

CONFORMATIONAL DYNAMICS AND CHARGE SEPARATION IN THE EXCITED STATE OF BRIDGED DONOR–ACCEPTOR COMPOUNDS

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The process of intramolecular charge separation was studied in three nearly identical donor–bridge–acceptor compounds (1–3) under jet-cooled conditions. Each consists of a vinylcyanonaphthalene group as a powerful electron acceptor and an anilino derivative as an electron donor, separated by a rigid hydrocarbon bridge. The only difference between the three compounds is the substituent at the *para* position of the anilino group, which directly influences the ionization potential of the donor. For compound 1, which has the weakest donor of the three, it is found that excitation at (or very near) the electronic origin of the acceptor chromophore results exclusively in local emission, while excitations with an excess energy $>60\text{ cm}^{-1}$ lead to a distinct red shift. Comparison with 2 and 3 shows that the red-shifted band can be attributed to a charge-separated state with an extended conformation, in which an electron has been transferred across three sigma bonds. Interestingly, this charge separation process appears to be more efficient in 2 and 3 than in 1, resulting in complete quenching of the local emission even at the lowest energy excitations. These observations are interpreted in terms of intramolecular radiationless transition theory and a comparison is made with the behaviour of (semi)flexibly bridged systems in which charge separation was shown earlier to be linked to a major, electrostatically driven reorganization.

1. INTRODUCTION

Linked donor (D)–acceptor (A) systems of the type D–bridge–A, in which the bridge is a saturated hydrocarbon moiety, have been developed into a major tool for studying various aspects of electron donor–acceptor interactions. Especially the phenomenon of photoinduced charge separation has been studied extensively,¹ i.e. electron transfer from donor to acceptor upon optical excitation of either of the chromophores to create the highly dipolar charge transfer (CT) state

$D^+ \text{--} \text{bridge--} A^-$. One of the most important conclusions to emerge from this work is that long-range electron transfer has been shown to be a remarkably efficient process for molecules incorporating sufficiently strong D–A couples and rigid bridges.² At the same time, it has become evident that the hydrocarbon bridge, originally only introduced to limit the range of distances and relative orientations available to D and A, can play an ‘active’ role in mediating interaction between D and A. In the condensed phase, however, such intra-molecular interaction is inevitably accompanied by interaction via the medium surrounding the D–bridge–A molecules.

Therefore, it is very interesting that in recent years it has been found that various D–bridge–A systems are

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amenable to study in the gas phase under jet-cooled conditions.^{3–13} In this way any assistance of the medium is eliminated and information may be obtained on the efficiency of purely internal processes in these isolated, solvent-free systems. These studies have until now mainly been focused on exciplex formation in (semi)flexibly bridged molecules and have revealed that the conformational changes required to convert the extended ground-state molecule to the folded, emissive exciplex can either occur by internal vibrational redistribution prior to charge separation or by electrostatically driven folding following long-range charge separation ('harpooning mechanism'), depending on the D and A groups attached. The latter process was discovered^{4,5} for compounds **1r**, **2r** and **3r** (see Scheme 1) and constituted the first experimental evidence for solvent-free long-range charge separation, involving a curve-crossing process in an extended conformation from the locally excited state to a charge separated state. Although the charge separation step in these and some related semi-rigid molecules¹⁰ such as **4** is endothermic, the consecutive folding process from a chair to a boat-like piperidine ring leads to an enormous gain in Coulomb energy, which easily ensures that the zero level of the emissive exciplex state lies far below that of the locally excited state.

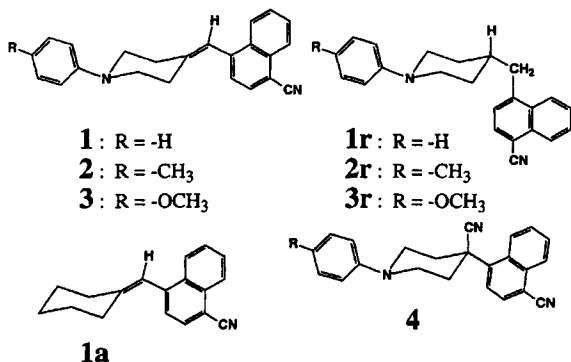
In this paper, mainly the behaviour of jet-cooled **1**, **2** and **3** is reported and a comparison is made with that observed for more flexible systems such as **1r–3r** and **4**, both in the gas phase and in solution. An interesting aspect of **1–3** is that the dipole moment of the emissive CT state in solution has been found to be of a magnitude (*ca* 25 D) consistent with an extended conformation, irrespective of the solvent dielectric constant.^{14,15} This may be attributed not so much to a higher steric barrier for folding from chair to boat as compared with **1r**, **2r** and **3r**, but more in particular to a much smaller gain in Coulomb energy resulting from such a folding, since the

folding process of the piperidine ring in **1** (as visualized in Figure 1) cannot lead to close contact of D and A as it does in **1r**.^{5,16} It therefore seemed likely that **1** may be considered to behave as a rigidly bridged system also in the gas phase.

Recently, it has been pointed out^{17,18} that in fully rigid D–bridge–A compounds the range across which charge separation could occur under isolated (jet-cooled) conditions must be limited, and in fact may be significantly smaller than in (semi)flexible systems where the charge-separated state can be stabilized by subsequent electrostatically driven folding. On the other hand, the rigid series **1–3** contain a stronger acceptor chromophore than the **1r–3r** series by an amount of *ca* 0.2 eV, as judged by the difference in reduction potentials between 1-vinyl-4-cyanonaphthalene (–1.76 V relative to SCE in acetonitrile¹⁴) and 1-cyanonaphthalene (–1.96 V relative to SCE in acetonitrile¹⁹), and it is therefore expected that their CT state is lower in energy at any given D–A distance. Furthermore, the sigma skeleton between D and A now consists of three σ bonds (instead of five), leading to a shorter charge separation distance and presumably larger electronic coupling.

The fluorescence of jet-cooled **1** was studied in our laboratory a few years ago and the preliminary results were described in a thesis by Hermant.¹⁵ It was found that excitations in excess of *ca* 170 cm^{–1} above the origin caused a red shift of the resulting emission band of *ca* 34 nm (from 338 to 372 nm), whereas the emission of the monochromophoric reference compound **1a** (see Scheme) was not affected by higher excitation energies and remained constant at 338 nm. Therefore, the red-shifted emission band of **1** was attributed to the CT state and it was concluded that only a very small barrier existed for electron transfer. Interestingly, extrapolation from the solution-phase CT fluorescence maxima to the gas phase, employing the Lippert–Mataga relation,²⁰ leads to a predicted CT maximum of *ca* 358 nm,^{14,21} i.e. within *ca* 1000 cm^{–1} of that found in the jet upon excitation with sufficient excess energy. This supports our assumption that the conformation of the emissive CT state of **1** is essentially unchanged in the gas phase.

The interpretation of the fluorescence spectra in the jet was hampered by the fact that the local and CT emission bands of **1** strongly overlap, particularly when detected via our broad-band (20 nm) monochromator, which does not resolve the local emission into the sharp features that are so characteristic of supersonic jet studies. Otherwise, a clear distinction between the broad and structureless CT fluorescence and the well resolved local fluorescence might have been observed, which would have allowed us to assign these emission bands with more confidence. Another way to confirm our interpretation would be to lower the CT level relative to the locally excited state, so that the CT emission band



Scheme 1. Structure of the rigidly bridged D–A systems **1–3** and related semi-flexibly bridged systems **1r–3r** and **4** and the acceptor model **1a**

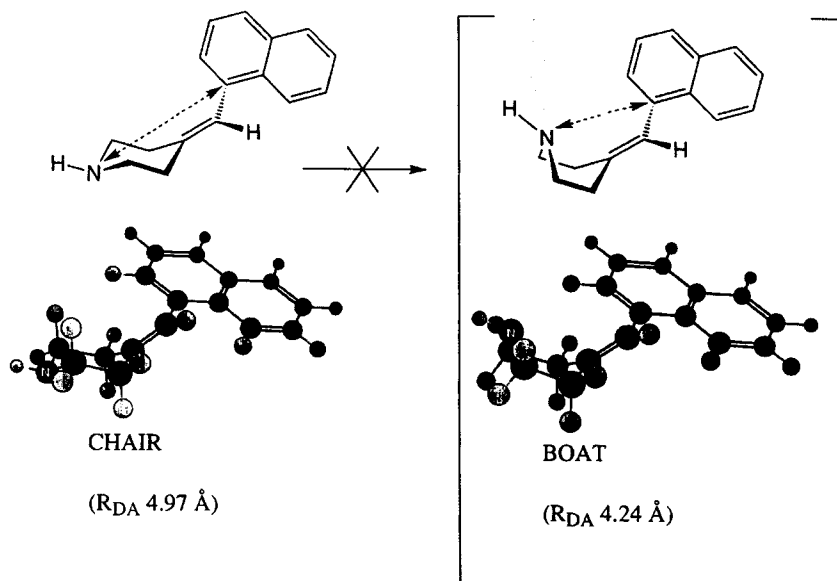


Figure 1. Effect of chair-boat conversion on D-A distance in a model system for 1-3 in which the donor is represented by an amino nitrogen and the acceptor by a vinyl-naphthalene unit. R_{DA} is measured from the nitrogen to C-1 of naphthalene. Note the relatively minor reduction in distance that would be achieved by a chair to boat conversion

would be shifted further to the red. Not only would this avoid the overlapping of the bands, but this shift of the CT band itself would be very convincing evidence for the nature of this fluorescence. Another interesting aspect would be that the apparent barrier to electron transfer might be lowered still further, possibly to the point where even 0-0 excitation would lead to charge separation.

For this purpose compounds 2 and 3 were synthesized. Again, as was the case for the series 1r, 2r and 3r,⁵ by introduction of a methyl or methoxy group at the *para* position of the donor moiety the molecule was only slightly modified, leaving the excitation spectrum, 0-0 transition energy, electron affinity and R_{DA} virtually unaltered. The only important difference is the lowering of the ionization potential of the donor $I(D)$ of 2 and 3 with respect to 1, which is expected to lead to a lowering of the CT energy level by the same amount.²² The results, described in this paper, are indeed as predicted above: by its dependence on $I(D)$ the red-shifted band could readily be identified as CT emission and furthermore the electron transfer in 2 and 3 is shown to require no excess energy at all. Moreover, the local emission of 2 and 3 is completely quenched at all excitation energies studied, testifying to an extremely high efficiency of electron transfer even in the gas phase. In the section on the dynamics of electron transfer, the factors responsible for this behaviour are discussed qualitatively in

terms of a radiationless transition in an isolated molecule.

To start with, the excitation spectra obtained during this study proved to contain some intriguing patterns, which are explained and interpreted below.

RESULTS AND DISCUSSION

Excitation spectra

The onset of the excitation spectra of jet-cooled 1, 2 and 3 shows a very rich vibrational structure in the region of the origin, which is already strongly congested and contains numerous regularly spaced peaks. In order to facilitate the interpretation of these spectra, the excitation spectrum of 1a was also measured and compared with that of 1 (see Figure 2).

Compound 1a functions as a model for the acceptor chromophore of 1, incorporating a 1-vinyl-4-cyanonaphthalene group with a six-membered aliphatic ring connected to it, but lacking the donor group. From the nearly identical position of the origins of 1 and 1a and the similarity of the vibrational patterns, it is clear that the spectra can be attributed to the 1-vinyl-4-cyanonaphthalene moiety, which has the lowest 0-0 transition at *ca* 325 nm. The 1-vinylnaphthalenes are known²⁴ to be non-planar in the ground state and four stable conformations are conceivable during a complete

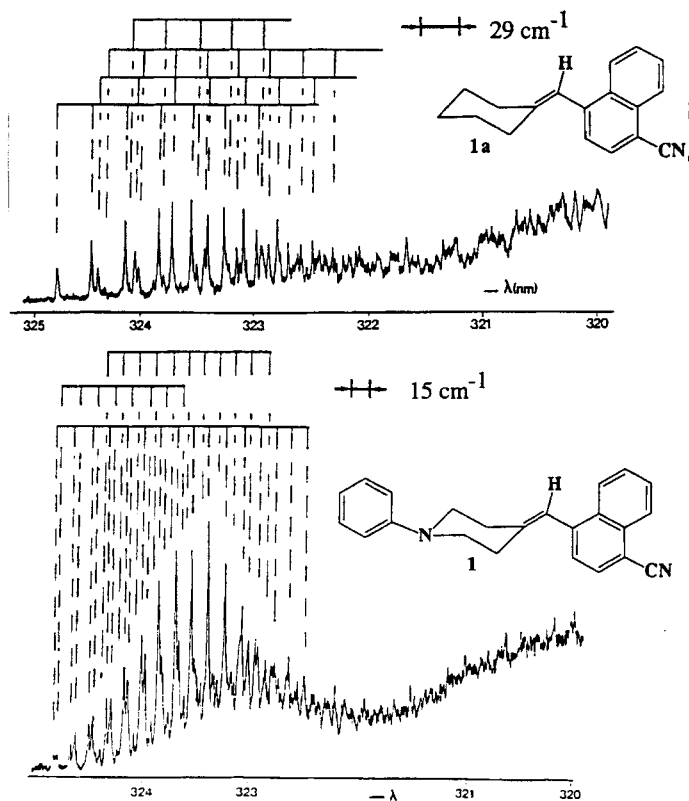


Figure 2. Excitation spectra of jet-cooled **1a** and **1** ($\lambda_{\text{det}} = 340\text{ nm}$, bandwidth 20 nm). In the spectra four (**1a**) and three (**1**) progressions are identified with a regular vibrational spacing amounting to 29 cm^{-1} in **1a** and 15 cm^{-1} in **1**.

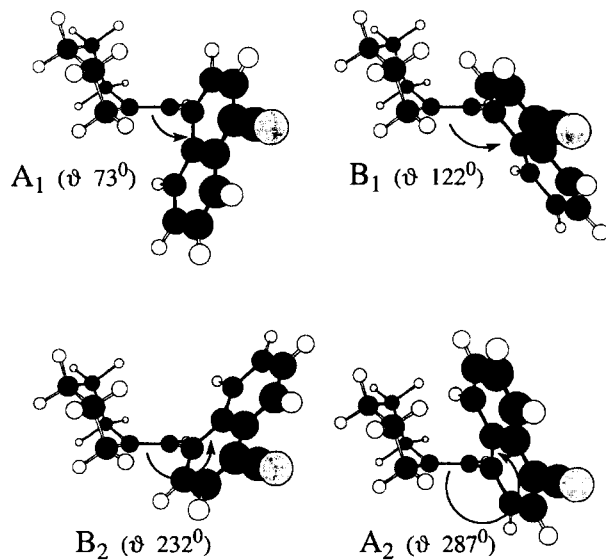


Figure 3. The four ground-state conformations of **1a** resulting from rotations around the vinyl naphthalene bond as calculated by AM1. The twist angle ϑ is defined as the dihedral angle between the vinyl and naphthalene planes, as indicated by the arrows

rotation around the bond joining the vinyl and naphthyl groups (dihedral angle ϑ). The angles and energies of these four conformational minima (depicted in Figure 3) were calculated for **1a** by means of the AM1 method²⁵ and are given in Table 1.

Each of these conformations might generate its own origin transition, especially since these conformational differences appear within the chromophore, so that even small effects will directly influence the transition energy. Indeed, this seems to be the case for **1a**, where four origins are observed in the excitation spectrum (see Figure 2), whereas for **1** only three are found.

The most striking aspect of these excitation spectra is that every origin has an extremely long and constant low frequency progression of 15 cm^{-1} (in **1**) and 29 cm^{-1} (in **1a**), which can be attributed to the torsional vibration around the single bond that connects the vinyl and naphthalene groups. The bell-shaped intensity distribution of the peaks within these progressions clearly indicates that the minima of the potential curves of the S_1 and S_0 states are displaced with respect to each other along the ϑ coordinate. We interpret this to result from the increased planarity of the S_1 state compared with S_0 , in which case the large difference in ϑ between S_0 and S_1 would be the cause of the long and constant progression. This situation has also been found for, e.g., biphenyl,^{26,27} which has a dihedral angle between the phenyl rings of 42° in S_0 and is planar in the S_1 state, while recently Cable and Westrick²⁸ reported similar findings for benzylidenecyclopentane (BCP) and benzylidenecyclohexane (BCH), where the amount of steric hindrance between the allylic hydrogens of the alkane ring and the aryl hydrogens is similar to that in **1** and **1a**.

Inspection of the excitation spectra of compounds **2** and **3** (see Figure 4) reveals that they display mainly the same features as described above for **1**. The lowest energy transition is located at 325.14 nm for all three molecules. Owing to the large displacement of the S_1 potential curve relative to the ground state, it might be that the true origins of these spectra cannot be observed, but for convenience we refer to these lowest transitions as origins.

For compound **2** three origins²⁸ (recognizable by the

Table 1. Heats of formation (kcal mol^{-1})^a and twist angles ϑ as calculated for **1a** by means of AM1

Conformer	$\vartheta(^{\circ})^b$	Energy (kcal mol^{-1})
A ₁	73	61.84
B ₁	122	61.14
B ₂	232	61.06
A ₂	287	61.94

^a $1\text{ kcal} = 4.184\text{ kJ}$

^b See Figure 3 for definition of ϑ

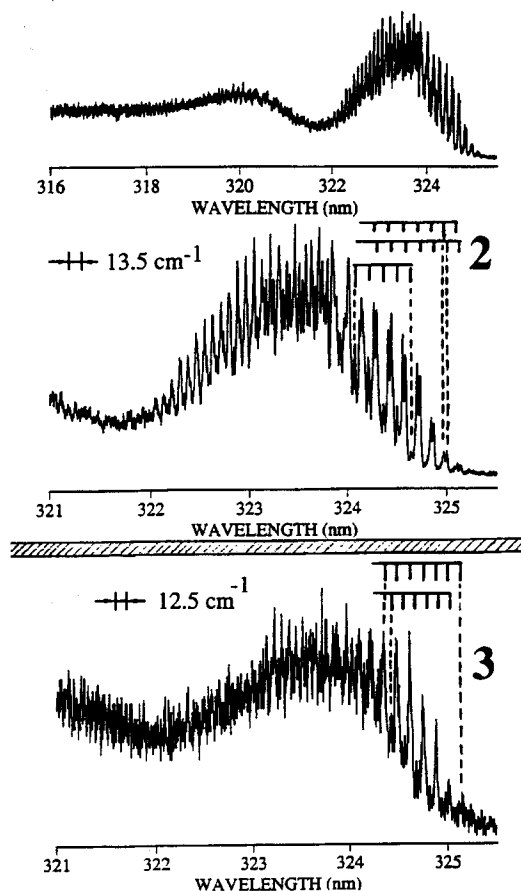


Figure 4. Excitation spectra of **2** (range $>316\text{ nm}$ and expansion of the range $>321\text{ nm}$) and of **3** (range $>321\text{ nm}$); $\lambda_{\text{det}} = 375$ and 395 nm , respectively

progressions built on them) are found, with frequencies and intensity ratios similar to those of **1**, whereas for **3** only two origins are discernible. As for the progressions themselves, the vibrational spacings are remarkably constant within one progression and also for the different progressions within one spectrum, but they decrease slightly from **1** to **3**, since the energy of torsional modes is a function of the reduced masses of the two parts of the molecule relative to the torsional axis. This is illustrated by the difference between **1** and **1a**, where the extra mass of the donor moiety leads to a sharp decrease of the torsional vibration energy from 29 to 15 cm^{-1} .

The values for **2** and **3**, 13.5 and 12.5 cm^{-1} , respectively, show that this vibration frequency is lowered further by introducing the donor substituent in the molecule, while that one with the heavier substituent (the methoxy group in **3**) has the lowest vibration

frequency, which nicely supports our interpretation of this low-frequency mode. In a way, this is a direct influence of the extra substituent at the other end of the molecule on the excitation spectrum of the acceptor (which we were trying to avoid, see Introduction), but this peculiar side-effect of the increased mass of the donor will obviously not alter the electronic properties of **2** and **3** to any significant extent.

In conclusion, the most important thing to emerge from this section is that the spectra of **1**, **2** and **3** are similar in appearance and that the transition energies involved in S_0 - S_1 excitation are equal for these compounds. It appears that our assumption that modification of the donor group should have little effect on the properties of the acceptor moiety and on the overall energy involved in electronic excitation of the molecule is fully justified. Therefore, it is all the more surprising that while the onset of the excitation spectrum of **1** was recorded with detection at 345 nm, the spectra of **2** and **3** had to be monitored at 375 and 395 nm, respectively, to obtain any sufficient signal! Apparently, although the initially excited species is clearly the same for the three (as judged by the similarity of the excitation spectra), the emitting species obviously is not, leading us to the conclusion that even these very low-energy excitations of **2** and **3** are followed by efficient relaxation to a state that is appreciably lower in energy than the DA^* state.

Emission spectra

The relaxation process described above for compounds **2** and **3** was earlier also found¹⁵ to take place in the excited state of **1**, as could be inferred from its emission spectra, but only for excitations above a certain threshold energy. Upon excitation of **1** near its origin, an emission band is observed at 338 nm, which can be attributed to local emission of the acceptor group.



Figure 5. Fluorescence spectra of jet-cooled **1** excitation at 324.41 nm (●—●) and 323.29 nm (●⋯●), corresponding to excess energies of 60 and 166 cm^{-1} , respectively.

Excitations in excess of ca 60 cm^{-1} lead to a broadening and red shift of this band, while still higher excitations (>170 cm^{-1}) ultimately result in a band centred at 372 nm (see Figure 5), attributed to CT emission which is calculated to be around that value in the gas phase (see Introduction), provided that the chair conformation of the piperidine ring is retained upon charge separation.²⁹

In contrast, such a threshold-like behaviour was not observed for **2** and **3**. Even the lowest energy excitations (at 325.01 and 325.04 nm) leading to sufficient fluorescence to allow a reliable estimate of its maximum do not result in any discernible local emission. Excitation of any of the vibrational peaks (or of the broad absorption region around 320 nm) always leads to a red-shifted emission with a maximum at ca 377 nm for **2** and 395 nm for **3**. In Figure 6, the fluorescence spectra of **2** and **3** are compared with that of **1**, at an excitation energy where the emission of **1** solely consists of the red-shifted band.

The differences between the maxima of **1**, **2** and **3** clearly testify to the influence of the donor substituent on the energy level of the emitting state, which can only be explained if the red-shifted emission band arises from the CT state. The differences in red shift of 360 cm^{-1} (0.045 eV) for **2** and 1570 cm^{-1} (0.195 eV) for **3** compared with **1** are close to the differences in oxidation potential²² of their donors, which forms convincing evidence for our assignment of this emission band to the CT state.

Furthermore, the already very low barrier for charge separation in **1** is apparently still further lowered in **2** and **3** by this shift in the CT state, making full charge separation in **2** and **3** possible in the gas phase without any excess energy being required. Nevertheless, the sharp and well resolved excitation spectra indicate that the locally excited state must have a definite lifetime before conversion to the CT state occurs. This is discussed in more detail below.

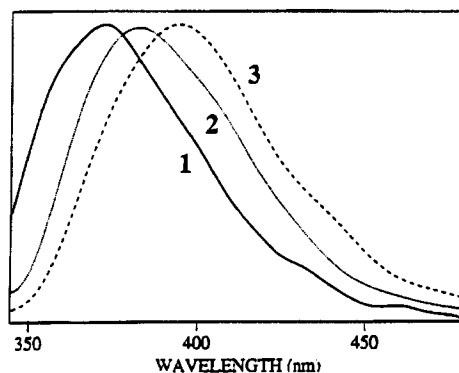


Figure 6. Smoothed fluorescence spectra of **1**, **2** and **3**. $\lambda_{\text{exc}} = 321$ nm.

Dynamics of electron transfer

The efficiency of the electron transfer process in these jet-cooled molecules is remarkable, especially in view of the fact that under solvent-free conditions there is no energetic stabilization of the polar CT state by a surrounding medium and furthermore, coupling to the nuclear motions of the solvent medium (which plays a key role in the Marcus theory^{30,31}) is obviously not possible. Both aspects will be discussed in this section, starting with the energetic feasibility of long-range electron transfer in these systems.

The main stabilization of the CT state in the gas phase is the Coulomb attraction between D^+ and A^- , which decreases strongly on increasing their relative distance. This severely limits the distance R_{ET} at which charge separation can occur, as can be estimated from the equation

$$R_{ET} \text{ (in \AA)} = 14.4/[I(D) - E(A) - E_{00}] \quad (1)$$

This equation was used earlier^{10,18} to calculate the R_{ET} of compounds such as **1r** and **3r**, giving good agreement with the actual distance R_{DA} obtained from molecular modelling studies. For compounds **1**, **2** and **3**, the electron affinity $E(A)$ is estimated³² to be 0.88 eV, the 0-0 excitation energy $E_{00} = 3.81$ eV and the ionization potentials $I(D)$ are 7.57, 7.37 and 7.30 eV, respectively.²³ With these values, equation (1) gives $R_{ET} = 5.0$ \AA for **1**, 5.4 \AA for **2** and 5.5 \AA for **3**.

For the actual R_{DA} in these molecules, we take the distance between the anilino-nitrogen and C-1 of the naphthalene group (see Figure 1), which represent positions reasonably close to the centres of the positive and negative charges developed in D and A upon charge separation. In the chair conformation this gives $R_{DA} = 4.97$ \AA. This corresponds well with the results of various measurements of the excited-state dipole moment in solution^{14,21} that gave a value of $R_{DA} = 4.8$ –5.0 \AA for **1**, **2** and **3**. Hence it can be concluded that for all members of this series R_{DA} is below R_{ET} , which makes charge separation energetically feasible without a significant reduction of the donor-acceptor distance imposed by the chair conformation of the bridging piperidine ring. This also implies that the excess energy of ≥ 60 cm^{-1} needed to induce charge separation in **1** cannot simply be attributed to the energy difference between the zeroth vibrational level of the CT state and the DA^* state, as will be discussed below.

Having established the energetic feasibility of charge separation in the absence of a solvent for this series of molecules, the next step is to investigate the mechanism that is operative in this process. As stressed before by Jortner and co-workers,^{17,34} the occurrence of electron transfer in jet-cooled molecules seems to be at variance with standard theory, which predicts that the rate of electron transfer approaches zero when the medium

reorganization energy (λ_s) is zero. However, if the CT state has a sufficiently high density of vibrational levels that are effectively coupled to and isoenergetic with those of the DA^* state, the intramolecular electron transfer in an isolated DA molecule may be regarded as a radiationless transition in the statistical limit,¹⁷ for which a theoretical formalism is available.^{35,36} In this approach, the rate of electron transfer (k_{ET}) is given by

$$k_{ET} = (4\pi^2/h)V^2FC\rho_{CT} \quad (2)$$

where V is the electronic coupling between D and A, FC is the nuclear Franck-Condon overlap between the locally excited and CT state and ρ_{CT} is the density of states in the CT manifold. In order for the charge separation to be so efficient in these compounds, all three factors should have relatively high values, which will be evaluated in the discussion below.

Starting with V , the photophysical behaviour of compounds **1**, **2** and **3** in solution²¹ is characterized by very fast electron transfer, high CT fluorescence quantum yields and large radiative rates, which clearly shows that the interconnecting bridge (consisting of three σ bonds) in this type of rigid molecules allows for rather strong electronic coupling between donor and acceptor. Recently this was evaluated quantitatively,³⁷ using a three-state model to analyse the electronic coupling elements between ground state, locally excited state and CT state. It appeared that especially V^* , the coupling between the S_1 and CT states, reaches high values (of a few thousand cm^{-1}) in non-polar media.

A high value of V might in principle lead to the possibility of direct excitation into the CT state, a situation we recently discussed¹¹ in our study of two jet-cooled rigid donor-bridge-acceptor compounds with powerful D-A pairs. The excitation spectra of these electronically strongly coupled systems consist of a very broad, structureless band, which could be attributed to CT absorption, i.e. direct population of the CT state from the ground state, implying that instantaneous charge separation occurs across three σ bonds in those molecules. For compound **1**, such a transition might be expected to occur somewhere in the vicinity of the 0-0 transition of the 1-vinyl-4-cyanonaphthalene chromophore, and for **2** and **3** possibly even to the red of that band, since their CT states appear to be appreciably lower in energy than the locally excited state. However, closer inspection of the excitation spectra of **1**, **2** and **3** gives no clear indication of the presence of a CT absorption band. All sharp spectral features in the region 322–325 nm correspond to the excitation of the DA^* state, as explained earlier, and no extra absorption band is found to the red of this spectrum. Furthermore, the broad maximum which occurs at *ca* 320 nm in all three spectra, which might be suspected to be a direct CT transition because of its lack of structure, does not shift with increasing donor strength. Therefore, this band cannot be ascribed to CT absorption, as it would be

expected to shift to the red by the same amount and for the same reason as the maxima of the CT emission bands. A further consequence of this is that the threshold-like behaviour of **1** cannot be attributed to the presence of an underlying CT absorption band. Apparently the extreme broadness of the region around 320 nm is simply due to vibrational congestion, as is often observed in this type of progressional transitions.³⁸ Thus, in contrast to the more strongly coupled DA systems¹¹ mentioned above, the direct transition to the D^+A^- state is apparently very weak relative to the strong local S_0-S_1 ($A-A^*$) transition for the present series, which is in line with the observation that their absorption spectra in solution also give no clear indication for the presence of a CT transition.

Returning to our discussion dealing with equation (2), the second important factor that determines k_{ET} is FC, the Franck–Condon vibrational overlap factor between both excited states. Chatteraj *et al.*¹² pointed out in their study of charge-shift reactions in a supersonic expansion that the geometry change between ‘reactants’ and ‘products’ upon electron transfer occurring in the gas phase is small owing to the lack of interaction of the charged chromophores with the medium. This would imply that the potential energy curves of the initial and final states are not much shifted from each other, resulting in poor vibrational overlap and small FC factors. We feel, however, that in general charge separation processes in the gas phase will be accompanied by an appreciable (internal) reorganization energy (λ_i) due to significant changes in bond lengths and angles in both the donor and acceptor moieties upon electron loss and capture, respectively. For instance, it was estimated¹⁸ from model calculations on the experimental excess vibrational energy dependence of the Franck–Condon overlap factors of jet-cooled **1r** and **3r** that λ_i amounts to 4000–5700 cm^{-1} for these isolated molecules. For the structurally related series **1–3** it may be assumed that a similar value applies. In fact, the energy difference between the fluorescence maxima of DA^* and D^+A^- in **1** (*ca* 8.3 kcal mol^{-1}) suggests that after passing the barrier of *ca* 60 cm^{-1} there is indeed an appreciable relaxation along one or more coordinates. Actually, this situation is reminiscent of the normal Marcus region (in solution), where electron transfer is an activated process due to the displacement between the two potential energy curves. Despite the fact that the original Marcus theory was not designed to account for electron transfer in the gas phase, taking into account the effect of internal reorganization allows one to discuss the interplay between ‘driving force’ ΔG_0 and reorganization energy ($\lambda = \lambda_i$) as the factors creating a barrier to electron transfer also in isolated molecules.^{18,39} Consequently, assuming a situation as in Figure 7, k_{ET} is expected to increase with increasing driving force. Indeed this seems to be the case for our compounds, as the molecules with the stronger donors (**2** and **3**) exhibit

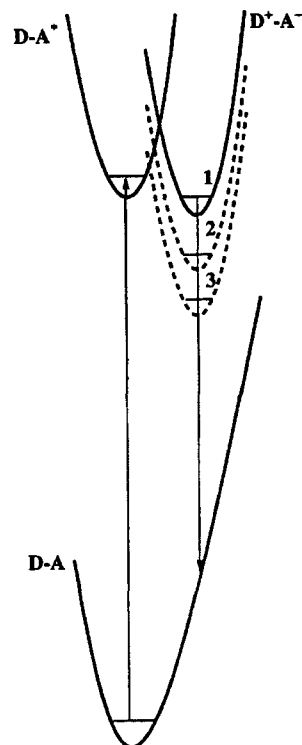


Figure 7. Schematic potential energy curves for the ground state (DA), locally excited state (DA^*) and CT state (D^+A^-) of **1**, **2** and **3**

more efficient electron transfer than **1**. This is in sharp contrast to the prediction of Chatteraj *et al.*,¹² where the assumption of a negligible reorganization energy automatically creates an ‘inverted region’ situation for any exothermic electron transfer, implying that the rate of electron transfer should drop upon increasing that exothermicity, i.e. in going from **1** to **3**. Evidently the actual situation in the series **1–3** corresponds to the Marcus normal region behaviour where the rate increases with increasing exothermicity.

The third and last factor to consider in equation (2) is ρ_{CT} , the density of background vibronic CT states in the vicinity of a vibronic level of the locally excited state. In the case of compounds **1r**, **2r** and **3r**, the CT level appeared to be higher in energy than the locally excited state, resulting in an unfavourably low density of states for the CT state. However, by means of the subsequent folding process, the relaxation of the initial DA^* state is mediated by the sparse manifold of the extended CT state into the quasi-continuum of the final, low-lying exciplex state. For the rigid compounds **1**, **2** and **3**, the relaxation mechanism is simpler, having only two relevant excited states, and the energy gap between the

origins of DA^* and D^+A^- is expected to supply a sufficiently large ρ_{CT} , especially for **2** and **3**. The situation for **1**, which has the smallest energy gap, seems to be slightly different, since excitation near its origin does not lead to charge separation, although slightly higher excitations already result in complete quenching of the local emission. This may be interpreted as a manifestation of the rapid increase of ρ_{CT} with increasing excess energy. The fact that the electron transfer process becomes so efficient within such a small energy domain might partly be due to the presence of the unusually low-frequency torsional mode of the DA^* state (as discussed earlier), which may be helpful in (a) effectively coupling this state to the CT state, thereby replacing the traditional solvent low-frequency vibrational modes, and (b) increasing the electron affinity of the vinylcyanonaphthalene group, by specifically channelling excitation energy into the torsional motion to planarity, and thereby increasing the pi-conjugation. It should be noted that the importance of low frequency internal vibrations for intramolecular electron transfer rates has been shown recently even for systems in the solution phase.⁴⁰

From the discussion above, it may be concluded that the efficient gas-phase electron transfer in these molecules seems to be generally in accord with equation (2), which indicates that the theory of intramolecular radiationless transitions gives a good description of the charge separation process.

One last point worth mentioning concerning the dynamics of the process is that, although the local emission is completely quenched (especially for **2** and **3**), the excitation peaks that are detected by monitoring the CT fluorescence are nevertheless very sharp and do not show any significant lifetime broadening. This seems surprising and is in contrast with the results for the rigid compounds we described earlier,¹¹ where not a single sharp feature was observed in the excitation spectra, owing to very rapid relaxation to the CT state. However, similar behaviour has been reported for cases involving intermolecular exciplexes⁴¹ and flexibly bridged exciplexes^{7,10} and a simple explanation can be given by considering that, although the absence of local emission requires electron transfer to be on the sub-nanosecond time-scale, no lifetime broadening is expected if the relaxation to the D^+A^- state occurs in >10 ps. Consequently, a rough measure of the electron transfer time-scale can be gathered from these two limits.

Comparison between rigidly and semi-flexibly bridged systems

It is of considerable interest to compare the behaviour of the virtually rigid systems **1–3** described above with that reported by us earlier for closely related semi-flexibly bridged systems such as **1r–3r** and **4**.

As mentioned above, charge separation in the latter systems under isolated conditions can only be induced by excitation with a significant excess energy, which amounts to $1700 \pm 200 \text{ cm}^{-1}$ for **1r** and **2r**,^{4a,5} $750 \pm 200 \text{ cm}^{-1}$ for **3r**⁵ and as high as 3800 cm^{-1} for **4**.¹⁰ This behaviour contrasts with the low to negligible excess energy required to induce charge separation in **1–3**.

Because the spectroscopic origins in the excitation spectra of all compounds are nearly identical (i.e. $E_{00} = 3.87 \text{ eV}$ for **1r–3r** and **4** and 3.81 eV for **1–3**), it is clear from, e.g. equation (1), that the lower excess energies required for charge separation in **1–3** must be due to the higher electron affinity of the acceptor and also a smaller charge separation distance, both of which stabilize the charge separated state.

Remarkably, however, the CT emission for **1–3** (see Figure 6) occurs at significantly higher energy than that observed⁵ for **1r–3r**. In fact, the CT fluorescence maximum of the latter compounds under isolated conditions occurs at $0.48 \pm 0.015 \text{ eV}$ lower energy than of **1–3**, while **4** fluoresces 0.44 eV to the red¹⁰ of **1**. As we have pointed out before,^{5,10} the huge Stokes shift which this implies for the CT fluorescence of **1r–3r** and **4** as compared with **1–3** under isolated conditions can only be understood if the former systems undergo a dramatic internal reorganization process subsequent to the initial charge separation, a process that brings D and A closer together by folding of the interposed semi-flexible bridge. We have reported earlier^{16,19,42–46} that in solution this electrostatically driven 'harpooning' process can be slowed sufficiently to make it kinetically resolvable by application of time-resolved spectroscopy and temperature variation. We now report that in solution also pressure variation has been found to influence significantly the conformational reorganization of the charge-separated state in, e.g., **4**.

A preliminary demonstration of this effect is provided by the fluorescence spectra obtained for **4** in methylcyclohexane at pressures ranging between 0 and 3.5 kbar (see Figure 8) at 30°C . At low pressure the spectrum is dominated by emission centred at *ca* 460 nm , which is known^{45,46} to stem from a folded CT-state with close D–A contact. At higher pressures, however, a marked shoulder around 400 nm develops, which stems^{45,46} from CT emission emerging in an extended conformation with much larger D–A separation. We note that we are confronted here with the counter-intuitive situation that the contribution of emission from an extended conformation increases at higher pressures! We consider it likely that this remarkable observation is largely due to a decrease in the rate of folding at higher pressures and this is under active investigation by application of pressure-dependent time-resolved spectroscopy, the results of which will be the subject of future publications.⁴⁷

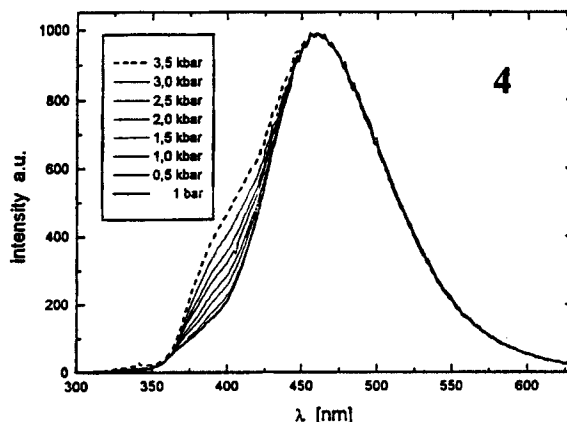


Figure 8. Pressure dependences of the fluorescence spectrum of **4** in methylcyclohexane solution at 30 °C

CONCLUSION

Whereas in earlier publications the feasibility of solvent-free, long-range, photoinduced charge separation was demonstrated either in systems that undergo a consecutive major conformational change or in systems where direct excitation via a charge-transfer transition is available, we have now shown that it can also be achieved via local excitation in systems such as **1–3** that do not undergo major conformational changes following charge separation.

EXPERIMENTAL

The synthesis of compounds **1–3** and **1r–3r** has been described elsewhere.⁴⁸

The fluorescence excitation and dispersed fluorescence spectra of isolated molecules were measured using a continuous free jet combined with a pulsed tunable UV laser system. Briefly, a laboratory-made expansion chamber is evacuated by a Roots pump (Edwards E4500, 500 m³ h⁻¹), backed by a rotary pump (Edwards E2M80, 80 m³ h⁻¹), resulting in a typical background pressure of 0.1 mbar during experiments with a helium pressure of 3 bar. An excimer laser (Lumonics HyperEX-460) operating at 80 Hz (in some cases 40 Hz) was used as excitation source, pumping a dye laser (Lumonics HyperDYE-300) at 308 nm (XeCl). A tunable UV laser beam was obtained by scanning the dye laser and simultaneously frequency doubling its output with KDP crystals, by means of a HyperTRAK-1000 system. Fluorescence from the jet-cooled compounds was collected by a spherical quartz condenser (Melles Griot 01MCP119, focal length = 50 mm) imaging on to the slit of a Zeiss M20 grating monochromator (spectral resolution 10–20 nm) and into an EMI S20, 9558QA photomultiplier. The

signal from the photomultiplier was fed into a gated integrator and boxcar averager from Stanford Research Systems (SR250) and the SR267 and SR277 programs were used on an IBM AT personal computer to acquire data from the boxcar with the SR245 computer interface module. The spectra were corrected for the intensity of the UV laser light and analysed using a laboratory-written spectrum analyser program.

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