

PHOTOCHEMISTRY OF BICHROMOPHORIC COMPOUNDS : SCOPE AND EXPECTATIONS

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Abstract - Excitation of molecules containing more than one chromophore leads to intramolecular interactions such as excimer-, exciplex- and product formation. It is shown in this paper that these interactions can occur even if the chain connecting them contains several (more than three) units. Different factors affecting these interactions and the relation between the photophysical and photochemical aspects in these systems is stressed.

If an intramolecular interaction is made impossible intermolecular reaction leads to high molecular weight products. The principles and the scope of this photopolymerization process is discussed.

INTRODUCTION

The photophysical and photochemical properties of species which interact only, or more strongly, in the excited state have, since the fascinating observations by the late prof. Förster (1), been the subject of interest for many a photochemist - be it an organic or physical oriented one.

Excited state interactions in polychromophoric systems, including biopolymers, play an important role in excitation (information) transfer, degradation, and in the analysis of chain conformation.

Bichromophoric compounds (2) are better defined models for the processes occurring in multichromophoric systems. Upon excitation of a bichromophoric compound with a conventional light source several processes can occur depending on the nature of the chromophores. If the respective energy levels are adequately situated energy transfer can occur (3). Intramolecular excited state interaction was first observed by Hirayama (4) in his study of the emission properties of α,ω -diphenylalkanes. His observation, that only the 1,3-diphenylpropane showed excimer emission and the analogous results by Chandross (5) in the α,α and β,β dinaphthylalkanes and by Klöpffer (6) with di-N-carbazolylalkanes led to the erroneous (7) so called n equals three rule. Also non symmetric bichromophoric compounds, such as α,ω -arylalkyl N-disubstituted amines (8 c-f), show intramolecular exciplex formation. The geometric requirements are however less strict in the hetero excimer.

Excited state properties of intramolecular charge transfer complexes, where interaction in the excited state is stronger than in the ground state, have been investigated by Mutai (9) Davidson (10) and particularly Verhoeven (10).

In most cases the attention was focussed on systems containing the magic three bridge units between the chromophores.

It is in the area of the intramolecular reactions that the first examples appeared of reaction in systems containing flexible chains with more than three units (12)(2).

The analysis of the intramolecular cycloaddition reaction of N,N'-alkalynbismaleimides (7) led us to postulate the notion that intramolecular reaction through an excited state complex is limited by the possibility of the formation of a favourable conformation within the lifetime of the excited state involved and by the extent of its stabilization. This assumption was validated by the recent observations by Kunhle and Zachariasse (13) in the non reacting α,ω -dipyrenyl alkanes, by Borkent (14) in some charge transfer systems and by ourselves (15) (vide infra).

All processes mentioned up to now are intramolecular in nature. Bichromophoric systems can be designed to prohibit intramolecular and to promote intermolecular processes leading to high molecular weight materials.

This process named photopolymerization (16 a-d) is in essence different from the radical or ionic photoinitiation polymerization process. The former is a multi-step process in which each propagation step is the direct result of a photochemical reaction, while the latter is a chain reaction process in which only the creation of the initiating species is a photochemical reaction. This type of photopolymerization can be subdivided in two classes :

a. The type a photopolymerization.

In this case the propagation step results from a reaction of an excited state with a ground state chromophore (eq. 1).



The general kinetic scheme for this type a photopolymerization has been worked out (17). This class can be subdivided in two subclasses the singlet and the triplet photopolymerization. The latter one has been exemplified by the photopolymerization of N,N'-alkylenebisdisubstituted maleimides (16) and the kinetic analysis of the process proves its multistep character. The former one will be part of the present discussion (*vide infra*).

b. The type b photopolymerization.

The propagation step in this type of photopolymerization consists of a recombination of two reactive ground state species formed in a prior photochemical process (eq. 2-4).

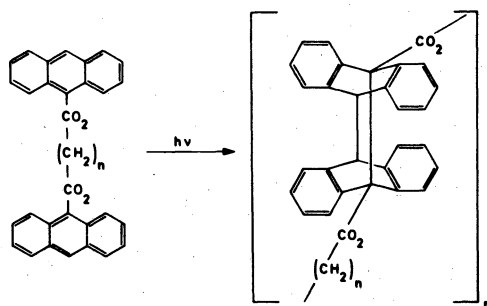


This type of photopolymerization has been exemplified in the photoreduction of α,ω -alkylenebisbenzophenones (18). A kinetic investigation of these systems proved the mechanism of propagation to be identical to the photoreduction of the model compound (19).

In the present paper the photochemistry of some anthracene derivatives and their contribution to the better understanding of some aspects of the excited state behaviour of bichromophores is discussed.

PHOTOPOLYMERIZATION OF ALKYLENE BIS-9-ANTHROATES (20)

Upon irradiation of a $2 \cdot 10^{-1}$ M solution of alkylene bis-9-anthroates (1a, $n=9$; 1b $n=11$) in dichloromethane filmforming polymers can be obtained resulting from the (4+4) π cycloaddition reaction of the anthracene moieties.



Photopolymerisation of nonamethylene -bis-9-anthroate

To establish the nature of the excited state involved in the reaction the lifetime of the reacting species was determined by quenching of the reaction by DTBN. From the linear Stern Volmer slopes, using a value of $8.3 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for the quenching rate constant (21), lifetimes of 7, 5.4 and 3.6 nanoseconds were obtained respectively for $2.5 \cdot 10^{-2} \text{ M}$, $0.5 \cdot 10^{-1} \text{ M}$ and $1 \cdot 10^{-1} \text{ M}$ solutions of component 1a in dichloromethane. On plotting $1/\tau$ as a function of the concentration of 1a (fig. 1), τ_0 an extrapolated lifetime, at infinitive dilution, was obtained of 10.5 nanoseconds. This value is identical to the one obtained by direct measurement at 10^{-5} M of the singlet lifetime (10 nanoseconds) of 1a by single photon counting technique. If an identical analysis is made for the hexyl-9-anthroate 2 in CH_2Cl_2 the extrapolated value for the lifetime is found to be 15 nanoseconds. Direct measurements by single photon counting give a value of 15 nanoseconds while a value of 14.6 can be obtained from fluorescence quenching with ditertylbutylnitroxides.

It should be pointed out that the singlet lifetime of the 1a is shorter than that of the model compound. This establishes the photopolymerization to occur via a singlet excited state (22). The following kinetic equations can be derived for this type of photopolymerization - type a process, singlet reaction only (17)-under conditions of total light absorption.

$$2,3 \quad \chi \log \left(\frac{1}{1-p} \right) + p = \frac{2 I_0 (t-t_0)}{[A_0]_0} \quad (\text{eq. 3})$$

where χ is the ratio of the monomolecular decay of the singlet over the product of the sum of bimolecular rate constants times the initial chromophore concentration $[A_0]_0$. In the present case, for high initial concentrations and low degree of conversion, p , the first part in the equation is negligible and the degree of conversion is linearly dependent of the time.

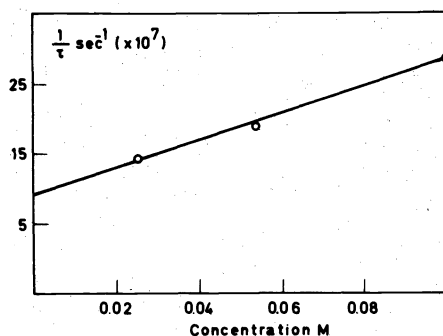


FIG. I : Reciprocal of the lifetime obtained by reaction quenching (DTBN) as a function of the initial concentration of 1a.

The degree of conversion at time t is related to the degree of polymerization, \bar{X}_n , in the following way :

$$\bar{X}_n = \frac{1}{1-p} \quad \text{or} \quad p = \frac{\bar{X}_n - 1}{\bar{X}_n} \quad (\text{eq. 4})$$

A plot of the change in optical density or the thereof derived degree of conversion as a function of time is given in fig.2. In the same figure the degree of conversion derived from the independently obtained degree of polymerization is plotted (23).

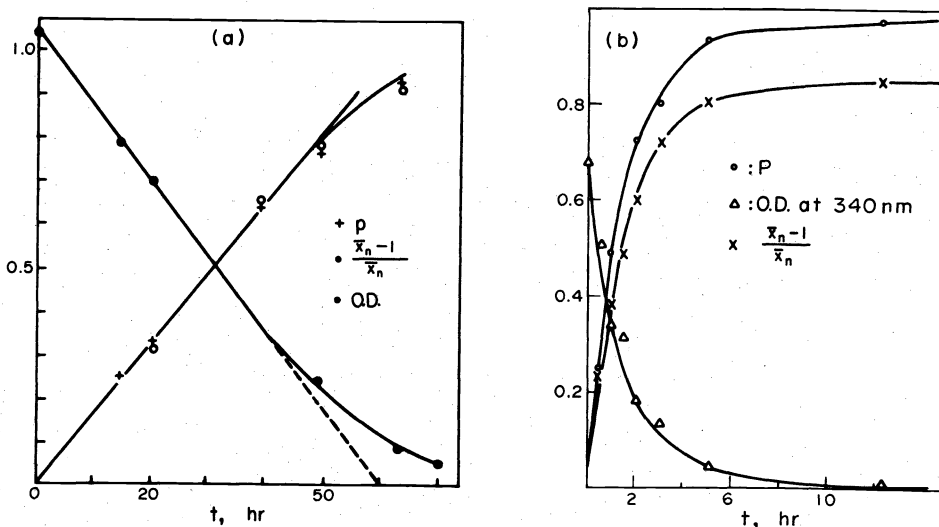


FIG.2 : Photopolymerization of 1a in dichloromethane.
 a) $[A_0]_0 = 4.10^{-1} \text{ M}$; b) $[A_0]_0 = 1.10^{-1} \text{ M}$
 x optical density at 340 nm; 500 times diluted
 ● degree of conversion derived from
 $\Delta \frac{\bar{X}_n - 1}{\bar{X}_n}$

At low conversion the experimental points fit the proposed equation indicating that the scheme is valid.

The change of the degree of conversion, p, obtained from absorption spectroscopy and of the value $\bar{X}_n - 1 / \bar{X}_n$ obtained by molecular weight measurements as a function of time should however be identical (24). From fig.2b it can be seen that the discrepancy between the two increases at higher conversion. One possible explanation for this observation would be that at higher conversion and lower concentration of chromophore an intramolecular process would become more and more competitive with the intermolecular addition. To check this the quantum yields of dimerization of hexyl-9-anthroate and of polymerization of 1a were determined as a function of chromophore concentration $[A_0]$ in the 10^{-3} to 10^{-1} M range. Assuming a scheme similar to the one proposed by Cowan (22) and plotting $1/\phi$ dimeris. versus $1/[A_0]$

a straight line should be obtained. This is observed for the dimerisation of the model compound but, at low concentration, it can be seen from fig.3 that the "photopolymerization" of 1a becomes independent of concentration indicating an intramolecular process.

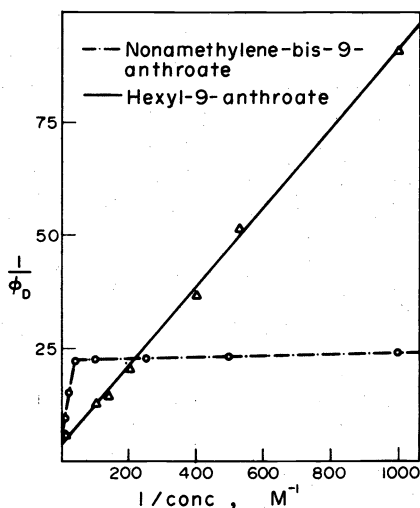
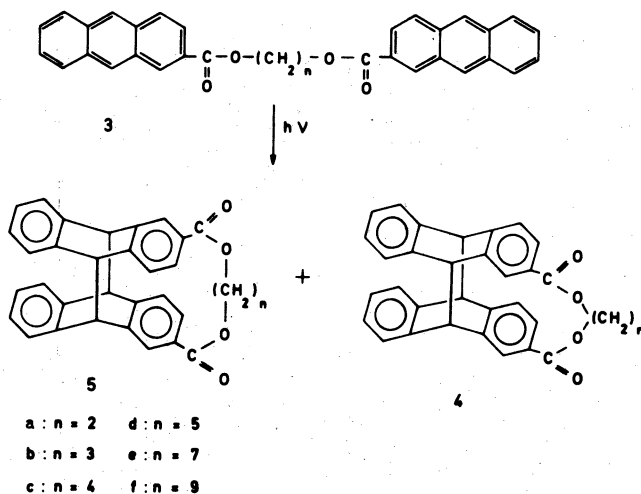


FIG.3 : Reciprocal of the photodimerization of hexyl-9-anthroate and of 1a in CH_2Cl_2 as a function of the reciprocal of their initial concentration.

Preparative irradiation of 1a at 10^{-4} M in dichloromethane leads to the formation of an intramolecular cycloadduct, with spectroscopic properties similar to those of the dimer of hexyl-9-anthroate indicating an head to tail cycloaddition.

INTRAMOLECULAR INTERACTION IN DIANTHRACENES

The excited state behaviour of anthracene and derivatives has been the subject of several studies from the photophysical and photochemical point of view (25). In a number of these studies excimer emission (26) has been reported and the relation between the photodimerization and excimer emission (27) has been discussed. In view of our statement on the mechanism of cyclomerization of N,N' -alkylenebismaleimides (7) the intramolecular photocycloaddition of some dianthracene derivatives was investigated in the hope to observe both excimer emission and intramolecular product formation and to be able to relate the two. Intramolecular cyclomerization of 9,9'-dianthracenes has been reported for systems in which two or three atoms separate the two anthracenes (28). Where normally addition at the 9,9',10,10' position occurs H. Bouas-Laurent has recently reported (29) an abnormal 9,10,1',4' addition. The cycloaddition of bisanthracenes linked in the 1,1' position or in the 2,2' position 3 has been reported earlier (30).



The ratio of the products formed on irradiation of 3 a-f, the quantum yield of product formation and of fluorescence are reported in table 1.

Table 1 : Photocyclomerization of 3 in dichloromethane solution at 20°C.
The samples are excited at 360 nm; concentration $5 \cdot 10^{-4}$ M.

| Compound | % 4 | % 5 | $\phi_{\text{cycl.}}$ | $\phi_{\text{fluor.}}$ |
|----------|-----|-----|-----------------------|------------------------|
| 3a | 90 | 10 | 0.07 | 0.21 |
| 3b | 80 | 20 | 0.09 | 0.17 |
| 3c | 70 | 30 | 0.08 | 0.13 |
| 3d | 65 | 35 | 0.11 | 0.07 |
| 3e | 60 | 40 | 0.06 | 0.11 |
| 3f | 48 | 52 | 0.05 | 0.145 |

From the data in table 1 it can be seen that the product ratio depends on the chain length, the formation of the more strained head to tail cyclomer becomes more easy when the chain length increases. On inspection of the emission properties of these compounds (fig. 4) an emission bathochromic to the one of the model compound, hexyl-2-anthroate, is observed for 1a-1d.

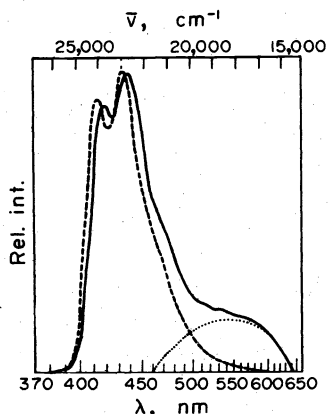


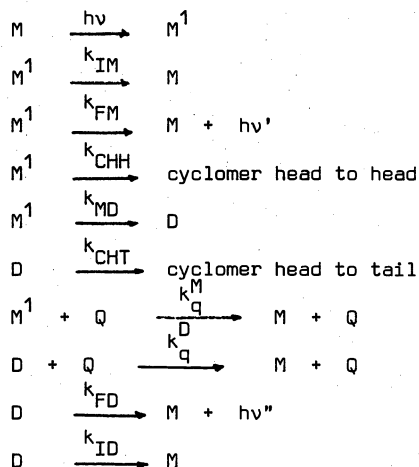
Fig.4 : Fluorescence spectra of 3b (—) and of hexyl-2-anthroate (---) in dichloromethane at 20°C.

The quantum yield of this bathochromic emission drops from 0.04 for 1a to 0.005 for 1d while the lifetime, determined by single photon counting in dichloromethane at room temperature, equals 46 nanoseconds for 1a and drops to 25 nanoseconds for 1c. The nature of this bathochromic emission was established by cleavage of cyclomers 4b and 5b in an ethanol glass at 77°K. Only the bathochromic emission was observed indicating that it originates from an excited species in which the two anthracene moieties are very close. These results indicate that intramolecular excimer emission can be observed for systems in which the $n=3$ rule does not hold. This was also illustrated very elegantly in the bispyrene system (13). The question then arises if the excimer lies on the path to product formation. A first hint in this direction is found in the decrease of the excimer emission when the amount of head to tail cyclomer increases. A second one is found in the preparative quenching of the photocyclomerization of 3b by di-*tert*-airbutylnitroxide in dichloromethane at 20°C. The percentage of 5b formed decreases on addition of the quencher and is totally absent when the quencher concentration equals $5 \cdot 10^{-1}$ M. This indicates that the head to tail cyclomer is preferably quenched and hence formed by a longer living species than the head to head cyclomer. In the cyclomerization of 3e and 3f, where no excimer emission is observed, the product ratio is independent of the quencher concentration. The lifetimes of 3e and 3f obtained by fluorescence quenching and reaction quenching with di-*tert*-air butylnitroxide are identical within experimental error and equal respectively 7.4 and 8.4 nanoseconds.

On the basis of these observations the scheme I can be proposed for the cyclomerization reaction.

In this scheme, where M stands for compound 3, k_{1M} denotes all monomolecular decay constants with the exception of k_{fM} , the rate constant for fluorescence, and of k_{DM1} and k_{DM2} , the rate constants for excimer formation. For 3e and 3f the rate constants for product formation, k_{CHH} and k_{CHT} , are much larger than any other deactivation pathway of D_1 and D_2 . However by increasing the steric constraints k_{fD} , the rate constant for excimer emission, does become competitive with k_{CHT} for 3b. From the quantum yield of excimer fluorescence and the lifetime a value of 10^6 sec^{-1} is determined for k_{fD} . Since the quantum yield of excimer fluorescence is of the same order of magnitude as the quantum yield of head to tail cyclomer formation, k_{CHT} should be at least 10^6 sec^{-1} . It should be pointed out that no back reaction of D_2 to M^1 is incorporated in the scheme. Further work is in progress to ascertain this point.

Scheme I



On the basis of this scheme, assuming stationary state conditions, the following expression for the quenching of the cyclomerization reaction can be derived :

$$\frac{\phi_r^0}{\phi_r} = \frac{(1 + k_q^M \tau^M [Q])(1 + k_q^D \tau^D [Q])}{1 + k_q^D \tau^D [Q] \cdot (R_0/1+R_0)} \quad (\text{eq. 5})$$

Using the independently measured values of k_q^M , k_q^D , τ^D , τ^M and of R_0 , the ratio of the head to head cyclomer over the head to tail cyclomer in absence of quencher, it was found that the calculated plot fits well the experimental points (fig. 5).

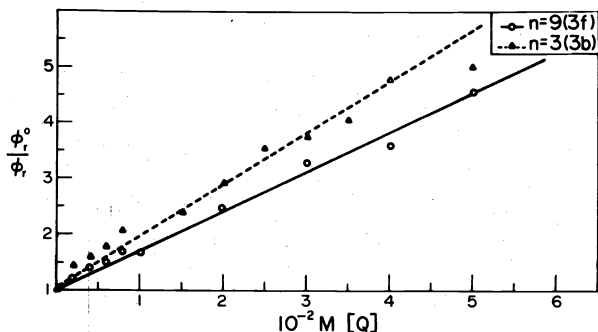
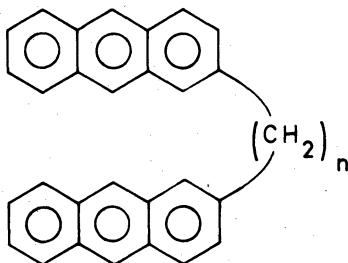


Fig. 5 : Quenching of the cyclomerization by di-*t*-butylnitroxide in CH_2Cl_2 ,
 o experimental data for 3f; Δ experimental data for 3b;
 ---- quenching curve for 3b, calculated according to equation 5,
 using the values

$$\begin{array}{l}
 k_1^M = 8,3 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}; \quad k_1^D = 2,3 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}; \quad \tau^D = 36 \text{ nanoseconds}; \\
 \tau^M = 8,9 \text{ nanoseconds}.
 \end{array}$$

From these data the intermediacy of the excimer on the pathway to product can be concluded. The question can now be asked if dianthracenes, linked in the two position, with a shorter chain, which would prevent reaction, show excimer emission. To look into this the emission properties of α, ω -2,2-dianthrylalkanes 6 were investigated.



6a $n=2$; 6b $n=3$; 6c $n=6$

The emission spectrum of 6c in methylcyclohexane is identical to that of 2-ethylanthracene. On irradiation it forms a cyclomer. The emission spectra of 6a and 6b, reported in figures 6 and figure 7, contains besides monomer emission, a bathochromic emission with maxima at 450 nm and 480 nm respectively. The excitation spectra of the broad bands are identical to that of the model and coincide with the absorption spectra. The bathochromic emission is not observed in a viscous solvent at low temperature.

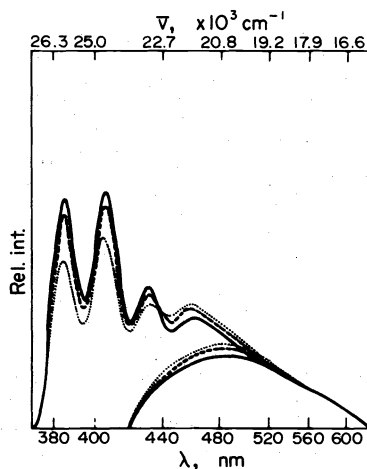


Fig.6 : Emission spectrum of 6a in methylcyclohexane at (· · ·) 9°C; (· · · ·) -7°C; (- - -) -26°C; (—) -37°C.

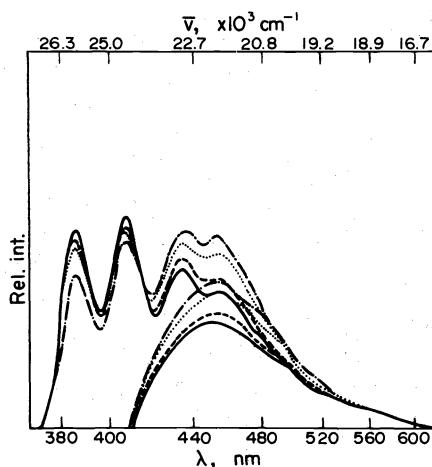


Fig.7 : Emission spectrum of 6b in methylcyclohexane at (· · ·) 9°C; (· · · ·) -7°C; (—) -19°C

The broad band can therefore be assigned to excimer emission. On excitation at low temperature in methylcyclohexane-isopentane glass at 77°K of the broken cyclomer of 6c an analogous broad band is observed (figure 8).

The quantum yield of fluorescence of 2-ethylanthracene, 6a and 6b, is reported in table 2.

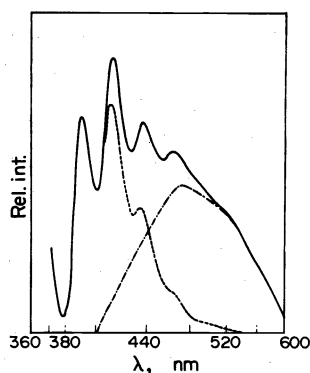


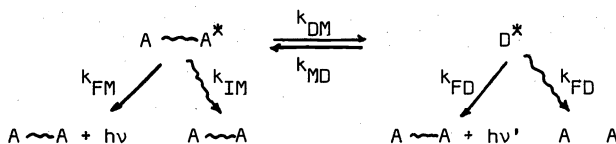
Fig.8 : Emission spectrum of the broken cyclomer at 77°K in methylcyclohexane-isopentane (—) compared with the emission of 2-ethylanthracene (---). (-.-.) Bathochromic broad band emission.

Table 2 : Fluorescence quantum yield of 2-ethylanthracene, 6a and 6b in methylcyclohexane at 20°C.

| Compound | $\phi_{\text{total}}^{\text{T}}$ | $\phi_{\text{monomer}}^{\text{F}}$ | $\phi_{\text{excimer}}^{\text{F}}$ |
|--------------------|----------------------------------|------------------------------------|------------------------------------|
| 2-ethyl anthracene | 0.26 | 0.26 | - |
| 6a | 0.26 | 0.10 | 0.16 |
| 6b | 0.26 | 0.13 | 0.13 |

From the temperature dependence of the emission of 6a (fig.6) and 6b (fig.7) it can be seen that in this temperature region a well defined isoemissive point exists at 410 nm for 6a and at 440 nm for 6b. The activation energy for the formation of the excimer of 6a was obtained from the Arrhenius plot of $\phi_{\text{excimer}}^{\text{F}} / \phi_{\text{monomer}}^{\text{F}}$ versus $1/\tau$. A value of 2,2 kcal/mol was found which differ from the value observed by Mataga (31) for 1,2-(di-1-anthryl)ethane. Assuming (32) that the rate constants for non radiative decay, k_{IM} , and for radiative decay, k_{FM} , of the monomeric excited species in 6a and 6b are identical to the respective rate constants of 2-ethylanthracene, the system can be analysed according to scheme II.

Scheme II



The notation follows that of Birks (34). From the linear Stern-Volmer plot of the fluorescence quenching of 2-ethylanthracene with di-t-butyl nitroxide a singlet lifetime of 10 nanoseconds is obtained assuming that the quenching occurs at a diffusion controlled rate. Using this lifetime the rate constants k_{FM} and k_{IM} can be calculated. By measuring the fluorescence intensities in absence and in the presence of oxygen under identical experimental conditions for the model and 6a and 6b all rate constants can be determined (35). The values obtained are reported in table 3.

Table 3 : Rate constants for 6a and 6b in methylcyclohexane at 20°C

| | k_{FM} | k_{IM} | k_{DM} | k_{MD} | k_{FD} | $k_{\text{ID}} \cdot 10^7 \text{ sec}^{-1}$ |
|----|-----------------|-----------------|-----------------|-----------------|-----------------|---|
| 6a | 2.6 | 7.4 | 26 | 2.3 | 1 | 2.6 |
| 6b | 2.6 | 7.4 | 17 | 0.3 | 0.3 | 1 |

Although the method lacks high accuracy, which can be obtained by other methods (6), three important observations can be made :

a. the rate constant for excimer formation drops with lengthening of the chain. Comparison with the value of k_{DM} for 1,3-dicarbazoylpropane (33) in cyclohexane at room temperature ($20 \cdot 10^7 \text{ sec}^{-1}$), 1,3-dinaphthylpropane (36) in ethanol ($12 \cdot 10^7 \text{ sec}^{-1}$) and for 1,3-diphenylpropane in cyclohexane (33)(37) ($110 \cdot 10^7 \text{ sec}^{-1}$) shows that they are of the same order of magnitude. The difference may reflect differences in solvent viscosity (38) and also differences in the bulk of the chromophores.

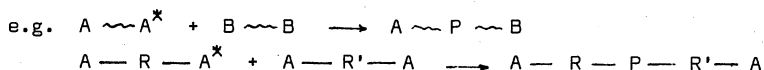
b. the rate constant k_{MD} is substantially larger for 6a than for 6b reflecting the larger strain in the excited state complex and hence its greater tendency to dissociate.

c. the rate constants k_{FD} is larger for 6a than for 6b. This reflects a difference in geometry and hence in overlap in the two excited state complexes. This is further substantiated by the difference in the wavelength of the emission spectrum. Identical observations were made in the α,ω -bispyrenylalkenes (13). Further work is in progress to get detailed information on the kinetics and the thermodynamics of these systems.

CONCLUSION

From the study of Zachariasse (13), Verhoeven (14), Winnik (39), Kanoaka (40) and ourselves it is now clear that intramolecular interaction - be it excimer, charge transfer, exciplex interaction or product formation - in bichromophoric systems is not limited to the $n=3$ cases. The notion that intramolecular interaction depends on the probability to reach within the lifetime of the excited state involved a favourable conformation and on the thermodynamics of the systems is verified. Theoretical models are being developed(41) and compared with experimental data of the "cyclization" probability. This will lead to a better understanding of the conformations of hydrocarbon chains and hopefully of other types of chains in solutions. Analysis of the photochemistry and photophysics of bichromophoric systems contributes to the better understanding of the excited state properties of complexes and their role as reactive intermediates.

Under certain conditions intermolecular reactions lead to the formation of high molecular weight materials. Where up to now emphasis was put on homopolymerization, it is within the scope of the process to develop the principles of photocopolymerization.



If chosen properly, truly alternating copolymers of well defined structure can be synthesized and from these well defined polymers the relationship between structure and the physical and chemical properties can be studied.

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