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LONG-RANGE EXCHANGE CONTRIBUTION TO SINGLET-SINGLET ENERGY TRANSFER IN A SERIES OF RIGID BICHROMOPHORIC MOLECULES

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Intramolecular singlet-singlet energy transfer is reported in a series of compounds containing a 1,4-dimethoxy-naphthalene chromophore as the energy donor and a cyclic ketone as the energy acceptor connected by rigid, elongated, saturated hydrocarbon bridges with an effective length of 4, 6, and 8 C-C σ bonds. The rate of energy transfer is found to be proportional to the spectral overlap – as varied by solvent variation – and to show an exponential distance dependence while its magnitude significantly exceeds that predicted for a dipole-dipole coupling mechanism. From this it is concluded that energy transfer occurs predominantly via an exchange mechanism. Exchange integrals of 60, 10, and 2.5 cm⁻¹ across 4, 6, and 8 σ bonds are calculated. The magnitude of these is proposed to signify through-bond exchange interaction between symmetry-matched donor ($\pi\pi^*$) and acceptor ($n\pi^*$) states.

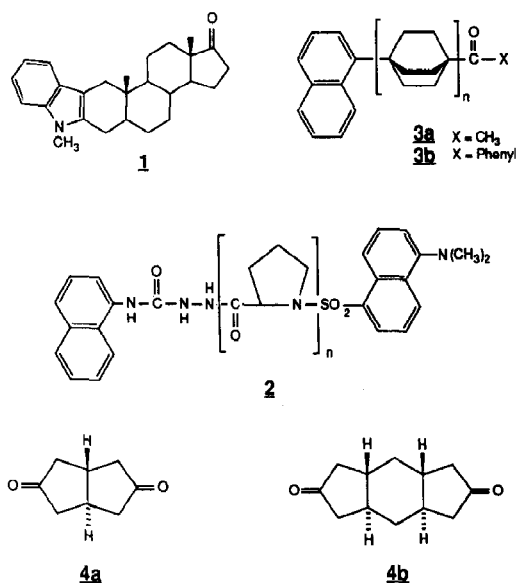
1. Introduction

Two major mechanisms for singlet-singlet energy transfer have been identified [1]. The Förster mechanism [2] operates via Coulombic interaction between transition moments and therefore requires no direct contact between energy donor and acceptor while the Dexter mechanism [3] depends upon electron exchange and thus requires spatial overlap. For both mechanisms theory predicts proportionality of the energy transfer rate constant and the spectral overlap^{#1} between donor emission and acceptor absorption. Experimentally this has been confirmed very elegantly [4] by studying the solvent dependence of intramolecular energy transfer in the bi-

chromophoric molecule **1** (see scheme 1) with fixed donor-acceptor separation, where the donor (indole) emission and the acceptor (carbonyl) absorption display opposite solvatochromism.

Discrimination between the Dexter and the Förster mechanism may be achieved by studying the effect of varying the donor-acceptor separation (R). The rate constant for the Dexter transfer is expected [1,3] to parallel the decrease of electronic overlap with increasing R , which may be approximated by an exponential function. For Förster dipole-dipole transfer, however, a more gradual fall-off with the inverse sixth power of R is predicted [2]. The latter prediction has been tested extensively for $R \geq 20$ Å, e.g. by studying [5] intramolecular energy transfer in a series of bichromophoric molecules **2** (see scheme 1) with a proline oligomer spacer that was varied between 20 Å ($n=4$) and 46 Å ($n=12$) as

^{#1} Note that the form of the expression used to define the spectral overlap is different in the Förster and Dexter treatments.



Scheme 1. Structure of molecules used in earlier studies on intramolecular energy transfer.

well as by studying [6] energy transfer across organized fatty acid monolayers of variable thickness.

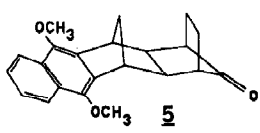
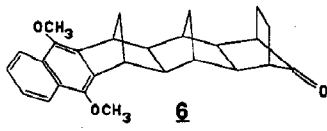
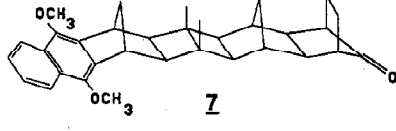
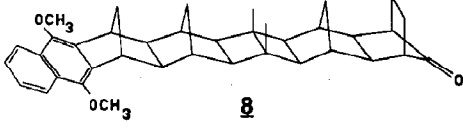
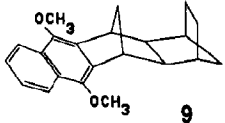
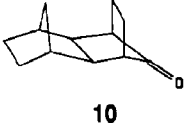
As yet little systematic study has been made of the distance dependence of singlet-singlet energy transfer for $R < 20$ Å. For **2** this was impossible since energy transfer becomes quantitative at $n \leq 4$. For **1** ($R \approx 10$ Å) no explicit effort was made to determine the relative contributions of Förster and Dexter energy transfer. The latter, however, was considered [4] to be unimportant and this seems to be supported by the results of several studies [7] on intramolecular triplet-triplet energy transfer. Such triplet-triplet energy transfer occurs by an exchange mechanism exclusively and for $R > 10$ Å its rate is found to be too slow to contribute on the time scale usually available for singlet-singlet energy transfer. Interestingly, a substantially larger variation of the intramolecular energy transfer rate than expected from an inverse sixth power dependence was observed by Zimmerman et al. [8] on comparison of **3** ($n=2$) and **3** ($n=1$). Thus the rate was found to increase 250-fold for **3a** and 39-fold for **3b** on going from $n=2$ ($R \approx 11.5$ Å) to $n=1$ ($R \approx 7.5$ Å), which corresponds to a 13.4-fold increase of R^{-6} . It was proposed that through-bond interaction via the bicyclooctane bridge provides sufficient electronic

coupling to make the Dexter mechanism operative for **3** ($n=1$), but not for **3** ($n=2$).

A similar conclusion was reached by Schippers et al. [9] from comparison of the rates of intramolecular singlet $n-\pi^*$ energy transfer in **4a** and **4b**. While the rate ($\leq 10^7$ s⁻¹) in **4b** is not incompatible with that predicted on the basis of dipole-dipole and quadrupole-quadrupole coupling, the rate ($\geq 10^{10}$ s⁻¹) in **4a** could only be explained if an exchange mechanism resulting from considerable delocalization of the carbonyl n and π^* orbitals towards the five-membered ring (i.e. through-bond interaction across four σ bonds!) is invoked. Recent studies [10-17] on the properties of various rigid bichromophoric molecules indicate that the effects of through-bond interaction may be felt over extended arrays of σ bonds considerably larger than the four- and the five-bond arrays in **4a** and **3** ($n=2$). Studies of intramolecular electron transfer [13-17] have been particularly revealing in this respect and have provided evidence for electronic coupling across rod-like rigid saturated bridges, extending up to twelve σ bonds [15-17]!

During our studies on intramolecular electron transfer we have recently developed [15-17] saturated hydrocarbon bridges that not only provide a rigidly defined donor-acceptor distance but also the possibility to vary this distance incrementally and at the same time maintain a well defined donor-acceptor orientation throughout the series. This latter property is of great advantage in the quantitative interpretation of energy transfer by the Förster mechanism. It thus seemed of particular interest to use this type of bridge to investigate the relative contribution of Förster- and Dexter-type energy transfer across a saturated bridge of variable length. To this end the bichromophoric systems **5-8** were studied (scheme 2). These contain a 1,4-dimethoxynaphthalene chromophore as an energy donor and a carbonyl group as an energy acceptor separated by extended arrays of four, six, eight and ten σ bonds corresponding to a centre-to-centre distance ranging from $R_c = 6.8$ Å to $R_c = 13.0$ Å and an edge-to-edge distance ranging from $R_e = 4.6$ Å to $R_e = 11.5$ Å.

The centre-to-centre distance (R_c) between donor and acceptor moieties is measured from the midpoint of the central C-C bond of the naphthalene system to the midpoint of the C-O bond of the ac-

	<u>Re (Å)</u>	<u>Rc (Å)</u>
 5	4.6	6.8
 6	6.8	8.7
 7	9.4	11.5
 8	11.5	13.0
 9		
 10		

Scheme 2. Structure of bichromophoric molecules (5–8) and model systems (9, 10), as well as chromophore edge-to-edge separation (R_e) and centre-to-centre separation (R_c) (see text for definitions).

ceptor. In addition the edge-to-edge distance (R_e) is measured between the bond that the donor shares with the bridge and the carbon atom of the carbonyl group. These distances were obtained from X-ray crystal structures of 7, 8, and an analogue of 6 [18]. Molecules 9 and 10 were used as models to study the properties of the isolated donor and acceptor chromophores.

2. Experimental

Syntheses of compounds 5–10 have been described elsewhere [12,17]. Samples for spectroscopic measurements were prepared in spectrograde solvents and carefully deoxygenated by purging with argon. Static absorption and emission measurements were performed using Hewlett–Packard 8451A and Spex Fluorolog instruments. Fluorescence lifetimes

were determined via time-correlated single-photon counting as described earlier [15,17]. Emission measurements were made on samples with a concentration of $\approx 2.5 \times 10^{-5}$ M, which implies A (1 cm) ≈ 0.1 at the excitation wavelength (300 nm). At this wavelength the extinction coefficient of the donor ($\approx 4000 \text{ M}^{-1} \text{ cm}^{-1}$ [17]) exceeds that of the acceptor (see fig. 1) by more than two orders of magnitude, which ascertains selective excitation of the former.

3. Results

In table 1 fluorescence properties of the isolated donor 9 are compiled in a number of solvents, while fig. 1 displays the corresponding emission spectra as well as the absorption spectrum ($n-\pi^*$ transition) of the acceptor model 10 in di-*n*-butyl ether. The latter

Table 1
Emission data for donor **9** in various solvents

Solvent	<i>n</i>	λ_{max} (nm)	Φ	τ (ns)
cyclohexane	1.4262	350	0.35	5.43
di- <i>n</i> -butyl ether	1.3992	354	0.33	4.78
diethyl ether	1.3524	357	0.27	4.82
ethyl acetate	1.3724	368	0.40	4.39
tetrahydrofuran	1.4072	370	0.24	4.26
acetonitrile	1.3441	386	0.33	4.78

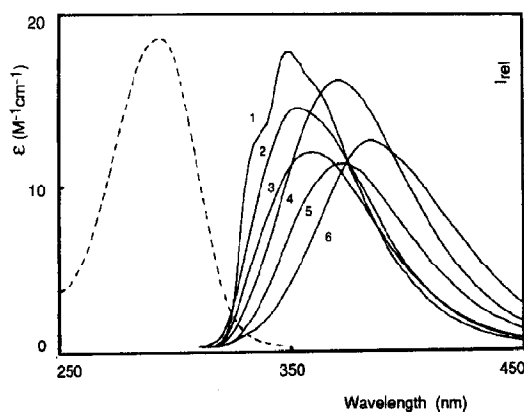


Fig. 1. Absorption spectrum (---) of the ketone **10** in di-*n*-butyl ether and fluorescence spectra (—) of the dimethoxynaphthalene derivative **9** in various solvents (see table 1).

shows only a minor solvent dependence but as reported earlier [16,17] the fluorescence of the donor undergoes a significant bathochromic shift with increasing solvent polarity.

The occurrence of energy transfer, following light absorption in compounds **5–8** is detected by observ-

ing the quenching of the local fluorescence of the 1,4-dimethoxynaphthalene chromophore. The rate of energy transfer can then be calculated via

$$k = [\Phi(9) - \Phi] / \Phi \tau(9). \quad (1)$$

Table 2 compiles the quantum yield of the donor fluorescence in compounds **5–7** in some solvents, and the energy transfer rates calculated via eq. (1). For **8** the fluorescence quantum yield was found to be equal to that of **9** in all solvents, within the experimental accuracy ($\pm 2\%$).

4. Discussion

4.1. Solvent dependence

For all bichromophoric systems the data in table 2 show that the degree of quenching increases in less polar solvents. This is an important observation since it allows us to conclude that energy transfer instead of electron transfer constitutes the quenching mechanism. The difference between the oxidation potential of the donor ($E_{\text{ox}} = +1.1$ V versus SCE in acetonitrile [17]) and the reduction potential of the carbonyl acceptor ($E_{\text{red}} = -2.5$ V versus SCE [19]) is so large that after excitation of the donor (zero-zero singlet excitation energy 3.78 eV [17]) electron transfer – if any – would be thermodynamically feasible [17] in extremely polar media only.

Both the Förster (dipole–dipole) and the Dexter (exchange) mechanism, however, require that the rate of energy transfer be proportional to the spectral overlap (J) of the donor emission and the acceptor absorption, which increases in less polar solvents!

Table 2
Donor fluorescence quantum yield (Φ) and calculated (via eq. (1)) rates of energy transfer (k) for **5**, **6** and **7** in various solvents at 20°C

Solvent	5		6		7	
	Φ	k (10^9 s^{-1})	Φ	k (10^7 s^{-1})	Φ	k (10^7 s^{-1})
cyclohexane	0.0042	15.0	0.11	39	0.27	5.3
di- <i>n</i> -butyl ether	0.0077	8.7	0.15	24	0.31	1.5
diethyl ether	0.0067	8.2	0.14	20	0.24	2.2
ethyl acetate	0.014	6.3	0.27	11	0.38	1.2
tetrahydrofuran	0.016	3.2	0.17	9.9	0.27	–
acetonitrile	0.049	1.2	0.30	2.0	0.33	–

Table 3

Förster and Dexter spectral overlap integrals calculated (via eqs. (2) and (3), respectively) by numerical integration of the $n-\pi^*$ absorption of the acceptor and the fluorescence of the donor (fig. 1) in various solvents

Solvent	J_{Dexter} (cm)	$J_{\text{Förster}}$ (cm ⁶ mmole ⁻¹)
cyclohexane	22.6×10^{-7}	25.9×10^{-20}
di- <i>n</i> -butyl ether	20.2×10^{-7}	19.3×10^{-20}
diethyl ether	14.6×10^{-7}	13.8×10^{-20}
ethyl acetate	7.01×10^{-7}	6.74×10^{-20}
tetrahydrofuran	5.23×10^{-7}	5.65×10^{-20}
acetonitrile	2.77×10^{-7}	3.27×10^{-20}

Convenient expressions to calculate this overlap are given by

$$J_{\text{Förster}} = \frac{\int F(\nu) \epsilon(\nu) \nu^{-4} d\nu}{\int F(\nu) d\nu}, \quad (2)$$

$$J_{\text{Dexter}} = \frac{\int F(\nu) \epsilon(\nu) d\nu}{\int F(\nu) d\nu \int \epsilon(\nu) d\nu}, \quad (3)$$

where $F(\nu)$ is the fluorescence intensity of the energy donor at wavenumber ν (in cm⁻¹), and ϵ is the molar extinction coefficient (in cm⁻¹ M⁻¹) of the energy acceptor. Table 3 compiles the overlap integrals calculated via eqs. (2) and (3) from numerical integration over the donor emission and the acceptor absorption (see fig. 1) in various solvents.

A significant increase of J with decreasing solvent polarity occurs, which mainly results from the blue-shift of the donor emission (see fig. 1). The solvent dependence of J (table 3) corresponds quite well with the solvent dependence of the rate of energy transfer observed for each of the bichromophoric molecules (see table 2) as demonstrated by the near unity slope in plots of $\log k$ versus $\log J$ (see fig. 2).

This result not only confirms earlier observations regarding the relation between spectral overlap and rate of energy transfer but mutatis mutandis also shows that in all solvents studied energy transfer is the process responsible for the quenching of the fluorescence observed in 5, 6 and 7 as compared to 9.

4.2. Distance dependence

While both the Förster and the Dexter mechanism are in line with the observed proportionality be-

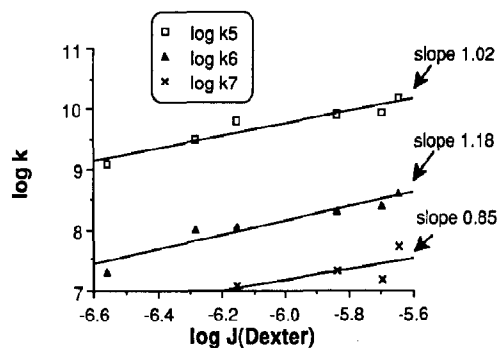


Fig. 2. Double logarithmic plots of the rate of intramolecular energy transfer (see table 2) versus spectral overlap (see table 3) for 5, 6 and 7.

tween the spectral overlap and the rate of energy transfer, these mechanisms predict a different distance dependence [1-3]. Thus, for dominant dipole-dipole interactions, the Förster mechanism leads to an inverse sixth power distance dependence given by

$$k_{\text{Förster}} = \frac{8.8 \times 10^{-25} K^2 \Phi J_{\text{Förster}}}{n^4 \tau R^6}, \quad (4)$$

while the Dexter mechanism is expected – in its simplest form – to lead to an exponential distance dependence,

$$k_{\text{Dexter}} = \frac{4\pi H^2 J_{\text{Dexter}}}{h} = \frac{4\pi^2 (H_0)^2 e^{-2R/L} J_{\text{Dexter}}}{h}. \quad (5)$$

In eq. (4) n is the solvent refractive index, Φ and τ are the fluorescence quantum yield and the fluorescence lifetime (in s) of the isolated donor, K is an orientation factor and R is the distance (in cm). In eq. (5) H is the coupling matrix element, which is assumed to show a single exponential distance dependence with a preexponential factor H_0 and a fall-off defined by the so-called Bohr radius L .

As shown in fig. 3 it is impossible even to approximate the observed distance dependence by an inverse sixth power behavior. Using the center-to-center distances (R_c) the best fit obtained would imply an inverse twelfth power dependence while even with edge-to-edge distances (R_e) an inverse ninth-power dependence is required to fit the data!

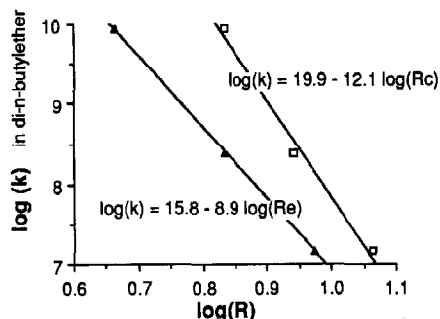


Fig. 3. Double logarithmic plots of the rate of intramolecular energy transfer in 5, 6 and 7 (solvent di-*n*-butyl ether) as a function of R_c and R_e .

On the other hand a single exponential distance dependence using the centre-to-centre chromophore distance (see fig. 4A) gives a reasonable fit with an effective Bohr radius $L = 1.5 \text{ \AA}$ (in di-*n*-butyl ether) while an even better fit (see fig. 4B) is obtained using not R_c but the number (n) of σ bonds separating donor and acceptor! This seems to suggest that an exchange mechanism is dominant even in 7. Since even for pure through-space interactions a single ex-

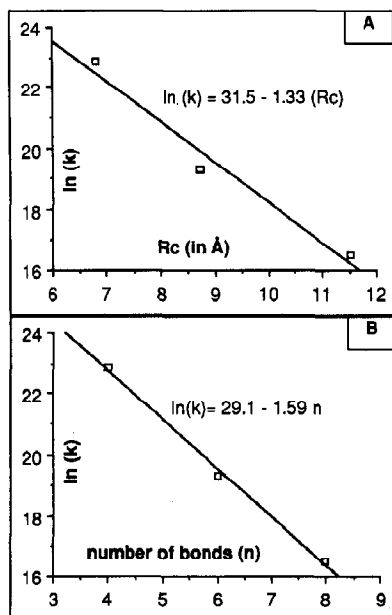


Fig. 4. Exponential fits for the rate of intramolecular energy transfer – in dibutyl ether – as a function of R_c (A) and of the number of σ bonds (B) separating the chromophores.

ponential distance dependence is only a first approximation, the improved fit using n instead of R_c cannot be considered as a proof but only as an indication for the through-bond character of the exchange interaction in 5–7.

Further confirmation that an exchange mechanism dominates in 5, 6, and even in 7 was obtained by comparison of the experimental rates of energy transfer with those calculated for the contribution of the Förster mechanism by application of eq. (4). The rigidity of our systems in principle makes such quantification achievable since the orientation factor K should be uniquely defined and furthermore X-ray structure data of 6 and 7 are available.

Under the overall C_s symmetry of our molecules the electronically allowed part ^{#2} of the carbonyl $n-\pi^*$ transition dipole strength must be polarized perpendicular to the plane of symmetry, i.e. in the trigonal plane of the carbonyl group and perpendicular to the C=O bond. This implies that the carbonyl stretching vibration cannot act as an optically active mode, which is in line with the lack (see fig. 1) of pronounced vibrational structure, in contrast to that observed in the $n-\pi^*$ transition of ketones like 4a and 4b [9] ^{#2} where the C_2 symmetry leads to an allowed component polarized along the C=O bond. If we furthermore assume that the S_0-S_1 transition of the donor chromophore corresponds to a long-axis polarized 1L_b transition of the parent naphthalene molecule this would give an orientation factor $K=0$. If, however, the methoxy substituents perturb the naphthalene chromophore sufficiently (vide infra) to give (partial) 1L_a character to the lowest singlet, the donor and acceptor transition dipole moments are parallel to each other and perpendicular to the connecting line, i.e. $K=1$. On substitution in eq. (4) together with other data obtained in cyclohexane this gives $k_7(\text{Förster}) = 1.6 \times 10^6 \text{ s}^{-1}$. This is more than an order of magnitude slower than actually observed

^{#2} It has been shown that for $n-\pi^*$ transitions in saturated ketones zero-point vibrations in general lead to sufficient lowering of the local symmetry to induce a dipole strength in the “forbidden” directions comparable to that in the “allowed” directions. This implies that the spectral overlap integrals (in table 3), calculated using the total spectral envelope of the $n-\pi^*$ absorption band, probably represent an overestimate of the overlap between the Franck-Condon allowed spectral envelopes, see ref. [20].

(see table 2) for 7 in cyclohexane and thus supports the conclusion that in 7 (and thus certainly also in the lower homologues 5 and 6) energy transfer occurs almost exclusively via an exchange mechanism! It is therefore of interest to evaluate the coupling matrix element H from the experimental data by application of eq. (5). Substitution of all experimental parameters obtained for 5, 6, and 7 in di-*n*-butyl ether as a solvent leads to $H(5) = 60 \text{ cm}^{-1}$, $H(6) = 10 \text{ cm}^{-1}$ and $H(7) = 2.5 \text{ cm}^{-1}$.

It should be realized that these sizeable coupling elements pertain to exchange between two locally excited states. It is interesting to note that whereas the $n-\pi^*$ excited state of the carbonyl group belongs to the A'' irreducible representation of the C_s molecular point group, the first excited singlet state of the naphthalene donor is either A' or A'' depending on whether the first transition is assumed to have 1L_b character (as in naphthalene) or 1L_a character. The magnitude of the exchange integrals derived above makes it very probable that the coupling occurs between states of the same symmetry since the part of the Hamiltonian determining the exchange interaction is totally symmetric and we thus propose that the methoxy substituents perturb the naphthalene π system sufficiently to give the lowest excited singlet 1L_a character. Low temperature polarized absorption and emission spectra may allow a definite assignment of the transition polarizations, and of the role of vibronic mixing.

In a parallel study [21] it was recently found that the radical anion of 5 displays a charge-transfer absorption indicating strong electronic coupling between the radical anion (resulting from one-electron reduction of the carbonyl group) and the dimethoxynaphthalene moiety. From similar data for related radical anions containing the more easily reducible 1,1-dicyanovinyl group electronic couplings of ≈ 1300 , ≈ 500 , and $\approx 250 \text{ cm}^{-1}$ across four, six, and eight σ bonds were calculated [21]. Basically the charge transfer in the radical anions can be described by interaction between two orbitals that exchange the single electron, i.e. the lowest unoccupied MO of the carbonyl group and the lowest unoccupied MO of the dimethoxynaphthalene moiety. The exchange interaction governing intramolecular energy transfer, however, requires [1,8] both interaction between these two orbitals and between the corresponding

highest occupied MOs [1,8]. It therefore seems interesting to note that the distance dependence of the exchange integrals derived from the present study on energy transfer in the ketones 5–7 is almost perfectly quadratic with respect to that of the electronic coupling found [21] from charge transfer in the corresponding radical anions!

5. Concluding remarks

The data presented above provide unequivocal evidence for the dominance of an exchange mechanism in singlet-singlet energy transfer in compounds 5–7 spanning distances up to and including 11.5 Å. The particular efficiency of the bridges interconnecting donor and acceptor in these molecules in mediating energy transfer via an exchange mechanism seems related to their ability to provide a pathway for rapid intramolecular electron transfer by a through-bond mechanism. The complete rigidity of the molecules 5–8 proved to be a very valuable property in quantification of the possible contribution of alternative (i.e. dipole-dipole) mechanisms to the energy transfer.

Acknowledgement

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