

FROM ANTHRACENE PHOTODIMERIZATION TO JAW PHOTOCHROMIC MATERIALS AND PHOTOCROWNS

Henri Bouas-Laurent, Alain Castellan and Jean-Pierre Desvergne

Laboratoire de Chimie Organique et Equipe de Recherche Associée au CNRS 167
(Photophysique et Photochimie Moléculaire), Université de Bordeaux 1,
33405 Talence Cédex, France.

Abstract - The inter and intramolecular photochemical reactions of anthracenes in the absence of oxygen is discussed. The intermolecular photodimerization of 9-substituted anthracenes in fluid solution usually leads to head-to-tail photodimers; it will be shown that this trend can be obviated by non bonding attractive interactions between substituents or by mixed photodimerization. The mechanistic aspects will be examined, next, in connection with the problem of excimer intermediacy.

Bis-9-anthracenes can form photocyclomers and, in certain cases, intramolecular excimers at room temperature. Those which display interesting photochromic properties, were called "jaw compounds"; some of them induce an unusual anthracene ring cyclomerization. A study of photophysical and photochemical processes by steady state and transient kinetic analysis of α, ω -bis-9-anthryl-n-alkanes (ethane to decane) and α, ω -bis-9-anthryl-polyoxaalkanes allows a deeper insight into the mechanism of photodimerization. By irradiation, the latter derivatives can generate "photocrowns"; this is the first photochemical synthesis of crown-ethers.

INTRODUCTION

There is a continuing and considerable interest in the photophysics and photochemistry of aromatic hydrocarbons in the solid state and in fluid solution (1). Certain polycyclic aromatic hydrocarbons and their derivatives undergo photodimerization and we have investigated their reactivity (in particular anthracenes, acenaphthylenes, phenanthrenes, benzanthracene and naphthacene) for several years (2 - 8). We will limit our account to the study of the anthracene chromophore in fluid solution. Indeed, the photodimerization of anthracene is one of the oldest known photochemical reactions (9) and a classical example of text-books (10). Anthracenes are unique in combining the advantages of having easily accessible absorption spectra, exhibiting monomer (and often excimer) fluorescence and high photoreactivity; they also have a fairly good solubility in organic solvents and, although sometimes with difficulty, a variety of derivatives can be prepared.

We will thus consider the anthracene ring as a model of a fluorescent and photoreactive chromophore, envisaging the study of the structure of the photodimers and the mechanism of photodimerization as well as the design of photochromic systems based on this reaction (bichromophores). The first part of the report will be devoted to intermolecular reactions and the second part to intramolecular processes. In this case, the formation of intramolecular excimers or photocyclomers (intramolecular "photodimers") is dependent on the conformational and dynamical properties of the chain.

I. INTERMOLECULAR INTERACTIONS

I₁ - The structure of the photodimers; the head-to-tail vs. head-to-head selectivity.

By irradiation in organic solvents through a Pyrex filter most anthracene derivatives readily form photodimers (2 a-b,13) the two halves are linked by position 9,10' and 10,9' as revealed by U.V. spectroscopy and, for anthracene and 9-formylanthracene, by X-ray structure analysis (2 a-b,11). The salient feature is the large length of the C₉-C_{10'} bond : 1.61 Å. An elegant explanation was recently proposed for this peculiarity (12). A number of 9-substituted anthracenes were shown by dipole moment measurement, NMR and chemical correlation (14, 2 a-b) to yield exclusively head-to-tail (h-t) rather than head-to-head (h-h) photodimers (fig.1). The generality of this mutual orientation was rationalized in terms of electronic (dissymmetry of charges) (14,15) electrostatic and steric effects of the substituents (14). Nevertheless, when the steric hindrance is not excessive and provided some attractive non bonding forces exist between the substituents, the usual trend towards h-t dimerization can be obviated. This was found to be the case with (9-anthryl)methyl acetate (I₁ ; Z = CH₂-O-CO-CH₃) and N-(9-anthryl)methylacetamide (I₂ ; Z = CH₂-NH-CO-CH₃). Irradiation of I₁ in CH₂Cl₂ at ca 350 nm gave a mixture of h-h and h-t photodimers in a 1 to 4 ratio (NMR) (16). An alcoholic solution (5 x 10⁻² M) of I₂ photodimerized in a Pyrex vessel to give a mixture of

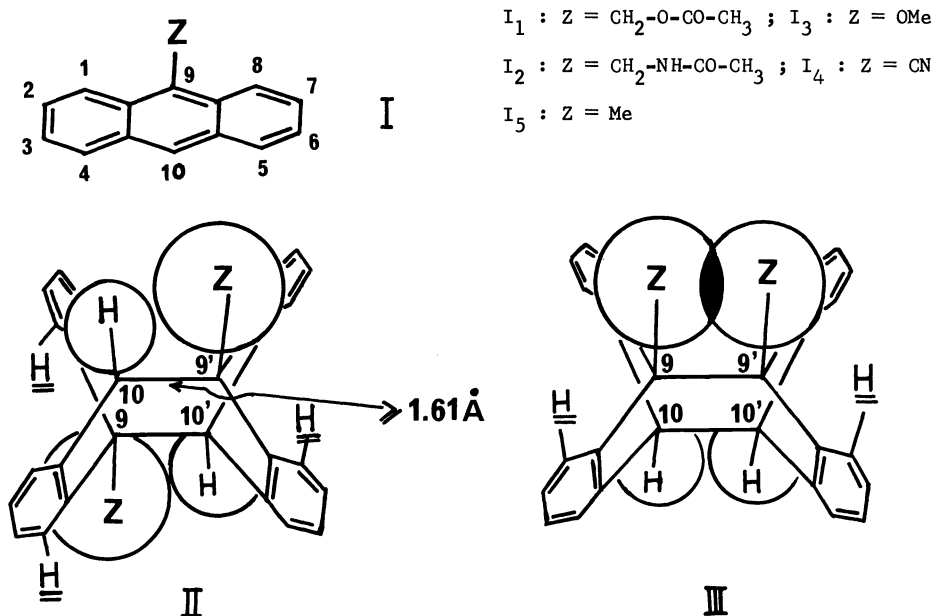


Fig. 1 - I) numbering of the anthracene ring. II) head-to-tail (h-t) photodimers. III) head-to-head photodimers. (schematic drawings). The underlined hydrogen atoms (so called peri hydrogens) play an important role in preventing h-h bonding as shown by space filling molecular models.

h-h and h-t photodimers (TLC, NMR) (17). But the h-h products, which are thermally labile, were not isolated. We believe that dipole-dipole interactions or hydrogen bonds are responsible for allowing the h-h orientation to compete with h-t orientation (fig.2).

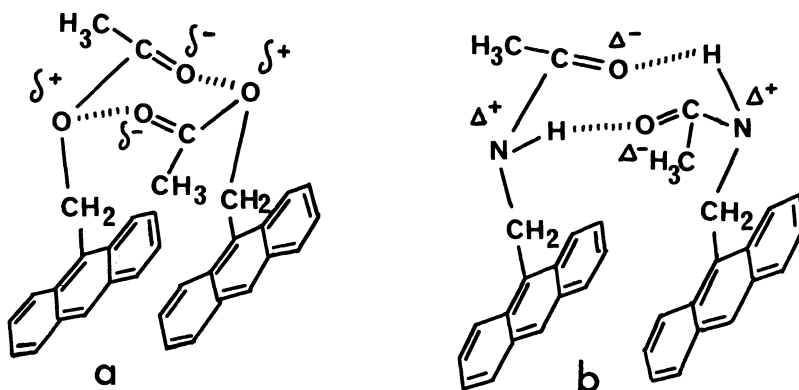


Fig. 2 - Possible structures of head-to-head complexes leading to h-h photodimers; (a) dipole-dipole interaction. (b) hydrogen bonds. The photodimers, not isolated, were characterized by NMR.

Another possibility of getting a h-h photodimer was to generate a crossed photodimer by irradiation of a mixture of a monomer substituted by an electron-releasing group and a monomer bearing an electron-withdrawing substituent; the size of the groups should be kept minimal to avoid steric hindrance and the use of non polar solvent was preferred to prevent formation of radical-ions through electron transfer (5). All these requirements were fulfilled with a 1 : 1 mixture of 9-methoxy (I_3 ; $Z = \text{OCH}_3$) and 9-cyano (I_4 ; $Z = \text{CN}$) anthracenes which, irradiated in ether, gave the h-h crossed photodimer (IV) in high yield with no trace of the h-t isomer. The other photoproducts were the homodimers of I_4 and I_3 . IV could be isolated and characterized by NMR but its thermal dissociation is fairly fast at room temperature. The photocyclization quantum yield of the 1 : 1 mixture of I_3 and I_4 (in benzene at 366 nm) is 0.29 (at 10^{-2} M) ; it is about three times the quantum yields of homophotodimerization of I_3 or I_4 separately (5).

Similar results were found in the phenanthrene series where a mixture of 9-methoxy and 9-cyano phenanthrenes exhibit an exciplex fluorescence at room temperature and generate the

crossed h-h syn photodimer (V) together with the h-t syn dicyano diphenanthrene (4) (fig.3).

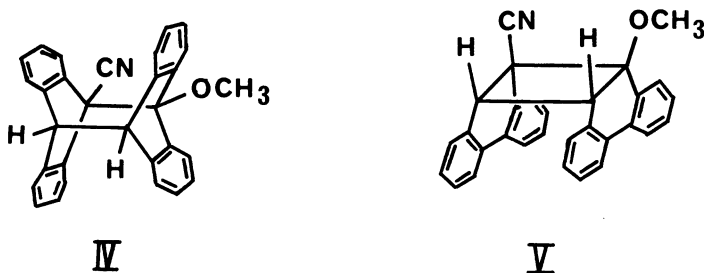
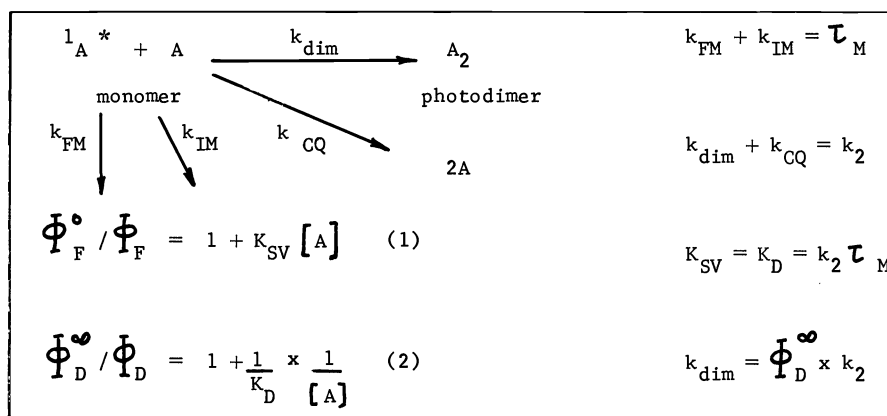


Fig. 3 - Head-to-head crossed photodimers of 9-methoxy A and 9-cyano A (IV) and of 9-methoxy and 9-cyano phenanthrene (V). 'A' represents the anthracene ring.

I₂ - On the mechanism of photodimerization of anthracene and its derivatives.

Since the pioneering work of Bowen (1954) a number of authors have examined the mechanism of photodimerization of anthracene and some of its derivatives, but we would like to stress the results of Cherkasov (2a,18) and Cowan (2a,10,19) who tackled the problem of substituent and solvent effects. In a parallel study we have investigated the mechanism of photodimerization of anthracene (A) 9-methyl (I₅; Z = Me), 9-cyano (I₄; Z = CN) and 9,10-dimethyl (DMA) anthracenes in degassed benzene. Our purpose was to get quantitative data on polar or steric effects of the substituents and, further, on the excimer reactivity (2a). It was shown that the triplet state is not directly responsible for the photodimerization (20). The simplest kinetic scheme, assuming that the photodimers are formed from the singlet state, is given below (scheme 1) together with the usual Stern-Volmer relationship for the fluorescence and a relationship between Φ_D^∞ (dimerization quantum yield extrapolated at infinite concentration) and Φ_D (dimerization quantum yield at any concentration [A]). A determination of fluorescence and reaction quantum yields versus concentration allows the derivation of slopes



Scheme 1 - Kinetic scheme for the photodimerization of anthracenes.

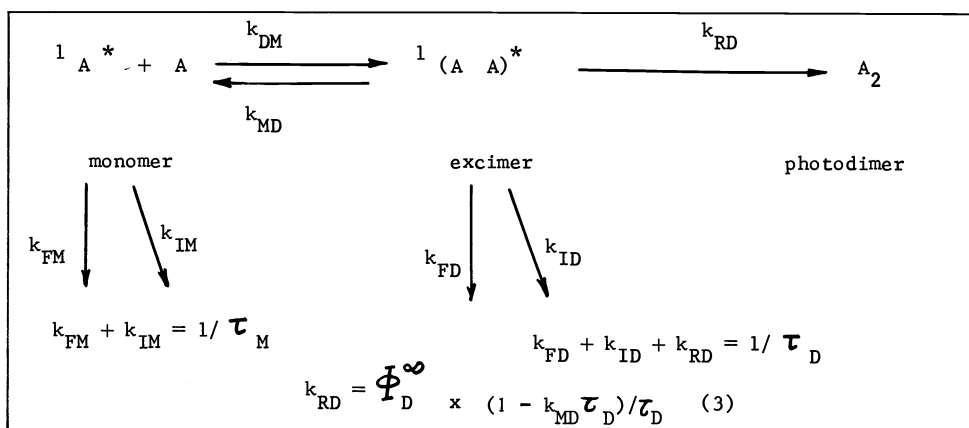
of relations (1) and (2). These independent measurements provided proximate values for K_{SV} and K_D ; then the kinetic scheme was considered as consistent; given τ_M , it was possible to calculate the rate constant k_{dim} . In table 1 we have collected some rate parameters k_{dim} and k_2 calculated from our own results, and Cherkasov's and Cowan's data (2a). For comparison, we have added data obtained for naphthacene (very approximate) and acenaphthylene (2d). From examination of k_{dim} values, we note that the reactivity of anthracenes is high, with little sensitivity to the polar effect of the substituents and apparently to the nature of solvents. Of interest also is the decrease of k_{dim} with the increasing bulk of the substituents. (We have checked that the DMA cyclizes at the 9-10' and 9'-10 positions). The rate parameter k_2 is generally very high as one would expect if the fluorescent state is quenched by formation of a stable excimer (21) and this was an argument to postulate the intermediacy of an excimer (2b) (see scheme 2). From this scheme, it is possible to derive equation (3) and with the assumption that $k_{MD} \ll k_{DM}$, to calculate k_{RD} if we know the excimer lifetime τ_D . Taking τ_D values determined by Yang (22) or Cohen (23) for anthracene (A) and Cherkasov (18) for 9,10-dimethylantracene (DMA) we found respectively: $k_{RD} (A) \approx 1.2 \times 10^8 \text{ s}^{-1}$ and $k_{RD} (DMA) \approx 2 \times 10^4 \text{ s}^{-1}$.

Table 1 - Rate constants of photodimerization ($k_{dim.}$) and bimolecular quenching (k_2) of the singlet excited state. a) Cherkasov's data. b) Cowans's data (ref. 2a).

Compound	Solvent	k_2 ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	k_{dim} ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Anthracene (A)	Benzene ^a	6.6	2.3
	Toluene ^a	14	2.2
9-MeA	Benzene ^a	9.2	2.8
	Toluene ^a	14	1.9
9-Et-A	" ^a	9.2	1.1
9-Pr-A	" ^a	8.4	0.6
9- ⁿ Bu-A	" ^a	6.4	0.5
9,10-Dimethyl-A	Benzene ^a	1.8	0.04
	Toluene ^a	7.6	0.03
9-CN-A	Benzene	5.4	1.3
9-COOH-A	EtOH (H ⁺) ^b	5.4	1.0
Naphthacene	Cyclohexane	(0.7) [*]	(0.3) [*]
Acenaphthylene [§]	Ether (aerated)	0.1	0.04

* very approximate values; see 2a.

§ see ref. 2d



Scheme 2 - Kinetic scheme for the photodimerization of anthracenes through the intermediacy of an excimer.

II. INTRAMOLECULAR INTERACTIONS

Another way of obtaining a h-h "photodimer" is to link the two anthracene chromophores by an aliphatic chain. The two aromatic halves are forced to adopt this geometry, and the reaction called photocyclomerization will become chain-controlled. It is a way of investigating bimolecular reactions at high dilution. Considerable work has been devoted to the photo-physics and photochemistry of non conjugated chromophores. The topic has been recently reviewed by De Schryver (24,25) who investigated, inter alia, bis-1,1' - and bis-2,2'-anthracenes. Photocyclomerization of bis-9,9'-anthracenes was studied by several authors (for a review see ref. 24 and 26); particular emphasis was given to 1,2-bis-(9-anthryl) ethane (27). We were interested in preparing photochromic materials and investigating the synthetic and mechanistic aspects of bis-9,9'-anthracenes and will successively consider the jaw compounds, the bis-9-anthrylalkanes and the "photocrowns".

II₁ - "Jaw" photochromic materials.

The purpose was to generate efficient and chemically stable photochromic materials. Inspection of models shows that the best overlap between the two aromatic rings is reached with a three-membered chain. This is in keeping with the well known Hirayama rule (1a,24). Sequences

such as $-\text{CH}_2\text{-O-CH}_2-$, $-(\text{CH}_2)_3-$, $-\overset{\text{O}}{\text{C}}\text{-NH-CH}_2-$ were chosen for their relative chemical inertness. For comparison, we have studied compounds such as $\text{A-Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_2\text{-A}$ and $\text{A-CH}_2\text{-S-CH}_2\text{-A}$ as well as dissymmetrical bichromophores (XI, XII); see chart 1. The photocyclomerization of compounds VI, or IX₁-XI₁ into their photoisomers VI₂ or IX₂-XI₂ and the thermal or photochemical dissociation of the latter mimic the closure and opening of a jaw; for this reason

$\text{R-A-CH}_2\text{-O-CH}_2\text{-A-R}'$	VI ₁	$\text{R} = \text{R}' = \text{H}$	a
		$\text{R} = \text{CH}_3$; $\text{R}' = \text{H}$	b
		$\text{R} = \text{C}_6\text{H}_5$; $\text{R}' = \text{H}$	c
		$\text{R} = \text{R}' = \text{C}_6\text{H}_5$	d
$\text{A-CO-NH-CH}_2\text{-A}$	VII ₁		
$\text{A-CH}_2\text{-S-CH}_2\text{-A}$	VIII ₁		
$\text{A-SiMe}_2\text{-O-SiMe}_2\text{-A}$	IX ₁		
$\text{A}_9\text{-CH}_2\text{-O-CH}_2\text{-A}_1$	X ₁		
$\text{A}_9\text{-CH}_2\text{-O-CH}_2\text{-Np}_1$	XI ₁		
$\text{A}_9\text{-CH}_2\text{-O-CH}_2\text{-Np}_2$	XII ₁		
$\text{A-(CH}_2)_n\text{-A}$	XIII ₁	sketched $\text{A-C}_n\text{-A}$	
A-mXy-A	XIV ₁		

Chart 1. Schematic representation of bichromophores. A is for 9-anthryl or 9,10 disubstituted anthracenes. R and R' represent atoms or substituents in position 10 and 10'. A₉, A₁, Np₁, Np₂ are respectively for 9-anthryl, 1-anthryl, 1-naphthyl and 2-naphthyl. The open form is numbered 1 and the cyclized form 2 (see fig.4).

they were called "jaw" photochromic materials or jaw compounds (fig.4). A series of derivatives of type VI₁ exhibited efficient photochromic properties (28) as can be estimated from

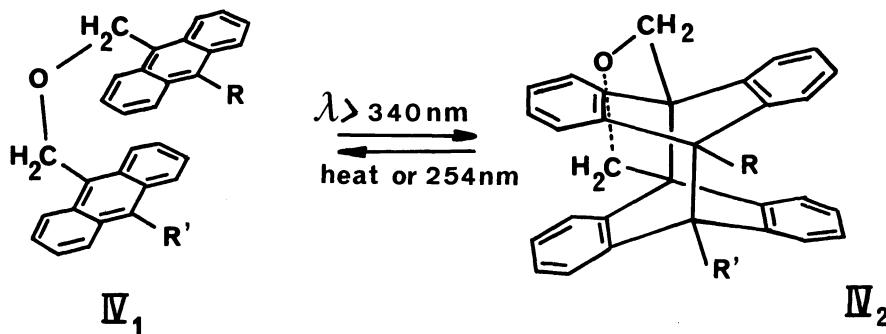


Fig. 4 - Jaw compounds ; photocyclomerization of IV₁ and dissociation of IV₂.

the values of the closure and reopening quantum yields of some of them (table 2). In particular the photocyclomerization of 1,3-bis-9 anthrylpropane appears to be less efficient than that of VI₁. Although it is not a comparison of the reactivities, it is tempting to ascribe this difference to a lower barrier of energy of rotation about a C-O bond than a C-C bond (30). This ether linkage has been used with success to yield intramolecular excimers with the benzene (31), naphthalene (32) pyrene (33) chromophores or to lead to photocyclomers in the case of bis-(1 naphthylmethyl)oxide (32) or compounds X, (29) XI₁ (34); see fig.8 and 10. Compounds VI 1 a-c do not show excimer fluorescence in Me-cyclohexane (MCH) at room temperature. However, it could be detected by the Chandross (39) method at 77K (fig.5). To allow the intramolecular fluorescence to compete with the photocyclomerization, bulky substituents were fixed in position 10 and 10' (VI₁); indeed the latter derivative was found photostable in our experimental conditions and has a high yield of excimer fluorescence in MCH at 20°C (fig.6 and table 2) and might be a useful fluorescing probe. Crowding the chain by substitution, for instance in replacing $-\text{CH}_2-$ by $-\text{Si}(\text{CH}_3)_2-$, led to IX₁ which exhibits

Table 2 - Photophysical and photochemical data of jaw compounds at R.T. solvent MCH. Photocyclomerization quantum yields $\Phi_{1 \rightarrow 2}$ were determined at 366 nm. Reverse quantum yields $\Phi_{2 \rightarrow 1}$ were determined at $\lambda < 300$ nm.

Compound	$\Phi_{1 \rightarrow 2}$	$\Phi_{2 \rightarrow 1}$	Φ_{FM}	Φ_{FD}	τ_M (ns)	k_R^f (10^8 s^{-1})
H-A-CH ₂ -O-CH ₂ -A-H	0.32	0.64	0.03		0.9	3.5
Me-A-CH ₂ -O-CH ₂ -A-H	0.32	0.38	0.07			
C ₆ H ₅ -A-CH ₂ -O-CH ₂ -A-H	0.19	0.27	0.09			
C ₆ H ₅ -A-CH ₂ -O-CH ₂ -A-C ₆ H ₅			0.21	0.34		
A ₉ -CH ₂ -O-CH ₂ -A ₁	0.15	0.66 ^a	0.028	0.007		
A ₉ -CH ₂ -O-CH ₂ -Np ₁	0.08		0.078	0.037	0.75 ^c	0.38 ^d
A ₉ -CH ₂ -O-CH ₂ -Np ₂	0.015 ^e		0.10		1.6	
A-CH ₂ -O-CH ₃			0.088		1.25	
A-SiMe ₂ -O-SiMe ₂ -A	0.10	0.8 ^a	0.022	0.051		
A-CH ₂ -CH ₂ -CH ₂ -A	0.14		0.47			
A-CH ₂ -CH ₂ -A	0.26 ^b	0.55 ^b	0.16 ^b			
A-CH ₂ -A	0.15	0.76 ^b	0.06 ^b		1.1 ^b	1.4

(b) in benzene, ref.26 (a) $\Phi_{2 \rightarrow 1}$ at 292 nm, J. Ferguson, personal communication.

(c) $1/\lambda_1 = 0.75 \text{ ns}$; $1/\lambda_2 = 6 \text{ ns}$ (d) $k_{RD} = 0.38 \times 10^8 \text{ s}^{-1}$ (scheme 3) (e) the photoproduct is of unknown structure (f) $k_R = \Phi_{1 \rightarrow 2} \times 1/\tau_M$

excimer fluorescence and photocyclomerization; but it was found that the reaction occurs at position 9-1' and 10-4' and not at the usual more reactive 9-9' and 10-10' sites (35). This is the first example of unsymmetrical anthracene photodimerization (fig.7). Assuming that this new reaction was due to conformation constraints, we prepared X₁ to compel the two anthracene moieties to react in the same way as IX₁ and isolated X₂ as the only photoproduct (fig.8). This new type of cyclomer has a characteristic U.V. spectrum (fig.9).

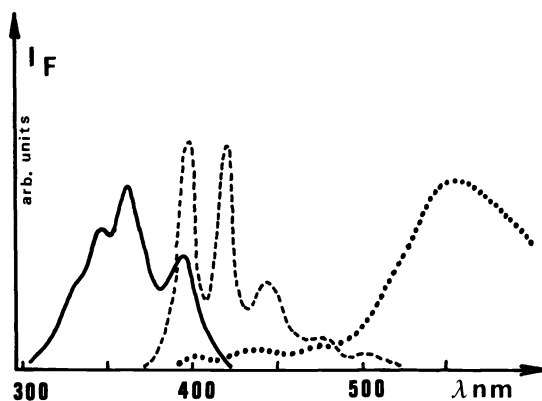


Fig. 5 - Fluorescence spectrum of the cleaved photocyclomer (VIa₂) in MCH glass at 77K (.....); excitation spectrum of the excimer (———). Spectrum obtained after softening the glass and refreezing at 77K (-----). Corrected spectra.

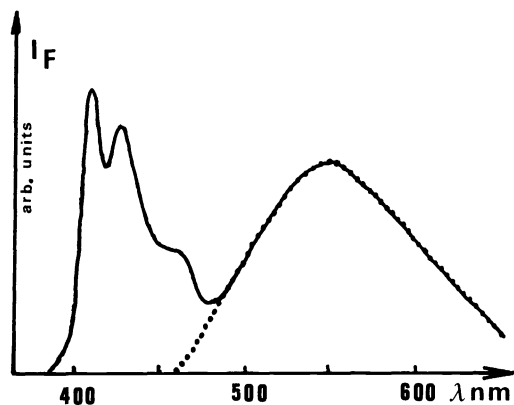
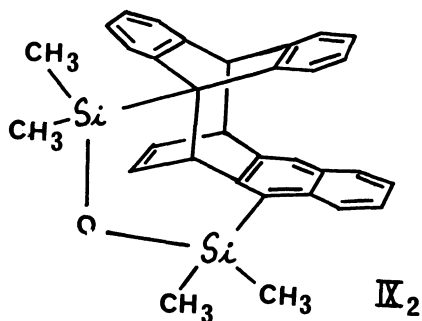
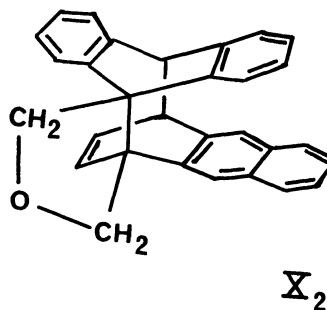


Fig.6 - Fluorescence spectrum of VI d₁ (———) Intramolecular excimer fluorescence (.....) $\lambda_{max} 550 \text{ nm}$. Solvent MCH; 20°C; conc. ca $5 \times 10^{-5} \text{ M}$. Corrected spectra.

Fig. 7 - Photocyclomer of IX₁Fig. 8 - Photocyclomer of X₁

Let us note that the hypochromicity (U.V. absorption intensity of the bichromophore compared to the model) of VIa₁ is certainly less important than claimed (28,29) (a check of the U.V. spectrum of 9-methoxymethylanthracene showed ϵ (383 nm) \approx 9,000 instead of 13,300) and it is possible that the other bichromophores do not exhibit large hypo or hyperchromism).

It was tempting to compare the photoreactivity of VIa₁ with that of the sulfur analog (VIII₁) which does not cyclomerize but splits out into anthrylmethyl radicals (36).

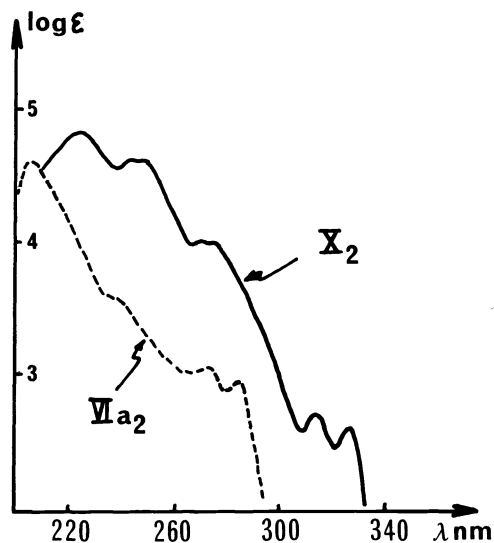
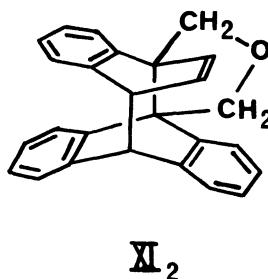


Fig. 9 - Electronic absorption spectra of IVa₂ (4 ortho-xylene chromophores) and X₂ (2 ortho-xylene and one 2,3-dimethyl naphthalene chromophores).

Fig. 10 - Photocyclomer of XI₁

By irradiation in degassed benzene (3×10^{-3} M), the amide VII₁ gave a mixture of photocyclomer VII₂ and an insoluble polymer (likely a dimer) which were separated and characterized by spectroscopic methods (17). Easy formation of a polymer (dimer), even at conc. ca 5×10^{-4} M, in competition with the photocyclomer, may be ascribed to the presence of intermolecular associations due to H bonds (17).

II₂ - α, ω -bis(-9 anthryl) n-alkanes.

In table 2 we have collected results concerning the first α, ω -bis(-9 anthryl) n-alkanes XIII, namely A-C₁-A, A-C₂-A and A-C₃-A and we observe they efficiently photocyclomerize. But, in their fluorescence spectra in methylcyclohexane (MCH) or benzene at room temperature it was not possible to detect intramolecular fluorescence (26,37). Increasing the number of -CH₂- links was expected to reduce the reactivity of the system, and consequently, favor intramolecular excimer fluorescence. Indeed, a study of α, ω -bis(-1 pyrenyl) n-alkanes (38) had shown the general occurrence of this type of fluorescence, even for long chains. A number of studies on the photophysics of bisaryllalkanes (40) (mainly propanes) and (dimethyl-

-amino n-alkanes (C₁-C₁₃ and C_{16,18,20}) have been published (41). A systematic study of α, ω bis(-9 anthryl) alkanes should reveal different properties of the chain, since the required intermolecular distance to form a photocyclomer is much smaller than that of an excimer.

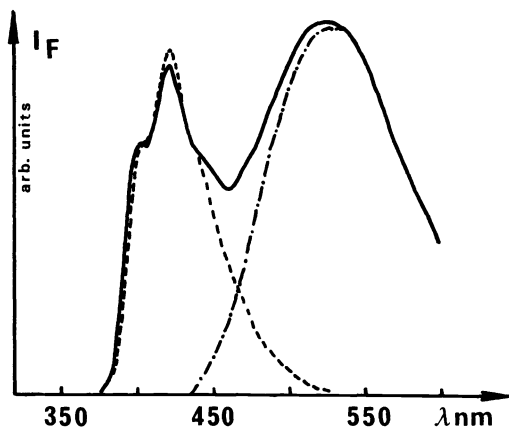


Fig. 11 - Corrected fluorescence spectra of IX₁(—) and of 9-trimethylsilylanthracene (-----) taken as the model compound. Difference spectrum (·····) is that of excimer emission (MCH ; 20°C ; 5 x 10⁻⁵M).

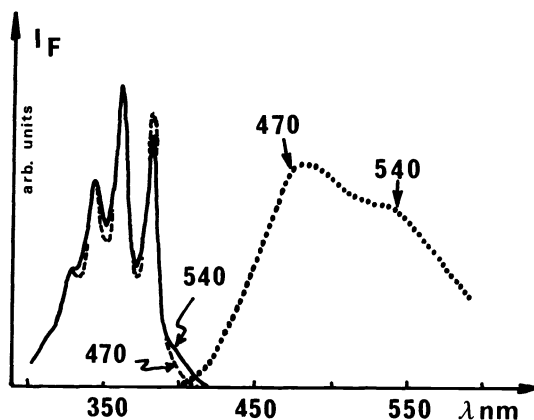


Fig. 12 - Corrected spectrum of cleaved photocyclomer IX₂ in MCH at 77K (·····); excitation spectra observed at emission wavelength of 470 nm (-----) and 540 nm (—).

In addition to -1,1' and -2,2' bisanthracenes (25) let us note papers dealing with A-C₁-A (26), A-C₂-A (26,27) A-C₃-A (42,44), A-C₄-A (42,43), A-C₆-A and A-C₁₂-A (44). We have investigated α, ω bis(-9 anthryl) n-alkanes (XIII, ethane to decane) and bis (-9 anthryl) meta-xylylene (A-mXy-A) (XIV) as well as the reference monomeric compounds 9-ethyl, 9-n-hexyl, 9-n-decyl and 9-(metatoluylmethyl)anthracenes (respectively termed 9-EtA, 9-HexA, 9-DecA and 9-mXyA). We have measured fluorescence and reaction quantum yields under steady state illumination and lifetimes by single photon counting in MCH and EtOH at room temperature (37). Fluorescence decays were analysed separately at two wavelengths : 391-394 nm ("monomer emission") and 530-540 nm (excimer emission). The monomer and excimer fluorescence response functions are assumed to be respectively the following (1) :

$$i_M(t) = C_M \left\{ \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) \right\}$$

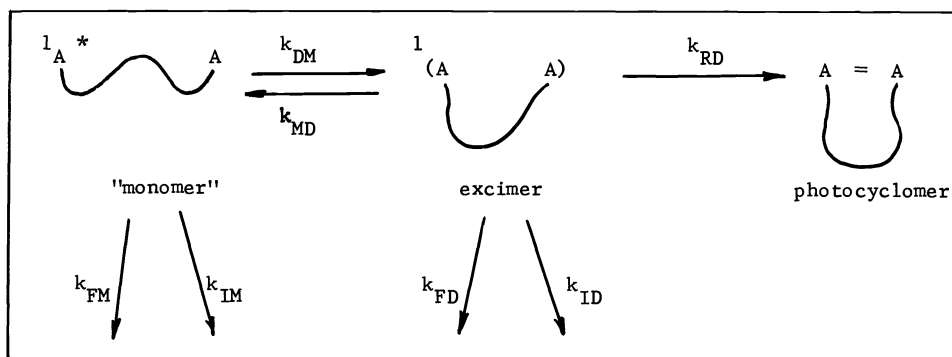
$$i_D(t) = C_D \left\{ \exp(-\lambda_1 t) - b \exp(-\lambda_2 t) \right\}$$

The fluorescence decay at ca 392 nm was most often best described by a biexponential which allowed the derivation of λ_1 , λ_2 and B (for A-C₃-A, we observed a monoexponential decay and A-C₇-A did not give us a good fit between experimental and computed curves). The excitation spectra of the short (391-394 nm) and long (530-540 nm) wavelength fluorescence emissions were identical. The four reference compounds gave a monomer fluorescence emission with a monoexponential decay which provided k_M values; from their fluorescence quantum yields, we deduced k_{FM} . As in the intermolecular case (2b) and in agreement with Ferguson's (45) and De Schryver's (25) results, we postulate the intermediacy of an excimer (scheme 3) although we cannot completely discard a possible competition between excimer and photocyclomer formation (scheme 4). The rate parameters k_{DM} , k_{MD} , k_D are obtained from the transient kinetic data (λ_1 , λ_2 , B) and k_M (ref. compounds) with the assumption that k_{FM} and k_{IM} are those of the model compounds. (This may not be quite true for A-C₂-A). For small values of $1/\lambda_1$ and when λ_1 and λ_2 are close to each other, there are difficulties in getting very accurate values of λ_1 , λ_2 and B and one should consider the rate parameters with some caution. k_{FD} and k_{RD} were obtained from the following equations : $k_{FD} = \Phi_{FD} \times W/k_{DM}$;

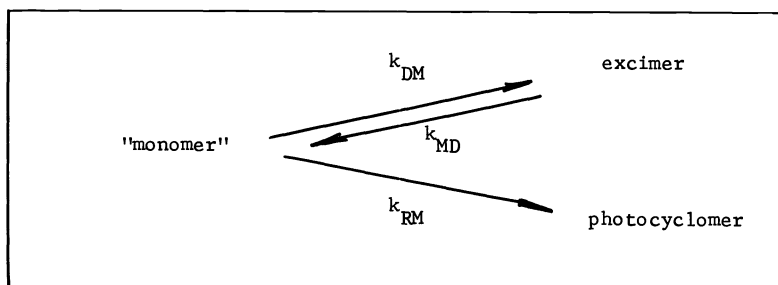
$$k_{RD} = \Phi_{RD} \times W/k_{DM} \text{ with } W = k_D k_M + k_{MD} k_M + k_{DM} k_D.$$

An example of fluorescence spectra in MCH (A-C₁₀-A) is depicted in fig. 13 where an intramolecular excimer fluorescence is observed and this corresponds to a low photochemical reactivity (table 3). The photocyclomers of A-C₂-A (27), A-C₃-A (42b) and A-C₄-A (43) have a classical dianthracene structure (fig.14) as well as for A-C₁₀-A but the other bis(-9 anthryl)n-alkanes we have examined lead to a mixture of cyclomers. A selection of physical and kinetic data obtained in MCH is given in table 3. (Results in EtOH show similar trends with higher values for k_{DM}). The ratio Φ_{FD}/Φ_{FM} is usually taken as a probe of the conformational properties of the bichromophores (1,31,38,41). We observe an irregular periodicity with maxima for A-C₅-A and A-C₉-A (fig.15) which is in contrast to those of bis-1-pyrenes (38) and bis-(dimethylamino)alkanes (41). Of note is the absence of detection of an excimer fluorescence in the spectrum of A-C₃-A in our conditions, even by single photon counting, in

contrast to other bisarylpropanes (46,47) or the bis(dimethylamino)propane (41) for which Φ_{FD} is a maximum. The photoreactivity of A-C₃-A is a partial explanation for this difference. The case of A-C₂-A is not simple. In keeping with previous observations (26,48), we could not detect an excimer fluorescence in the fluorescence spectrum but the fluorescence decay at 394nm does not correspond to a single exponential but to a biexponential with a contribution of an emitting species of whom the decay was observed at 540 nm; the latter behaves kinetically like an excimer with a lifetime of 3 ns. The bisarylalkanes are a mixture of interconverting conformers, each of which having a different reactivity; therefore k_{DM} may be an apparent rate constant and must be taken as an approach to the knowledge of dynamical properties of the chains. The salient feature is the high values of k_{DM} of A-mXy-A compared with that of A-C₅-A, due to the role of the rigid hinge between the two chromophores (fig. 16).



Scheme 3 - Kinetic scheme of photocyclomer formation through intramolecular excimer. $k_M = k_{FM} + k_{IM}$; $k_D = k_{FD} + k_{ID} + k_{RD}$; k_{RD} and k_{FD} of table 3 were calc. according to this scheme.



Scheme 4 - Kinetic scheme in which photocyclomerization is in competition with intramolecular excimer formation.

It is interesting to consider k_{DM} of bisarenes with the same chain and different terminal groups (table 4) obtained by others (25,46,47). Of note also is the generally large value of k_{MD} (except for $n = 4,5,6$) which correspond to high values of k_{FD} consistent with weak excimer stability (47). The reactivity rate parameters k_{RD} regularly decrease from $n = 2$ to $n = 4$ and then abruptly to $n \gg 5$. It reflects the strain experienced by the system when the two rings get to a bonding distance. A-mXy-A is a remarkable example of a significant difference between the rate constant to reach the excimer state ($\approx 10^9 \text{ s}^{-1}$) and a low cyclomerization rate ($\approx 10^4 \text{ s}^{-1}$). In a parallel study a temperature dependent analysis of these systems has been done (49).

II₃ - Photocrowns (photocyclomers of bis-(9 anthryl) polyoxa-n-alkanes).

X-ray structure analysis has shown that, in contrast to the planar zig-zag arrangement of a polymethylene chain, a polyethylene oxide chain has a helical structure in the crystalline state (50). It has also been shown experimentally and by calculations that, in organic solvent, the lowest energy structure of the polyethylene oxide resembles approximately the helical conformation occurring in the crystal (50). We anticipated that linking two anthracene rings by these chains would greatly facilitate photocyclomerization; moreover, these systems would provide the first photochemical synthesis of crown-ethers (50). Indeed compounds XV₁ ($n = 1-4$) (chart 2) smoothly led to their photocyclomers XV₂ ($n = 1-4$) but the latter are thermally unstable at room temperature (fig.17). We have measured the rates of thermal dissociation (table 5); it appears that an enlargement of the polyoxacyclane increases the thermal stability. Addition of salts (v.g. alkali metal perchlorates) does not change the cyclomerization quantum yield but considerably increases the thermal stability of the cyclomers which become "cation locked". Then, heating of the solids XV (M⁺) does not regenerate the open form (XV). Unlocking is performed by shaking XV₂ with a polar solvent such as CH₃CN.

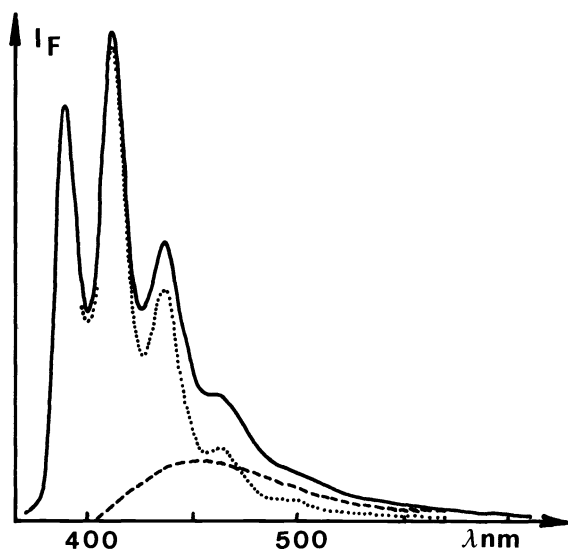


Fig.13 - Corrected fluorescence spectra of A-C₁₀-A (—) and 9-Dec-A (.....) in MCH at 20°C ($\lambda_{exc.}$: 366nm; $\approx 10^{-5}$ M). The excimer spectrum (-----) is obtained by difference of A-C₁₀-A and the ref. compound normalized at the first vibronic band.

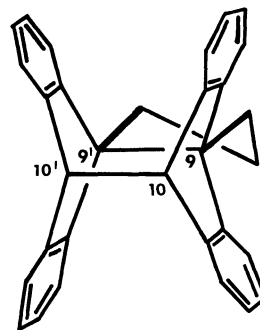


Fig. 14 - Structure of photocyclomer XIII₂ (n = 3) (ref. 42b).

Table 3 - Monomer (Φ_{FM}), excimer (Φ_{FD}) fluorescence and reaction (Φ_R) quantum yields. Rate parameters of α, ω -bis(9 anthryl)alkanes calculated according to scheme 3. (Solvent : MCH 20°C).

Compounds	k_{DM}	k_{MD}	k_D	k_{FD}	k_{RD}	Φ_{FM}	Φ_{FD}	Φ_R	$\lambda_{max.}$
	$(10^6 s^{-1})$				$(10^4 s^{-1})$	exp	exp	(366nm) (10^{-4})	Excimer nm
A-C ₂ -A	580 ^a	270 ^a	355 ^a	59 ^a	13,830 ^a	0.22 ^b	0.10 ^b	2,400	
A-C ₃ -A						0.47		1,400	
A-C ₄ -A	46	3	89	8	2,600	0.34	0.02	610	550-560
A-C ₅ -A	96	10	9	7	5	0.31	0.16	11	490
A-mXy-A	1,080	67	8	11	3	0.21	0.47	13	470
A-C ₆ -A	14	12	9	18	30	0.38	0.06 ₆	11	490-500
A-C ₇ -A						0.37		12	460
A-C ₈ -A	58	110	66	89	20	0.33	0.14	11	450
A-C ₉ -A	62	77	65	112	27	0.30	0.21	6	450
A-C ₁₀ -A	37	117	11	52	27	0.39	0.08 ₄	4	450

a) approximate values due to uncertainties on λ_1 and λ_2 and on "monomer" rate parameters.

b) calculated from Φ_{FM} exp. and rate parameters obtained from transient kinetic analysis (monomer fluorescence decay is biexponential).

A mechanistic study similar to that has been described for bis (9-anthryl) alkanes was achieved (solvent benzene) and the main results are collected in table 5. One can see that these systems have a fairly high reactivity (k_{RD}) for long chains, especially in comparison with bis (9-anthryl)n-alkanes except A-C₂-A and A-C₄-A and this in keeping with the expected properties of the chain. Compounds XV also exhibit excimer fluorescence. In order to generate fluorescent probes in the series, we prepared two 10-substituted derivatives (XVI and XVII). The first one is a very interesting compound, under current investigation, which probably forms two excimers at room temperature and two or more photoproducts, one of them by 9-1' closure. The second derivative (XVII) is also photoreactive, generating an unsymmetrical photocyclomer (9-1' closure characterized by U.V. absorption) with a low quantum yield. In line with crown-ethers synthesis, we prepared the anthracenophane XVIII (n = 1) for the selective complexation of lithium cations (fig.18). Shortly after appeared a report of the synthesis of XVIII (n = 2) (52) designed for the complexation of sodium cations. The authors found a thermal dissociation rate constant of $\approx 1.2 \times 10^{-3} s^{-1}$ at 30°C for the photocyclomer of XVIII (n = 2); compare with $k_{diss} \approx 5.8 \times 10^{-3} s^{-1}$ at 20°C for XVIII (n = 1) (table 5).

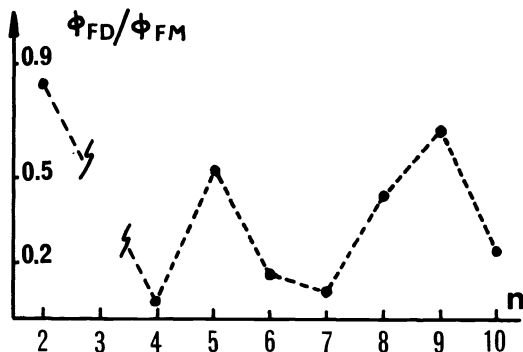


Fig. 15 - Variation of the ratio excimer/monomer fluorescence quantum yields (Φ_{FD}/Φ_{FM}) with the number of methylenes (n) of the chain in MCH, at 20°C.

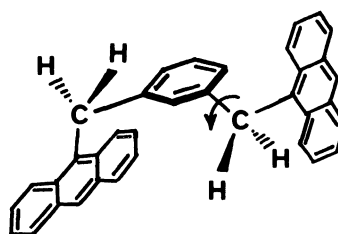


Fig. 16 - Schematic representation of a conformer of XIV_1 ; the rigid metaxylylene hinge favors the excimer formation.

Table 4 - Rate constant (k_{DM}) of intramolecular excimer formation of 1,3-bisarylpropanes at room temperature. CH : cyclohexane MCH : methylcyclohexane.

Chromophore	Phenyl	2-Naphthyl	N-Carbazolyl	2-Anthryl	1-Pyrenyl	1-Biphenyl
$k_{DM}(10^6 \text{ s}^{-1})$	1.100	300	280	170	123	73
solvent (ref)	CH (46)	MCH (47)	CH (46)	MCH (25)	MCH (47)	MCH (47)

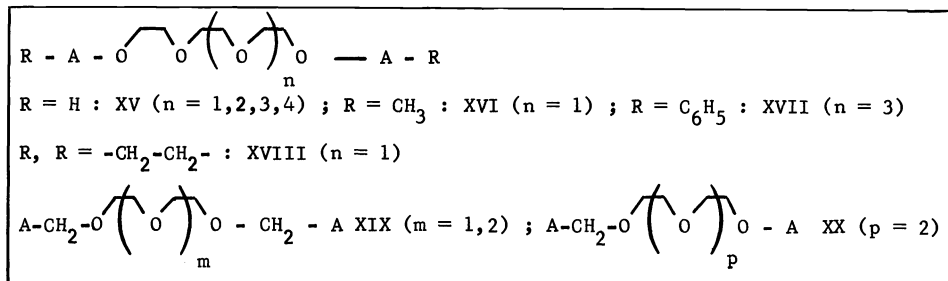


Chart 2 - Schematic formulae of the α, ω bis(-9 anthryl) polyoxaalkanes investigated. "A" represents 9-anthryl or 9,10-disubstituted anthracenes; R groups are located in position 10.

We also measured the monomer and excimer lifetimes and the fluorescence and cyclomerization quantum yields of XVIII ($n = 1$) (table 5).

Thermal instability being probably due to electrostatic repulsion between the oxygen atoms, we prepared compounds XIX ($m = 1, 2$) where the anthracene rings are linked to a methylene group rather than an oxygen atom. In fact, the photocyclomers were found more stable (see k_{diss} , table 5) but slowly reverted to the open form at room temperature. A still more important improvement of the stability of photocrowns was obtained by the synthesis of the dissymmetrical XX (designed to get a methylene group facing an oxygen atom) as one can observe in table 5 (see also fig.20).

Of note is the contrast between XIX ($m = 1$) and XIX ($m = 2$). The first forms an intramolecular excimer with a high rate constant ($2 \times 10^9 \text{ s}^{-1}$) and exhibits a high ratio Φ_{FD}/Φ_{FM} (fig.19) and a relatively low k_{RD} ($\approx 10^6 \text{ s}^{-1}$); the second has lower excimer lifetime and Φ_{FD} although a much higher reactivity ($k_{RD} \approx 79 \times 10^6 \text{ s}^{-1}$). Another result which emerges from table 5 (see also table 3) is that there is no direct relationship between excimer wavelength and stability when the chain influence is so important.

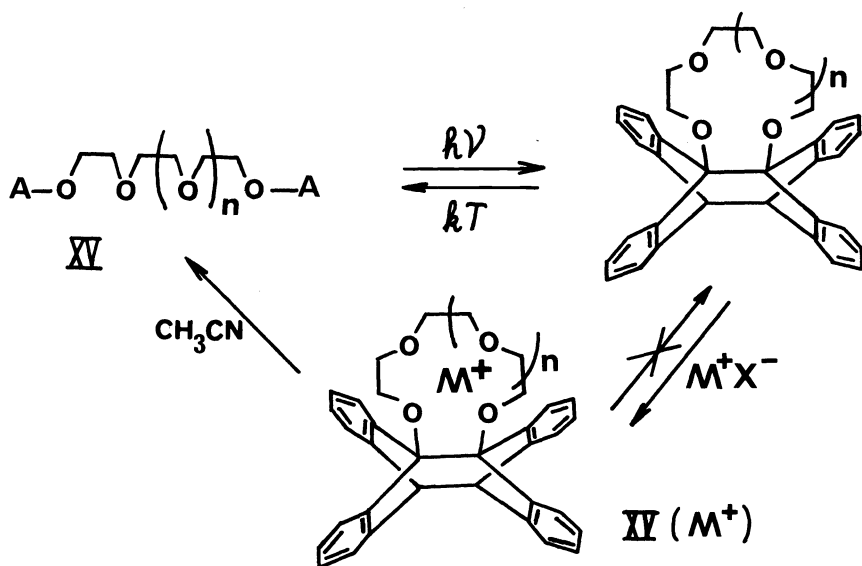


Fig. 17 - Photochemical synthesis of crown-ethers with four to seven oxygens. Thermal stability is gained by cation complexing. $XV (M^+)$ readily revert to the open form by competing solvation with a polar solvent.

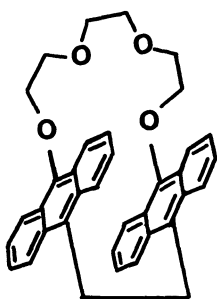


Fig. 18 - [2,10] 1,9-anthracenophane XVIII ($n = 1$) m.p. : 233-234°C; for other physical data see table 5.

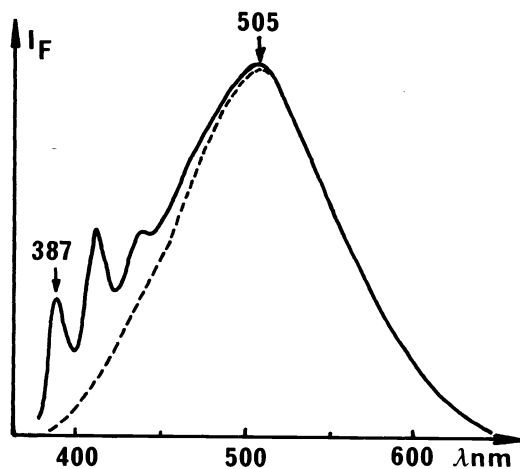


Fig. 19 - Corrected fluorescence spectrum of 1,9-bis(9-anthryl)-2,5,8-trioxanonane (XIX $m = 1$) in MCH; 20°C; $10^{-5}M$. See table 5. Excimer fluorescence spectrum (-----) λ_{max} : 505 nm.

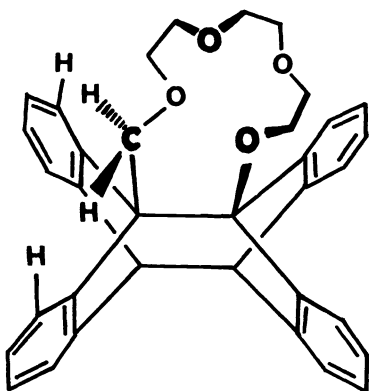


Fig. 20 - Possible conformation of the photocyclomer of XX (dissymmetrical photocrown).

Table 5 - Monomer (Φ_{FM}), excimer (Φ_{FD}) and cyclomerization (Φ_R) quantum yields; rate parameters of α, ω bis(-9 anthryl) polyoxaalkanes calculated according to scheme 3. Temperature : 20°C.

Compounds	k_{DM}	k_{MD}	k_D	k_{FD}	k_{RD}	Φ_{FM}	Φ_{FD}	Φ_R	λ_{max}	thermal
	10^6 s^{-1}			(10^4 s^{-1})		exp	exp	(10 ⁻⁴)	excim. (nm)	k.diss. (10 ⁻⁶ s ⁻¹)
^a XV n = 1	570	5	111	3.5	3,500	0.10	0.023	2,600	470	5,800
^a XV n = 2	540	10	111	2.5	3,400	0.10	0.015	2,500	470	300
^a XV n = 3	420	5	103	2.1	2,900	0.10	0.01	2,150	510	370
^a XV n = 4	310	22	111	1.8	3,200	0.17	0.01	2,000	510	230
^b XVIII n=1 ^c						0.095	0.053	1,750		5,800
^b XIX m = 1 ^d	2,050	6	15	5.3	104	0.024	0.18	450	505	147
^b XIX m = 2 ^d	946	13	245	5.6	7,880	0.034	0.01	1,700	540	146
^b XX p = 2						0.034	0.004	1,900	530	3

a) solvent : benzene ; ref cpd. was A-(O(CH₂)₂)₃-OCH₃ ; b) solvent : MCH ; c) $1/\lambda_1 = 2.7 \text{ ns}$; $1/\lambda_2 = 5.5 \text{ ns}$; B = 0.08 ; d) ref. cpd. A-CH₂-O-CH₃ ($\Phi_{FM} : 0.088$, $\tau_M = 1.25 \text{ ns}$ in MCH).

SUMMARY AND CONCLUSION

We have examined the anthracene ring as a representative of aromatic molecules which undergo excimer formation and photodimerization, there being a connecting thread between the early studies of photochemistry of anthracenes and the present approach to the knowledge of bichromophoric interactions. The problem of photodimerization can be considered in terms of increasing intramolecular or external constraints.

1° In fluid solutions, anthracene can take any mutual orientations to form the photodimer. Under these experimental conditions, the intermediacy of an excimer seems very likely (as it was demonstrated in a dianthracene matrix where $k_{RD} \approx 5 \times 10^8 \text{ s}^{-1}$ (45)) and the rate constant of collapse to the photodimer should be of the order of $1 \times 10^8 \text{ s}^{-1}$.

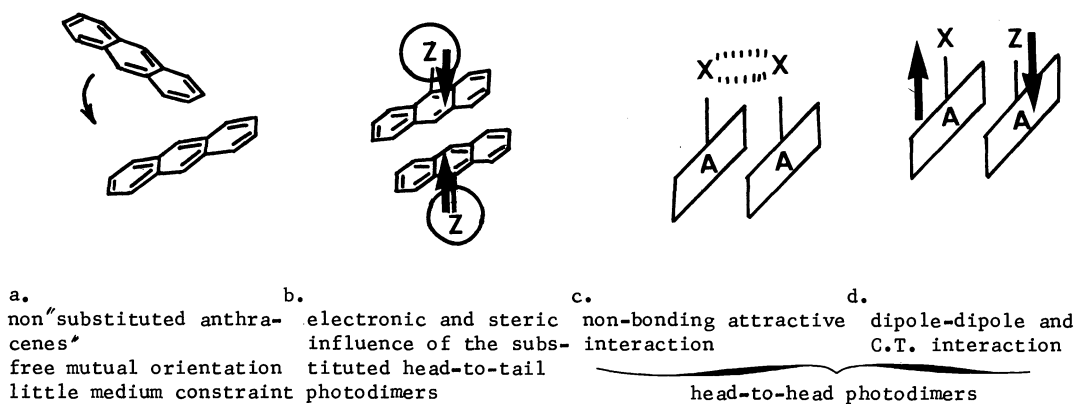


Fig. 21 - Schematic representation of the mutual orientation of the two rings in the intermolecular photodimerization of anthracenes in fluid solution.

2° The steric, electronic and electrostatic properties of the substituent (especially in position 9) force the rings to a mutual head-to-tail orientation, unless some special non bonding interactions between the substituents compete towards a head-to-head structure (fig.21). When the substituents are different (one is electron-donor and the other electron-acceptor) and not too bulky, the head-to-head orientation may be exclusive (fig. 21d).

3° In bis-9-anthracenes, the reactivity of the two terminal groups is governed by the

flexibility of the chain. The rate of excimer collapse to photocyclomer is high for 1,2-(bis-9 anthryl)-ethane ($k_{RD} \approx 1.4 \times 10^8 \text{ s}^{-1}$ in MCH) and decreases abruptly as the chain length increases. k_{RD} depends on the excimer conformation and on the non bonding interaction in the cyclic transition state (fig. 22) and does not show the same pattern as k_{DM} . In certain cases the chain may alter the mode of cycloaddition, ring closure occurring by the 9-1' and 10-4' positions exclusively (29) or in competition with the usual 9-9' reactivity (A-C₅-A to A-C₉A and A-mXy-A). (For comparison of k_{RD} values see table 6).

Table 6 - Rate constants of photodimer or photocyclomer formation from an excimer intermediate at room temperature. Some are estimated values (see text and other tables).

Compound	Solvent	k_{RD} (10^6 s^{-1})
A	dianthracene crystal	500 ^a
A	benzene	120
DMA	benzene	0.02
A-C ₂ -A	MCH	140 ^b
XV n = 1	benzene	35
9-A-CH ₂ -O-CH ₂ -Np1	MCH	38
XIX (m = 1)	MCH	1
XIX (m = 2)	MCH	79

a) extrapolated at room temperature (Ref.45); b) tentative value; see table 3

The polyoxyethylene chains of α,ω (bis-9 anthryl) polyoxaalkanes undergo less severe strain by cyclization and the rate parameters k_{DM} and k_{RD} are high even if the photocyclomers are thermally unstable. Conversely, the rate parameters (tables 3-5) can give informations about the dynamical properties of the chains or the physical properties (v.g. viscosity) of the medium.

It is possible to increase the constraint by including the bichromophores into a rigid matrix at low temperature or by forming a cyclophane (fig.23b). Ferguson, in particular, is studying this aspect (43).

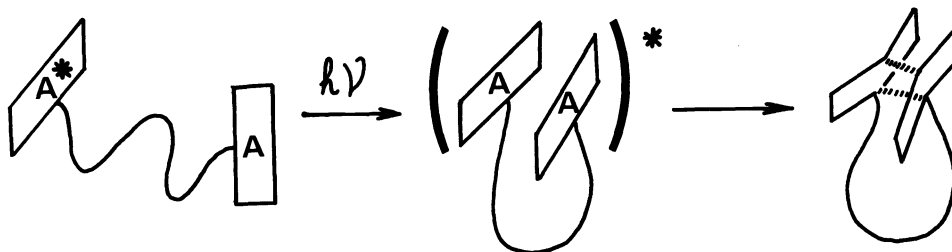


Fig. 22 - Chain controlled photocyclomerization of bis-9-anthracenes in fluid solution.

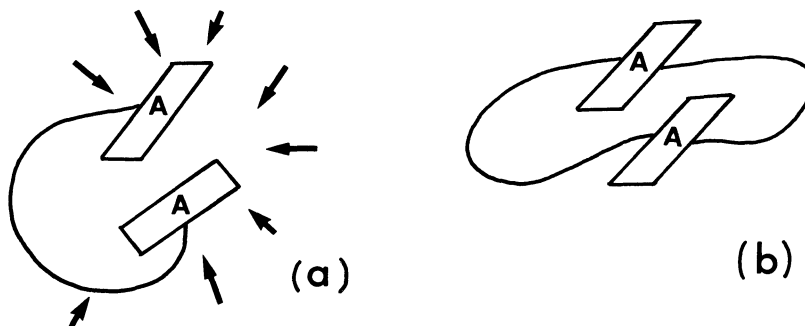


Fig. 23 - Chain + matrix (a) or double chain (b) controlled photocyclomerization of bis-9-anthracenes.

Acknowledgements - We are grateful to the CNRS, the Ministère de l'Education Nationale and the DGRST for financial support. We are particularly indebted to Drs. Lapouyade, Lesclaux, Ewald, Soullignac and Mr. Bitit for valuable assistance in several aspects of this

work. We express our best thanks to Dr. J.M. Ferguson for providing some samples and results prior to publication and to Prof.R.S. Davidson, visiting professor, for his assistance in the English version of the manuscript. Last, but not least, we would like to express our gratitude to Prof. J. Jousset-Dubien, Correspondant de l'Institut, for his enthusiastic direction of the Bordeaux Photochemistry Team.

REFERENCES

1. a) Photophysics of Aromatic Molecules, J.B. Birks, Wiley, London, 1970. b) Organic Molecular Photophysics, J.B. Birks, Wiley, London, 1 (1973), 2 (1975).
2. Photocycloaddition des hydrocarbures aromatiques polynucléaires en solution.
a) Part I - A. Castellan, R. Lapouyade and H. Bouas-Laurent, Bull.Soc.Chim.Fr. 201-209 (1976). b) Part II - A. Castellan, R. Lapouyade and H. Bouas-Laurent, Ibid, 210-216 (1976). c) Part III - A. Castellan, G. Dumartin, R. Galante and H. Bouas-Laurent, Ibid, 217-222 (1976). d) Part IV - A. Castellan, G. Dumartin and H. Bouas-Laurent, Tetrahedron, 36, 97-103 (1980). e) Part V - R. Lapouyade, A.Nourmamode and H. Bouas-Laurent, Tetrahedron, 00, 000 (1980). f) A. Castellan, C.R. Acad.Sc., 281C, 221-224 (1975).
3. J-P. Desvergne, H. Bouas-Laurent, R. Lapouyade, J. Gaultier, C. Hauw and F. Dupuy, Mol. and Liquid Cryst. 19, 63-85 (1972).
4. H. Bouas-Laurent, R. Lapouyade, A. Castellan, A. Nourmamode and E.A. Chandross, Z.f.Phys. Chem., N.F. 101, 39-44 (1976).
5. A. Castellan, R. Lapouyade, H. Bouas-Laurent and J.Y. Lallemand, Tetrahedron Letters, 2467-2470 (1975).
6. R. Lapouyade, A. Castellan and H. Bouas-Laurent, Tetrahedron Letters, 3537-3540 (1969).
7. H. Bouas-Laurent and R. Lapouyade, J.C.S. Chem. Comm., 817-818 (1969).
8. H. Bouas-Laurent and A. Castellan, J.C.S. Chem. Comm., 1648-1649 (1970).
9. I. Fritzsche, J. Prakt. Chem. 101, 333 (1867).
10. D.O. Cowan and R.L. Drisko, Elements of Photochemistry, Plenum Press, New York (1976). The authors have used the photochemistry of anthracenes as models to illustrate a chapter of their book.
11. M. Ehrenberg, Acta Crystallogr. 20, 177-182 (1966) ; B 24, 1123-1125 (1968).
12. D.A. Dougherty, W. Douglas Hounshell, H.B. Schlegel, R.A. Bell and K. Mislow, Tet.Letters 3479-3482 (1976).
13. R. Calas and R. Lalande, Bull. Soc. Chim. Fr., 763-769 (1959) ; 770-772 (1959).
14. a) R. Lalande and R. Calas, Bull. Soc. Chim. Fr., 144-147 (1960).
b) F.D. Greene, Bull. Soc. Chim. Fr. 1356-1360 (1960).
15. H. Bouas-Laurent and C. Leibovici, Bull. Soc. Chim.Fr., 1847-1848 (1967).
16. F.C. De Schryver, L. Anand, G. Smets and J. Switten, Polym. Letters, 9, 777-780 (1971).
17. Unpublished results by G. Felix, J. Parrot, H. Bouas-Laurent et al.
18. T.M. Vember, T.V. Veselova, I.E. Obyknovennaya, A.S. Cherkasov and V.I. Shirokov, Izvest. Akad. Nauk, S.S.S.R., Ser. Fiz. 37, 837 (1973) and ref. therein.
19. D.O. Cowan and W.W. Schmiegel, J. Am. Chem. Soc., 94, 6779-6788 (1972).
20. a) E.J. Bowen, Advances in Photochem., Noyes, Hammond and Pitts Jr., Wiley, New York 1, 23-42 (1963). b) H.L.J. Bäckström and K. Sandros, Acta Chem. Scand. 12, 823 (1958).
c) S.M. de B. Costa and E.C.C. Melo, J.C.S. Faraday II, 76, 1-13 (1980).
21. a) B. Stevens and J.T. Dubois, Trans Faraday Soc. 62, 1525 (1966) b) E.A. Chandross and C.J. Dempster, J. Am. Chem. Soc. 92, 3586-3593 (1970).
22. J.K. McVey, D.M. Shold and N.C. Yang, J. Chem. Phys. 65, 3375-3376 (1976).
23. V. Yakhot, M.D. Cohen and Z. Ludmer, Advances in Photochemistry, Pitts, Hammond, Gollnick and Grosjean, Wiley New-York, 11, 489-523 (1979).
24. F.C. De Schryver, N. Boens and J. Put, Advances in Photochemistry, Pitts, Hammond and Gollnick, Wiley New York, 10, 359-465 (1977).
25. F.C. De Schryver, N. Boens, J. Huybrechts, J. Daemen, M. De Brackeleire, Pure and Appl. Chem. 49, 237-247 (1977).
26. W.R. Bergmark, G. Jones II, Th. E. Reinhardt and A.M. Halpern, J. Am. Chem. Soc. 100, 6665-6673 (1978).
27. B.F. Anderson, J. Ferguson, M. Morita and G.B. Robertson, J. Am. Chem. Soc., 101, 1832-1840 (1979) and references therein.
28. A. Castellan, J-M. Lacoste and H. Bouas-Laurent, J. Chem. Soc. Perkin II, 411-419 (1979).

29. A. Castellan, J-P. Desvergne and H. Bouas-Laurent, Nouv. J. Chim. **3**, 231-237 (1979).
30. J. Dale, Tetrahedron **30**, 1683-1694 (1974).
31. M. Goldenberg, J. Emert and H. Morawetz, J. Am. Chem. Soc. **100**, 7171-7177 (1978).
32. a) R.S. Davidson and T.D. Whelan, J.C.S. Chem. Comm. 361-362 (1977).
b) R. Todesco, J. Gelan, H. Martens, J. Put, N. Boens and F.C. De Schryver, Tet. Letters 2815-2818 (1978).
33. D. Georgescauld, J-P. Desmazes, R. Lapouyade and M.A. Winnik, Photochem. Photobiol., in the press.
34. Unpublished results of J-P. Desvergne et al.
35. G. Felix, R. Lapouyade, H. Bouas-Laurent and B. Clin, Tet. Letters, 2277-2278 (1976).
36. A. Couture, A. Lablache-Combier, R. Lapouyade and G. Felix, J. Chem. Res. (S) 258-259 (1979) (M) 2887-2897 (1979).
37. A. Castellan, J-P. Desvergne and H. Bouas-Laurent, Chem. Phys. Letters, accepted for publication.
38. K. Zachariasse and W. Kühnle, Z. für Phys. Chem. N.F. **101**, 267-276 (1976).
39. E.A. Chandross, J. Chem. Phys. **43**, 4175 (1965).
40. For a review of the photophysics of bisarylalkanes see ref. 37, 38 and 41.
41. A.M. Halpern, M.W. Legenza and B.R. Ramachandran, J. Am. Chem. Soc., **101**, 5736-5743(1979)
42. a) M. Daney, R. Lapouyade, G. Felix and H. Bouas-Laurent, F.P. (Anvar) Appl. 75/18, 558 ; June 13, 1975 ; C.A. **87**, 690, 134837 h. (1977).
b) A. Dunand, J. Ferguson and G.B. Robertson, in the press.
43. A. Dunand, J. Ferguson, M. Puza and G.B. Robertson, J. Am. Chem. Soc. **102**, 3524-3530 (1980).
44. T. Kobayashi, S. Nagakura and M. Szwarc, Chem. Phys. **39**, 105-110 (1979).
45. J. Ferguson and A.W.H. Mau, Mol. Phys. **27**, 377-387 (1974).
46. W. Klöpffer in ref. 1 b) vol. 1, 357-402.
47. K.A. Zachariasse, W. Kühnle, A. Weller, Chem. Phys. Letters, **59**, 375-380 (1978).
48. T. Hayashi, T. Suzuki, N. Mataga, Y. Sakata and S. Misumi, J. Phys. Chem. **81**, 420-423 (1977).
49. J. Ferguson, Chem. Phys. Letters, accepted for publication.
50. J-P. Desvergne and H. Bouas-Laurent, a) J.C.S. Chem. Comm., 403-404 (1978) and ref. therein. b) Israel J. Chem., N° 3-4, 220-226 (1979) and ref. therein.
51. J-P. Desvergne, A. Castellan and R. Lesclaux, Chem. Phys. Letters, **71**, 228-231 (1980).
52. I. Yamashita, M. Fujii, T. Kaneda, S. Misumi and T. Otsubo, Tet. Letters **21**, 541-544 (1980).