Design of an Antenna System for the Collection of Singlet Excitation Energy. Exciton Diffusion among Concentrated 9,10-Diphenylanthracene Centers in Polystyrene

Clifford L. Renschler and Larry R. Faulkner*[1]

Contribution from the Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. *Received July 23, 1981*

Abstract: Fluorescence decay kinetics of 9,10-diphenylanthracene (DPA) were examined at [DPA] = 16–181 mM in spin-cast polystyrene films of ~2000-Å thickness. Exponential decays with lifetimes ranging from 6.94 ns at low concentration to 6.34 ns at 180 mM were observed in unquenched systems. In the presence of tetrabromo-*o*-benzoquinone (TBBQ), added at 12.0 mM as a quenching probe, the decay kinetics were modified. At very low concentrations of DPA, nearly pure Förster kinetics were observed. Extrapolation of behavior to [DPA] = 0 gave a critical transfer radius for Förster transfer from DPA to TBBQ of 28 Å. Calculations from spectral data gave 29 Å. As the concentration of DPA increased, quenching became progressively more efficient and the time dependence of decay showed evidence of excitation diffusion by hopping from DPA site to DPA site. Diffusion coefficients were evaluated by two-parameter fits of decays to curves predicted from the Yokota–Tanimoto theory based on a Padé approximant. Values of the diffusion coefficient increased with [DPA] to 7.9×10^{-6} cm^2/s at [DPA] = 180 mM. The corresponding diffusion length is 55 Å. The meaning of the results to the construction of an antenna system for collection of photonic energy into photochemical reaction centers is discussed.

The conversion of light into chemical energy holds high current interest.[2-4] Many strategies have been employed. In each, photons are absorbed to produce excited species, which then engage in other processes such as electron transfer, at reaction centers. Among the centers that have been studied are species in micelles,[5-7] supported monolayers and multilayers,[8-10] vesicles,[10,11] zeolites,[12-14] semiconductors,[2-4,15] and thin molecular films.[16] The focus has been the tailoring of the reaction center's structure to promote efficient primary chemistry, e.g., to force electron transfer in the desired direction and prevent recombination.

Another element of the overall energy conversion problem is the efficient collection of photonic energy into the reaction centers. Many artificial systems are optically dilute and would benefit from a coupling with apparatus for collecting energy from outlying regions.[16,17] Such a scheme is analogous to the so-called "antenna pigment" system operative in photosynthetic organisms.[18-21] Emerson and Arnold[22] first demonstrated that groups of chlorophyll molecules gather light for each primary conversion reaction in bacterial photosynthesis. Their concept has been refined by much further research, but the basic idea remains current that several hundred chromophores receive energy on behalf of each specialized reaction center where primary charge transfer takes place.[18-21]

The goal of our work is to understand the fundamentals of energy migration and collection, together with techniques of molecular assembly, so that artificial energy collection apparatus based on the antenna concept can be developed. The work involved here stresses singlet excitation energy.

Earlier reports from this laboratory[16,23] dealt with fluoranthene as an antenna chromophore dispersed in a polystyrene film about 2500 Å thick. On the film's surface, perylene was deposited as a trap. The fluoranthene absorption centers were able to feed energy fairly efficiently to the accessible perylene surface layer; thus interest arose in the prospects for exciton diffusion among fluoranthene molecules. Such a process would increase the range from which energy could be captured by reaction centers that might be rationally substituted for the perylene traps. Migration would have to occur by energy transfer over distances larger than contact radii, because the rigid matrix prohibits motion of the molecules.

Excitation migration among concentrated chromophores in an inert matrix has received some attention, mainly with respect to chlorophyll dispersions as models for natural chloroplasts. In studies of monolayers, Tweet et al.[24] showed that at high dilution with an inert surfactant, chlorophyll *a* undergoes singlet excitation transfer by inductive resonances in a single step. Moreover, they provided evidence for multistep migration of the singlet excitation energy in undiluted films. A number of workers have shown the existence of energy transfer processes among chlorophyll sites in rigid matrices by polarization measurements,[25-28] although extensive migration involving multiple steps could not be demonstrated in this manner. In virtually all of these systems, chlorophyll *a* exhibits a concentration quenching effect, which has been studied in detail by Porter, Patterson, and associates.[27,29] Their research, which featured measurements of quantum yield, lifetime, and polarization did provide substantial evidence of multistep migration. The quenching was explained in terms of nonemissive

---

(1) To whom correspondence should be addressed.
(2) Archer, M. D. *Photochem.* **1978**, *9*, 603.
(3) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.
(4) Wrighton, M. S., Ed. *Adv. Chem. Ser.* **1980**, *No. 184*.
(5) Thomas, J. K.; Piciulo, P. *Adv. Chem. Ser.* **1980**, *184*, 97.
(6) Grätzel, M. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 981.
(7) Grätzel, M. *Faraday Discuss. Chem. Soc.* **1980**, *70*, 359.
(8) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 82.
(9) Grimaldi, J. J.; Boileau, S.; Lehn, J. *Nature (London)* **1977**, *265*, 229.
(10) Calvin, M. *Faraday Discuss. Chem. Soc.* **1980**, *70*, 383.
(11) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507.
(12) Jacobs, P. A.; Uytterhoeven, J. B.; Beyer, H. K. *J. Chem. Soc., Chem. Commun.* **1977**, 128.
(13) Kuznicki, S. M.; Eyring, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 6790.
(14) Faulkner, L. R.; Suib, S. L.; Renschler, C. L.; Green, J. M.; Bross, P. R. In "Chemistry in Energy Production"; Wymer, R. G., Keller, O. L., Eds.; American Chemical Society: Washington, D.C.; *ACS Symp. Ser.* **1980**, 99.
(15) Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139.
(16) Faulkner, L. R.; Tachikawa, H.; Fan, F.-R.; Fischer, S. G. *Adv. Chem. Ser.* **1980**, *No. 184*, 113.
(17) Fromherz, P.; Arden, W. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 1045.
(18) Rabinowitch, E. "Photosynthesis"; Govindjee, Ed.; Wiley: New York, 1969.
(19) Knox, R. S. In "Bioenergetics of Photosynthesis"; Govindjee, Ed.; Wiley: New York, 1975.
(20) Sauer, K. *Accounts Chem. Res.* **1978**, *11*, 257.
(21) Witt, H. *Biochim. Biophys. Acta* **1979**, *505*, 355.
(22) Emerson, R.; Arnold, W. *J. Gen. Physiol.* **1932**, *15*, 391; *16*, 191.
(23) Tachikawa, H.; Faulkner, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 8025.
(24) Tweet, A. G.; Bellamy, W. D.; Gaines, G. L., Jr. *J. Chem. Phys.* **1964**, *41*, 2068.
(25) Trosper, T.; Park, R. B.; Sauer, K. *Photochem. Photobiol.* **1968**, *7*, 451.
(26) Gorshkov, V. K. *Biophysics (Engl. Transl.)* **1969**, *14*, 25.
(27) Kelly, A. R.; Porter, G. *Proc. R. Soc. London, Ser. A* **1970**, *315*, 149.
(28) Wong, D.; Vacek, K.; Merkelo, H.; Govindjee, *Z. Naturforsch., A* **1978**, *33A*, 863.
(29) Kelly, A.; Patterson, L. K. *Proc. R. Soc. London, Ser. A* **1971**, *324*, 117.

0002-7863/82/1504-3315$01.25/0

traps identified as closely situated pairs of chlorophyll molecules cast randomly into the matrix. The excitation is thought to migrate until it encounters such a site, radiates, or undergoes some other decay process. Theoretical work has been advanced to explain the shapes of quenching curves.[30-32] Ferreira and Porter[33] later studied perylene in polystyrene, which develops an emissive dimeric trap.[33,34] Its increasing contribution to the emission spectrum with increasing concentration of perylene gave evidence of similar migration phenomena. Johnson[35] has recently reported measurements of lifetimes of *N*-isopropylcarbazole at high concentrations in polystyrene. Additions of small amounts of perylene or dimethyl terephthalate to this matrix effected a quenching that was interpreted in detail via a mechanism of extensive exciton diffusion among *N*-isopropylcarbazole sites. The transfer of energy between these sites was interpreted as occurring by dipole–dipole (Förster) coupling.[36-39]

Other types of excitation migration have been observed but are less relevant to our interest here. Much work has involved molecular crystals[39-41] where the interactions between chromophores are so substantial that concepts of localized excitation have limited meaning. Intermediate between molecular crystals and dispersions of chromophores are polymers with chromophores attached as pendant groups on a backbone. Many qualitative and some quantitative studies of singlet and triplet migration have been reported.[39,42-44] In molecular crystals and polymers, one encounters numerous difficulties with trap formation at defects and at random pairs, which limit diffusion lengths. Moreover, these phases are not very versatile with respect to the ultimate goal of coupling to reaction centers.

For dispersions of chromophores in rigid matrices, only Johnson[35] has attempted to evaluate diffusion lengths of singlet excitation. Burkhart and Lonson have reported some data for triplet motion.[45] Even for crystals and polymers, only a few quantitative results are available, most being rough estimates of diffusion lengths.[39,42] Before one can understand and manipulate singlet diffusion in any of these systems, reliable, precise diffusion coefficients are needed for systems that can be constructed reproducibly. Moreover, one would like to minimize the effect of energy trapping at dimeric sites built fortuitously into the phase under study. This consideration has led us to stress work with chromophores that do not form excimers or undergo self-quenching in fluid media.

Our initial research has recently been reported.[46] The work involved thin films of polystyrene (PS), in which fluoranthene (FA) and tetrabromo-*o*-benzoquinone (TBBQ) were homogeneously dispersed. Quite high concentrations (up to 1.2 M) of FA were used in order to produce average nearest neighbor spacings less than 10–20 Å. TBBQ served as a quenching center. After light absorption, FA singlets can undergo dipole-dipole resonance energy transfer[36-39] to TBBQ. Our approach was to see if strict Förster kinetics would apply, or instead, if complications would appear, reflecting the diffusion of excitons among fluoranthene sites. New experimental methods were developed, and they play important roles in the work described here. We found that the decay of FA singlets adhered strictly to Förster kinetics. No hint of diffusion could be detected.

An antenna system based on fluoranthene is not feasible, because the resonance between fluoranthene sites in the polymer is too weak. The electronic transition itself is not strong, and there is poor overlap in the distribution of downward transitions among transmitting sites and upward transitions at receiving locations. A superior new chromophore is needed. This article describes results with 9,10-diphenylanthracene (DPA) in polystyrene, whose singlet excitons indeed engage in appreciable diffusion at sufficient concentrations of chromophores.

Experimental Section

DPA and TBBQ were obtained from Aldrich Chemical Co. Some DPA samples were recrystallized one to three times from benzene, but for most work the material could be used as received. Sublimed TBBQ did not differ in performance from the material supplied by Aldrich. Also used as purchased was Aldrich 99% *p*-xylene. Polystyrene was obtained from Polysciences (Warrington, PA) and was treated with three cycles of dissolution in toluene, followed by reprecipitation with methanol. It was then dried in vacuo for 48 h.

Thin films were formed by a spin-coating technique[16,47] in which a xylene solution containing appropriate ratios of PS, DPA, and TBBQ was dropped onto a rapidly spinning (~6000 rpm) 1 in. × 1 in. × 1 mm float glass slide manufactured by Erie Scientific (Portsmouth, NH). Evaporation of the xylene left a dry, smooth film on the slide. Details are available elsewhere.[16,48] Prior to the film casting step, the slides were cleaned with distilled water and lens paper. In all work, the casting solution contained 3.47% w/v PS. The thicknesses of the resulting films were on the order of 2000 Å.[48] Precise values are not important here. Prior work has shown that the films are free of voids[49] and solvent[50] and that they have a density essentially that of polystyrene.[49] The mole ratios of solutes and polystyrene used in the casting solution are preserved in the films,[16,48] and this fact was used to calculate the concentrations of DPA and TBBQ in the films.

Fluorescence decay curves were obtained with an EG&G ORTEC Model 9200 time-correlated single photon counting apparatus, which was connected through a custom-built interface to a Data General Nova 820 minicomputer. The computer acted as a multichannel analyzer. Operating characteristics and procedures have been described elsewhere.[46] The air-gap flashlamp used as an excitation source exhibited a width at half intensity of 1.5–2.0 ns.

A colored glass filter passing light from 330 to 360 nm was used between the flashlamp and the sample. Two interference filters, one centered at 420 nm and one at 430 nm (both with 7-nm band-pass and both manufactured by Ditric Optics, Hudson, MA), were placed between the sample and the detector.

Emission spectra were taken by using an Aminco-Bowman spectrophotofluorometer with a Hamamatsu R928 photomultiplier. A band-pass of 6 nm and front-surface geometry were used. Absorption spectra were recorded by using a Beckman Acta M-VI or a Perkin-Elmer 552 spectrophotometer. Correction of fluorescence emission spectra was carried out by the method of Melhuish.[51]

All measurements of fluorescence spectra and lifetimes were carried out with the films in air. The use of a nitrogen atmosphere did not change the lifetime of DPA singlets in PS appreciably.

Digitization of spectra was accomplished with a Summagraphics Data Tablet operating with the Nova 820 computer, which later implemented routines for correction and analysis of data.

Results and Discussion

Manifestations of Diffusion. For a system whose rate of fluorescence quenching is governed strictly by Förster transfer from the excited donor singlet to an energy acceptor, without migration of the donor singlet from its original point of creation, the fluorescence decay function takes the form[36-39]

$$I = I_0 \exp(-t/\tau_M) \exp(-2\gamma t^{1/2}/\tau_M^{1/2}) \qquad (1)$$

where I is the fluorescence intensity at time t after Δ-function

---

(30) Beddard, G. S.; Porter, G. *Nature (London)* **1976**, *260*, 366.

(31) Altmann, J. A.; Beddard, G. S.; Porter, G. *Chem. Phys. Lett.* **1978**, *58*, 54.

(32) Dalton, J. *J. Chem. Soc., Chem. Commn.* **1980**, 78.

(33) Ferreira, J. A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 340.

(34) Tachikawa, H.; Faulkner, L. R. *Chem. Phys. Lett.* **1976**, *39*, 436.

(35) Johnson, G. E. *Macromolecules* **1980**, *13*, 145.

(36) Förster, Th. *Naturwissenschaften* **1946**, *33*, 166.

(37) Förster, Th. *Ann. Phys. (Leipzig)* **1948**, *2*, 55.

(38) Förster, Th. *Faraday Discuss. Chem. Soc.* **1969**, *27*, 7.

(39) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970.

(40) Silbey, R. *Annu. Rev. Phys. Chem.* **1976**, *27*, 203.

(41) Kopelman, R. *Top. Appl. Phys.* **1976**, *15*, 297.

(42) Allen, N. S.; McKellar, J. F. *Photochemistry* **1978**, *9*, 559.

(43) Rippen, G.; Kaufmann, G.; Klöpffer, W. *Chem. Phys.* **1980**, *52*, 165.

(44) Kim, N.; Webber, S. E. *Macromolecules* **1980**, *13*, 1233.

(45) Burkhart, R. D.; Lonson, E. R. *Chem. Phys. Lett.* **1978**, *54*, 85.

(46) Renschler, C. L.; Faulkner, L. R. *Faraday Discuss. Chem. Soc.* **1980**, *70*, 311.

(47) De Forest, W. S. "Photoresist: Materials and Processes"; McGraw-Hill: New York, 1975.

(48) Fischer, S. G. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1981.

(49) Walker, T. K. B.S. Thesis, University of Illinois at Urbana-Champaign, 1977.

(50) Eaton, D. R. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1978.

(51) Melhuish, W. H. *J. Opt. Soc. Am.* **1962**, *52*, 335.

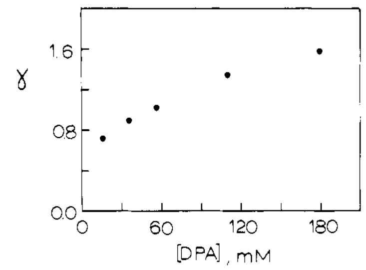

Figure 1. Dependence of γ on DPA concentration ([TBBQ] = 12.0 mM).

excitation at $t = 0$, I_0 is the intensity at $t = 0$, γ is an energy-transfer parameter discussed below, and τ_M is the unquenched lifetime of the donor. The quantity γ can be expressed as $[Q]/[Q]_0$, where [Q] is the molar quencher concentration and $[Q]_0$ is the so-called "critical molar concentration", defined as

$$[Q]_0 = 3/2\pi^{3/2}N'R_0^3 \qquad (2)$$

Here, N' is Avogadro's number per millimole and R_0 is the critical transfer radius, which is the distance of separation between donor and acceptor at which there are equal probabilities for energy transfer and donor decay by any other process.

Adherence to this kinetic form can be tested experimentally[35,46] by (a) normalizing fluorescence decay curves for quenched and unquenched systems to unit height at $t = 0$ and (b) taking the ratio of the two curves on a point-by-point basis to obtain a time-dependent ratio function that embodies the effects of quenching alone. For pure Förster kinetics, one can see from eq 1 that

$$R = \exp(-2\gamma t^{1/2}/\tau_M^{1/2}) \qquad (3)$$

Other R functions are expected for other types of quenching, and the shape of R can be used diagnostically to define the mechanism.[46] With pure Förster kinetics, plots of $-\ln R$ vs. $t^{1/2}$ should be linear and can provide values of γ for each quencher concentration employed. Then, plots of γ vs. [Q] can be used to obtain $[Q]_0$, which in turn yields R_0. This kinetically determined value for R_0 can be compared with an independent figure computed from spectroscopic data.[36-39] In the previous studies of concentrated fluoranthene chromophores with dilute TBBQ as quencher,[46] all of these expectations were met, and there was excellent quantitative agreement between kinetic and spectroscopic R_0 values.

If a system follows these kinetics, as does the FA/TBBQ/PS system,[46] values of γ are independent of the fluorophore concentration, because there is no interaction between fluorophores leading to excitation migration, and no relative movement of donor and acceptor centers occurs during the donor lifetime. In contrast, thin PS films containing DPA as the donor and TBBQ as the acceptor yield γ values that increase with [DPA], as shown in Figure 1. This effect indicates that the quenching efficiency increases as the mean DPA site separation decreases, and it can be explained in terms of successive hopping of the excitation from one DPA site to the next by Förster interactions, prior to quenching by a final transfer into a TBBQ site. The consequent diffusion of energy would lead to an increased likelihood of ultimate capture by TBBQ.

Another manifestation of diffusion effects is found in individual plots of $-\ln R$ vs. $t^{1/2}$ as shown in Figure 2. Cases are shown for low and high concentrations of DPA. At the low concentration, the mean spacing between DPA sites is large, hence the interactions between them are weak, the hopping frequency is low, and the diffusion length during a lifetime is small. The linear relation between $-\ln R$ and $t^{1/2}$ indicates that pure Förster kinetics, applicable to the nondiffusing system, are being approached. In the opposite limit of a diffusion length much larger than R_0, $-\ln R$ becomes a linear function of t.[46,52] An intermediate time dependence characterizes the transition domain of behavior, where the effect of diffusion moves from insignificance to dominance; therefore measurable degrees of diffusion are indicated by a departure of $-\ln R$ from linearity with $t^{1/2}$. The results in Figure 2 for the system of high DPA concentration clearly show the effects of diffusion.

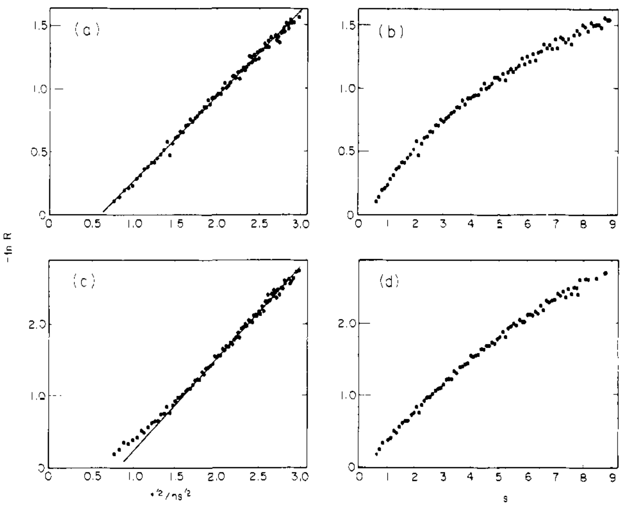

Figure 2. Dependence of $-\ln R$ on t and $t^{1/2}$. (a) and (b) are for 35.9 mM DPA and 12.0 mM TBBQ. (c) and (d) are for 181 mM DPA and 12.0 mM TBBQ. Lines through later-time data are only to emphasize advent of curvature in (c).

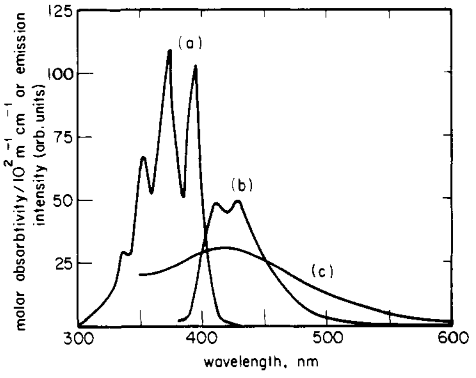

Figure 3. Spectra of DPA and TBBQ: (a) DPA absorption in xylene; (b) DPA emission from 11.9 μM solution in xylene (excitation at 366 nm); (c) TBBQ absorption. Spectrum b is uncorrected, but a digitized, corrected version of it was used in calculations of R_0.

Behavior at Infinite Dilution. As [DPA] increases, the values of γ lose quantitative significance, because pure Förster kinetics become inadequate for describing the system, and the nonlinearity in $-\ln R$ vs. $t^{1/2}$ becomes marked. A plot like that in Figure 1 serves mainly as a qualitative detector of diffusion effects. Even so, it is useful to consider the value of γ extrapolated to infinite dilution of DPA, where pure Förster kinetics should be strictly valid. The value of 0.60 at [TBBQ] = 12.0 mM corresponds to $R_0 = 28$ Å for the quenching of ^{1}DPA* by TBBQ.

An independent calculation of R_0 can be had by using Förster's theory,[36-39] in which R_0 is related to spectroscopic parameters

$$R_0^6 = \frac{(9 \ln 10)\kappa^2}{128\pi^5 n^4 N'} \phi_f \int_0^\infty f_M(\bar{\nu})\epsilon_Q(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (4)$$

where ϕ_f is the fluorescence quantum yield of the donor in the absence of quencher, n is the refractive index of the medium, $\epsilon_Q(\bar{\nu})$ is the molar absorptivity of the quencher vs. wavenumber, and $f_M(\bar{\nu})$ is the emission spectrum of the donor normalized to unit area. The parameter κ accounts for the mean relative orientations of the donor and acceptor transition moment vectors. Maksimov and Rozman[53] give $\kappa^2 = 0.475$ for species randomly dispersed in a rigid medium.

---

(52) Faulkner, L. R. *Chem. Phys. Lett.* **1976**, *43*, 552.

(53) Maksimov, M. Z.; Rozman, I. M. *Opt. Spektrosk.* **1962**, *12*, 337.

Table I. Lifetime of DPA Fluorescence in Polystyrene Films[a]

[DPA] in film, mM	τ_M, ns	[DPA] in film, mM	τ_M, ns
18.0	6.94	108	6.73
35.9	6.94	180	6.34
53.9	6.96		

[a] Spin coated from 3.47% w/v polystyrene in xylene.

The DPA emission and TBBQ absorption spectra shown in Figure 3 were digitized at 1-nm spacing and an overlap integral was computed numerically. Then with $n = 1.6$ for polystyrene[54] and $\phi_f = 1.0$ for DPA,[55] R_0 was calculated to be 29.0 Å. This figure agrees excellently with the kinetically determined value obtained from extrapolated γ.

Evaluation of Diffusion Coefficients. In order to quantify the efficiency of diffusion of DPA singlet energy within the films, a more sophisticated kinetic treatment is needed. Specifically, the model should describe the decay kinetics of systems in which long-range energy transfer to a quencher and diffusion are both possible. Several theoretical treatments of this problem have been developed and critically compared.[39,56] We chose one advanced by Yokota and Tanimoto,[57] which features a Padê approximant to deal with the effects of diffusion as a perturbation on the limiting case of pure Förster kinetics. Our choice of this "YT Padê" approach is based on its demonstrated ability[52] to predict accurately experimental results for systems in which the diffusion length is less than, or of the same order as, R_0. The model was also attractive for the ease with which it lent itself to curve fitting. The YT Padê treatment yields the decay relations[57]

$$I = I_0 \exp(-t/\tau_M) \exp(-K[\mathrm{Q}]) \quad (5)$$

$$K = \tfrac{4}{3}\pi^{3/2}N'(\alpha t)^{1/2}B \quad (6)$$

$$B = [(1 + 10.87x + 15.50x^2)/(1 + 8.743x)]^{3/4} \quad (7)$$

where $\alpha = R_0^6/\tau_M$ and $x = D\alpha^{-1/3}t^{2/3}$. Here, R_0 is the critical transfer radius from fluorophore to quencher and D is the coefficient for diffusion of excitation.[58]

Fluorescence decay curves were taken for five types of films, each containing 12 mM TBBQ and different concentrations of DPA varying from 18 to 180 mM. Each curve was fitted to the YT Padê kinetic equations with the gradient-expansion algorithm of Marquardt,[59] modified by an added perimeter search.[60] A two-parameter fit was used, with I_0 and D left as variable quantities. The zero-time intensity was fitted rather than defined, since significant distortions in the first nanosecond of the decay are induced by the finite width of the excitation pulse. The value of R_0 was taken as 29 Å, as determined by calculation from the overlap integral. Appropriate data for τ_M were measured experimentally, with an average value determined from four successive unquenched decay profiles taken for each DPA concentration. We emphasize that this approach leaves D as the single parameter describing the shape of decay. The remaining parameter I_0 simply controls vertical scaling.

There was a systematic lowering of τ_M with increasing [DPA], as one can see in Table I. The effect is similar to the trend observed earlier for fluoranthene in PS.[46] Its origin is unclear. It could reflect a self-quenching effect or a change in oscillator strength based on an increase in the refractive index of the film at higher [DPA].

In carrying out the fits, $t = 0$ was taken as the maximum in the full emission transient, and the fit was made over the time range from 1.3 to 8.8 ns. With the lowest concentration of DPA, a 6-fold intensity change took place over this interval. The fitted curve matched the data essentially perfectly through the fitting range and did not deviate significantly from the measurements over the larger range from 0.2 to 15 ns. At shorter times the fitted curve deviated positively because the data were distorted by the finite flash width, and at longer times the fit deviated negatively because background counts became significant in the measured signal. With the highest concentration of DPA, a 20-fold decrease in intensity took place over the fitting interval, and the fit matched the data essentially perfectly from 0.2 to 12 ns.

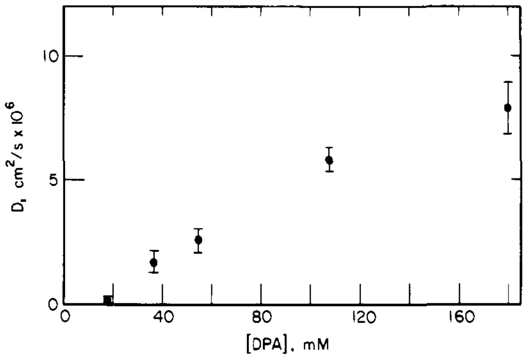

Figure 4. Dependence of D on DPA concentration. Films contained 12.0 mM TBBQ. Error bars encompass four standard deviations of the mean.

A plot of D vs. [DPA] is shown in Figure 4. Each value is an average computed from fits of four decays. Clearly, the rate of diffusion of DPA singlets rises with the chromophore concentration. In fact, at higher concentrations the values of D begin to approach figures characteristic of molecular diffusion in the usual fluid solutions. From the largest value 7.9×10^{-6} cm²/s, one calculates a root-mean-square diffusion length of 55 Å over the unquenched lifetime [$(6D\tau_M)^{1/2}$ for a three-dimensional random walk[61]].

A diffusion length of this magnitude is possible because of the relatively large overlap between the DPA fluorescence emission and absorption spectra shown in Figure 3. An R_0 value for resonance transfer from one DPA site to another was computed from the overlap integral to be 23.4 Å, as compared with only 7.5 Å for FA–FA resonance transfer.[46] Consequently the likelihood that a DPA singlet will be localized on a site close enough to another DPA site to undergo transfer is much higher than for the analogous FA system at equal fluorophore concentrations.

Interactions on the Molecular Scale. The diffusion coefficient in a three-dimensional system of random walks can be rewritten as $l^2/6\tau$, where l^2 is the average square step length and τ is the step frequency.[61] If we consider l to be the mean nearest neighbor distance,[61] $0.554[\mathrm{DPA}]^{-1/3}$, which is 11.6 Å at [DPA] = 180 mM, then $\tau \approx 3 \times 10^{-10}$ s. The rate constant for migration k'_{mig} is then $1/\tau$ or $\sim 3 \times 10^9$ s^{-1}. The intermolecular interaction energy between a locally excited site and its nearest neighbor can be estimated from the uncertainty principle as $\Delta E \approx hk'_{\mathrm{mig}}$, which is 0.1 cm^{-1} or 10^{-5} eV. These values for ΔE and k'_{mig} are both several thousand times smaller than their counterparts for crystalline anthracene.[39] They both seem reasonable, given the substantially larger nearest-neighbor spacings in our castings. Thus, our results suggest that the average exciton takes ~20 steps before it decays in an unquenched system.

From the Förster theory[36-39] one can estimate k'_{mig} in a different manner as $(R_0/l)^6/\tau_M$, where R_0 is the critical transfer radius for the DPA–DPA interaction and l is again taken as the nearest-neighbor distance. By this route, k'_{mig} is obtained as 1×10^{10} s^{-1}. This figure is comparably close to the value obtained above, considering both the very sensitive dependence on the value of l, and the fact that we regard movement as involving only nearest neighbors. These considerations all show that the diffusion phenomena observed here are quite reasonable on physical grounds.

---

(54) Hodgman, C. D., Ed. "Handbook of Chemistry and Physics", 42nd ed.; CRC Press: Cleveland, 1960.

(55) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1965.

(56) Reference 52 and Kinka, G. W.; Faulkner, L. R. *J. Am. Chem. Soc.* **1976**, *98*, 3897 provide reviews.

(57) Yokota, M.; Tanimoto, O. *J. Phys. Soc. Jpn.* **1967**, *22*, 779.

(58) Our parameter D is equivalent to Λ as used in the literature on polymers. See ref 35.

(59) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

(60) Faulkner, L. R. *J. Electrochem. Soc.* **1975**, *122*, 1190.

(61) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.

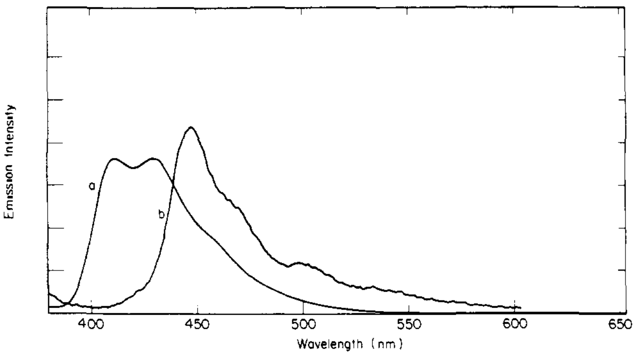

Figure 5. DPA emission spectra: (a) 11.9 μM solution in xylene; (b) thrice-recrystallized DPA powder. Both spectra were excited at 366 nm and both are uncorrected. Digitized versions of these spectra were corrected and used for resolution of film spectra. A spectrum identical with (b) was recorded with 250 nm excitation.

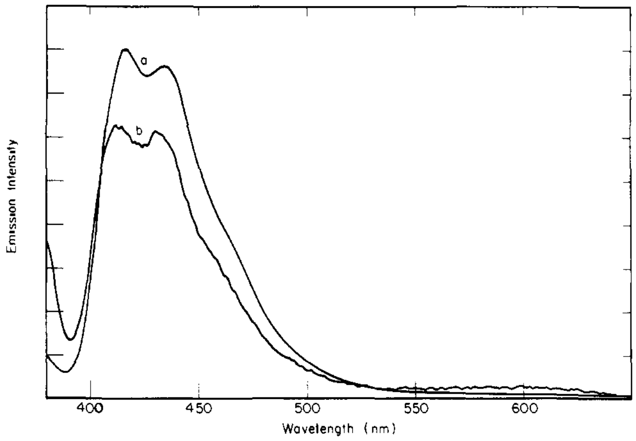

Figure 6. Fluorescence emission spectra of DPA in polystyrene films: (a) 181 mM DPA; (b) 35.6 mM DPA (excitation at 366 nm). These spectra are uncorrected, but digitized versions of them were corrected before the resolution into components.

Spectral Search for Microcrystallites. One always must be alert to the possibility that aggregates or microcrystalline domains affect results of this sort, either as regions of high exciton conductivity or as traps. The solubility of DPA in xylene was found to be 46 mM. Only two of the five films used in studies of γ or in evaluations of D had a concentration of DPA less than that figure. If the solubility of DPA in polystyrene is similar to the solubility in xylene, as seems likely, microcrystallites might well be expected to form in some of the films. On the other hand, the speed of casting and drying (a process measured in milliseconds) might engender amorphous, supersaturated films, free of microcrystals.

A search for aggregates and microcrystallites was carried out by careful examination of the fluorescence emission spectra of the films. Spectra were recorded for (a) a series of five films with DPA concentrations equal to the values used in the study of γ vs. [DPA], but without TBBQ, (b) an 11.9 μM xylene solution of DPA, and (c) a crystalline powder sample of thrice-recrystallized DPA. Some of these spectra are shown in Figures 5 and 6. Each spectrum was digitized at a 1-nm spacing, and then the film spectra were analyzed numerically.

The analysis algorithm took the solution spectrum as representing emission from an isolated DPA site in a medium of polarizability similar to that of polystyrene. The crystal spectrum was regarded as representative of emission from an aggregated site. The object was to find the linear combination of these two components that best matched each film spectrum. All spectra were corrected and normalized to unit area before this process was carried out. Only two parameters, the weighting factors for the components, were used. At each wavelength, the intensity of the film emission was taken as the weighted sum of the intensity of the solution and that of the crystal. A least-squares routine found the pair of weighting factors that gave the best match between the predicted composite and the actual film spectrum. A variant in the procedure allowed upscale or downscale shifting of either component in 1-nm units before least-squares analysis was carried out. The quality of fit was judged by visual inspection of plots and by the slopes and linear correlation coefficients of plots of measured intensity vs. the calculated intensity of the linear combination.

Table II. Percentage Crystal Spectral Component in Film Spectra vs. DPA Concentration[a]

[DPA] in film, mM	red-shift in soln spectrum, nm	percentage of crystal component
16.6	0	4.4
35.9	1	2.8
55.7	1	5.2
101	3	2.4
181	4	0.6

[a] Best fits by quantitative criteria described in text.

In Figure 5, there are obvious differences between solution-phase and crystalline spectra, and they make the two emissions easily resolvable in any composite containing appreciable components of both. The larger question is the value of the crystal spectrum as a representative of aggregated forms. Reabsorption effects and trapping of singlet excitons at defects are known to affect the shapes of crystalline anthracene spectra to a marked degree.[39,62,63] Reabsorption probably would not be manifested in our thin film samples, but defects like those prevalent in recrystallized DPA might be. This ambiguity must be borne in mind as the results of the dissection are considered.

Figure 6 contains spectra from films with the lowest and highest DPA concentrations. Visual inspection alone indicates that the film spectra are predominantly solution-like and that a slight red-shift occurs with increasing [DPA]. The results of the spectral analysis are shown in Table II. With unshifted solution and crystal spectra, the best fits imply a 4–12% crystal-like component. On the other hand, we found that superior matches to the film emission could be achieved by red-shifting the solution spectrum slightly before analysis. The best overall fits gave slopes and linear correlation coefficients for plots of measured intensity vs. calculated intensity that were unity within 2% and one part per thousand, respectively. A 1–2-nm mismatch in spectra might be expected, given the intrinsic precision of the Aminco-Bowman instrument. A larger shift would require justification on physical grounds. The upshot of the data in Table II is that essentially the whole emission from the films can be considered as originating in solution-like (nonaggregated) sites. What might first appear to be an increase in crystal-like emission with increasing [DPA] is better regarded as a slight red-shift in emission from isolated sites. Such a shift could reflect a change in dispersion interactions as the more polarizable DPA makes up a larger percentage of the medium.

Conclusion. We believe that this work has demonstrated the existence of exciton diffusion among DPA chromophores and has produced valuable measurements of diffusion coefficients as a function of concentration. The experimental tools that have been further developed here offer considerable advantages over those available previously, and they ought to enable a general, quantitative attack on the problem of excitation migration in rigid systems.

According to the results in Figure 4, the coefficient for diffusion of DPA singlet excitons depends on a fractional power of concentration. In this respect, our results differ from those of Johnson,[35] who reported that the coefficient for diffusion of *N*-isopropylcarbazole singlet excitons in polystyrene was proportional to the four-thirds power of concentration. The origin of this difference is unclear at present. It could represent effects of undetected aggregation in one or both of our systems or it could be fundamentally related to the diffusion process. Theory of the

---

(62) Birks, J. B.; Wright, G. T. *Proc. Phys. Soc., London, Sect. B* **1954**, *67*, 657.

(63) Wright, W. H. *Chem. Rev.* **1967**, *67*, 581.

type being developed by Blumen and co-workers,[64–66] in concert with additional experimental data should clarify the matter soon.

The diffusion lengths attained here are interestingly large but are insufficient for the ultimate purpose of efficiently collecting photonic energy for supply to a reaction center. Distances greater than 200 Å will probably be needed. In order to achieve diffusion coefficients that would lead to such distances, one must find systems giving greater resonance interactions between antenna chromophores. This study has highlighted the desirability of large oscillator strength in the relevant transition and rigidity in the molecule. In addition, we have called upon steric aspects of molecular structure to minimize the formation of dimeric traps in the cast films. All these elements should be preserved in any new system. Equation 4 suggests additionally that the resonance interaction could be improved substantially by going to a chromophore with a much redder transition. This is probably the most fruitful change that could be made to improve the diffusion coefficient.

Acknowledgment. We are grateful to the U.S. Department of Energy for supporting this work through Contract DE-AC02-76-ER01198, administered by the Materials Research Laboratory of the University of Illinois.

Registry No. DPA, 1499-10-1; polystyrene, 9003-53-6.

---

(64) Blumen, A.; Zumofen, G. *Chem. Phys. Lett.* **1980**, *70*, 387.
(65) Blumen, A.; Klafter, J.; Silbey, R. *J. Chem. Phys.* **1980**, *72*, 5320.
(66) Blumen, A. *J. Chem. Phys.* **1981**, *74*, 6926.

Diradicalar or Ionic Twisted Excited States in the Singlet Cis–Trans Isomerization of Polyenes?

Ignacio Nebot-Gil[†] **and Jean-Paul Malrieu***

Contribution from the Laboratoire de Physique Quantique (E.R.A. 821), Université Paul Sabatier, 31062 Toulouse Cedex, France. *Received June 29, 1981*

Abstract: Ab initio extensive CI's are performed on singlet excited states of butadiene, hexatriene, and styrene in their planar and twisted geometries. Size dependance of both ionic and diradicalar excited states is studied. The π conjugation and proper geometrical distortions allow some stabilization of the ionic twisted minima, but these minima remain rather high in energy (above 110 kcal/mol) and twisted diradicalar excited states are always present (for more than two conjugated double bonds) *below* the ionic minima. Since the vertical absorption energy decreases when the dimension of the conjugated system increases, for large enough polyenes, the cis–trans isomerization from the "ionic" absorbing state must proceed through an internal conversion to the lower diradicalar excited surfaces.

I. Introduction

The ^1B_u absorbing state of linear polyenes is known to correspond to the homo → lumo transition[1] and to be "ionic" in nature when treated in the VB approach. The size dependence of the vertical transition energy follows the empirical law[2]

$$\Delta E = A + B/2n$$

(n being the number of double bonds), which received partial theoretical demonstrations.[3] Recent theoretical[4] treatments and experimental evidences[5,6] support the possible existence of lower ^1A_g excited states. These excited states are "neutral" in the sense of VB theory and have important components on the $(\text{homo} \rightarrow \text{lumo})^2$ doubly excited determinant. Experience fails to see such a neutral (forbidden) state below the lowest ^1B_u state in butadiene[7] and hexatriene,[8] but an ^1A_g neutral state is definitely found 0.5 eV below the ^1B_u state in octatetraene,[5,6] and this should be the rule[9] for larger polyenes.

Twisted singlet excited states of polyenes have received much attention. For ethylene the twisted excited singlet is much lower in energy than the vertical $\pi \rightarrow \pi^*$ absorption, and further pyramidalization of one carbon stabilizes the excited state and breaks the symmetry in favor of one of the M^+M^- resonant ionic components of the wave function, allowing an important dipole to appear ("sudden" polarization phenomenon[10]). The resulting minimum has been located at 5.81 eV above the ground state planar energy by accurate extensive CI calculations;[11,12] this funnel in the ionic singlet surface is supposed to play the main role in the cis–trans isomerization. Such ionic minima may be supposed to occur in polyenes, whatever the twisted bond, and are usually supposed to be responsible for the cis–trans isomerization after the vertical allowed transition to the ionic ^1B_u state. A lot of efforts have been devoted to the problem of the polarization of these twisted minima. For butadiene and terminally twisted polyenes, it is well established now that an important dipole moment occurs in the ionic excited state minimum.[13,14] Controversy has taken

---

[†] On leave from Departamento de Química-Física, Facultad de Ciencias Químicas, Dr. Moliner s/n, Burjasot (Valencia), Spain.

(1) See, for instance: L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966, p 379.
(2) B. Hudson and B. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437 (1974); F. Sondheimer, D. A. Ben-Ephraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **95** 575 (1973).
(3) (a) W. Kutzelnigg, *Theor. Chim. Acta*, **4**, 417 (1966); H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949); P. Karadakov, O. Castano, F. Fratev, and V. Enchev, *Chem. Phys. Lett.*, **78**, 560 (1981); D. R. Yarkony and R. Silbey, *Chem. Phys.*, **20**, 193 (1977). (b) See also: A. Szabo, J. Langlet, and J. P. Malrieu, *ibid.*, **13**, 173 (1976).
(4) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972).
(5) B. S. Hudson and B. E. Kohler, *Chem. Phys. Lett.*, **14**, 299 (1972).
(6) (a) M. F. Granville, G. R. Holton, and B. E. Kohler, *J. Chem. Phys.*, **72**, 4671 (1980); (b) J. R. Andrews and B. S. Hudson, *Chem. Phys. Lett.*, **57**, 600 (1978).
(7) J. P. Docsing and R. McDiarmid, *J. Chem. Phys.*, **73**, 3617 (1980).
(8) W. M. Fliker, O. A. Mosher, and A. Kuppermann, *Chem. Phys. Lett.*, **45**, 492 (1977).
(9) A. C. Lasaga, R. J. Aerni, and M. Karplus, *J. Chem. Phys.*, **73**, 5230 (1980).
(10) V. Bonacic-Koutecky, P. Bruckmann, P. Hiberty, J. Koutecky, C. Leforestier, and L. Salem, *Angew. Chem., Int. Ed. Engl.*, **14**, 575 (1975); for reviews, see L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979), and J. P. Malrieu, *Theor. Chim. Acta*, **59**, 251 (1981).
(11) G. Trinquier and J. P. Malrieu, *Chem. Phys. Lett.*, **72**, 328 (1980).
(12) R. J. Buenker, V. Bonacic-Koutecky, and L. Pogliani, *J. Chem. Phys.*, **73**, 1836 (1980); P. R. Brooks and H. F. Schaefer III, *J. Am. Chem. Soc.*, **101**, 307 (1979).
(13) P. Bruckmann and L. Salem, *J. Am. Chem. Soc.*, **98**, 5037 (1976).

0002-7863/82/1504-3320$01.25/0