Registry No. PPTox, 82639-45-0; PPTox$^-$, 82639-46-1; PPTH$_2$, 82639-48-3; PPT^{2-}, 82639-47-2; N^5-EtPPTH$_2$, 85222-30-6; N^5-EtPPT$^{-\cdot}$, 85249-96-3; N^5-EtPPTox, 82639-50-7; N^5-MePPTox, 85222-31-7; N^5-EtPPT-4α-OH, 82639-52-9; acetaldehyde, 75-07-0; formaldehyde, 50-00-0; *m*-hydroxybenzaldehyde, 100-83-4; cysteine, 52-90-4; dithiodiglycolic acid, 505-73-7; *N*-benzylnicotinamide, 2503-55-1; *N*-benzyl-1,4-dihydro-3-quinolinecarboxamide, 17260-79-6; nicotinamide adenine dinucleotide, 53-84-9; NaCNBH$_3$, 25895-60-7.

Kinetic Studies of Intramolecular Excimer Formation in Dipyrenylalkanes

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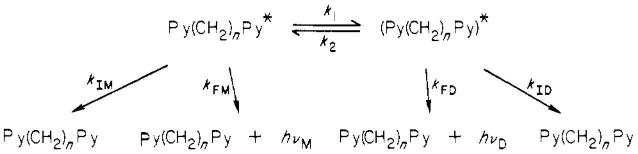
Abstract: The kinetics of excimer formation in 1,3-bis(1-pyrenyl)propane and 1,10-bis(1-pyrenyl)decane have been studied in a range of solvents. In neither case does the excimer formation rate show a marked dependence on solvent bulk viscosity. In the case of 1,3-bis(1-pyrenyl)propane the results indicate two initial conformation groups that on excitation form the excimer with different average rate constants.

Introduction

Dipyrenylalkanes are suitable for the investigation of intramolecular excimer formation. It is known that, in addition to a structured monomer fluorescence band with a maximum near 375 nm, the emission spectra of these compounds exhibit a broad, structureless band with maximum intensity in the vicinity of 480 nm, which is due to fluorescence from intramolecular excimers.[1] Two features of pyrene account for this intramolecular excimer formation and the consequent suitability of pyrene (Py) as a probe for studying the kinetics of conformational change in alkanes. First, the stabilization energy of pyrene excimers is large (0.34 eV in cyclohexane).[2] This means that if an excited and a ground-state pyrene achieve the appropriate configuration, then the excimer readily forms and there is little tendency for subsequent dissociation. Second, the long fluorescence lifetime of pyrene derivatives increases the chance of a suitable configuration being attained within the excited pyrene lifetime. Studies have been undertaken using steady-state measurements of fluorescence intensities in the series pyrene–(CH$_2$)$_n$–pyrene with n = 2–16 and 22 in methylcyclohexane.[1] While several investigations have made use of the relative intensities in the monomer and excimer regions,[3-5] fewer direct kinetic treatments have been reported.[6] Intramolecular excimer emission is strongest for dipyrenylpropane, which has been used as a fluorescent probe for micellar interiors. It has been clamined that the excimer formation rate decreases essentially linearly with increasing viscosity in highly viscous solvents.[4] However, doubts as to the validity of using dipyrenylpropane as a probe of microviscosity have been raised.[5]

Scheme I



The interaction between an excited and a ground-state pyrene chromophore linked by an alkane chain can be represented by the familar Scheme I,[7] where k_{IM} and k_{FM} are respectively the radiationless and radiative decay rates of the excited pyrene monomer and k_{1D} and k_{FD} are the corresponding rates for the excimer. Kinetic analysis of the photostationary situation yields for the ratio of the excimer and monomer emission intensities

$$\frac{I_{\mathrm{ex}}}{I_{\mathrm{mon}}} = \frac{k_1\tau_{\mathrm{D}}}{1 + k_2\tau_{\mathrm{D}}}\frac{k_{\mathrm{FD}}}{k_{\mathrm{FM}}}$$

where $\tau_{\mathrm{D}} = (k_{\mathrm{FD}} + k_{\mathrm{ID}})^{-1}$. For the steady excimer to monomer emission intensity ratio to be a measure of viscosity requires, in the most general case, that k_1, k_2, τ_{D}, k_{FD}, and k_{FM} all depend only on viscosity. It has already been shown that at least one of those constants does not comply with this condition.[5] Two simplifying assumptions can be envisaged for the above scheme. In the first, $k_2\tau_{\mathrm{D}} \ll 1$ and thus

$$I_{\mathrm{ex}}/I_{\mathrm{mon}} \simeq k_1\tau_{\mathrm{D}}k_{\mathrm{FD}}/k_{\mathrm{FM}}$$

In the second (excited-state equilibrium) $k_2\tau_{\mathrm{D}} \gg 1$ and

$$I_{\mathrm{ex}}/I_{\mathrm{mon}} \simeq (k_1/k_2)(k_{\mathrm{FD}}/k_{\mathrm{FM}})$$

Although it seems likely that the radiative rate ratio, $k_{\mathrm{FD}}/k_{\mathrm{FM}}$, would be approximately independent of solvent, it is much less certain that the remaining constants depend only viscosity. Rate constants for excimer formation and dissociation in methylcyclohexane have already been reported,[6] but the method has been criticized.[5] The effect of solvent has not been studied. In this work k_1, k_2, and τ_{D} are determined for the compounds with n = 3 and 10 in four low-viscosity solvents. The results indicate that in the n = 10 case neither of the foregoing limiting situations applies. In the n = 3 case, although the data point to k_2 being negligible, other complications arise.

While excimer formation between free molecules in solution is diffusion controlled, departures from this behavior might be expected in constrained systems where the chromophores are linked by short alkane chains. In a study of intramolecular excimer formation and dissociation, Johnson reported that for 1,3-bis(*N*-carbazolyl)propane, in a group of chemically and structurally

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(2) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, Ser. A.* **1963**, *275*, 575.

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different solvents, the rate constants did not directly correlate with the macroscopic solvent viscosity.[8] It was suggested that the microstructure of the solvent surrounding the solute was of greater significance in limiting the motion of the two interacting groups than the bulk solvent viscosity. This work aims to provide some insight into the importance of the nature of the chromophore as well as the length of the alkane chain during intramolecular excimer formation.

Experimental Section

1,10-Bis(1-pyrenyl)decane, 1,3-bis(1-pyrenyl)propane, 1-ethylpyrene, and 1-octylpyrene were supplied by Molecular Probes Inc. We are grateful to Dr. R. P. Haugland of Molecular Probes Inc. for preparing a pure sample of 1,10-bis(1-pyrenyl)decane using a Wittig synthesis. It was found that samples of this compound prepared by other techniques contained a short-lived fluorescent impurity, most likely a dipyrenyl ketone, which absorbed to the red of free pyrene and exhibited a broad emission with maximum near 425 nm.

Spectroscopic grade ethanol (Merck) and benzene (Ajax Chemicals) were used. Cyclohexane was purified by passing through a column packed with silica (BDH 60–120 mesh), and toluene was freshly distilled after removal of sulfur-containing impurities.[9] Solution concentrations were less than 10^{-5} M in pyrene to ensure the absence of intermolecular excimers. Dilution by a factor of 10 did not alter the measured parameters. All solutions were degassed to better than 5×10^{-3} torr by freeze–pump–thaw cycles.

Absorption spectra were measured on a Cary-17 spectrophotometer. Uncorrected emission and excitation spectra were recorded by using a Perkin-Elmer MPF 44A fluorimeter. The excitation spectra of all solutions, monitoring emission at 370 and 500 nm, were indistinguishable from those for monomer absorption. Fluorescence decay data were obtained by the time-correlated single-photon counting method using an Applied Photophysics nanosecond spectrometer, Model SP2X, with a nitrogen-filled spark lamp operating at 15 kHz. Samples were excited with vertically polarized light, and emission was observed at 90° to the excitation direction with a polarizer set at 54.7° to the vertical plane. The excitation wavelength was 325 nm, and separate decay curves of 50 000 peak counts were collected, with a 360-nm cutoff filter (Schott) combined with a 370-nm interference filter (Pomfret Research Optics) or a 515-nm cutoff filter (Schott) to isolate the monomer and excimer decay regions. Each measurement was done at least three times, and the goodness of fit of the data to a nonlinear least-square fitted curve was assessed by examination of the residuals between the experimental and computed curves. Fluorescence lifetimes were reproducible to within 5%. All measurements were made at 20 °C unless stated otherwise. Low temperatures were achieved by use of an Oxford Instruments DN704 cryostat.

Results and Discussion

The fluorescence intensity–time profiles of the excited monomer and excimer for the kinetic scheme outlined above are respectively of the form[10]

$$i_{\mathrm{M}}(t) = [k_{\mathrm{FM}}(\lambda_2 - X)/(\lambda_2 - \lambda_1)][\exp(-\lambda_1 t) + A \exp(-\lambda_2 t)]$$

and

$$i_{\mathrm{D}}(t) = [k_{\mathrm{FD}}k_1/(\lambda_2 - \lambda_1)][\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]$$

where

$$\lambda_{1,2} = \tfrac{1}{2}\{X + Y \mp [(Y - X)^2 + 4k_2k_1]^{1/2}\}$$

and

$$A = (X - \lambda_1)/(\lambda_2 - X)$$

$$X = k_{\mathrm{FM}} + k_{\mathrm{IM}} + k_1 \qquad Y = k_{\mathrm{FD}} + k_{\mathrm{ID}} + k_2$$

Analysis of the experimental decay curves collected in the monomer and excimer emission regions as a sum or difference of two exponentials, by use of a nonlinear least-squares convolution method, provided λ_1, λ_2, and A. In addition to measurement of $i_{\mathrm{M}}(t)$ and $i_{\mathrm{D}}(t)$, it is necessary to obtain a value of $k_{\mathrm{M}} = k_{\mathrm{FM}} + k_{\mathrm{IM}}$, the rate of monomer decay by means other than excimer formation, and then combination of the above equations enables k_1, k_2, and $k_{\mathrm{D}} = k_{\mathrm{FD}} + k_{\mathrm{ID}}$ to be determined.[10] It has been assumed that k_{M}, the total monomer decay rate in the absence of excimer formation, is the same in the dipyrenyl derivative as in the monopyrenyl derivative of approximately equal hydrocarbon chain length. Thus fluorescence lifetimes were obtained in each solvent for 1-ethylpyrene and 1-octylpyrene, as these compounds resemble the species of interest without the possibility of intramolecular excimer formation. An alternative procedure has been suggested that requires separate study of the reaction in the presence of two different quenchers over a range of quencher concentrations.[11] The implication is that neither quencher interferes with the process of excimer formation, and this may not always be true. Values of k_{M} used in our calculations are given in Table I, from which it is evident that, while the presence of a 1-alkyl substituent appreciably lowers the fluorescence lifetimes from those of free pyrene, the length of the alkane chain has only a small effect on k_{M}. Therefore the ethyl- and octyl-substituted models provide reasonable estimates for k_{M} in the molecules with propane and decane chains.

Table I. Fluorescence Lifetimes for Pyrene and Relevant Derivatives in Various Solvents

	τ_{f}, ns		
solvent	pyrene, 25 °C[12]	1-ethylpyrene	1-octylpyrene
toluene		176	173
benzene	311	167	158
cyclohexane	430	237	225
ethanol	373	217	210

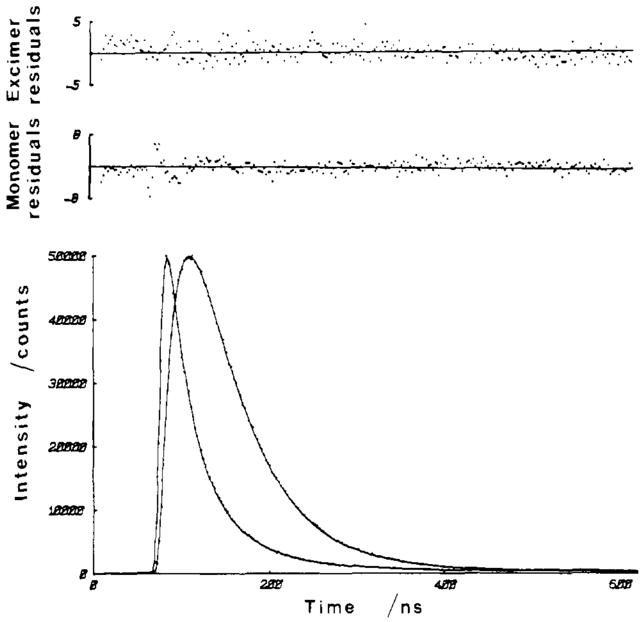

Figure 1. Typical intensity–time profiles and weighted residuals plots for monomer and excimer emissions of 1,10-bis(1-pyrenyl)decane in benzene: (···) experimental points convolved with lamp-response function (not shown); (—) fitted curve; (left curve) monomer $\lambda_1 = 4.4 \times 10^7$ s^{-1}, $\lambda_2 = 1.9 \times 10^7$ s^{-1}, $A = 0.6$; (right curve) excimer, $\lambda_1 = 4.6 \times 10^7$ s^{-1}, $\lambda_2 = 1.9 \times 10^7$ s^{-1}, preexponentials, $(-1.61 \pm 0.05) \times 10^5$, $(+1.70 \pm 0.05) \times 10^5$.

For 1,10-bis(1-pyrenyl)decane the experimental decays closely followed the expected form. The observed monomer and excimer fluorescence profiles were initially fitted to general double-exponential functions in which the preexponential factors and

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Table II. Photophysical Data and Kinetic Parameters for Excimer Formation in 1,10-Bis(1-pyrenyl)decane

solvent	η, cP	λ_{abs}^{max}, nm	λ_{em}^{max}, nm	$I_{ex}{}^a/I_{mon}$	$10^{-6} \times k_1$, s^{-1}	$10^{-6} \times k_2$, s^{-1}	$10^{-6} \times k_D$, s^{-1}
toluene	0.59	346	478	0.61	28	6	23
benzene	0.65	346	477	0.63	31	6	23
cyclohexane	1.0	344	472	1.3	54	8	22
ethanol	1.2	343	476	1.7	92	9	21

[a] Ratio of excimer to monomer fluorescence intensities determined at band maxima from uncorrected spectra.

lifetimes were independently variable. This led to the conclusion that, for the excimer fluorescence, the preexponential factors were of equal magnitude (within experimental accuracy) and of opposite sign, and the values of λ_1 and λ_2 were the same for the monomer and excimer. Figure 1 shows a pair of fitted experimental curves. (The lamp-response function is not shown.) The difference in temporal behavior of the monomer and excimer emissions can be seen. Hence the proposed kinetic scheme is verified, and rate parameters have been determined. These are presented in Table II together with steady-state absorption and emission characteristics. While k_D is almost constant in the solvents investigated, environmental influences are seen to be important during excimer formation and dissociation. The bulk solvent viscosity can only be of minor importance as k_1 is greatest in ethanol, the solvent of highest viscosity studied here.

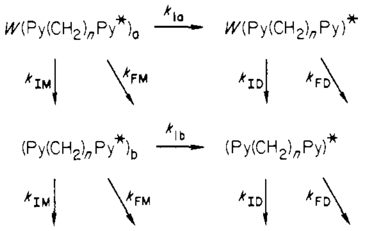
The chain linking the chromophores is capable of exerting several influences on excimer formation rates. Interaction of the chain with the solvent could alter its extension and flexibility. In a solvent such as ethanol, where alkane–solvent contacts would be unfavorable, it might be expected that the chain would be compact and the distance between pyrenes quite small. On the other hand, in a hydrocarbon solvent the chain might be extended, thus enabling a greater average separation of the chromophores. However, as well as influencing the distance between pyrene molecules, solvent influences on the chain flexibility may also be of importance in hindering motion and restricting the alignments achievable by these groups.

It is also likely that interactions between the pyrenes will be significant as the alkane chain is small in comparison to the end groups. Free pyrene in polar solvents has a tendency to aggregate,[13] and while no spectroscopic evidence of ground-state aggregation was obtained for these solutions, it is likely that in ethanol the pyrenes remain, on averge, quite close together to minimize solvent contacts. The ten-unit chain provides sufficient freedom for a range of separations to be possible and an optimum condition could be achieved. On excitation only a small motion would then be required in order to attain the excimer configuration that would rapidly form. In aromatic solvents, in which the end groups are highly soluble, the chromophores initially would be as widely separated as the connecting chain allowed. The rate of excimer formation then would be more strongly influenced by the motion of the chain in solution. Theoretical studies on a model system of a single nine-unit polymer show, by comparison with a chain in the absence of solvent, the importance of including the effect of solvent during calculation of end-to-end autocorrelation functions.[14] Thus even for such short chains a range of behavior might be expected in differing solvents.

The rates of dissociation of the excimer are also of interest. If k_2 were negligible then $i_M(t)$ would become a single exponential. Attempts to fit these data to a single-exponential function led to significant deviations from a random distribution of the residuals between the calculated and experimental curves. As the excimer energies are similar in each solvent, the difference in dissociation rate results from the effect of solvent on the chain linking the chromophores, and although excimer formation is most efficient in ethanol, it is also in this solvent that the excimer dissociates most rapidly.

As a contrasting case, 1,3-bis(1-pyrenyl)propane was studied.

Scheme II



In this case the linking chain is sufficiently small that solvent effects on the chain should be less important. It was found that the time profiles of emission intensities would not fit the earlier equations. While $i_M(t)$ could be analyzed as a sum of two exponentials, $i_D(t)$ did not take the form of a difference between two exponentials. If constrained to this form, the values obtained for $\lambda_{1,2}$ were different from those for the monomer decay. However, by fitting $i_D(t)$ to a triple-exponential function,

$$i_D(t) = A_1 \exp(-\lambda_1't) + A_2 \exp(-\lambda_2't) + A_3 \exp(-\lambda_3't)$$

it was found that λ_1' and λ_2' were the same as those extracted from $i_M(t)$ and the sum of A_2 and A_3 equalled $-A_1$, within experimental error.

It has been stated earlier[1] that the excimer formed between pyrenes with three linking carbons is highly stable, and this is compatible with the lower energy of the excimer band of this compound relative to that in dipyrenyldecane. In a related study of intramolecular excimer formation in bis((1-pyrenylmethoxy)carbonyl)alkanes,[15] it was found that the excimer emission maxima for the compounds with one to four linking CH_2 groups were blue-shifted with respect to the intermolecular excimer emission maximum of a model compound. This was interpreted in terms of a strained excimer configuration. Considering also the fewer degrees of freedom for rotation of the propane chain, this suggests that excimers formed in 1,3-bis(1-pyrenyl)propane would resist dissociation. This is in accord with the work of Zachariasse,[6] who claimed a low rate of dissociation for this compound in methylcyclohexane. Assuming a nondissociative excimer, a kinetic scheme consistent with the observations is provided by a system that has two distinct groups of ground-state conformer. This system is then described in Scheme II, where W is the weighting factor representing the ratio of conformers of type a to type b present in solution. The effective rate constants k_{1a} and k_{1b} result from the effect of all the motions required to bring the excited monomer species into the excimer configuration. With the assumption that k_{IM} and k_{FM} are equal for each initial species it follows that

$$i_M(t) = k_{FM}[W \exp(-\lambda_1't) + \exp(-\lambda_2't)]$$

and

$$i_D(t) = W\frac{k_{FD}k_{1a}}{\lambda_3' - \lambda_1'}[\exp(-\lambda_1't)] + \frac{k_{FD}k_{1b}}{\lambda_3' - \lambda_2'}[\exp(-\lambda_2't)] - \left(W\frac{k_{FD}k_{1a}}{\lambda_3' - \lambda_1'} + \frac{k_{FD}k_{1b}}{\lambda_3' - \lambda_2'}\right)\exp(-\lambda_3't)$$

where $\lambda_1' = k_{1a} + k_M$, $\lambda_2' = k_{1b} + k_M$, and $\lambda_3' = k_D$.

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The literature contains several reports that show that the kinetic scheme appropriate to intermolecular excimer formation may not be applicable to intramolecular complexes.[16] Johnson presented a kinetic scheme that allowed for the existence of two intrachain excimer states in poly(*N*-vinylcarbazole),[17] and this concept has since received further support.[18] This model is one simplification of a general kinetic treatment for a system of three excited species capable of interconverting, fluorescing, or undergoing radiationless relaxations during their excited lifetimes.[19] The importance of distinguishing different types of rotational conformers for the excited monomer state was recognized by Goldenberg et al. during a study of intramolecular excimers.[20] Conformers from which a single hindered rotation can lead to excimer formation were distinguished from others that must undergo a more complex rearrangement before the excimer alignment can be achieved. Similar ideas have been advanced by Todesco et al.[21] The kinetics of 1,3-dicarbazolylpropane have been reinterpreted in terms of such a scheme, where the long-lived excited monomer conformations convert to the confirmation group from which excimer formation is rapid.[19] More generally, van der Auweraer et al. have pointed out three alternative schemes that, under stated assumptions, lead to triple-exponential exciplex emission and could be considered when multiexponential decays are observed.[22] In addition to the aforementioned process whereby the "slow" excimer-forming conformations pass through an intermediate state before the exciplex can result, another model was proposed with two different sets of starting conformation that form the exciplex at different rates. In this case, interconversion between the starting configurations was much slower than all other processes. The kinetics of ω-phenyl-α-(dimethylamino)alkanes with 2, 3, or 4 methylene groups were interpreted in terms of this scheme, while in the molecule with 11 groups separating the amine and phenyl substituents, the effect of initial conformational differences disappeared.[23] The exponents obtained from the time evolution of the emissions are the same for each of these models, and when the fast and slow rates of excimer formation are very different, the preexponential factors differ only slightly. Therefore, a choice between these two schemes may be difficult to make. The important point is that deviation (of whatever type) from the conventional scheme for excimer formation may not be observed by steady-state measurements.[22] Kinetics measurements are then essential for the correct identification of either scheme.

A further model involving an equilibrium between the excited monomer and a nonfluorescent intermediate on the pathway to the exciplex has also been proposed.[22] However, for this model the present values of the exponents are only compatible with two growth terms and a single decay, which is contrary to our observations.

Although the concept of two conformation groups will satisfactorily explain our observations and the literature cited gives support to the idea, it should be noted that for irreversible excimer formation, as above, nonexponential decay of the monomer could possibly be explained on a different basis. Conversion of the various possible conformations to the excimer configuration, and to each other, is described by a series of coupled differential equations. Analysis of such a system predicts a number of discrete relaxation times. In the case of a large number of interconverting conformers, the spectrum of relaxation times is such that the experimentally observed monomer decay function is expected to approximate to a single exponential. However, in the case of a molecule with a small number of degrees of freedom, a distribution of relaxation times such that the monomer decay can be approximated by a double-exponential function becomes a possibility.[24] To investigate this possibility would require extensive calculation involving consideration of the molecular potential-energy surface as a function of torsional angles and the rate of diffusional passage from one conformation to another. This is beyond the scope of the present paper. Moreover, other data to be presented are compatible with the idea of two conformation groups.

The fluorescence intensity–time profile for the dipyrenylpropane excimer was fitted to a general triple-exponential function with variable exponents and preexponential factors. In each case $\lambda_1' > \lambda_3' > \lambda_2'$, which results in the first term in $i_D(t)$ being negative and the other two terms being positive. Rate parameters were obtained using W, λ_1', and λ_2' from the monomer decay and λ_3' from the excimer curve. The equations are $k_{1a} = \lambda_1' - k_M$, $k_{1b} = \lambda_2' - k_M$, and $\lambda_3' = k_D$. It must be emphasized that a reasonable fit to the excimer fluorescence data is only possible by allowing more than two exponential terms. Although the reliability of numbers extracted by this method is limited by the quality of the data, the triple-exponential fit does provide useful confirmation of the values of λ_1' and λ_2'. However, the parameters of most concern are k_{1a} and k_{1b}, and these are obtained from the double-exponential fit for the monomer. Attempts to fit $i_M(t)$ to a triple-exponential function were unsuccessful and yielded two identical values. This supports the assumption that dissociation of the excimer does not occur within its lifetime.

Results of this analysis are given in Table III. In each solvent most of the excimers are rapidly formed, and an 8% contribution is provided by excimers from a less flexible ground-state configuration. Hence the predominant ensemble of structures must have pyrenes separated in such a way that only a comparitively simple movement of the chromophores is required in order to form the sandwiched excimer. A second type of conformation encounters a high resistance to excimer formation as greater rearrangement about C–C bonds is necessary before the configuration can be achieved where all hydrogens are pointing away from the overlapping pyrenes as is required for the excimer. We note a considerable difference between our results and those reported for this compound in the similar solvent methylcyclohexane.[6] Zachariasse et al. obtained λ_1 and λ_2 and treated their results in terms of k_1 and k_2 without observation of a second ground-state conformer group. They also found that the monomer decay showed negligible deviation from a single-exponential decay with a short lifetime. This is consistent with their very high excimer to monomer ratio[3] compared to that obtained both here and by Henderson et al.[5] Although a free monomer contaminant could be responsible for the appearance of a long-lived component in the monomer decay, this should be eliminated from the excimer data by the chosen filters. If the longest lived component ($1/\lambda_2'$) in both the monomer and excimer curves was due to an impurity emitting in both the monomer and excimer regions, then this would mean that the excimer growth and decay was conventional and A_1 should be equal to $-A_3$. The values of k_D obtained for dipyrenylpropane are somewhat lower than those for dipyrenyldecane. In view of the comments made earlier about the likely difference in excimer binding in the two cases, some difference is not surprising.

Support for the present model can be gained by undertaking experiments at low temperatures, at which the equilibrium between the conformations will shift. The slow ensemble which accounts for only a small proportion of the molecules at room temperature is apparently less stable and will thus decline in importance as the temperature is lowered. In that event, the kinetics should simplify to give a single-exponential decay for $i_M(t)$ provided dissociation of the excimer is still noncompetitive. Although the excimer emission at low temperatures is too weak to enable accurate measurement of $i_D(t)$, it was found that $i_M(t)$ did become

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Table III. Photophysical Data and Kinetic Parameters for Excimer Formation in 1,3-Bis(1-pyrenyl)propane

solvent	η, cP	λ_{abs}^{max}, nm	λ_{em}^{max}, nm	I_{ex}^{a}/I_{mon}	W	$10^{-6} \times k_{1a}$, s^{-1}	$10^{-6} \times k_{1b}$, s^{-1}	$10^{-6} \times k_D$, s^{-1}
toluene	0.59	348	492	1.1	12	102	3	17
benzene	0.65	348	488	1.2	13	112	2	17
cyclohexane	1.0	346	487	1.7	13	119	3	15
ethanol	1.2	344	487	1.4	13	120	2	14

[a] Ratio of excimer to monomer fluorescence intensities determined at band maxima from uncorrected spectra.

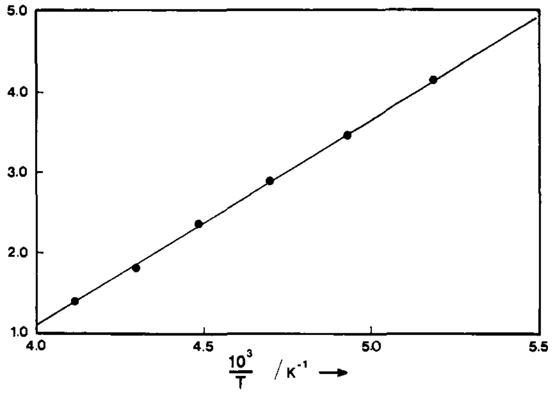

Figure 2. Arrhenius plot for the rate constant of excimer formation for 1,3-bis(1-pyrenyl)propane in the temperature range 193–243 K.

single-exponential below 243 K, for dipyrenylpropane in toluene. This solvent was selected for its low freezing point and high solubility of the probe molecule. Steady-state emission intensities were also measured in the temperature range where $i_M(t)$ is single exponential. The excimer to monomer emission intensity ratio is then related to the rate constants by $I_{ex}/I_{mon} = (k_{FD}/k_{FM})k_1\tau_D$, and it was found that a plot of ln (I_{mon}/I_{ex}) vs. $1/T$ was linear (Figure 2). The single-exponential character of the monomer emission confirms that excimer dissociation can be ignored, and with the assumption that k_D is temperature independent over the small temperature range covered, it follows that the slope of this graph yields the activation energy for k_1. The value of 21 kJ mol^{-1} determined for this system is significantly higher than that required for rotational motion about carbon–carbon bonds in alkanes[25] and probably contains contributions from solvent displacement effects.

None of the rate parameters for 1,3-bis(1-pyrenyl)propane are a strong function of solvent properties in the range studied. The absence of an influence of solvent viscosity in the low-viscosity region is in contrast to an earlier reported decrease of k_1 with increasing η,[4] and indeed, with use of the earlier calibration curve[3] and our steady-state result the viscosity of ethanol would be determined as 50 cP.

It is interesting to compare the present results with those obtained by Johnson in a study of excimer formation in 1,3-bis(*N*-carbazolyl)propane.[8] As in this work Johnson reported no dependence on bulk viscosity for chemically and structurally different solvents. Among related solvents the excimer formation and dissociation constants decreased with increasing viscosity with the effect being more dramatic in some solvent groups than others. Johnson rationalized these results in terms of the free volume available for intramolecular rearrangement. A poorer solvent, which packs more loosely round the solute, should give a greater free volume and a less marked dependence on viscosity is then expected. There are difficulties with this interpretation as can be seen by an examination of Johnson's results. Better solvents should give closer solvent packing and less free volume, and this in turn leads to a greater viscosity dependence of the rate constants. At the same time better solvents would be expected to lead to smaller rate constants as there would be greater tendency for the interacting chromophores to drag with them solvent molecules. Johnson cites the reduction of the excimer formation and dissociation constants in the "good" solvents acetone and the acetates as an example. However, the data for the alkanes and alcohols do not entirely fit this picture. The viscosity dependence is more marked in alcohols, suggesting, as expected, a lower free volume and tighter packing of the solvent in comparison to the alkanes. However, the rate constant for excimer formation is actually greater in alcohols compared to alkanes, although the reverse is the case for the dissociation constant. Thus no single explanation seems able to explain the extent of the viscosity dependence of the rate constants and at the same time their absolute values.

There will be little tendency for solvation of the end groups in the bis(1-pyrenyl)alkanes, and any association between the solvent and pyrene end groups would be expected to be similar in both the propane and decane compounds. Thus it seems more likely that any difference between the two compounds will arise from differing solvent influences on the rigidity of the connecting hydrocarbon chain. In the case of the dipyrenylpropane it is possible that the initial configurations corresponding to rapid excimer formation prevent solvent access to the hydrocarbon chain to some extent. However, the slower excimer formation rate might be expected to be just as sensitive to bulk solvent viscosity as is the excimer formation rate in the decane. In fact only the excimer formation rate in dipyrenyldecane shows a strong dependence on the solvent. Thus it appears that the different behavior of the two compounds is due to different degrees of solvent–hydrocarbon chain interaction associated with the different chain lengths connecting the chromophores.

This work has shown that the rate parameters for excimer formation or dissociation do not depend solely on the bulk solvent viscosity for either 1,3-bis(1-pyrenyl)propane or 1,10-bis(1-pyrenyl)decane in low-viscosity solvents. While the kinetics of the former compound are virtually independent of the solvent, environmental influences are important in the species linked by ten methylene units as both the solvation properties of the chain and the end groups can affect the rates.

Acknowledgment. We thank Dr. R. J. Robbins for helpful discussions on this problem. Support from the Australian Research Grants Scheme is gratefully acknowledged.

Registry No. 1,3-Bis(1-pyrenyl)propane, 61549-24-4; 1,10-bis(1-pyrenyl)decane, 61549-31-3.

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