

Electron transport via saturated hydrocarbon bridges: 'exciplex' emission from flexible, rigid and semiflexible bichromophores

Jan W. Verhoeven

Laboratory of Organic Chemistry, The University of Amsterdam,
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.

Abstract - The photophysical properties are compared of systems containing electron donor-acceptor (D/A) pairs linked by saturated hydrocarbon bridges with various degrees of flexibility. It is concluded that even in fully extended conformations rapid (subnanosecond) photoinduced electron transfer can occur, thus providing a mechanism for quenching of 'local' fluorescence that is not restricted by the conformational dynamics of the bridge. Especially in solvents of low dielectric constant electrostatic forces strongly modify the conformational dynamics occurring after the initial charge separation ('harpooning mechanism'). Furthermore it is shown that the extended charge separated state may undergo radiative recombination resulting in the observation of 'exciplex-like' emission. For flexibly bridged systems this allows the occurrence of multiple 'exciplex' emission from widely different conformations ranging from fully extended to fully folded. The distance across which charge separation and radiative recombination occur with significant rate can be extended by through-bond interaction (TBI) via the bridge, but even if the bridge structure and conformation do not allow for important TBI these rates can be quite significant for bridges with a length up to that corresponding to an extended pentamethylene chain.

1. INTRODUCTION

In the wake of the discovery of *intermolecular* excimer and exciplex formation (ref. 1) extensive studies have emerged on *intramolecular* excimer and exciplex formation in bichromophoric molecules of the general structure D-bridge-A, where D and A denote the chromophores connected by a nonconjugated 'bridge' (ref. 2, 3). Initially bridges consisting of methylene groups ($-(\text{CH}_2)_n-$) have been employed most widely to restrict the configuration space available to the chromophores and at the same time provide sufficient conformational flexibility to allow efficient intramolecular 'complexation'. Fig. 1 provides a simplified representation of the mechanistic schemes employed to describe the photophysical dynamics of such flexibly linked bichromophores.

Whereas especially for longer polymethylene bridges a large number of conformations can be envisaged, we have - for the sake of clarity - subdivided these in 'extended' and 'folded' conformations in Fig. 1 to discriminate between those in which direct contact of the chromophores is absent or present respectively.

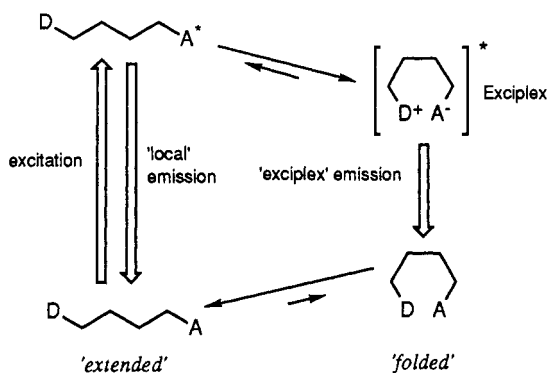


Fig. 1. Simplified kinetic scheme for intramolecular exciplex formation.

Assuming a negligible contribution of folded conformations to the ground state equilibrium, the process of conformational folding in the excited state is an essential step in the exciplex formation and thus rate limiting in the appearance of exciplex emission as well as in the quenching of local emission from the primarily excited chromophore. This feature has in fact been employed widely to investigate the conformational dynamics of polymethylene- and related bridges by studying the time resolved photophysics of intramolecular exciplex and especially excimer formation (ref. 2, 4, 5). While schemes adapted from that in Fig. 1 appear to be universally successful (see however ref. 6) in the description of intramolecular excimer formation (i.e. for D=A), in a number of cases anomalous behaviour has been observed for systems capable of forming polar intramolecular exciplexes. In this paper we discuss these observations in the light of recently emerged insight on long-range electron transfer as well as new results concerning the conformational requirements for exciplex-type emission provided by the study of rigidly and semiflexibly bridged bichromophores.

2. DEPHASING OF LOCAL-FLUORESCENCE QUENCHING AND EXCIPLEX FORMATION IN FLEXIBLY BRIDGED SYSTEMS; EXCIPLEX FORMATION BY A HARPOONING MECHANISM

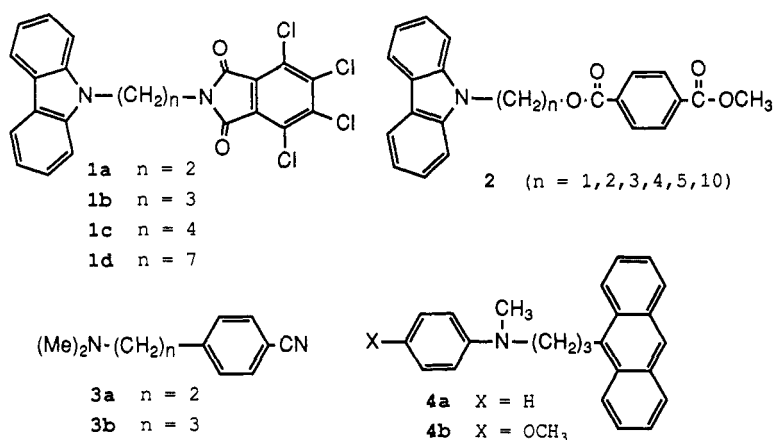


Fig. 2. Flexible D/A systems for which photoinduced charge separation and intramolecular exciplex formation have been inferred to occur non-concerted in a low polarity environment.

As early as 1976 (ref.7, 8) we studied intramolecular exciplex formation in systems **1** (see Fig. 2), which incorporate the powerful carbazole/tetrachlorophthalimide D/A pair that makes photoinduced charge separation (and concomitant quenching of local fluorescence) thermodynamically feasible even in saturated hydrocarbon solvents. Complete quenching of the local (carbazole) fluorescence was found for **1a-c** in all solvents including *n*-hexane implying a quenching mechanism with a rate $\geq 4 \times 10^{10} \text{ s}^{-1}$. For these systems in *n*-hexane an exciplex emission was found with an equally high growth-rate. While these rates at room temperature already exceed those generally found for intramolecular excimer formation across similar bridges we furthermore observed that the full quenching of the local fluorescence in **1a-c** persists at low temperature. For the higher homologue **1d** in saturated hydrocarbon solvents both intramolecular exciplex emission and a weak residual local fluorescence are detected that display virtually identical growth and decay rates respectively ($5 \times 10^9 \text{ s}^{-1}$ at 20°C). Amazingly, no significant effect of solvent viscosity on these rates could be detected. Furthermore from the temperature dependence of the quenching process for **1d** in diethylether this quenching process was concluded to involve an apparent barrier of only 1.2 kcal/mol. These observations forced us to conclude that the quenching of local fluorescence in **1** occurs before any major conformational reorganization occurs, i.e. by long-range electron transfer. Furthermore we suggested that, especially in the low dielectric media employed, subsequent exciplex formation is assisted by electrostatic attraction in analogy to the 'harpooning' model developed by Polanyi (ref. 9) in the description of gas-phase electron transfer processes.

It is important to stress that we were neither the first nor the only to note the possibility of electron-transfer quenching in more or less extended conformations of flexibly bridged D/A systems. In general, however, indications for such a process have been limited to measurements in polar solvents (ref. 10-14) where the lack or weakness of exciplex emission hampers a study of the relation between the processes of quenching and (emissive) exciplex formation.

Interesting exceptions to this situation are constituted by **2**, **3** and **4** (see Fig. 2). Thus for the lower members of **2** ($n=1, 2, 3$) Hatano et al. (ref. 15) reported that while lowering the temperature of a solution in methyl tetrahydrofuran abolishes the intramolecular exciplex emission, the degree of quenching of the local carbazole fluorescence hardly diminishes. Quite similar observations were reported more recently by Van der Auweraer (ref. 16) for **3a** and **3b** that display full quenching of the local cyanobenzene fluorescence even in an isopentane glass at 77 K. Even more revealing is the recent report of Yang et al. (ref. 17) concerning the behaviour of **4a,b** in saturated hydrocarbon solvents of various viscosity. While the quenching rate of local anthracene fluorescence in **4a** diminishes with increasing solvent viscosity, it is virtually viscosity independent in **4b** which contains a stronger electron donor moiety. At the other hand the exciplex emission quantum yield of **4a** is nearly viscosity independent, while that of **4b** diminishes at higher solvent viscosity. These data were interpreted to indicate a harpooning mechanism of exciplex formation in **4b** but not in **4a**.

In conclusion, from studies on flexibly bridged bichromophores many indications arise that the simple kinetic scheme of Fig. 1, while generally adequate for intramolecular excimer formation (see however ref. 6), breaks down for a description of intramolecular exciplex formation in a situation where photoinduced electron transfer is thermodynamically feasible over distances beyond those encompassed by the conformational energy well of the (emissive) exciplex state. This situation obtains for systems containing strong D/A pairs and/or embedded in a strongly solvating medium.

Little definitive information, however, can be gained from the study of such flexibly bridged systems about the actual distance at which charge separation occurs nor about the geometry of the exciplex from which the eventual 'exciplex'-emission observed emerges. In the next sections we try to answer these questions in more detail employing conformationally restricted bridges.

3. LONG-RANGE PHOTOINDUCED ELECTRON TRANSFER IN RIGIDLY BRIDGED DONOR-ACCEPTOR SYSTEMS

While studies on flexibly bridged D/A systems have occasionally provided evidence for the occurrence of photoinduced long-range electron transfer (see previous section) it were especially studies on systems containing rigid, extended hydrocarbon bridges that have in the past decade revealed the ubiquitous occurrence of this phenomenon (ref. 3).

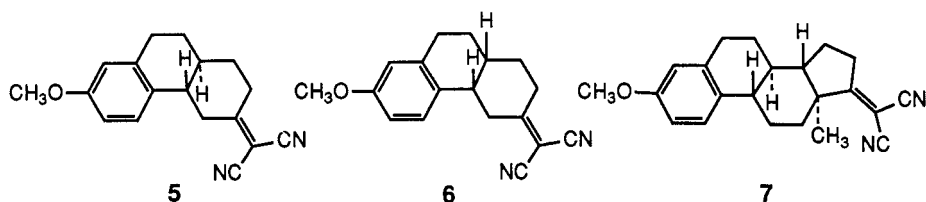
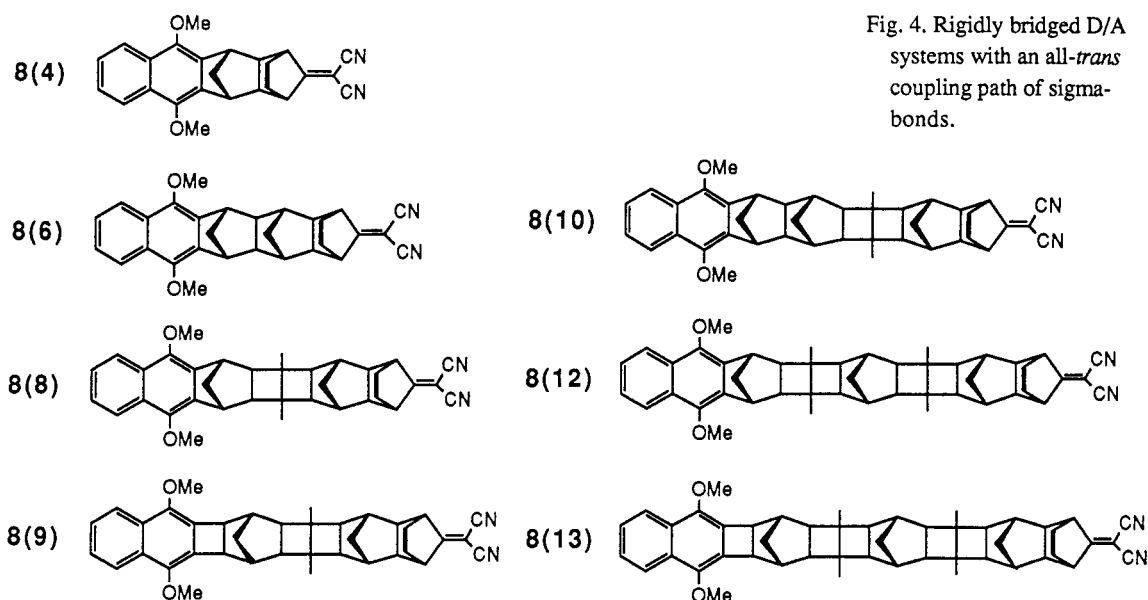


Fig. 3. Rigidly bridged D/A systems studied by Pasman et al. (ref. 18-20).

Amongst the earliest examples of such systems synthesized and studied in our laboratory (ref. 18-20) are compounds **5**, **6**, and **7** (see Fig. 3), that contain a methoxybenzene/dicyanovinyl D/A pair connected by a *trans*-decaline (**5**), a *cis*-decaline (**6**) and a steroidal (**7**) bridge respectively. For all three systems, up to and including **7** where the steroidal spacer keeps D and A at an edge-to-edge separation of at least 5.8 Å, we observed complete quenching of the donor fluorescence irrespective of solvent polarity. This was attributed to intramolecular electron transfer with a rate $\geq 10^{11} \text{ s}^{-1}$.

Extension of these studies in collaboration with the groups of M.N. Paddon-Row, N.S. Hush and J.M. Warman (ref. 21-23) has since dramatically confirmed and enhanced these conclusions. Instrumental in these studies was especially the series of compounds **8(n)** (see Fig. 4) in which rigid bridges comprising arrays of n ($n = 4-13$) C-C sigma bonds interconnect the dimethoxynaphthalene/dicyanovinyl D/A pair. For **8(4)** the rate of photoinduced electron transfer escaped detection in analogy to the situation we met before in **5**, **6**, and **7** where the number of bonds separating D and A amounts to 3, 3, and 5 respectively. For **8(6)** and the higher members of the series, however, rates of photoinduced charge separation (k_{ct}) were measured by picosecond time correlated single pho-



ton counting techniques, that were found to display only a moderate solvent dependence and to obey closely an exponential distance dependence in each separate solvent. Fig. 5 demonstrates this for tetrahydrofuran as a solvent (ref. 24), where a least squares fit of the data gives eqn.(1), R_e being the edge-to-edge D/A distance in Å:

$$k_{et} (s^{-1}) = 10^{14} \exp(-0.92n) \approx 10^{14} \exp(-0.80R_e) \quad (\text{corr. coeff. } r^2=0.994) \quad (1)$$

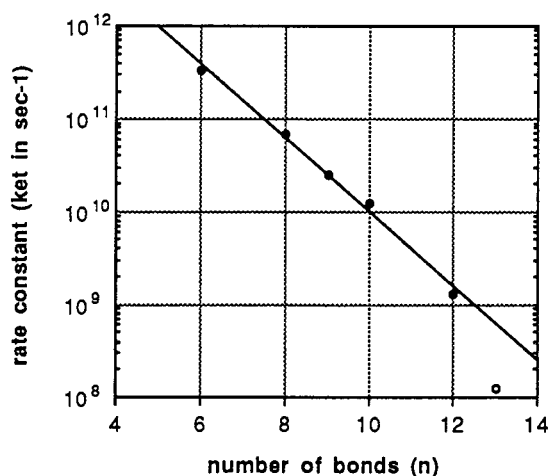


Fig. 5. Mono-exponential fit (see eqn(1)) of the rate of photoinduced charge separation in $8(n)$ as a function of the number of bonds separating D and A (solvent: tetrahydrofuran at 20°C)

Note that the rate for $n=13$ has been omitted in the regression analysis since this rate would require a significant correction for the increase of the barrier at high values of n (see ref. 23).

Similar studies (ref. 25) on thermal electron transfer in radical-anions and radical-cations employing another type of rigid or semirigid, saturated hydrocarbon bridges recently provided a significantly higher value (i.e. 1.36 per bond or 1.1 Å⁻¹) for the exponential factor, which implies a much faster attenuation of the rate with increasing length of the bridge (i.e. with a factor 3.9 per bond while in the series $8(n)$ this is only 2.5 per bond). As stressed before (ref.21-24) the fast electron transfer and its slow attenuation across the bridges incorporated in systems $8(n)$ appears to be connected to efficient through-bond interaction (TBI) (ref. 26) between the D and A chromophores via the all-*trans* arrays of C-C sigma-bonds provided by the bridges. While extensive theoretical and experimental evidence is available to support that an all-*trans* arrangement optimizes TBI, it should be stressed that this is not a *conditio-sine-qua-non* for the occurrence of rapid long-range electron transfer. Thus, while the rate of photoinduced

electron transfer in **9(6)** and **9(8)**, that lack the all-*trans* bridge configuration (see Fig. 6) typical for **8(n)**, was found (ref. 27) to be slowed down significantly high rates still can be obtained across such 'bent' bridges.

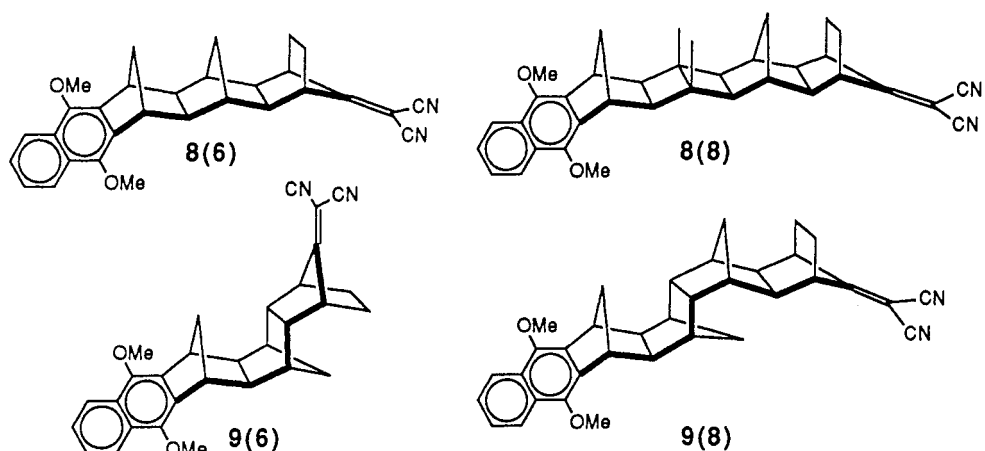


Fig. 6. Rigidly bridged D/A systems with (**8**) and without (**9**) an all-*trans* array of sigma-bonds in the coupling path.

Interestingly, however, a more pronounced solvent dependence of the rate in **9(n)** than in series **8(n)** was observed. As a result the ratio of the k_{et} values for **8(8)** and **9(8)** varies from 13.6 in the polar but rather non-polarizable solvent acetonitrile to only 2.9 in the polarizable solvent benzene. From this it appears likely that not only TBI via the bridge but also superexchange via the solvent plays a vital role in mediating long-range electron transfer. The latter corroborates earlier studies (ref. 28) on intermolecular electron transfer in rigid methyl tetrahydrofuran glasses that provided a distance dependence for optimally exothermic (i.e. 'barrier-free') intermolecular electron transfer given by eqn(2):

$$k_{et} = 10^{13.9} \exp(-1.20R_e) \quad (2)$$

While this expression predicts significantly lower rates at equal separation than eqn(1), it still implies formidable rates at D/A separations far beyond the Van der Waals contact distance and in the absence of a bridge capable of efficient TBI. Thus at $R_e = 7 \text{ \AA}$, corresponding to the length of a fully extended pentamethylene chain, eqn(2) provides an estimate of $k_{et} = 1.8 \times 10^{10} \text{ s}^{-1}$.

In conclusion the results of various studies on long-range electron transfer lend support to the hypothesis (see § 2) that even in fully or partly extended conformations of flexibly bridged $D-(CH_2)_n-A$ systems intramolecular photoinduced charge separation is possible on a subnanosecond time scale competitive with the rotational conformational changes occurring in such polymethylene bridges. While through-bond interaction can significantly extend the length of the bridges across which electron transfer is sufficiently fast to compete with other relaxation pathways the importance of this mechanism is restricted by conformational requirements. Across bridges comprising the equivalent of \leq five methylene groups, however, subnanosecond charge separation remains feasible even in the absence of TBI which appears to corroborate the harpooning mechanism presented in § 2 as an explanation for the dephasing of local fluorescence quenching and exciplex formation in some $D-(CH_2)_n-A$ systems. In fact, as we will discuss in a later section, thermodynamic restrictions rather than a lack of electronic interaction probably prevent the occurrence of harpooning in most flexibly bridged D/A systems studied.

4. 'EXCIPLEX' EMISSION FROM RIGIDLY BRIDGED DONOR-ACCEPTOR SYSTEMS

Already in an early stage of our studies on extended, rigidly bridged D/A systems we noted that not only rapid photoinduced electron-transfer occurs in such systems, but also that the dipolar state thus populated apparently can undergo radiative relaxation leading to the appearance of 'exciplex'-type fluorescence (ref. 29,30). Thus while, as discussed in § 2, the fluorescence of the aromatic chromophore in **5-7** (see Fig. 3) is fully quenched as a result of

extremely fast intramolecular electron transfer, these systems display (ref. 18-20) a structureless emission at longer wavelength (see Fig. 7, 8) which via its strong solvatochromism is identified to emerge from a highly dipolar excited state.

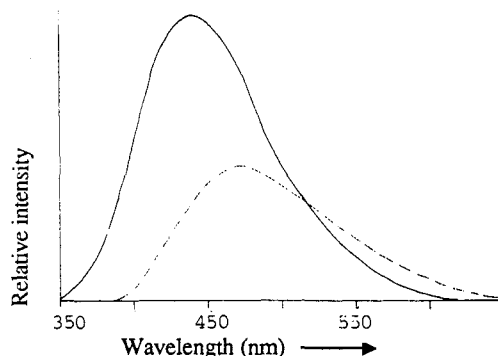


Fig. 7. Exciplex-type fluorescence of **5** in diethyl ether (—) and in chloroform (- - -).

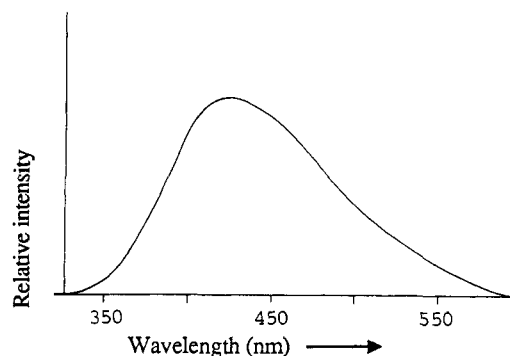


Fig. 8. Exciplex-type fluorescence of **7** in diethyl ether.

Also in the more extended series **8(n)** such observations were made (ref. 23) and in a few solvents weak longwavelength emission emerging from the charge separated state could even be detected for **8(10)** (ref. 31). These observations clearly reveal the semantic and conceptual problems one meets in comparing intermolecular and intramolecular interactions. It appears widely accepted that the process of intermolecular charge separation should be discussed in terms of the formation and eventual equilibration of (emissive) exciplexes, being equivalent to contact ion pairs, and of (non-emissive) solvent separated ion pairs (refs. 32). We note that while long-range charge separation across extended bridges might be compared with direct formation of a solvent separated ion pair, the now demonstrated emissive nature of the giant dipoles produced in the former process makes this comparison problematic. We furthermore note that since formation of the (emissive) charge separated state in rigidly bridged D/A systems clearly cannot involve large conformational changes it is inappropriate to refer to the emission as exciplex emission and that 'charge-transfer' emission appears a more appropriate term. This is corroborated by the observation that the electronic absorption spectra of the bridged systems often provide evidence for a finite vertical transition probability between the ground-state and the charge separated state (ref. 29-31) i.e. for a charge-transfer absorption band. We finally note that the fluorescence quantum yield of 'giant dipoles' formed by intramolecular charge separation across conformationally extended hydrocarbon bridges can reach very high values. Thus we recently demonstrated that systems like **10** (see Fig. 9) retain their extended conformation after photoinduced charge separation from the anilino donor to the vinylaromatic acceptor and that the dipolar state thus produced displays an intense (quantum yield up to 85%) and highly solvatochromic emission which makes these molecules an interesting class of fluorescent probes for medium polarity (ref. 33, 34) and mobility (ref. 35, 36).

In conclusion, the results discussed in this section not only support the occurrence of photoinduced charge separation across extended hydrocarbon bridges but also provide definite proof that from the extended charge separated state thus populated discrete 'exciplex-like' longwavelength fluorescence may emerge. The consequences of this finding for the interpretation of the photophysical behaviour of more flexibly bridged D/A systems are discussed in the next section.

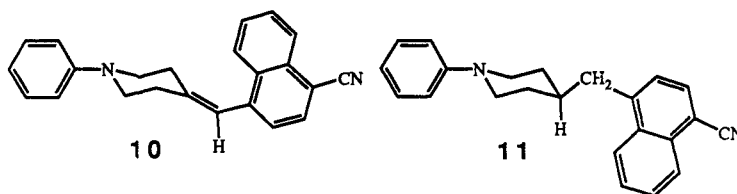


Fig. 9. A virtually rigid (**10**) and a closely related semiflexible (**11**) D/A system.

5. CHARGE-TRANSFER EMISSION FROM FOLDED AND EXTENDED CONFORMATIONS OF A BRIDGED DONOR-ACCEPTOR SYSTEM WITH LIMITED FLEXIBILITY

The results obtained with rigidly bridged D/A systems presented in § 3 and 4 suggest that in extended conformations of flexible $D-(CH_2)_n-A$ molecules not only photoinduced charge separation can occur but also that the extended charge separated state thus produced might be able to undergo emissive charge recombination leading to the observation of fluorescence similar to that normally attributed to an intramolecular exciplex involving direct D/A contact. Evidently the low rotational barriers in polymethylene chains allow very fast (subnanosecond) conformational changes that make it difficult to discriminate eventual charge transfer emission from different conformations. For that purpose, it would be desirable to have a molecule with higher energy barriers between the conformations, but still sufficiently flexible to allow conformational changes to occur within the nanosecond time scale typical for excited state lifetimes. Compound **11** (see Fig. 9), synthesized in our laboratory (ref. 37,38), represents such a semi-flexible molecule. Both X-ray diffraction and NMR spectroscopy confirm that **11**, as expected, has a stretched ground-state conformation since the central piperidine ring adopts a chair conformation while both the phenyl group and the 4-cyano-1-methylenenaphthyl group occupy stereochemically preferred equatorial positions. Compound **11** incorporates an anilino moiety as a powerful electron-donor and the cyanonaphthalene unit as an acceptor, interconnected by an array of five sigma-bonds, analogous to that present in systems of the type $D-(CH_2)_4-A$. In the latter essentially 'free' rotations around the C-C bonds, with estimated barriers of 2-3 kcal/mol, can convert the molecule from a fully stretched into an optimally folded conformation. Such a process is highly restricted in **11**, where it requires a chair-boat interconversion of the piperidine ring which is estimated (ref. 38) to involve a barrier of at least 10 kcal/mol.

Fluorescence of **11** at room temperature

The fluorescent behaviour of **11** in solution at room temperature has been described previously (ref. 37,38). Excitation of the cyanonaphthalene chromophore at 300 nm does not lead to local fluorescence, which would be expected at 345 nm. Instead a new, broad emission band is observed in many solvents. The maximum of this emission shows a large bathochromic shift which increases with increasing solvent polarity, typifying an exciplex-type emission from a state with strong charge transfer character (see Table 1).

The maximum of the intramolecular 'exciplex' band of **11** in n-hexane (452 nm) closely resembles that of the intermolecular exciplex between 1-cyanonaphthalene and N,N-diethylaniline in the same solvent (ref. 39). Thus, at least in this solvent, the fluorescence appears to arise from a folded conformation which brings D and A as close together as in the intermolecular exciplex, which probably has a sandwich-type orientation.

TABLE 1. Charge transfer fluorescence maxima of **10** and **11** in various solvents at 20°C.

Solvent	Δf	$\nu_{ct} \mathbf{10}$ (1000 cm ⁻¹)	$\nu_{ct} \mathbf{11}$ (1000 cm ⁻¹)
n-hexane	0.092	24.60	22.12
c-hexane	0.100	24.40	22.07
di-n-butyl ether	0.194	21.50	20.83
diisopropyl ether	0.237	20.40	20.75
diethyl ether	0.251	19.50	20.20
ethyl acetate	0.292	17.50	17.42
tetrahydrofuran	0.308	17.50	17.42
dichloromethane	0.319	17.30	17.21
acetonitrile	0.393	14.40	-

Fluorescence spectra of **11** as a function of temperature and solvent

The observation described above for **11** in an apolar solvent, i.e. full quenching of the local emission and the appearance of emission from a 'folded' exciplex is not inconsistent with the harpooning mechanism we postulated in § 2 and which we substantiated (ref. 38) for **11** in the gasphase by supersonic jet experiments. In this harpooning mechanism electrostatic forces play a vital role in determining the kinetics of the conformational changes occurring after the initial charge-transfer. Especially in a solvent of low dielectric constant these electrostatic forces might be able to attenuate the high barrier to folding expected for **11** sufficiently to allow for rapid folding at room temper-

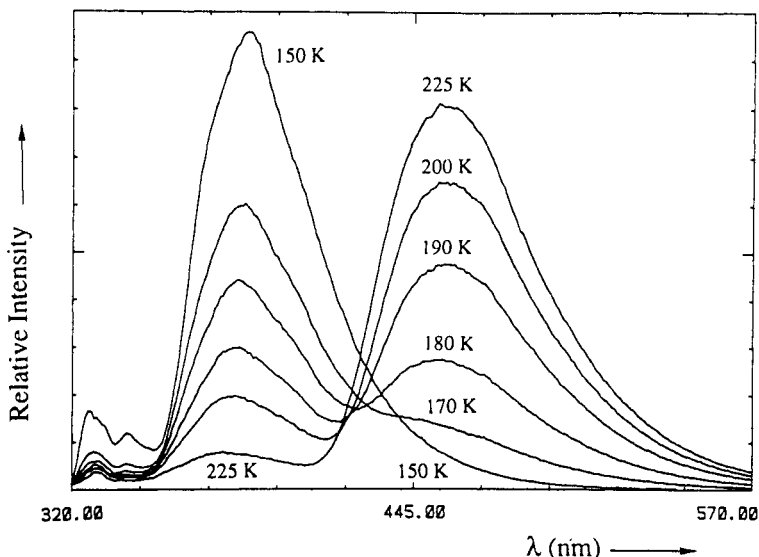


Fig. 10. Temperature effect on fluorescence spectrum of **11** in methyl cyclohexane. Excitation wavelength 300 nm.

perature. It thus appeared interesting to study the fluorescent behaviour of **11** at low temperature as well as in solvents of higher dielectric constant.

As demonstrated in Fig. 10 the long wavelength 'exciplex' emission at 454 nm does indeed decline upon cooling a methylcyclohexane (MCH) solution even at temperatures far above that where solidification occurs (130 K), thus testifying to the relatively high barrier involved in formation of this exciplex. Furthermore, in line with the occurrence of long-range electron transfer, no significant increase of the local emission (at 345 nm) occurs. Most interesting, however, is the observation that a new broad emission around 380 nm appears. This even persists after complete solidification of the solvent and thus appears to emerge from an excited state which has a conformation very similar to that of the ground-state. The excitation spectrum of this band is virtually indistinguishable from that of the 454 nm band and agrees very well with the absorption spectrum of **11**, so the band cannot be ascribed to an impurity.

Since the behaviour demonstrated in Fig. 10 also turns out to be independent of concentration, we were forced to attribute the 380 nm band to an intramolecular excited state identified as the conformationally extended charge separated state postulated as a precursor of the folded exciplex emitting at 454 nm. This kinetic link was recently confirmed by time resolved measurements (ref. 40). Only when the interconversion has slowed down sufficiently does this extended state have the chance to emit, otherwise it is effectively quenched by the very rapid Coulomb-induced conformational change.

Important further support for the correctness of the interpretation of the emissive behaviour of **11** in apolar solvents comes from a comparison with its behaviour in more polar solvents. In Fig. 11 we plot the charge transfer fluorescence frequency (ν_{CT}) of both **11** and the related but even less flexible **10** as a function of the solvent polarity as defined by the parameter Δf (see Table 1).

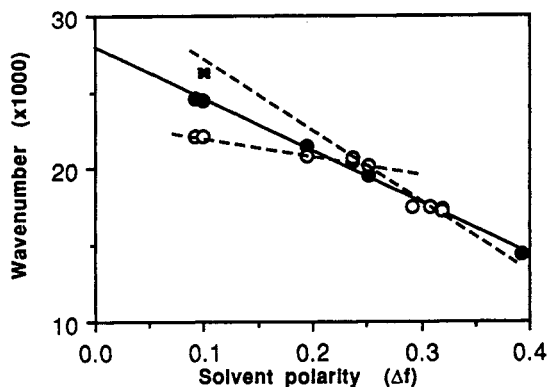


Fig. 11. Influence of solvent polarity (Δf scale) on the charge transfer fluorescence maxima of **10** (filled circles) and **11** (open circles) at room temperature. The additional charge transfer fluorescence displayed by **11** at low temperature (see Fig. 10) is indicated by an asterisk.

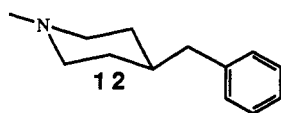
For emission from an excited state with dipole moment μ_e much larger than that of the ground state eqn (3) can be derived in which $\nu_{ct}(0)$ denotes the gasphase frequency, ρ the effective radius of the cavity that the molecule occupies in the solvent, ϵ the solvent dielectric constant, n its refractive index, h Planck's constant and c the velocity of light.

$$\nu_{ct} = \nu_{ct}(0) - (2\mu_e^2/hc\rho^3)\Delta f \quad (3)$$

with $\Delta f = (\epsilon-1)/(2\epsilon-1) - (n^2-1)/(4n^2+2)$

While the fluorescence frequency of **10** shows a solvent dependence (ref. 33,34) which nicely follows that predicted by eqn (3) this linear relation clearly breaks down in the case of **11** for solvents of low dielectric constant, where the slope is much less pronounced than that in more polar solvents. According to eqn (3) this implies that for **11** the dipole moment of the fluorescent state is smaller in apolar solvents than in polar solvents. In the light of the discussion above this may be interpreted to indicate that whereas the emission in apolar solvents emerges from a 'folded' exciplex state it emerges from a more extended charge separated state in polar solvents. Interestingly extrapolation of the fluorescence frequencies observed in polar solvents into the apolar regime leads to an estimate of $\nu_{ct} \approx 27,100 \text{ cm}^{-1}$ (370 nm) in methylcyclohexane, which corresponds remarkably well with the fluorescence attributed to an extended charge transfer state (380 nm) in the low temperature spectra obtained in this solvent (see Fig. 10). In the literature deviations from the linear solvent dependence predicted by eqn (3) have occasionally been reported (ref. 41,42) for flexibly bridged D/A systems. These deviations have mostly been attributed to changes in the electronic structure of the exciplex as a function of solvent polarity, by e.g. increased mixing of the charge separated and locally excited configurations in apolar solvents resulting in a decrease of the exciplex dipole moment (ref. 42). Noteworthy, however, is that Masaki et al. (ref. 41) in an early stage already explicitly considered the possibility of conformational changes of the emissive exciplex as a function of solvent. The present results dramatically confirm this possibility and furthermore prove that systems $D-(CH_2)_n-A$ may not only undergo rapid photoinduced charge separation but can even display 'exciplex' type emission in a fully extended conformation. Since in solvents of high dielectric constant the driving force for formation of a folded conformation following charge separation is strongly diminished, this may have important implications with regard to the interpretation of exciplex-type emission observed for flexible systems in polar solvents.

Fig. 12 displays preliminary results of calculations (ref. 43) on the influence of the solvent dielectric properties on the conformational energies of fully extended and optimally folded conformations in the ground-, the locally excited- and the charge separated-state of **11**. For this purpose we used the simplified model **12** to calculate via molecular mechanics (ref. 44) the relative steric energies as well as the electrostatic effects as a function of the conformation and of the medium dielectric constant.



The charge separated state was mimicked by putting a localized positive unit charge on N and an evenly distributed negative unit charge on the aromatic ring of **12**. The calculated energy of the charge separated state was corrected for the solvation energy without differentiating the two conformations by the Born equation for an ion pair with an average ion radius r via eqn(4):

$$\Delta E_{\text{solv}} = -(e^2/r)(1-1/\epsilon) \quad (4)$$

For r we took $r = 3.3 \text{ \AA}$, which is a reasonable value in view of literature data (ref. 23, 25, 32). Subsequently the energies of the excited states (i.e. the locally excited state and the charge separated state) were offset relative to the ground state to reproduce (i) the gasphase zero-zero excitation energy of the cyanonaphthalene chromophore (89 kcal/mol) (ref. 38), and (ii) the CT fluorescence energy of the extended conformation in saturated hydrocarbon solvents ($\approx 380 \text{ nm}$; 75 kcal/mol). As expected, in the ground state as well as in the locally excited state the extended conformation is by far the most stable irrespective of the medium dielectric properties. In the charge separated state, however, this order is reversed for medium dielectric constants ranging from $\epsilon = 1$ to 4, i. e. for media ranging from the gasphase to about the polarity of diethyl ether. This is in reasonable agreement with the conclusion drawn above from the solvent effect on charge-transfer fluorescence of **11** (see Table 1 and Fig. 11) which indicates a change-over of the geometry of the emitting state in this polarity region. Evidently this point is bound to shift to higher dielectric constants for more flexible systems than **11** but, as discussed by Weller et al. (ref. 32), even for intermolecular systems a change-over from a contact ion-pair (i.e. an exciplex) to a solvent separated ion pair being more stable is expected to occur at $\epsilon \geq 7$.

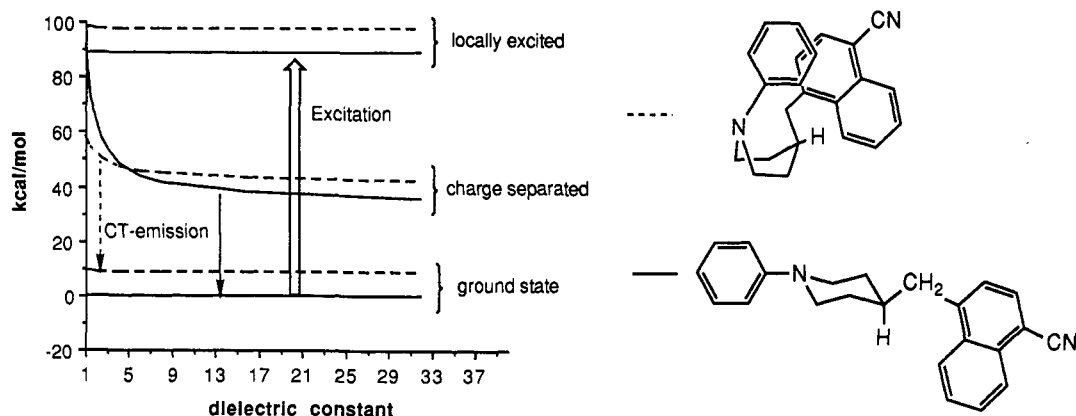


Fig. 12. Calculated (see text) energy of the charge separated state relative to the ground- and the first locally excited singlet state of **11** in fully extended and folded conformation as a function of the dielectric constant of the medium.

While in view of the approximations made Fig. 12 must be considered to be highly qualitative it serves to explain the reasons why **11** displays all features of the harpooning mechanism. Most importantly the D/A pair incorporated is sufficiently strong to make electron transfer in an the extended conformation feasible over the full range of dielectric constants including the low dielectric constant regime in which subsequent, electrostatically driven, 'folding' is to be expected. In fact supersonic jet studies (ref. 38) showed that in vacuum the 'vertical' energy gap separating the locally excited and charge separated states amounts to no more than 1700 cm^{-1} or 4.85 kcal/mol . For weaker D/A pairs electron transfer in apolar solvents requires prior adoption of a folded conformation in the ground- or locally excited state or the application of highly polar solvents that counter act folding once electron transfer has occurred. It's important to note that freezing of the solvent decreases the conformational mobility of any solute *as well as* the solvating capacities of the solvent. This implies that (re)appearance of local fluorescence upon freezing solutions of flexibly bridged D/A systems in polar solvents is no proof for the electron transfer in mobile solution being conformationally restricted.

Acknowledgements

The author gratefully acknowledges the important contributions of P. Pasman, who led the way to the development and study of rigidly bridged systems in our laboratory, as well as those of H. Oevering and J. Kroon who expanded the scope of these studies in a fruitful collaboration with M.N. Paddon-Row and his coworkers (University of New South Wales), with N.S. Hush (University of Sydney) and with J.M. Warman and M.P. de Haas (University of Delft). The recent progress in revealing the dynamics and consequences of intramolecular harpooning effects would have been impossible without the dedication and cooperation of G.F. Mes, H.J. van Ramesdonk, B. Wege-wijs, R.M. Hermant, D. Bebelaar and R.P.H. Rettschnick.

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