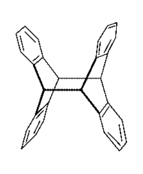
Photodimerization of anthracenes in fluid solutions: (part 2) mechanistic aspects of the photocycloaddition and of the photochemical and thermal cleavage†



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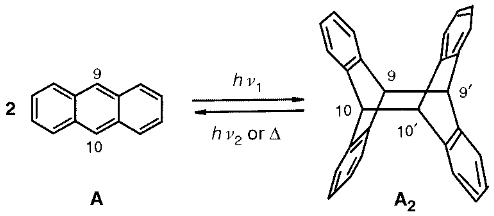
One of the classics in photochemistry, the photodimerization of anthracenes can be considered as a paradigm of the photocycloaddition of non saturated hydrocarbons. The historical steps of the mechanistic studies are reviewed: based on fluorescence quenching, cyclization quantum yields measurement, the influence of dioxygen and solvents, they support a singlet state pathway; the dimerization rate constants are found to be generally high for reactions occurring within a few nanoseconds unless they are slowed down or inhibited by steric strain. In several cases, excimers have been demonstrated to be intermediates and it is shown that excimer fluorescence and cyclization are competitive processes. Another intermediate known as pericyclic minimum (or conical intersection) is postulated to form a sort of floppy cycloadduct where the reacting centres are at mutual distances shorter than in excimers and longer than in dimers. For intermolecular dimerizations, the triplet state is also reactive but through triplet–triplet annihilation in dilute solutions. Intramolecular photocycloadditions have also been carefully examined, for the role of multiple excimer formation, regioselectivity (9,10 : 1′,4′ and 9,10 : 1′,2′ cyclization) and solvent polarity. The triplet state reactivity is shown to lead to 4π + 2π or 4π + 4π cycloadducts, depending on geometric factors. In the latter case when intersystem crossing is favoured by the substituents, cyclization quantum yields as high as 0.65–0.72 have been observed. Photodissociation quantum yields are generally high and the reactions are partly adiabatic, leading to excimer and monomer fluorescence, but the major part follows another pathway not fully elucidated by flash photolysis. Thermodynamic and kinetic parameters for the thermal cleavage are given; they reveal a large gamut of stability for the photocycloadducts.

1 Introduction

The late 1950s marked the beginning of a new era in photochemistry because of the systematic investigation of photochemical reactions in relation to singlet and triplet excited state reactivity, fluorescence and phosphorescence quenching, influence of the reaction phase, flash photolysis, actinometry…. These studies led to a better understanding of mechanisms.

Photodimerization which is of special interest in synthesis has been the object of extensive studies.[1–3,10] One of the oldest known photodimerizations is that of anthracene[1–12] outlined in Scheme 1.



Scheme 1 The 'classical' photodimerization of anthracene (A) ; the photodimer (A_2) reverts to monomers by photochemical or thermal dissociation ; this reaction is undergone by many mono and polysubstituted derivatives of anthracene.[1]

Because the photoaddition process results in the reduction of the conjugated system (from anthracene to *ortho*-disubstituted benzene) the photodimers do not absorb light of wavelength > 300 nm as shown in the UV spectra of A and A_2 (Fig. 1). Such a shift between the absorption spectra is an advantage for kinetic studies and provides photochromic properties to the system.

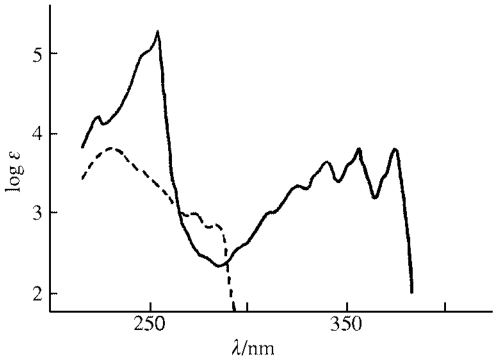


Fig. 1 Electronic absorption spectra of anthracene (**A**—) and its photodimer (**A**$_2$- - -) in cyclohexane. Irradiation of a solution of anthracene (conc ≅ 10^{-3}–10^{-2} M) at *e.g.* $\lambda \approx$ 365 nm leads to $\mathbf{A_2}$ without photoproduct absorption interference.

Provided the substituents (*e.g.* –NO_2 or –COR) do not introduce n–π* electronic transitions, this photocycloaddition

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† Part 1: see H. Bouas-Laurent, A. Castellan, J.-P. Desvergne and R. Lapouyade, *Chem. Soc. Rev.*, 2000, **29**, 43.

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involving a pure π–π^* state is a 'clean' reaction; this photodimerization can be considered as a paradigm for the $(4\pi + 4\pi)$ photocycloaddition. Much progress was accomplished in the 1960s, and the discovery of excimers by Förster and Kasper in 1954[2,3,7,13] raised the question of their intermediacy. Furthermore, from 1965, the Woodward–Hoffmann rules[14] stimulated the search for concerted processes in photocycloaddition reaction.

Several accounts and reviews dealing with this topic have appeared since 1963.[1,3–8,10–12] Here we present a more complete and updated report covering the essentials of the mechanistic aspects of the photodimerization of anthracenes *in fluid solution*, as announced in the conclusion of the review on structural aspects;[1] it focusses on the $(4\pi + 4\pi)$ cycloaddition involving the 9,10 positions of one nucleus and the 9′, 10′ (or 1′, 4′) positions of the other nucleus. The other types of cycloadditions of anthracenes, $(4\pi + 2\pi)$, $(2\pi + 2\pi)$, $(6\pi + 6\pi)$[1] are not so much documented. The intermolecular as well as the intramolecular photocycloadditions are described. As the reaction is reversible, the photochemical and thermal dissociation mechanisms are also considered.

2 Mechanism of photodimerization

2.1 Intermolecular photodimerization

2.1.1 The singlet excited state (S_1) as the reactive state The mechanism was investigated as early as 1905 by Luther and Weigert[12] and the photophysical aspects were studied sporadically until 1950 by several authors especially Suzuki.[12] Then, Bowen (1953–1960)[4] measured the anthracene disappearance quantum yield at 366 nm as a function of concentration of

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Alain Castellan received his thesis in 1974 from the University of Bordeaux on the 'Photodimerisation of aromatic hydrocarbons in solution'. He spent one year (1975–1976) at the University of Utah in the laboratory of Professor Josef Michl working on the photoreactivity of polycyclobutenes from upper excited states and on magnetic circular dichroism spectroscopy. In 1985 he earned a full professor position at Université Bordeaux 1 in organic chemistry and for four years has been the Director of the 'Laboratoire de Chimie des Substances Végétales' at the 'Institut du Pin'. His current research focuses on the chemistry and photochemistry of lignocellulosics in relation to wood and paper science.

Jean-Pierre Desvergne obtained his thesis degree from the University of Bordeaux in 1973, after spending one year (Leverhulme visiting fellowship) in Aberystwyth (Wales) with Professor Sir John Meurig Thomas to study the surface chemistry and photochemistry of organic crystals. He has been a member of CNRS since 1970 and is currently Director of Research at Université Bordeaux 1. He is presently head of the 'Laboratoire de Chimie Organique et Organométallique' (LCOO), a mixed CNRS and University Unit. His domains of expertise and research interests span solid state molecular photochemistry, the photochemistry and photophysics of aromatic hydrocarbons, polymer photochemistry, molecular and cation recognition, as well as the structural and spectroscopic studies of gels of organic liquids. He was co-editor of the book 'Chemosensors of Ion and Molecule Recognition' with Professor A.W. Czarnik, in 1997.

René Lapouyade obtained his thesis degree in 1969 with Professor H. Bouas-Laurent at the University of Bordeaux. He received the Adrian award from the Société Chimique de France for his work on 'Peri effect and photochemical reactivity of anthracene derivatives'. After one year of postdoctoral research at the Photochemistry Unit of the Western Ontario University, Canada, with Professor Paul de Mayo, he joined the photochemistry group at Bordeaux headed by Professor Jacques Joussot-Dubien. He was named CNRS Research Director in 1976. He participated in the creation of a new research group in the Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB) from 1994 to 1998 and is now working in the Laboratory of Chemical Analysis from Molecular Recognition (LACReM) in the Ecole Nationale Supérieure de Chimie et Physique de Bordeaux (ENSCPB). His research interests include synthesis and photophysical studies of new supramolecular fluorophores for the selective recognition of ions and molecules. Currently he is engaged in the design of new photochromic ionophores to detect ions and achieve fast ion concentration jumps and spin transitions.


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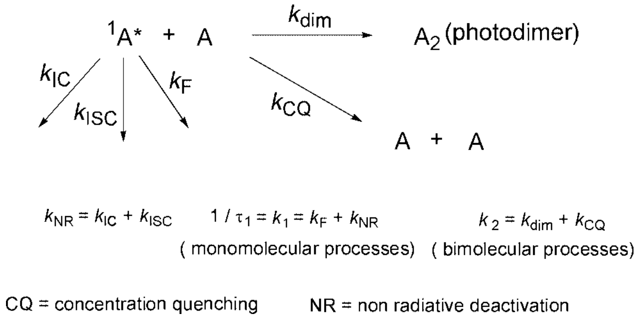
anthracene (A) and showed that a limit is reached at high concentration because of the trend to aggregation of anthracenes; the aggregates have a specific reactivity close to that of the solid state. In parallel with the increase of photodimerization quantum yield, Bowen observed a self quenching of fluorescence and proposed the S_1 state ($^1A^*$) as the reactive state.[4] Bowen and others also noted that heavy atom solvents such as CS_2 or C_6H_5Br completely inhibit photodimerization.[4]

It is known that heavy atoms favour intersystem crossing and therefore trigger the formation of the triplet state ($^3A^*$) which, at that concentration ($\approx 10^{-2}$ M), does not lead to photodimer. But, at low concentration ($[A] \leqslant 10^{-3}$M) in heavy atom solvents and in the presence of dioxygen, the latter was found to add to the 9,10 position to generate 9,10-epidioxyanthracene (AO_2, the so-called endoperoxide).[2,3] It was demonstrated that AO_2 results from the addition of singlet oxygen sensitised by the triplet state[2,3] to the most reactive positions of anthracene.$^3A^* + {}^3O_2 \longrightarrow {}^1A + {}^1O_2^{*}{}^1A + {}^1O_2^* \longrightarrow AO_2$Such a reaction is not competitive with photodimerization in deoxygenated solvents and at substrate concentration $\geqslant 10^{-3}$M.

The first measurements of the fluorescence quenching and photodimerization quantum yields, were extended later to several derivatives by Vember *et al.* 1973,[7] Cowan and Schmiegel 1972[3,7,12] and Castellan *et al.*[7] (see Table 1) who determined a series of rate constants. The above experimental observations can be expressed in Scheme 2.



Scheme 2 Kinetic scheme of photodimerization of anthracenes from the S_1 state. This Scheme implies the use of classical lamps and excludes two photon irradiation.

Finally Pereira *et al.* in 1971[7] showed that the photodimerization quantum yield of anthracene in the absence of O_2 at room temperature, at conc. 0.8 to 1.2×10^{-2} M in cyclohexane does not change within experimental errors when excited at 230, 254 or 365 nm. It was then concluded that the reaction is not dependent on wavelength.

From Scheme 2 one derives the following equations for the expressions of fluorescence (ϕ_F) and photodimerization (ϕ_{dim}) quantum yields, assuming the steady state approximation for the anthracene singlet excited state:

$$1/\phi_F = \{k_1 + k_2[A]\}/k_F \tag{1}$$

$$\phi^{\circ}_F/\phi_F = 1 + K_{SV}\,[A]$$
$$\text{Stern–Volmer equation } (K_{SV} = k_2\tau_1) \tag{2}$$

ϕ°_F is the fluorescence quantum yield determined at high dilution ($\leqslant 10^{-5}$ M);

$$\phi_{dim} = k_{dim}\,[A]/\{k_1 + k_2\,[A]\} \tag{3}$$

$$\phi^{\infty}_{dim} = k_{dim}/k_2 \quad ([A] \longrightarrow \infty) \tag{4}$$

$$1/\phi_{dim} = k_2/k_{dim} + k_1/\{k_{dim}\,[A]\} \tag{5}$$

$$1/\phi_{dim} = 1/\phi^{\infty}_{dim} + 1/\{\phi^{\infty}_{dim}\,K_D[A]\} \quad (K_D = k_2/k_1 = k_2\tau_1) \tag{6}$$

This mechanism requires that the experimental values of K_{SV} and K_D are equal. To *illustrate the method,* fluorescence (eqn. 1) and disappearance quantum yields data (eqn. 6) are plotted in the following graphs (Fig. 2 and Fig. 3) for anthracene in degassed benzene.

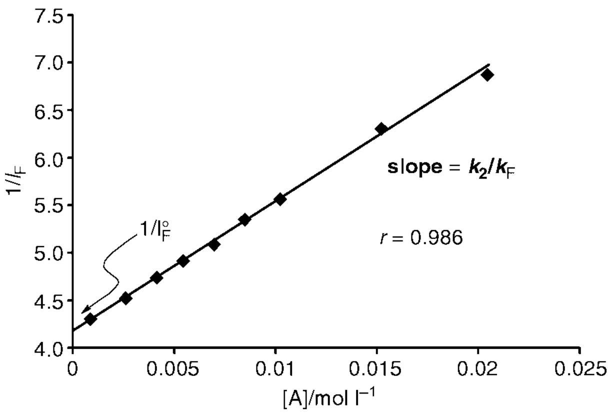


Fig. 2 Fluorescence quenching plots (eqn. 1) of anthracene in degassed benzene. I_F is proportional to ϕ_F. Adapted from reference 7, with permission.

Table 1 Rate constants of bimolecular events from the S_1 state at ambient temperature and other relevant data, according to Scheme 2.1. For the derivation, see eqns. 1–9. A denotes the anthracene nucleus

Monomer	τ_1/ns	ϕ^{∞}_{dim}	K	k_2	k_{dim}	k_{CQ}	Solvent	Ref.
				10^9 M^{-1} s^{-1}	10^9 M^{-1} s^{-1}	10^9 M^{-1} s^{-1}		
A	4	0.16	56	14	2.25	11.75	Toluene	a
A	4.1	0.34	27	6.6	2.28	4.32	Benzene	b
A		0.35		9.8			Cyclohexane	c
9 Me A	9.5	0.14	130	13.7	1.90	11.80	Toluene	a
9 MeA		0.16		4.9			Cyclohexene	c
9 EtA	9.2	0.115	85	8.15	1.05	9.20	Toluene	a
9 Pr^{n}A	9.4	0.067	79	8.4	0.55	7.85	Id	a
9 Bu^{n}A	9.7	0.075	62	6.4	0.48	5.92	Id	a
9,10 diMeA	12.5	0.02	23	1.84	0.04	1.80	Benzene	b
9,10 diMeA		—		1.7			Cyclohexane	c
9 MeOA	6.6	0.164	65	9.8	1.60	9.80	Toluene	a
9 CNA	13	0.24	70	5.4	1.30	4.10	Benzene	b
9 COOHA	4.5	0.19	25	5.45	1.05	4.40	EtOH + H$^+$	d
9 COONaA	1.5	0.10	11	7.3	0.73	6.57	H_2O	d

[a, b]: in degassed solvents. [a] Vember *et al.* 1973.[7,8,10] [b] Castellan *et al.*[7] [c] Bendig *et al.* 1981.[10] [d] Cowan and Schmiegel 1972.[3,7,12] Adapted from reference 7, with permission.

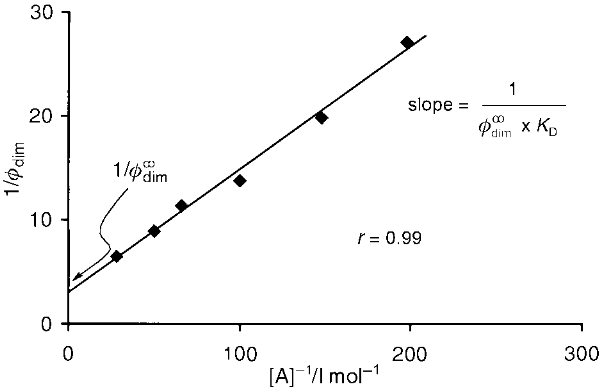


Fig. 3 Photodimerization quantum yields plots of anthracene in degassed benzene (eqn. 6). For rate constant values, see eqns. 7–9 and Table 1. Disappearance quantum yields were measured at < 10% conversion rate. Adapted from reference 7, with permission.

K_{SV} was found to be equal to K_D within experimental errors.[7] In Table 1, K represents the average value. From K, ϕ_{dim} and τ_1 (determined experimentally by phase fluorimetry or by single photon counting) one derives the following equations:

$$k_2 = K/\tau_1 \quad (7)$$

$$k_{dim} = \phi^{\infty}{}_{dim} \times k_2 \quad (8)$$

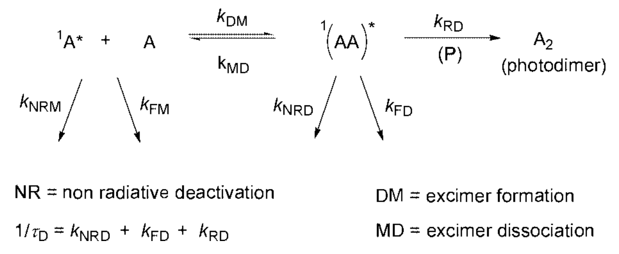
$$k_{CQ} = k_2 - k_{dim} \quad (9)$$

It should be emphasized that the 'k_{dim}' reported values imply an elementary step, *i.e.* without intermediate (*vide infra* the role of excimers). Some selected rate constants have been collected in Table 1.

The values of Table 1 show that the photodimerization is a very fast reaction: k_{dim} being *ca.* 0.5–2.3 × 10^9 M^{-1} s^{-1} (except 9,10-dimethylanthracene whose reactivity is much lower: 0.04 × 10^9 M^{-1} s^{-1}, *i.e.* 57 fold less than anthracene); these high rates are consistent with reactions occurring during the singlet state lifetime (4–13 ns).

The bulk increase of 9-alkyl substituents is reflected by a decrease of rate constants (k_{dim}), even if the differences are small. The rate decrease is much more pronounced for 9,10-dimethylanthracene which exhibits a clear steric effect. In our hands, neither 9,10-diethylanthracene nor its homologues were found to photodimerize and there is little probability that this will be observed under usual conditions. $\phi^{\infty}{}_{dim}$ is indicative of the probability that an encounter leads to a cycloaddition (1/3 for A and 1/50 for diMeA in benzene). Worth noting, although the results are not in Table 1, the photodimerization rates (k_{dim}) in ethanol of 9-anthroate esters (9-(COOR)A with R = Me, Et, Bu^n, Bu^t) were found by Shon *et al.* 1975[10,12] to be in the range 0.63–0.78 × 10^9 s^{-1}; the ester group crowding does not affect significantly k_{dim} because it is relatively remote from the reaction centre.

2.1.2 The role of excimers Here we consider only *singlet excimers.* They are 1 : 1 complexes (one molecule in the excited state and one in the ground state) stable in the excited singlet state and dissociative in the ground state. For aromatic hydrocarbons, they are characterized by a broad red shifted fluorescence band.[6,9,13] For the most stable excimers, theoretical calculations and experimental evidence favour a slightly staggered *sandwich configuration* with the best overlap between π electrons, as suggested by the geometry of molecular pairs in pyrene crystals [13], and in some bispyrenes or bisanthrylcyclophanes (Bouas-Laurent *et al.* 1986[10,12]). Birks[13] determined the rate constants of Scheme 3 for pyrene (which is not reactive: k_{RD} negligible) in cyclohexane and other solvents and found that the rate of excimer formation is diffusion limited *i.e.* k_{DM} ≈ 10^{10} M^{-1} s^{-1} in organic solvents. The same author believed that *photodimerization is an 'extreme case of excimer formation'* and if the dimerization is inhibited, that excimer fluorescence is observed because the two processes compete as expressed in Scheme 3.



Scheme 3 Kinetic scheme of photodimerization of anthracene including a fluorescing excimer as intermediate. The scheme implies the use of a classical lamp (one photon reaction). The notations are taken from Birks.[13] (P) denotes a pericyclic minimum (see Fig. 6).

However, the alternative mechanism of a competitive formation of the excimer (diversion or blind alley) and of the photodimer was proposed by others (Vember *et al.* 1973[7,8,10]):

$$^1A^* + A \rightarrow {}^1(AA)^*$$

$$^1A^* + A \rightarrow A_2$$

$$^1A^* + A \rightarrow 2A$$

Anthracene does not show excimer fluorescence under usual experimental conditions in solution but in 1965 Chandross[15] photodissociated its photodimer in a methylcyclohexane matrix at 77 K, at 254 nm, producing a pair of adjacent anthracene molecules which are held in mutual contact in the rigid matrix and emit a broad fluorescence similar to that of excimer (λ_{max} ≈ 470 nm).

The first evidence of the intermediacy of an excimer on the way to the photodimer was given in the solid state by Ferguson and Mau, 1974,[8–10] who by using the Chandross technique with the *photodimer crystal* as the matrix, measured the excimer fluorescence quantum yield *versus* the photodimerization quantum yield from 20 to 200 K (Fig. 4); under these experimental conditions, these two processes were found to be strictly competitive (a 'crossover' point at 123 K represents values of 0.5 for each process).

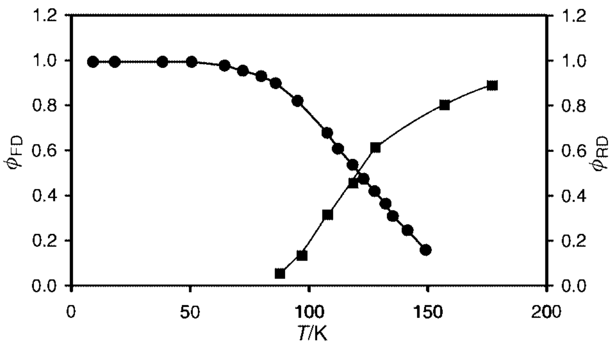
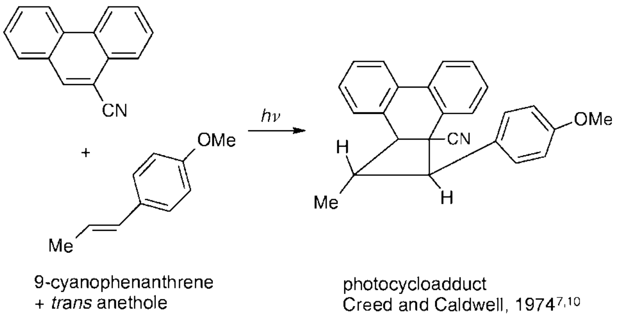


Fig. 4 Temperature dependence of the photodimerization (ϕ_{RD}) and excimer fluorescence (ϕ_{FD}) quantum yields of the anthracene sandwich pair in dianthracene matrix. Taken from Ferguson and Mau 1974[8–10] with permission.

In parallel, Creed and Caldwell, 1974[7,10] provided kinetic evidence, *in solution,* of the intermediacy of *an exciplex* (heteroexcimer) in the (2 + 2) photocycloaddition of 9-cyanophenanthrene to *trans*-anethole, observing the stereospecific collapse of the maximum overlap sandwich exciplex to the cycloadduct.

For *anthracene in solution*, the demonstration of the existence of an *excimer* whose fluorescence is not detected (except under special conditions, *vide infra*) came from Cohen *et al.* in 1976.[2,7,10] The authors selected an energy acceptor



(rhodamine B) which has an absorption spectrum overlapping weakly with the monomer fluorescence but strongly with the emission assumed from the 'non emitting' excimer; therefore, energy transfer from the excimer (not from the monomer) to the dye was expected if the excimer lifetime is greater than the time for energy transfer; irradiation of anthracene at 375 nm leads to sensitised emission from the dye, thus confirming the formation of the excimer. Kinetic analysis of the results was interpreted in terms of excimer intermediacy and allowed an estimate of 1–1.5 ns for its lifetime in a toluene–ethanol 4 : 1 mixture which is in good agreement with other authors' data (Ferguson and Mau 1974[8,9,10]). Shortly after, McVey *et al.* 1976[8] published the first direct observation and characterization of the anthracene excimer in solution (0.2 M in $CHCl_3$).

The same year, Boens *et al.*, 1976[10,12] demonstrated kinetically the competition between *intramolecular excimer* fluorescence emission and photocycloisomerization for trimethylene bis-2-anthroate in a dilute dichloromethane *solution*. Ferguson *et al.*[16] in 1981, gave clear evidence of the intermediacy of an *intramolecular excimer* in the unsymmetrical photocycloisomerization of 1,3-bis-(9-anthryl)-1,1,3,3-tetramethyldisiloxane ($ASiMe_2OSiMe_2A$) in a glass forming mixture of solvents: methylcyclohexane (MCH) and isopentane (IP). The fluorescence quantum yields have been measured from 100 K to 300 K and the photocycloaddition quantum yield was found to be 0.17 at 300 K. In Fig. 5, one observes that, at 220 K, there is an important change in the ϕ_{FD} and ϕ_Q curves; by extrapolation to 300 K it appears that the increase of quenching (0.17) can be accounted for by the photoreaction quantum yield which has the same value within experimental errors.

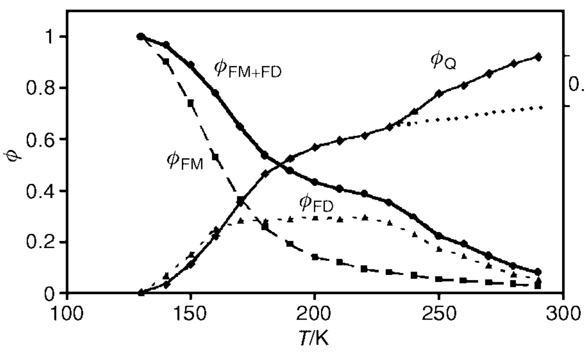
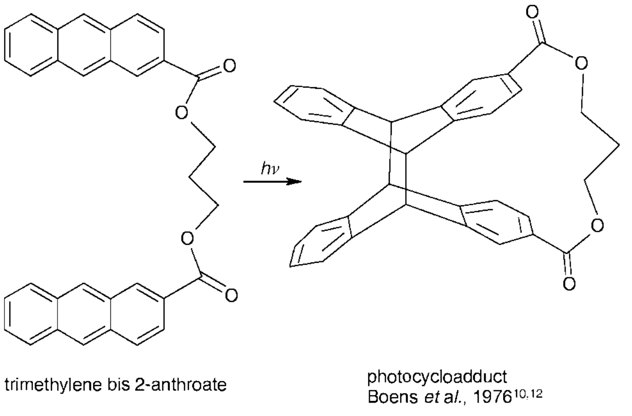


Fig. 5 Temperature variation of the fluorescence quantum yields (ϕ) of $ASiMe_2OSiMe_2A$ in a degassed mixture of methycyclohexane (MCH) and isopentane (IP). MCH : IP = 1 : 3. FM = monomer fluorescence; FD = excimer fluorescence; Q = quenching. $\phi_Q = 1 - \phi_{FM+FD}$. Taken from ref. 16 with permission.



Consequently, if we postulate that all fluorescing excimers are intermediates in the photocycloaddition, and assume the steady state approximation for $^1A^*$ and $^1(AA)^*$, the following equations are derived from kinetic Scheme 3 (eqns. 10–20).

$$\phi^{\circ}_{FM}/\phi_{FM} = 1 + K_{SV}[A] \tag{10}$$

$$\text{with } K_{SV} = k_{DM}\tau_M\,(1 - k_{MD}\tau_D) \tag{11}$$

$$\phi^{\infty}_{FD} = k_{FD}\tau_D/(1 - k_{MD}\tau_D) \tag{12}$$

$$\phi^{\infty}_{RD}/\ \phi_{RD} = 1 + 1/(K_{RD}[A]) \tag{13}$$

$$\phi^{\infty}_{RD} = k_{RD}\tau_D/(1 - k_{MD}\tau_D) \tag{14}$$

$$K_{RD} = k_{DM}\tau_M\,(1 - k_{MD}\tau_D) \tag{15}$$

$$K = \tfrac{1}{2}\,(K_{SV} + K_{RD}) \tag{16}$$

$$\mathrm{k}_{RD} = \phi^{\infty}_{RD}\,(1 - k_{MD}\tau_D)/\tau_D \tag{17}$$

$$k_{FD} = \phi^{\infty}_{FD}\,(1 - k_{MD}\tau_D)/\tau_D \tag{18}$$

$$k_{DM} = K/\tau_M(1 - k_{MD}\tau_D) \tag{19}$$

$$k_{NRD} = 1/\tau_D - (k_{RD} + k_{FD} + k_{MD}) \tag{20}$$

From the experimental values of ϕ^{∞}_{RD}, ϕ^{∞}_{FD}, τ_M, τ_D and $K = \tfrac{1}{2}(K_{SV} + K_{RD})$, and a reasonable estimate for k_{MD} ($\approx 10^6\ s^{-1}$, Birks[13]) it was possible to determine the rate constants given in eqns. 17–20; they have been listed in Table 2 for anthracene and 9,10-dimethylanthracene.

Owing to experimental uncertainties, these data should be taken with caution but they suggest that the anthracene excimer in solution should yield the photodimer with a probability of 0.35 whereas the latter is *ca.* 0.004 for 9,10 DMA, in agreement with steric hindrance. Moreover the competitiveness between excimer fluorescence ($k_{FD} \approx 2 \times 10^6\ s^{-1}$)) and photoreactivity ($k_{RD} \approx 140–500 \times 10^6\ s^{-1}$) is apparent in Table 2; it is largely in favour of photoreactivity and non radiative deactivation ($k_{NRD} \approx 260–430 \times 10^6\ s^{-1}$) for anthracene and this can explain why the excimer fluorescence is so difficult to observe in solution.

Table 2 Rate constants of excimer formation and of its deactivation channels at ambient temperature for anthracene (A) and 9,10-dimethylanthracene (9,10-DMA).

Compound	ϕ^{∞}_{RD}	ϕ^{∞}_{FD}	K	τ_D ns	k_{DM} 10^9 $M^{-1}s^{-1}$	k_{MD} 10^6s^{-1}	k_{RD} 10^6s^{-1}	k_{FD} 10^6s^{-1}	k_{NRD} 10^6s^{-1}	Solvent
A	0.35	0.004	56	2.5	14	1	140	2	260	T[a]
A				1.5			235	2.5	430	B[b]
A							500			D.M.[c]
9,10-DMA	0.004	0.34	95	200	8	1	0.015	1.4	2.6	T[d]

[a] In toluene (T), using Vember's data,[7] except ϕ^{∞}_{RD}. [b] In benzene (B) using τ_D: 1.5 ns from McVey[7] in $CHCl_3$. [c] From Ferguson and Mau 1974[8–10] in a dianthracene matrix (D.M.). [d] In toluene (T), using Vember's and our own data.[7] Adapted from reference 7, with permission.

2.1.3 Energy profile According to the Woodward–Hoffmann rules,[14] $2\pi_s + 2\pi_s$ (as well as $4\pi_s + 4\pi_s$) cycloaddition is photochemically allowed; a state diagram for this concerted reaction correlates the first excited states (addends to adducts) and the doubly excited states (D) to the addend and product ground states, respectively. As the *singlet state photoadditions* have been observed to be *diabatic*, there must be an excited state potential energy surface crossing to the ground state surface even if the two states have the same symmetry (in such a case, there is an avoided crossing). Michl and coworkers[17] in 1976 performed *ab initio* calculations on a model four electron, four orbital system (H_4) which showed that the avoided crossing (at the so-called pericyclic minimum) can turn into a *conical intersection* (or funnel) at a rhomboidal geometry (*i.e.* far from idealized symmetric reaction path geometries). Hereafter, it will be denoted *Michl's* pericyclic minimun. The first *ab initio* verification of this result for *real organic molecules* has been realized recently.[18,19] A simplified energy profile (one coordinate) for inter- or intramolecular *photocycloaddition of anthracenes* is represented in Fig. 6. An important feature is the excimer energy minimum relative situation. The main profile sketches the observation of both excimer fluorescence and photocycloaddition (*e.g.* for A, 9-MeA, 9,10-diMeA, $A(CH_2)_4A$, $ASiMe_2OSiMe_2A$)[8] whereas two other profiles, as predicted by Gerhartz *et al.*,[17] are represented in inserts: (a) formation of cyclophotoadduct without excimer fluorescence (*e.g.* for ACH_2OCH_2A and $AOCH_2OA$);[10] (b) excimer fluorescence not accompanied by cycloadduct formation (*e.g.* C_6H_5–ACH_2OCH_2A–C_6H_5).[8]

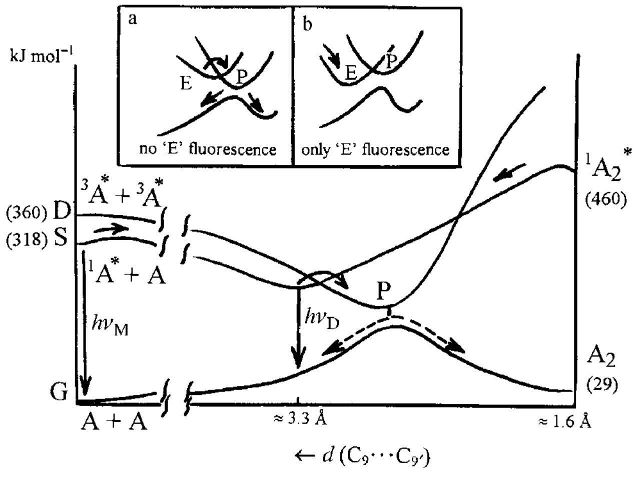


Fig. 6 Simplified energy profile for the photodimerization of anthracenes (inter-and intramolecular processes). The reaction coordinate is the distance (not to scale) between the 9 and 9′ carbons of the two reacting rings. 'A' denotes the anthracene nucleus; E the excimer, P the pericyclic minimum named also funnel, hole…, S singly excited state, D doubly excited state. Recent *ab initio* calculations have shown that, in many cases, the pericyclic minimum can turn into a *conical intersection* (multidimensional potential surface touching). *Insert a*: formation of phocycloadduct A_2 without excimer fluorescence; *insert b*: excimer fluorescence not accompanied by cycloadduct formation. Adapted with permission, from reference 17, copyright 1976, American Chemical Society.

The energy profile represented in Fig. 6 illustrates the three cases encountered experimentally; in case 'a' excimer fluorescence is not observed because the activation energy to reach the doubly excited state surface which generates a pericyclic intermediate (P), is negligible. If the activation energy is higher or if the temperature is lowered excimer fluorescence is liable to compete. Some authors (Kaupp 1973,[10] Bergmark *et al.* 1978[8,12]) have described this intermediate as a diradical (Fig. 7) in analogy with other diradicals which have been characterized by chemical trapping and flash spectroscopy;[20] but so far, no intermediate has been trapped. The same argument is applied to linked anthracene systems such as bis-9-anthrylmethanes and bis-anthrylethanes which generate very short lived transients (Section 2.2.2); the pericyclic diradicaloid intermediate proposed by Michl[17] (which can have zwitterionic character) seems in agreement with the theory of concerted reactions (see Fig. 7).

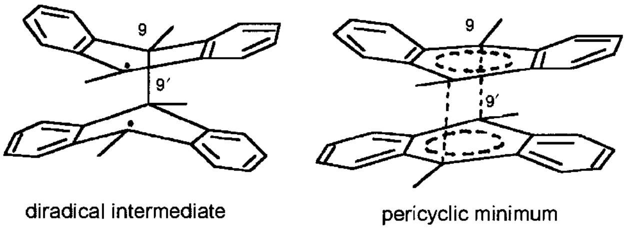


Fig. 7 Left: diradical intermediate; there is no bonding between 10 and 10′ positions. **Right**: pericyclic intermediate; there is partial bonding between the meso positions. Some authors (Bergmark *et al.* 1978[8,12]) do not make a difference between these two representations.

2.1.4 Intermolecular regioselectivity. *2.1.4.1 Head to-head versus head to-tail photocycloadducts.* In the case of 9-monosubstituted anthracenes head to head (*hh*) and head to tail (*ht*) geometries are possible for the photodimers. Each of them may be characterized by its *own excimer* and its *own pericyclic minimum.* Simple perturbation theory favours the *hh* excimer (as long as steric factors are not prominent); but according to Michl's considerations,[21] the *ht* arrangement should lead to the deepest pericyclic minimum (all other factors being the same). The profiles, pictured in Fig. 8, suggest that relative yields of the *hh* and *ht* cycloadducts are difficult to predict.

In practice, even for substituents whose steric bulk does not prevent the formation of *hh* photodimers (such as Cl, Br, CN, CH_3, CH_2OH, CH_2OCOCH_3, CH_2OCH_3, OCH_3…) *only the ht* cycloadducts were *isolated* under thermodynamic control and purified by recrystallization in *boiling* solvents such as ethanol, benzene or chloroform. However, after the advent of NMR, the crude photoproduct of the *ambient* temperature irrradiation was found to be constituted of a *mixture of hh and ht* photocycloadducts[1] reflecting *kinetic* rather than thermodynamic control; for instance, Kaupp, 1980,[1,10] found that 9-methylanthracene gave an *hh*:*ht* ratio of 40:60 by irradiation in benzene, and assigned to the *hh* isomer the signals that disappeared by heating the benzene solution. In pure fluid solvents, the ratio *ht*:*hh* was always found to be higher than 50:50 but Wolff[22] showed that the *hh* isomer can be favoured for 9-methoxyanthracene (and other derivatives) irradiated in *polar micelles*; then strong intermolecular forces (H bonds) may change the relative (*hh*:*ht*) stability[1] along the reaction pathway especially in the excimer and in the pericyclic minimum.

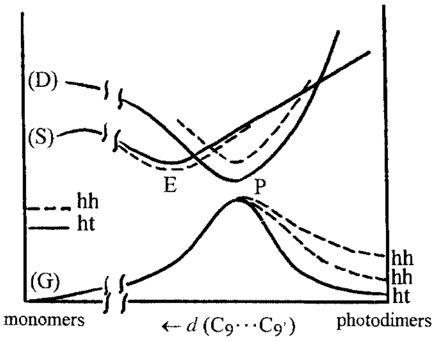
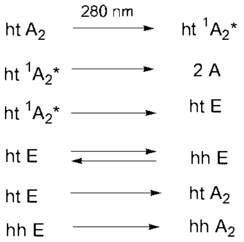


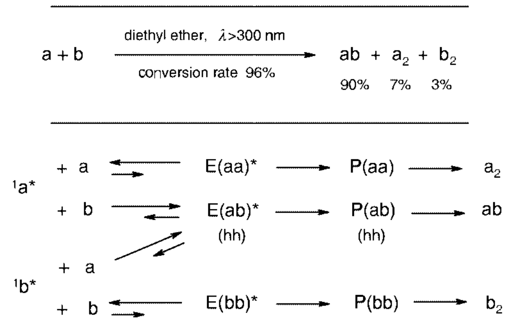
Fig. 8 Simple energy profile, not to scale, for concerted head-to-head and head-to-tail photodimerization of 9-monosubstituted anthracenes; (—) refers to *ht* and (---) to *hh* arrangements (two isomers of different stability are pictured). In most cases the reaction being under thermodynamic control, the *ht* cycloadduct was found to be the sole product (adapted from Bonačić-Koutecký *et al.*,[21] with permission).

The *hh* isomer can also be generated in an indirect fashion which implies the existence of intermediates such as excimers (E) and the pericyclic minimum (P). Wolff [22] irradiated the *ht* photodimer (A_2) of 9-methylanthracene in *n*-hexane at a *concentration* (10^{-5} M) too low for the photodimerization to compete with the other processes and at a *wavelength* (280 nm) where the molar absorption coefficient of the photodimer is comparable to that of the monomer; under these conditions, significant amounts of the photodimer *hh* A_2 was produced in addition to some A. The author interpreted this result in postulating the intermediacy of *hh* and *ht* excimers in rapid interconversion (see Scheme 4)



Scheme 4 Proposed mechanism (Wolff 1985[22]) for the formation of head-to-head (*hh*) photodimer by irradiation of the head-to-tail (*ht*) photodimer of 9-methylanthracene (A) in *n*-hexane (conc ≈ 10^{-5} M).

Such an interpretation is backed up by the preferential formation of *the hh crossed* photodimer by irradiation of a 1 : 1 mixture of 9-cyanoanthracene (a) and 9-methoxyanthracene (b) (Castellan *et al.*, 1975[8,12]) at ambient temperature, in diethyl ether: crossed dimer/pure dimers: 90/10. This result supports an interconversion between excimers and exciplexes E (aa)*, E (ab)*, E (bb)* rather than a thermal dissociation of the pure photodimers (which are stable under the reaction conditions); the crossed dimer (ab) is thermally less stable than a_2 and b_2 and decomposes *slowly* into the starting monomers at ambient temperature (see Scheme 5). One might also consider the interconversion to occur at the pericyclic (P) stage but the binding energy between the two monomers seems higher than in the excimers (exciplexes).



Scheme 5 Proposed mechanism for the preferential formation of the crossed photodimers 'ab' whose yield largely exceeds that expected from statistical collisions. a = 9-cyanoanthracene; b = methoxyanthracene; E = excimer; P = pericyclic minimum. See Castellan *et al.* 1975.[8,12]

2.1.4.2 Non classical photodimers. Photocycloaddition occurring through 9,10 : 1′,4′ positions have been observed for 2,6-bis(decyloxy)anthracene (Fages *et al.* 1988[1,12]), 1-acetylanthracene (Becker *et al.* 1996[1]) and methyl anthracene-1-carboxylate (Becker *et al.* 1996[1]) in addition to the classical process. No mechanistic investigations have been performed so far.

2.1.5 The triplet state reactivity (triplet–triplet annihilation) Anthracene photodimerization can also be *triplet sensitized* with biacetyl as shown by Bäckstrom *et al.* in 1958[7,23] but the rate was found to be extremely slow (as triplet sensitizer, one can also use fluorenone). Saltiel *et al.* 1983[12] as well as previous authors have shown that the self-quenching of triplet anthracene with ground state anthracene leads exclusively to ground state anthracene monomer.$^3A^* + A \rightarrow 2\ A$

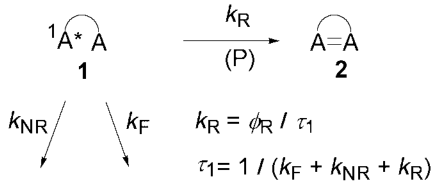
However, Saltiel *et al.*[23] demonstrated that triplet–triplet annihilation (TTA) generates a singlet excimer which collapses to the photodimer. A complete kinetic study incorporating the data concerning the dependence of dianthracene (A_2) quantum yield for direct A excitation on absorbed light intensity I_a, allowed a quantitative evaluation of the TTA component in photodimer formation.[23]$^3A^* + {}^3A^* \rightarrow {}^1(AA)^*$ + other species$^1(AA)^* \rightarrow A_2{}^1(AA)^* \rightarrow A + A{}^3A^* + A \rightarrow A + A$

In air saturated solutions, dioxygen quenching of $^3A^*$ eliminates the TTA contribution to A_2 formation. At high anthracene concentration ($> 5 \times 10^{-3}$ M) self quenching reduces $^3A^*$ lifetime and inhibits the TTA process. For *degassed dilute solutions*, A_2 quantum yield was shown by the authors to be proportional to the square of light intensity, reflecting the contribution of TTA to A_2 formation. These fundamental results provide experimental evidence in favour of the postulated intermediacy of a doubly excited state in photocycloaddition (see Fig. 6). This mechanism (TTA) was later proposed by Becker *et al.*, 1993,[1] for the photodimerization of 9-benzoylanthracene in toluene, under argon, at a concentration as high as 5×10^{-2} M (see Section 2.2.4).

2.2 Intramolecular photocycloaddition

These reactions have to be performed under high dilution ($< 10^{-3}$ M) to avoid intermolecular processes. Accordingly, the kinetic schemes are different from those for the intermolecular processes (*vide infra*).

2.2.1 Excimer fluorescence is not observed It is therefore not relevant to introduce an excimer species in the kinetic Scheme 6 (the energy profile corresponds presumably to that of insert 'a' in Fig. 6). The photocycloaddition rate (k_R) is consequently related directly to the singlet state lifetime and to the reaction quantum yield (ϕ_R). The reactivity k_R is a weighted average of the rate constants from the rapidly interconverting conformers. A selection of relevant data are listed in Table 3.



Scheme 6 Kinetic scheme for intramolecular photocycloaddition. No fluorescing excimer is observed.

Table 3 Fluorescence and reaction quantum yields (ϕ_F, $\phi^{366}_{R(1\text{-}2)}$) singlet state lifetimes (τ_1) and photocycloaddition rates determined according to Scheme 6 of selected non conjugated 9-substituted anthracene bichromophores (A–Z–A) at ambient temperature, in non polar solvents; A = 9-anthryl; MCH = methylcyclohexane; B = benzene

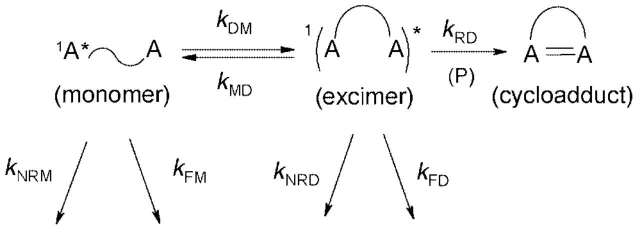
Z	ϕ_F	$\phi^{366}_{R(1\text{-}2)}$	τ_1 (ns)	$k_R/10^7$ s^{-1}	Solvent	Ref.
CH_2	0.06	0.15	1.1	13.5	B	[a]
$(CH_2)_3$	0.47	0.14	6	2.3	MCH	[b]
$(CH_2)_4$	0.37	0.08	4.6	1.7	MCH	[c]
CH_2OCH_2	0.03	0.30	0.9	33.0	MCH	[b]
OCH_2O	0.06	0.38	0.4	95.0	MCH	[d]
$O(CH_2)_2O$	0.22	0.22	3.8	5.8	MCH	[c]

[a] Bergmark *et al.* 1978.[8,12] [b] Bouas-Laurent *et al.* 1980.[8] [c] Desvergne *et al.* 1988.[24] [d] Desvergne *et al.* 1995.[24]

From Table 3 and other data, it appears that the shorter the chain, the more efficient the reaction, provided the best overlap between the two aromatic rings is reached during the excited singlet lifetime (0.4–6 ns) of the bichromophore. The highest rate is obtained for three linkage chains where two CH_2 are replaced by two oxygen atoms which is known to reduce the rotational energy barrier. An interesting feature not reported in Table 3 is the observation by Castellan *et al.* 1979[8] and Desvergne *et al.* 1995[24] of a clear increase of ϕ_R with solvent polarity; these unexpected results are commented upon below (Section 2.2.2.2).

2.2.2 Excimer fluorescence is observed.

2.2.2.1 Classical reaction scheme. As discussed earlier (Section 2.1.2) a fluorescing excimer is now accepted as an intermediate as described in Scheme 7.



$$k_M = k_{FM} + k_{NRM} \qquad k_M = 1/\tau_M$$

$$k_D = k_{FD} + k_{NRD} + k_{RD} \qquad k_D = 1/\tau_D$$

Scheme 7 Kinetic scheme for intramolecular photocycloaddition *via* a fluorescing excimer. Birks' notations[13] are used.

Experimental quantum yields ϕ_{FD} and ϕ_{RD} together with the transient kinetic analysis give access to the rate constants of Scheme 7. The fluorescence decay measurements were performed by using the time correlated single photon counting technique. The decay parameters (accuracy *ca.* 10%) can be determined by a non-linear least square deconvolution method (see for example Desvergne *et al.*[24] and Marquis *et al.*[25]).

A biexponential decay obeys the following equation:

$$I_F(t) \propto A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$

Then the time evolution of the emission from the locally excited species $I_M(t)$ and from the excimer $I_D(t)$ could be expressed as follows, respectively:

$$I_M(t) \propto k_{FM} (\lambda_2 - X) [\exp(-\lambda_1 t + A\exp(-\lambda_2 t)]/(\lambda_2 - \lambda_1)$$

$$I_D(t) \propto k_{FD}k_{DM} [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] /(\lambda_2 - \lambda_1)\lambda_{1,2} = \tfrac{1}{2}\{(X + Y) \pm [(X - Y)^2 + 4 k_{DM}k_{MD}]^{1/2}\}$$

$X = k_{DM} + k_M$, corresponds to the deactivation channels of the locally excited monomer.

$Y = k_{MD} + k_D = \lambda_1 + \lambda_2 - X$, corresponds to the deactivation channels of the excimer state. $A = A_2/A_1 = (X - \lambda_1)/(\lambda_2 - X)$; X and Y can be expressed as a function of A, λ_1, λ_2 and thus deduced from the experimental data:

$$X = (A\lambda_2 + \lambda_1)/(A + 1)$$
$$Y = (A\lambda_1 + \lambda_2)/(A + 1)$$

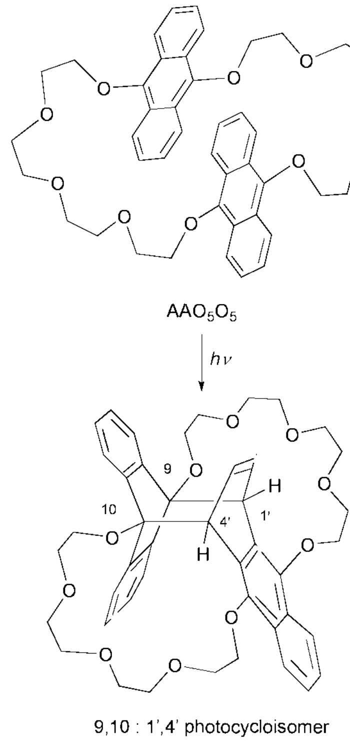
$$k_M = 1/\tau_M \text{ (monochromophoric kinetic parameters)}$$
$$k_{DM} = [A\lambda_2 + \lambda_1 - k_M(A + 1)]/(A + 1)$$
$$k_{MD} = (X - \lambda_1)(\lambda_2 - X)/k_{DM}$$
$$k_D = [(A\lambda_1 + \lambda_2) / (A + 1)] - k_{MD}$$
$$k_{FD} = \phi_{FD}(k_M k_D + k_M k_{MD} + k_D k_{DM})/k_{DM}$$
$$k_{RD} = \phi_{RD}(k_M k_D + k_M k_{MD} + k_D k_{DM})/k_{DM}$$

Kinetic parameters (k_{DM}, k_{MD}, k_D, k_{FD} and k_{RD}, Scheme 7) are evaluated from the preceding equations based on the Birks model (fluorescence decay of *one* locally excited species and *one* excimer). The expressions of k_{RD} and k_{FD} were established with the assumption that the stationary state approximation applies to 'monomer' and excimer concentrations.[8,10,13,25]

Relevant kinetic data are listed in Table 4. They show the easy formation of excimers (rate 5×10^8 to 2×10^9 s^{-1}) which is controlled by intramolecular bond rotations in the tether (Z) to reach the appropriate excimer geometry; the photocycloaddition rates are contrasted ($k_{RD} \approx 0.1$–35×10^6 s^{-1}) reflecting the relative steric crowding at the reaction centres; the latter is severe with the disilyl compound; in this case the photocycloaddition was shown to occur between the 9,10 positions of one nucleus and the 1′,4′ positions of the other one (Desvergne *et al.* 1988[24]).

2.2.2.2 More complex processes. As shown earlier, Scheme 7 involves one 'monomer' (a set of rapidly interconverting conformers) and one 'excimer'; hereafter are described two examples of more complex processes with two 'monomers' and two 'excimers', respectively.

(a) Two consecutive 'monomer' conformations. Such a mechanism (Scheme 8) has been proposed for describing the fluorescence decay of a macrocyclic compound AAO_5O_5

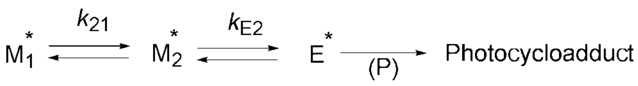


9,10 : 1′,4′ photocycloisomer
Marquis *et al.*[25]

Table 4 Monomer (ϕ_{FM}), excimer (ϕ_{FD}), fluorescence and reaction (ϕ_{RD}) quantum yields; excimer formation and excimer deactivation rate constants for non conjugated α,ω-di(9-anthryl) derivatives A–Z–A, at ambient temperature. B = benzene; MCH = methylcyclohexane. For simplification 'CH_2' is denoted by 'C'

Z	ϕ_{FM}	ϕ_{FD}	ϕ_{RD}	$k_{DM}/10^6$ s^{-1}	$k_{MD}/10^6$ s^{-1}	$k_{FD}/10^6$ s^{-1}	$k_D/10^6$ s^{-1}	$k_{RD}/10^6$ s^{-1}	Solvent	Ref.
O-C(COC)$_2$C-O	0.10	0.023	0.26	570	5	3.5	111	35	B	[a]
C-(OCC)$_2$O-C	0.024	0.18	0.045	2.050	6	5.3	15	1	MCH	[b]
SiMe$_2$C$_2$SiMe$_2$	0.085	0.025	0.0008	1.000	87	3		0.1	MCH	[c]

[a] Desvergne *et al.* 1980.[10,12] [b] Desvergne *et al.* 1984.[12] [c] Desvergne *et al.* 1988.[24]



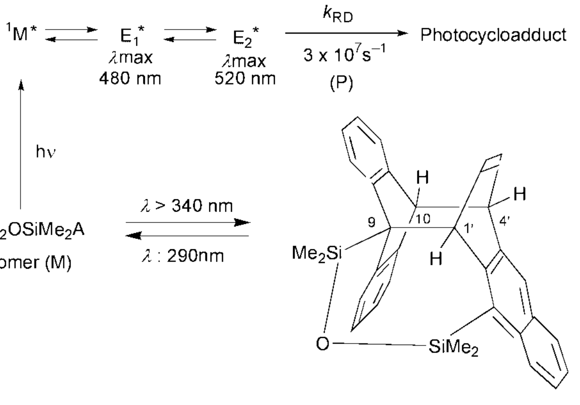
solvent	$k_{21}(s^{-1})$	$k_{E2}(s^{-1})$
CH_3OH	9.10^7	5.10^8
MCH	2.10^7	1.10^8

Scheme 8 Kinetic scheme showing the presence of two sets of fluorescent monomers, one of them collapsing into excimer E*, postulated to be the precursor of the photocycloadduct.[25]

(decaoxa[13.13]-9,10-anthracenophane) which generates an unsymmetrical (9,10 : 1′,4′) photocycloadduct.[25]

The transient kinetic analysis was performed over a large temperature range, in several solvents and at two wavelengths; the fluorescence profiles were fitted with two or three exponentials. Some rates constants (k_{21} and k_{E2}) at ambient temperature, given in Scheme 8, represent the dynamics of transformation of conformers M_1 into M_2 and that of excimer formation from the suitable conformers.

(b) Two consecutive fluorescing excimers are on the reaction pathway. This case has been observed for the 9,10 : 1′,4′ photocycloaddition of A–$SiMe_2OSiMe_2$–A (Scheme 9). A careful fluorescence study (Ferguson *et al.*[16]) as a function of temperature has demonstrated that the unsymmetrical photoproduct is formed from the second excimer E_2* whose geometry is likely to exhibit partial overlap. A similar mechanism applies to 9–A–CH_2OCH_2–1–A.



Scheme 9 Photocycloaddition through a two excimer route. The rate of cycloadduct formation at ambient temperature from excimer E_2* was derived from Ferguson's data.[16]

2.2.2.3 α,ω-Dianthrylalkanes. (a) Influence of solvent polarity. As fluorescing excimers can be characterized as intermediates in the photocycloaddition, an extensive study has been performed of α,ω-dianthrylalkanes [A–$(CH_2)_n$–A], n = 2–11.[26]

For long polymethylene chains ($n \geqslant 4$) the excimer formation was shown not to depend on solvent polarity;[26] however the latter affects the shorter chain bichromophores; the best documented are 1,2-dianthrylethanes (n = 2) which *are developed below*; the others (n = 0, 1, 3) are briefly commented upon: it has been demonstrated by flash photolysis that the excited state of 9,9′-dianthryl (n = 0) has an ion pair structure in polar solvents. In the case of 1,1-dianthrylmethanes, no excimer emission was detected in the study of photocycloaddition in benzene solutions either for 1,3-di-9-anthrylpropane in benzene or ethanol or after cleavage of their photocycloisomer (Ferguson *et al.* 1977[9]) (nevertheless excimer emission was claimed for 1-(9-anthryl)-3-(1-anthryl)propane but the authors indicated to have observed no photocycloadduct formation (Itoh *et al.* 1980[12])).

(b) 1,2-Di(9-anthryl)ethanes (AC_2A). Because the excimer geometry requires that the ethane link be in an eclipsed conformation, which AC_2A would not reach spontaneously, Ferguson *et al.*[27] and Anderson *et al.* 1979[9] used the Chandross photodissociation method to generate two anthracene nuclei from the photocycloisomer in a *very rigid matrix* to maintain them in close proximity selecting as host the photocycloadduct crystal at very low temperature (< 10 K); under these extreme conditions, splitting occurred at 10 K and a broad red (λ_{max} ~ 580 nm) emission appeared, followed, at higher temperature, by a yellow green emission (λ_{max} ~ 530 nm); this species can be rephotocyclized > 100 K, *i.e.* when sufficient activation energy is available. Because the ethanobridge imposes a rotation towards *gauche* and *anti* conformations, on further heating of the matrix, a blue structured species was finally formed where little overlap subsists between the two nuclei; this conformation cannot be cyclized again;[27] see Fig. 9.

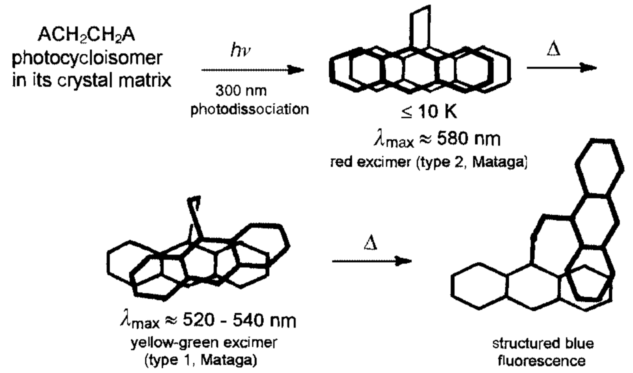
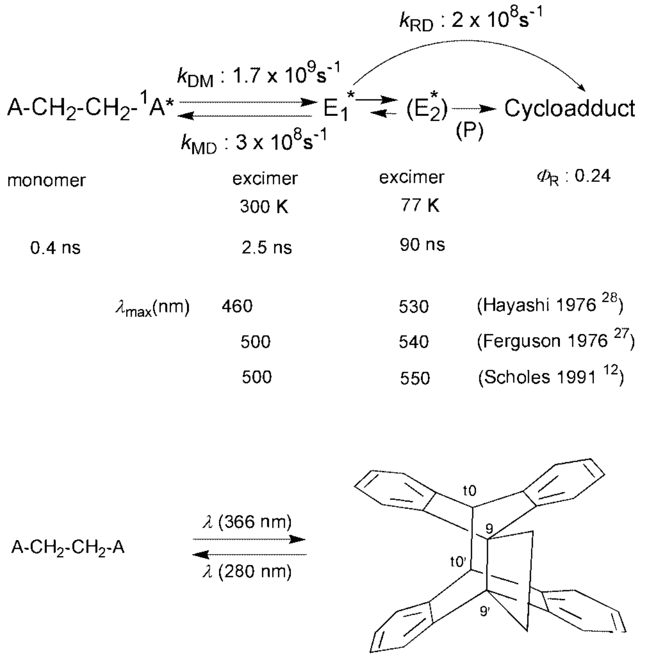


Fig. 9 Proposed structure for selected conformations of 1,2-di(9-anthryl)-ethane obtained by photodissociation of the photocycloisomer at 300 nm at very low temperature, followed by gradual softening of the crystal matrix. Adapted from Ferguson *et al.* 1976,[27] with permission. Adapted with permission from Anderson *et al.* 1979,[9] copyright 1979 American Chemical Society.

Another important result was presented by Ferguson[9] in 1980 based on the temperature dependent quenching of AC_2A fluorescence, in MCH-D: methylcyclohexane–decalin. From $T \cong 200$ K, $\phi_{F\ (lim)} \cong 0.45$, to T = 298 K, ϕ_F = 0.21, the fluorescence quenching ($\Delta\phi_F$ = 0.24) corresponds to the observed photocycloaddition quantum yield, at 298 K: ϕ_{RD} = 0.24. The author concluded that once a nearly overlapped conformation of two A rings is attained during the lifetime of the excited state, the consequence is either fluorescence or photoreaction or both depending on temperature. In that case, according to Ferguson, there is no need of partitioning in another intermediate (called pericyclic minimum in this account) (see Fig. 6). This case might correspond to a partitioning coefficient $\alpha \geqslant 0.95$, *i.e.* the photoreaction is too fast to allow another channel to compete. A similar statement was made for ACH_2A by Ferguson in 1981.[9]

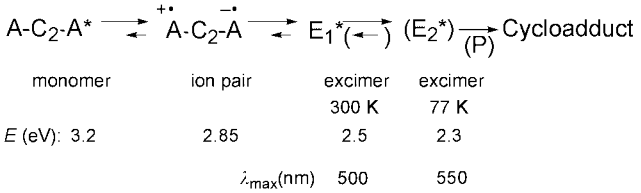
These experiments were complemented later with extensive calculations by Scholes *et al.* 1991[12] using semi-empirical methods (SCF-MO-CI treatment of valence π electrons). Computation of the ground state and excited state surfaces allowed the description of the geometry of two excimers (E_1, E_2) at $\lambda_1 \cong 500$ nm and $\lambda_2 \cong 550$ nm. Scholes also studied the room temperature fluorescence decay using the time correlated single photon counting technique and found two pure components (kinetic parameters: 1/λ: 0.43 ns, A : 20690 and 1/λ′ : 2.5 ns, A′: 4426 in methylcyclohexane/isopentane: MCH/IP) which he assigned to the locally excited state and to excimer E_1, respectively. From these data and the experimental photocyclization quantum yield and according to equations derived from Scheme 7, the rate constants for excimer E_1 formation and its transformation into photoisomer were determined (Scheme 10).

In a study of the *solvent influence* by picosecond flash photolysis, Yao *et al.*[28] demonstrated the ultrafast formation of



Scheme 10 Photocycloisomerisation of 1,2-di(9-anthryl)ethane (A–CH_2CH_2–A) *in MCH*:*IP*; excimer (E_2^*), characterized at 77 K, was not observed at ambient temperature presumably because the fluorescence cannot compete with the photoreaction. The 'monomer' is a mixture of ground state conformers. (P) denotes the pericyclic minimum (see Fig. 6).

an ion-pair (i.p.) by intramolecular electron transfer in acetonitrile (Scheme 11, and spectra in section 3.1.2); this was not unexpected by the authors who derived a value of 2.85 eV for the i.p. energy, (*E*½ $A^{+\bullet}$/A: + 0.96; *E*½ $A^{-\bullet}$/A: −1.99 eV *vs.* SCE in CH_3CN); the S_1 level being ≈ 3.2 eV, the electron transfer should be exothermic by *ca.* 0.35 eV. It was also shown that the i.p. collapses to excimer E_1. Therefore, a slightly different mechanism is proposed for polar solvents in Scheme 11.

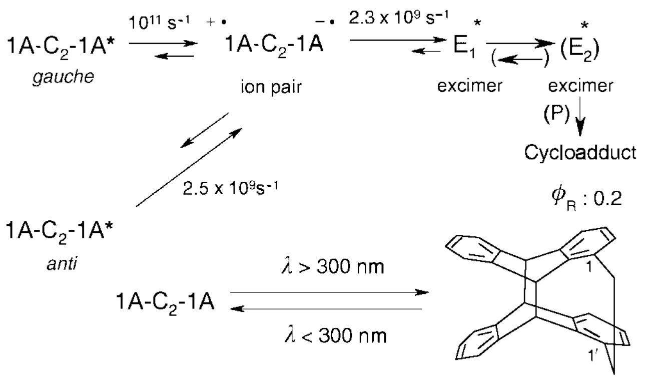


Scheme 11 Possible reaction scheme for 1,2-di(9-anthryl)ethane (AC_2A) photocycloisomerization *in acetonitrile* at ambient temperature. Excimer (E^*_2) was characterized only at low temperature (Hayashi *et al.* 1976.[28]). The ion pair was detected by ps flash photolysis (Yao *et al.*[28]). *E* (eV) ≡ excited state energy. For other symbols see Scheme 10.

(c) 1,2-Di(1-anthryl)ethane (1A–C$_2$–1A). This molecule, studied by Hayaschi *et al.* 1976, 1977[28] was shown to photocyclize into the 9,9′:10,10′ cycloadduct. Using picosecond flash photolysis, Yao *et al.*[28] could measure the kinetics of the i.p. and excimer E_1 formation in acetonitrile, the latter implying probably some harpooning effect.[29] But despite the intermediacy of the i.p., the cyclization quantum yield was found to be similar in MCH and acetonitrile (ϕ_R : 0.2), presumably because, in this case, the slow step is the transformation of E_1 into the cycloadduct (Scheme 12).

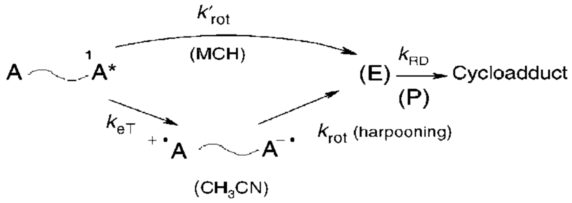
As noticed by Yao *et al.*,[28] 1,2-dianthrylethanes are examples of a composite system with identical halves that undergo solvation induced symmetry breaking in the S_1 state and whose symmetry is restored by excimer formation (contrary to 9,9′-dianthryl); this is due to the exceptional redox properties of anthracene.

2.2.3 Other dianthryls with short flexible chains In section 2.2.1, two remarkable bichromophores ACH_2OCH_2A and $AOCH_2OA$ have been reported to undergo a very efficient photocyclization (Table 3), attributed to an exceptional flexibility of the chain linking the two reactive entities. Furthermore, the reaction quantum yield was shown to increase with solvent polarity.ϕ_R (ACH_2OCH_2A): MCH = 0.30, CH_3CN = 0.50 (Castellan *et al.* 1979[8])ϕ_R ($AOCH_2OA$): MCH = 0.38,CH_3CN = 0.43, MeOH = 0.54 (Desvergne *et al.* 1995[24])



Scheme 12 Proposed reaction scheme for the photocycloisomerization of 1A–C_2–1A *in acetonitrile*. The two sets of conformers react at different rates and the ion pair was shown to collapse to excimer E_1* which probably involves some harpooning effect.[29] For further details see Schemes 10 and 11. Possible back electron transfer from the ion pair to 1A–C_2–1A ground state has not been included in the Scheme.

These solvent effects are surprising for symmetrical bichromophores. In view of the preceding results on 1,2-dianthrylalkanes, it is tempting to propose the formation of an ion pair as intermediate which could accelerate the cycloadduct formation by some sort of harpooning effect[29] (Scheme 13). No excimer emission has been detected. Nevertheless, more work is necessary to ascertain the mechanism.



Scheme 13 Suggested mechanism for photocycloaddition of ACH_2OCH_2A or $AOCH_2OA$ in non polar (MCH) or polar (CH_3CN, CH_3OH) solvents; k_{rot}, k'_{rot} denote bond rotation rate constants to attain a non fluorescent excimer (E) geometry; eT denotes electron transfer. It is assumed that k_{RD} >> k_{rot} and k'_{rot}.

2.2.4 Intramolecular regioselectivity (a) A dissymmetrical mode of cyclization, the *9,10*:*1′,4′ closure* has been found for some bichromophores incorporating dimethylsilyl groups in the linking chain: $ASiMe_2OSiMe_2A$[16] and $ASiMe_2$–$(CH_2)_n$–$SiMe_2A$ (*n* = 1, 2) (Desvergne *et al.* 1989[12]). The photoreactivity of the first compound is considered elsewhere in this account (sections 2.2.2.2 and 3.1.2). These derivatives seem to follow the same singlet state mechanism as the classical bichromophores (Schemes 7 and 9) and involve one lateral ring for *steric reasons*. This is borne out by the exclusive 9,10 : 1′,4′ closure of 9-(1-anthrylmethoxymethyl)anthracene (1A–CH_2OCH_2–9A) (Castellan *et al.* 1979[8]).

(b) Another mode of cyclization is undergone by some bichromophores bearing a short linking chain (1 to 3 links); it consists of an intramolecular Diels–Alder reaction involving a *9,10*:*1′,2′ closure*. Most of them cyclize through a triplet state route and are examined in the next section (2.2.5). Here it is worth highlighting the *singlet state reactivity* of some alkyl anthranilates (Fig 10). Becker *et al.* 1989[12] found that the reaction proceeds in solution with high quantum yield, the latter is not affected by dioxygen; remarkably also, the closure, which

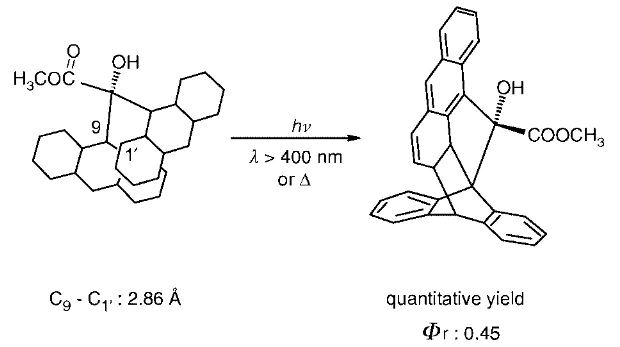


Fig. 10 9,10 : 1′,2′ (Diels–Alder) photocycloisomerization of methyl 9-anthrilate in toluene. The reaction is stereospecific and proceeds smoothly at ≈ 200 °C (Becker *et al.* 1989.[12]).

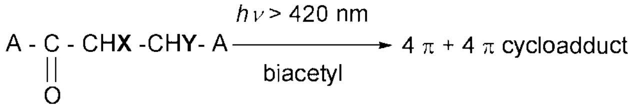
can proceed smoothly by melting (≈ 200 °C) is quantitative and stereospecific. These results are suggestive of a *hot ground-state reaction* due to geometric constraints as evidenced by the short C_9–C_1', distance and the broadening and bathochromic shift of the UV spectrum. Di(9-anthryl)dimethylsilane (ASi-Me_2A) might react in the same way (Daney *et al.* 1985[12]) but experimental evidence for such a mechanism is lacking.

2.2.5 The triplet state reactivity The intramolecular cyclization can proceed efficiently through the triplet state, as has been demonstrated by biacetyl triplet sensitization and dioxygen quenching: the triplet reactivity was observed for short chain bisanthracenes, especially (but not exclusively) when the compounds include a *9-anthroyl group*. The regioselectivity 9,10 : 1′,2′ or 9,10 : 9′,10′ seems to depend on geometric factors. Some typical examples are given below:

4 π + 2 π cycloaddition. Becker and coworkers[12] have observed this closure for *cis*-di(9-anthryl)ethylene, di(9-anthryl) ketone, 1,2-di(9-anthryl)ethanone and a series of 1,2-di(9-anthryl) ethanes. In the latter case, a competition occurs between the singlet state route (more efficient) and the triplet pathway which must be sensitized, unless there are substituents favouring intersystem crossing such as X = C_6H_5CO (Fig. 11).

4π + 4π cycloaddition. The triplet sensitized cycloisomerizations were observed by Becker and Amin, 1989[12] to give 4π + 4π cycloadducts if the molecular geometry of the ground state facilitates parallel alignment of the anthracene moieties as is the case for propano-linked systems where the *reaction quantum yields* were found to be *remarkably high* and to exceed those of the corresponding excited singlet state reactions (Scheme 14). Such is the case, also, for an ethanolinked bichromophore, the 1,1′, 5,5′-tetrachloro-di(9-anthryl)ethane (Becker and Anderson, 1985[12]), which by biacetyl sensitization, is transformed exclusively into two isomeric 4π + 4π cycloadducts in high yield (ϕ_R = 0.43).

Despite the great interest of these results, no in-depth mechanistic study has been performed so far on the intramolecular triplet reactivity.



X	Y	Φr	Φr (air saturated)
H	H	0.65	< 0.02
H_3C	H	0.72	0.02

Scheme 14 Typical example of triplet sensitized cycloisomerization of some propanolinked bisanthracenes. The quantum yields are the highest observed for the cycloaddition of anthracenes.

2.3 Effective molarity

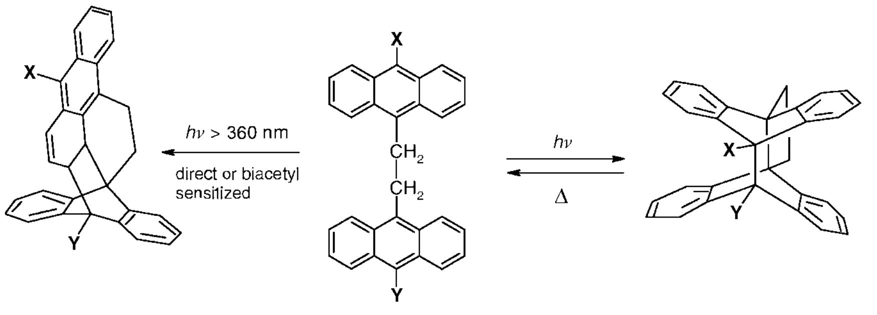
The effective molarity (EM) is the ratio of intra- over intermolecular rates of cycloaddition; it is therefore an indicator of the concentration under which the ring formation predominates over the polymerization. For photocyclomerization without excimer (2.2.1) it follows that:k_R (intra) = k_{dim} (inter) [EM]k_R was observed to be in the range: (2–90) × 10^7 s^{-1} for shorter chains (Table 3) and k_{dim} ≅ 1–2 × $10^9 M^{-1}s^{-1}$ in the absence of significant steric effect (Table 1). It is therefore advisable to have: [EM] < 2 × 10^{-2} M but for very high closure rates, [EM] can reach 4 × 10^{-1}M.

When a fluorescing excimer is observed, the comparison should be made between k_{DM} (inter) which was found to be diffusion controlled ≅ 10^{10} M^{-1} s^{-1} (Table 2) and k_{DM} (intra) reported to be in the range (3–20) × 10^8 s^{-1} (Table 4). It follows that:k_{DM} (intra) = k_{DM} (inter) x [EM]Consequently the effective molarity should be: [EM] < 3 × 10^{-2}M. For longer chains, lower values of [EM] should be considered.

3 Mechanism of photochemical and thermal dissociation

3.1 Photodissociation

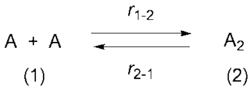
3.1.1 Photodissociation quantum yield By irradiation in the range 250–290 nm, anthracene photodimers (or intramolecular



Φr		X	Y		Φr
0.1	← biacetyl	H	H	direct →	0.26
0.005	← direct	COC_6H_5	H	↛	—

Fig. 11 Direct and triplet sensitized (typically AC_2A 2 × 10^{-3} M in benzene at 420 nm, with biacetyl 2 × 10^{-1} M under argon) irradiation of di(9-anthryl)ethane derivatives. The phosphorescence of biacetyl has been found to be quenched at nearly diffusion controlled rate.

cycloadducts) photodissociate into two anthracene nuclei; but at those wavelengths, the monomers redimerize. Eventually, a photostationary state is reached when the two rates ($r_{1 \rightarrow 2}$ and $r_{2 \rightarrow 1}$) are equal (Scheme 15).



Scheme 15 Rates of photodimerization ($r_{1 \rightarrow 2}$) and of photodissociation ($r_{2 \rightarrow 1}$)

These rates are expressed as a function of the quantum yields:

$$r_{1-2} = \phi_{1-2} \times I_{a1}$$

$$r_{2-1} = \phi_{2-1} \times I_{a2}$$

I_{a1} is the intensity absorbed by the monomer which is proportional to $I_0 \times (OD_1)_\lambda$. I_{a2} is proportional to $I_0(OD_2)_\lambda$ at the excitation wavelength λ (OD denotes optical density instead of absorbance A which is used as a symbol for anthracene); therefore, it becomes:$\phi_{1-2} \times I_0 \times (OD_1)_\lambda = \phi_{2-1} \times I_0 \times (OD_2)_\lambda \phi_{2-1} = \phi_{1-2} \times (OD_1)_\lambda/(OD_2)_\lambda$

Assuming that ϕ_{1-2} does not depend on wavelength *i.e.* is the same at 366 nm and 250–290 nm as shown by Pereira *et al.* 1971[7] for anthracene, and knowing $(\varepsilon_1)_\lambda$ it is easy to derive ϕ_{2-1}. The values obtained for some intermolecular and intramolecular processes are collected in Table 5.

Table 5 Intermolecular and intramolecular photocycloaddition and photodissociation quantum yields of some anthracenes at ambient temperature in diverse solvents. $\phi_{2-1} = \phi_{diss}$

Compound	ϕ^{∞}_{dim} (intermol.) λ: 366 nm	ϕ_{1-2} (intramol.) λ: 366 nm	ϕ_{diss} λ: 254 nm	Solvent
A	0.35		0.63 0.55$^{(i)}$	CH[a] AN[b]
9MeA	0.16		0.81	CH[c]
ACH_2A		0.15	0.76	B[d]
ACHOHA		0.29	0.81	B[d]
$A(CH_2)_2A$		0.24	0.80$^{(ii)}$	MCH-D[e]
ACH_2OCH_2A		0.30	0.64	MCH[f]
$ASiMe_2OSiMe_2A$		0.17	0.81	MCH : IP[g]

(i) 269 nm (ii) at 283 nm. MCH = methylcyclohexane; AN = acetonitrile; CH = cyclohexane; B = benzene; D = decalin; IP = isopentane. $\phi_{diss}(A_2)$ = 0.35 (93 K), 0.22 (83 K), 0.55 (300–100 K) (Yamamoto and Grellmann[30]) [a] Kei Sin Wei and Livingston, 1967.[10] [b] Kaupp, 1971.[7] [c] Bendig *et al.*, 1981.[10] [d] Bergmark *et al.*, 1978.[8,10,12] [e] Ferguson, 1980.[9] [f] Castellan *et al.*, 1979.[8,10] [g] Ferguson *et al.*, 1981.[16]

It is noticeable that the sum of the two processes (direct and back reaction) most often amounts to 1 within experimental errors and this has been an argument in favour of the existence of a common intermediate between photocycloaddition and photocycloreversion (see energy profile, Fig. 6). This point is developed in the next section.

3.1.2 Mechanism of photodissociation The first results were reported by Menter and Förster 1972[30] on the photocleavage of di-9-methylanthracene $(MeA)_2$ in acetonitrile (10^{-4} M) at $\lambda_{exc.}$: 270 nm. The authors observed the fluorescence emission from the excimer and from the excited monomer in low yield, indicating a partial *adiabatic pathway*. Moreover they showed, by dioxygen quenching experiments, that the main fraction of excited monomer MeA* is formed directly from the excited photodimer $(MeA)_2$*. Their results were found to be consistent with the following equations:

$$(MeA)_2 \rightarrow (MeA)_2^* \ (\lambda_{exc.}\ 270\ nm)$$

$$(MeA)_2^* \rightarrow 2\ MeA + kT$$

$$(MeA)_2^* \rightarrow (MeAAMe)^* (MeA)_2^* \rightarrow (MeA)^* + MeA$$

$$(MeAAMe)^* \rightarrow 2MeA + h\nu_D \text{ (excimer fluorescence)-} (MeAAMe)^* \rightarrow 2MeA + kT$$

$$(MeA)^* \rightarrow MeA + h\nu_M \text{ (monomer fluorescence)} (MeA)^* \rightarrow MeA + kT$$

Because of the very low yields of the adiabatic pathways, it was concluded that the *major fraction* of the photochemically reacting molecules prefer a *diabatic path*.

In 1977 and 1978, Ferguson and coworkers[9] also observed an *excimer fluorescence emission* as a product of the photodissociation of the photodimers of anthracene (A_2), 9-methylanthracene $(MeA)_2$, the photoisomers of 1,2-di(9-anthryl)ethane, 1,3-di(9-anthryl)propane and other related compounds; the experiments were conducted in hydrocarbon matrices at various temperatures (100 – 298 K). The recognition of a thermally activated rate for the formation of the excimer implies the existence of a non-fluorescent precursor representating the primary photodissociated product state in the reaction and this was believed by the authors to be an excited state of Michl's pericyclic minimum.

In 1981, Ferguson *et al.*[16] investigated the photodissociation of the photocyclomer of 1,3-di(9-anthryl)-1,1,3,3-tetramethyldisiloxane $ASiMe_2OSiMe_2A$ whose closure has been examined in section 2.2.2.2 (see Scheme 9); the dissymmetrical photocycloadduct incorporates a *2,3-disubstituted naphthalene chromophore* which was excited at 290 nm. Interestingly, the photocycloisomer cyclo(ASiOSiA)* emits fluorescence whose intensity changes with temperature; at 100 K, the emission is characteristic of the naphthalene chromophore and lies in the ultraviolet. At ≈ 120 K, a broad excimer band appears in the visible region and grows, at the expense of the naphthalene emission, until the temperature reaches 225 K and then drops (Fig. 12). The excimer fluorescence quenching was interpreted as due to photocycloaddition.[16] However, the photodissociation (quantum yield = 0.81 at ambient temperature) is not totally accounted for by the above experiments.

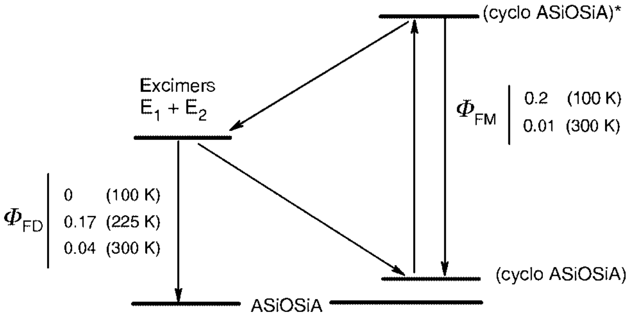


Fig. 12 Photodissociation of cyclo($ASiMe_2OSiMe_2A$) abbreviated ASiOSiA at 290 nm in a glass forming solvent composed of methylcyclohexane and isopentane (1 : 3), the fluorescence quantum yields of the excimers (E_1 + E_2) ϕ_{FD} were determined in the temperature range 100–300 K. See ref. 16.

An in-depth study was undertaken at the same time by Yamamoto and Grellmann[30] on dianthracene (A_2) and di(9-methylanthracene) $(MeA)_2$ in 2-methyltetrahydrofuran (MTHF) (10^{-4} M, λ_{exc} = 270 nm) in the 100–300 K temperature range. The authors recorded the fluorescence of A_2* (λ_{max} 315 nm), A* (λ_{max} 380, 400, 424 nm) and of the excimer (AA)* (λ_{max} ≈ 540 nm) following excitation and the variation of the fluorescence yields *versus* temperature. In agreement with previous work (Menter and Förster 1972,[30] Ferguson[9]), they found a distinct temperature dependent excimer emission; from flash photolysis (20 ps pulse of 265 nm light, time resolution 400 ps), the build-up and decay of excimer fluorescence was determined and it allowed the calculation of temperature activated parameters. These experiments and others led to the establishment of a mechanistic diagram which implies an intermediate (electronically excited tight complex

Xs) through which the major part of the singlet state proceeds at 293 K. At lower temperature, the dissociation proceeds through the triplet state which should also involve an intermediate Xt partitioning into A and A_2. The triplet route has been shown to be exclusive at 77 K. The proposed pathways are sketched in Fig. 13. In addition, it should be emphasized that the authors established that the photodissociation is wavelength dependent. These studies were extended to the anthracene–tetracene crossed photodimer (Yamamoto and Grellmann, 1982[10]).

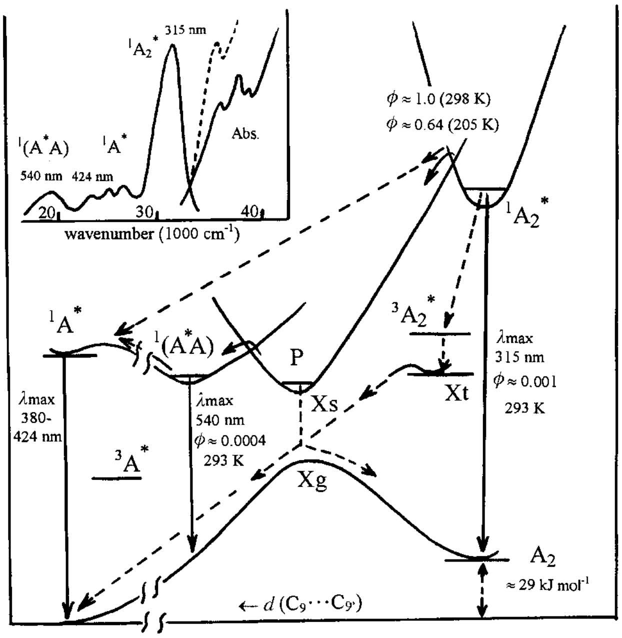
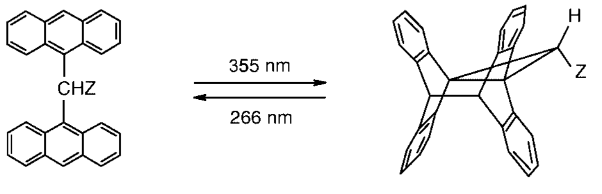


Fig. 13 Proposed energy profile for the photodissociation of the photodimers of dianthracene (A_2) and di(9-methylanthracene) $(MeA)_2$ in MTHF. At 293 K, the splitting occurs in the singlet state proceeding mainly through an electronically excited tight complex Xs (the pericyclic minimum) and partially through an excimer $^1(AA)^*$; the fluorescence quantum yields were found to be temperature dependent and very low at 293 K. At lower temperatures, the dissociation was shown to follow the triplet ($^3A_2^*$) route which is exclusive at 77 K. **Insert**: absorption and uncorrected fluorescence spectra of a degassed 10^{-4} M solution of A_2 in MTHF at 293 K ($\lambda_{exc.}$ 270 nm). Adapted from Yamamoto and Grellmann,[30] with permission.



1 a Z = H
b Z = OH
2

Scheme 16 Photocyclomerization of di(9-anthryl)methane (**1a**) and di(9-anthryl)methanol (**1b**) at 355 nm and photodissociation of their photocycloisomers **2a** and **2b** at 266 nm using picosecond laser absorption spectroscopy with a pulse width of 25 ps. **1** $\rightarrow$ **2** conversion was $\leqslant 5$ % and **2** $\rightarrow$ **1** $\leqslant 2$ %. (Manring *et al.* 1985.[24])

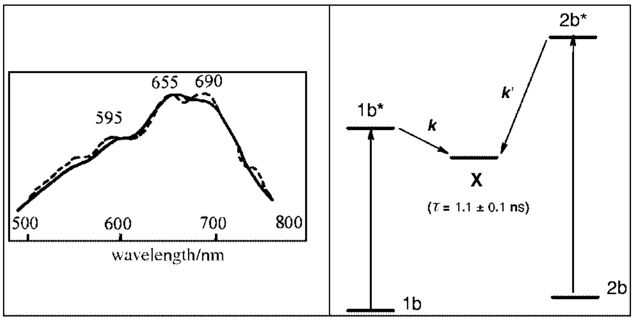


Fig. 14 Left: Spectra observed in CH_3CN after 60 ps: — (355 nm excitation of **1b**), ----- (266 nm excitation of **2b**); the two spectra have been normalized to show their identity. The shape of the transient does not vary with time (lifetime: 1.1 ± 0.1 ns). **Right**: proposed energy profile featuring the formation of the transient X (k, $k' \geqslant 1.5 \times 10^{10} s^{-1}$). Adapted with permission from Manring *et al.* 1985,[24] copyright 1985 American Chemical Society.

Manring *et al.* (1985[24]) studied the photocycloisomerization of two di(9-anthryl)methanes (Scheme 16) and their dissociation in various solvents by picosecond laser absorption spectroscopy in order to characterize a *common intermediate* (CI) (presumably the Michl pericyclic minimum). The transients were probed between 500 and 800 nm. Clear results were obtained in acetonitrile where laser excitation at 355 nm (of **1a**, **1b**) and at 266 nm (**2a**, **2b**) produced similar transient spectra within 60 ps of the laser flash (Fig. 14). The peak at 595 nm was assigned by the authors to the $S_n^* \leftarrow S_1^*$ absorption, which becomes the more intense in the non polar solvents, suggesting that the two other peaks (655nm and 690 nm) belong to a species with a charge transfer character. The authors describe this transient as a *common intermediate with an intramolecular ion-pair structure* and they consider that it coincides with *an excimer* in acetonitrile. Similar spectra were observed in ethanol but, in ether, the nature of the transients could not be defined.

Further picosecond laser absorption spectroscopy was accomplished by Yao *et al.*,[28] who were able to describe an intramolecular electron transfer in acetonitrile for 1A–CH_2CH_2–1A (see Section 2.2.2.2c) in comparing the spectrum obtained 60 ps after the flash with the absorption spectra of the S_1 state, the anion radical and the cation radical, respectively of 1-methylanthracene (Fig. 15). It is clear that the transients observed by Manring *et al.* 1985[24] do not correspond to those of ion pairs and therefore their assignment is questionable. The spectra (Fig. 14) also cannot be assignable to that of an excimer. Such a spectrum has been obtained by Dvornikov and Rentzepis[31] as the first transient, 100 ps after photolysis, of di(9-methylanthracene) $(MeA)_2$ at 266 nm in 1,2-dichloroethane; it is characterized by a wide absorption with bands at 480, 780 and 860 nm (Fig. 16) and a lifetime likely to be that of the excimer of 9-methylanthracene.

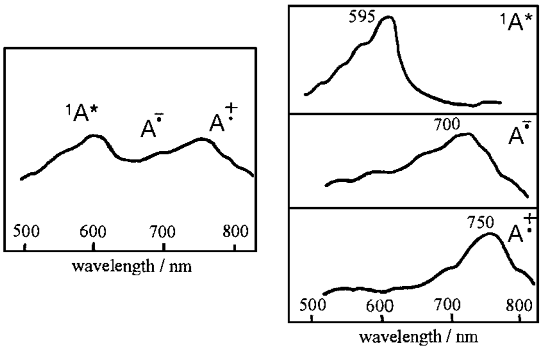


Fig. 15 Left: Spectrum observed in CH_3CN after 60 ps of 1A–CH_2CH_2–1A, the absorption at 595, 710 and 740–750 nm are characteristic of the locally excited ($^1A^*$) and of an ion-pair. **Right**: reference absorption spectra of the S_1 state, the anion radical and the cation radical in acetonitrile of 1-methylanthracene, respectively. Adapted with permission from Yao *et al.*,[28] copyright 1989 American Chemical Society.

In conclusion, the photodissociation mechanism of anthracenes photodimers or photocycloisomers does not seem to be as well understood as that of the photocycloaddition. Most studies have been conducted on dianthracene, di(9-methylanthracene) and the photoisomers of 1,2-di(9-anthryl)ethane, 1,2-di(1-anthryl)ethane and di-9-anthrylmethane, in various solvents and under different conditions. An adiabatic path leading to an excimer has been well established by fluorescence spectroscopy

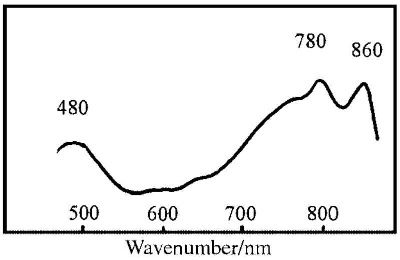


Fig. 16 Transient absorption of the photodimer of 9-methylanthracene in 1,2-dichloroethane 100 ps after excitation at 266 nm (30 ps laser excitation); all the broad bands were found to decay with the same lifetime (≈ 3 ns). Adapted from Dvornikov and Rentzepis[31] with permission.

and picosecond absorption spectroscopy but in low yield and the major part of the singlet state path proceeds through a non-emitting intermediate (diabatic process), presumably the pericyclic minimum. At low temperature, the triplet pathway is favoured.

3.2 Thermal dissociation

3.2.1 Kinetic and thermodynamic factors Photocycloadducts are split by melting the solid or by heating a degassed solution in an appropriate solvent; the cycloreversion can be quantitative.

The first order kinetics were followed by measuring the UV absorption in the 350–400 nm range *versus* time at a given temperature. NMR spectrometry was also used for monitoring the cleavage. Several kinetic parameters were obtained and selected values are reported in Table 6 in the Arrhenius form. Half lifetimes at ambient temperature have been calculated to compare the stability of different compounds as a function of the structure. Nevertheless, these data have been obtained by different authors in several solvents and under various experimental conditions; therefore they should be taken with caution.

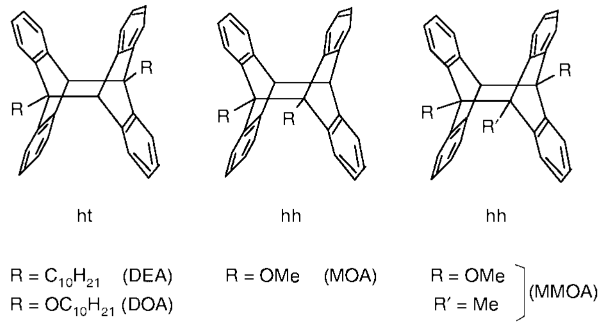
Despite this scattering of results, several trends emerge from Table 6. Some photodimers (A_2, *ht* photodimers and the cycloadduct of 1,2-di(9-anthryl)ethane are stable for many years at ambient temperature; this *thermal bistability* (open and cyclic forms) is an attractive feature for applications.[10,31] Another important result is the contrast between *hh* and *ht* photodimer stabilities; these data help understand the experimental difficulties encountered in the isolation of the *hh* isomers.

The intramolecular cycloadducts thermal stability can be modulated by small variation of structure. Thus cycloadducts of α,ω-di(9-anthryl)polyoxaalkanes were found to exhibit a variety of half lifetimes in benzene, at ambient temperature $AO(CH_2CH_2O)_3A$ $t_{1/2} \approx 2$ min; $ACH_2(OCH_2)_2OCH_2A$ $t_{1/2} \approx 78$ min; $ACH_2(OCH_2CH_2)_3OA$ $t_{1/2} \approx 64$ h (Desvergne *et al.* 1984[10]). Moreover, great enhancement of the rate of dissociation can be effected by chemical means. For instance, 9-anthraldehyde photodimer thermal reversion (with CF_3COOH 0.043 M in benzene at 25 °C) is *ca.* 3 × 10^5 times faster than under neutral conditions (Greene, 1960[8,10]).

The interesting question of synchronous *versus* stepwise thermal cleavage of 9,9′ and 10,10′-bonds has been addressed by Greene (1960[8,10]). From an elegant study of the dissociation kinetics of the *ht* photodimers of 9-bromoanthracene and 9-formylanthracene [compared with the cophotodimers (crossed dimers) of 9-bromoanthracene and 9-formylanthracene, respectively, with anthracene] he concluded that the 'bulk of the free energy of activation is associated with the *rupture of the 9,9′-bond* with some concomitant breaking of the 10,10′-bond', the extent of which being dependent on the substituent. The study was extended to two bis-anthracenes [photocycloisomers of 9-anthroic anhydride and of di(9-anthryl)methanol] and it was shown that the dissociation is also *largely* associated with the cleavage of only one of the two bridgehead bonds.

Due to the very low solubility of the photodimers, the experimental determination of the *thermal dissociation enthalpy* has been obtained either by measuring the heat of combustion of monomer and photodimer (Bender and Farber, 1952[32]) or of 9,10-dihydroanthracenes (Bendig *et al.* 1981[10,32]) or by calorimetry using the photodimer (or photocycloadduct) as solid (Donati *et al.* 1972,[32], Bergmark *et al.* 1978[8,12,24]). In this process, the caloric peak is strongly disturbed by the heat of melting; therefore these results cannot reflect the enthalpies in solution.

Recently calorimetric measurements (Grimme *et al.*[32]) using differential scanning calorimetry (DSC) were performed on *soluble ht* photodimers (substituted by long alkyl or alkoxy chains) and on *hh* photodimers (which are more soluble in organic solvents than the *ht* isomers); the concentrations used were $\geqslant 10^{-2}$ M, in cyclic hydrocarbons or tetrachloroethane (see Scheme 17 and Table 7).



Scheme 17 Pure and crossed photodimers used for the determination of dissociation enthalpy (Δ*H*) and kinetics. See Table 7.

The measured enthalpy difference between the *ht* dimer of DEA does not show a significant solvent influence; therefore this is also assumed for the other cases under study. Moreover, it may be accepted that the long alkyl chain (in DEA and DOA) is not an important factor to induce the difference of enthalpy between the photodimer and the monomers. Thus, it is

Table 6 Kinetic parameters for the first order thermal dissociation of anthracene (A) and 9-monosubstituted A in solution. The half lifetimes ($t_{1/2}$) are in years (y) or hours (h). B = benzene; TE = tetraline; CH = cyclohexane; DCB = *o*-dichlorobenzene; E = ether; θ(1 h) is the temperature at which $t_{1/2}$ is one hour, see Table 7 for comparison.

Compound	E_a /kJ mol^{-1}	$\log_{10}A$	$t_{1/2}$ (300 K)	θ (1 h) /°C	Solvent	Ref.
A_2	154	13.8	3 × 10^5 y	185	B	[a]
ht (9A-CHO)$_2$	131	14.3	9 y	110	B	[a]
ht (9A-CH$_3$)$_2$	160	16	2 × 10^4 y	149	TE	[b]
hh (9A-CH$_3$)$_2$	111	14.8	6 h	38	E	[b]
ht (9A-CH$_2$OH)$_2$	153	15.2	7 × 10^3 y	148	DCB	[b]
hh (9A-CH$_2$OH)$_2$	113	15	9 h	41	E	[b]
cyclo[A(CH$_2$)$_2$A]^i	143	14.8	3 × 10^2 y	129	DCB	[c]

i: Photocycloisomer of 1,2-di(9-anthryl)ethane. [a] Greene 1960,[8,10] measured between 45 and 130 °C. [b] Wolff *et al.* 1983.[22] [c] Becker *et al.* 1982.[12]

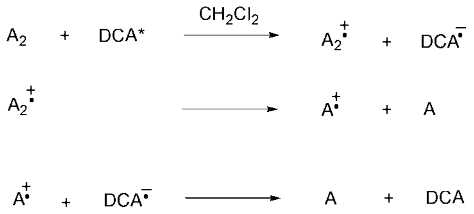
Table 7 Thermodynamic and kinetic parameters average values of several measurements for the thermal dissociation of some photodimers. See Scheme 17 for DEA, DOA, MOA and MMOA

Compound	Solvent	$-\Delta H^{a}_{\text{av.}}$/kJ mol^{-1}	θ^{b}(1 h)$_{\text{av.}}$/°C
ht DEA	DMCH[c]	28.3	119
	Tetralin	27.4	119
ht DOA	Tetralin	29.6	97
hh MOA	TCE[d]	43.1	42
hh MMOA	TCE[d]	43.6	55

[a] Precision ±3 kJ mol^{-1}. [b] The temperature at which $t_{1/2}$ of the reaction is one hour (±1 °C). [c] 1,3-Dimethylcyclohexane. [d] 1,1,2,2-Tetrachloroethane. Taken from Grimme *et al.*[32] with permission.

reasonable to conclude that the molar *dissociation enthalpy is ca. 15 kJ mol^{-1}* higher for a *hh* than for a *ht* photodimer (Grimme *et al.*[32]) (at least for these types of substituents). Furthermore the θ (1 h) data (Table 7) illustrate quantitatively the relative *kinetic instability* of the *hh* photodimers. *Quantum mechanical computations* give energy differences in reasonable agreement with the reaction enthalpies observed in solution. These are the more complete computational studies on anthracene photodimers effected with the most recent methods (Grimme *et al.*[32]).

3.2.2 Cleavage by photoinduced electron transfer Irradiated in the presence of molecular electron acceptors such as 9,10-dicyanoanthracene (DCA) or chloranil, dianthracene was shown to dissociate into the monomers. It was found by Roth and Schilling 1982[10] and Barber *et al.* 1982[10] that the reaction proceeds through electron transfer and the cation radical dimer ($A_2^{+\cdot}$) splits into neutral anthracene (A) and the anthracene cation radical ($A^{+\cdot}$), which is subsequently neutralized by the anion radical formed as outlined in Scheme 18.



Scheme 18 Mechanism proposed for the dissociation of anthracene photodimers catalysed by sensitised electron transfer. DCA = 9,10-dicyanoanthracene; other electron acceptors such as chloranil, cadmium disulfide and tetracyanoethylene were used.

A similar catalytic reaction has also been studied by Masnovi and Kochi 1985[10] in the presence of tetracyanoethylene. Barber *et al.* 1982[10] also used a suspension of cadmium disulfide along the same lines.

4 Conclusion

The mechanistic aspects of the *photodimerization* and the *cycloreversion* of anthracenes in fluid solution have been reviewed.

It has been shown that such clean and apparently simple reactions may involve complex kinetic schemes. The present account shows that much progress has been accomplished in the understanding of the mechanism; nevertheless, although the mechanistic pathways have been illuminated by monomer and excimer fluorescence, some dark areas still remain. Particularly, there is a need of sophisticated calculations to settle the controversial problem of the pericyclic minimum (conical intersection) which is believed to be a common intermediate in the singlet state mechanism. To that end, further ultra-fast flash photolysis studies should be undertaken to try to intercept other elusive transients; an in-depth study of the intramolecular triplet state reactivity might establish a mechanistic scheme and answer the question of concerted *vs* stepwise (expected for a triplet intermediate) pathway.

It is our hope that this review will be useful to those who are considering the use of anthracene derivatives as subunits in supersystems[33,34] in order to incorporate several functions such as switches for light emission, electron transfer relay, information storage… in molecular assemblies, artificial membranes, polymers and diverse materials.

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