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The Mechanism of Short-Range Intramolecular Electronic Energy Transfer in Bichromophoric Molecules

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A study of intramolecular energy transfer (intra-ET) in a series of bichromophoric molecules consisting of cyclic α -diketones incorporating an ortho-, meta-, or para-substituted benzene ring is reported. Most spectroscopic properties of these molecules are described by a superposition of those of their constituent chromophores. Unique for the bichromophore molecule is the fact that, depending on the molecular geometry, energy absorbed by the aromatic chromophore is transferred in part to the α -diketone and both chromophores emit their characteristic fluorescence spectra. An extensive study was made of the intramolecular electronic energy transfer process in solution as a function of temperature. The results indicate that the transfer efficiency is strongly structure dependent suggesting that a Dexter type exchange interaction is responsible for singlet-singlet intra-ET between close chromophores in a bichromophoric molecule. The thermal dependence observed in some cases is attributed to conformational factors. A general theoretical analysis of intra-ET in bichromophoric molecules provides expressions for donor fluorescence decay and for its fluorescence quantum yield in terms of the average distance between donor and acceptor moieties and the flexibility of the chains connecting donor and acceptor. Comparison with the present experimental data supports the predictions of this analysis. It is concluded that intra-ET in bichromophoric molecules is indeed governed by short-range exchange interactions.

Introduction

Electronic energy transfer (EET) processes involve systems composed of at least two molecular species.¹ In addition to intramolecular radiative and nonradiative decay channels, excitation energy can be exchanged between molecules in an intermolecular electronic energy transfer (inter-ET) process. In some molecular species intramolecular relaxation involves, in addition to vibrational and electronic transitions, intramolecular electronic energy transfer (intra-ET) between two chromophores incorporated in a single molecule as a separate process.

Energy transfer (ET) processes are usually described in terms of bimolecular quenching



where the excitation energy is transferred from an excited donor D^* molecule to a ground-state acceptor molecule A , resulting in quenching of D^* and sensitization of A . For D^* , process 1 adds to its existing decay routes another nonradiative decay channel and thus its overall decay rate k is given by the Stern-Volmer relation²

$$k = 1/\tau_D + k_Q[A] \quad (2)$$

where k_Q is the bimolecular quenching rate constant and τ_D is the emission lifetime of D^* .

In all EET processes to be discussed, a resonance condition between the initial state of the system $D^* + A$ is required. In solution EET is slow compared to vibrational relaxation in D^* and A^* so that the initial and final states are vibrationally relaxed and the ET transitions are determined by the Frank-Condon principle at the common overlap frequency of D and A .³

Thus ET is possible if the overlap integral

$$J = \int_0^\infty F_D(\bar{\nu}) \bar{\epsilon}_A(\bar{\nu}) d\bar{\nu} \quad (3)$$

is nonzero, where $F_D(\bar{\nu})$ and $\bar{\epsilon}_A(\bar{\nu})$ are the normalized emission spectrum of D and the extinction coefficient of A , respectively

$$\int_0^\infty F_D(\bar{\nu}) d\bar{\nu} = \int_0^\infty \bar{\epsilon}_A(\bar{\nu}) d\bar{\nu} = 1 \quad (4)$$

The initial state of the system can be described by the wave function

$$\psi_i = (1/2^{1/2})(\psi_D^{(1)}\psi_A^{(2)} - \psi_D^{(2)}\psi_A^{(1)}) \quad (5)$$

and its final state by

$$\psi_f = (1/2^{1/2})(\psi_D^{(1)}\psi_A^{(2)*} - \psi_D^{(2)}\psi_A^{(1)*}) \quad (6)$$

Interaction leading to EET can be described by an interaction Hamiltonian H' and an interaction matrix element β^3

$$\beta = \int \psi_i H' \psi_f d\tau = (1/2) \int \psi_D^{(1)}\psi_A^{(2)} H' \psi_D^{(1)}\psi_A^{(2)} d\tau - (1/2) \int \psi_D^{(1)}\psi_A^{(2)} H' \psi_D^{(2)}\psi_A^{(1)} d\tau \quad (7)$$

The first term in eq 7 is the Coulombic interaction and the second one is the exchange interaction term. When expanding in series, the first term in the Coulombic contribution is the dipole-dipole interaction which is given by

$$\beta_{d-d} \sim \bar{M}_D \cdot \bar{M}_A / R^3 \quad (8)$$

where \bar{M}_D and \bar{M}_A are the transition dipole moments of the $D^* \rightarrow D$ and $A \rightarrow A^*$ transitions, respectively, and R is the distance between D and A molecules. The exchange interaction is a quantum mechanical effect arising from symmetry properties of the wave functions with respect to exchange of spin and space coordinates of two electrons separated by a distance r_{12} in the D - A system. The space part of this interaction is given by

$$\beta_{ex} = \int \phi_D^{(1)}\phi_A^{(2)}(e^2/r^{12})\phi_D^{(2)}\phi_A^{(1)} d\tau \quad (9)$$

The transfer rate k_{ET} is given by the "golden rule"

$$k_{ET} = (2\pi/\hbar)\beta^2\rho \quad (10)$$

where ρ is the density states related to the overlap integral J .³ Substitution of (8) and (9) in (10) yields the Förster⁴⁻⁶ relation for long-range dipole-dipole ET rate, k_{ET}^{d-d} , and the Dexter⁷ relation for the short-range exchange interaction ET rate, k_{ET}^{ex}

(4) Förster, Th. *Z. Naturforsch.* **1949**, *49*, 321; *Z. Elektrochem. Angew. Phys. Chem.* **1949**, *53*, 93.

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(3) Mataga, N.; Kubota, T. "Molecular Interactions and Electronic Spectra"; Marcel Dekker: New York, 1970.

$$k_{ET}^{d-d} = \tau_D^{-1}(R_0/R)^6 \quad (11)$$

where R_0 is the critical transfer radius

$$R_0 = (9000 \ln 10 \chi^2 \Phi_D / 128 \pi^2 n^4 N_0) \int_0^\infty \bar{\nu}^{-4} F_D(\bar{\nu}) \epsilon_A(\bar{\nu}) d\bar{\nu} \quad (12)$$

Here χ is an orientation factor for A and D dipoles ($\chi^2 = 2/3$ for random distribution) and n is the refractive index of the medium, Φ_D is the fluorescence quantum yield of D, and $\epsilon_A(\bar{\nu})$ is the molar extinction coefficient of A in $L \text{ mol}^{-1} \text{ cm}^{-1}$.

The Dexter exchange interaction ET rate is given by⁷

$$k_{ET}^{ex} = (2\pi/\hbar) K J \exp(-2R/L) \quad (13)$$

where R is the distance between D and A molecules, L is the average orbital radius involved in ψ_i and ψ_f , and K is a constant which, unlike R_0 , is not related to any experimental parameter and thus, since J involves normalized $\bar{\epsilon}_A(\bar{\nu})$ (in contrast to $\epsilon_A(\bar{\nu})$ in eq 12) energy transfer via forbidden transitions in A are allowed by exchange interactions while they are much less probable in the Förster mechanism. Thus, we may conclude that unless $R_0 < 10 \text{ \AA}$ energy will be transferred mainly by the Förster mechanism. There are, however, instances in which the Förster transfer is forbidden or involves higher multipolar interactions.

Molecular diffusion may play a role in the ET process in solution. In the limiting case where $R_0 < 10 \text{ \AA}$, exchange interaction is noticeable and the ET rate may become diffusion controlled³

$$k_Q = 8RT/3000\eta \quad (14)$$

where η is the viscosity of the medium. In other words, the rate-determining step in a short-range inter-ET process in solution is the rate of molecular encounters; the transfer itself is fast and is governed by eq 13. In general, even for large R_0 , the transfer kinetics in solution do not follow the simple Förster formula, and various modifications have been suggested.^{3,8,9}

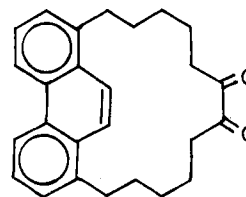
However, when D and A moieties are *fixed* in close proximity in a *single* bichromophoric molecule D-A, diffusion is no longer involved in the ET process. Instead, intra-ET governed by short-range interactions (eq 13) might be observed.

Recently Bourson et al.¹⁰ reported studies of intra-ET in a bichromophoric molecule composed of two dye moieties connected by a *flexible* $-(CH_2)_3$ -chain. The authors suggested that changing the chain length will provide them with information regarding the mechanism of the intra-ET process. Such an approach is not likely to yield the desired information as earlier investigations reported by Weber¹¹ and by Schnepf and Levy¹² have indicated. These authors reported that compounds of the type D- $(CH_2)_n$ -A gave only fluorescence of the acceptor moiety after excitation of the donor chromophore. The quantum yield was independent of the number of methylene groups separating the two chromophores. Later workers¹³ examined similar systems involving isolated chromophores. In some cases,^{13d} the donor and acceptor were attached to a rigid system so that their spatial relationship was known to a considerable degree (unfortunately, geometrical variations in such a rigid system were not feasible). The occurrence of intra-ET could be readily evaluated from knowledge

of the excitation and emission spectra of each moiety alone and comparison with spectra of the bichromophoric species.

In all of these cases, complete quenching of D fluorescence was observed with concomitant emission *solely* from A. This was true even for donor chromophores with high fluorescence quantum yields. However, observed yields of emission from A* were less than the theoretical maximum, implying that D* in the bichromophoric molecule decayed nonradiatively to ground electronic states through channels unavailable to the separate D chromophore. Residual D* emission might be anticipated in systems where nonradiative decay is not enhanced in the bichromophoric molecule and/or where intra-ET is similar in rate to fluorescence decay of D* due to combination of weak spectral overlap (low J) and weak spatial overlap of D and A orbitals (large R).

Earlier work in this laboratory¹⁴ provided the first example of a bichromophoric molecule which, in fact, exhibited *dual* fluorescence due to *partial* intra-ET between D* and A. The macrocyclic compound I containing phenanthrene D and α -di-

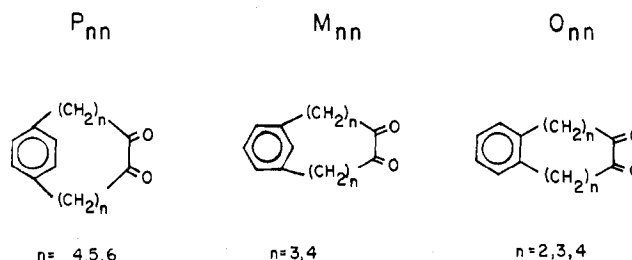


I

ketone A moieties was synthesized¹⁵ for intra-ET and photochemical studies. Comparison of the absorption spectra of I with model separate D and A compounds showed negligible overlap of the absorption and fluorescence spectra of the chromophores. Emission spectra were determined at various temperatures with CW and time-resolved (nano- and picosecond) laser excitation. Fluorescence from both chromophores was observed upon excitation of the phenanthrene moiety. The combined results established that very rapid intra-ET (A* emission rise time $< 2 \text{ ns}$) occurs from higher vibrational states of the phenanthrene moiety or higher energy conformers of I. A similar example has been provided by Zimmerman et al.¹⁶

These compounds do not suffer from the *flexibility* characteristic of a single- $(CH_2)_n$ -chain and, in addition, have very poor spectral overlap, assuring low intra-ET efficiency which results in dual fluorescence. These properties are essential in order to allow elucidation of the transfer mechanism.

The results obtained with I showed that macrocyclic α -diketones incorporating an aromatic ring are excellent substrates for studies of intra-ET. Compounds chosen for further study were the *p*- and *m*-cyclophanes (P_{nn} and M_{nn}) and the ortho analogues, benzocycloalkenediones (O_{nn}). These compounds have been syn-



II

thesized¹⁶ and preliminary results¹⁷ with the para series, P_{nn} ,

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(16) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933.

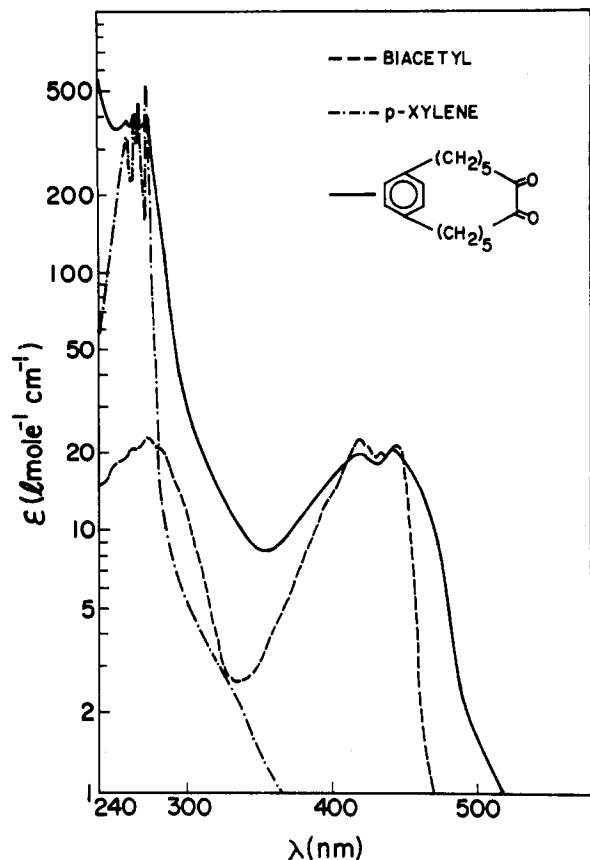


Figure 1. Absorption spectra for the bichromophoric molecule P₅₅ (full curve) together with the corresponding spectra for *p*-xylene (---) and biacetyl (— · —) dissolved in methylcyclohexane/isopentane.

indicated that the transfer efficiency is strongly dependent on the D-A separation R which is determined by the length of the $(\text{CH}_2)_n$ bridges. Since this bridge has limited flexibility, a distribution of R 's contributes to the observed effect.¹⁸ Further studies with the bichromophoric molecules II are reported in the present paper. It is shown here that Dexter's theory⁷ predicts the correct distance dependence for the intra-ET process.

Experimental Section

A laser fluorimeter based on nitrogen laser excitation (Molelectron UV 400), on nitrogen laser-pumped dye laser excitation (Molelectron DL 200), or on 268-nm excitation provided by frequency doubling the coumarin 153 dye laser was employed. The details of the system are given elsewhere.¹⁴ In some cases time-correlated single-photon counting was used for lifetime determination.

Continuous wave corrected fluorimetry measurements were performed on a Perkin-Elmer MPF-4 fluorescence spectrophotometer. Cary 14 and 15 spectrophotometers were used for absorption measurements.

Synthesis of the bichromophoric molecules is described separately;¹⁹ a sample of O₂₂ was obtained from Prof. Gleiter (University of Heidelberg). A 1:1 mixture of methylcyclohexane (spectrograde) and isopentane (analytical grade) was used as solvent for all studies. The solvent was purified by passing through a column of activated alumina. Typically, concentrations of 3×10^{-3} M were used. Samples in quartz cells were degassed by five freeze-pump-thaw cycles.

(17) Hassoon, S.; Lustig, H.; Rubin, M. B.; Speiser, S. *Chem. Phys. Lett.* **1983**, *98*, 345.

(18) Speiser, S.; Katriel, J. *Chem. Phys. Lett.* **1983**, *102*, 88.

(19) Rubin, M. B.; Migdal, S.; Speiser, S.; Kaftory, M. *Isr. J. Chem.*, in press. In this paper, evidence is given to support our conclusion that the temperature dependence is inherently related to the conformational changes. Moreover, no T dependence is observed for P₄₄, P₆₆, and O₃₃, compounds which have only one stable conformer.

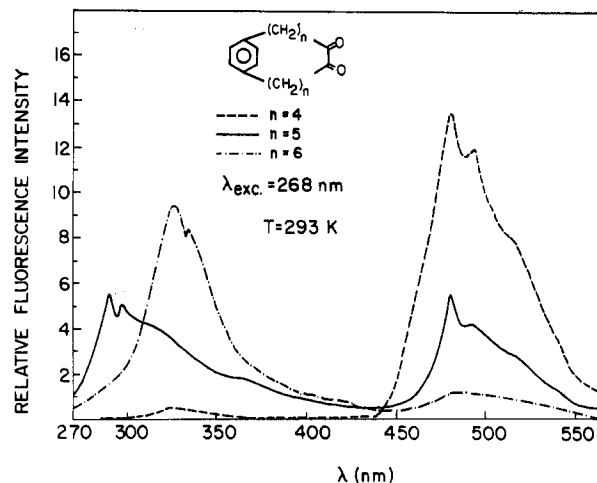


Figure 2. Fluorescence spectra for the bichromophoric molecules P_{nn} excited by 268-nm laser light.

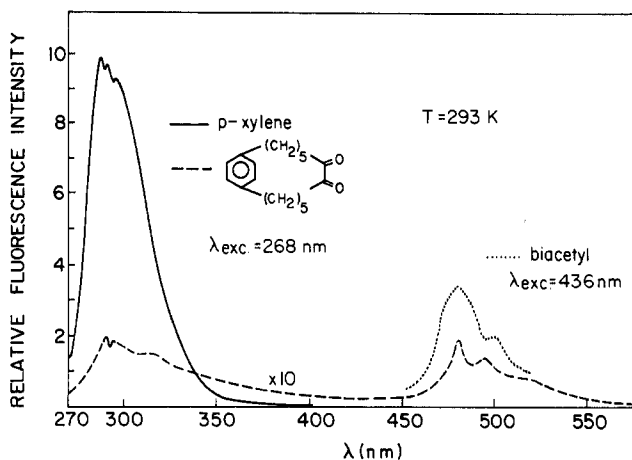


Figure 3. Fluorescence spectra of P₅₅ (— · —) compared to *p*-xylene (full curve) (at the same concentration) both excited by 268-nm laser light at 293 K and of biacetyl (···) excited at 436 nm.

Results and Discussion

The absorption spectrum of P₅₅ together with the absorption spectra of the separate D and A chromophores is shown in Figure 1. It is clearly evident that the spectrum of the bichromophoric molecule is a simple superposition of *p*-xylene and biacetyl absorption spectra. The same behavior was observed for all compounds. The fluorescence emission spectra obtained by 268-nm excitation of P_{nn} are shown in Figure 2. Comparison of the fluorescence spectra of *p*-xylene and biacetyl with those for P_{nn} identifies the dual emission as that of the benzene and α -diketones moieties in P_{nn} (Figure 3). Dual fluorescence could also be observed from mixtures of *p*-xylene and biacetyl in fluid solution but disappeared in frozen solution as expected for an inter-ET process. This is in contrast to the behavior of the bichromophoric molecules for which intra-ET is manifested by dual fluorescence even in frozen solution. Figure 2 shows an almost complete intra-ET for P₄₄, a partial intra-ET and dual fluorescence for P₅₅, and almost no transfer for P₆₆. Thus, small changes in the $-(\text{CH}_2)_n-$ bridge are manifested in a dramatic change in the transfer efficiency. Similar results for the meta-M_{nn} and ortho-O_{nn} analogues of P_{nn} are shown in Figures 4 and 5.

The calculated spectral overlap integral, eq 3, for xylene emission and biacetyl absorption is $J = 2 \times 10^{-7}$ cm. Using eq 12 we find that $R_0 = 10$ Å, indicating that ET due to dipole-dipole Förster type⁴⁻⁶ interaction is not highly probable as expected for the weak $r \rightarrow \pi^*$ transition of the α -diketone A. On the other hand, the average distance between the two moieties in the bichromophoric molecules II is short enough¹⁹ to promote transfer via Dexter's exchange interaction mechanism.⁷ Here one expects an exponential dependence of the transfer efficiency on the D-A

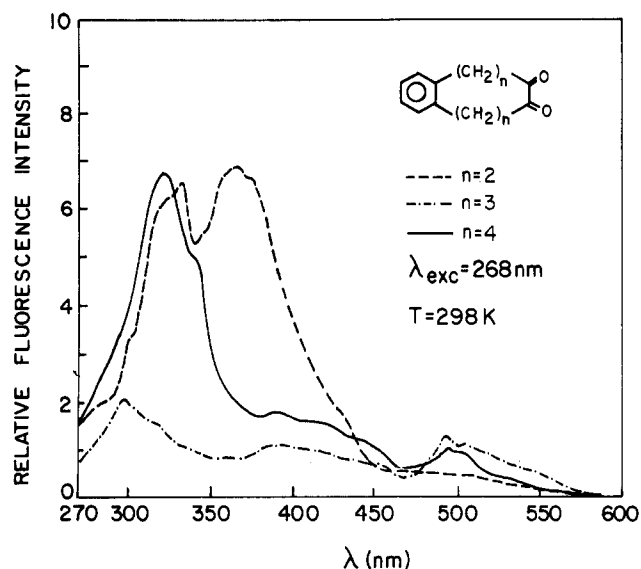


Figure 4. Fluorescence spectra for O_m excited by 268-nm laser light at 293 K.

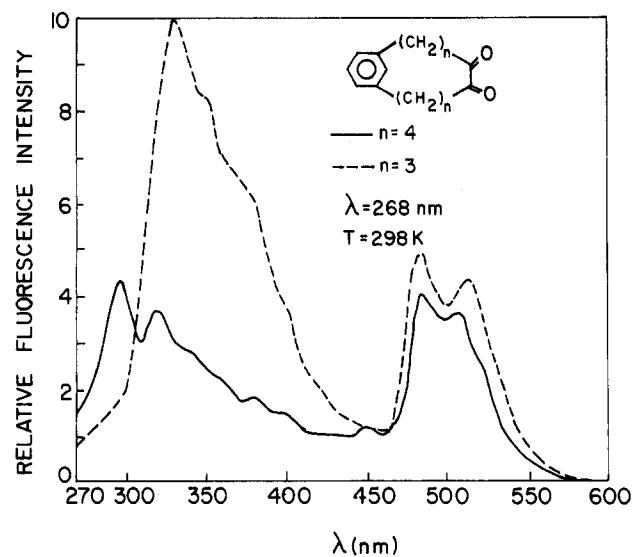


Figure 5. Fluorescence spectra for M_m excited by 268-nm laser light at 293 K.

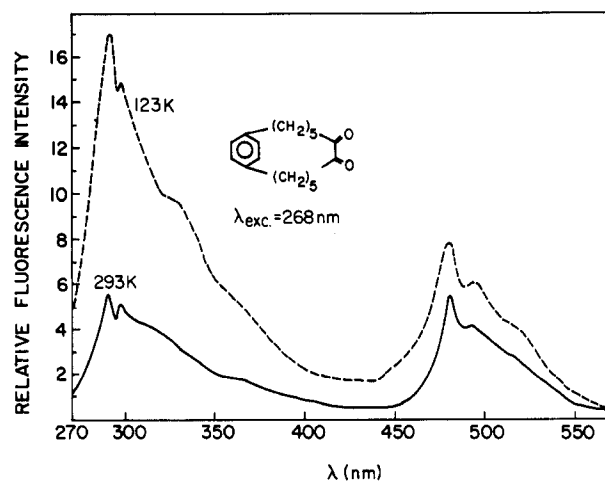


Figure 6. Temperature-dependent fluorescence spectrum of P_{55} .

separation distance eq 13. The geometry effect observed is indicative of a very strong distance dependence for the intra-ET process that cannot be accounted for by the mild R^{-6} dependence characteristic of Förster type interactions.⁴⁻⁶ We provide evidence

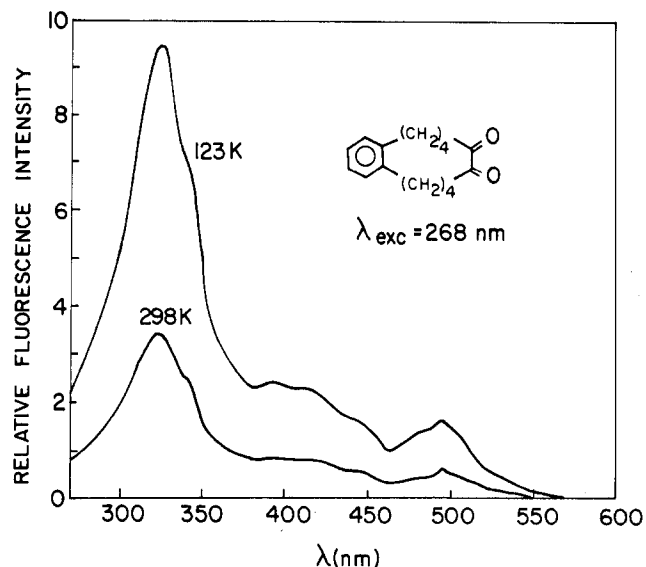


Figure 7. Temperature-dependent fluorescence spectrum for O_{44} excited by 268-nm laser light.

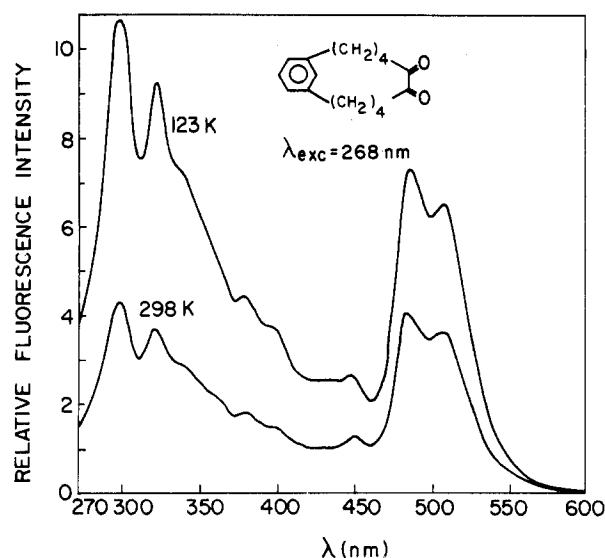


Figure 8. Temperature-dependent fluorescence spectrum for M_{44} excited by 268-nm laser light.

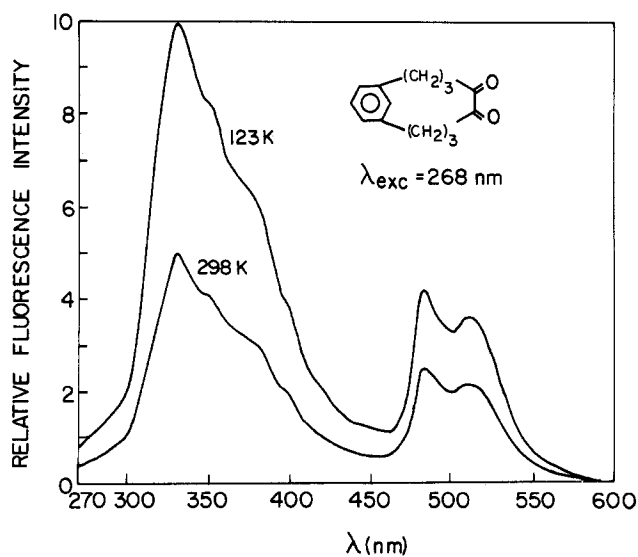


Figure 9. Temperature-dependent fluorescence spectrum for M_{33} excited by 268-nm laser light.

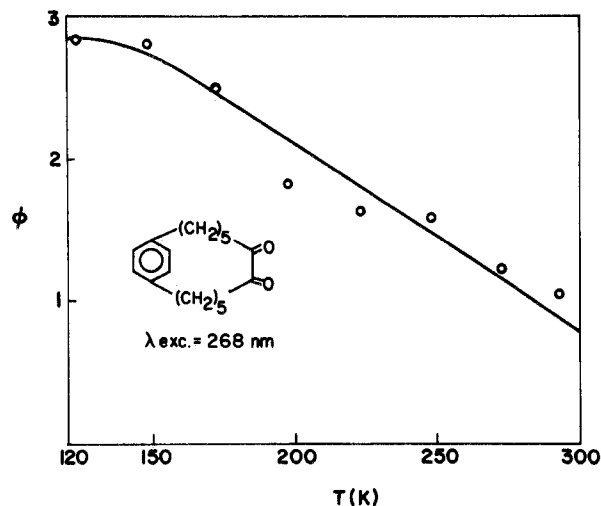


Figure 10. Temperature-dependent fluorescence quantum yield ϕ for the benzene chromophore of P_{55} .

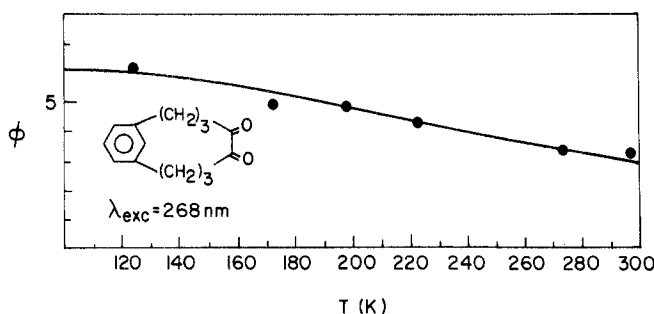


Figure 11. Temperature-dependent fluorescence quantum yield ϕ for the benzene chromophore of M_{33} .

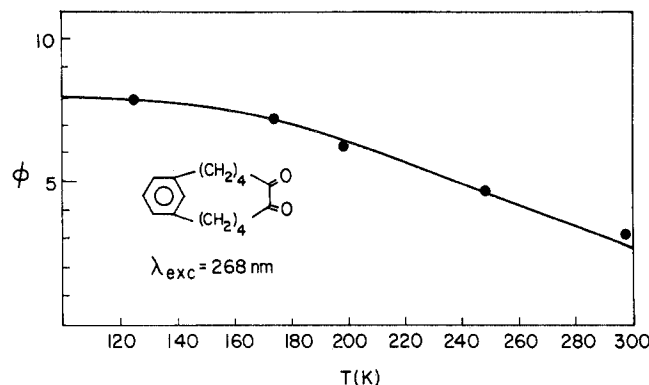


Figure 12. Temperature-dependent fluorescence quantum yield ϕ for the benzene chromophore of M_{44} .

for an exponential dependence on R based on Dexter's theory.⁷

It is expected that this type of intra-ET will be very sensitive to temperature changes which affect the ET efficiency either by specific vibronic interactions or by conformational changes.¹³ Temperature-dependent intra-ET in the bichromophoric molecules II was studied and the results are shown in Figures 6–9. The general behavior of the donor fluorescence yield ϕ , measured from integrated emission spectra, vs. T is similar to that observed earlier for I¹⁴ (Figures 10–13). The enhancement observed in the fluorescence intensity of the α -diketone chromophore (Figures 6–9) is typical of α -diketones in general and was found identical with that observed for biacetyl. Moreover, the xylene fluorescence quantum yield was found to be temperature independent. Thus we may conclude that the observed temperature dependence is directly related to the intra-ET process.

A kinetic scheme for the analysis of intra-ET in bichromophoric molecules D–A involving the conformational change $(D-A)_1 \rightleftharpoons (D-A)_2$ is shown in Figure 14. Here $\sigma_D I$ is the pumping rate

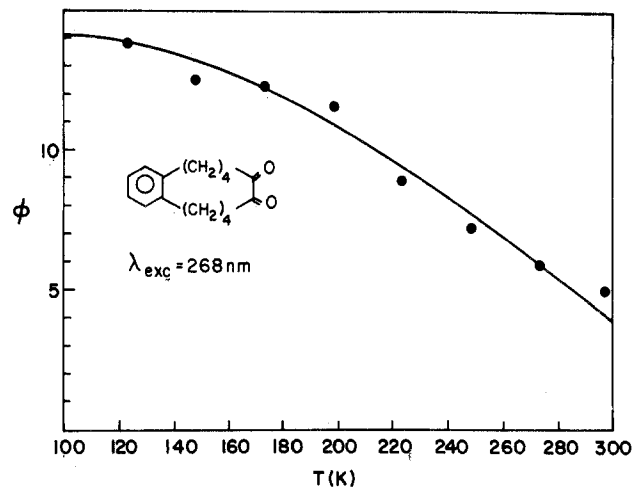


Figure 13. Temperature-dependent fluorescence quantum yield ϕ for the benzene chromophore of O_{44} .

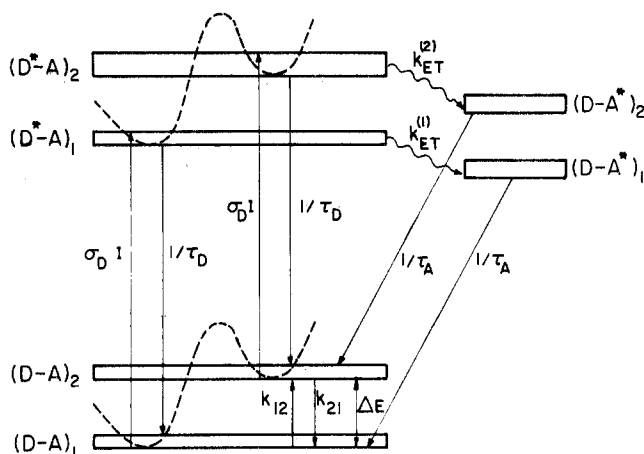


Figure 14. Kinetic scheme for intra-ET in bichromophoric molecules D–A involving conformational change.

of the donor moiety having an absorption cross section σ_D by a laser pulse of intensity I , and τ_D and τ_A are the fluorescence lifetimes for D and A molecules, respectively. The equilibrium constant for the two conformers $(D-A)_1$ and $(D-A)_2$ is given by $k_{12}/k_{21} = \exp(-\Delta E/RT)$. Intra-ET rate constants for $(D^*-A)_1$ and $(D^*-A)_2$ are $k_{ET}^{(1)}$ and $k_{ET}^{(2)}$, respectively. Utilizing this scheme we obtain the following result for the donor fluorescence quantum yield:

$$\phi_0/\phi = 1 + \tau_D k_{ET}^{(1)} (1 + \tau_D k_{ET}^{(2)}) [1 + \tau_D k_{ET}^{(2)} + (1 + \tau_D k_{ET}^{(1)}) \exp(-\Delta E/RT)]^{-1} + \tau_D k_{ET}^{(2)} (1 + \tau_D k_{ET}^{(1)}) [1 + \tau_D k_{ET}^{(1)} + (1 + \tau_D k_{ET}^{(2)}) \exp(-\Delta E/RT)]^{-1} \exp(-\Delta E/RT) \quad (15)$$

where $\phi_0 = \tau_D k_r$, k_r being the radiative decay rate of A.

For large temperature range $1 + \tau_D k_{ET}^{(2)} \gg (1 + \tau_D k_{ET}^{(1)}) \exp(-\Delta E/RT)$, thus

$$\phi_0/\phi = 1 + \tau_D k_{ET}^{(1)} + \tau_D k_{ET}^{(2)} [1 + \tau_D k_{ET}^{(2)}]^{-1} \exp(-\Delta E/RT) = \frac{1 + \tau_D k_{ET}^{(1)} [1 + \delta \exp(-\Delta E/RT)]}{1 + \tau_D k_{ET}^{(2)} [1 + \delta \exp(-\Delta E/RT)]} \quad (16)$$

where

$$\delta = \tau_D k_{ET}^{(2)} / [\tau_D k_{ET}^{(1)} (1 + \tau_D k_{ET}^{(2)})] \quad (16a)$$

From Figures 9–11 we can obtain the extrapolated value of ϕ at $T \rightarrow 0$, $\Phi_0 = \phi_0 [1 + \tau_D k_{ET}^{(1)}]^{-1}$. Rewriting eq 16 in terms of Φ_0 we obtain

$$\phi^{-1} - \Phi_0^{-1} = \delta \Phi_0^{-1} \tau_D k_{ET}^{(1)} \exp(-\Delta E/RT) \quad (16b)$$

The Arrhenius behavior for ϕ predicted by eq 1b is obeyed by compounds II as shown in Figures 15–18. The range of ΔE values are typical of conformational changes involving the $-(CH_2)_n-$

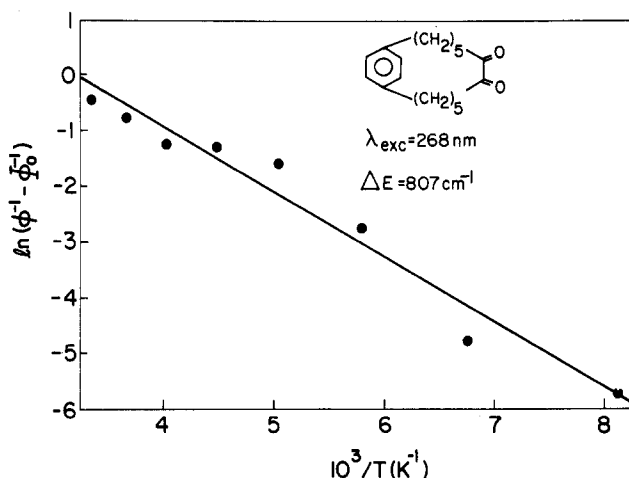


Figure 15. Arrhenius plot (eq 16b) of the temperature-dependent fluorescence quantum yield of the donor moiety in P₅₅.

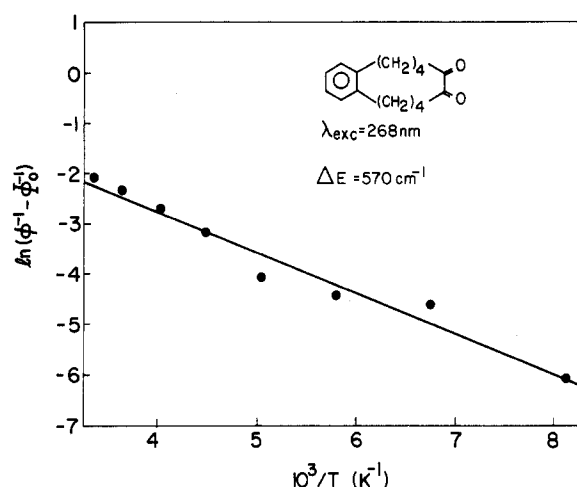


Figure 16. Arrhenius plot (eq 16b) of the temperature-dependent fluorescence quantum yield of the donor moiety in O₄₄.

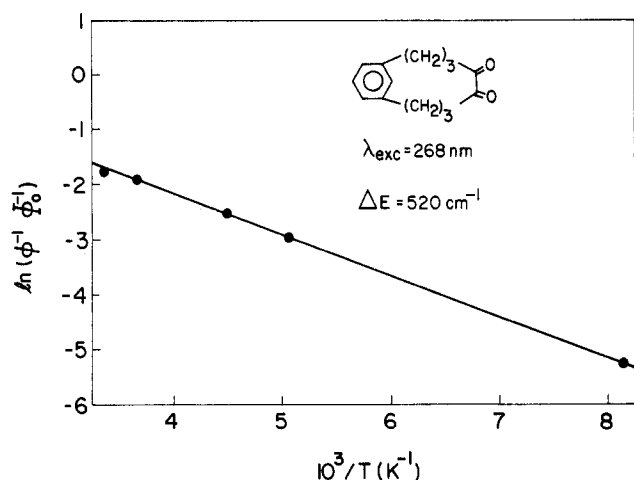


Figure 17. Arrhenius plot (eq 16b) of the temperature-dependent fluorescence quantum yield of the donor moiety in M₃₃.

bridge.¹⁹ Different bridges are likely to yield different ΔE values. No temperature dependence is expected for highly efficient intra-ET or when only one stable conformer exists, as is the case for P₄₄, P₆₆, and O₃₃.¹⁹

For O₂₂ the fluorescence spectrum reveals the existence of an additional emission band around 380 nm (Figure 4). Conformational analysis and NMR studies show a unique structure for this molecule as compared to all other bichromophoric molecules II. Due to the close proximity of the two chromophores in O₂₂

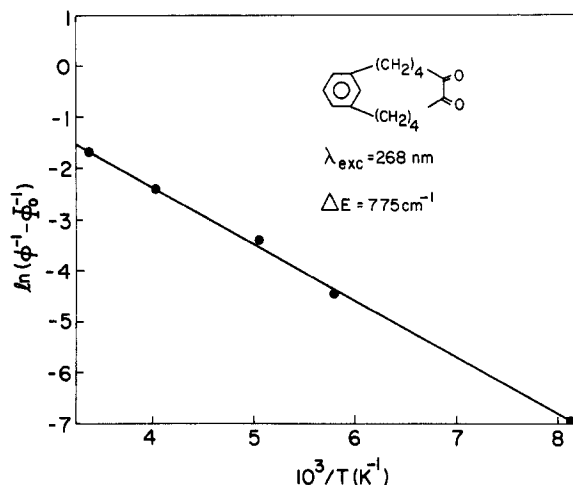


Figure 18. Arrhenius plot (eq 16b) of the temperature-dependent fluorescence quantum yield of the donor moiety in M₄₄.

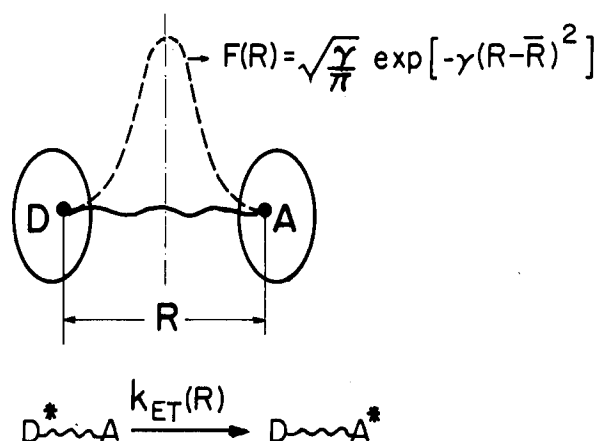


Figure 19. Intramolecular electronic energy transfer in bichromophoric molecule D-A. The D and A moieties are connected by a bridge of limited flexibility resulting in a distribution of D-A distances R .

it is possible that an intramolecular exciplex is formed or that through-bond interactions are operative, resulting in an additional band at about 380 nm. This effect masks any intra-ET process in this molecule. Further details concerning structural analysis of compounds II will be published elsewhere.¹⁹

In order to account for the dependence of ϕ on the molecular geometry (Figures 2, 4, and 5) one has to examine the general case of intra-ET in randomly distributed bichromophoric conformations resulting in some experimental average value for ϕ . For any bichromophoric molecule there may be a distribution of spatial arrangements, $F(R)$ (Figure 19), which must be taken into account when relating experimental results to molecular structure.

Steinberg et al.²⁰ have studied intra-ET in *large* bichromophoric molecules possessing long flexible polymer chain bridges where the average D-A separation is larger than 15 Å and the microscopic ET process due to dipole-dipole interaction, described by eq 11, is modified by using an appropriate $F(R)$.²¹

(20) (a) Hass, E.; Wilchek, M.; Katchalski-Katzir, E.; Steinberg, I. Z. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1807. (b) Hass, E.; Katchalski-Katzir, E.; Steinberg, I. Z. *Biochemistry* **1978**, *17*, 11, 5064.

(21) It should be noted that in cases of inter-ET a macroscopic sample has to be considered where energy is transferred from each D to randomly distributed A's. In this case one has to average over all possible donors thus requiring double averaging over a distribution of ET rates and a given distribution of molecules, $F(R)$. Thus, for inter-ET the average decay signal for N acceptor molecules in a macroscopic sample is³

$$P(t) = [\exp(-t/\tau_D)] \left\{ \int \exp[-k_{ET}(R)t] F(R) dR \right\}^N$$

with eq 11 and eq 13 expressions of $\bar{P}(t)$ for inter-ET via dipole-dipole interaction³ and exchange interaction, respectively,^{22,23} are obtained.

(22) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978.

(23) Blumen, A. *J. Chem. Phys.* **1980**, *72*, 2632.

We are interested in intra-ET in *small* bichromophoric molecules with bridges of limited flexibility and with poor spectral overlap between the D-A moieties. For our purposes it is useful to rewrite eq 13 in the form

$$k_{ET}^{\text{ex}} = (1/\tau_D) \exp[-\beta(R - R_0')] = \alpha \exp(-\beta R) \quad (17)$$

where $\beta = 2/L$ and

$$(2\pi/\hbar)KJ = \exp(\beta R_0')/\tau_D \equiv \alpha \quad (18)$$

R_0' being the critical transfer radius for which $k_{ET}^{\text{ex}} = 1/\tau_D$ which, unlike R_0 (eq 12), cannot be calculated from spectroscopic data on D and A. The limited bridge flexibility and the molecular axial symmetry can be described by a narrow Gaussian distribution

$$F(R) = (\gamma/\pi)^{1/2} \exp[-\gamma(R - \bar{R})^2] \quad (19)$$

Equation 19 is an approximation with two fitting parameters \bar{R} and γ . It might be that other $F(R)$, symmetrical around \bar{R} , may fit as well, slightly affecting the analysis which follows. In eq 19 \bar{R} is the most probable D-A separation for a given bichromophoric molecule and γ^{-1} is a temperature-dependent width measuring the D-A bridge flexibility. Although exchange interaction will in general depend on the relative orientation of D and A orbitals this is not taken into account in $F(R)$. However, for molecules II we have found that conformational changes do not involve significant changes in orientation of the two chromophores¹⁹ with the exception of O₄₄. As is shown below our results justify the use of a one-dimensional distribution of R 's.

The average decay signal, $\bar{P}(t)$, is given by

$$\bar{P}(t) = \int \exp(-t/\tau_D)(1 + \tau_D k_{ET}) F(R) dR \quad (20)$$

Substituting eq 17 and 19 in eq 20 yields²¹

$$\begin{aligned} \bar{P}(t) &= (\gamma/\pi)^{1/2} \int_{-\infty}^{\infty} \exp\{(-t/\tau_D)[1 + \exp[-\beta(R - R_0')]]\} \times \\ &\quad \exp[-\gamma(R - \bar{R})^2] dR = (\gamma/\pi)^{1/2} \exp(-t/\tau_D) \times \\ &\quad \int_{-\infty}^{\infty} \exp\{(-t/\bar{\tau}) \exp[-\beta(R - \bar{R})]\} \exp(-\gamma(R - \bar{R})^2) \times \\ &\quad dR = (\gamma/\pi)^{1/2} \exp(-t/\tau_D) \int_{-\infty}^{\infty} \exp\{(-t/\bar{\tau}) \times \\ &\quad \exp(-\beta\rho)\} \exp(-\gamma\rho^2) d\rho \quad (21) \end{aligned}$$

where we have used the substitutions

$$\rho \equiv R - \bar{R} \quad (22)$$

$$\bar{\tau} \equiv \tau_D \exp[\beta(\bar{R} - R_0')] = \alpha^{-1} \exp(\beta\bar{R}) \quad (23)$$

Equation 21 can be integrated numerically. For rigid bichromophoric molecules, however

$$\beta(R - \bar{R}) \sim \beta/(2\gamma)^{1/2} < 1 \quad (24)$$

where $1/(2\gamma)^{1/2}$ measures the standard deviation from \bar{R} for a Gaussian distribution of R 's. Thus eq 21 can be approximated by

$$\begin{aligned} \bar{P}(t) &= (\gamma/\pi)^{1/2} \exp(-t/\tau_D) \int_{-\infty}^{\infty} \exp\{(-t/\bar{\tau}) \times \\ &\quad [1 - \beta\rho + (\beta^2/2)\rho^2] - \gamma\rho^2\} d\rho = [2\gamma/(2\gamma + t\beta^2/\bar{\tau})]^{1/2} \times \\ &\quad \exp\{(-t/\tau_D)[1 + \tau_D/\bar{\tau}] + (t/\bar{\tau})^2\beta^2(2\beta^2t/\bar{\tau} + 4\gamma)^{-1}\} \quad (25) \end{aligned}$$

Equation 25 predicts nonexponential behavior for donor fluorescence (phosphorescence) decay due to intra-ET via exchange interaction in bichromophoric molecules. For small t an exponential decay is obtained

$$\bar{P}(t) = \exp\{(-t/\tau_D)(1 + \tau_D/\bar{\tau})\} = \exp(-t\theta/\tau_D) \quad (26)$$

where due to intra-ET the donor lifetime is reduced by a factor of θ

$$\theta = 1 + \tau_D/\bar{\tau} = 1 + \exp[\beta(R_0' - \bar{R})] = 1 + \tau_D \bar{k}_{ET} \quad (27)$$

where

$$\bar{k}_{ET} \equiv k_{ET}^{\text{ex}}(\bar{R}) = \alpha \exp(-\beta\bar{R}) \quad (27a)$$

Accurate fluorescence lifetime measurements will usually require nanosecond or subnanosecond excitation. Our 10-ns experimental time resolution did not provide us with a means of checking the validity of eq 27. However, τ_D was always smaller (<10 ns) than the 30-ns fluorescence lifetime of xylene. Therefore most intra-ET studies will involve determining the donor fluorescence (or phosphorescence) quantum yield ϕ relative to its value in the absence of A, ϕ_0 . The average donor fluorescence (phosphorescence) quantum yield ϕ is given by

$$\phi = k_r \int_0^{\infty} \bar{P}(t) dt \quad (28)$$

where k_r is the donor radiative decay rate. Using eq 21 we obtain

$$\begin{aligned} \phi &= k_r (\gamma/\pi)^{1/2} \int_{-\infty}^{\infty} \exp[-\gamma(R - \bar{R})^2] dR \int_0^{\infty} \exp\{(-t/\tau_D) \times \\ &\quad [1 + \exp(-\beta(R - R_0'))]\} dt = \tau_D k_r (\gamma/\pi)^{1/2} \int_{-\infty}^{\infty} dR \{1 + \\ &\quad (\tau_D/\bar{\tau}) \exp[-\beta(R - \bar{R})]\}^{-1} \exp[-\gamma(R - \bar{R})^2] = \\ &\quad \phi_0 (\gamma/\pi)^{1/2} \int_{-\infty}^{\infty} [1 + (\tau_D/\bar{\tau}) \exp(-\beta\rho)]^{-1} \exp(-\gamma\rho^2) d\rho \quad (29) \end{aligned}$$

where $\phi_0 = \tau_D k_r$ (vide supra).

For poor spectral overlap $(\tau_D/\bar{\tau}) \exp(-\beta\rho) \ll 1$ so that

$$\phi \sim \phi_0 (\gamma/\pi)^{1/2} \int_{-\infty}^{\infty} [1 - (\tau_D/\bar{\tau}) \exp(-\beta\rho)] \exp(-\gamma\rho^2) d\rho \quad (30)$$

or

$$\phi = \phi_0 [1 - (\tau_D/\bar{\tau}) \exp(\beta^2/4\gamma)] \quad (31)$$

Using eq 23 and 27a we can write

$$\begin{aligned} Q \equiv 1 - \phi/\phi_0 &= \exp(\beta^2/4\gamma) \exp(\beta R_0') \exp(-\beta\bar{R}) = \\ &= \tau_D \alpha \exp(-\beta\bar{R}) \exp(\beta^2/4\gamma) = \tau_D \bar{k}_{ET} \exp(\beta^2/4\gamma) \quad (32) \end{aligned}$$

Equation 32 predicts a linear dependence of $\ln Q$ vs. \bar{R} with a slope of $-\beta$, a property amenable to experimental verification.

Using eq 17 and 18 and comparing eq 32 with eq 16 we obtain

$$\begin{aligned} 1 + \tau_D \bar{k}_{ET} [1 + \delta \exp(-\Delta E/RT)] &= \\ 1/[1 - \tau_D \bar{k}_{ET} \exp(\beta^2/4\gamma)] \quad (33) \end{aligned}$$

thus relating γ to T . For very narrow distribution corresponding to $\gamma \gg 1$, eq 33 yields

$$\exp(\beta^2/4\gamma) = 1 + \delta \exp(-\Delta E/RT) \quad (34)$$

or

$$\gamma^{-1} \approx (4\delta/\beta^2) \exp(-\Delta E/RT) \quad (35)$$

To a first approximation we assume that the chain flexibility can be represented by a single harmonic mode of a frequency ω and a reduced mass μ . The variance, σ , of the mode amplitude, x , is given by²⁴

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = (\hbar/\mu\omega) \{1/2 + 1/[\exp(-\hbar\omega/kT) - 1]\} \quad (36)$$

Hence

$$\begin{aligned} \gamma &= 1/2\sigma^2 = \\ &= (\mu\omega/\hbar) \{[\exp(\hbar\omega/kT) - 1]/[1 + \exp(-\hbar\omega/kT)]\} \quad (37) \end{aligned}$$

The low temperature limit of γ^{-1} is

$$\begin{aligned} \gamma^{-1} &= (\hbar/\mu\omega) [1 + 2 \exp(-\hbar\omega/kT)] \exp(-\hbar\omega/kT) \approx \\ &= (\hbar/\mu\omega) \exp(-\hbar\omega/kT) \quad (38) \end{aligned}$$

which can be compared with γ^{-1} of eq 35. It is satisfying to note that these two expressions are qualitatively of the same form.

Table I summarizes the results of earlier studies of intra-ET for several bichromophoric molecules, together with relevant photophysical parameters. It is evident that for the α -naphthyl

TABLE I: Experimental Results of Intra-ET Studies in Several Bichromophoric Molecules

D-A molecules		\bar{R} , Å	τ_D/θ , ns	τ_D , ns	ϕ_0/ϕ	ref
D	A					
α -naphthyl	acetyl	7.5	3	64	38	16
		15	45	64	1.28	16
α -naphthyl	benzene	7.5	0.25	64		16
		15	8.32	64		16
β -naphthyl	benzoyl	7.5	<0.1	64		16
fluorene	norbornylene	7.0			120	13f,g
phenanthrene	biacetyl	6.0			12	14

TABLE II: Relative Quantum Yield ϕ/ϕ_0 for the Benzene Chromophore Fluorescence in the (Benzene)-(α -Diketone) Bichromophoric Molecules as a Function of Molecular Geometry

molecule	\bar{R} , Å	ΔE , kcal/mol	ϕ/ϕ_0	$\gamma(300\text{ K})$, Å ⁻²
P ₄₄	3.60		0.01	
P ₅₅	4.42	2.32 ± 0.15	0.14	9.0
P ₆₆	5.33		0.74	
M ₃₃	3.80	1.50 ± 0.02	0.16	2.4
M ₄₄	4.12	2.23 ± 0.03	0.09	7.7
O ₃₃	4.20		0.23	
O ₄₄	6.00	1.64 ± 0.11	0.98	3.0

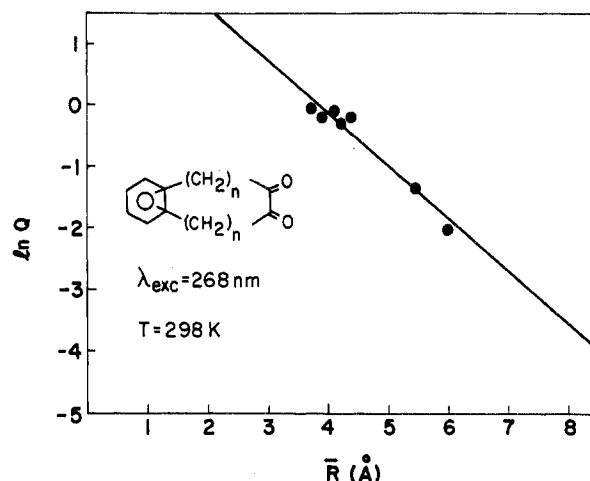
(D)-acetyl (A) molecules ϕ and τ_D are strongly dependent on \bar{R} . However, these data are not sufficient to test the validity of eq 27 and 32.

Our results for ϕ in the bichromophoric molecules II are summarized in Table II. The values for \bar{R} were obtained from X-ray analysis and molecular mechanics force-field calculations of the conformations.¹⁹ These ϕ vs. \bar{R} values were analyzed in terms of eq 32. The results are shown in Figure 20. From the slope and the intercept of the $\ln Q$ vs. \bar{R} plot (eq 32) we obtain $\beta = (0.89 \pm 0.25) \text{ Å}^{-1}$ and $R_0' = 3.84 \text{ Å}$, using eq 34 and assuming $\delta \sim 1$. The fit to the present analysis of intra-ET is reasonable, resulting in the following novel photophysical parameters:

1. $L = 2/\beta = 2.32 \text{ Å}$, a reasonable value for the average orbital van der Waals radius of eq 13.
2. $\gamma = 9 \text{ Å}^{-2}$ for P₅₅ at 300 K, and moderately dependent on temperature indicating a limited flexibility and narrow distribution of conformations.
3. $R_0' = 3.84 \text{ Å}$, indicating poor overlap as expected for $J = 2 \times 10^{-7} \text{ cm}$.
4. $\alpha = 2.7 \times 10^9 \text{ s}^{-1}$, a reasonable nonradiative decay rate for ET at close contact ($\bar{R} = 0$) of two chromophores with poor spectral overlap.
5. $K = 2.33 \times 10^{-12} \text{ dyn}$, obtained from α and the spectroscopically measured J (eq 19). The *first* measurement of its kind.

Concluding Remarks

It is shown that the mechanism of short-range singlet-singlet intra-ET can be studied in appropriately constructed bichromo-

**Figure 20.** Plot of $\ln Q \equiv \ln [1 - (\phi/\phi_0)]$ vs. \bar{R} (eq (32)) for the bichromophoric molecules II.

phoric molecules. The condition necessary for observing intra-ET via exchange interaction is poor spectral overlap between the emission spectrum of the donor chromophore and the absorption spectrum of the acceptor chromophore. Moreover, the electronic transition of the donor chromophore involved in the intra-ET should be forbidden in order to avoid ET due to dipole-dipole interactions. These conditions were met by the bichromophoric molecules prepared for this study and allowed investigation of singlet-singlet intra-ET via exchange interaction as a function of temperature and molecular geometry. A complementary study of triplet-triplet intra-ET in the same molecular systems is in progress.

With an appropriate averaging procedure, expressions were obtained for the fluorescence lifetime and fluorescence quantum yield of a donor moiety undergoing an intra-ET process via exchange interaction to an acceptor moiety in bichromophoric molecules. These photophysical parameters are functions of the molecular geometry and are expressed in terms of the average distance separating the chromophores and the temperature-dependent width of the distribution of these distances. Temperature-dependent dual fluorescence data supports the present analysis.

In conclusion we note that the present paper provides, for the *first time*, experimental and theoretical means for obtaining the photophysical parameters incorporated in Dexter's exchange interaction formulation of electronic energy transfer.

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