.7 , -6.1 , and -5.7 kcal/mol for 2-methylbutane, methylcyclohexane, and *trans*-decalin, respectively. The gain in Coulomb energy shows a minor temperature effect due to the variation of the dielectric constant ϵ_s with temperature. For example, when *trans*-decalin is cooled to 240 K, the dielectric constant is increased by only 3%.³⁹ And although the dielectric constant of 2-methylbutane responds more strongly to temperature changes, an increase of only 8% is reached at 200 K compared with room temperature.⁴⁰ Taken the change of 8% in ϵ_s , the Coulomb energy gain ΔE_C in 2-methylbutane will be reduced from -6.7 (293 K) to -6.2 kcal/mol at 200 K. The small temperature effects in ϵ_s were thus neglected and using the ΔE_C values and the E_a values of method C (Table 1), the steric barrier is calculated from eq 10. This yields 11–12 kcal/mol for the semirigidly bridged D–A systems (except for WS2), which is in fact close to the aforementioned barrier for a piperidine chair–boat interconversion determined by dynamic NMR experiments³⁵ and again indicates that no additional barrier is presented by solvent viscosity.

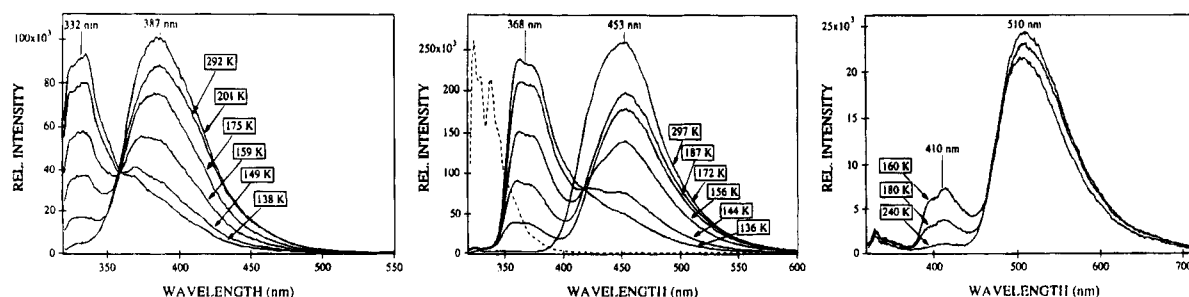


Figure 6. Steady-state spectra of the flexibly bridged DA systems at different temperatures: (a) **WW1** in methylcyclohexane (left), (b) **WS1** (solid line), and 1-methyl-4-cyanonaphthalene at 150 K (dashed line) in methylcyclohexane (middle) and (c) **SS1** in 2-methylbutane (right).

The absence of a viscosity effect on the activation energy for the ECT-to-CCT conformational change in the piperidine-bridged systems is somewhat unexpected as there are many examples in the literature for which a conformational change (e.g., the *cis*–*trans* photoisomerization of *trans*-stilbene^{41–43} and diphenylbutadiene^{44,45}) was shown to be viscosity dependent. In our experiments we have strongly varied the viscosity (η) of the solvents studied by lowering the temperature. The viscosity of *trans*-decalin increases from 1.82 cP at 300 K to 7.89 cP at its freezing point (≈ 240 K); with cooling from room temperature to 200 K, η varies from 0.23 to 0.85 cP for 2-methylbutane and from 0.73 to 5.03 cP for methylcyclohexane. It is known that the dependence of the viscosity η with temperature can be described⁴⁶ by an Arrhenius-like equation: $\eta = \eta_0 e^{-E_{\text{vis}}/RT}$, where η_0 (in centipoise) and E_{vis} (in kcal/mol) are the preexponential factor and activation energy for viscosity respectively. By plotting $\ln \eta$ (from literature data⁴⁷) versus $1/T$, activation energies were obtained of 1.7, 2.4, and 3.5 kcal/mol for 2-methylbutane, methylcyclohexane, and *trans*-decalin,³⁶ respectively. Assuming that solvent viscosity provides an additional barrier to the “harpooning” mechanism, it is thus expected that the activation energies for the piperidine-bridged compounds in *trans*-decalin should be increased by about 1.8 kcal/mol compared to 2-methylbutane.

The data of Table 1 show that the E_a values are in fact rather similar for all piperidine-bridged systems. This observation can be understood within the theoretical framework developed by Kramers.³⁴ According to Kramers’ model, the molecular motion can be viewed as a crossing of a one-dimensional potential energy barrier. The rate equation for a thermally activated barrier crossing in the presence of friction is given by

$$k = \frac{\omega_0}{4\pi\omega'\tau_c} \{ \sqrt{1 + (2\omega'\tau_c)^2} - 1 \} e^{-E/RT} \quad (12)$$

In this expression (12) ω_0 is the frequency of the potential well of the initial minimum and ω' the frequency of the barrier maximum, E is the barrier height and τ_c is the velocity relaxation time which is related to the friction coefficient (ζ). Two limiting cases are commonly distinguished: (a) the low-viscosity (weak coupling) limit and (b) the high-viscosity (strong coupling) limit.

(a) In the weak coupling limit τ_c is very long compared to “free motion” time scales, which means that the frictional forces are only a small perturbation on the molecular motion ($\tau_c\omega' \gg 1$). In this case, eq 12 becomes independent of viscosity:

$$k = \frac{\omega_0}{2\pi} e^{-E/RT} \quad (13)$$

(b) The other limit to consider is when the motion is sufficiently strongly coupled to the medium and friction is very large. Now τ_c is short compared to the characteristic time scales of free motion on the potential surface ($\tau_c\omega' \ll 1$). In this

Smoluchowski limit the rate expression is given by eq 14, which follows by Taylor expansion from eq 12:

$$k = \frac{\omega_0\omega'\tau_c}{2\pi} e^{-E/RT} \propto \frac{1}{\zeta} e^{-E/RT} \quad (14)$$

The rate constant becomes inversely proportional to the frictional coefficient ζ and to the viscosity η , assuming a hydrodynamical model in which $\zeta \propto \eta$.

In the studies on *cis*–*trans* photoisomerizations the influence of viscosity on the conformational change was successfully interpreted within the Smoluchowski limit as the isomerization rates were found to decrease with increasing viscosity,^{41–45} while the other limiting case (a) appeared to apply for the photochemical isomerization of DODCI.⁴⁸ Recently, Li and Peters studied⁴⁹ the diffusional separation of intermolecular exciplexes (*trans*-stilbene/fumaronitrile) into solvent-separated ion pairs in alkyl nitrile solvents of different viscosity. They found a clear viscosity effect on the rate of radical ion pair separation and showed that the kinetics could also be successfully described within the Smoluchowski limit of Kramers’ theory.³⁴ Wegewijs showed that the activation energies of the folding process in a related piperidine-bridged compound are mainly determined by viscosity.³⁶ Our results on the conformational change of the semirigidly bridged systems on the other hand can be understood as a case of “weak coupling”. Apparently the steric barrier associated with the folding process although lowered by electrostatic attraction is still large compared to the viscosity barrier and consequently no viscosity effect is observed.

As will be shown below this situation is quite different for the analogous flexibly bridged systems. Replacement of the piperidine ring by a trimethylene chain reduces the sterically imposed barrier for folding to only 2–4 kcal/mol,⁵⁰ which is easily reduced to zero by electrostatic attraction. Consequently it is expected that viscosity will significantly affect the folding rates of the flexibly bridged systems.

Flexibly Bridged Donor–Acceptor Systems. In Figure 6 the steady-state emission spectra of **WW1** in methylcyclohexane, **WS1** in methylcyclohexane, and **SS1** in 2-methylbutane are given to illustrate the different behavior of “weak” and “strong” D–(CH₂)₃–A systems at low temperatures. For **WW1** the CCT emission at 387 nm disappears upon cooling, and at the same time an emission typical for the locally excited state of D or A develops in the 330 nm region. The behavior of the systems with stronger DA pairs, **WS1** and **SS1** is remarkably different from that of **WW1**. Upon cooling, the CCT emission diminishes as expected, but no emission typical for the locally excited state of either D or A arises. As shown in Figure 6b, the structured local emission of the acceptor chromophore (1-methyl-4-cyanonaphthalene) is found at ~ 335 nm (at 150 K). Instead a new emission arises at ~ 370 nm for **WS1**, which is attributed to an ECT state as this emission is close to the position of the emission shown by **WS2** in nonpolar solvents^{23b} (see

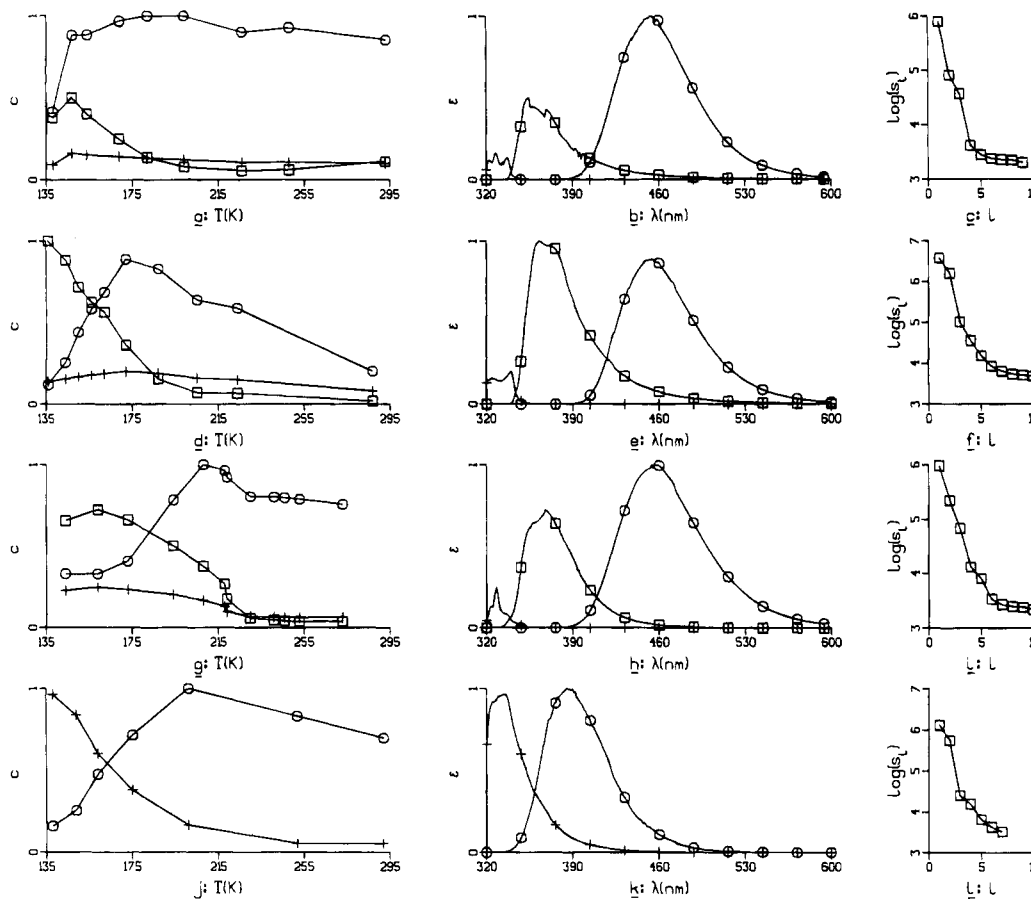


Figure 7. Decomposition of steady-state spectra of flexibly bridged systems **WS1** and **WW1** at different temperatures using the spectral model as in Figure 4: (a)–(c) **WS1** in 2-methylbutane; (d)–(f) **WS1** in methylcyclohexane; (g)–(i) **WS1** in *trans*-decalin, and (j)–(l) **WW1** in methylcyclohexane.

Figure 3). As shown in Figure 6c **SS1** displays a behavior analogous to **WS1** with both emissions about 50 nm red-shifted. This shift affirms our interpretation of the charge-transfer nature of the CCT emission and especially of the emission attributed to the ECT species, as the lowering of the donor oxidation potential ($E_{1/2}^{ox} \approx 0.2$ eV lower due to the 4-methoxy substitution in the aniline donor^{30b}) in **SS1** should be reflected in a red-shift of both the CCT and ECT emissions compared to **WS1**.

The decomposition of the steady-state spectrum of **WS1** in methylcyclohexane (Figure 6b) is shown in Figure 7d–f together with the spectra in 2-methylbutane (Figure 7a–c) and *trans*-decalin (Figure 7g–i).

As reported in our previous study^{30b} the time-resolved data revealed that the CCT emission consists in fact of two highly overlapping CCT emission bands. A separation of these bands is not possible from steady state data. The behavior of the amplitudes in Figure 7a,d,g is analogous to that shown in Figure 4, but the dominance of the ECT emission appears at a much lower temperature. Interestingly the temperature at which the contribution of the ECT species becomes equal to that of the CCT species in Figure 7 is different for the three solvents and increases from about 138 K in 2-methylbutane to ~180 K in *trans*-decalin, thus already suggesting a solvent viscosity effect. This was corroborated by taking decay traces of **WS1** in these solvents. The results of the analysis are compiled in Table 5S–7S [supplementary material]. As noted earlier^{30b} with the decomposition of the room-temperature fluorescence decay data, a complication arises with the flexibly bridged systems, because next to the dominant CCT component a minor, more blue-shifted CCT emission is present. The 300 K DAS of **WS1** in methylcyclohexane are shown in Figure 8a. The negative

amplitudes of the fast decay (squares) again indicate harpooning. However, assuming model II with an independently decaying minor CCT emission (triangles), the ECT spectrum (squares) possesses a hump in the red region. Thus this model is most probably an oversimplification. At 190 K, well below the lowest temperature where harpooning occurs in the semirigidly bridged systems, the ECT spectrum is much more satisfactory (Figure 8e). At still lower temperatures the situation becomes more complicated: at 150 K a second component appears with a maximum at 360 nm (plus signs in Figure 8h), but there is still some harpooning present (negative amplitudes of squares in Figure 8g) resulting in a CCT state with a temperature-independent spectral shape (compare circles in Figure 8b,e,h).

The behavior of **SS1** in methylcyclohexane was found to be very similar to **WS1**, although the CCT and ECT emissions are shifted to ca. 510 and 420 nm, respectively, and the decay rates are greater (Table 6S). From the ECT decay rates of **WS1** and **SS1** (tabulated in Table 5S–7S) and the spectra, the relative folding rate constants were calculated and plotted logarithmically versus the reciprocal temperature (Figure 9). The fits of $k_{fold,rel}$ against $1000/T$ in Figure 9 for both compounds are qualitatively comparable to those of the semirigidly bridged systems in Figure 5. The slopes found are somewhat smaller (last two columns of Table 1, but we must add that the simple model II used here is probably an oversimplification). Inspection of the activation energies of **WS1** in Table 1 shows that a viscosity effect may be present here, although it must be admitted that only a limited data set is available to back this conclusion. Nevertheless, the value of E_a obtained increases by 1.9 kcal/mol from 2-methylbutane to *trans*-decalin, which agrees well with the 1.8 kcal/

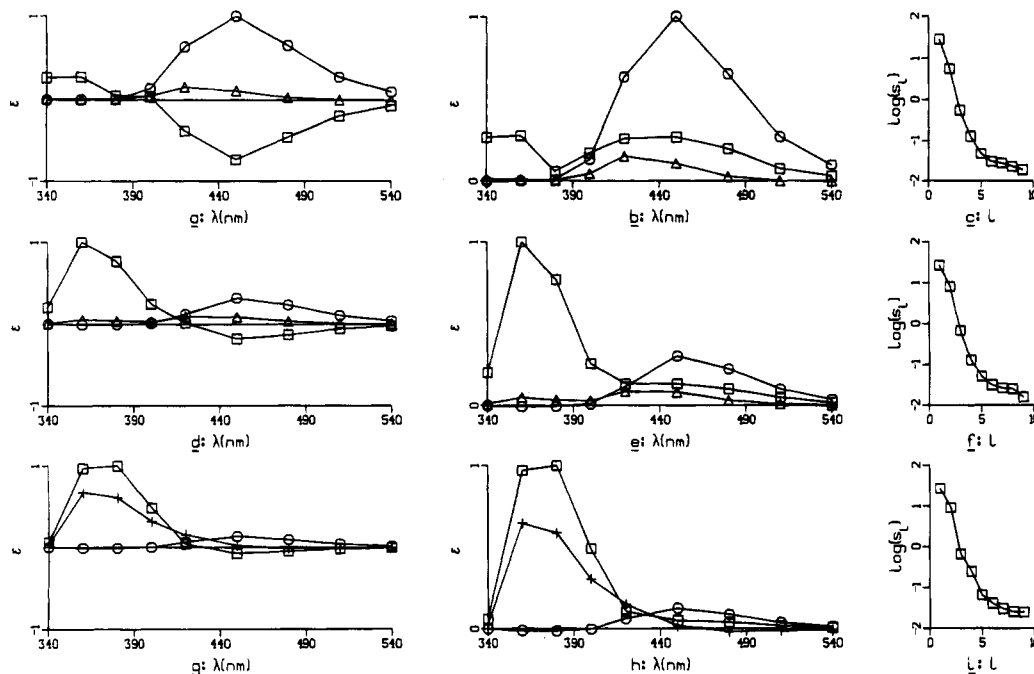


Figure 8. Decomposition of the trace data of **WS1** in methylcyclohexane at three temperatures using two kinetic models as in Figure 2. At 300 and 190 K the minor CCT component (triangles) is treated as an independent decay. At 150 K a third component (origin unclear) is also treated as an independent decay (plus signs). (a)–(c) $T = 300$ K, $k_1 = 0.95 \times 10^9$ s $^{-1}$, decay rate of ECT (squares); $k_2 = 0.0139 \times 10^9$ s $^{-1}$, decay rate of major CCT (circles); $k_3 = 0.057 \times 10^9$ s $^{-1}$, decay rate of minor CCT (triangles). (d)–(f) $T = 190$ K, $k_1 = 0.234 \times 10^9$ s $^{-1}$, $k_2 = 0.0122 \times 10^9$ s $^{-1}$, $k_3 = 0.044 \times 10^9$ s $^{-1}$. (g)–(i) $T = 150$ K, $k_1 = 0.252 \times 10^9$ s $^{-1}$, $k_2 = 0.0130 \times 10^9$ s $^{-1}$, $k_3 = 0.066 \times 10^9$ s $^{-1}$.

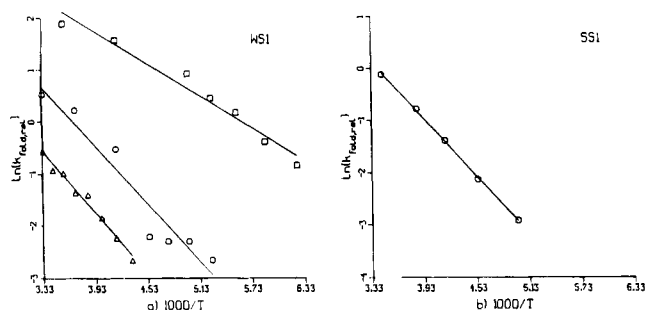


Figure 9. Plot of $\ln(k_{\text{fold,rel}})$ versus $1000/T$. Solvents: 2-methylbutane (squares), methylcyclohexane (circles), and *trans*-decalin (triangles): (a) **WS1**; (b) **SS1**.

mol difference in barrier expected when this depends solely on solvent viscosity (E_{vis}) as analyzed in the previous section.

At first sight it might seem remarkable that activation energies of 2–4 kcal/mol are found for both **SS1** and **WS1**, since the low rotational barrier of the trimethylene chain is expected to be totally cancelled by the Coulombic energy gain, if exciplex formation proceeds according to the “harpooning” mechanism (see also ref 30b). However, it should be realized that although the calculated value of E_a with eq 10 would indeed yield a negative value and the intrinsic conformational barrier thus becomes zero by the gain in Coulomb energy going from ECT to CCT, the dynamic nature of the viscosity barrier means that it cannot be lowered by electrostatic effects. The fact that the calculated activation barriers for **WS1** in Table 1 are close to the barriers induced by viscosity, especially for 2-methylbutane and *trans*-decalin, supports this view and confirms for these flexibly bridged systems that the Smoluchowski limit of Kramers’ theory applies.

Finally, we present some results on the weak acceptor flexibly bridged compound **WW1**. The decomposition of the steady state spectra of **WW1** in methylcyclohexane (Figure 6a) is shown in Figure 7j–l. We find a peak around 330 nm which is attributed to local emission (compare plus signs in Figure

7e,k). From solvatochromic shift analysis^{30b} we know that the red emission consists of two strongly overlapping CCT emissions, whose separation is impossible with time-integrated (steady-state) data. Again the contributions of the local emission grow at the expense of the CCT emissions upon cooling. With decay traces (Table 6S) we find three components (three significant singular values in Figure 10c,f,i). At 260 and 200 K we have two CCT emissions (circles and triangles in Figure 10a,b,d,e), plus a fast decaying local emission (plus signs). The DAS of the last possesses negative amplitudes, which indicates that the CCT emission is formed from the local emission. Thus in this case a conformational change precedes charge transfer, analogous to the **P3** system studied by Mataga and co-workers.¹⁵ Interestingly, **WW1** is the only one of the compounds reported here whose behavior is consistent with Scheme 1. As was the case with **WS1**, the detailed kinetics of this three-component system cannot be extracted from the data. Most probably there are interrelations between the CCT emissions that are formed from the locally excited state. At 150 K only the red CCT emission has remained (circles in Figure 10h) which is formed from local emission (negative amplitudes in Figure 10g), while the third component largely overlaps the local emission. Perhaps both donor and acceptor local emissions are present, analogous to the semirigidly bridged counterpart **WW2** (cf. Figure 9 in ref 30b).

Conclusions

The present investigations show that the “harpooning-mechanism” in which an extended CT species changes to a more compact CT species provides a satisfactory description of the observed dynamic behavior of semirigid D–bridge–A systems incorporating strong donor–acceptor pairs in nonpolar media. It is found that the folding process of the piperidine bridged systems takes place above ≈ 200 K and results in dual charge-transfer emission from two strongly different conformations. By a study of the effect of temperature on the folding rate constants, activation energies are obtained for the piperidine

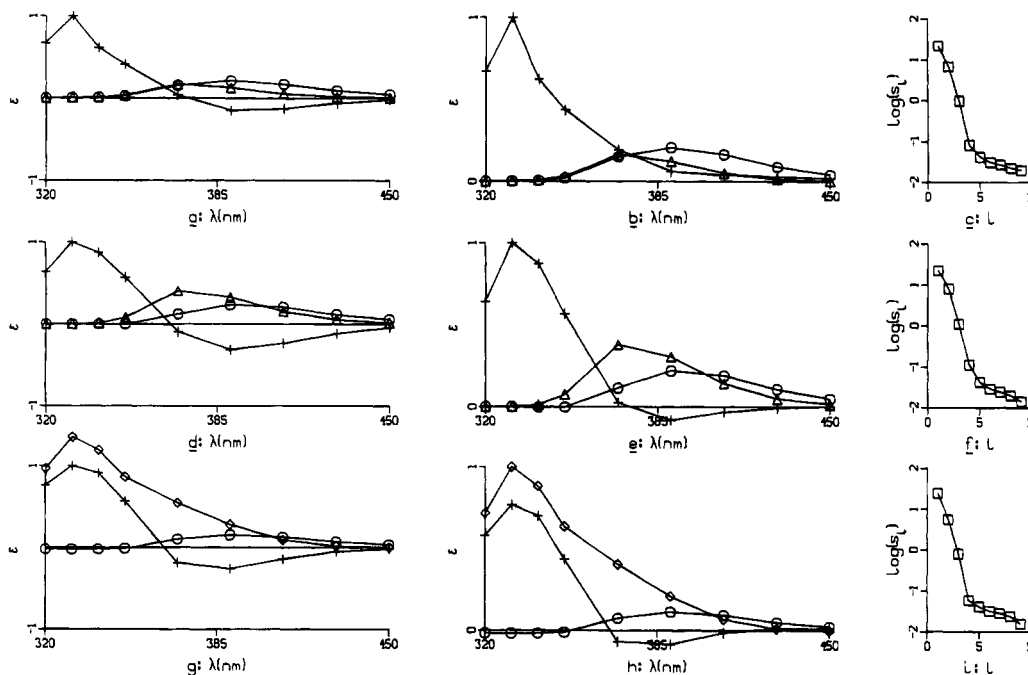


Figure 10. Decomposition of the trace data of WW1 in methylcyclohexane at three temperatures using two kinetic models as in Figure 2. At 260 and 200 K a second, more blue, CCT component (triangles) is treated as an independent decay. At 150 K a third component (origin unclear) is also treated as an independent decay (diamonds): (a)–(c) $T = 260$ K, $k_1 = 2.0 \times 10^9$ s $^{-1}$, decay rate of local fluorescence (plus signs); $k_2 = 0.0293 \times 10^9$ s $^{-1}$, decay rate of redmost CCT (circles); $k_3 = 0.093 \times 10^9$ s $^{-1}$, decay rate of second CCT (triangles). (d)–(f) $T = 200$ K, $k_1 = 0.46 \times 10^9$ s $^{-1}$, $k_2 = 0.0262 \times 10^9$ s $^{-1}$, $k_3 = 0.059 \times 10^9$ s $^{-1}$. (g)–(i) $T = 150$ K, $k_1 = 0.42 \times 10^9$ s $^{-1}$, $k_2 = 0.0258 \times 10^9$ s $^{-1}$, $k_3 = 0.063 \times 10^9$ s $^{-1}$.

bridged systems of 4–6 kcal/mol. These activation energies are much lower than the steric barrier for ring inversion because the Coulombic attraction in nonpolar solvents reduces this barrier significantly. This barrier reduction is calculated to amount to 6–7 kcal/mol using a simple point charge model, which implies that the steric barrier is 11–12 kcal/mol for ring inversion, in accordance with NMR studies.³⁵

Furthermore it is shown that the “harpooning mechanism” is not restricted to systems which have a rather high ground-state barrier between “extended” and “folded” conformations. The trimethylene-bridged systems WS1 and SS1, which also incorporate a strong donor/acceptor couple that allows for rapid long-range electron transfer in nonpolar solvents, show harpooning even at temperatures down to 140 K (Figure 8). Flexibly bridged D–A systems which have a weak D/A pair (WW1) show no harpooning and electron transfer can occur only in a folded conformation.

Although our limited time resolution did not allow a complete evaluation of the kinetics, which moreover are complicated by the presence of more than two CT conformations, we could estimate activation energies of 2–4 kcal/mol for the folding process of WS1 and SS1. These are attributed mainly to solvent viscosity, as the low rotational barrier imposed by the trimethylene chain is compensated completely by the large gain in Coulomb energy. These results indicate that the Smoluchowski limit of Kramers’ theory can be applied to the flexibly bridged systems as the friction is important for this essentially barrierless process.

However, the Smoluchowski limit does not apply to the semirigidly bridged systems, which are found to be independent of viscosity (Table 1). Apparently the intramolecular motion of the folding process for these systems is not sufficiently strongly coupled to the medium and the frictional forces are only a small perturbation on the molecular motion of these systems. Thus, our observations as well as those reported in another recent study⁵¹ are consistent with the notion that high

barrier cases are more potential controlled or inertial, and low barrier cases are more diffusive or viscosity controlled.

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Supplementary Material Available: Tables 2S–7S contain the decay rates of the seven compounds as function of temperature in the solvents studied (3 pages). Ordering information is given on any current masthead page.

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