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Intramolecular Excimer Formation in Bichromophoric Molecules Linked by a Short Flexible Chain

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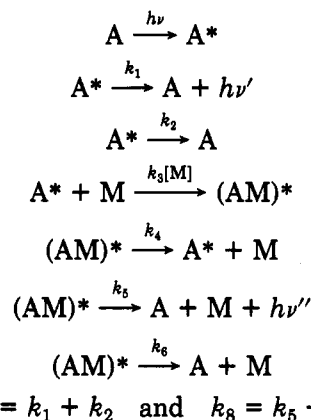
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Since the first report of the pyrene excimer by Förster,¹ intermolecular excited-state interactions have become a key subject in photochemistry and photophysics. If the two chromophores are identical, the stabilizing interaction between a molecule in the ground state and a molecule in the excited state can be described by the configuration interaction model.² An alternative way to estimate the stabilization energy takes into account properties such as electrostatic interactions, exciton resonance, intermolecular repulsion, charge-transfer interactions, dispersion forces, and overlap repulsions.³ If the two chromophores are different, an exciplex or an heteroexcimer can be formed.⁴ The stabilization of an excimer depends strongly on the overlap between the two chromophores. Calculations suggest a picture of the excited-state complex in which the two chromophores, if they are planar, are at an optimum distance of 3.5 Å in a planparallel orientation.

Intermolecular excited-state complex formation can be described by the kinetic Scheme I.⁵ In this scheme A* represents the locally excited state (LE) and (AM)* is the excited-state complex (E); in the case of an excimer M and A are identical. The fluorescence spec-

trum consists of the emission of LE, $h\nu'$, at higher energies and of the complex E, which emits at lower energies, $h\nu''$.⁶

Scheme I



At sufficiently low temperatures where $k_4 \ll k_8$ the decay of the fluorescence of the locally excited state is

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Frans C. De Schryver was born in Belgium in 1939. He received his doctoral degree in chemistry from the University of Leuven under the direction of Prof. G. Smets. After postdoctoral studies with C. S. "Speed" Marvel, T. Förster, and A. Weller he became professor at the University of Leuven. His research interests are in the area of photochemistry and photophysics of polymers, electron transfer, and complex formation in bichromophoric molecules, colloids, and other ordered systems.

Mark Van der Auweraer is a research scientist of the Belgian National Science Foundation and a permanent member of the research group in Leuven. His interests are centered around excited-state properties of donor-acceptor systems and photoelectrochemistry in monolayers.

Pol Collart, Jan Vandendriessche, Rudy Goedeweeck, and AnneMie Swinnen are co-workers whose stimulating enthusiasm has strongly contributed to the development of the ideas presented in this Account.

monoexponential while that of the complex can be described by a difference of two exponentials. When k_4 is of the same order of magnitude as k_8 , the decay of the fluorescence of the locally excited state can be described as a sum of two exponentials and the decay of the complex can be described as a difference of two exponentials. The ratio of the preexponential terms in the excimer region should be equal to -1 .⁷ An analysis of the decay functions according to Scheme I permits the determination of all relevant rate constants.⁸

In this Account we will discuss two important aspects of excimer formation when two chromophores are linked in one molecule by a short flexible chain.

Local vs. Overall Concentration

The first obvious consequence of the chromophores being linked is the greatly enhanced local concentration of the chromophores which are no longer randomly distributed, and this permits the observation of an excited-state complex at very low (10^{-5} M) overall concentration. The first report of such an intramolecular excimer was made by Yanari⁹ in a study of the fluorescence spectrum of polystyrene in 1963. Almost at the same time Hirayama¹⁰ showed that in a series of di- and triphenylalkanes only those with two phenyl groups separated by three aliphatic carbon atoms led to excimer emission. This and the observation of intramolecular excimer formation in other 1,3-diarylalkanes such as 1,3-dicarbazolypropane¹¹ led to the introduction of the so-called $n = 3$ rule (never intended by Hirayama), which states that two chromophores linked by a chain need to be separated by three methylene groups to be able to reach a planparallel sandwich geometry of the excimer and a gauche⁺ gauche⁻ (g^+g^-) conformation of the chain. It has since been demonstrated that both shorter¹² and longer¹³ chains permit excimer formation. Our claim¹⁴ that "intramolecular excimer formation is limited by the probability to reach within the lifetime of the excited state a conformation suitable for complex formation and by the stabilization of the complex" is particularly well demonstrated by the elegant work of Winnik^{15b} and Cuniberti^{15a} on macromolecular chains end-capped by 1-pyrenyl groups and of Zachariasse^{13b} on α,ω -1-dipyrenylalkanes.

Intramolecular excimers have been observed in a large number of homo- and copolymers containing phenyl, naphthyl, carbazoyl, anthryl, or pyrenyl groups. This body of information has been recently reviewed by

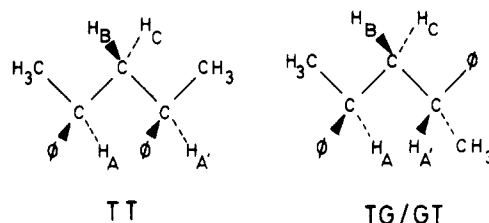


Figure 1. Conformations of importance in *meso*-2,4-diaryl-pentanes 1_{xy} .

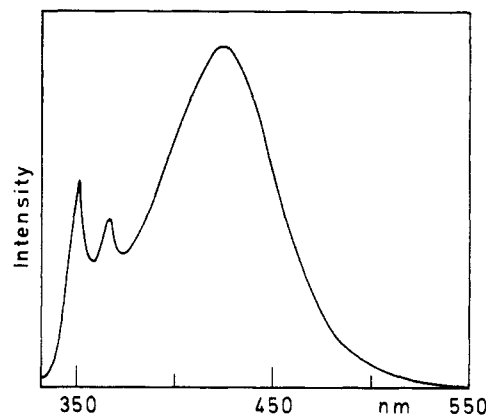
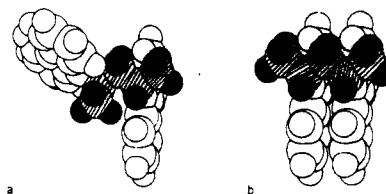


Figure 2. Fluorescence spectrum of 1_{a} in dibutyl ether at room temperature showing emission of the locally excited state at 350 nm and of the excimer at 420 nm. Space-filling models (a) of the ground state or locally excited state (TG) and (b) excimer (TT) are inserted.

Frank and Phillips.¹⁶ In most of the studies reported until the late 1970s information was gathered by using intensity ratios, corrected or uncorrected, of the fluorescence spectrum, and with the exception of one contribution (vide infra) little or no attention was given to conformational aspects in the analysis. However, in studying the temperature-dependent kinetics of intramolecular complex formation in α -(*N,N*-dimethylamino)- ω -phenylalkanes, we became aware that at least in systems where the chromophores were linked by short flexible chains concentration effects alone could not account for the observed behavior.¹⁷ At the same time deviations of Scheme I were observed for polymers¹⁸ and for 1,3-di-1-pyrenylpropane.¹⁹ This led us to evaluate in more detail configurational and conformational aspects of bichromophoric compounds.

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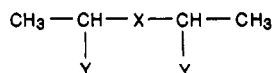
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Configurational and Conformational Aspects

In 1965 Bovey and Longworth,²⁰ in a study of 2,4-diphenylpentanes as model units of polystyrene, observed a substantial difference in the fluorescence spectrum of the meso and the racemic diastereoisomers. They also applied ¹H NMR to obtain information concerning the conformational distribution within each diastereoisomer.²¹ This conformational distribution was also studied for 2,4-diphenylpentanes by infrared,²² ultrasonic relaxation,²³ and theoretical calculations.²⁴ These studies indicate that at room temperature the TG conformation and to a very small extent the TT conformation contribute to the ground state of the meso isomer (Figure 1) while for the racemic isomer the TT and the GG conformations are the main contributors (vide infra). The symbol T indicates a methyl group between the two hydrogens of the methylene group, the symbol G indicates an aryl group between the two methylene hydrogens, and \bar{G} indicates a proton between two methylene hydrogens. The importance of this observation and the consequences on the kinetic aspects of intramolecular excimer formation in bichromophoric molecules and in multichromophoric compounds such as poly(vinylaromatics) were only realized when a systematic study of molecules of the general structure 1 was undertaken. As an example, the emission spectrum of **1_ca** is given in Figure 2.

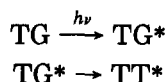


$1_x y$ if meso and $1_x y'$ if racemic
 X = O or CH₂ (indicated by subscript o or c)
 Y = *N*-carbazoyl = a
 Y = phenyl = b
 Y = 2-pyrenyl = c
 Y = 9-anthryl = d
 Y = 1-pyrenyl = e
 Y = 1-naphthyl = f
 Y = 2-naphthyl = g

The Meso Diastereoisomer

Analysis of the fluorescence decay of **1_ca**,²⁵ **1_cb**,²⁶ and **1_cc**²⁷ led to the conclusion that in solvents of low viscosity the excited-state complex formation could be described by a monomolecular equivalent of Scheme I (Scheme II). Analysis at different wavelengths within

Scheme II



the excimer band further indicated that the decay parameters as well as their contribution did not vary. This clearly supports the formation of only one excimer.

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Table I.
Kinetic and Thermodynamic Parameters of Excimer Formation of **1_ca-c** in Isooctane

parameter	1_ca	1_cb	1_cc
fwhm, ^a cm ⁻¹	3400	3900	3800
emission max, ^a nm	420	330	485
E_a , kJ mol ⁻¹	16	10	17
k_3 , ^b 10 ¹⁰ s ⁻¹	310	10	60
k_8 ⁻¹ (20 °C), ns	37	22	145
ΔH° , kJ mol ⁻¹	-20 ± 3		-16
ΔS , J K ⁻¹ mol ⁻¹	-17 ± 5		-42

^a Excimer emission, fwhm = full width at medium height.

^b Preexponential term.

On the basis of ¹H NMR analysis of the vicinal coupling constants of the methylene protons, it could be shown that in the temperature region between -70 and +30 °C these compounds are mainly (>95%) in the TG conformation and the excimer-forming step is one chain rotation around one bond to form the TT conformation in which the two chromophores overlap extensively in a planparallel fashion, as can be seen in Figure 2 for **1_ca**. Important parameters of the photophysics of **1_ca-c** as far as available are assembled in Table I.

Substitution of the central methylene group by an oxygen no longer permits the use of the above-mentioned NMR method to obtain information on the conformational distribution for the meso diastereoisomer. The analysis of the luminescence behavior of **1_cc**²⁷ reveals a single-exponential decay at -70 °C in isooctane when analyzed in the locally excited state, an activation energy for excimer formation of 17.6 kJ mol⁻¹ in isooctane, and the presence of only one excimer with a k_8 ⁻¹ of 85 ns and a fwhm of 3800 cm⁻¹. These data suggest for **1_cc** a TG ground-state conformation. It should be pointed out that Becker,²⁸ using absorption spectroscopy and the observation of differences in the chemical shift of the aryl protons of the anthryl group in **1_d**, concluded that in the ground state this compound has a TT rather than a TG conformation.

These results permit the conclusion that intramolecular excimer formation in a bichromophoric molecule linked by three sp³ carbons or in the ether analogue can be analyzed by Scheme II if there is a well-defined single conformation of the chain, if the bond linking the chromophores to the chain is a C₂ axis of the chromophore, and if there are no interactions in the ground state.

The next question then is What complication can arise if in a meso-2,4-diarylpentane or ether analogue the chromophore is not substituted symmetrically? This is the case in compounds **1_xe-g**. NMR analysis of **1_e** indicated that the meso isomer in alkane solvents at room temperature has mainly (>95%) a TG chain conformation while at lower temperatures only the TG conformation is present. The time profile of the fluorescence at -50 °C cannot be analyzed as a single exponential, but good fits are obtained upon analysis of the locally excited state as a sum of two exponentials. Spectral information clearly indicates that at this temperature no back-dissociation of the complex occurs.²⁹ A substantial shift of the excimer emission maximum, a broadening of the full width at medium height of the

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Table II.
Excited-State Properties of $1_c e$ and $1_o e$ in Isooctane

parameter	$1_c e$	$1_o e$
$\lambda_{\max}(298 \text{ K}),^a$ nm	480	472
$\lambda_{\max}(183 \text{ K}),^a$ nm	500	492
fwhm(298 K), ^a cm^{-1}	4300	4800
fwhm(183 K), ^a cm^{-1}	3800	4400
$\alpha_1/\alpha_2(450 \text{ nm})^b$	1.44	1.5
$\alpha_1/\alpha_2(520 \text{ nm})^b$	8.5	15
$\beta_1^{-1}(450 \text{ nm}),^c$ ns	80	160
$\beta_2^{-1}(450 \text{ nm}),^c$ ns	47	80
$\beta_1^{-1}(520 \text{ nm}),^c$ ns	80	161
$\beta_2^{-1}(50 \text{ nm}),^c$ ns	47	80
$k_{3,fo},^d$ 10^{10} s^{-1}	150	330
$E_{3,fo},^e$ kJ mol^{-1}	21	19
$k_{3,po},^f$ 10^{10} s^{-1}	2	7
$E_{3,po},^g$ kJ mol^{-1}	12	8

^a Of the excimer emission. ^b Ratio of the preexponential terms of the two-exponential decay function describing the time profile of the excimer emission measured at 298 K in isooctane. ^c $\beta_{1,2}$ exponential terms of the decay function. Since the amount of back-dissociation at this temperature is very small, they can be set equal to k_8^{-1} . ^d Preexponential term of the rate constant for formation of the long-lived excimer. ^e Activation energy of the rate constant for formation of the long-lived excimer. ^f Preexponential term of the rate constant for formation of the short-lived excimer. ^g Activation energy of the rate constant for formation of the short-lived excimer.

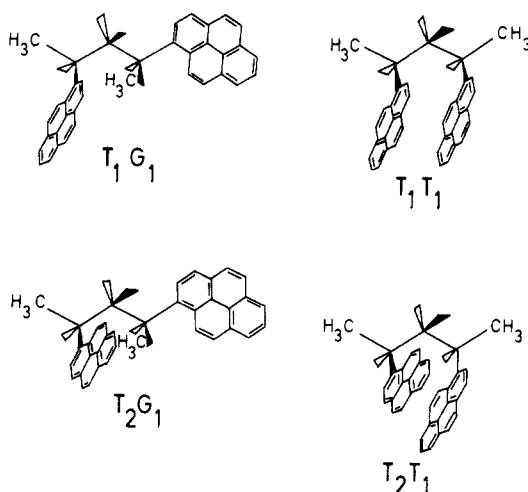


Figure 3. Representations of the different rotamers of $1_c e$ leading to excimers with different overlap.

excimer emission, and the analysis of the fluorescence decay across the excimer band clearly established the presence of two excimers. Analogous results were obtained for $1_o e$ (Table II).

The formation of two excimers starting from one chain conformation was related to the presence of different rotamers of the nonsymmetrically substituted 1-pyrenyl group in the TG conformation (Figure 3). The longer lived excimer is formed from the $T_1 G_1$ conformer and has a k_8^{-1} value at room temperature which is close to the one observed for *meso*- $1_c c$ and *meso*- $1_o c$ and emits at longer wavelengths. At low temperature it is the main contributor to the excimer emission. Transient picosecond absorption spectroscopy³⁰ of $1_c c$ and $1_o e$ substantiates this interpretation. Since a TT conformation of $1_o c$ results in a full overlap of the two pyrene groups, a similar spatial arrangement can be suggested for this long-lived excimer. The se-

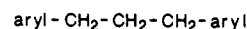
ond excimer formed from other rotamer(s) will have only partial overlap of the two chromophores. An unequivocal assignment of the decay parameters to the different rotamers forming the two different excimers could be made by the analysis of the decay of the locally excited state and the excimer decay at 205 K where the long-lived excimer is the sole contributor, and the locally excited state can be correlated with the growing in of this excimer. This suggests that the rate of rotation of the chromophores should be smaller than the rate of excimer formation. Broadening of the ^1H NMR signal of the pyrene group at 185 K indicates slow rotation of this group on the NMR time scale and, hence, certainly on the time scale of the photophysical experiment. The difference in activation energies and preexponential terms can be understood by inspection of the rotational motion from TG to TT.

The partially overlapping excimer has a lower activation energy of formation due to the fact that a stabilizing interaction due to exciton resonance between the two pyrene groups starts earlier along the reaction coordinate, decreasing the activation barrier. The activation energy for formation of the full overlap excimer in the nonsymmetrically substituted compounds $1_c e$ and $1_o e$ is comparable within experimental error to the activation energies observed for $1_c c$ and $1_o c$, respectively. Similar observations concerning the formation of more than one excimer in the *meso* diastereoisomer were first made for $1_o f$ and $1_o g$.^{18b,31} Theoretical calculations for *meso*- $1_o g$ ³² indicate three ground-state energy minima, two of which are due to a TG conformer with different rotameric orientation of the naphthyl group and a third one due to a TT conformer with partial overlap of the naphthalene rings. A conformational study of *meso*- $1_o g$ ³³ did not consider these different rotamers and analyzed the fluorescence decay of this compound³⁴ within the framework of only one excimer, for which an activation energy of formation of 20 kJ mol^{-1} was observed.

These results indicate that the complexity of the fluorescence decay of bichromophoric compounds with nonsymmetrically substituted chromophores even if only chain conformation is present is due to the possibility that more than one excimer may form in these systems.

1,3-Diarylpropanes

The next question to be dealt with is, What are the consequences if the chromophores are linked by a short chain for which more than one ground-state chain conformation contributes substantially? This aspect can be considered by a study of 1,3-diarylpropanes (structure 2) and of the racemic diastereoisomers of structure 1.



2

aryl: a, carbazolyl; b, phenyl; c, 2-pyrenyl; d, 9-anthryl;
e, 1-pyrenyl; f, 1-naphthyl; g, 2-naphthyl; h, 4-biphenyl

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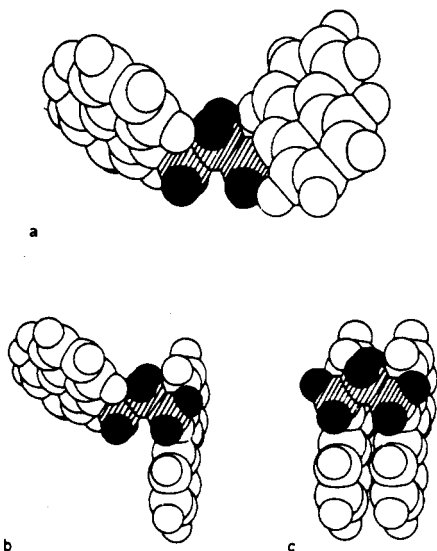


Figure 4. Ground-state conformations of 2a: (a) tt conformation, (b) tg conformation, (c) g^+g^+ or g^+g^- conformation.

Intramolecular excimer formation of 2a was first reported by Klöpffer¹¹ and Johnson.³⁵ A recent analysis of this compound^{25b} with picosecond pulse excitation and single-photon detection showed that the decay of 2a in the excimer region can be described as a difference of two exponentials and that the ratio of the preexponential terms is equal to -1 . Only one excimer is formed, and its properties, such as the emission spectrum, the excimer decay, and the picosecond transient absorption spectrum,³⁶ can be compared with those of the excimer formed in 1_ca. The fluorescence of the locally excited state can be analyzed as single exponential at temperatures below -60°C and as a sum of two exponentials above this temperature. The values of the two-exponential terms correspond to those observed in the excimer region. At first sight one could conclude that the system is identical with 1_ca. However, a 1,3-disubstituted propane can adopt a tt or a tg^\pm chain conformation. For *n*-pentane the tg^\pm conformation is about 3 kJ mol^{-1} higher in energy than the tt conformer and separated by a barrier of 10 kJ mol^{-1} . Calculations have shown^{24b} that the energy barrier for rotation from tt to g^+g^- is very high, suggesting that excimer formation can be formulated according to Scheme III. If the equilibrium between the conformers is slow, this should result in a more complex decay than the one observed. This thus indicates that the rate constants for rotation gauche to trans, k_{gt} , and trans to gauche, k_{tg} , are much larger than the rate constant for excimer formation k_a . The observed rate constant k_{obsd} equals $f_{tg^\pm}k_a$, where f_{tg^\pm} represents the fraction of molecules in the tg^\pm conformation. The observed activation energy, E_{obsd} , relates to the real activation energy of excimer formation, E_a , as

$$E_{\text{obsd}} = E_a + \frac{\Delta H^\circ_M}{1 + K_M} \quad (1)$$

where ΔH°_M is the enthalpic difference and K_M the equilibrium constant of the preequilibrium in Scheme III at temperature T . Scheme III is illustrated by the

Table III.
Kinetic and Thermodynamic Data of Structures 2a, 2c, and 2h

parameter	2a ^a	2c ^b	2h ^c
fwmh, cm^{-1}	3400	3980	4500
emission max, ^d nm	420	486	377.5
E_0 , kJ mol^{-1}	17	20.8	18.4
k_0' , ^e 10^{10} s^{-1}	23	52	11
k_8^{-1} , ^f ns	33.5	140.5	28.5
ΔH° , kJ mol^{-1}	-18.5	-20	-25
ΔS° , $\text{J K}^{-1}\text{ mol}^{-1}$	-45	-31	-65

^a In isoctane.^{25b} ^b In methylcyclohexane.³⁷ ^c Reference 38.
^d Excimer emission. ^e Preeponential term of the observed activation energy of excimer formation. ^f At room temperature.

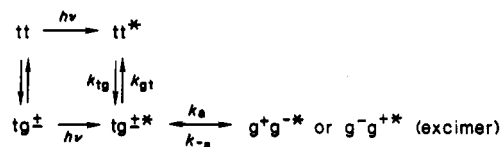
Table IV.
Kinetics and Thermodynamic Parameters of 2e in Heptane³⁷

parameter	excimer 1	excimer 2
k_3' , 10^{10} s^{-1}	1	60
E_3 , kJ mol^{-1}	12	22
k_8^{-1} , ^a ns	154	76
ΔH° , kJ mol^{-1}	-20	-20
ΔS° , ^b $\text{J K}^{-1}\text{ mol}^{-1}$	-28	-51

^a At 334 K. ^b As calculated from ref 42, Table 2.

space-filling models of 2a represented in Figure 4. The relevant data are assembled in Table III.

Scheme III



Comparison of the data obtained for 1_ca and those of 2a permits the following statements. The activation energy for excimer formation is very similar in both cases. Transient spectroscopy shows that the structures of the excimers are identical,³⁶ and a full overlap of the chromophores is realized. The binding energies are identical for both excimers. An important difference is however observed for the change in entropy upon excimer formation; it is substantially smaller in the case of 1_ca. A similar comparison can be made between 1_cc and the results obtained by Zachariasse³⁷ for 2c (Table III). Independently, he came to the conclusion that the complexity of the fluorescence decay of 1,3-diarylpropanes is not due to the conformation of the chain. However, in his analysis the importance of the preequilibrium on the observed values is not taken into account.

The preexponential factor of t to g or g to t rotation in 1,3-dibromopropane⁴⁰ equals $3 \times 10^{13}\text{ s}^{-1}$, that of excimer formation in 1_ca equals $3 \times 10^{12}\text{ s}^{-1}$, and that of excimer formation in 2a equals $2 \times 10^{11}\text{ s}^{-1}$. It is clear that the difference between the first and second value reflects the increased ordering in the excimer-forming

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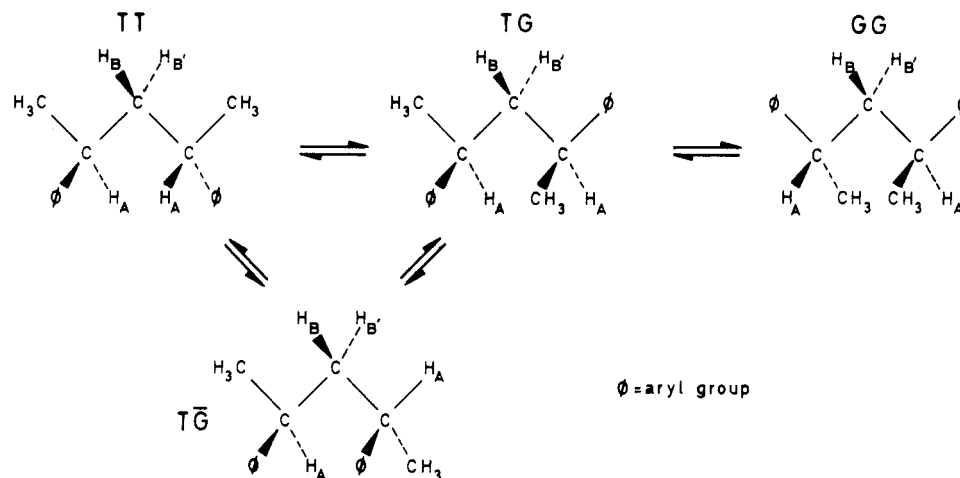
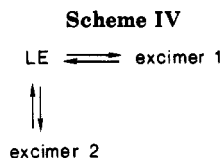


Figure 5. Conformations of importance in *rac*-2,4-diarylpentanes $1_{xy'}$.

step starting from a situation in which the carbazole group already cannot freely rotate. The difference between the second and the last value reflects in addition the preordering of the carbazole ring upon going from *tt* to *tg*.

In a discussion of the time profile of the fluorescence of a number of 1,3-diarylpropanes,³⁷ Zachariasse showed that, in contrast to **2c**, compound **2e** forms two excimers similar to 1_{ce} but arising from an ensemble of locally excited states that behaves as one component (Scheme IV). The results of this analysis as reported are presented in Table IV.



The lifetime of the two excimers (k_8^{-1}) corresponds within experimental error to the values reported for 1_{ce} . Comparison of the lifetime and/or transient spectra of the long-living excimer of **2e**³⁷ and of 1_{ce} with the data on **2c**, 1_{cc} , 1_{cc} , and [3.3](2,7)pyrenophane³⁷ suggests that this excimer has a symmetric structure. This conclusion was reached independently by Zachariasse³⁷ and our group.²⁹ The other, shorter living, excimer would then have a less symmetric structure. It is therefore surprising that the second excimer of **2e** should have such a highly negative entropy change. Similar values were observed for **2a**, **2c**, and **2h**, all forming only a symmetric excimer. Furthermore, in our analysis of 1_{ce} , where we could distinguish between -80 and -50 °C, the two different species leading to the two different excimers, the more symmetric one had a higher preexponential term as well as a higher barrier for formation than the other one. The activation energy of the symmetric excimer agrees well with those observed for **2c** and 1_{cc} in comparable solvents. The greater relative importance of the shorter living species in 1_{ce} at higher temperature was related to a change in the distribution of the two sets of rotational isomers. From the analysis of **2e** based on Scheme IV apparently the reverse emerges. One possible explanation could be that the observed rate constants are not real rate constants but contain information on the fraction of the locally excited state leading to each excimer in the same way as the rate constant of excimer formation in **2a**

contains information on the *tt*, *tg* equilibrium.

Zachariasse³⁸ also indicated that **2g** falls into the same category as **2e**. Whether complex decays will be observed will depend either upon the analytic resolving power of the curve fitting to a more exponential decay⁴¹ when differences in decay parameters or the contribution of a decay component becomes small or upon the stabilization that can be achieved by the excimer(s) and the relative value of the rate of excimer formation vs. the rate of rotation of the chromophore.

Racemic Diastereoisomers

The racemic diastereoisomers $1_{xy'}$ in as far as they have been analyzed are also systems in which the chain is present in different conformations (Figure 5). Calculations²⁴ as well as experimental analyses²¹⁻²³ indicate that $1_{cb'}$ at room temperature is 75% *TT* conformation and 25% *GG* conformation. Experimentally, it was found that $1_{cc'}$ and $1_{cc'}$ at room temperature in chloroform or cyclohexane are present for 70% to 80% in the *TT* conformation while at low temperature the latter conformation is the only one.²⁷

The steady-state fluorescence spectra of $1_{cc'}$ and $1_{cc'}$ have an excimer fluorescence band that is completely superimposable with that of their respective meso diastereoisomers at all temperatures investigated. This suggests an identical geometrical structure of the excimer and, hence, also the presence of only one excimer. The fluorescence decay curves of $1_{cc'}$ and $1_{cc'}$ monitored at 377 and 500 nm can be described by the same decay laws used for the respective meso diastereoisomers.

The molecular dynamics of the racemic diastereoisomer upon excitation are more complicated than those of the meso diastereoisomers due to the presence of two ground-state conformations. Since the decay laws used for meso diastereoisomers can also be applied to the racemic diastereoisomer, all the rate constants describing the equilibrium between the ground-state conformations must be large compared to the rate constant of excimer formation. The question however still remains regarding the conformation from which excimer formation takes place. It could be shown that excimer formation occurs from the *TT* conformation.²⁷ The preequilibrium between the *GG* and the *TT* chain

(41) Van de Zegel, M.; Boens, N.; Daems, D.; De Schryver, F. C. *Chem. Phys.* 1986, 101, 311.

Table V.
Kinetic and Thermodynamic Data of 1_{cb} , 1_{cc} , and 1_{cc} in Isooctane

parameter	1_{cb}	1_{cc}	1_{cc}
emission max, ^a nm	330	485	485
fwhm, ^a cm ⁻¹	3900	3800	3900
k_0 , ^b 10 ¹⁰ s ⁻¹	40	10	33
E_0 , ^b kJ mol ⁻¹	20	20	22
k_8 , ^c ns	23	145	85

^a Of the excimer. ^b Observed value. ^c At room temperature.

conformation should therefore be taken into account by using the following equations:

$$k_{\text{obsd}} = f_{\text{TT}}k_3 \quad (2)$$

$$f_{\text{TT}} = \frac{K_1K_2}{1 + K_1 + K_1K_2} \quad (3)$$

$$K_1 = k_a/k_{-a} \quad (4)$$

$$K_2 = k_{-b}/k_b \quad (5)$$

$$E_{\text{obsd}} = E_3 + \frac{\Delta H^{\circ}_2 + (1 + K_2)\Delta H^{\circ}_1}{1 + K_1 + K_1K_2} \quad (6)$$

In these equations k_{obsd} and E_{obsd} are the observed rate constant and activation barrier of excimer formation. The fractions of the TT or TG conformations at a given temperature are represented by f_{TT} and f_{TG} . It could be shown²⁷ that since the fraction of the TT conformation is considerable and decreases with increasing temperature, this path should lead to a negative deviation from linearity in the Arrhenius plot of the rate constant of excimer formation. This could be experimentally verified. In Table V the kinetic and thermodynamic properties of 1_{cb} , 1_{cc} , and 1_{cc} are reported.

Inspection of the emission spectrum of 1_{ca} at room temperature in isooctane shows the presence of an emission at 370 nm which can be ascribed to a partially overlapping excimer.²⁵ It could be demonstrated that the TT conformation, present for more than 85% at room temperature and the only conformation at 140 K, results in substantial overlap of the carbazole rings, as indicated by shifts in the NMR signals. The difference in the nature of this excimer and the one observed in the meso diastereoisomer was also substantiated by picosecond transient spectroscopy,³⁶ which further revealed that this excimer was formed within a few picoseconds after excitation and did not require important motion of the carbazole groups. A similar complication due to sidewise extending chromophores leading to overlap in the ground state as evidenced by NMR was observed in 1_{cd} .²⁸ Analysis of 1_{ce} reveals a similar complexity as observed for the meso diastereoisomer. Time-correlated single-photon counting at low temperature permits the identification of at least two excimers with lifetimes identical with those observed in 1_{ce} .^{29,37}

The different structures discussed up to now permit the following conclusion: *If two identical chromophores are linked by three sp^3 carbons in a propane or a pentane chain or by a carbon-oxygen-carbon bond in the ether analogues, then the conformational change of the backbone chain is always faster than the excimer-forming step. An exception to this observation is found when the chromophores already overlap in a*

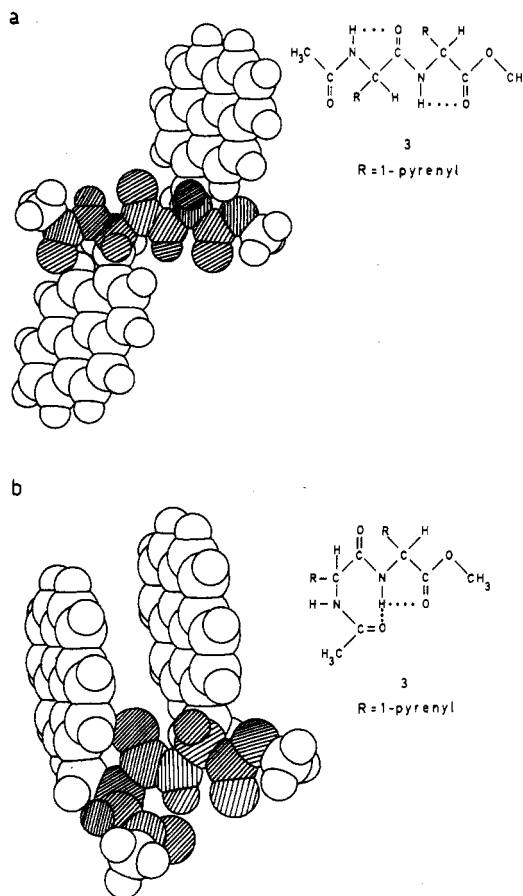


Figure 6. Structure of *N*-acetyldi-1-pyrenylalanine methyl ester (3) and the representation of (a) the C_5 and (b) the C_7 chain conformation.

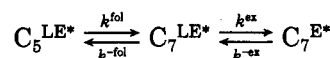
ground-state rotamer. If the chromophore is substituted nonsymmetrically, more than one excimer can be formed.

The Dipeptide Chain

The next question to address then is the evaluation of a system in which the conformational change of the chain is slower or of the same order than excimer formation. For this reason a dipeptide containing 1-pyrenyl chromophores (structure 3) was studied.

N-Acetyldi-1-pyrenylalanine methyl ester can occur in two diastereoisomeric forms, threo (3t) and erythro (3e). In inert solvents, not capable of forming hydrogen bonds, the ratio of excimer emission over emission from the locally excited state is substantially higher than in solvents which can accept hydrogen bonds.⁴² The decrease of the emission ratio can be correlated with an increase of the basicity according to the Taft basicity parameter.⁴³ In very acidic solvents, in terms of the Taft acidity parameter, high values are obtained for the emission ratio. These observations and the fact that in a given solvent 3e always has a higher efficiency of excimer formation than 3t were explained by the consecutive kinetic Scheme V. In this scheme two con-

Scheme V



(42) Collart, P.; Toppet, S.; De Schryver, F. C., submitted for publication.

(43) Goedeweck, R.; De Schryver, F. C. *Photochem. Photobiol.* 1984, 39, 515.

formations of the peptide chain are considered (Figure 6): an extended chain conformation, C_5 , with alternate side chains and a folded conformation, C_7 , with quasi-parallel side chains. The latter one is supported by an intramolecular hydrogen bond between the carbonyl function of the acetyl protecting group and the amine function of the second pyrenylalanine residue. Only the C_7 conformation allows rotation of the aromatic side groups to a partially overlapping excimer geometry within the lifetime of the excited pyrene moiety. This point could be proven by the substitution of the hydrogen involved in the hydrogen-bond formation in the C_7 conformation by a methyl group,⁴⁴ resulting in the disappearance of the excimer band in the emission spectrum.

In inert solvents a dipeptide chain is stabilized by folding, leading to a high C_7 population, and hence a more intense excimer emission than in hydrogen-bonding solvents. These solvents shift the conformational distribution in the ground state to more of the C_5 conformer. When compared in the same solvent, the threo diastereoisomer has a lower folded population than the erythro in part due to increased steric hindrance and in part due to the absence of a stabilizing N-H pyrene interaction. This interpretation was confirmed by measuring the decay of the locally excited state.⁴⁵ At temperatures where excimer dissociation, k^{-ex} , can be neglected, a two-exponential decay of the locally excited state is observed. Analysis of the fluorescence decay across the excimer band revealed the formation of only one excimer with a k_8^{-1} of 45 ns at room temperature. The two decay parameters of the locally excited state could therefore be associated with two ground-state chain conformations. From the decay times, the ratio of the preexponential terms of the decay, and the fluorescence lifetime of the unquenched chromophore, all the rate constants associated with Scheme V and the ratio C_7/C_5 could be calculated. In toluene at -20°C ratios of 3 and 0.75 were calculated for **3e** and **3t**, respectively, while in ethyl acetate these values decrease to 0.8 and 0.4. These results confirm the influence of the solvent on the conformational equilibrium of the dipeptide.

Conclusion and Outlook

In this Account, the role of configurational and conformational isomers in excimer formation between two identical chromophores linked by a short flexible chain has been discussed. A correlation is drawn between the ground-state stereochemical characteristics and the

excited-state behavior. This opens the possibility for using intramolecular excimer formation in the analysis of the dynamics of linked systems in a time window different from that of other techniques such as NMR. A strong interest currently exists in evaluating solvent effects on intramolecular rotations for molecules in the excited state. Some of the above-described systems can and will contribute to that area of study.⁴⁶ It is also important to note that some of these systems are the base units of polychromophoric molecules. The study of the 2,4-diarylpentanes has led to a better understanding of the fluorescence properties of poly(vinylaromatic) compounds.⁴⁷ The extension of the number of chromophores linked to the chain, as in 2,4,6-triphenylheptane,⁴⁷ has shown that excitation energy transfer between identical chromophores at an heterotactic junction (meso-racemic) is important in the photophysics of poly(vinylaromatic) compounds.

Although our concern about the effect of ground-state stereochemistry on excited-state properties started with 1-phenyl-3-(*N,N*-dimethylamino)propane,¹⁷ there still is less information currently available on the role of conformational and configurational aspects on intramolecular exciplex formation or electron transfer. Additional complexity could arise from the fact that long-distance electron transfer can proceed or compete with exciplex formation. We could show that at least in 1-aryl-3-(*N,N*-dimethylamino)propanes the rotation around the carbon-nitrogen bond does influence the excited-state behavior where this is not the case if the *N,N*-dimethylamino group is replaced by an indole moiety.⁴⁸ Interest in systems in which two or more different chromophores are linked has recently strongly increased since such molecules can be considered as models for the photosynthetic unit, permitting the study of fundamental and maybe practical aspects of charge creation and separation by light.

It is a pleasure to thank all the co-workers who over the years have contributed to our understanding of this area of research. Particular thanks are due to Dr. N. Boens, who developed the single-photon counting systems to the level of sophistication that permitted this work. I also remember the late Prof. Förster, who introduced me to the wonderland of excimers, and thank the Belgian National Science Foundation for their continuous support.

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