

Study of Non-conjugated Bichromophoric Systems. Part 3.¹ The Photocyclomerization of 9-(1-Naphthylmethoxymethyl)anthracene and 9-(2-Furylmethoxymethyl)anthracene. Interest of the CH₂-O-CH₂ Link

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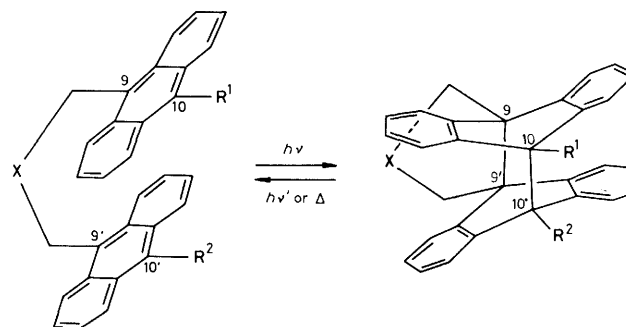
The title compounds (1a) and (3a), easily synthesized by the Williamson method, were prepared in order to study the photophysical and photochemical interactions of anthracene and, respectively, naphthalene and furan at high dilution. By irradiation, (1a) and (3a) both readily yield single photocyclomers, respectively (1b) and (3b). Under the same experimental conditions, the photocyclomerization quantum yield of (1a) is ten times higher than that of 1-(9-anthryl)-3-(1-naphthyl)propane (2a). This shows that the CH₂-O-CH₂ link is more efficient than the (CH₂)₃ chain in bringing together the two reacting terminal groups during the excited state lifetime. The fluorescence of the bichromophores was studied under photostationary conditions and a transient kinetic analysis was performed by single photon counting. It allowed the determination of the rate parameters of a kinetic scheme where the exciplexes of (1a) (emitting) and (3a) (non-emitting) are postulated as intermediates. These kinetic results, compared with others, are discussed in terms of influence of the chromophores, chain, and medium on the intramolecular reactions.

Interactions between two chromophores have been extensively studied in systems where the two groups are linked together by a u.v. transparent chain whose conformational mobility allows the terminal groups to collide.² Among these systems, bisanthracenes are especially interesting in displaying both excimer fluorescence emission and photocyclomerization.³ Following the Hirayama results, the propane link was recognized as inducing strong interactions between the two aromatic rings;⁴ however, we recently showed the advantage of using the ether chain -CH₂-O-CH₂- for a more efficient photocyclomerization⁵ (Scheme 1); in addition, the syntheses of these bichromophores proved easier.

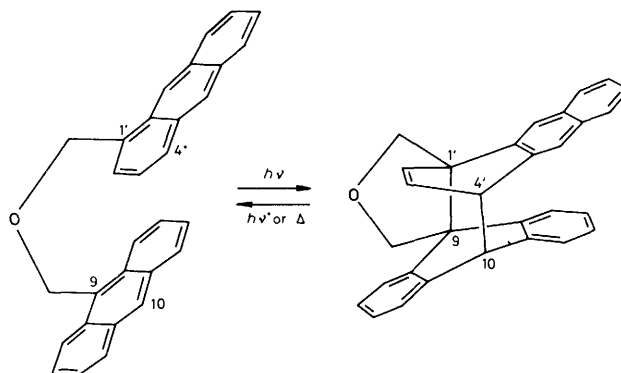
We also observed that the short linkage -CH₂-O-CH₂- between the 9- and 1'-positions of the anthracene moieties does not permit a sandwich overlap of the two rings but leads to a novel unsymmetrical cyclomerization process in this series¹ (Scheme 2).

By using this short linkage to prepare new bichromophoric systems to study the specific interactions between the anthracene ring and other aromatic chromophores (phenyl, naphthyl, phenanthryl, pyrenyl, *etc.*), we found that some of these molecules exhibit new intramolecular fluorescent exciplexes but no intramolecular photocycloaddition.⁶

By contrast, 9-(1-naphthylmethoxymethyl)anthracene (1a) and 9-(2-furylmethoxymethyl)anthracene (3a) smoothly undergo photocyclomerization. In the present paper, we report the synthesis of (1a) and (3a), the structure of the photocyclomers and a kinetic analysis of these systems with particular emphasis on fluorescence under stationary and dynamic (single photon counting) conditions. Compound (4a) is used as the monochromophoric reference. Compound (1a) will be compared with the already known compound (2a) where the link is the propane chain.⁷⁻⁹



Scheme 1

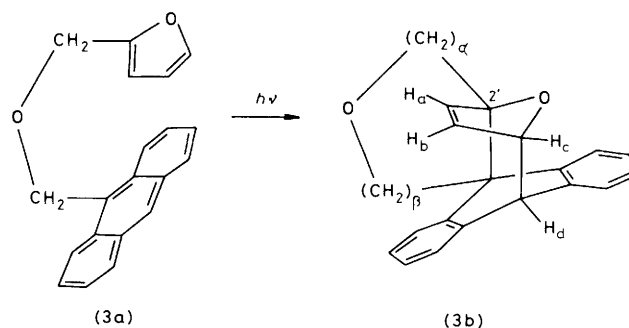
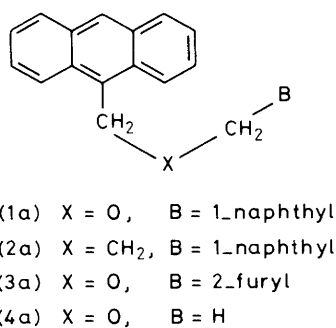


Scheme 2

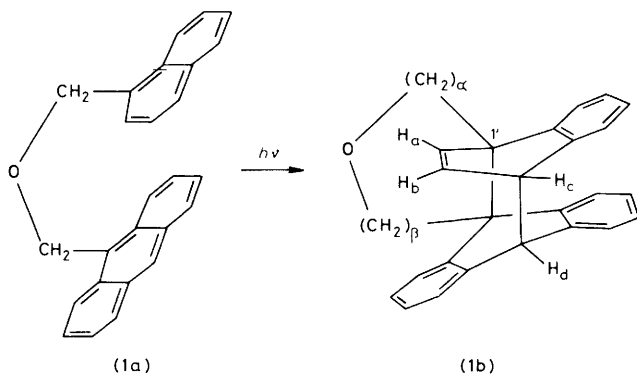
Results and Discussion

I Preparation and Structure of the Photoproducts.—1 Compound (1a). Compound (1a) was prepared in 50% yield by treatment of 1-hydroxymethylanthracene first with sodium hydride in dimethylformamide (DMF) and then with 9-chloromethylanthracene for 2.5 h at room temperature. Spectral

(i.r., u.v., m.s., and ¹H n.m.r.) data and elemental micro-analysis are as expected for (1a). Comparison of the u.v. spectra of (1a) and of the reference compound (4a), in methylcyclohexane (MCH), shows that absorption of (1a) must be due to independent contributions of the naphthalene and anthracene chromophores; this indicates an absence of important interaction between the two rings in the ground state.



Scheme 4



Scheme 3

2 Photocyclomer (1b).—In degassed diethyl ether or MCH solutions irradiation of (1a) (ca. 5×10^{-5} M, room temperature) with a high-pressure mercury lamp through Pyrex and liquid filter ($\lambda \geq 335$ nm) gave a single photoproduct which was quantitatively isolated and identified by u.v. and ^1H n.m.r. spectrometry as the photocyclomer (1b) (Scheme 3). The main features of the ^1H n.m.r. spectrum are reported in the Experimental section. The signals were assigned unambiguously by using first-order or AB pattern analyses. The $(\text{CH}_2)_\beta$ group exhibits a single peak whereas the $(\text{CH}_2)_\alpha$ protons, close to the chiral C(1'), appear, as expected, as an AB pattern. The structure of (1b) is similar to that of (2b) [photocyclomer of (2a)] previously determined by Chandross⁷ and then by Ferguson *et al.*⁸ who performed an X-ray structure analysis.

Crystals of (1b) are thermally stable at room temperature. On irradiation at short wavelength (254 nm) at very low concentration ($\approx 10^{-5}$ M in degassed MCH), (1b) was not found to revert quantitatively to (1a), giving a complex reaction which was not further investigated. Under thermal conditions, where the photocyclomers of the so-called 'jaw photochromic materials'^{1,5} smoothly revert to the starting materials, (1b) does not give back (1a).

3 Compound (3a).—This was synthesized (65% yield) by reacting NaH with 2-hydroxymethylfuran in DMF and subsequently adding 9-chloromethylantracene. Spectroscopic data (i.r., u.v., m.s., and ^1H n.m.r.) and elemental microanalysis are in agreement with the proposed structure (see Experimental section). The u.v. absorption spectrum of (3a) in MCH does not exhibit any significant shift from the sum of the spectra of the furan ring and (4a), indicating that there are no important interactions between the two chromophores in the ground state. Further, it was not possible to detect a charge-transfer band as the spectra in polar aprotic (CH_3CN) or protic (MeOH) solvents are very similar to the spectrum in MCH.

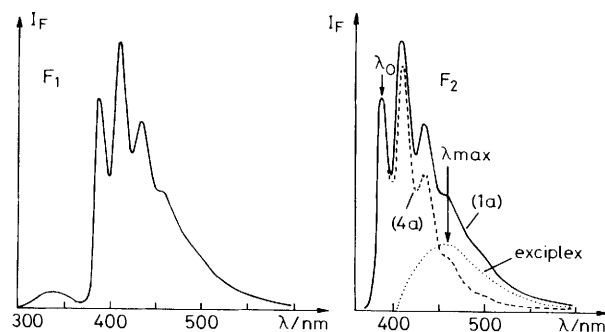


Figure 1. Fluorescence spectra of (1a) in methylcyclohexane at room temperature. F₁, λ excitation 282 nm, concentration ca. 4×10^{-6} M; F₂, λ excitation 365 nm, — (1a), concentration ca. 7×10^{-6} M; - - - (4a); ···· exciplex spectrum derived by subtraction of spectrum of (4a) from that of (1a) normalized at λ_0 388 nm

4 Photocyclomer (3b).—In degassed ether, (3a) ($\approx 10^{-4}$ M, room temperature) smoothly gives (3b) (Scheme 4), by irradiation with the same set up and conditions as those used for (1a). After 10 h, a single photoproduct (70% yield) was isolated. Spectral (i.r., u.v., m.s., and ^1H n.m.r.) data and elemental microanalysis are in accord with the proposed structure (see Experimental section). Analysis of the ^1H n.m.r. spectrum, similar to that of (1b), allowed the assignment of all the non-aromatic protons. The protons of both CH_2 groups display an AB pattern; the $(\text{CH}_2)_\alpha$ protons, which experience the higher difference in chemical shift, should be nearer to the chiral C(2') than are the $(\text{CH}_2)_\beta$ protons.

Under the experimental conditions experienced by (1b), (3b) does not readily revert, thermally or photochemically, to (3a).

II Fluorescence and Photoreactivity.—1 *Photostationary conditions.* a Reference compound (4a). The fluorescence emission of reference compound (4a) is typical of a 9-alkyl-substituted anthracene (Figure 1); however, the quantum yield (ϕ_F 0.09) is weaker than those usually found for 9-alkylantracenes.^{10,11}

b Compounds (1a) and (2a). Figure 1 shows the fluorescence spectra of (1a) recorded for two different excitation wavelengths at room temperature. When the bichromophore is excited at 365 nm, *i.e.*, only in the anthracene ring, a double fluorescence emission is observed; it is identified to the sum of a locally excited state ('monomer') and an exciplex emission; assuming that the monomer emission of (1a) is identical to that of the reference compound (4a), it is possible to deduce the exciplex spectrum (Figure 1) by subtraction of

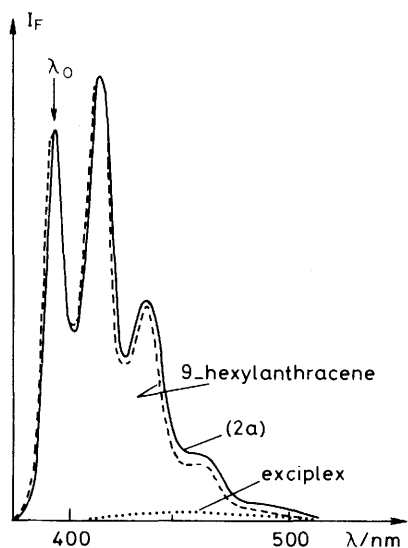


Figure 2. — Fluorescence spectrum of (2a) in methylcyclohexane at room temperature; λ excitation 365 nm, concentration *ca.* 10^{-5} M. - - - Fluorescence spectrum of 9-hexylanthracene.¹¹ ···· Exciplex spectrum derived by subtraction between (2a) and reference spectra normalized at λ_0 390 nm

the monomer spectrum from the bichromophore spectrum, both being normalized at the first vibronic band (λ_0).

The fluorescence spectrum of (2a), recorded for comparison under the same conditions as for (1a), is represented in Figure 2 and both monomer and exciplex emissions are also apparent. For (1a) and (2a) the same excitation spectra were observed for all the fluorescence (short and long wavelength) emission bands and they correspond to the u.v. absorption spectra; this establishes that the monomer and exciplex emissions have the same origin. The relative quantum yield of exciplex (ϕ_{FD}) over monomer (ϕ_{FM}) fluorescence is in favour of (1a) (see Table 3). The exciplex fluorescence of (2a) had been recorded by Chandross⁷ in a matrix at 77 K after photodissociation of the photocyclomer (2b) and by Ferguson^{8,9} at 20 °C after partial photocleavage of (2b) in a microcrystal of the photocyclomer acting as a matrix. Under the same experimental conditions, 9-(2-naphthylmethoxymethyl)anthracene, an isomer of (1a), displayed a fluorescence spectrum identical to that of (4a) and no exciplex emission was detected.⁶

When (1a) is excited at 282 nm, the naphthalene ring absorbs almost all the incident light but the larger part (96.5%) of the emitted light originates from the anthracene ring and *ca.* 3.5% from the naphthalene chromophore (Figure 1). This observation is reminiscent of the results of Ferguson *et al.*⁸ who reported for (2a) in MCH at 77 K a very weak naphthalene fluorescence (0.03%). We also observed a very weak naphthalene emission under our conditions (MCH; room temperature) by exciting (2a) in the naphthalene ring. Schnepf and Levy¹² had not detected any naphthalenic emission for a series of (9-anthryl)(1-naphthyl) $\alpha\omega$ -alkanes in MCH at room temperature.

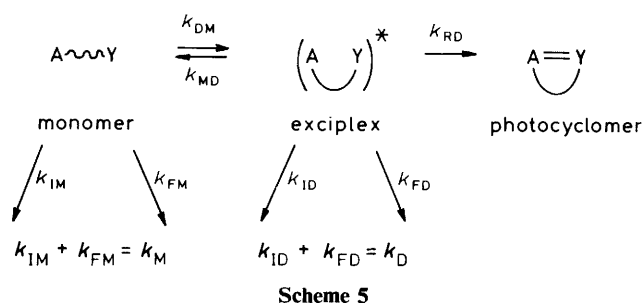
We also observed a naphthalene fluorescence (*ca.* 3%) for 9-(2-naphthylmethoxymethyl)anthracene.

A very crude estimation of excimer (exciplex) stability may be provided by the energy difference ($\Delta\tilde{\nu}_{0,max}$) between the first monomer vibronic band ($\tilde{\nu}_0$) and the maximum of excimer emission ($\tilde{\nu}_{max}$). Table 1 allows a comparison of $\Delta\tilde{\nu}_{0,max}$ of several exciplexes (1a) and (2a) and excimers made of symmetrical anthracene or naphthalene bichromophores. A

Table 1. Shift ($\Delta\tilde{\nu}_{0,max}$) between the monomer first vibronic fluorescence band ($\tilde{\nu}_0 = 1/\lambda_0$) and excimer (exciplex) fluorescence maximum ($\tilde{\nu}_{max} = 1/\lambda_{max}$) in methylcyclohexane (MCH) at room temperature

Compound	λ_0 /nm	λ_{max} /nm ^a	$\Delta\tilde{\nu}_{0,max}$ /cm ⁻¹ ^a
ACH ₂ OCH ₂ N	388	455	3 900
A(CH ₂) ₃ N	390	450–470	3 900
NCH ₂ OCH ₂ N ^b	325	415	6 700
N(CH ₂) ₃ N ^c	330	420	6 500
ACH ₂ OCH ₂ A ^d	393	550	7 300

^a Approximate values. ^b Ref. 20, solvent iso-octane. ^c E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, 1970, **92**, 704, temperature 77 K. ^d Ref. 5, temperature 77 K. A = 9-Anthryl; N = 1-naphthyl.



higher $\Delta\nu_{0,max}$ appears for excimers as it was already observed for other bichromophores⁶ linked with the same chain.

c Compound (3a). In MCH, at 20 °C, (3a) ($\approx 10^{-5}$ M) shows the typical monomer fluorescence emission of the reference compound (4a). No exciplex fluorescence was detected under our experimental conditions. However, transient reaction kinetics (see below) indicate the participation of an exciplex in equilibrium with the locally excited state; the exciplex fluorescence quantum yield must be too low to permit detection under stationary state-conditions.

d Quantum yields. The monomer (ϕ_{FM}) and exciplex (ϕ_{FD}) fluorescence quantum yields determined in MCH ($\approx 10^{-5}$ M) at room temperature are listed in Table 2.

2 *Transient reaction kinetics.* A fluorescence decay. It has been established, on several occasions, that excimers are intermediates on the reaction pathway towards photodimers or photocyclomers.^{13,14} Ferguson⁸ has also shown the intermediacy of the emitting exciplex in the photocyclomerization of (2a) in a crystal matrix of (2b). We thus postulate a kinetic scheme where exciplexes are intermediates in the photocyclomerization of (1a)–(3a) in MCH at room temperature (Scheme 5).

Assuming steady-state approximation, we can derive equations (1) and (2) for k_{RD} and k_{FD} .

$$k_{RD} = \phi_R \frac{(k_D k_M + k_{MD} k_M + k_{DM} k_D)}{k_{DM}} \quad (1)$$

$$k_{FD} = \phi_{FD} \frac{(k_D k_M + k_{MD} k_M + k_{DM} k_D)}{k_{DM}} \quad (2)$$

The rate constants are calculated from the fluorescence and reactivity quantum yields, on the one hand and from kinetic analyses (λ_1, λ_2, B) of the monomer and exciplex fluorescence

Table 2. Monomer (ϕ_{FM}), exciplex (ϕ_{FD}), and photocyclomerization (ϕ_{RD}) quantum yields of bisaryls linked by polymethylene or oxygen-containing chains. Kinetic data determined by single photon counting and rate parameters computed according to Scheme 5. Solvent methylcyclohexane (MCH), room temperature

Compound	λ_1^{-1}/ns	λ_2^{-1}/ns	B	$10^6 k_{DM}/\text{s}^{-1}$	$10^6 k_{MD}/\text{s}^{-1}$	$10^6 k_{FD}/\text{s}^{-1}$	$10^6 k_{RD}/\text{s}^{-1}$	ϕ_{FM} calc.	ϕ_{FM} exp.	ϕ_{FD}	$10^{-4} \phi_{RD}$
ACH ₂ OCH ₂ N (1a)	0.75	6	0.075	450	195	18	38	0.07 ₈	0.07 ₈	0.03 ₇	780
A(CH ₂) ₃ N (2a)									0.44	0.02	70
ACH ₂ OCH ₂ F (3a)	1.2	8	0.003	53	27		57	0.08 ₆	0.08 ₄		280
ACH ₂ OCH ₃ ^b (4a)	1.25					(70) ^c					
ACH ₂ CCH ₂ A ^d								0.03			3 200
ACH ₂ CH ₂ CH ₂ A ^d								0.47			1 400
A(OCH ₂ CH ₂) ₃ OA ^d								0.10		0.02 ₃	2 600
A(CH ₂) ₁₀ A ^d								0.39		0.08 ₄	4

^a At 365 nm. ^b $k_M = k_{FM} + k_{IM} = 800 \times 10^6 \text{ s}^{-1}$. ^c k_{FM} . ^d Ref. 3. A = 9-Anthryl; N = 1-naphthyl; F = 2-furyl.

decay^{10,11,15} (single photon counting) on the other. Monomer and exciplex fluorescence intensity response *versus* time are

$$i_M(t) = C_M [\exp(-\lambda_1 t) + B \exp(-\lambda_2 t)] \quad (3)$$

$$i_D(t) = C_D [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (4)$$

given by equations (3) and (4) with $2\lambda_1, \lambda_2 = (X + Y) \pm [(Y - X)^2 + 4k_{DM}k_{MD}]^{1/2}$ where $X = k_M + k_{DM}$, $Y = k_D + k_{MD}$ and $B = (X - \lambda_1)/(\lambda_2 - X)$. k_{DM} , k_M and then k_{FD} and k_{RD} (Table 3) were computed as already shown^{10,11,15} from λ_1 , λ_2 , B and ϕ_{FM} , ϕ_{FD} , ϕ_{RD} for (1a) and (3a). Subsequently ϕ_{FM} , calculated from the above kinetic constants, was found to be in close agreement with the experimental values; this points to the consistency of the kinetic scheme.

It should be noted that k_{DM} , k_{MD} , and k_{RD} include, *a priori*, all the different sets of conformational populations of the bichromophores assumed to be in dynamic equilibrium; therefore, they should be considered as average values.

But kinetic analysis of the fluorescence decay of (2a) was not possible with Scheme 5. Distinct conformational geometries of the chain should probably be taken into account¹⁵ as recently shown by De Schryver^{16a} for a bisnaphthalene. This point deserves a study in itself and will not be considered further in this paper.

b Photoreactivity. All the reactions were carried out in degassed media; the intramolecular photocycloadditions were examined at concentrations of *ca.* 10^{-5}M . The reaction quantum yields, measured at 365 nm, are collected in Table 2. From inspection of these values, it appears that the *intramolecular* additions of naphthalene or furan to anthracene are of some efficiency. It is not the same for the *intermolecular* process. Chandross⁷ had already tried without success to obtain a mixed photodimer between anthracene and naphthalene. Similarly, by irradiating either a solution of anthracene in furan or mixtures of (4a) with a large excess of 2-hydroxymethylfuran in diethyl ether, we have only isolated the anthracene photodimers. However, it is noteworthy that Sakurai *et al.*^{17a} have photochemically added furan, 2-methylfuran, and 2,5-dimethylfuran to 9-cyanoanthracene; the latter has a much stronger electron affinity^{17b} than anthracene. A weak fluorescence exciplex emission was also detected by the authors, only with dimethylfuran.

Comparison of exciplex (k_{DM}) and photocyclomer (k_{RD}) formation rate constants of (1a) and (3a) with published values for bichromophores linked with chains of different nature and length is possible (Table 3). Rate parameters calculated from Arrhenius activation parameters obtained by Ferguson for (2a) in rigid media are also included in Table 3. The rate constants (k_{DM}) are found to be dependent not only on

Table 3. Intramolecular excimer (exciplex) formation (k_{DM}) and photocyclomerization (k_{RD}) rate parameters of some bisanthracenes or dissymmetrical bisaryls in fluid or rigid media at room temperature.

Compound	Medium	$10^6 k_{DM}/\text{s}^{-1}$	$10^6 k_{RD}/\text{s}^{-1}$
ACH ₂ OCH ₂ N (1a)	MCH	450	38
A(CH ₂) ₃ N (2a)	Crystal ^a		400 ^b
A(CH ₂) ₃ N (2a)	MCH-IP ^c		280 ^b
A(CH ₂) ₃ N (2a)	MCH-D ^c		130 ^b
ACH ₂ OCH ₂ F (3a)	MCH	53	57
A(CH ₂) ₄ A ^d	MCH	26	46
A(OCH ₂ CH ₂) ₃ OA ^e	MCH	570	35

^a Crystal of (2b).^{8a} ^b Calculated from Arrhenius activation parameters. ^c Ref. 8b; MCH = methylcyclohexane; IP = isopentane; D = decalin. ^d Ref. 11. ^e Ref. 15. A = 9-Anthryl; N = 1-naphthyl; F = 2-furyl.

the chromophores but also, expectedly, on the chain. However, in fluid solutions, the k_{RD} values do not seem to vary significantly and they increase distinctly in rigid matrices.

9-(2-naphthylmethoxymethyl)anthracene [isomer of (1a)] neither displays an exciplex fluorescence⁶ nor gives intramolecular photocyclomerization;⁶ geometrical constraints are likely to inhibit good overlap between the two rings and an adequate approach to the reactive centres; a similar explanation was proposed by Chandross for some dinaphthylpropanes.¹⁸

Conclusions.—From the above results, the utility of linking the chromophores in (1a)—(3a) is apparent. Moreover, several features emerge which show some distinct advantages of using a CH₂-O-CH₂ link to study the photophysical and photochemical interactions between different chromophores at high dilution. (i) Of note are the straightforward syntheses of (1a) and (3a) starting from the corresponding easily accessible aldehydes. (ii) Although this ether chain (CH₂-O-CH₂) has also been used by us and others for the study of photophysical and photochemical interactions in other symmetrical (benzene,¹⁹ naphthalene,¹⁹⁻²¹ phenanthrene,²² anthracene,^{1,5,6} and pyrene²³) or unsymmetrical⁶ (anthracene with respectively benzene, naphthalene, phenanthrene, and pyrene) bisaryls, a comparison of the results obtained with different chains of the same length was made on very rare occasions. The parallel study of (1a) and (2a) in fluid solution provides a second example of the compared efficiency (in terms of reaction quantum yields) of the CH₂-O-CH₂ and (CH₂)₃ chains. There is no doubt that the replacement of one CH₂ group by an oxygen enhances the photocyclomerization quantum yield (ϕ_{RD}) (see Table 2). Similar behaviour was also recognized in

bisanthracenes containing three-membered or longer chains (Table 2). Interestingly, although ϕ_R is systematically higher for the bisaryls linked by an oxygenated chain, the monomer fluorescence yield (ϕ_{FM}) is smaller.

Our observations on excited state reactions are in line with results obtained by other authors for the ground state:^{24,25} comprehensive kinetic studies on intramolecular electron transfer²² or cyclizations²⁵ in systems containing polyethyleneoxy or polymethylene chains have clearly shown the accelerating role of the oxygen atom in the reactions investigated.²⁵

Experimental

Solvents.—Methylcyclohexane (MCH) (Prolabo; u.v. spectrograde) was used without further purification. No fluorescent impurities were detected under experimental conditions. Diethyl ether (Prolabo) was distilled from LiAlH_4 before use.

Starting Materials.—1-Hydroxymethylnaphthalene and 2-hydroxymethylfuran were commercial (Aldrich). 9-Anthraldehyde was easily prepared from anthracene by the Vilsmeier-Haack method. 9-Anthraldehyde underwent smooth reduction to 9-hydroxymethylanthracene²⁶ on treatment with NaBH_4 by the usual procedure; the latter compound is transformed into 9-chloromethylanthracene by SOCl_2 without difficulty.²⁶

Physical Methods. Apparatus.—M.p.s were taken with a Kofler block. Elemental analyses were performed at the CNRS microanalysis centre. N.m.r. spectra were measured with a Bruker WH 90 Fourier transform spectrometer (reference Me_4Si , solvent CDCl_3). Electronic absorption spectra were recorded with a Cary 219 instrument. I.r. spectra were taken with a Perkin-Elmer 412 and mass spectra (70 eV) with a V.G. Micromass type 16F instrument. Fluorescence spectra were obtained with a Hitachi-Perkin-Elmer MPF 44 fluorimeter, corrected for excitation and emission. The fluorescence lifetimes were measured by single photon counting, as described elsewhere,¹⁵ using an Applied Photophysics apparatus. The sample vessels were degassed on a high vacuum by several freeze-pump-thaw cycles and sealed. H.p.l.c. was carried out with an LDC set equipped with a Pye-Unicam u.v. detector.

The fluorescence quantum yields were determined in degassed MCH relative to quinine sulphate in *N*-sulphuric acid as standard (ϕ_F 0.55) by the usual method²⁷ taking into account the refractive index correction. The determination of the reaction quantum yields was performed in MCH, with degassed samples, at 365 nm as previously described.^{1,5}

Preparation of Compounds.—Compound (4a) was prepared according to Stewart's procedure²⁶ and was purified by column chromatography (silica gel, ligroin) followed by h.p.l.c. (15 μ octadecylsilane SiC_{18} Spherisorb, methanol as eluant).

9-(1-Naphthylmethoxymethyl)anthracene (1a).—At room temperature, to a solution of sodium hydride (0.10 g, 4.4×10^{-3} mol) in DMF (10 ml), was added dropwise with stirring 1-hydroxymethylnaphthalene (Aldrich) (0.7 g, 4.4×10^{-3} mol) in DMF (50 ml). Stirring was continued for 30 min after the end of the addition. A DMF solution (30 ml) of 9-chloromethylanthracene²⁸ (1 g, 4.4×10^{-3} mol) was then introduced dropwise and stirred for 2.5 h at room temperature. The solution was hydrolysed with water (slightly acidified with dilute HCl). The precipitate formed was filtered, dried, and chromatographed on a silica gel column. After elution with ligroin-diethyl ether (1 : 1), crystallization

from the same solvent mixture afforded crystals of (1a) (1.53 g, 74%), m.p. 111 °C, ν_{max} (KBr) 3 070, 2 980, 2 940, 2 880, 1 630, 1 605, 1 520, 1 445, 1 350, 1 130, 1 075, 1 040, 900, 800, and 740 cm^{-1} ; δ (CDCl_3) 5.13 (2 H, s), 5.50 (2 H, s), and 7.20—8.60 (16 H, m); λ_{max} (MCH) 385 (log ϵ 3.98), 365 (3.99), 347 (3.80), 330.5 (3.48), 313.5 (3.65), 292.5 (3.68), 281.5 (3.83), 255.5 (5.19), and 223.5 nm (4.95); m/z 248 (50%, M^+), 192 (100), 191 (81), 189 (23), 179 (81), 178 (34), 141 (36), and 142 (15) (Found: C, 89.65; H, 5.85. $\text{C}_{26}\text{H}_{20}\text{O}$ requires C, 89.65; H, 5.75%).

9-(2-Furylmethoxymethyl)anthracene (3a).—The experimental procedure was the same as above. The compounds used were 9-chloromethylanthracene (1.4 g, 6.18×10^{-3} mol), 2-hydroxymethylfuran (Aldrich) (0.6 g, 6.20×10^{-3} mol), sodium hydride (0.15 g, 6.20×10^{-3} mol), and DMF (60 ml). Chromatography on silica gel and elution with ligroin-diethyl ether (1 : 1) and crystallization in the same solvent mixture yielded yellow crystals of (3a) (1.2 g, 67%), m.p. 78 °C, ν_{max} (KBr) 3 105, 3 085, 3 060, 2 890, 2 880, 1 625, 1 500, 1 480, 1 450, 1 445, 1 400, 1 360, 1 340, 1 265, 1 245, 1 150, 1 070, 1 040, 1 015, 990, 920, 890, 755, 730, 710, 625, 605, and 535 cm^{-1} ; δ (CDCl_3) 4.40 (2 H, s), 5.33 (2 H, s), 6.20 (2 H, m), and 7.2—8.3 (10 H, m); λ_{max} (MCH) 385 (log ϵ 3.92), 365 (3.94), 346 (3.74), 330 (3.45), 256 (5.19), and 249 nm (4.94); m/z 288 (58%, M^+), 192 (100), 191 (88), 179 (83), 178 (54), 149 (50), and 81 (31) (Found: C, 83.0; H, 5.9. $\text{C}_{20}\text{H}_{16}\text{O}_2$ requires C, 83.35; H, 5.55%).

Preparation of the Photocyclomers.—**Compound (1b).** A degassed solution of (1a) (40 mg, 1.15×10^{-4} mol) in diethyl ether (750 ml) was irradiated in a Pyrex vessel at $\lambda > 335$ nm [liquid filter, lead acetate (7 g)—sodium bromide (540 g)—water (1l)] with a high-pressure mercury lamp (Philips SP 500) for 8 h. After solvent removing, (1b) was obtained as a powder (40 mg, 100%), m.p. (decomp.) 192—194 °C, ν_{max} (KBr) 3 080, 3 050, 2 940, 2 900, 2 860, 1 640, 1 480, 1 460, 1 390, 1 290, 1 130, 1 080, 960, 790, 740, 730, 720, and 670 cm^{-1} ; m/z 348 (M^+); δ (CDCl_3) 3.94 (A), 4.38 (B) [2 H, $(\text{CH}_2)_{2z}$, J_{AB} 11 Hz], 4.78 [2 H, $(\text{CH}_2)_\beta$], 3.98 (1 H, m, H_c , J_{cd} 8.6, J_{bc} 6.7, J_{ac} 1 Hz), 4.73 (1 H, d, H_d , J_{cd} 8.6 Hz), 5.72 (1 H, m, H_a , J_{ab} 8.3, J_{ac} 1 Hz), 6.12 (1 H, m, H_b , J_{ab} 8.3, J_{bc} 6.7 Hz), and 6.6—7.5 (12 H, m); λ_{max} (MCH) 285 (log ϵ 3.06), 281.5 (3.08), 272.5 (3.10), 255 (3.23), 220 (4.48), and 203.5 nm (4.59).

Compound (3b). Under preceding irradiation conditions, (3a) (42 mg, 1.46×10^{-4} mol) in degassed diethyl ether (350 ml) after 10 h exposure and ether evaporation gave a yellow solid which was chromatographed on silica gel (ligroin-diethyl ether, 1 : 1). Compound (3b) was obtained (30 mg, 72%) as a solid, m.p. (decomp.) 188—190 °C, ν_{max} (KBr) 3 066, 3 026, 2 980, 2 940, 2 880, 1 460, 1 450, 1 390, 1 350, 1 230, 1 180, 1 140, 1 060, 1 010, 940, 880, 816, 745, 706, 630, and 616 cm^{-1} ; δ (CDCl_3) 3.93 (A), 4.07 (B) [2 H, $(\text{CH}_2)_\beta$, J_{AB} 10.8 Hz], 4.44 (A), 4.77 (B) [2 H, $(\text{CH}_2)_{2z}$, J_{AB} 10 Hz], 4.14 (1 H, d, H_d , J_{cd} 6.7 Hz), 4.66 (1 H, m, H_c , J_{bc} 1.9, J_{dc} 6.7 Hz), 5.7 (1 H, m, H_a , J_{ab} 6 Hz), and 5.9 (1 H, m, H_b , J_{ba} 6, J_{bc} 1.9 Hz); λ_{max} (MCH) 281 (log ϵ 3.27), 273 (3.10), 265 (2.93), and 214 nm (4.50).

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