Molecular Triplet Excimers

EDWARD C. LIM

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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Introduction

Molecular excimers are dimeric species which are formed by the association of an electronically excited molecule with the corresponding ground state molecule.[1] The excimer (E*) may be singlet or triplet, depending

$$^{1,3}M* + {}^1M \rightarrow {}^{1,3}E*$$
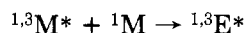
pending upon the spin multiplicity of the electronically excited molecule (M*) from which it is formed. Although the structure and spectra of the singlet excimers of aromatic hydrocarbons have been well characterized[1] soon after their discovery[2] in 1954, relatively little has been known about the triplet excimers until very recently. The primary reason for this lies with the experimental difficulties associated with the detection of triplet excimers in fluid solutions via phosphorescence measurements. Nevertheless, recent experiments on naphthalene and related compounds in this and other laboratories reveal some fascinating information concerning the unusual geometry of the triplet excimers and photophysical consequences thereof. The purpose of this Account is to describe our efforts to identify and characterize triplet excimers of aromatic molecules, especially naphthalene. In order to highlight the chronological sequences of these efforts, and the difference between singlet and triplet excimers, we begin with a brief descritpion of singlet excimers.

Emission Characteristics and Conformation of Singlet Excimers

Figure 1 presents the concentration dependence of fluorescence of pyrene which led to the discovery of molecular singlet excimers by Förster and Kasper.[2] Curve a is the fluorescence spectrum of a dilute solution of pyrene, which can be identified as the normal fluorescence of monomeric species. As the concentration of the solution is increased, a broad structureless fluorescence band appears at the lower energy side of the normal fluorescence, and its intensity increases with increasing concentration. Since the absorption spectrum of the sample was independent of concentration (and remained monomeric in character), the anomalous fluorescence was attributed[2] to a dimeric species which is formed by the association of pyrene in its lowest excited singlet state with a molecule in the ground state. The term "excimer" was introduced by Stevens and Hutton[3] to distinguish this product of photoassociation from the excited state of a stable ground-state dimer.

The diffuse character of the excimer fluorescence and its lower energy relative to the normal fluorescence can

be explained in terms of the potential energy diagram first used by Stevens and Hutton[3] (Figure 2). Since the ground state of the excimer is repulsive (i.e., unstable), the potential energy of the molecular pair increases with decreasing intermolecular separation in the ground electronic state. When one of the molecules is electronically excited, it can fluoresce or form an excimer by association with a ground-state molecule. The lower energy of the excimer fluorescence relative to the normal fluorescence is easily seen from the diagram, while the diffuse character of the excimer fluorescence can be ascribed to the repulsive character of the ground-state potential.

The temporal characteristics of the excimer fluorescence was first studied by Birks and his co-workers,[4] whose results are shown in Figure 3. Unlike the normal fluorescence which has no measurable buildup time, the time dependence of the excimer fluorescence is characterized by a buildup to a maximum intensity followed by a decay. As expected, the buildup time of the excimer fluorescence increases as the viscosity of the solvent increases, and decreases with increasing concentration of the sample.

The experiments following these early studies have established the formation of singlet excimer as a general property of aromatic hydrocarbons.[1,2] Studies of fluorescence of crystals,[5,6] sandwich dimers,[7,8] and diarylalkanes[9,10] all indicate that the preferred conformation of singlet excimer is a symmetrical sandwich structure (or one very close to it) with an interplanar separation of 3–4 Å. Thus, the molecular crystals of perylene and pyrene, which contain two molecules arranged in sandwich-pair conformation in the crystal lattice, emit broad structureless fluorescence characteristics of excimer, as do the sandwich pairs of aromatic hydrocarbons produced by photolytic dissociation of the corresponding photodimers in rigid organic glasses. In fluid solutions of diphenylalkanes and 1,n-di-α-naphthylalkanes, intramolecular excimer formation is observed only in the diarylpropanes. The result is illustrated for 1,n-di-α-naphthylalkanes in Figure 4. It turns out that the 3-methylene chain is the only species for which the symmetric sandwich arrangement of two aromatic rings is possible.[9,10]

(1) See, for review: Birks, J. B. *Rep. Prog. Phys.* **1975**, *38*, 903. Stevens, B. *Adv. Photochem.* **1971**, *8*, 161.
(2) Förster, Th.; Kasper, K. *Z. Phys. Chem.* (*Munich*) **1954**, *1*, 275.
(3) Stevens, B.; Hutton, E. *Nature* **1960**, *186*, 1045.
(4) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, A* **1963**, *275*, 575.
(5) Stevens, B. *Spectrochim. Acta* **1962**, *18*, 439.
(6) Ferguson, J. *J. Chem. Phys.* **1958**, *28*, 765.
(7) Chandross, E. A.; Ferguson, J.; McRae, E. G. *J. Chem. Phys.* **1966**, *45*, 3546.
(8) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 704.
(9) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.
(10) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.

Edward C. Lim is Professor of Chemistry, and Distinguished Faculty Fellow, at Wayne State University. Following his graduate studies (M.S., 1957; Ph.D., 1959) at Oklahoma State University, he taught 9 years at Loyola University (Chicago), before moving to Wayne State in 1968. His primary research interest is in the area of molecular photophysics.
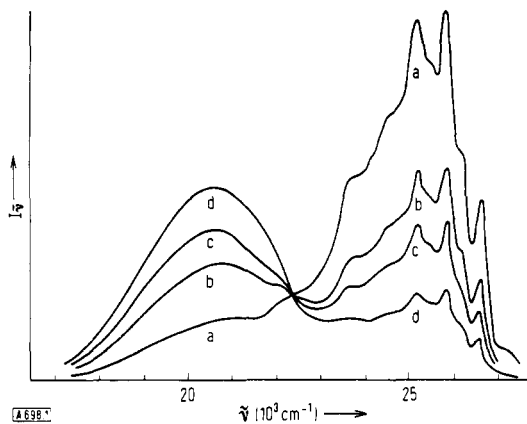
Figure 1. Concentration dependence of fluorescence of pyrene in cyclohexane at room temperature. The concentration increases in going from (a) to (d).
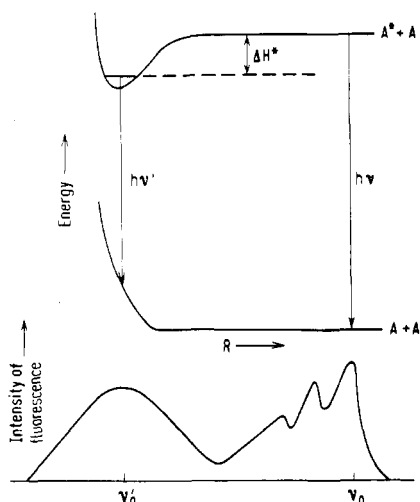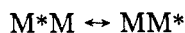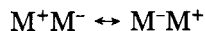
Figure 2. Potential energy as a function of the intermolecular separation.

Theoretical Descriptions of Singlet Excimers

Theoretical considerations[11-13] suggest that the binding in molecular excimer is essentially due to the exciton resonance

$$M^*M \leftrightarrow MM^*$$

with smaller contributions coming from charge resonance

$$M^+M^- \leftrightarrow M^-M^+$$

The exciton resonance arises from the dipole–dipole interaction between excited and unexcited molecules, while the charge resonance arises from the coulombic interaction of the positive and negative molecular ion states. Calculations of Konijnenberg,[11] Murrell and Tanaka,[12] Azumi, Armstrong, and McGlynn,[13] Vala et al.,[14] and those of our own,[15] indicate that the configurational mixing between the exciton resonance and charge resonance structures can account for the binding energies of singlet excimers at an intermolecular separation very close to that deduced from experiments. An

(11) Konijnenberg, E. Doctoral Thesis, Free University of Amsterdam, Holland, 1963.
(12) Murrell, J. N.; Tanaka, J. *Mol. Phys.* **1964**, *45*, 363.
(13) Azumi, T.; Armstrong, A. T.; McGlynn, S. P. *J. Chem. Phys.* **1964**, *41*, 3839.
(14) Vala, M. T.; Hiller, I. H.; Rice, S. A.; Jortner, J. *J. Chem. Phys.* **1966**, *44*, 23.
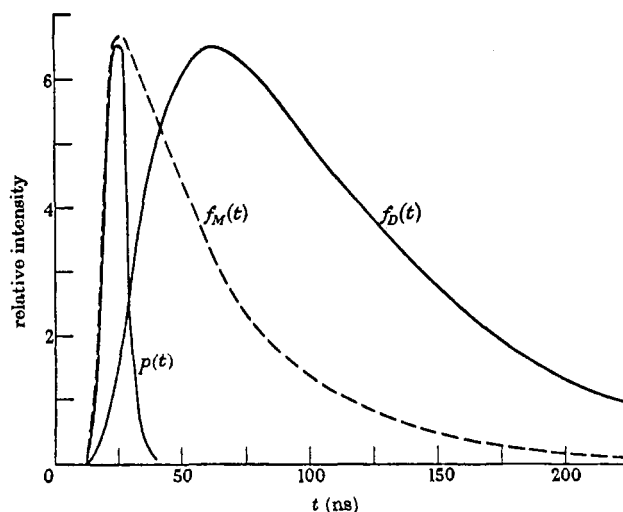(15) Chandra, A. K.; Lim, E. C., unpublished results.

Figure 3. Temporal characteristics of excimer fluorescence (f_D) and monomer fluorescence (f_M) for pyrene in cyclohexane at room temperature. P represents the exciting light pulse used for the experiment.

alternative approach to the above theoretical description of a singlet excimer was proposed by Chandra and Lim,[16] in which the excimer was treated as a super-molecule whose molecular orbitals are composed of the molecular orbitals of the monomer.[17] This approach allows a direct correlation of the energy of excimer fluorescence in terms of the energy of the corresponding monomer fluorescence. In what follows, we present a brief outline of this theoretical approach, as it is relevant to the discussion of the triplet excimers.

We assume that the excimer of an aromatic hydrocarbon, e.g., naphthalene, has the D_{2h} configuration in which one aromatic molecule is exactly superposed over the other, in a perfect sandwich-pair structure. Let the number of π-electrons in one molecule be $2m$ and the molecular orbitals these electrons occupy in the ground state be 1,2,3,...,m, where m is the highest filled orbital. Using a super-molecule approximation we designate the Hückel-type dimer orbitals as $\phi_1, \phi_2, ..., \phi_{2m}$ so that ϕ_{2m} represents the highest filled orbital. In addition to the orthogonality between the highest filled (m or m') and the lowest vacant orbitals [$(m + 1)$ or $(m + 1)'$] of the same molecule, it is assumed that orthogonality exists between m and $(m + 1)'$ and between $(m + 1)$ and m'. The coordinates of the two molecules in the excimer are chosen such that $S' > 0$ and $\beta' < 0$, where S' and β' are, respectively, the intermolecular overlap and resonance integrals. The energies and the normalized wave functions of the dimer orbitals are then given by

$$E_{2(m+n)} = E_{m+n} - \beta'$$

$$E_{2(m+n)-1} = E_{m+n} + \beta'$$

$$\phi_{2(m+n)} = 2^{-1/2}[(m + n) - (m + n)']$$

$$\phi_{2(m+n)-1} = 2^{-1/2}[(m + n) + (m + n)'] \tag{1}$$

where $n = 0,1,2,...$ and S' is assumed to be zero. The dimer orbitals are therefore split by an energy $2\beta'$. The orbital energy diagram for the monomer and excimer is shown in Figure 5.

The configurational wave functions for the excited states of the dimer (i.e., excimer states) can be con-

(16) Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1968**, *48*, 2589.
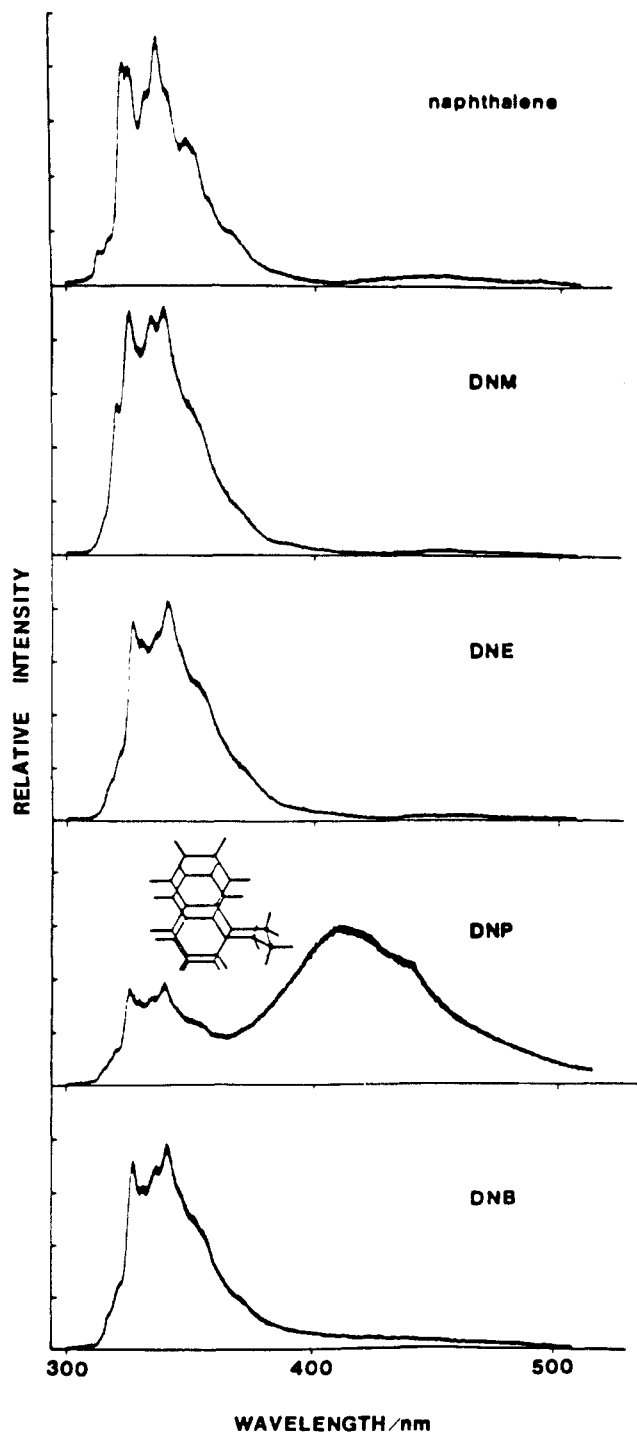(17) Azumi, T.; Azumi, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 279.
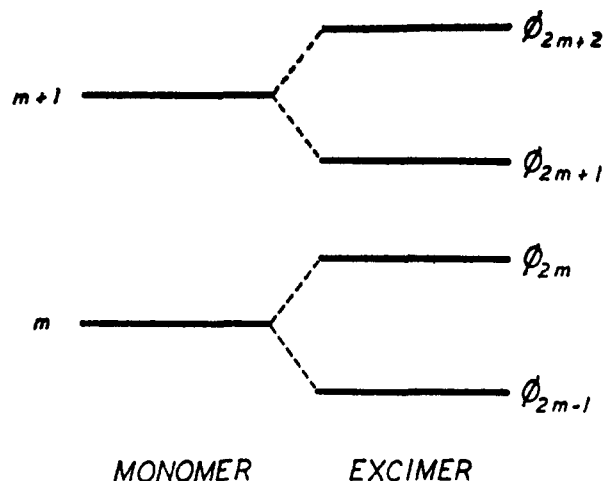
MONOMER   EXCIMER

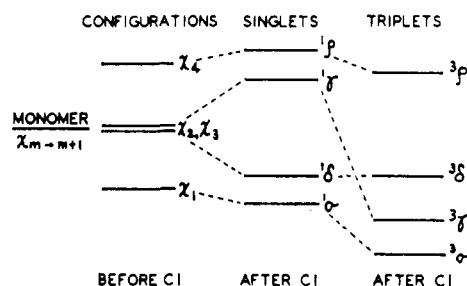**Figure 5.** Orbital energy diagram for the monomer and excimer.

Figure 6. Effects of configuration interaction on the singlet and triplet states of an excimer with sandwich-pair conformation.

essentially the sum of two Slater determinants, are either symmetric (S) or antisymmetric (A) with respect to reflection in a plane that lies midway between, and parallel to, two monomers. The configuration χ_2 and χ_3 are degenerate in the Huckel approximation. The matrix elements of the total Hamiltonian $[H = \sum_i H_i^{core} + \frac{1}{2}\sum_{i,j}(r_{ij})^{-1}]$ between two configurations of different symmetry are zero, but they do not vanish for those having the same symmetry. An interaction element of this type removes the degeneracy between χ_2 and χ_3 and leads to the following four states of an excimer:

$$\sigma: \ (1 + \lambda^2)^{-1/2}(\chi_1 + \lambda\chi_4)$$

$$\rho: \ (1 + \lambda'^2)^{-1/2}(\chi_1 + \lambda'\chi_4)$$

$$\delta: \ 2^{-1/2}(\chi_2 - \chi_3)$$

$$\gamma: \ 2^{-1/2}(\chi_2 + \chi_3) \tag{3}$$

where λ and λ' are the configurational mixing coefficients in the lower and higher energy states, respectively. The effect of configuration interaction on the singlet states of an excimer is illustrated in Figure 6. Note that the excimer fluorescence corresponds to the radiative transition from the σ state to the repulsive ground state in this scheme. The energy of the excimer fluorescence $E(\sigma)$ is related to that of the $m \rightarrow m + 1$ transition of the monomer by the expression

$$E(\sigma) = (1 - K)E(p) +$$

$$K[\Delta E - \langle m,m|(m + 1)',(m + 1)'\rangle] - 2\left(\frac{1 - \lambda^2}{1 + \lambda^2}\right)\beta' -$$

$$\left(1 + \frac{2\lambda}{1 + \lambda^2}\right)\langle m,(m + 1)|m',(m + 1)'\rangle \tag{4}$$

where $E(p)$ represents the energy of the p (Clar nota-

WAVELENGTH/nm

Figure 4. Fluorescence spectra of 1,n-di-α-naphthylalkanes in isooctane at room temperature. Concentration of the sample was 10^{-5} M. DNM, DNE, DNP, and DNB represent 1,1-di-α-naphthylmethane, 1,2-di-α-naphthylethane, 1,3-di-α-naphthylpropane, and 1,4-di-α-naphthylbutane, respectively.

structed from these dimer orbitals. Thus, for the four low-lying excited singlet states, we write

$$\chi_1 = \phi_{2m}\phi_{2m+1} \quad A$$

$$\chi_2 = \phi_{2m}\phi_{2m+2} \quad S$$

$$\chi_3 = \phi_{2m-1}\phi_{2m+1} \quad S$$

$$\chi_4 = \phi_{2m-1}\phi_{2m+2} \quad A \tag{2}$$

where $\phi_k\phi_l$ represents a configuration in which an electron is promoted from an occupied orbital ϕ_k to an unoccupied orbital ϕ_l. These configurations, which are
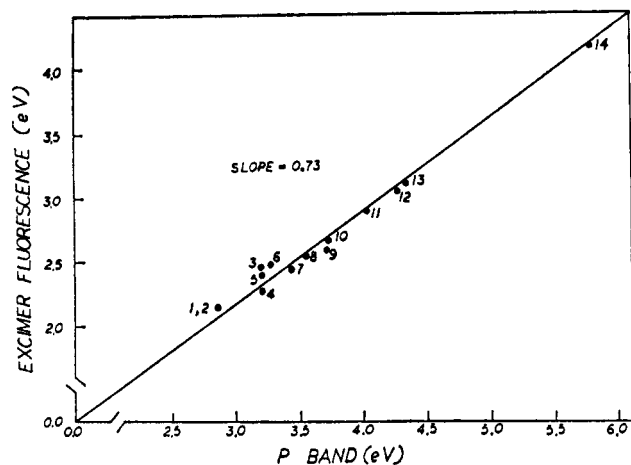
Figure 7. A plot of the energy of excimer fluorescence against the energy of the corresponding monomer P(or L_a) absorption band. See ref 16 for the identity of the aromatic hydrocarbons.

tion)[18] or L_a (Platt notation)[19] band of the monomer, corresponding to the $m \rightarrow m + 1$ transition, ΔE is the energy difference between the lowest vacant and highest filled orbitals of the monomer, and K is given by $^1/_2\{1 - [2\lambda/(1 + \lambda^2)]\}$. The bracketed terms in eq 4 represent the two electron integrals over the dimer orbtials, involving the operator $\sum (r_{ij})^{-1}$. Numerical evaluations of the terms on the right-hand side (R.H.S.) of eq 4 show that the sum of the second, third, and fourth terms are very small compared to the first term.[16] Thus, the calculation predicts a linear relationship between the energy of the excimer fluorescence and the energy of the p absorption band of the corresponding monomer. This prediction is indeed borne out by the results in Figure 7, which show that the observed energy of excimer fluorescence (measured at the peak of emission) is approximately proportional to the energy of the monomer p band for polycyclic aromatic hydrocarbons for which excimer fluorescence has been observed.

Stability of Triplet Excimers with Sandwich-Pair Geometry

Encouraged by the results of the previous section, we have applied the supermolecule description of excimers to explore the stability of triplet excimers having sandwich-pair geometry.[20] The difference between the energy of the triplet excimer ($^3\sigma$) and the sum of the energies of a triplet monomer (^3P) and a ground state monomer (M) can be written as[20]

$$E(^3\sigma) - E(^3P) - E(M) = -2\left(\frac{1 - \lambda^2}{1 + \lambda^2}\right)|\beta'| -$$
$$\frac{1}{2}\left(1 - \frac{2\lambda}{1 + \lambda^2}\right)[\langle m,m|(m + 1)',(m + 1)'\rangle -$$
$$\langle m,m|(m + 1),(m + 1)\rangle] + x$$
$$(5)$$

where x represents the repulsion energy of the dimeric ground state. The sum of the first two terms on the R.H.S. of eq 5 turns out to be smaller than the estimated repulsion energy (x) of the ground dimeric state.[20] The result therefore suggests that the triplet excimer is not likely to be stable if its conformation is

(18) Clar, E. *Polycyclic Hydrocarbons*; Academic: London, New York; Springer-Verlag: Berlin, 1964.
(19) Platt, J. R. *J. Chem. Phys.* 1949, *17*, 484.
(20) Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* 1968, *49*, 5066.
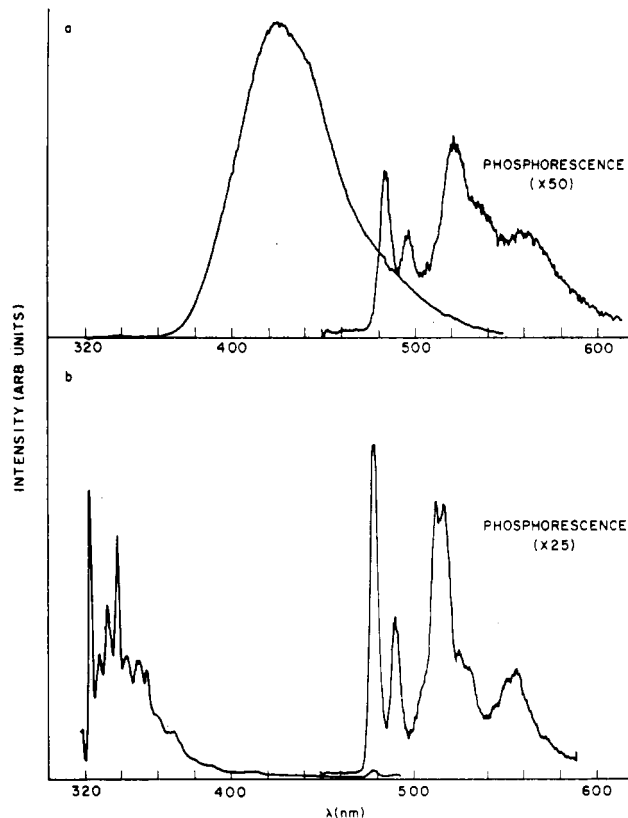

Figure 8. Fluorescence and phosphorescence of a sandwich dimer of naphthalene (top) and those of naphthalene monomer (bottom), in methylcyclohexane glass at 77 K.

the same as that favored by the corresponding singlet excimer, namely a symmetric sandwich configuration of two aromatic rings.[20]

This prediction was dramatically confirmed by the experiment of Chandross and Dempster.[8] In their experiment, 1,3-di-α-naphthylpropane was irradiated to form the photocycloaddition product, which was subsequently photolyzed in rigid methylcyclohexane glass (at 77 K) to yield a sandwich dimer of naphthalene. The dimer exhibits structured phosphorescence resembling that of a naphthalene monomer, despite the fact that its fluorescence is distinctly excimerlike in character. The results, which are shown in Figure 8, demonstrate the very small binding energy associated with the "triplet excimer" of sandwich-pair geometry.

Excimer Phosphorescence in Fluid Media

Although the results of the preceding section show that naphthalene in its triplet state does not interact with the ground-state molecule to form a stable triplet excimer of parallel sandwich-pair conformation, they do not rule out the formation of triplet excimers whose conformation is significantly different from the sandwich structure. In fact, there are reasons to expect the preferred conformation of the triplet excimer to be different from the sandwich-pair conformation favored by the singlet excimer (vide infra).

We have therefore set out,[21] as have others,[22] to look for weak phosphorescence from fluid solutions of

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(22) Takemura, T.; Baba, H.; Shindo, Y. *Chem. Lett.* 1974, 1091. Takemura, T.; Aikawa, M.; Baba, H.; Shindo, Y. *J. Am. Chem. Soc.*, 1976, *98*, 2205.
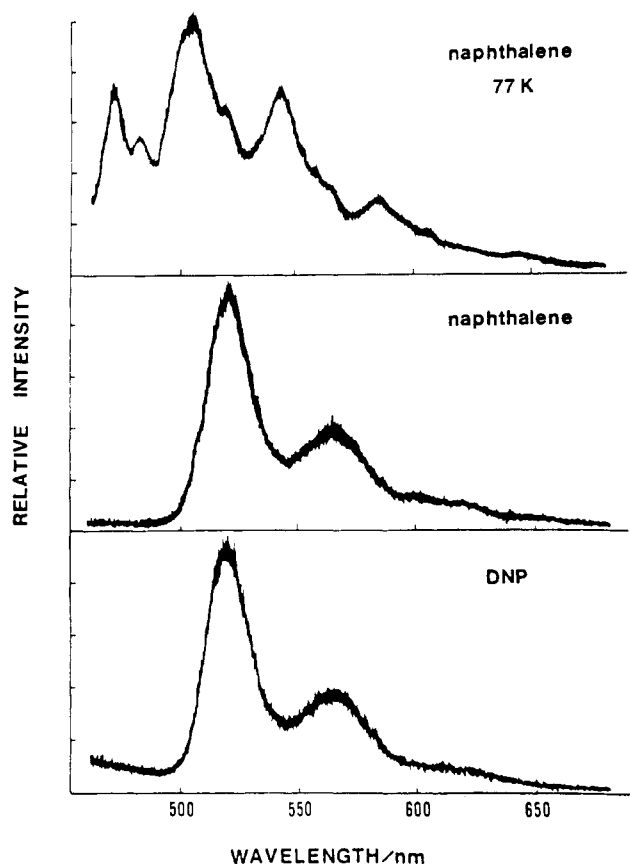
Figure 9. Room-temperature phosphorescence spectra of naphthalene (middle) and 1,3-di-α-naphthylpropane (bottom) in isooctane and low-temperature phosphorescence spectrum of naphthalene in methylcyclohexane glass at 77 K (top). Concentration: $\sim 10^{-5}$ M.

naphthalene and related compounds, using a homemade spectrophosphorimeter which combines the high intensity of a repetitively pulsed flash lamp (excitation source) and the high sensitivity of photon counting (detection system). The results for chromatographically pure samples of naphthalene and 1,3-di-α-naphthylpropane are shown in Figure 9 (center and bottom). It should be noted that the phosphorescence spectra of the two compounds are essentially identical with each other and they differ from their respective low-temperature phosphorescence spectra (top). Since the excitation spectra of the room-temperature phosphorescence are identical with the absorption spectra of these species, we assign the room-temperature phosphorescence to the emission from triplet excimers. Consistent with this assignment the room-temperature phosphorescence of these compounds exhibit a rise time which depends strongly on the viscosity of the solvent (see Figure 10). Concentration dependence of the intensity of the "excimer phosphorescence" indicates that the emission from naphthalene is due to intermolecular triplet excimers, while that from the dinaphthylpropane is due to intramolecular triplet excimers (i.e., the triplet excimer is formed from the two naphthalene molecules joined by the methylene chain).[21,23]

The study of the phosphorescence from the series of 1,n-di-α-naphthylalkanes (n = 1–4) in fluid solutions reveals that the ability of the species to form a sandwich-pair conformation of two naphthalene rings is not
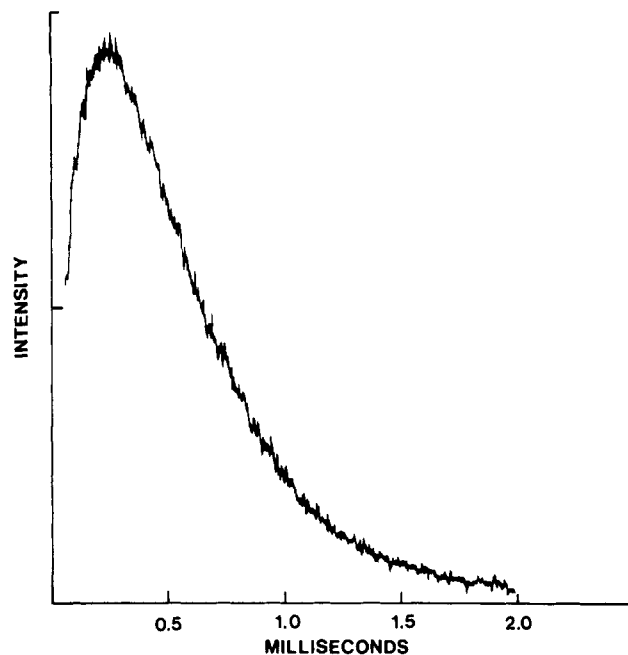
(23) Lim, B. T.; Lim, E. C. *J. Chem. Phys.* 1983, 78, 5262.

Figure 10. Temporal characteristics of the excimer phosphorescence of 1,1-di-α-naphthylmethane in isooctane at room temperature. Concentration: $\sim 10^{-5}$ M.
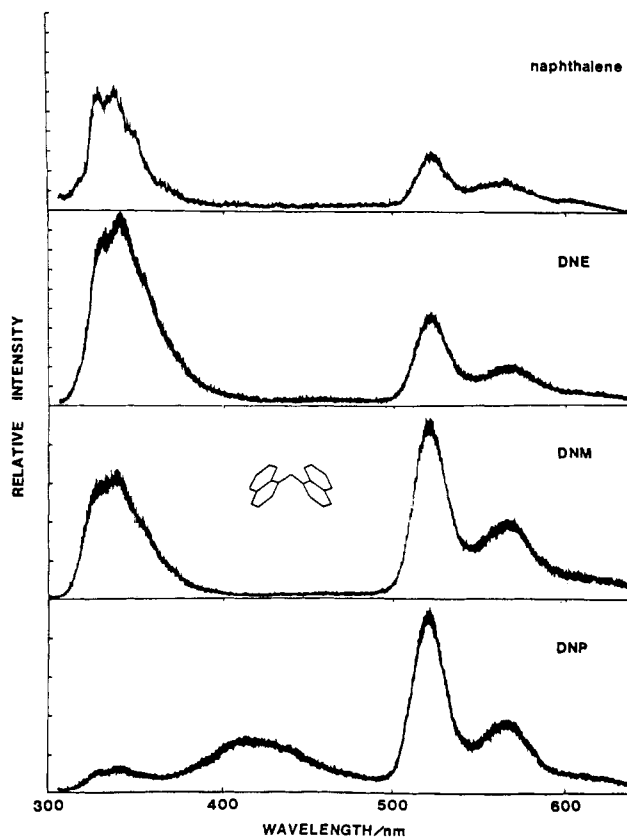

Figure 11. Excimer phosphorescence of naphthalene, 1,1-di-α-naphthylmethane (DNM), 1,2-di-α-naphthylethane (DNE), and 1,3-di-α-naphthylpropane (DNP) in isooctane at room temperature. Concentration is $\sim 10^{-5}$ M except for naphthalene, which is $\sim 10^{-4}$ M.

a prerequisite for the observation of excimer phosphorescence.[21,23] Thus, 1,1-di-α-naphthylmethane, 1,2-di-α-naphthylethane, and 1,4-di-α-naphthylbutane all exhibit excimer phosphorescence, despite the fact that their fluorescence is clearly monomerlike in char-
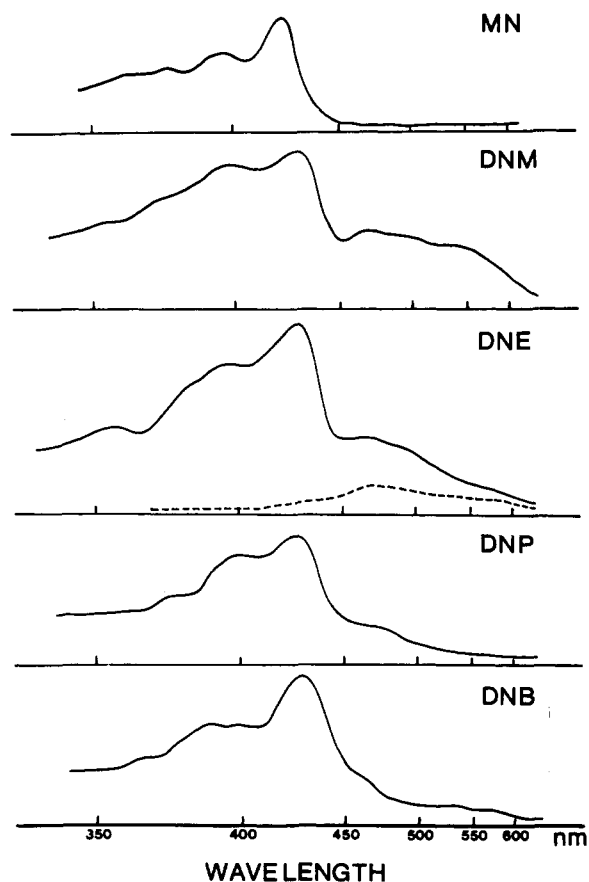
Figure 12. Laser-induced transient absorption spectra of dilute solutions ($\sim 10^{-5}$ M) of 1,n-di-α-naphthylalkanes and α-methylnaphthalene in isooctane at room temperature. The time delay between the excitation and probe pulses was 5 μs, except for the dashed curve in DNE, which was 150 μs.
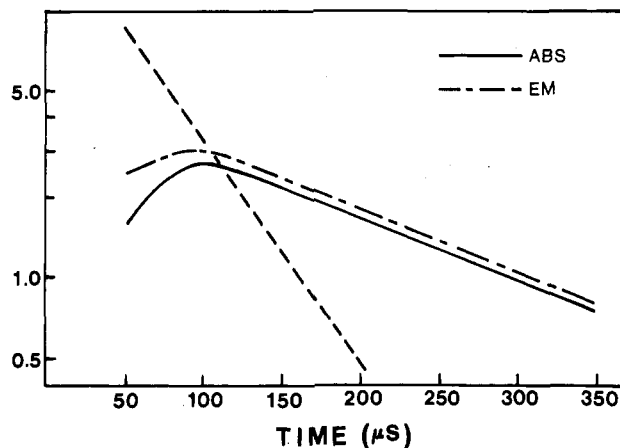

Figure 13. Temporal characteristics of transient absorption due to the triplet monomer (- - -) and triplet excimer (—) for 1,1-di-α-naphthylmethane in isooctane at room temperature. The dash-dot (- $\cdot$ -) curve represents the temporal characteristics of the excimer phosphorescence taken under identical experimental conditions.

acter. The results, which are displayed in Figure 11, prove that the geometry of the triplet excimer is different from a sandwich-pair geometry favored by the singlet excimer. The proof for the highly skewed structure of the triplet excimer is especially evident from the remarkable observation of excimer phosphorescence from the dinaphthylmethane. The minimum information that can be gained from these results is that the short axes of the two naphthalene rings are highly nonparallel in the triplet excimers of the dinaphthylalkanes. Since the excimer phosphorescence of naphthalene is essentially identical with those of the dinaphthylalkanes we can conclude that the intermolecular triplet excimer of naphthalene also has a highly skewed conformation. The likely conformation of the triplet excimer will be described in a later section.

Absorption Spectra of Triplet Excimers

If the triplet excimer is a stable entity which can be identified by its emission, it must also have an absorption which is different from that of the corresponding triplet monomer. The transient absorption spectra of the dinaphthylalkanes, obtained by a flash photolysis technique, indeed show evidence of the absorption due to the triplet excimer.[24] Figure 12 compares the transient absorption spectra of the dilute solutions of dinaphthylalkanes with the spectrum of α-methylnaphthalene recorded under identical exper-

imental conditions. Although the absorption spectrum of α-methylnaphthalene corresponds to the well-known triplet–triplet absorption of naphthalene-like molecules (i.e., monomeric species) the dinaphthylalkane spectra display, in addition, a broad absorption to the red of the monomer absorption. This absorption (centered at about 480 nm) appears only in low viscosity solvents, and its time dependence is characterized by a buildup to maximum absorbance, followed by an exponential decay. The buildup (or rise) and the decay rates of the absorption are identical with those of the emission which has been assigned to the excimer phosphorescence (Figure 13). The identity indicates that the new transient absorption is the triplet–triplet absorption of the excimers. In contrast, the triplet–triplet absorption of the monomer at shorter wavelengths shows no measurable buildup time, and it decays considerably faster than the triplet–triplet absorption of the excimer. The disparity in the two decay rates allows recording of the absorption spectra of the triplet excimer via time-resolved spectroscopy, as illustrated for the dinaphthylethane (Figure 12).

Transient absorption, attributable to triplet excimers, has also been observed in poly(2-vinylnaphthalene),[25] in the neat liquids of α-methyl- and α-chloronaphthalenes,[26] are in bis[1-(1-pyrenyl)ethyl] ethers.[27]

Dynamics of Triplet Excimer Formation

The temporal characteristics of the triplet–triplet absorption in the dinaphthylalkanes indicate that the triplet excimer is formed from the triplet monomer following a simple kinetic scheme:[24]

$$^3M^* \xrightarrow{k_a} {}^3E^*$$

$$k_b \downarrow \qquad\qquad \downarrow k_E$$
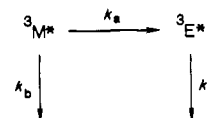
Here, k_a is the rate constant for the excimer formation,

(24) Subudhi, P. C.; Lim, E. C. *Chem. Phys. Lett.* **1978**, *56*, 59.

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(27) Masuhara, H.; Tanaka, J. A.; Mataga, N.; De Schryver, F. C.; Collart, P. *Polymer J. (Tokyo)* **1983**, *15*, 915.

and k_b and k_E are the combined rate constants for various unimolecular decay channels (radiative and nonradiative) for the triplet monomer and triplet excimer, respectively. Denoting $k_a + k_b = k_M$, an analysis of the above kinetic scheme yields

$$[^3M^*] = [^3M^*]_0 e^{-k_M t} \qquad (6)$$

$$[^3E^*] = \frac{k_a}{k_E - k_M}[^3M^*]_0(e^{-k_M t} - e^{-k_E t}) \qquad (7)$$

For the dinaphthylalkanes k_M is significantly greater than k_E (see, for example, Figure 13), so that eq 6 and 7 indicate that the buildup rate of the triplet excimer should be identical with the decay rate of the triplet monomer, k_M. This prediction is borne out by the experiment (Figure 13) which shows that the decay rate of the monomer absorption is approximately the same as the buildup rate of the excimer absorption at short times. The time required for the excimer absorption to build up to a maximum is given by

$$t_{max} = \frac{1}{k_M - k_E} \ln \frac{k_M}{k_E} \qquad (8)$$

Using k_M ($\sim 2.0 \times 10^4$ s^{-1}) and k_E ($\sim 3.3 \times 10^3$ s^{-1}) obtained from the decay curves of the absorptions, we obtain t_{max} of 107 μs for the dinaphthylmethane, which is in excellent agreement with the observed value (Figure 13). As expected for a process involving association of $^3M^*$ and ^1M, t_{max} increases with increasing length of the methylene chain and increasing viscosity of the solvent.

The unusually small rate constant of the excimer formation, as evidenced by the long rise time of the excimer absorption (or excimer emission), is believed to be due to a large activation energy resulting from the highly limited, and skewed, geometry of the triplet excimer (vide infra).

Bimolecular Interaction of Triplet Excimers Leading to Delayed Fluorescence

The identification of the triplet excimer of the dinaphthylalkanes based on the phosphorescence and transient absorption is further strengthened by the observation of delayed fluorescence (a long-lived emission spectrally identical with normal fluorescence) from fluid solutions of the dinaphthylalkanes.[28]
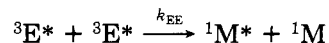
It is well known that the interactions of two molecules in their lowest triplet state (T$_1$) can lead to formation of an excited singlet states (S$_n$) and the ground state (S$_0$)

$$T_1 + T_1 \rightarrow S_n(n \geq 1) + S_0$$
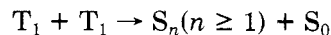
which can be monitored through delayed fluorescence.[29] For the interactions of two triplet monomers

$$^3M^* + {}^3M^* \xrightarrow{k_{MM}} {}^1M^* + {}^1M$$
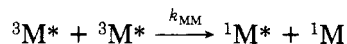
and two triplet excimers

$$^3E^* + {}^3E^* \xrightarrow{k_{EE}} {}^1M^* + {}^1M$$

leading to the formation of the excited singlet state of

(28) Subudhi, P. C.; Lim, E. C. *Chem. Phys. Lett.* **1978**, *58*, 62.
(29) Parker, C. A.; Hatchard, C. G. *Proc. R. Soc. London A* **1962**, *269*, 574.
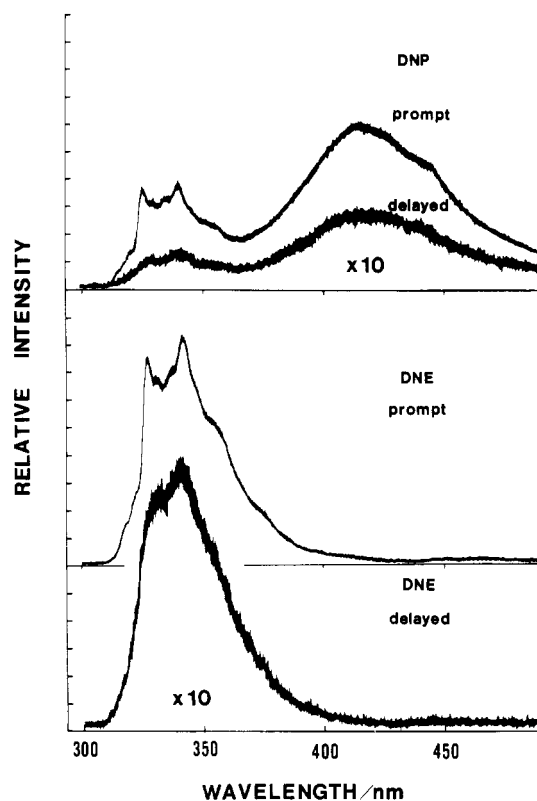

Figure 14. Prompt (normal) and delayed fluorescence of 1,2-di-α-naphthylethane (DNE) and 1,3-di-α-naphthylpropane (DNP) in isooctane at room temperature. Concentration: $\sim 10^{-4}$ M.

the monomer ($^1M^*$), the time dependence of the concentration of $^1M^*$ can be written as

$$\frac{d[^1M^*]}{dt} = -(k_r + k_{nr})[^1M^*] + \frac{1}{2}k_{MM}[^3M^*]^2 + \frac{1}{2}k_{EE}[^3E^*]^2 \qquad (9)$$

where k_r and k_{nr} represent the radiative and nonradiative decay rates of $^1M^*$, respectively. Substituting (6) and (7) into (9) and integrating, we obtain[30]

$$[^1M^*] = $$

$$\frac{\frac{1}{2}k_{MM}[^3M^*]_0^2 + \frac{1}{2}k_{EE}\left([^3M^*]_0\frac{k_a}{k_E - k_M}\right)^2}{(k_r + k_{nr}) - 2k_M}e^{-2k_M t} +$$

$$\frac{\frac{1}{2}k_{EE}\left([^3M^*]_0\frac{k_a}{k_E - k_M}\right)^2}{(k_r + k_{nr}) - 2k_E}e^{-2k_E t} +$$

$$\frac{k_{EE}\left([^3M^*]_0\frac{k_a}{k_E - k_M}\right)^2}{(k_r + k_{nr}) - (k_M + k_E)}e^{-(k_M+k_E)t} \qquad (10)$$

The result (which neglects triplet–triplet annihilation between an excimer and a monomer) shows that the delayed fluorescence is composed of three major components. One decays exponentially with a rate of $2k_M$, i.e., twice the decay rate of the triplet monomer, the second decays with twice the decay rate of the triplet excimer ($2k_E$), and the third decays with the rate $k_M + k_E$.

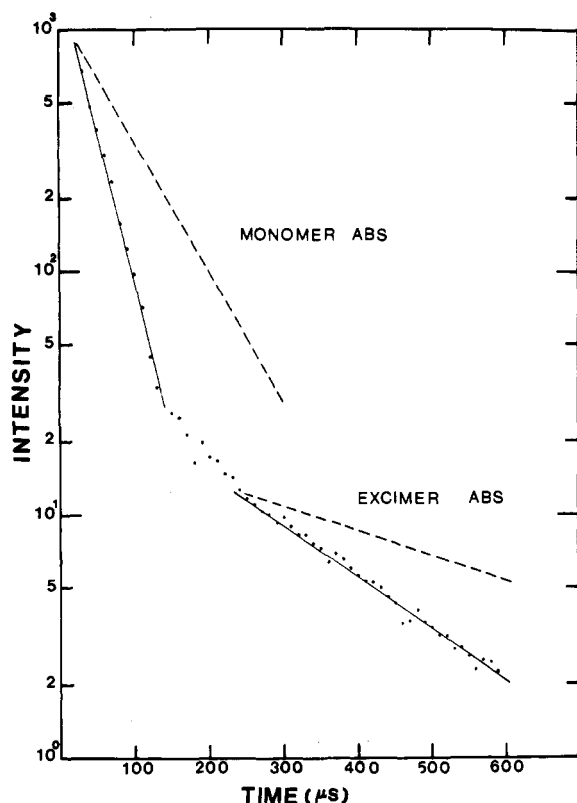(30) Original equation in ref 29 has a missing term.

Figure 15. Comparison of the temporal characteristics of delayed fluorescence (—) with those of the triplet–triplet absorption (- - -) for isooctane solution of 1,2-di-α-naphthylethane at room temperature.

Figure 14 presents the time-resolved fluorescence of the dinaphthylethane. Note that the spectral characteristics of the delayed fluorescence are virtually identical with that of the normal (prompt) fluorescence. The temporal characteristics of the delayed fluorescence are compared with those of the triplet–triplet absorptions in Figure 15. The delayed fluorescence is composed of two major decaying components. The shorter lived component decays with a lifetime approximately half that of the triplet monomer, while the longer-lived component decays with a lifetime half that of the triplet excimer. These results indicate that the shorter lived component of the delayed fluorescence is due to the triplet–triplet annihilation of monomers, while the longer lived component is due to the interaction of two triplet excimers.

It should be noted from Figure 15 that the intensity of the shorter lived component is much greater than that of the longer lived one, indicating that the concentration of the triplet monomers far exceeds that of the triplet excimers (we do not expect the annihilation efficiency to be much less for the excimers as compared to the monomers).

The behavior of the dinaphthylmethane and dinaphthylbutane is very similar, but the dinaphthylpropane and naphthalene display delayed excimer fluorescence, in addition to the delayed monomer fluorescence (Figure 14).[28] The temporal characteristics of the delayed excimer fluorescence are identical with those of the delayed monomer fluorescence, and they both exhibit the shorter and longer lived components. As in the dinaphthylmethane, dinaphthylethane, and dinaphthylbutane, the shorter-lived component decays

with a lifetime half that of the triplet monomer. The ratio of the intensities of the shorter lived component to the longer lived component does not change in going from the spectral region of the monomer fluorescence to that of the excimer fluorescence. Furthermore, the ratio of the excimer component to the monomer component in the delayed fluorescence is identical with the corresponding ratio in the prompt fluorescence, within experimental error (Figure 14). These results show that the singlet monomer is a precursor of the singlet excimer, both in the prompt and delayed fluorescence. Thus, the triplet–triplet annihilation of the excimers does not directly lead to the production of singlet excimers. The inability of the triplet–triplet annihilation of excimers to directly produce singlet excimers is very probably a consequence of the fact that the interaction between two triplet excimers of highly skewed structure yields singlet species of skewed geometry, which is not a favorable conformation for the singlet excimer. The species generated by the annihilation process therefore dissociate into $^1M^*$ and ^1M, before rearranging to form an intramolecular singlet excimer of sandwich-pair conformation.

Conformation and Binding Energy of Triplet Excimers

The stability of the sandwich-pair geometry of singlet excimers can be attributed to exciton resonance which is largest for the face-to-face arrangement of the two aromatic molecules (see Theoretical Descriptions of Singlet Excimers). For the triplet excimers, however, exciton resonance is not expected to be the major source of their binding energy since the transition moments associated with singlet–triplet transitions are extremely small (exciton resonance interaction is proportional to the square of the transition moment[31]). One might therefore expect that the conformation of a triplet excimer differs from that of the corresponding singlet excimer. As we have already discussed, the evidence for the highly skewed geometry of the triplet excimer is provided by the observation of excimer phosphorescence from 1,1-di-α-naphthylmethane. The result establishes that the short axes of the two naphthalene rings are highly nonparallel in the triplet excimer, but it is mute to the question of the relative orientation of the two long axes.

In order to more exactly define the conformation of the naphthalene triplet excimer, we have compared[23] the emission characteristics of naphthalene and 1,n-di-α-naphthylalkanes with those of the rigid symmetric model compound of the dimethylnaphthalene, cis-6b,12b-dihydroacenaphth(1,2-a)acenaphthylene[32] (hereafter referred to as the Agosta dimer). Figure 16 presents the phosphorescence spectra of naphthalene, 1,1-di-α-naphthylmethane, and Agosta dimer in isooctane at room temperature. It should be noted that the emission spectra of all compounds are essentially identical with each other and they can be identified as excimer phosphorescence. These results establish that the intermolecular triplet excimer of naphthalene and the intramolecular triplet excimers of the dinaphthylalkanes have identical, or very nearly identical, conformations that can be attained by the Agosta dimer.

(31) See, for example: Hoytink, G J. *Z. Elektrochem.* 1960, *64*, 156.
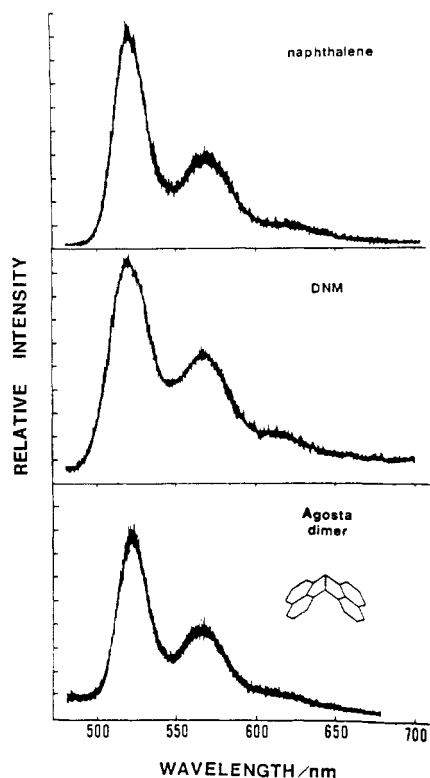(32) Agosta, W. C. *J. Am. Chem. Soc.* 1967, *89*, 3505.

Figure 16. Excimer phosophorescence of naphthalene, 1,1-di-α-naphthylmethane (DNM), and Agosta dimer in isooctane at room temperature. Concentration was $\sim 10^{-5}$ M for DNM and Agosta dimer and $\sim 10^{-4}$ M for naphthalene.

The major deduction that can be made from these results is that the long axes of the two naphthalene rings are very nearly parallel in the triplet excimer. Although the range of possible conformation is greatly narrowed by this conclusion, there still remains the question of the angle between the two short axes. Thus, in the dinaphthylmethane with parallel long axes, this angle is $\sim 109.5°$ (tetrahedral angle), while in the Agosta dimer the tilt angle is close to $120°$. The tetrahedral angle might be closer to the angle preferred by the triplet excimer, since the formation of the triplet excimer in the Agosta dimer is strongly temperature-dependent (i.e., phosphorescence spectrum is monomer-like at lower temperatures). We are therefore tempted to conclude that the conformation of naphthalene triplet excimer is very close to the most symmetric "L-shaped" conformation of the dinaphthylmethane. This conclusion is supported by the observation[33] of the excimerlike phosphorescence from low-temperature rigid glass solutions of 7,14-endoxy-7H,14H-cycloocta[1,2,3-de:5,6,7-$d'e'$]dinaphthalen-7-ol,[32] (hereafter referred to as the hydroxy dimer), which closely mimics the symmetric L-shaped conformation of 1,1-di-α-naphthylmethane. Interestingly, all four dinaphthylalkanes can adopt this L-shaped structure without inducing any strong repulsive forces.

Theoretically, the L-shaped structure of the naphthalene triplet excimer could be rationalized in terms of the electrostatic and dispersion forces, which are the primary attractive forces responsible for the formation of ground-state van der Waals dimers. In naphthalene, the leading contribution to the classical electrostatic

interaction between the molecular charge distribution comes from quadrupole–quadrupole interactions. Recent calculations[34,35] of the quadrupole moment, using a double-ζ basis set, indicate that the normal (i.e., perpendicular to the molecular plane) component of the quadrupole tensor is negative, while the in-plane long-axis component is positive, for both the ground and triplet states of naphthalene (the ground state, in addition, has a positive in-plane short axis component). Thus, the electrostatic interactions would preclude sandwich and co-planar structures, and favor a T-shaped structure for triplet excimer (this is the rationale which has been advanced[36,37] to account for the stability of T-shaped van der Waals dimers in benzene[38-40] and s-tetrazine[41,42]). For the T-shaped excimer, however, the dispersion force is not expected to be nearly as large as in a cofacial structure. The preference for an L-shaped structure of the naphthalene triplet excimer may therefore be interpreted as a compromise between the dispersion force which favors a cofacial structure and the electrostatic force which favors a T-shaped structure. Interestingly, the proposed structure of the naphthalene triplet excimer is not too dissimilar to the ground-state van der Waals dimer of anthracene[43] in which the long axes of two anthracene molecules are parallel and the short in-plane axes make an angle of $\simeq 60 \pm 15°$.

Radiative Properties of Triplet Excimers

$T_1 \rightarrow S_0$ radiative transitions owe their appearance to spin–orbit coupling. The spin–orbit coupling introduces some singlet character into the triplet state, whereby the spin-forbidden $T_1 \rightarrow S_0$ radiative transition derives its intensity from the spin-allowed S_k $(k \geq 1)$ $\rightarrow S_0$ radiative transition.[44] In aromatic hydrocarbons, where the molecular plane allows separation of σ and π orbitals, the spin–orbit coupling between $\pi\pi^*$ states is very weak, so that $T_1(\pi\pi^*) \rightarrow S_0$ radiative transition borrows intensity from weakly allowed, high-energy, $^1\sigma\pi(^1\sigma\pi^*$ or $^1\pi\sigma^*) \rightarrow S_0$ radiative transitions (the one-center spin–orbit coupling between $^3\pi\pi^*$ and $^1\sigma\pi$ states is much more efficient than the three-center coupling between two $\pi\pi^*$ states).[44] Consequently, the transition moments from $T_1(\pi\pi^*)$ to the ground state are generally very small in aromatic hydrocarbons, and they lie normal to the molecular plane. In triplet excimers, however, the strict orthogonality between σ and π orbitals does not exist, since the σ-electrons in one moiety can interact with the π-electrons in the other, leading

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to a breakdown of the separability of σ- and π-electrons.[45] An important consequence of this σ–π interaction is to introduce a small amount of $\sigma\pi^*$ and $\pi\sigma^*$ characters into the $\pi\pi^*$ states (singlet and triplet), which allows the $T_1(\pi\pi^*) \rightarrow S_0$ radiative transition of the excimer to borrow intensity from the strongly allowed $^1\pi\pi^* \rightarrow S_0$ radiative transitions, via one-center spin–orbit coupling.[45] This will lead to a large enhancement of $T_1 \rightarrow S_0$ radiative transition probability for the excimer as compared to the corresponding monomer. This prediction sharply contrasts the radiative properties of the singlet excimers, whose transition moment to the ground state is generally much smaller than that of the corresponding singlet monomer.[1]

There are at least two experimental results which point to the large radiative decay rates of the intramolecular and intermolecular triplet excimers of naphthalene. First, the room-temperature phosphorescence from fluid solutions of the dinaphthylalkanes and naphthalene is almost exclusively due to the excimer emission (see Excimer Phosphorescence in Fluid Media), despite the fact that the concentration of the triplet monomers far exceeds that of the triplet excimers (as demonstrated by the dominance of the monomer absorption in the transient spectra and the dominance of the shorter lived component in the delayed fluorescence). Secondly, the lifetime of the excimer-like phosphorescence of the hydroxy dimer in rigid glass at 77 K is much shorter than that of the corresponding monomer (naphthalene and its methyl derivatives) phosphorescence, taken under identical experimental conditions ($\sim$4 ms vs. $\sim$2500 ms).[33] Since the measured phosphorescence yields (as defined by the number of T_1 molecules emitting divided by the number of molecules reaching T_1 by $S_1 \rightarrow T_1$ intersystem crossing) are similar for these compounds,[46] the T_1 radiative decay rate of the dimer (therefore, triplet excimer) must be substantially greater than that of the monomer. Although more quantitative measurements of the radiative decay rate of triplet excimers are desirable, the existing data are at least qualitatively consistent with the supposition that the breakdown of the σ–π separation (in excimers) leads to a large enhancement of the radiative and nonradiative decay rates for the triplet excimers. The infusion of the $\sigma\pi^*$ and $\pi\sigma^*$ characters into the $\pi\pi^*$ states of the excimer is suggested by the polarization of the phosphorescence of the hydroxy dimer, which exhibits considerable in-plane character.[46]

Concluding Remarks

Although naphthalene and 1,n-di-α-naphthylalkanes have been the primary focus of the past research in triplet excimers, there is no reason to expect the formation of triplet excimers to be limited to these species. Indeed, the observation of triplet excimers has also been reported for quinoxaline,[47] phenanthrene,[48] certain diphenanthrylalkanes,[49] and bis[1-(1-pyrenyl)ethyl] ethers.[27] With the advent of sensitive detection techniques (e.g., photon-counting spectrophosphorimeter) and theoretical advances in calculating intermolecular potential for polycyclic aromatic hydrocarbons,[50] we may see a period of rapid progress in the identification and characterization of triplet excimers and in the understanding of the forces responsible for triplet excimer formation. The spectroscopic and photophysical characteristics of the naphthalene triplet excimers, described in this Account, provide ample promises for the fascinating information that will emerge from future studies.

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