Tetrahedron Vol. 45, No. 15, pp. 4751 to 4766, 1989
Printed in Great Britain.

0040-4020/89 \$3.00+.00
Maxwell Pergamon Macmillan plc

CHARGE-TRANSFER ABSORPTION AND EMISSION RESULTING FROM LONG-RANGE THROUGH-BOND INTERACTION; EXPLORING THE RELATION BETWEEN ELECTRONIC COUPLING AND ELECTRON -TRANSFER IN BRIDGED DONOR-ACCEPTOR SYSTEMS.

H. Oevering and J.W. Verhoeven*,
Laboratory of Organic Chemistry, University of Amsterdam,
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.
M.N. Paddon-Row*,
Department of Organic Chemistry, University of New South Wales,
P.O.Box 1, Kensington, N.S.W. 2033, Australia.
J.M. Warman*,
I.R.I., Delft University of Technology, Mekelweg 15, 2600 GA Delft, The Netherlands.

(*Received in USA* 9 *December* 1988)

Abstract.
The electronic absorption- and emission spectra of seven (D)onor-(A)cceptor systems are studied with the general structure D-bridge-A, where the bridge consists of an extended, rigid, saturated hydrocarbon skeleton that separates D and A by distances ranging from 3 to 12 C-C σ-bonds. Across bridges with a length up to six σ-bonds sufficient electronic interaction occurs to cause a detectable perturbation of the electronic absorption spectra and for lower homologues this leads to the appearance of discrete intramolecular charge-transfer absorptions with an intensity that is strongly enhanced by intensity borrowing from symmetry-matched local transitions. In the fluorescence spectra discrete charge-transfer (CT) type emission has been detected for bridge lengths up to ten σ-bonds. The radiative transition probability of this CT emission provides a direct measure for the electronic coupling matrix element (H_{da}) between the charge-separated- and the groundstate. The magnitude of H_{da} is found to decrease exponentially with the number of intervening σ-bonds from 850 cm^{-1} at 3-bond separation to 17.6 cm^{-1} at 10-bond separation. Furthermore the rate of charge-recombination in the compounds studied is found to be proportional to the square of H_{da}, thus providing an experimental verification of this often implied "golden rule" relation.

1. INTRODUCTION

Intramolecular electron transfer between redox centres interconnected, but held spatially apart, by various types of more or less rigid, saturated hydrocarbon bridges has recently been reported by a number of research groups[1-36].

Already in an early stage Pasman et al. [32-35] suggested, that *through-bond interaction* of the electron-donor (D) and the electron-acceptor (A) moieties via the bridge σ-orbitals is very likely involved in mediating the electron transfer in such systems, implying that the electronic coupling occurs via a special form of super-exchange. The structural and conformational aspects of the saturated hydrocarbon skeleton, that comprises the interconnecting bridge, must then play an important role in defining the extent of such interaction and thereby the efficiency of electron-tunneling through the bridge.

These suggestions have led to a recent upsurge of attempts[12, 37-43] to provide a theoretical framework, that allows prediction of the through-bond coupling between redox-centres via various types and lengths of saturated hydrocarbon bridges. This is not an easy task since it requires quantitative evaluation of the tunneling matrix element (H_{da}) resulting from the very weak interaction between the 'tails' of the D and A wavefunctions as they extend into the bridge. Clearly experimental evaluation of this matrix element for various series of conformationally fully defined systems, each series spanning a large range of D-A distances with a single type of bridge structure, would provide an important gauge to measure the success of any such theoretical treatment.

For a series of three closely related mixed valence systems, this goal has been achieved via the extremely elegant studies of Stein et al.[21], who demonstrated that it is possible to observe directly the intramolecular intervalence absorption of these molecules. The intensity of this absorption band carries information

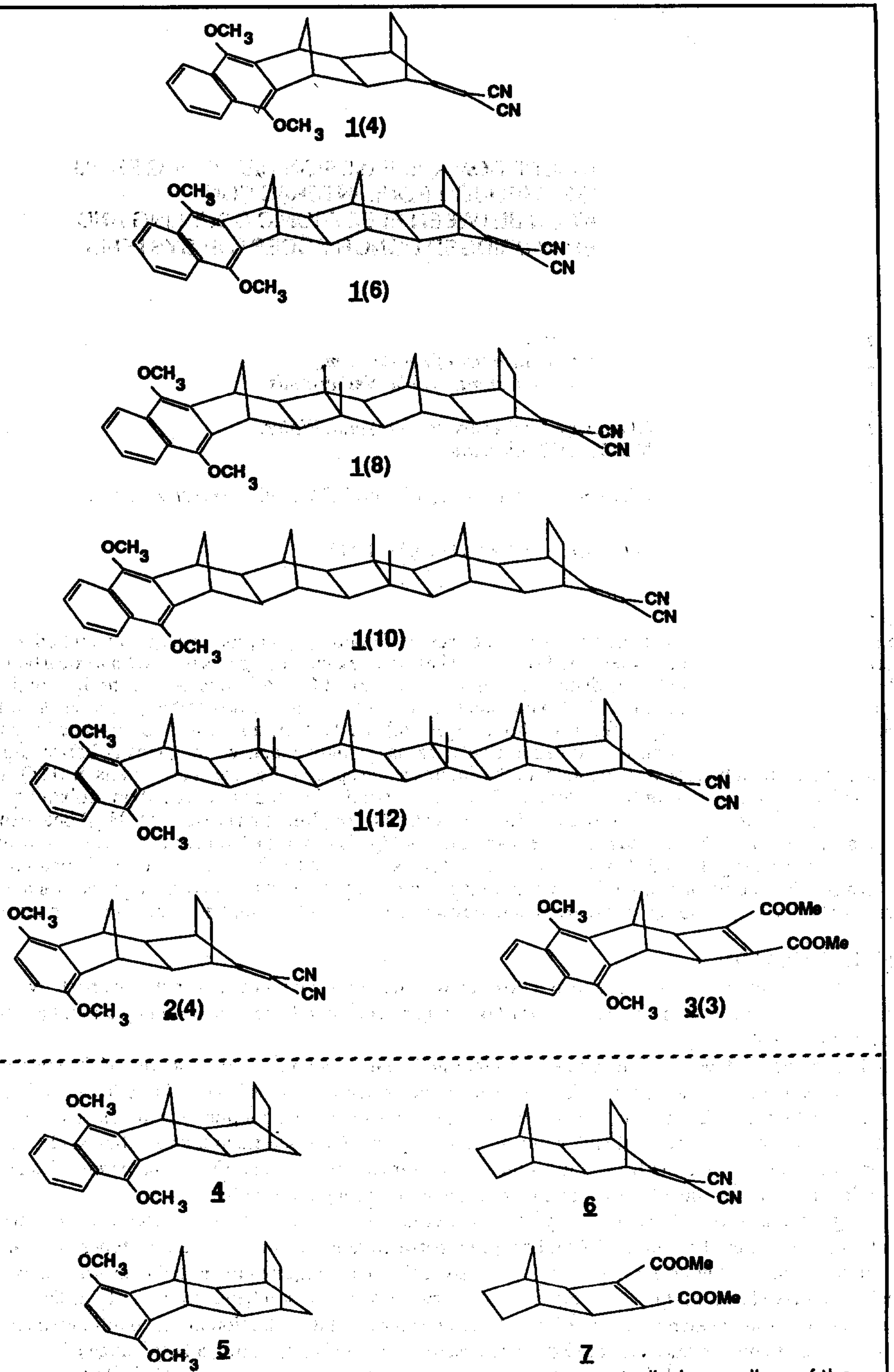

Figure 1 Structures of the bridged donor-acceptor systems studied as well as of the isolated donor modelsystems (4 and 5) and the isolated acceptor modelsystems (6 and 7).

about the coupling between the redox centres and can be related theoretically with the rate of intramolecular electron exchange between these centres[21, 37]. The latter, however, appears not to be accessible for direct experimental evaluation in these systems.

For a number of other bridged D-A systems the rate of photoinduced or thermal intramolecular electron transfer has been measured and efforts have been made[11, 13, 18-20] to calculate therefrom the coupling occurring either 'through-bond' or 'through-space'. This, however, rests heavily upon the ability to evaluate the Franck-Condon factors involved (*vide infra*). Furthermore most of the systems studied, either lack full conformational rigidity - which severely complicates any theoretical treatment - or comprise series that span a very limited range of D-A separations.

We have recently reported[26,53] the synthesis of a series of molecules **1**(n) (see Fig. 1) that contain a single D/A pair (D = 1,4-dimethoxynaphthalene and A = 1,1-dicyanovinyl) held at a rigidly defined orientation by norbornylogous bridges, spanning distances up to about 15 Å (centre to centre) where D and A are interconnected by a sigma-bonded framework comprising the shortest path of n carbon-carbon bonds. We now also report the first members - **2**(4) and **3**(3) - of two series that contain different D/A combinations (see Fig. 1). In addition Fig. 1 shows the structure of 'isolated donor modelsystems' **4** and **5** as well as 'isolated acceptor modelsystems' **6** and **7**.

Clearly the conformational uniformity of the bichromophoric compounds shown in Fig. 1 and the large range of D-A distances covered, makes this series very attractive for theoretical treatment provided that quantitative experimental verification of the strength of D/A coupling can be realized. It was shown before that photoinduced electron-transfer[22-29] occurs in all members of the series **1**(n). The rate of this process has been determined[26, 28, 29] for n = 6, 8, 10 and 12, while for n = 4 it occurs within the limits of the instrumental time resolution. Furthermore the rates of direct charge-recombination in this series have been determined by following the decay of the highly dipolar charge-separated state via time resolved microwave conductivity (TRMC) measurements[23, 25, 27]. Thus measurements of the rates of photoinduced charge-separation and thermal charge-recombination have provided an, albeit rather indirect, measure for the strength of D/A coupling in **1**(n). It should be realized that the rates of photoinduced charge-separation are related to such coupling between the locally excited state (D^*A) and the charge separated state (D^+A^-) while the rates of charge-recombination are related to the coupling between (D^+A^-) and the electronic groundstate (DA).

In this paper it will be shown that a careful study of the electronic absorption and especially of the electronic emission spectra of compounds **1**(n) (n = 4, 6, 8 and 10), **2**(4) and **3**(3) allows evaluation of the radiative transition probability between ground state and charge-separated state, thereby providing a <u>direct</u> measure for the coupling between these states.

2. RESULTS AND DISCUSSION

2.1 Electronic absorption spectra

The systems under study contain two chromophores which are nonconjugatively connected and seem spatially sufficiently apart for one to expect that their absorption spectra are simply the sum of those of the isolated chromophores. Absorption spectra of the four separate reference chromophores are given in Fig. 2.

The absorption spectra of the higher homologues in series **1**(n) (i.e. n ≥ 8) fulfill the classical expectation for nonconjugatively connected chromophores, their absorption spectra being virtually indistinguishable from the sum spectrum of **4** and **6**. This situation is quite different, however, for **1**(6) and especially for **1**(4). Thus (see Fig. 3) a significant broadening of several absorption bands seems to occur in **1**(6), while for **1**(4) very drastic changes occur.

The most pronounced features are: (i) a hypsochromic shift and concomitant intensity decrease of the bands in the 220 - 240 nm region, where both isolated chromophores show their strongest transition, and (ii) the appearance of a strong 'new' absorption at 256 nm. In addition to this a weak absorption tail appears in the 300 - 350 nm region at the long wavelength side of the first donor absorption.

These features are born out more clearly in the difference spectrum shown in Fig. 4. From this it may be concluded that two 'new' absorption bands occur in the spectrum of **1**(4) that cannot be attributed to either

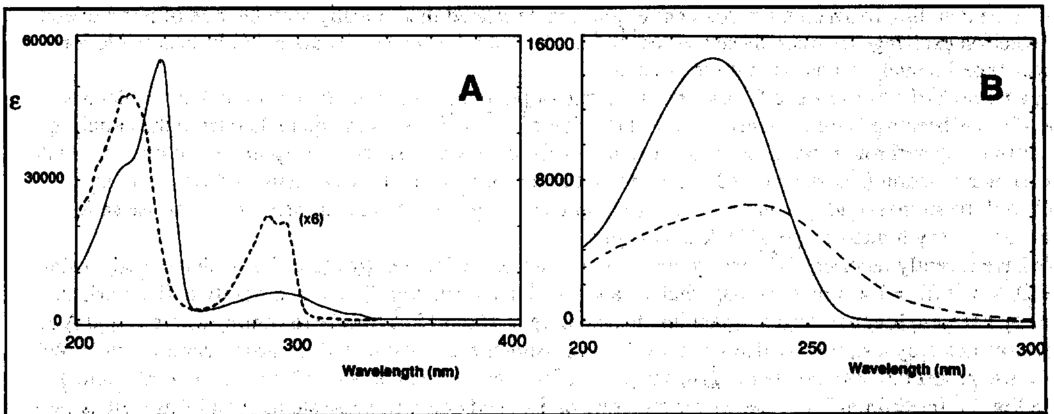

Figure 2 Absorption spectra, in cyclohexane, of the two donor chromophores (A) (**4**(——) and **5**(- - -)) and the two acceptor chromophores (B) (**6** (——) and **7** (- - -)).

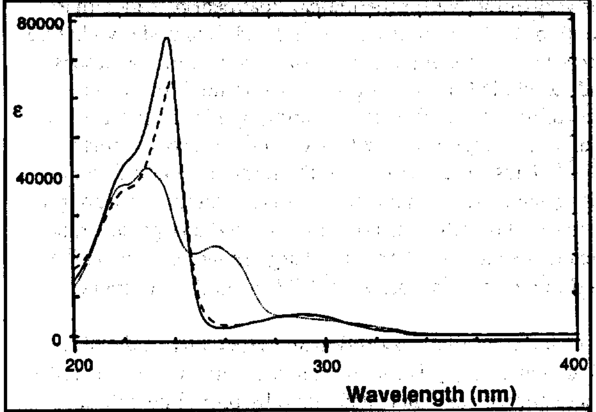

Figure 3 Absorption spectra of **1**(4) (.....) and **1**(6) (- - -) as well as the sumspectrum of **4** and **6** (——) in cyclohexane.

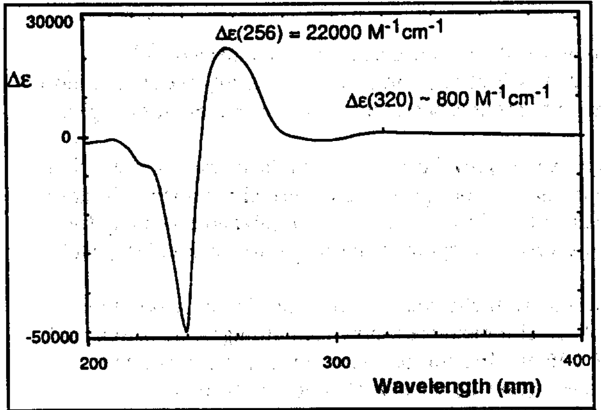

Figure 4 Absorption difference spectrum obtained by subtracting the sumspectrum of **4** and **6** from that of **1**(4).

of the isolated chromophores.
Thus the new absorption maximum already evident in Fig. 3 shows up as a strong band ($\varepsilon = 22000\ M^{-1}cm^{-1}$) at 256 nm in this difference spectrum, while the long wavelength tail is now identified as a weak ($\varepsilon \sim 800\ M^{-1}cm^{-1}$) band with a maximum around 320 nm. Furthermore the hypochromicity of the donor and/or acceptor transitions in the 220 - 240 nm region leads to a strongly negative amplitude of the difference spectrum in this region. The absorption spectrum of **2**(4) (see Fig. 5), in which the 1,4-dimethoxynaphthalene unit is substituted by a 1,4-dimethoxybenzene system, displays very similar features.Thus a strong new band ($\lambda_{max} = 258$ nm; $\varepsilon = 14000\ M^{-1}cm^{-1}$) and a much weaker new absorption feature at longer wavelength (λ(sh) = 300 nm; $\varepsilon = 1500\ M^{-1}cm^{-1}$) arise.

From the electronic absorption spectra of **1**(4) and **2**(4), it is evident that in these compounds extensive electronic interaction between the constituting chromophores occurs, leading to the appearance of new absorptions in the near UV region. In view of the electron donor/acceptor nature of the chromophores it seems logical to attribute these absorptions to transitions with an intramolecular charge- transfer (CT) character. From the extensive literature[44] on intermolecular CT interaction it is well known that multiple CT transitions can be observed if the donor possesses closely spaced ionization potentials and/or the acceptor possesses closely spaced electron affinities. The for-

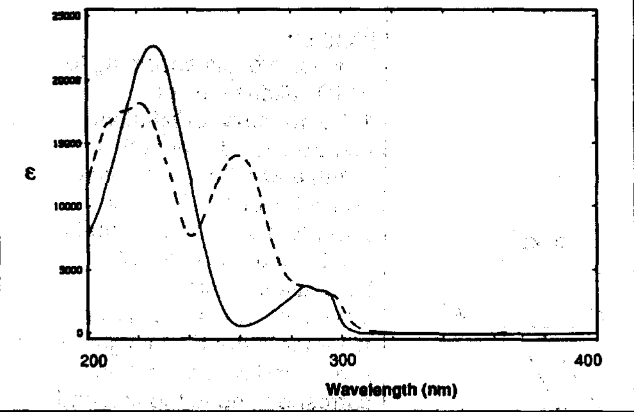

Figure 5 Absorption spectrum of **2**(4) (- - -) and the sum spectrum of **5** and **6** (——) in cyclohexane.

mer situation applies in the present systems as evidenced by HMO calculations and by the observation[26] of two CT transitions at 700 nm and at 495 nm for the complex between the reference donor **4** and the strong electron acceptor tetracyanoethylene (TCNE). The strong bathochromic shift of the CT bands in the **4**/TCNE complex as compared to those in **1**(4) may largely be attributed to the much stronger acceptor properties of TCNE (E_{red} = +0.24 V vs s.c.e. in acetonitrile[44]) as compared to the dicyanovinyl unit (E_{red} = -1.7 V vs s.c.e. in acetonitrile[26]) in **1**(4). This difference in acceptor properties could thus account for a hypsochromic shift of 1.94 eV upon substitution of TCNE by the acceptor incorporated in **1**(4).

Furthermore it should be realized that the intramolecular donor/acceptor separation in **1**(4) is certainly larger than in the intermolecular complex. For the latter a sandwich type orientation with an interplanar separation of ~3.5 Å is most likely, whereas in **1**(4) the closest atom to atom distances amount to 4.6 Å[26]. Because of this larger separation less Coulombic stabilization of the CT states occurs by (14.45/ε)(1/3.5 - 1/4.6) eV if D^+ and A^- are treated as point charges and if ε represents the dielectric constant of the medium between these. Substitution of ε = 2 (i.e. the dielectric constant of saturated hydrocarbons) indicates a further hypsochromic shift of 0.49 eV of the CT transitions in **1**(4) as compared to those in the intermolecular complex. This shift, together with the shift due to the difference in redox potentials gives extrapolated positions of 295 nm and 251 nm for the CT transitions in **1**(4), which is remarkably close to the positions observed (320 nm and 256 nm, see Fig.4) considering the crudeness of the assumptions made !

While the positions of the two 'new' absorptions in **1**(4) (as well as in **2**(4)) are compatible with their assignment to intramolecular CT transitions, the enormously different intensity of these two CT transitions deserves further comment.

As we have pointed out earlier[45, 46] symmetry factors may be of more importance in determining the intensity of CT transitions in rigid systems than in a rather loose intermolecular complex. The symmetry of the low lying CT excited configurations is readily derived from that of the frontier MO's between which the electron transfer formally occurs. Relevant frontier MO's as calculated by simple HMO are shown in Fig. 6. Thehighest occupied and first vacant MO's in donor and acceptor are indicated as d, d* and a, a*, respectively, while the penultimate occupied donor orbital and the next vacant donor orbital are indicated as d-1 and d*+1. Symmetry labels A' and A" are assigned according to the C_s point group of molecule **1**(4) (and **3**(3)).

Recent CNDO/S calculations[42,43] have confirmed the correctness of these symmetry predictions made by the HMO method. The first CT transition in **1**(4) (d → a*) leads to a CT configuration with a symmetry different from the groundstate while the second CT transition (d-1 → a*) leads to a CT configuration with a symmetry identical to that of the groundstate. In a simple two state description the transition dipolemoment of the CT transitions is directly proportional to the amount of mixing between the groundstate and the particular CT excited state and such a model might thus seem to rationalize the differentiation of the intensities of the first and the second CT transition in **1**(4) as well as in **2**(4).

That the situation is in fact more complicated became evident upon studying the absorption spectrum of **3**(3), see Fig.7. This molecule also features C_s symmetry, but now the first vacant acceptor MO (a*) belongs to the A" representation, see Fig. 6. Consequently the symmetry properties of the first and second

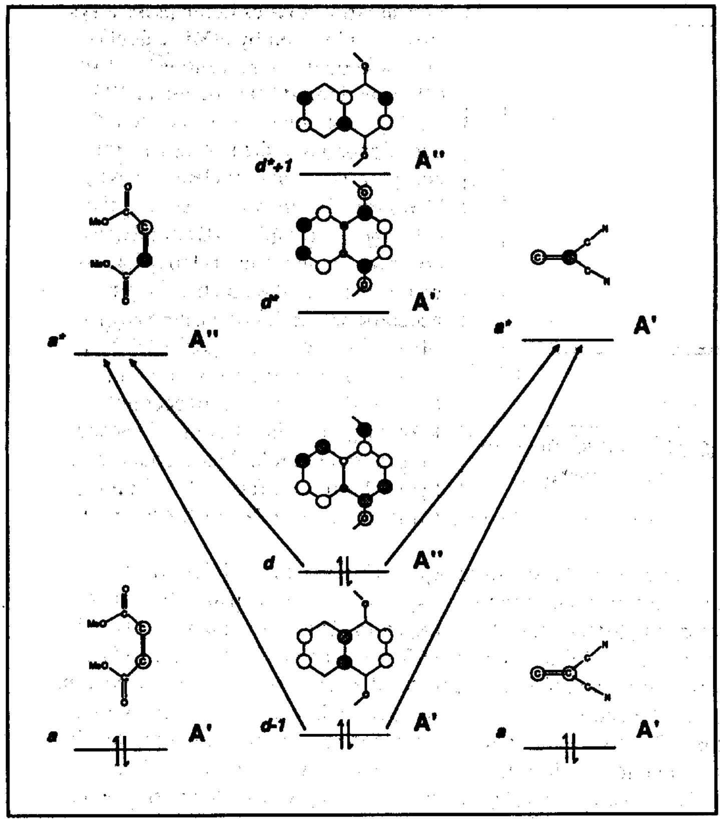

Figure 6
Frontier orbitals according to HMO calculations of 1,4-dimethoxynaphthalene (centre), 1,1-dicyanoethylene (right) and 1,2-dimethoxycarbonylethylene (left). In the acceptors only the MO coefficients on the C-C double bond are indicated.
The symmetry labels (A' and A'') refer to the C_s pointgroup. Arrows indicate excitations corresponding to the first and second CT transitions.

CT configuration are reversed with respect to those in **1**(4). Even though the donor and acceptor are now separated by three sigma-bonds instead of four only minor additional longwavelength absorption in the 250-350 nm region is detected and furthermore the spectrum for **3**(3) lacks the very strong hypochromicity in the 220 - 240 nm region typical for **1**(4) and **2**(4). From these observations we conclude that the very high intensity of the second CT transition in **1**(4) and **2**(4) is not just a result of a matching between the symmetries of the groundstate and the second excited CT configuration, because then the first CT transition of **3**(3) should have shown a comparably high intensity. A more likely explanation is that in **1**(4) and **2**(4) the symmetry of the second excited CT configuration also matches that of one or more local excited states that are connected with the very strong transitions in the 220 -240 nm region. Mixing between these states and the energetically nearby second CT configuration can then lead to extensive intensity transfer from the local transitions to the second CT transition thus explaining both the high intensity of the latter and the strong hypo-

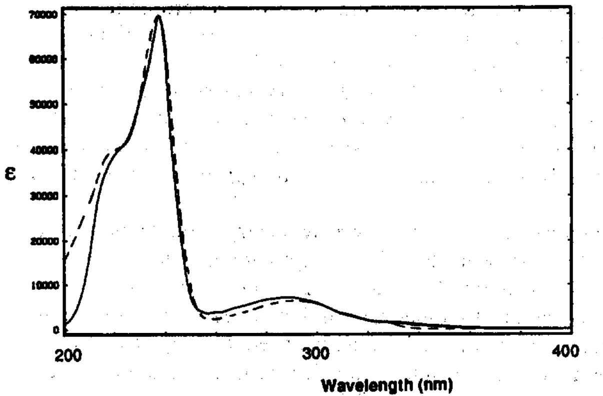

Figure 7 Absorption spectrum of **3**(3) (——) and the sumspectrum of **4** and **7** (- - -) in cyclohexane.

chromic effect observed for the former.
From CNDO/S + CI calculations[42] on the chromophores incorporated in **1**(4) it may be concluded that both chromophores indeed display at least one strong transition of the correct symmetry in the 220 -240 nm region. Thus the first $\pi \rightarrow \pi^*$ transition (λ_{max} = 228 nm; ε = 15500 $M^{-1}cm^{-1}$, see Fig. 2) of acceptor **6** related to the a → a* excitation leads to an A' excited state. Furthermore strong configuration interaction occurs between the configurations corresponding to d-1 → d* and d → d*+1 excitations of 1,4-dimethoxynaphthalene. This produces two states of A' symmetry, the lower of these is probably connected to the weak transition which appears as a shoulder at 328 nm, while the upper is connected to the strongest transition of the chromophore in the near UV region around 240 nm. Intensity borrowing from the strongest transition by the second CT transition is then symmetry allowed and might, as already stipulated above, be quite efficient because of the small energy gap involved. While earlier CNDO/S-CI calculations[42] on **1**(6) gave no indications for such intensity borrowing, more recent calculations on **1**(4) seem to support its occurrence[47].

Clearly this situation is quite different in **3**(3). Here it is the first CT transition (d → a*) which leads to an A' state but the large energy gap between this transition and the strong A' transition of the donor prevents extensive intensity transfer. The second CT transition (d-1 → a*) now leads to an A" state which matches the symmetry of the first acceptor excited state (a → a*) (λ_{max} = 240 nm; ε = 6600 $M^{-1}cm^{-1}$), but this local acceptor transition is not particularly strong and consequently neither of the two CT transitions is significantly enhanced in **3**(3).

The model discussed above seems to account qualitatively well for the interesting absorption features of the bichromophoric systems and indicates that a more accurate description should at least involve quantitative evaluation of the configuration interaction between locally excited configurations and CT excited configurations. The latter is not a trivial task, however, as evident from the results of CNDO/S + CI calculations on **1**(6)[42,43] and **1**(4)[47] by Larsson et al.. While these calculations gave a fair description of the local transitions, the CT transitions are calculated at much too high energy which, as also suggested by Larsson et al., may largely be due to the omission of solvent molecules in these calculations. As we have shown before[26], the large D-A distances involved cause the energy required for 'vertical' charge-separation to be quite sensitive towards the polarizability of the surrounding medium and its inclusion thus seems crucial in calculations that seek to quantify the configuration interaction between locally- and CT-excited configurations in donor-acceptor systems[48].

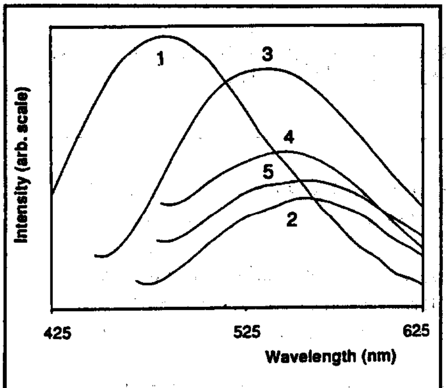

Figure 8
Charge transfer fluorescence of **1**(4) in a number of solvents.
1 = cyclohexane, 2 = benzene,
3 = di-n-butylether, 4 = diisopropylether and 5 = diethylether.

2.2. Electronic emission spectra

As reported earlier[22, 24, 26], photoinduced electron-transfer in **1**(n) causes a substantial or even complete quenching of the local donor fluorescence. The weakness or even complete absence of any fluorescence attributable to one of the separate chromophores, resulting from efficient intramolecular photoinduced electron-transfer, allows for sensitive detection of eventual fluorescence ($h\nu_{CT}$) resulting from radiative deactivation of the charge separated state:

$$D^{+}\text{-}A^{-} \longrightarrow D\text{-}A + h\nu_{CT} \qquad (1)$$

The detectability of such charge-transfer fluorescence is further enhanced by its significant Stokes-shift[26], which tends to move it into a region not overlapped by the residual donor or acceptor emissions, even if the related charge transfer absorption is strongly overlapped by local D → D* or A → A* transitions.

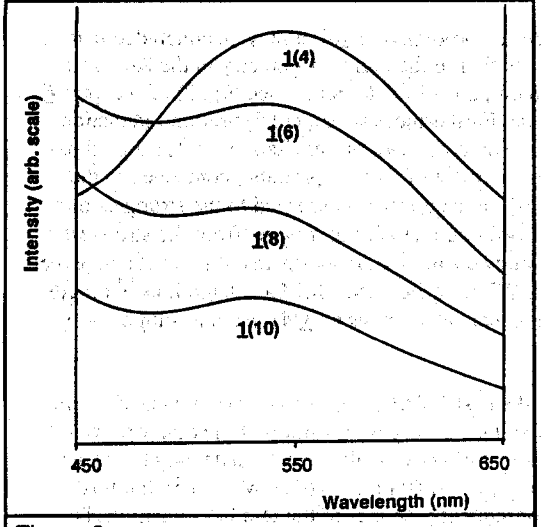

Figure 9
Charge transfer fluorescence of **1**(4), **1**(6), **1**(8) and **1**(10) in benzene.

Systems **1**(4), **2**(4) and **3**(3) provide convincing examples of the situation described above. As discussed in the previous section, the first CT-absorption in these systems can only be detected with great difficulty because of its weakness and its location in a region where stronger $D \rightarrow D^*$ transitions occur. In a number of solvents, however, a broad longwavelength emission is detected which can be attributed[26] to radiative deactivation of the charge- separated state. Fig. 8 displays this emission as observed for **1**(4) in a number of solvents.

Table I
CT fluorescence maxima, quantum yields and lifetimes of compounds :
1(4, 6, 8, 10) in a number of solvents at room temperature

	1(4)			1(6)			1(8)			1(10)		
solvent	λ (nm)	τ (ns)	ϕ	λ (nm)	τ (ns)	ϕ	λ (nm)	τ (ns)	ϕ	λ (nm)	τ (ns)	ϕ
n-hexane	475±10	8	0,03	443±10	55	0,042						
cyclohexane	475±10	9	0,034	447±10	47	0,038						
benzene	565±30	0,8	0,0008	555±30	6	0,0007	538±35	40	0,002	526±35	410	0,0041
di-n-butylether	530±15	2	0,0024	525±20	10	0,0018	520±30	49	0,002	520±35	340	0,0034
diisopropylether	555±25	1,3	0,001	550±25	8	0,0005						
diethylether	563±30	0,7	0,0005	572±30	1,2	0,0002						

For the higher homologues **1**(6), **1**(8) and **1**(10) of series **1**(n) CT-fluorescence has also been observed, although for **1**(8) and **1**(10) only in two solvents, benzene and di-n-butylether. In more polar solvents the emission is too weak to be observed. Furthermore, as shown earlier[26], there is no driving force for electron transfer in **1**(10) in saturated hydrocarbon solvents, by dint of thermodynamic features, while in these solvents **1**(8) shows substantial delayed donor fluorescence[29] resulting from thermal repopulation of the D^*A state by back electron transfer from the D^+A^- state. This results in the absence or the obscurance of CT-fluorescence for both compounds in solvents other than benzene and di-n-butylether.

Due to the broadness, the weakness and the location of the CT-fluorescence on a tail of the much stronger donor fluorescence (especially for the higher homologues) the determination of the fluorescence maximum becomes critically dependent on the fluorescence apparatus used, more specifically on the correction factors for the wavelength sensitivity of the detector.

It is evident, however, (see Fig. 8) that the CT-fluorescence undergoes a very large bathochromic shift upon increasing solvent polarity, which confirms that the emission results from the deactivation of a highly dipolar state. Emission spectra for other members of the series **1**(n) displaying the long wavelength CT type emission in benzene are shown in Fig. 9.

Table I compiles the lifetimes and the quantum yields determined for these long wavelength fluorescences as determined in a number of solvents. Despite the large influence of the correction factors for the wavelength sensitivity of the fluorescence detector on the fluorescence maximum the effects on the quantum yields of the CT-fluorescence are much less dramatic. However, it still remains difficult to obtain these

Table II

Dipolemoment and lifetime of the charge separated state as measured by TRMC [refs.23, 25, 27] in benzene at 20 C.

compound	μ (Debye)	τ (ns)
1(4)	26*	1
1(6)	37	6
1(8)	55	32
1(10)	68	360
1(12)	77**	740

*) Determined in cyclohexane since the lifetime in benzene is too short for accurate determination of the dipolemoment.

**) Corrected for the incomplete (~ 50%) quantumyield of the photoinduced charge separation.

Table III

CT-fluorescence quantum yields, lifetimes and maxima of compounds 2(4) and 3(3) in a number of solvents at room temperature.

		3(3)			2(4)	
solvent	λ (nm)	Φ	τ (ps)	λ (nm)	Φ	τ (ns)
cyclohexane	516 ± 5	0.014	2000	420 ± 5	0.034	20
benzene	604 ± 20	0.00044	6	530 ± 15	0.0053	6
di-n-butylether	564 ± 15	0.0018	420	490 ± 10	0.0088	8
diisopropylether	580 ± 15	0.0008	220	510 ± 10	0.0038	4.1
diethylether	592 ± 20	0.00038	120	530 ± 10	0.0018	2.7

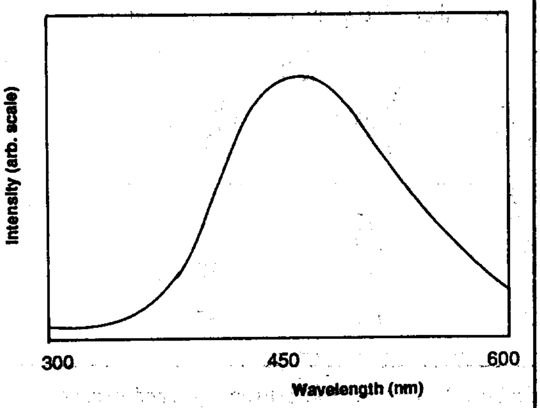

Figure 10 Charge transfer fluorescence of 3(3) in the gasphase at 473 K.

quantum yields especially for the longer homologues where the weak CT-fluorescence and the residual donor fluorescence overlap. Thus the quantum yields can be estimated within no better than 10% accuracy. As reported earlier[23, 25, 27] time resolved microwave conductivity (TRMC) measurements allow direct determination of the dipole moment and the lifetime of the charge separated state. Results of these measurements are compiled in Table II. The identity of the dipolar transients detected by these TRMC measurements and the state responsible for the long wavelength emission now observed for 1(n) (n = 4, 6, 8 and 10) is supported by the virtual identity of their decay times as evident from the comparison of the data in Table II with those given in Table I in the same solvent (benzene). Strongly solvatochromic CT fluorescence has also been observed for compounds 2(4) and 3(3) in a series of solvents. Quantitative data on quantum yields and lifetimes are given in Table III. For compound 3(3) it was even possible to obtain a fluorescence spectrum in the gasphase at 473 K (see Fig. 10). The spectrum shows only CT-fluorescence with a maximum at ~ 470 nm and no donor fluorescence at all, indicating that for 3(3) even in the gasphase the charge-separated state lies below the locally excited donor state, thereby allowing very fast electron transfer to occur!

2.3. Estimation of the through-bond matrix coupling element H_{da}

From the data compiled in Tables I and III it is simple to calculate the radiative (k_r) and the radiationless (k_q) decay rates of the charge transfer states via:

$$k_r = \Phi/\tau \qquad (2)$$

and

$$k_q = 1/\tau - k_r \qquad (3)$$

The values thus calculated for **1**(n), n = 4, 6, 8 and 10 are compiled in Table IV and those for **2**(4) and **3**(3) these values are compiled in Table V.

Table IV

The radiative- (k_r) and the radiationless (k_q) decay rate from the CT-state of compounds **1**(n), n = 4, 6, 8 and 10 calculated via eqs. (2) and (3) from the data in Table I in a number of solvents at room temperature.

solvent	**1**(4)		**1**(6)		**1**(8)		**1**(10)	
	k_r (x 10^4) [s^{-1}]	k_q (x 10^6) [s^{-1}]	k_r (x 10^4) [s^{-1}]	k_q (x 10^6) [s^{-1}]	k_r (x 10^4) [s^{-1}]	k_q (x 10^6) [s^{-1}]	k_r (x 10^4) [s^{-1}]	k_q (x 10^6) [s^{-1}]
n-hexane	380	120	76	17				
cyclohexane	380	120	81	21				
benzene	100	1200	12	150	5.0	25	1.0	2.4
di-n-butylether	120	500	18	100	4.1	20	1.0	2.9
diisopropylether	80	760	6	120				
diethylether	70	1400	17	830				

Table V

The radiative- (k_r) and the radiationless (k_q) decay rate from the CT-state of compounds **2**(4) and **3**(3) calculated via eq. (2) and (3) from Table III in a number of solvents at room temperature.

solvent	**3**(3)		**2**(4)	
	k_r (x 10^5) [s^{-1}]	k_q (x 10^7) [s^{-1}]	k_r (x 10^5) [s^{-1}]	k_q (x 10^7) [s^{-1}]
n-hexane	70	49	-	-
cyclohexane	70	49	17	4.8
benzene	(730)	(170000)	8.8	17
di-n-butylether	43	240	11	12
diisopropylether	36	450	9.3	24
diethylether	32	830	6.7	37

From these data it appears that a specific (intermolecular CT ?) interaction between **3**(3) and benzene occurs. Furthermore the Tables show that the radiative decay rate from the charge separated state to the groundstate is much less solvent dependent than the radiationless processes. A small decrease of k_r upon increasing solvent polarity was also found by Pasman[49] for some rigid D-A systems, where it was

explained by the fact that upon increasing solvent stabilization of the charge transfer state there will be a decrease in the admixture of locally excited states and hence a decrease in intensity "borrowing" from the local donor or acceptor transitions. Furthermore it should be noted that in more polar solvents extensive solvent reorganization occurs upon creation of the charge transfer state, which must have a substantial effect upon the Franck-Condon factors for the charge-recombination process.
Neglecting such effects the oscillator strength (f) of the CT transition corresponding to the CT fluorescence can be approximated[50] from the k_r values via eq. (4),

$$k_r = \upsilon^2 f \qquad (4)$$

where υ is the CT-transition maximum (in cm^{-1}).The oscillator strength is related[50] to the molar extinction coefficient of the absorption band via eq. (5),

$$f = 4.3x10^{-9} \int \varepsilon d\upsilon \approx 4.3x10^{-9} \varepsilon_{max} \Delta\upsilon_{1/2} \qquad (5)$$

where ε_{max} is the molar extinction coefficient at the maximum of the absorption band and $\Delta\upsilon_{1/2}$ is the full width at half height (fwhm) of the absorption band. On using for υ the maximum of the CT-absorption as obtained in Fig. 4 for **1**(4) (320 nm ≈ 31250 cm^{-1}), with a fwhm of 2000 cm^{-1} and the k_r in cyclohexane we calculate an ε_{max} of 450 $M^{-1}cm^{-1}$, which is remarkably close to the value (800 $M^{-1}cm^{-1}$) determined by difference spectroscopy (see Fig. 4). From the rapid decrease of k_r with increasing D-A separation (see Table IV) it is thus evident why no detectable CT absorption is found in the absorption spectra of systems **1**(n), with n ≥ 6. The oscillator strength of the direct DA ↔ D^+A^- transition as determined via eq. (4) is related to the transition dipolemoment of this transition via eq. (6),

$$f = 10^{-5} \upsilon \, |er_i|^2 \qquad (6)$$

where $|er_i|$ is the transition dipolemoment and υ is the CT transition-frequency (in cm^{-1}). For a pure CT type transition the transition dipolemoment can be given from a two state (DA / D^+A^-) mixing model[37] via by eq. (7), which seems a good approximation in solvents that lower D^+A^- sufficiently relative to locally excited states. From Table IV it appears that this is the case for solvent polarities beyond that of saturated alkanes where k_r becomes fairly constant.

$$|er_i| = e R_c H_{da} / (E_g - E_{CT}) \qquad (7)$$

In (7) $E_g - E_{CT}$ is the energy difference between ground- and charge-transfer state, which we will assume to equal the CT-fluorescence maximum (in cm^{-1}), R_c is the centre to centre donor-acceptor distance (in Å) and H_{da} is the electronic coupling matrix element between the groundstate and the charge-separated state.

Table VI

The coupling matrix elements for the series of molecules **1**(n), n = 4, 6, 8 and 10 and for the molecules **2**(4) and **3**(3) calculated via eq. (4), (6) and (7) from the radiative decay rates of the charge-transfer state (k_r) in di-n-butylether as compiled in Tables IV and V.

compound	number of bonds	R_e (Å)	R_c (Å)	H_{da} (cm^{-1})
1(4)	4	4.6	6.8	370
1(6)	6	6.8	8.7	112
1(8)	8	9.4	11.5	40
1(10)	10	11.5	13.0	17.6
3(3)	3	3.7	5.8	850
2(4)	4	4.6	6.1	381

The coupling matrix elements for the series **1**(n), n = 4, 6, 8 and 10, and for **2**(4) and **3**(3) as calculated via eq. (4), (6) and (7) from the radiative decay rates of the charge transfer state (k_f) in di-n-butylether are compiled in Table VI. For the series of molecules **1**(n), n = 4, 6, 8 and 10, the values of H_{da} compiled in Table VI provide a direct measure for the coupling between a single donor/acceptor pair over arrays of 4, 6, 8 and 10 bonds.

In a plot of H_{da} vs. the number of bonds (n) or the edge to edge distance (R_e) an exponential distance dependence of the through-bond coupling matrix element can be demonstrated (see Fig. 11), given by eq. (8) .

$$H_{da}\,(\text{in cm}^{-1}) = 2440 \exp(-0.44\,R_e) = 2566 \exp(-0.51\,n) \qquad (8)$$

where R_e is in Ångstrøm. For comparison the data of **2**(4) and **3**(3) have also been plotted in Fig. 11 , and interestingly these are found to deviate only marginally from the values predicted from eq. (8).

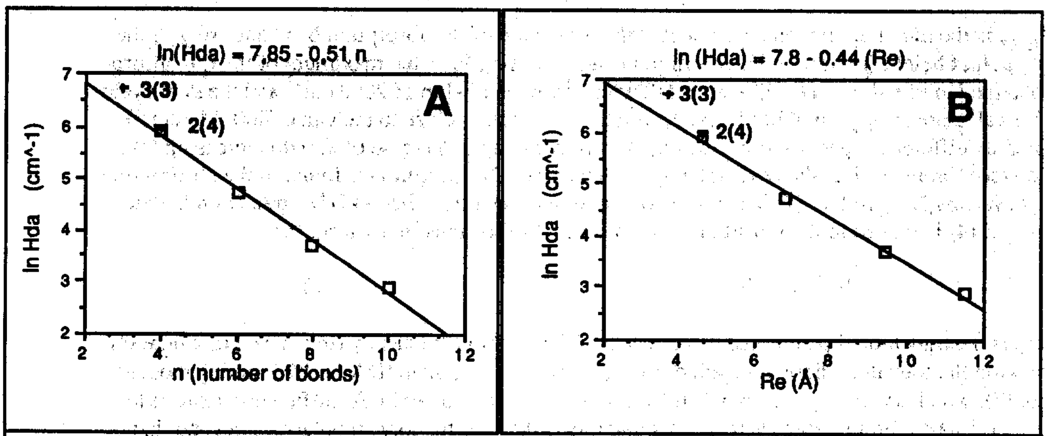

Figure 11 Estimated (see Table VI) coupling matrix elements (H_{da}) for the coupling between the charge-separated state and the groundstate as a function of the minimum number of separating sigma-bonds (n) **(A)** and the edge to edge donor-acceptor distance (R_e) **(B)** in di-n-butylether. The line drawn gives the least squares fit to the data for the series **1**(n), (n = 4, 6, 8 and 10) while datapoints for **2**(4) and **3**(3) have been added for comparison.

It should be noted that at this point we have collected data for the rate of charge-recombination ($k_{cr} = 1/\tau$, see Tables I- III) in our compounds as well as - via an independent route - for the electronic coupling matrix element (H_{da}, see Table VI) between the states involved ($D^+A^- \rightarrow DA$). This allows us to verify the applicability of the "golden rule" expression (9) that relates the rate of electron-transfer with the electronic coupling between D and A according to non-adiabatic electron-transfer theories.

$$k_{cr} = (4\pi^2/h)\, H_{da}^{\,2}\, FC \qquad (9)$$

This expression has in fact been relied upon extensively in cases where only rates[18-20, 11, 13] or H_{da} (from CT-transition oscillator strengths[21, 30, 37]) were accessible. That procedure, however, is complicated by the necessity to evaluate the Franck-Condon factor (FC), which is related to the energy difference between the two states and to the molecular- and solvent reorganization energies, and which can in most cases only be estimated using rather simplified models and under the assumption that it is constant in a series of 'related' systems.

Fig. 12 now shows a double logarithmic plot of the k_{cr} values as determined from fluorescence decay

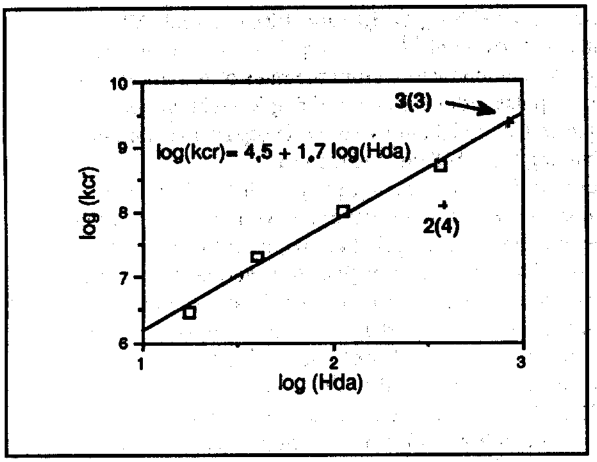

Figure 12
Double logarithmic plot of the decay rate of the charge separated state as a function of the coupling matrix element H_{da}, where the line drawn corresponds to the least squares fit to the data for the series **1**(n), (n = 4, 6, 8 and 10) while datapoints for **2**(4) and **3**(3) have been added for comparison.

(Table I and Table III) measurements versus H_{da} values determined (Table VI) from the radiative transition probability between D^+A^- and DA states (all in di-n-butylether). The datapoints for series **1**(n) (n = 4, 6, 8 and 10) indeed define a linear correlation with slope reasonably close to 2 (i.e. $k_{cr} \sim H_{ab}^2$). Once again the datapoints for **2**(4) and **3**(3) do not deviate dramatically from the correlation found for **1**(n), but especially for **2**(4) the deviation seems sufficiently large to suggest a significant change in Franck-Condon factors!

We have shown elsewhere[27] that the distance dependence of k_{cr} (as determined by TRMC in several solvents) in the series **1**(n) is described quite well by the exponential expression given in eq. (10),

$$k_{cr} = v_{cr} \exp(-0.88\, R_e) \qquad (10)$$

where the preexponential factor v_{cr} is strongly solvent dependent. Comparison of (10) with the exponential distance dependence found for H_{da} ($H_{da} \sim \exp(-0.44\, R_e)$, see Fig. 11) also nicely demonstrates that k_{cr} is indeed proportional to $(H_{da})^2$ as predicted by theory. This appears to be the first experimental verification of this proportionality in such a series of D/A systems and thereby provides important support for the application of eq. (9) to determine H_{da} from k_{cr} or *vice-versa* in systems where one of these parameters is not accessible via experiment.

2.4. Comparison of the magnitude and distance dependence of H_{da} in 1(n) with other systems

Recently Penfield et al.[30] reported the electronic absorption spectra of the radical anions of **1**(4), **1**(6) and **1**(8) created by pulse radiolysis. In these radical anions the negative charge is highly localized in the acceptor moiety (D-A⁻) but in the electronic spectra a long wavelength band can be detected which is attributed to an intramolecular CT transition transferring charge to the naphthalene moiety (D⁻-A). From the shape and intensity of these bands (λ_{max} = 633 nm; $\varepsilon \sim 2000\ M^{-1}cm^{-1}$, λ_{max} = 599 nm; $\varepsilon \sim 500\ M^{-1}cm^{-1}$ and λ_{max} = 555 nm; $\varepsilon \sim 125\ M^{-1}cm^{-1}$ in THF for the radical anions of **1**(4); **1**(6) and **1**(8) respectively), electronic couplings of 1300 cm^{-1}, 484 cm^{-1} and 242 cm^{-1} between the D-A⁻ and D⁻-A states in these radical anions were derived. These values are significantly larger than those given in Table VI for the parent neutral molecules. It should, however, be realized that they refer to different types of coupling as may be appreciated from simple one-electron considerations. Thus, in a charge-recombination process (D^+-A^- → D-A) the leading orbital interaction (see Fig. 6) is d/a*, while for charge-migration (D-A⁻ → D⁻-A) in the radical-anions it is d*/a* . The latter is in fact more closely related to the very fast photoinduced charge-separation[26] process in the neutral molecules.

Another series of fully rigid compounds for which electronic coupling matrix elements were determined are the mixed valence systems with spirocylobutane bridges studied by Stein et al.[21]. In these systems H_{da} values of 170 cm^{-1}, 68 cm^{-1} and 32 cm^{-1} across 4, 6 and 8 sigma bonds were estimated from the intensity of the intramolecular intervalence transition, which thus show more resemblance both in absolute magnitude and in distance dependence with those estimated for **1**(4), **1**(6) and **1**(8), see Table VI. The same applies to the H_{da} values calculated recently by Closs et al.[11,13] via eq (9) - and making a partial correction for the distance dependence of the Franck-Condon factor - from the rates of intramolecular electron transfer in a series of anion-radicals, created by pulse radiolysis, comprising 2-naphthyl and 4-biphenyl groups linked by cyclohexane, *trans*-decaline and steroidal units to provide separations ranging from 4 to 10 sigma-bonds and yielding H_{da} values ranging from 168 cm^{-1} to 6.2 cm^{-1}.

Although the rotational freedom of the chromophores with respect to the bridges presents additional problems in interpreting the latter results, together with those presented in this paper and with the data of Stein et al. they provide convincing evidence that effective through-bond coupling allowing for fast long-range electron transfer is by no means limited to a single type of hydrocarbon bridges. However, as indicated by the results of Closs et al. concerning the effect of the orientation (axial/equatorial) of D and A with respect to the bridge and by the effect of the internal configuration of the bridge demonstrated[51, 52] very recently by us, the actual magnitude of H_{da} is not simply determined by the number of intervening bonds.

Large H_{da} values require a mode of attachment of D and A to the bridge that allows for optimal 'hyperconjugative' overlap of the relevant frontier π-orbitals of D and Awith the σ-system of the bridge, and furthermore require a specific configuration in the relay of σ-bonds provided by the bridge, in accordance with the earliest predictions made on the conformational requirements for through-bond interaction. The all-*trans* configuration of the relay of C-C σ-bonds in the bridges of the present compounds (see Fig. 1) provides such an optimal situation and as we have shown very recently[51,52] a drastic lowering of the coupling efficiency results from changes in that situation thus allowing a fine-tuning of the rate of electron-transfer by molecular engineering of the bridge.

3. CONCLUSIONS

In this paper we have demonstrated that absorption measurements provide direct evidence for through-bond interaction in molecules **1**(4), **2**(4) and **3**(3) by the observation of "extra"-absorption bands not attributable to local donor- or acceptor transitions. These charge transfer absorption bands enable direct electron-transfer from the groundstate to the charge-separated state upon excitation with light. Radiative decay of the charge-separated state directly to the groundstate has been observed for compounds **1**(n), n = 4, 6, 8 and 10, **2**(4) and **3**(3) in a number of solvents. From the bathochromic shift of this charge-transfer fluorescence upon increasing solvent polarity and especially from Time Resolved Microwave Conductivity measurements the highly dipolar character of the charge-separated state has been shown.

Quantitative analysis of the transition probability for CT-emission enabled us to determine the through-bond electronic coupling matrix elements H_{da} between the groundstate and the charge-separated state. H_{da} shows, as expected for weak electronic coupling, a single exponential distance dependence and furthermore the proportionality between the square of H_{da} and the rate of charge-recombination, predicted by non-adiabatic electron-transfer theory, was substantiated.

4. EXPERIMENTAL

Synthesis and identification of the compounds are described elsewhere [26, 53, 54].

Samples for emission measurements were made in spectrograde solvents, with an absorption at the excitation wavelength between 0.1 and 0.2 and furthermore they were carefully deoxygenated by purging with argon for at least 15 minutes. The static fluorescence measurements were performed on a SPEX Fluorolog II instrument, with a Hamamatsu R928 detector and an excitation wavelength of 300 nm. The quantum yields are measured relative to diphenylanthracene in cyclohexane ($\Phi = 1$), upon variation of solvents there has been corrected for the change in refractive index of the solvents. For the time resolved fluorescence measurements on a nanosecond time scale the 308 nm line of a XeCl filled Lambda Physik EMG-101 excimer laser has been used as excitation source. The emitted light was detected via a Zeiss M4QIII monochromator by a RCA C-31025 C GaAs photomultiplier, from which the electric signal was fed into a Biomation 6500 transient digitizer coupled to a Tandy TRS80 model III microcomputer for data handling. For the subnanosecond time resolved fluorescence measurements a time correlated single photon counting equipment has been used, which has been described extensively before[26]. Static absorption measurements were performed with a Hewlett Packard 8451A diode-array spectrophotometer.

Acknowledgements

We express our thanks to Dr. S. Larsson for discussion of the absorption spectra and for making available results of CNDO/S-CI calculations on **1**(4) prior to publication.

The present investigations were supported by the Australian Research Grants Scheme and by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Research (NWO).

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