Polar-Solvent Effect on the Photocycloisomerization of Symmetrical Bis[anthracenes]: A Transient Ultrafast Kinetic Study

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

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Bis[anthracenes] are the few among the fluorescing nonconjugated bichromophores that possess photoreactive properties. The 9,9′-[methylenebis(oxy)]bis[anthracenes] **1** ($AOCH_2OA$) exhibit the highest known intramolecular photocycloaddition quantum yield from the S_1 state and, moreover, display a higher yield in polar solvents, an unexpected result for symmetrical systems. No excimer fluorescence was detected in solution at room temperature. The 10,10′-dimethoxy derivative **1b** was studied by picosecond (ps) laser spectroscopy. In nonpolar solvents (methylcyclohexane), $S_n \leftarrow S_1$ was the only transient absorption detected, whereas, in polar solvents (MeCN), the growth and the decay of a second transient were recorded, and the second transient was attributed to a zwitterion $A^{+\bullet}-A^{-\bullet}$. The kinetics data were derived, and it was concluded that electron transfer and ion recombination should be at the origin of the observed rate enhancement of cycloadduct formation in polar solvents.

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1. Introduction.

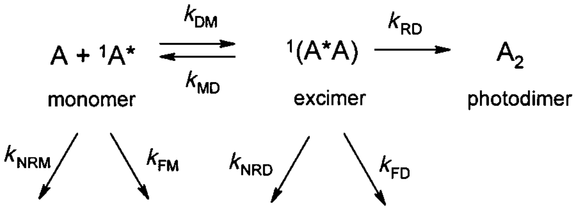
– A great number of studies have been devoted to the structural [1a] and mechanistic [1b] aspects of the photodimerization of anthracenes [2–5]. For the parent molecule and most derivatives, it has been shown that the singlet state is the reactive state at concentrations $\geq 10^{-3}$ M; this is outlined in *Scheme 1.*

Scheme 1. *Kinetic Scheme for the Dimerization of Anthracene and Substituted Anthracenes* (A) *from the S_1 State.* F, fluorescence; NR, nonradiative decay; CQ, concentration quenching; dim, photodimerization (*Birks*' notations [6]).

$$\begin{array}{llll} {}^1A^* & \longrightarrow & A & (k_F + k_{NR}) \\ {}^1A^* + A & \longrightarrow & A + A & (k_{CQ}) \\ {}^1A^* + A & \longrightarrow & \underset{\text{photodimer}}{A_2} & (k_{dim}) \end{array}$$

In several cases, it has been demonstrated that excimers (1:1 complexes in the excited state) are intermediates [1b][4][5][7], and it is now generally accepted that whenever a fluorescing excimer is detected, the kinetic scheme should be modified as shown in *Scheme 2*.

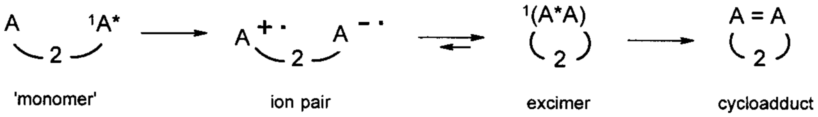
Scheme 2. *Kinetic Scheme for the Dimerization of Anthracenes Involving the Intermediacy of a Fluorescing Excimer.* k_F, fluorescence rate constant; k_{NR} nonradiative rate constant; M, monomer; D, excimer (*Birks*' notations [6]).



Nonconjugated bichromophores (bis[anthracenes]) such as 9,9′-(alkane-α,ω-diyl)-bis[anthracenes] $A-(CH_2)_n-A$ were found to be more convenient for mechanistic studies, because kinetics are first order at low concentration [4][5][8][9], and the problems due to aggregation are avoided.

The 9,9′-(ethane-1,2-diyl)bis[anthracene], represented as A2A for simplification, has been particularly investigated [10–12]. *Ferguson* and co-workers [10], and *Mataga* and co-workers [11][12] showed the role of intramolecular excimers in the formation of the photocycloadduct. *Yao et al.* [12], using picosecond (ps) spectroscopy, demonstrated the formation of an intramolecular ion pair and its transformation into an excimer in MeCN. These results are shown in *Scheme 3*; ion pairs were not formed in nonpolar solvents. *Mataga* and co-workers noted that *'A2A constitutes an example 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. This is due to the exceptional redox properties of anthracene'.* Despite the formation of an ion pair in MeCN, the cyclization quantum yield (0.2) was found to be the same in MeCN and methylcyclohexane (Mechx).

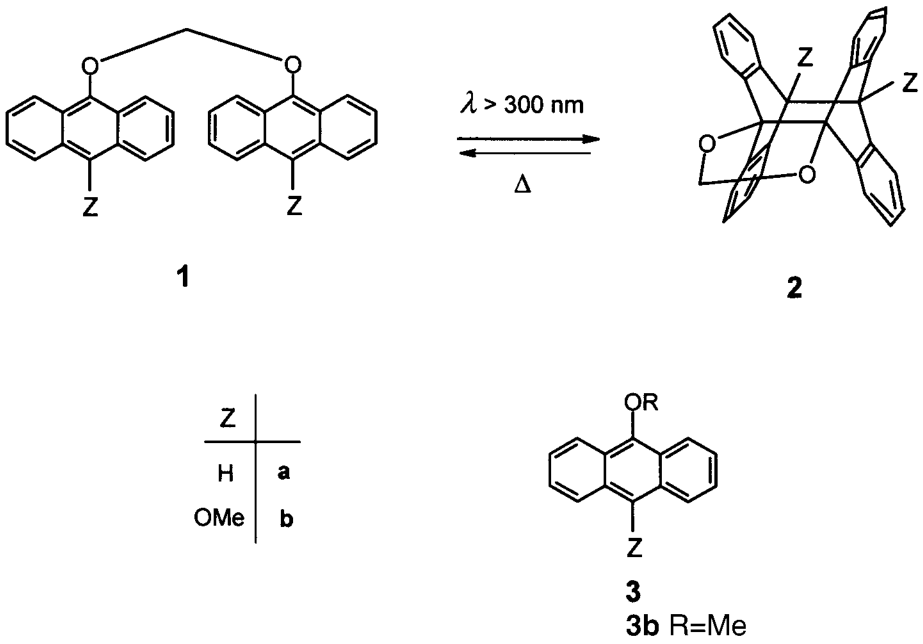
Scheme 3. *Proposed Mechanism for the Photocycloisomerization of A2A in MeCN at Room Temperature.* A = 9-Anthryl.



The system with the shortest chain ACH_2A, denoted A1A, was also carefully studied [13a–c]. No excimer fluorescence was observed. A laser flash photolysis study *in MeCN* revealed that transients were similar whether obtained from the open or the closed form and were assigned to a 'common intermediate'. However, in less polar solvents the results were not clear.

An important factor governing the cyclization efficiency is the molecular dynamics of the chain linking the two reactive chromophores; this was examined by the *Bordeaux* group [4][5][14–16] who discovered that the most efficient tether to date is OCH_2O, as depicted in **1a**,**b** (*Scheme 4*); compound **1a** was found to have the highest cyclization quantum yields (0.38 in Mechx, 0.43 in MeCN) from the singlet state; the apparent polar-solvent effect (within exper. errors) seems to vanish for the 10-MeO derivative **1b** (see below, *Table*). Moreover, in contrast to the case of A2A, no fluorescing excimer was detected [14], and single exponential decays were observed, as reported in a previous short communication [17], but the lifetimes in MeCN (< 0.4 ns) could not be determined by their single-photon timing system.

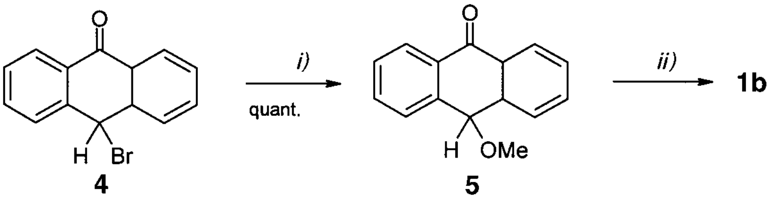
Scheme 4. *Photocycloisomerization of 9,9′-[Methylenebis(oxy)]anthracenes* **1**. The photocycloadduct **2** reverts thermally to the bis[anthracene] at room temperature. Compounds **3** are the reference molecules.



It was deemed of interest to investigate further the photocyclization of compounds **1** by the ps spectroscopy for a deeper insight into the kinetics and the role of solvent polarity. The absorbance of compounds **1** had to be high enough at 401 nm (exciting laser wavelength); only **1b** meets this requirement. The 9,10-dimethoxyanthracene (**3b**) was used as the reference molecule. Here, we report the synthesis of **1b**, a spectroscopic study of **1b** and **3b**, and their transient kinetics at room temperature in several solvents, to show the influence of solvent polarity on the photocycloaddition mechanism.

2. Synthesis. – The preparation of **1a** was described previously [14]. Methoxy derivative **1b** was obtained from 10-methoxyanthracen-9(10*H*)-one (**5**) by the *Dehmlow* [18] procedure (liquid-solid phase catalysis), CH_2Cl_2 acting as reactant and solvent (*Scheme 5*). The preparation is fully described in the *Exper. Part*. Compound **5** was known to be generated from 10-bromoanthracen-9(10*H*)-one [19], and we found that the reaction works smoothly in the presence of calcium carbonate; 10-bromoanthracen-9(10*H*)-one is easily obtained from Br_2 and anthracen-9(10*H*)-one according to [19b], but in CCl_4 instead of CS_2.

Scheme 5. *Synthetic Scheme for the Preparation of* **1b**



i) $CaCO_3$, MeOH, reflux. *ii*) Solid KOH, CH_2Cl_2, $(Et_4N)HSO_4$ (*Dehmlow*'s procedure [18]).

3. Spectroscopic and Photochemical Studies. – The electronic absorption spectra of **1a** and **1b** are represented in *Fig. 1*. Whereas solutions of **1a** are pale yellow, those of **1b** are bright yellow, in accordance with the *ca.* 15-nm (950 cm^{-1}) shift, usually observed between 9-substituted and 9,10-disubstituted derivatives [20]. For **1a**, it has been previously shown that there is no significant interaction between the chromophores in the ground state in solution; this was corroborated in the gas phase by means of the supersonic free jet technique indicating that the lowest excited state of **1a** corresponds to a locally excited (LE) anthracene transition [14].

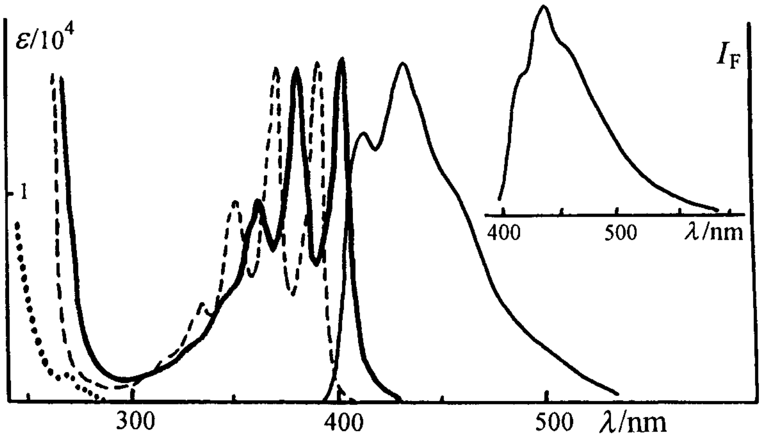
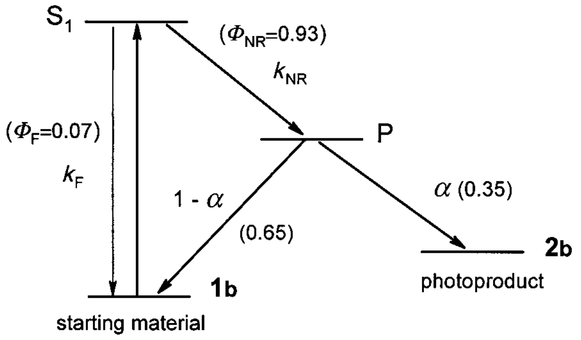


Fig. 1. *UV Absorption spectra* (left-hand) *of* **1a** (- - - -), **1b** (——), *and* **2b** (· ····) *in methylcyclohexane* (Mechx) (conc. *ca.* 10^{-4} M) *and fluorescence emission* (right-hand) *of* **1b** (——) *in Mechx*, $\lambda_{exc.}$ *370 nm*. Inset: fluorescence spectrum of **3b**.

Irradiation of **1b** in *Pyrex* vessels ($\lambda \geq 320$ nm) with a high-pressure Hg lamp in Et_2O provided the photocyclomer **2b** (*Scheme 4*), which was isolated and recrystallized (white crystals) in satisfactory yield (not optimized), as detailed in the *Exper. Part*. The electronic absorption spectrum is shifted to deep UV ($\lambda < 300$ nm) as shown in *Fig. 1*; this large shift is accompanied by marked differences in other physical properties [1a][5]. Photocyclomer **2b** reverted to **1b** slowly at room temperature and much faster upon heating. Therefore, compound **1b** exhibits the same photochromic properties as **1a**, which was shown previously to undergo several closure-opening cycles in degassed solvents [21].

The fluorescence spectrum of **1b** in solution at room temperature is represented in *Fig. 1*. It resembles that of the reference compound **3b** and does not reveal the presence of an excimer. This is, also, borne out by the single exponential fluorescence decay ($\tau = 1.2$ ns in Mechx) observed by the single-photon timing technique (SPT) (see *Table*). In MeCN, the decay ($\tau < 0.3$ ns) cannot be measured with the SPT equipment (*vide infra*). As shown in the *Table*, the fluorescence quantum yields ϕ_F are low, especially in MeCN, and much lower than those of the reference **3b**, which have been found to be 0.86 in Mechx ($\tau_F = 14.7$ ns) and 0.69 in MeCN ($\tau_F = 15$ ns) [16a]. Such low fluorescence intensities have also been observed for other short-link-containing bis[anthracenes], *e.g.*, ACH_2OCH_2A ($\phi_F = 0.03$ (Mechx) [22]) and ACHOHA ($\phi_F = 0.02$ (hexane, benzene) [13a][23] or 0.003 (MeCN) [23]). In contrast, 9,9′-(propane-1,3-diyl)bis[anthracene] displays a higher fluorescence intensity ($\phi_F = 0.47$ (MeChx), $\tau_F \approx 6.0$ ns), compared to that of the reference molecule, 9-decylanthracene ($\phi_F = 0.43$, $\tau_F \approx 6.3$ ns) [9]. For the majority of anthracene derivatives, it has been found that the main nonradiative deactivation channel is intersystem crossing, *i.e.*, $\phi_F + \phi_{ISC} \approx 1$ [6][24]. In the case of $AO(CH_2)_2OA$, it was confirmed that ϕ_{ISC} is negligible ($\phi_{ISC} < 0.1$ at 20°) [16a]. If this holds for **1b** (*vide infra*), we can infer that the major nonradiative channel ($\phi_{NR} = 1 - \phi_F$) reflects intramolecular interactions between the aromatic moieties on the way to the photocycloadduct. As the reaction quantum yield ϕ_R is lower than ϕ_{NR}, there must be at least one intermediate inducing partitioning between product and starting material (the chemical yield is quantitative). This intermediate is likely to be the pericyclic minimum (P; see *Scheme 6*, according to *Michl*'s model [25]). The assumption that ϕ_{ISC} is negligible and the strong decrease of ϕ_F from Mechx to MeCN were addressed by ps spectroscopy that is developed in the next section.

Scheme 6. *Proposed Energy Profile for the Photocycloaddition of* **1b** *in Methylcyclohexane* (Mechx). $\phi_R = 0.33$; $\phi_F = 0.07$ (ϕ_{ISC} negligible), $\phi_{NR} = 0.93$, and $\alpha = \phi_R/\phi_{NR} = 0.35$ (see *Table*).



4. Ultrafast Spectroscopy. – Laser excitation (401 nm, 0.06–0.1 mJ) of **1b** in nonpolar solvents (Mechx ($\varepsilon = 2.0$) or toluene ($\varepsilon = 2.4$)) produces similar transient absorption profiles to that of the reference compound **3b**, with a maximum centered at 570 nm (*Fig. 2*). Their shape does not vary with time and corresponds to the $S_n \leftarrow S_1$ absorption of the anthracene chromophore LE (locally excited anthracene) [1][4–6]. Indeed, the signal decays exponentially with a time constant of 1.05 ns in Mechx and

Table. *Photocycloisomerization* (ϕ_R; 366 nm), *Fluorescence* (ϕ_F), *and Nonradiative Deactivation* (ϕ_{NR}) *Quantum Yields of Compounds* **1** *and Related Bis[anthracenes] at Room Temperature.* The partition coefficient α is derived from $\phi_R = \alpha\ \phi_{NR}$; k_R which denotes the photocyclomerization rate constants is calculated from $\phi_R = k_R\tau$

	Solvent[a])	ϕ_R	ϕ_F	$\tau_1/10^{-9}$ s[b])	$\tau_1/10^{-9}$ s[c])	ϕ_{NR}	α
1a	Mechx	0.38	0.040	0.4		0.96	0.39
	MeCN	0.43	0.003	–		0.99	0.43
1b	Mechx	0.33	0.070	1.2	1.05	0.93	0.35
	MeCN	0.31	0.002	–	0.045	0.99	0.31
ACH_2OCH_2A [22]	Mechx	0.30	0.03	0.9		0.97	0.31
$A(CH_2)_3A$ [9]	Mechx	0.14	0.47	6.0		0.53	0.26
$AO(CH_2)_2OA$ [16a]	Mechx	0.22	0.22	3.8		0.78	0.28

[a]) Mechx = methylcyclohexane. [b]) From degassed solutions by the single-photon timing technique (SPT). [c]) From aerated solutions by laser (ps) flash spectroscopy.

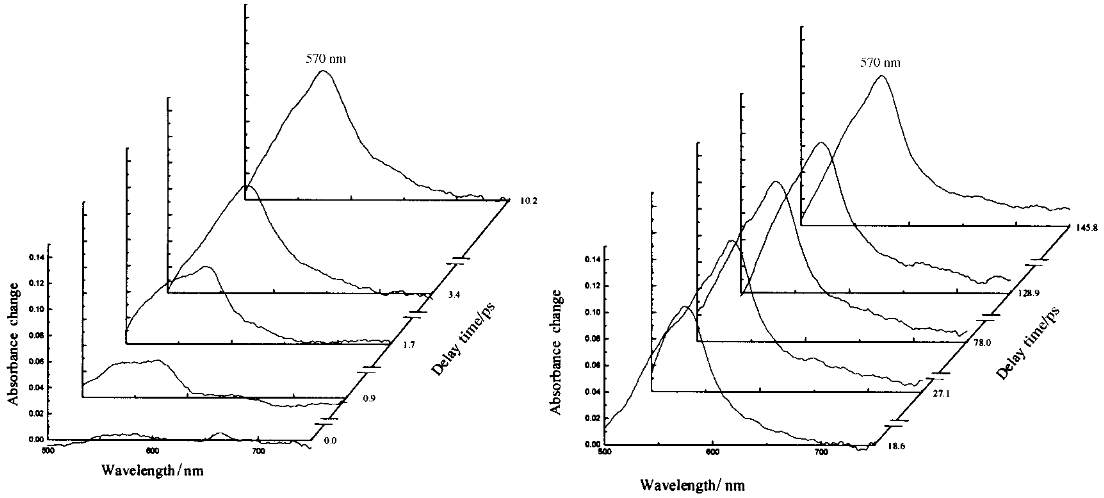


Fig. 2. *Absorbance change* vs. *wavelength at various delay times* (0.9 – 145.8 ps) *after excitation of* **1b** *in methylcyclohexane* (Mechx) *solution at room temperature* (transient 1)

0.8 ns in toluene, in excellent agreement with the fluorescence lifetimes obtained by single-photon counting.

This model is also enforced by the similarity of the transient absorption spectra displayed by **1b** and **3b** and the absence of other emitting species involving an intramolecular through-space interaction between the two chromophores in **1b**. In addition, no broadening of the signal delivered by **1b** is noticed upon increasing the delay time, in contrast to the observations reported by *Mataga et al.* [26] for 9,9′-(ethane-1,2-diyl)bis[anthracene] (the profile broadening being ascribed to intramolecular excimer formation).

Under the same experimental conditions in MeCN and other polar solvents, laser excitation of the reference compound **3b** always produces, as expected, the same transient spectrum as in methylcyclohexane (*Fig. 2*), in accordance with a $S_n \leftarrow S_1$

absorption profile. In contrast to **3b**, totally different time-resolved spectra are displayed by **1b** in polar solvents (MeCN ($\varepsilon = 36$), MeOH ($\varepsilon = 32.6$), ethyleneglycol ($\varepsilon = 38$), propylene carbonate ($\varepsilon = 66$)), as shown in *Fig. 3*.

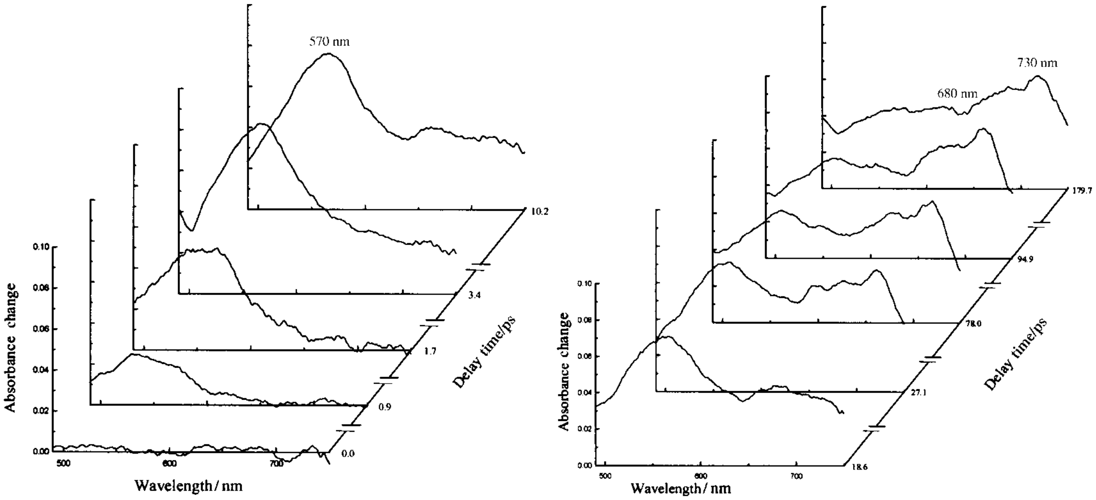


Fig. 3. *Absorbance change* vs. *wavelength at various delay times* (0.9 – 179.7 ps) *after excitation of* **1b** *in acetonitrile* (MeCN) *solution at room temperature.* Similar spectra are observed in the other polar solvents used (transient 1 and transient 2).

Indeed, the absorption profile for a 1.7 – 3.4 ps delay is very similar to the $S_n \leftarrow S_1$ spectrum given by **3b** (see *Fig. 2*). With an increase of the delay time (> 50 ps), the spectrum presents a second transient scaling between 650 and 760 nm, with two bands culminating at *ca.* 680 and 730 nm, respectively. Thus, after 50 ps, a remarkable enhancement of this new absorption is observed, which grows at the expenses of the $S_n \leftarrow S_1$ band (*Fig. 3*) and completely decays after 600 ps. The common rise of this dual transient absorption (45 ps, $k = 2.3 \cdot 10^{10}\ s^{-1}$) corresponds to the decay of the $S_n \leftarrow S_1$ absorption band (45 ps, $k = 2.2 \cdot 10^{10}\ s^{-1}$). The kinetics of the transient-1 decay ($\tau \approx$ 45 ps) and the transient-2 rise ($\tau \approx 45$ ps) are determined by the absorbance changes *vs.* time (*Fig. 4*) and found to be first order (*Fig. 5*).

It is noteworthy that the decay at 570 nm has the same contribution for both the two components (680 and 730 nm), which decay similarly. This long-wavelength transient absorption is very similar in shape and position to that issued from the superposition of anion and cation anthracenyl radicals spectra, as reported and discussed by *Mataga et al.* [12]. These ionic species would be formed in polar solvents after symmetry breaking between the two identical aromatic halves *via* a fast intramolecular photoinduced electron transfer. This electron transfer, which requires two closely linked anthracene moieties, does not occur in the reference material. Thus, we propose that a zwitterionic species $A^{+\bullet} - A^{-\bullet}$ is produced for **1b** in polar solvents. Such an electron transfer is supported by the redox potentials obtained [27] for **3b** (E_{ox} (*vs.* SCE) = 0.98 V in MeCN; E_{red} (*vs.* SCE) = – 1.90 V in DMF); therefore, the reaction should be exothermic ($\Delta G^{o} \approx -0.32$ eV).

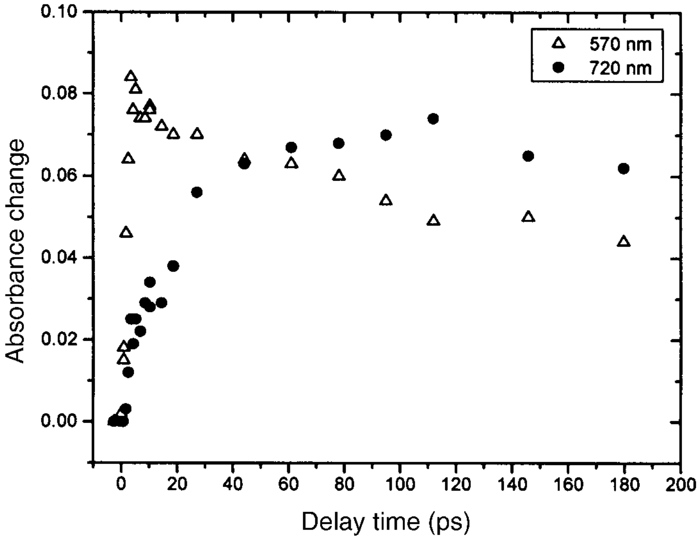


Fig. 4. *Kinetics of intermediates induced by excitation of* **1b** *in acetonitrile* (MeCN) *solution.* Absorbance change plotted as a function of time delay between excitation and probe pulses. Kinetics are measured at 570 nm (transient 1) and 720 nm (transient 2). The absorbance at 570 nm is due both to the transient 1 and transient 2.

At longer delay times (100–600 ps), after the disappearance of transient 1, the transient 2 decay kinetics can be measured. We find that they obey first-order kinetics with a lifetime of 230 ps ($k = 4.3 \cdot 10^9$ s^{-1}), see *Fig. 6*. The zwitterionic species may deactivate *via* charge recombination (rate constant k_P) leading to the pericyclic minimum (P) and back electron transfer to the ground state (rate constant k_{beT}).

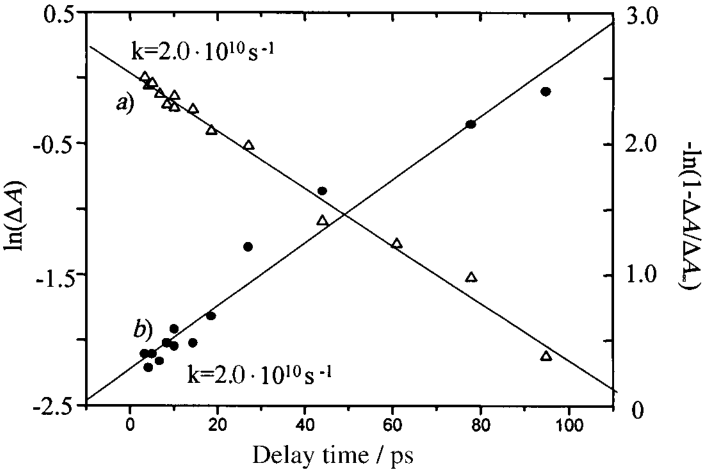


Fig. 5. *Kinetics of intermediates induced by excitation of bis[anthracene]* **1b** *in acetonitrile* (MeCN) *solution in logarithmic coordinates:* a) *decay of transient 1*, b) *growth of transient 2*. The 'pure' kinetics of transient 1 is deduced by subtracting the contribution of transient 2 at 570 nm.

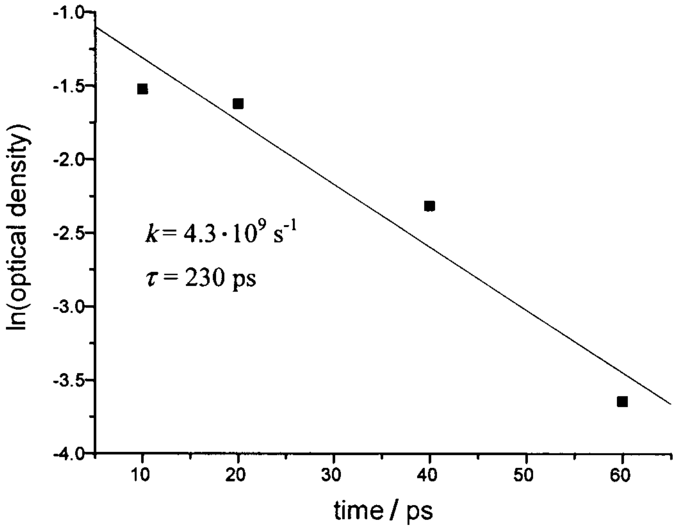


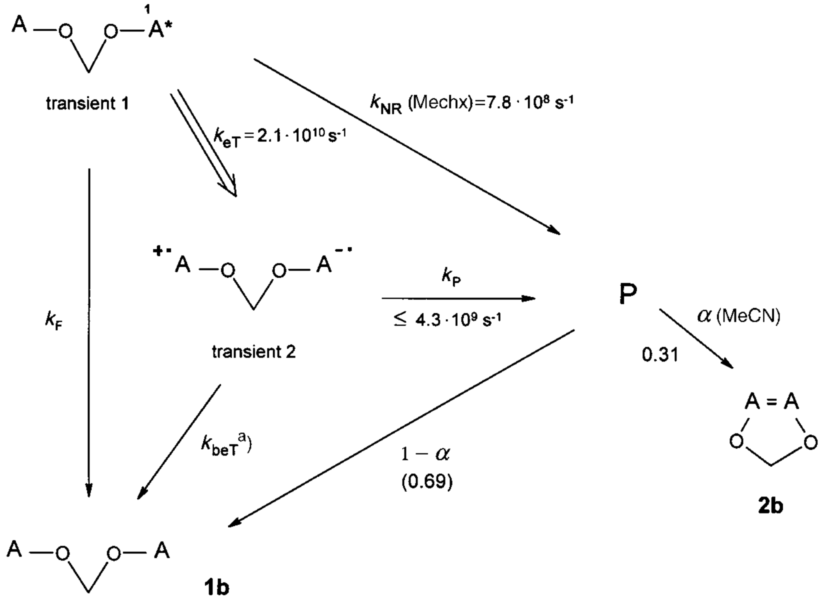
Fig. 6. *Decay kinetics of transient 2 for* **1b** *in acetonitrile* (MeCN), $\lambda = 720$ *nm*

The singlet state of **1b** deactivates *via* three channels as depicted in *Scheme 7*, namely fluorescence (k_F), a nonradiative process as in Mechx (k_{NR}), and an electron transfer (k_{eT}); the total rate constant is $2.2 \cdot 10^{10}$ s^{-1}; consequently: $2.2 \cdot 10^{10}$ s$^{-1} = k_F + k_{NR} + k_{eT}$. The fluorescence rate konstant k_F is $\leq 10^8$ s^{-1} (for **3b**, $\phi_F = 0.86$ and $\tau_F = 14.7$ ns), and k_{NR} (Mechx) is $7.8 \cdot 10^8$ s^{-1} ($0.93/1.2 \cdot 10^{-9}$ s^{-1}; see *Table*). Consequently $k_F + k_{NR} \ll k_{eT}$ and $k_{eT} \geq 2.1 \cdot 10^{10}$ s^{-1}. The experimental cycloaddition quantum yield ϕ_R is thus expressed as $\phi_R = [k_P/(k_P + k_{beT}) \cdot \alpha$; $0.31 = [k_P/(k_P + k_{beT})] \cdot 0.31$. As the transient 2 rate decay is *ca.* $4.3 \cdot 10^9$ s^{-1}, it results $k_P \leq 4.3 \cdot 10^9$ s^{-1} and $k_{beT} \ll k_P$. As noted earlier, this scheme is based on the assumption that the intersystem-crossing channel is negligible. Its validity was verified by conducting experiments in the ns time scale with a Nd-YAG 8 ns laser; compound **1b** fails to reveal any triplet-triplet absorption, whereas, under the same conditions, the reference compound **3b** displays a strong T-T absorption centered at *ca.* 430 nm, as expected [28]. These data are shown in *Fig. 7*.

Considering *Scheme 7*, one observes that the photocycloaddition rate that is already fast in Mechx is accelerated by approximately five times in MeCN. This is probably the result of a harpooning effect [29] due to charge recombination, which brings the two anthracene reactive centres to the best mutual positions.

Conclusion. – Ultrafast spectroscopy has allowed us to complete previous mechanistic studies of the intramolecular photocycloaddition of bis[anthracene] **1b**. In methylcyclohexane and other nonpolar solvents, the only observed transient is identified to be the S_1 state, and its lifetime is determined to be 1 ns, in excellent agreement with previous measurements. In MeCN, and other polar solvents, two transients are observed: transient 1 is identified as the S_1 state ($\tau \approx 45$ ps) and transient 2 as a zwitterion with a lifetime of 230 ps. We showed, based on the data, that *a very fast*

Scheme 7. *Proposed Kinetic Scheme for the Photocycloaddition of* **1b** *to* **2b** *in Acetonitrile* via *Electron Transfer.* P denotes the pericyclic minimum. The partition coefficient α is taken equal to that calculated in MeCN (see *Table* and *Scheme 6*).



a) k_{beT} is negligible within experimental error.

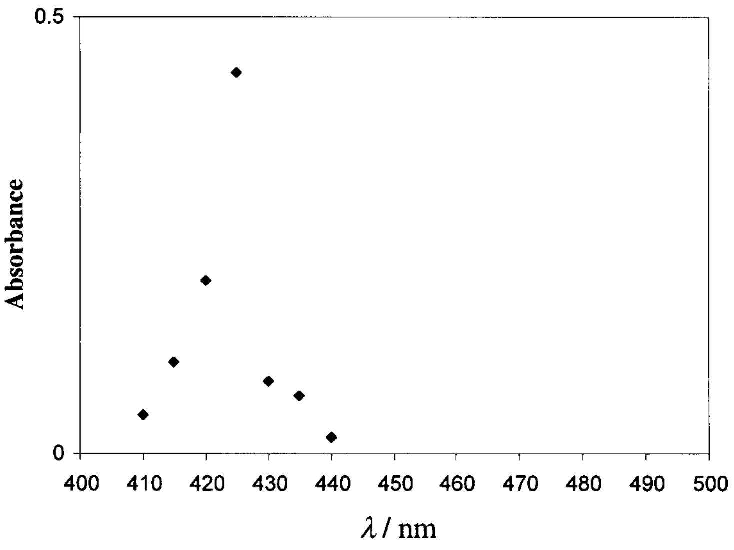


Fig. 7. *Triplet-triplet absorption spectrum measured after excitation of* **3b**, *in methylcyclohexane solution, by a 355-nm, 6-ns laser pulse*

intramolecular electron transfer between two identical moieties is the factor for the rate enhancement.

Further studies are considered for other bis[anthracenes] in protic solvents to get a deeper insight into this unique reaction.

NATO Grant GRG 971516 is gratefully acknowledged. *J.-P. D.* and *H. B.-L.* thank the *CNRS* and University Bordeaux 1 for financial support, *Matthias Gotta* (*ERASMUS* student, Darmstadt, Germany) and *CESAMO* for assistance. Finally, we are particularly indebted to Dr. *R. Bonneau* and Dr. *A. Credi* for informative discussions.

Experimental Part

General. Compound **1a** was prepared as already described [14], and 10-bromoanthracen-9(10*H*)-one (**4**) and 10-methoxyanthracen-9(10*H*)-one (**5**) were prepared according to literature procedures [19]. Column chromatography (CC): silica gel (*SDS, Chromagel Silice 60 A C.C*). UV/VIS Spectra: *Hitachi U-3300* spectrophotometer; λ_{max} in nm, ε in M^{-1} cm^{-1}. Emission spectra: *Hitachi F-4500* fluorescence spectrophotometer, corrected for emission and excitation, resp. IR Spectra: *Fourier-Transform Perkin-Elmer Paragon-1000-PC* spectrophotometer; 1% in KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AC250* spectrometer; δ in ppm rel. to $SiMe_4$ (=0 ppm). Electron-impact mass spectra (EI-MS): *Hewlett Packard HP-MS 5988A*; in *m/z* (rel. %). HR-MS: *Autospec-EQ* spectrometer.

10,10′-Dimethoxy-9,9′-[methylenebis(oxy)]bis[anthracene] (**1b**). A mixture of **5** (4.0 g, 17.85 mmol), KOH (2.5 g, 44 mmol), $(Et_4N)HSO_4$ (1.0 g, 4.8 mmol), and CH_2Cl_2 (150 ml, 2.34 mol) was stirred for 18 h at r.t. under N_2. The dark yellow precipitate was then filtered and the soln. neutralized, dried (Na_2SO_4), and evaporated. The orange powder was purified by CC (silica gel, CH_2Cl_2/pentane 7:3), crystallization from CH_2Cl_2/Et_2O 1:1 (*v/v*) and recrystallization from benzene/heptane 1:1: 2.6 g (63%) of **1b**. Bright yellow crystals. M.p. 181°. UV (cyclohexane): 252 (205000), 260 (322000), 343 (2500), 360 (10300), 380 (17100), 402 (17400). IR: 3060, 3040, 3000, 2980, 2960, 2830, 1670, 1620, 1450, 1430, 1350, 1300, 1280, 1190, 1170, 1140, 1120, 1100, 1080, 1050, 1020, 980, 760, 750, 680, 670. ^{1}H-NMR ($CDCl_3$): 4.2 (*s*, 2 MeO); 6.1 (*s*, CH_2); 7.35–7.8 (*m*, 8 arom. H); 8.3–8.6 (*m*, 8 arom. H). FAB-MS (pos.): 460 (100, $M^{+\bullet}$), 307 (48), 223 (52). HR-MS: 460.166453 ($C_{31}H_{24}O_4^+$; calc. 460.167460). Anal. calc. for $C_{31}H_{24}O_4$: C 80.85, H 5.25, O 13.90; found: C 80.77, H 5.26, O 13.65.

*8,9-Dihydro-8,9-dimethoxy-3a,8[1′,2′]:9,13b[1:2′]-dibenzenodibenzo[3,4:7,8]cycloocta[1,2-*d*]-1,3-dioxole* (**2b**). A soln. of **1b** (100 mg, *ca.* 0.22 mmol) in Et_2O, degassed by the freeze and thaw technique, was irradiated in a *Pyrex* flask for 18 h with a medium-pressure Hg lamp, at r.t. After filtration, the yellowish powder was recrystallized from Et_2O: 60 mg of **2b**. White crystals (68%). IR: 3060, 3030, 2960, 2940, 2880, 2840, 2770, 1720, 1660–1550, 1460, 1360, 1280, 1240, 1200, 1180, 1140, 1070, 1050, 1020, 760, 740. ^{1}H-NMR ($CDCl_3$): 3.6 (*s*, 2 MeO); 6.3 (*s*, CH_2); 7.1–7.7 (*m*, 16 arom. H). FAB-MS (pos.): 460 (96, M^+), 223 (100).

Spectrophotometric Measurements (see also *General*). A microbalance (*Mettler UM 3*, sensitivity 0.1 μg) was used to weigh the samples to be dissolved in spectroscopic-grade solvents for spectrophotometric measurements. No fluorescent contaminants were detected upon excitation in the wavelength region of exper. interest. The fluorescence quantum yields were determined by comparison with quinine sulfate as standard [30], and a refraction-index correction was effected. Fluorescence decay measurements were performed by the single-photon timing technique as already described [16a][31]. The samples (concentration $< 10^{-5}$M) were degassed by freeze-pump-thaw cycles on a high-vacuum line and sealed under vacuum. The fluorescence decay, recorded at r.t., was fitted by a single exponential ($i(t) \propto A\ \exp(-\lambda t)$) with the Decan 1.0 program [32]. Distribution of residuals, the *Durbin-Watson* parameter, and χ^2 were used to evaluate the goodness of fit.

Experimental Set for Transient Absorption Spectroscopy. A schematic representation of the experimental system used for transient absorption spectra and ultrafast kinetics measurements is shown in *Fig. 8*. For our measurements, we employed a subpicosecond laser system, which consists of a mode-locked Ti:sapphire laser (*Tsunami*, *Spectra-Physics*) coupled to a regenerative amplifier (*Spitfire*, *Spectra-Physics*). The output of the regenerative amplifier consisted of 1.5-ps pulses at 1 kHz repetition rate and a wavelength centered at 802 nm. The fundamental beam was frequency-doubled to the 401 nm pulse and used for excitation. This pump pulse was separated from the fundamental by a dichroic beam splitter and focused behind the sample by a 1000 mm focal length lens. The pump pulse energy was, typically, 60–100 μJ, and the beam diameter, in the sample, was 1 mm. To generate a ps supercontinuum probe pulse, a part of the fundamental beam was focused into a 1-cm thick cell containing deionized H_2O. The spectrum of the supercontinuum was found to cover the 420–840 nm wavelength range. The continuum beam was collimated after the cell and split into two beams which formed the probe and reference beams. The probe beam was focused to a 0.1 mm diameter spot inside a 2 mm thick sample cell by a 250 mm focal length lens and was intersected by the pump beam. The reference beam passed through a 2-mm reference cell, which contained the same soln. as the sample cell. The probe and reference beams were focused onto two different spots of the slit of a monochromator. A 16 bit 256 × 1024 pixels CCD detector (pixel size 26 μm, *Princeton Instrument LN/CCD 1024EUV*) was mounted at the output end of the monochromator and was used to monitor the spectra of the probe and reference beams. We utilized 120 pixel vertical binning to form two horizontal strips, which cover the spectra of the probe and reference beams. To measure the kinetics, the arrival of the probe pulse in the cell was delayed by a certain period of time with respect to the pump pulse. For each delay time, two consecutive measurements were made, one with excitation and the other without excitation. Including the reference, four spectra were used to calculate the transient absorption spectrum. This procedure minimized the possible shot to shot energy fluctuations in the continuum and the excitation pulses. For the measurement of each spectrum, 2500 pulses were averaged. With this exper. system, absorbance changes as small as $5 \cdot 10^{-3}$ were observed and resolved.

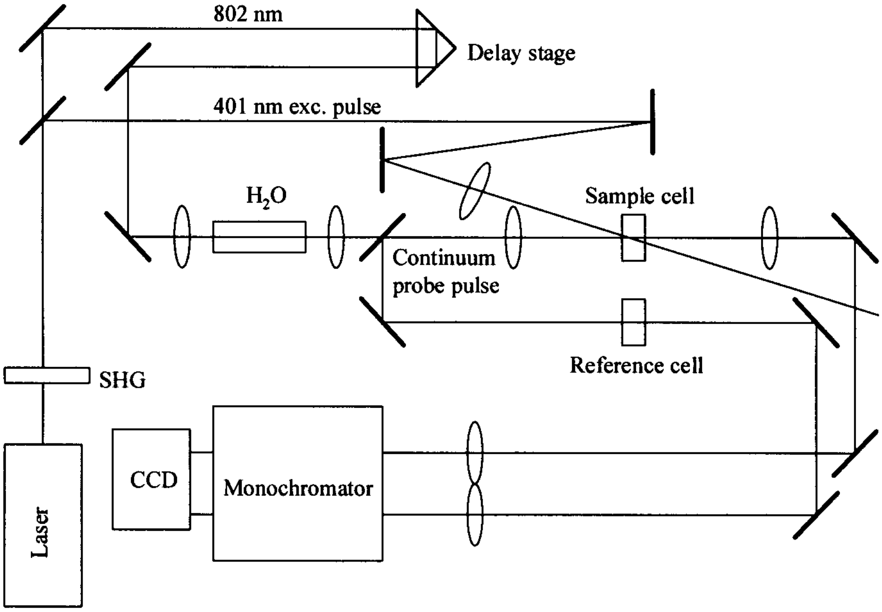


Fig. 8. *Schematic diagram of the experimental system for picosecond transient absorption spectra and kinetics measurements*

The optical densities of solns. of **1b** in MeCN and Mechx were 0.348 and 0.531, resp., at excitation wavelength 401 nm.

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Received May 26, 2001