

## Through-bond charge transfer interaction and photoinduced charge separation

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**Abstract** - A series of bichromophoric molecules was studied containing a 1,4-dimethoxynaphthalene donor (D) chromophore and a 1,1-dicyanoethylene acceptor (A) chromophore, interconnected by five different, rigid, saturated hydrocarbon bridges. The length of the bridges varies with increments of two sigma bonds from 4 to 12 to provide donor-acceptor separations up to 15 Å.

In all cases excitation of D is followed by rapid intramolecular electron transfer from D to A. Through-bond interaction involving  $\sigma/\pi$  interaction between the bridges and the chromophores is proposed to explain the very high rates of electron transfer. The observation of intramolecular charge transfer absorption and emission confirms the operation of such through-bond interaction.

### INTRODUCTION

Various lines of experimental evidence (ref. 1-4) have led to the conclusion that single electron transfer may occur between molecular species separated by a distance exceeding the sum of their van der Waals radii. In fact many biological electron transport processes -including the primary steps of photosynthesis (ref. 5)- involve such "long-range" electron transfer events. Much progress has been made in the study of the general distance dependence of electron transfer by measuring the time resolved evolution of the number of electron transfer events in dilute rigid solutions containing donor and acceptor species (ref. 2). From such measurements, however, no information about specific orientational effects nor about the effect of solvation dynamics on the rate of electron transfer can be achieved. We now present data from our studies (ref. 1) on photoinduced electron transfer in molecules containing an electron donor-acceptor pair in a rigidly defined relative orientation and at a rigidly defined distance, the latter being varied in discrete steps. The molecules studied in the present paper (I(n), n = 4, 6, 8, 10, 12 c.f. Fig. 1) incorporate a 1,4-dimethoxynaphthalene chromophore as the photoexcitable electron donor and a 1,1-dicyanoethylene unit as an electron acceptor, the minimum number of carbon-carbon sigma bonds separating donor and acceptor being n. Molecules II and III (see Fig. 1) will be used as models to study the properties of the "isolated" donor and acceptor systems.

### RESULTS AND DISCUSSION

#### Photoinduced electron transfer between II and III

Table 1 compiles some relevant photophysical and electrochemical data for the model systems II and III.

TABLE 1. Photophysical data (in cyclohexane and acetonitrile) and electrochemical data (in acetonitrile) for II and III.

	Solvent	Absorption			Fluorescence			Cyclic voltammetry (Volts vs. sce)
		$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (l.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\lambda_{\max}$ (nm)	$\phi$	$\tau$ (ns)		
II	cyclohexane	290	5700	350	0.35	5.43	-	
	acetonitrile	292	5300	386	0.33	4.78	+1.1 (E <sub>ox</sub> <sup>II</sup> ) <sup>a</sup>	
III	cyclohexane	230	15000	-	-	-	-	
	acetonitrile	228	16000	-	-	-	-1.7 (E <sub>red</sub> <sup>III</sup> ) <sup>b</sup>	

<sup>a</sup>Midpoint of the reversible first oxidation-reduction wave.

<sup>b</sup>From the peak potential (-1.73 V) of the irreversible reduction wave.

Note a: The co-authors are: M.N. Paddon-Row (University of New South Wales), N.S. Hush (University of Sydney), H. Oevering and M. Heppener (University of Amsterdam).

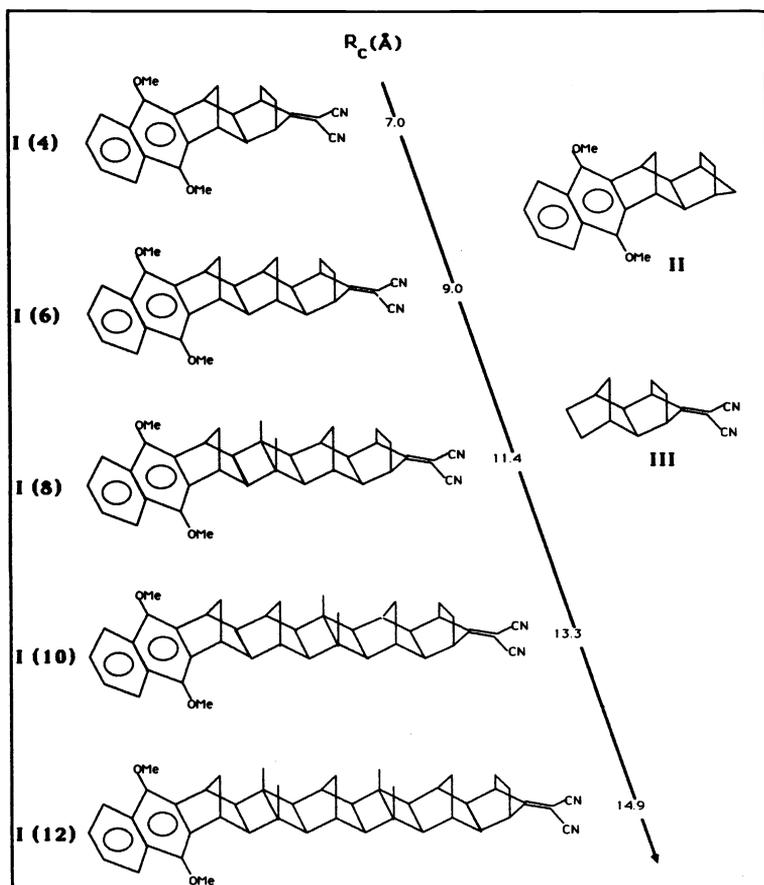


Fig. 1. Structure of bichromophoric molecules (I(*n*), *n* = 4, 6, 8, 10 and 12) and model systems (II, III) studied.  $R_c$  gives the distance between the centre of the naphthalene unit and the centre of the ethylenic bond in the 1,1-dicyanoethylene unit. Account has been taken of the curvature of the bridges as revealed by X-ray studies of I(6), I(8) and I(10), which makes  $R_c$  slightly shorter than expected (ref. 1) from molecular models with an essentially linear bridge.

Whereas the absorption spectra of II and III show little solvent dependence, the fluorescence of II undergoes a distinct bathochromic shift in more polar solvents while its quantum yield ( $\Phi$ ) and lifetime ( $\tau$ ) remain virtually unchanged. As expected III is non-fluorescent (ref. 6), furthermore III was found to quench the fluorescence of II in a virtually diffusion limited process in polar as well as in apolar media. The absorption data excluding energy transfer from II to III, electron transfer quenching seems the most plausible quenching mechanism. The thermodynamic driving force ( $\Delta G^*$ ) for such electron transfer in acetonitrile is rather accurately given (ref. 7) by eqn (1):

$$\Delta G^*(\text{CH}_3\text{CN}) = F(E_{\text{ox}}^{\text{II}} - E_{\text{red}}^{\text{III}}) - E_{\text{o,o}}^{\text{II}} - \frac{e^2}{R_c \epsilon} \quad (1)$$

The last term in eqn (1) corrects for the Coulombic attraction energy between the radical-ions at a centre to centre separation  $R_c$ . In a solvent with high dielectric constant like acetonitrile ( $\epsilon = 37$ ) this term is almost negligible (ref. 7) ( $\sim 0.03$  eV). The  $E_{\text{II}}^{\text{II}}$  term represents the electronic energy stored in II upon photoexcitation. For this we take the mirror point between its absorption and emission (320–340 nm corresponding to  $3.75 \pm 0.1$  eV, see Table 1) which leads to  $\Delta G^*(\text{CH}_3\text{CN}) = -0.98$  eV. In less polar solvents the driving force of the electron transfer is expected to decrease substantially.

It has been proposed (ref. 7) that eqn (2) can be used to calculate the Gibbs free energy change for photoinduced electron transfer in a medium with dielectric constant  $\epsilon$  employing electrochemical data obtained in acetonitrile ( $\epsilon = 37$ ). In eqn (2)  $r_{\text{d}^+}$  and  $r_{\text{a}^-}$  represent the effective ionic Born-radii of the donor radicalcation and the acceptor radicalanion.

$$\Delta G^* = F(E_{\text{ox}}^{\text{II}} - E_{\text{red}}^{\text{III}}) - E_{\text{o,o}}^{\text{II}} - \frac{e^2}{\epsilon R_c} - \left(\frac{e^2}{2}\right) \left(\frac{1}{r_{\text{d}^+}} + \frac{1}{r_{\text{a}^-}}\right) \left(\frac{1}{37} - \frac{1}{\epsilon}\right) \quad (2)$$

If we take  $r_{d+} = r_{a-} = r$  (in Å), and furthermore introduce the appropriate experimental data, eqn (2) reduces to eqn (3):

$$\Delta G^* = -0.95 - \frac{14.45}{\epsilon R_c} - \left(\frac{14.45}{r}\right) \left(\frac{1}{37} - \frac{1}{\epsilon}\right) \text{ eV} \quad (3)$$

This implies that in cyclohexane ( $\epsilon = 2$ ) and at the formal contact distance ( $R_c = 2r$ ) the driving force is given by  $\Delta G^* = -0.95 - (3.22/r)$ . From the (nearly) diffusion controlled quenching of II by III in cyclohexane it may be concluded (ref. 8) that even in this apolar medium a driving force of at least 0.2-0.25 eV remains for photoinduced electron transfer in a contact pair. From this value  $r \geq 4.5$  Å is suggested for the effective ionic radii. With this tentative value eqn (3) was now used to calculate  $\Delta G^*$  as a function of  $R_c$  in solvents of various dielectric constants (see Fig. 2).

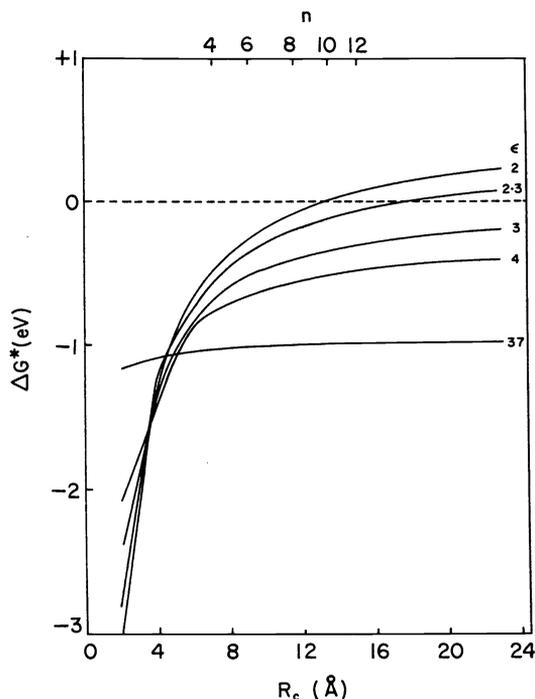


Fig. 2. Calculated (see text) Gibbs free energy change versus centre to centre distance for photoinduced electron transfer between II and III in media with various dielectric constants ( $\epsilon$ ). At the top the  $R_c$  values for I( $n$ ),  $n = 4, 6, 8, 10$  and  $12$ , have been indicated.

#### Photoinduced, intramolecular electron transfer in I ( $n = 4-12$ )

The plots in Fig. 2 suggest that photoinduced electron transfer between II and III is thermodynamically feasible in saturated hydrocarbon solvents ( $\epsilon = 2$ ) up to  $R_c \approx 13$  Å and that this range is extended rapidly upon increasing solvent polarity. The photophysical data of I ( $n = 4-12$ ) dramatically show that in these molecules photoinduced electron transfer over such large distances is not only thermodynamically but also kinetically feasible. Thus at concentrations excluding intermolecular quenching the lifetime and quantum yield of the dimethoxynaphthalene fluorescence for I(10) and I(12) is substantially reduced in solvents with  $\epsilon \geq 2.3$  as compared to that of II, while for the shorter homologues almost complete quenching of the dimethoxynaphthalene fluorescence occurs in all solvents including the saturated hydrocarbons. For I(8), I(10) and I(12) the residual dimethoxynaphthalene fluorescence was sufficiently strong to determine its lifetime by time-correlated single photon counting (see Table 2). From this the rate constant ( $k_{et}$ ) of the intramolecular, photoinduced electron transfer was determined by comparison with the fluorescence lifetime of II via eqn (4):

$$k_{et} = \frac{1}{\tau_I} - \frac{1}{\tau_{II}} \quad (4)$$

While for the two shorter homologues I(4) and I(6) only a lower limit  $k_{et} \geq 10^{11} \text{ s}^{-1}$  can be given, the results for I(8), I(10) and I(12) (see Table 2) clearly show a distance dependence of  $k_{et}$ . Extension of the bridge with two sigma-bonds decreases  $k_{et}$  by about one order of magnitude.

Remarkably enough the solvent dependence at a fixed distance is very small, except for the "trivial" effect of saturated hydrocarbon solvents that make (see Fig. 2) electron transfer thermodynamically impossible for I(10) and I(12). We (ref. 9) and others (ref. 10) have argued before that a minor influence of solvent polarity on the rate of electron transfer can be understood from the compensatory roles of the large solvent induced changes in overall free energy (see Fig. 2) and in solvent reorganization energy. The present data strongly reinforce this view.

TABLE 2. Lifetime ( $\tau$ ) of dimethoxynaphthalene fluorescence (detected at 360 nm) and calculated rate ( $k_{et}$ ) of intramolecular, photoinduced electron transfer for I(n),  $n = 8, 10, 12$  in various solvents at 24°C.

Solvent	$(\epsilon)$	I(8)		I(10)		I(12)	
		$\tau$ (ps)	$k_{et}$ ( $s^{-1} \times 10^8$ )	$\tau$ (ps)	$k_{et}$ ( $s^{-1} \times 10^8$ )	$\tau$ (ps)	$k_{et}$ ( $s^{-1} \times 10^8$ )
cyclohexane	(2.015)	48	210	5400	< 0.1	5400	< 0.1
benzene	(2.28)	19	520	135	72	1030	7.3
diethylether	(4.20)	21	470	190	51	1740	3.7
ethylacetate	(6.02)	22	450	115	85	1160	6.3
acetonitrile	(37.5)	33	300	380	24	2710	1.6

### Through-bond interaction in I

The data presented above demonstrate unequivocally that rapid, photoinduced, intramolecular electron transfer can occur in molecules I even if the saturated bridge keeps the donor and acceptor chromophores at a distance far beyond the contact distance of the isolated donor and acceptor. We have proposed before (ref. 1, 6) that the saturated bridge may play a decisive role in mediating electron transfer by a through-bond mechanism. For the shorter homologues I(4) and I(6) the absorption spectra (cf. Fig. 3) deviate significantly from the sum spectrum of the model systems, thus supporting the occurrence of through-bond electronic interaction.

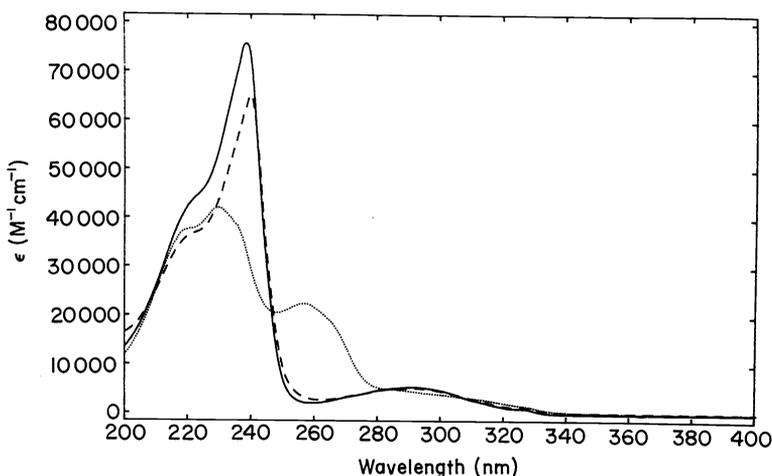


Fig. 3. Absorption spectra of I(4) (....) and I(6) (----) as well as the sumspectrum of II and III (—) in cyclohexane.

The occurrence of through-bond charge transfer interaction in I is further confirmed by the emission spectra of the shorter homologues (i.e. I(4), I(6) and (8)). While as discussed in a previous section the characteristic emission of the dimethoxynaphthalene chromophore is almost completely quenched in these molecules, a new, weak and broad longwavelength emission is observed for I(6) and especially for I(4) in a limited number of solvents with low polarity, while I(8) shows a very weak longwavelength tail on the residual donor emission. For I(6) we were able to detect this emission in cyclohexane ( $\lambda_{max}$  450 nm) but for I(4) it could also be studied in slightly more polar solvents although its intensity drops steeply as the polarity of the medium is increased. The large bathochromic shift which occurs in more polar solvents (see Table 3) identifies this emission as arising from an excited state with a highly dipolar character, i.e. an intramolecular charge transfer excited state.

It can be shown (ref. 11) that eqn (5) describes the solvent dependence of the emission maximum ( $\tilde{\nu}$  in  $cm^{-1}$ ) for molecules with a large excited state dipole moment ( $\mu_e$  in Debye) and negligible ground state dipole moment.

$$\tilde{\nu} = \tilde{\nu}_o - \frac{2\mu_e^2}{hc\epsilon^3} \left[ \frac{(\epsilon-1)}{(2\epsilon+1)} - \frac{(n^2-1)}{(4n^2+2)} \right] = \tilde{\nu}_o - \frac{10106 \mu_e^2}{\epsilon^3} (\Delta f) \quad (5)$$

TABLE 3. Longwavelength emission ( $\lambda_{\max}$  in nm) observed for I(4), I(6) and I(8) at 20°C in various solvents (excitation at 320 nm).

Solvent	( $\Delta f$ )	I(4)	I(6)	I(8)
1. n-hexane	(0.092)	475	-	-
2. cyclohexane	(0.100)	475	450	$\leq 430^a$
3. benzene	(0.116)	530	-	-
4. di-n-butylether	(0.194)	560	-	-
5. di-isopropylether	(0.237)	570	-	-
6. diethylether	(0.251)	600	-	-

<sup>a</sup>Extremely weak tail on residual donor fluorescence.

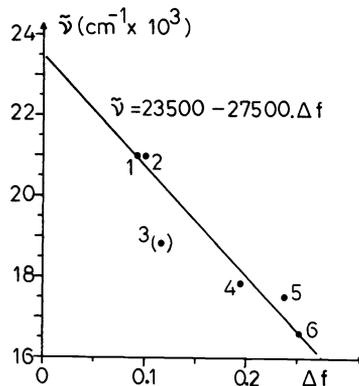


Fig. 4. Solvent dependence of the intramolecular charge fluorescence observed for I(4) (see Table 3).

In eqn (5) the solvent dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) are used to define an effective polarity parameter ( $\Delta f$ ). Furthermore  $e$  (in Å) denotes the effective radius of the cavity in which the molecule resides. For extended molecules a  $e$ -value equal to 40% of the long axis is used. For I(4) application of eqn (5) leads to a reasonable correlation (see Fig. 4). From the slope (27500  $\text{cm}^{-1}$ ) a value  $\mu_e = 20$  Debye is calculated using  $e = 5.2$  Å. Because of the small number of data points and the limited polarity range they span, this  $\mu_e$  value represents only a crude estimate (Note b). Its high value, however, confirms beyond doubt the charge transfer nature of the emissive state.

### Concluding remarks

The data presented above provide unequivocal proof for the occurrence of charge transfer interaction and very fast electron transfer across saturated hydrocarbon bridges. We have argued earlier (ref. 6) that through-bond interaction (TBI) plays a dominant role in the electronic coupling responsible for these phenomena. Furthermore we have demonstrated before (ref. 6) the stereochemical dependence of TBI as well as the large efficiency of TBI across bridges related to those incorporated in I (ref. 13). In this context it seems important to draw attention to earlier reports of Kuhn (ref. 3) and Möbius (ref. 14) describing remarkably rapid electron transfer across monolayers (20-30 Å thickness) of saturated fatty acid molecules. Much more information will be required to understand in detail the influence of the "intervening medium" upon electron transfer. Rigid systems like I appear of great value to obtain such information as well as in studies directed to quantification of the energetics and dynamics of solvation processes of dipolar species.

### EXPERIMENTAL

Synthesis of compounds I, II and III is described elsewhere (ref. 15).

Electrochemical measurements were performed using a glassy carbon working electrode and an Ag/AgCl/KCl (sat.) reference electrode (-40 mV relative to the saturated calomel electrode (sce)) in acetonitrile containing 0.1 mol.l<sup>-1</sup> tetraethylammonium tetrafluoroborate as a supporting electrolyte.

Static absorption and emission measurements were performed using Hewlett-Packard 8451A and Spex Fluorolog instruments.

Fluorescence lifetimes have been obtained by time correlated single photon counting. The experimental set-up is an improved version of the one developed by de Vries et al. (ref. 16). Excitation pulses (7 ps fwhm) are created by synchronously pumping a Rh6G dye laser (Coherent 490 with extended cavity) with a mode-locked Ar<sup>+</sup> laser (coherent CR8, repetition rate 94 MHz). The second harmonic of the dye laser is then generated by means of a 90° phase-matched ADA crystal, at the exit of which the fundamental frequency is filtered off with a Schott UG5 filter. The wavelength of the UV pulses thus created was 303 nm.

Fluorescence of the samples was focussed onto the entrance slit of a Zeiss M20 monochromator by means of a quartz condenser and a Dove prism. Light detection was performed by means of a Hamamatsu R1564 U-01 microchannel plate photomultiplier. The output of this photomultiplier was amplified by an ENI 500 LM amplifier. The amplified pulses were fed into a Tennelec 455 constant fraction discriminator producing the start pulses for a calibrated Ortec 457 time-to-amplitude-converter (TAC). Care was taken that the rate of start pulses did not exceed

Note b: Time resolved microwave conductivity measurements (see ref. 12) lead to an estimate of 25 Debye for the excited state dipole moment of I(4).

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10 of the laser repetition rate to ensure good statistics. Stop pulses for the TAC were derived directly from the sync. output of the modelock driver. The output of the TAC (a voltage proportional to the time elapsed between start and stop pulse) was digitized and accumulated in an EG&G 918 multichannel buffer coupled to an IBM personal computer. The overall time response of the system was measured to be 70 ps fwhm by directly recording the stray light from a milky suspension of Al<sub>2</sub>O<sub>3</sub> in water. Recorded spectra were analysed by means of a homewritten program based on iterative reconvolution. This allows for the presence of more than one exponential decay and automatically corrects for non-linearity in the TAC time-base and for residual emission resulting from previous excitation pulses. The quality of a fit was judged from the normalized residuals and the value  $\chi^2$ , the latter being always smaller than 1.6. Realistic simulations have shown that this program is capable of determining lifetimes as short as 20 ps to within 5 ps accuracy.

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