Resonance Transfer of Electronic Excitation Energy *via* Coupling of $S_0 \leftrightarrow S_1$ and $T_0 \leftrightarrow T_1$ Transition Moments[1]

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Summary Data for energy-transfer between diphenylmethylene (donor)–eosin (acceptor) and 9,10-dichloroanthracene (donor)–diphenylmethylene (acceptor) indicate that the coupling of $S_0 \leftrightarrow S_1$ and $T_0 \leftrightarrow T_1$ transition moments is well described by the inductive resonance theory.

THE theory for transfer of electronic excitation energy between two molecules[2] (or chromophores) at distances substantially larger than molecular diameters was originally developed by Perrin[3] and Förster[4] who postulated a nonradiative coupling of isoenergetic oscillators in the donor and acceptor moieties. Despite some necessary approximations, the predictions of the resonance concept have been reasonably confirmed by most experiments carried out either with binary mixed solutions of appropriate donor and acceptor molecules[4–7] or with model compounds having the two chromophores attached to the same molecular frame.[8] The elegant experiments of Kellogg and Bennett[6] demonstrated that Förster-type interaction may involve not only $S_0 \leftrightarrow S_1$ but also $T_1 \leftrightarrow S_0$ and $T_1 \rightarrow T_2$ transition moments. Admittedly, quantitative transfer experiments involving $T_1 \rightarrow T_2$ transitions are rather difficult mainly because known concentrations of spectroscopic triplets are not easily prepared, because the $T_2 \rightarrow T_1$ transition is nonradiative, and because accurate emission measurements are frequently complicated by interference from transitions to and within the singlet manifold. The use of ground-state-triplet molecules could remove most inconveniences associated with spectroscopically prepared triplets.

We present a quantitative evaluation of resonance transfer between ground-singlet and ground-triplet molecules *via* coupling of their $S_0 \leftrightarrow S_1$ and $T_0 \leftrightarrow T_1$ oscillators. We determined the separation dependence and rate constants for the following two pairs: diphenylmethylene (DPM) donor–eosin (EOS) acceptor and 9,10-dichloroanthracene (DCA) donor–DPM acceptor. The carbene was generated in its ground triplet state by near-u.v. irradiation of diphenyldiazomethane (DPD) in a rigid matrix. Mixed solutions of DPD and either EOS or DCA in frozen MeOH–ETOH (4 : 1) glass at 77K were photolysed until virtually all the diazoalkane was converted into carbene DPM and then examined for individual emissions in the Aminco–Bowman Spectrofluorometer. In parallel experiments we established that neither EOS nor DCA undergo any photochemical reaction or change in the emission or absorption spectra when irradiated under the same conditions.

The singlet–singlet absorption and emission of eosin[9] and 9,10-dichloroanthracene[10] and the triplet–triplet absorption and fluorescence of diphenylmethylene[11] are well known. These spectra are reproduced together in the Figure mainly to exhibit the sensitizer-emission–acceptor-absorption overlap for each of the two pairs investigated. Since the molar ratio of donor and acceptor was maintained the same in all samples, each component absorbed the same fraction of incident light. Consequently, the gradual changes in the relative fluorescence intensities of the two chromophores with dilution were caused only by the separation-dependent transfer process. The usual steady-state treatment of a photokinetic scheme containing absorption by each component, their unimolecular radiative and radiationless deactivations, and a second-order transfer step,[12] yields for the EOS–DPM pair $I_{\text{EOS}}/I_{\text{DPM}} = (Q_{\text{EOS}}/Q_{\text{DPM}})\ \{(\beta + K[\text{EOS}])/\alpha\}$ where I_{EOS} and I_{DPM} are the EOS and DPM fluorescence intensities in the presence of energy transfer, Q_{EOS} and Q_{DPM} are their respective quantum yields in the absence of transfer, α and β are the fractions of incident light absorbed by DPM and EOS respectively, at the excitation wavelength, and K the quenching constant equal to $K = k\tau_{\text{DPM}}$ with k the bimolecular transfer rate constant and τ_{DPM} the lifetime of the first excited triplet of DPM in the absence of acceptor. With α and β evaluated from the extinction coefficients of the two components at 300 nm, $Q_{\text{EOS}} = 0{\cdot}79$, and[13] $Q_{\text{DPM}} = 0{\cdot}23$, a plot of $\alpha[(I_{\text{EOS}}Q_{\text{DPM}}/I_{\text{EOS}}Q_{\text{DPM}}) - (\beta/\alpha)]$ against EOS at five concentrations of eosin between 10^{-4} and 5×10^{-4} M gave an excellent straight line with slope $K = 3{\cdot}1 \times 10^{3}\ \text{l mole}^{-1}$. With the fluorescence lifetime[14] of DPM $\tau_{\text{DPM}} = 22 \pm 1 \times 10^{-9}$ s, the transfer rate constant is k *ca.* $1{\cdot}4 \times 10^{11}\ \text{l mole}^{-1}\ \text{s}^{-1}$. The separation distance at which the rate of transfer equals all other rates of donor deactivation, R_0, calculated[2] from absorption and emission spectra of DPM and EOS was 43·4 Å. This value agreed well with that estimated[15] from transfer data which gave *ca.* 41 Å. Since both the magnitude of the bimolecular transfer rate constant and the value of R_0 for the DPM–EOS pair are comparable with those previously reported for singlet–singlet resonance transfer,[5–8,12] it seems that the coupling of the $S_0 \leftrightarrow S_1$ and $T_0 \leftrightarrow T_1$ transition moments is also adequately described by Förster's inductive resonance theory.

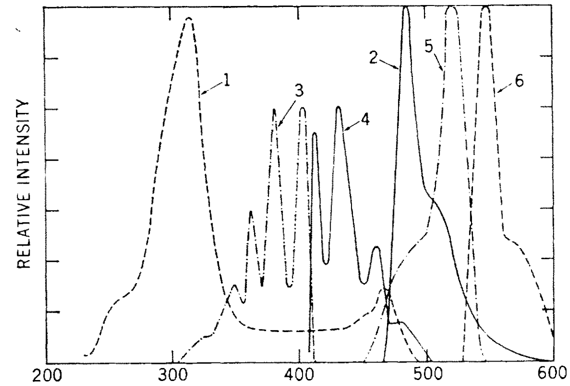

FIGURE. *Excitation* (1, 3, *and* 5) *and fluorescence* (2, 4, *and* 6) *spectra of* DPM, DCA, *and* EOS, *respectively. Intensity units are arbitrary; no comparison between different curves is implied. The spectra of* DPM *and* EOS *are uncorrected.*

The spectrofluorometric measurements on the DCA–DPM pair in which the acceptor is a ground-triplet molecule, were somewhat less accurate because of partial spectral overlap of the two emissions. Nevertheless, the estimated[16] transfer parameters (k *ca.* $2 \times 10^{9}\,\mathrm{l\,mole^{-1}}$ and R_0 *ca.* 23 Å) again tend to verify the applicability of the resonance concept to cases in which the donor or the acceptor undergoes a triplet–triplet transition.

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[1] Taken in part from the Ph.D. thesis of J. R. Bunting, George Washington University, 1970.

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[13] The emission quantum yields were determined in the usual manner by comparison with appropriate standards. Q_{EOS} and Q_{DCA} agreed within 8% with previously published values in refs. 9a and 10, respectively. Q_{DPM} was measured using quinine sulphate as standard. For details on the procedure, see for example C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, ch. 3.

[14] Measured on a TRW decay-time fluorometer.

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[16] The procedure is virtually indistinguishable from that used for the DCA–DPM pair. The lower k and R_0 values are undoubtedly the result of a comparatively shorter donor lifetime ($8{\cdot}5 \times 10^{-9}$ s) and a less extensive spectral overlap.