Non-conjugated Bichromophoric Systems. Part 4.[1] Synthesis and Photochemical Study of Bis-9-anthryls with a Four-membered Chain; Influence of the Replacement of Methylene Links by Oxygen Atoms or Dimethylsilyl Groups on the Formation of Intramolecular Excimers and Photocyclomers

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Bichromophoric systems (I_{CC}, I_{OO}, I_{O1} I_{O2}, and I_{SiC}) incorporating various four-membered links were prepared in order to study the influence of the nature of the linkages upon the photophysical and photochemical properties; these systems are bisanthracenes A–Z–A where A = 9-anthryl and Z = $(CH_2)_4$ (I_{CC}), $O(CH_2)_2O$ (I_{OO}), $O(CH_2)_3$ (I_{O1}), $CH_2O(CH_2)_2$ (I_{O2}), and $SiMe_2(CH_2)_2SiMe_2$ (I_{SiC}). By irradiation at high dilution, each of these compounds yields a single photocyclomer P_{XX} linked through the 9,10 positions of one ring and the 9′,10′ positions of the other, except for I_{SiC} where the bonds were formed between the 9,10 and 1′,4′ positions. The reaction quantum yields were measured at 365 nm in methylcyclohexane. The fluorescence was examined in the same solvent under stationary conditions at different temperatures and by transient kinetic analysis (single-photon counting). Three of these compounds (I_{CC}, I_{OO}, I_{O1}) did not display any intramolecular excimer fluorescence; a thermodynamic study indicates that the non-radiative decay of the S_1 excited state leads essentially ($\varphi_{i.s.c.}$ being very small) to the photoproduct P_{XX} and the starting material I_{XX} *via* a minimum of the potential surface (pericyclic minimum) with respective partition coefficients α and $(1 - \alpha)$: $\alpha = 0.13$ (I_{CC}), 0.28 (I_{OO}), 0.27 (I_{O1}). This shows the influence of the replacement of a CH_2 group by oxygen. The other two derivatives (I_{O2} and I_{SiC}) exhibit locally excited and excimer fluorescence, the latter being suggestive of large overlap between the aromatic rings. The excimers were postulated to be on the reaction pathway; the first collapses readily to the photocyclomer P_{O2} (φ_R 0.28) whereas the second, due to steric strain, leads to P_{SiC} with a very low yield (φ_R 8×10^{-4}; k_{RD} *ca.* 10^5 s^{-1}). It was observed that the introduction of an oxygen atom instead of a CH_2 group enhances the cycloaddition efficiency but the second oxygen did not show any further improvement. The presence of the bulky $SiMe_2$ groups helped the excimer state to be reached (rate of formation at room temperature k_{DM} *ca.* 10^9 s^{-1}) but strongly hindered the formation of the photocyclomer (k_{RD} *ca.* 10^5 s^{-7}). The last result clearly shows that photocyclomerization depends first on the intra-chain interactions controlling the rate of formation of an overlapping conformation and then on possibly more severe inter-linkage and chain-ring (with the so-called 'peri' hydrogens) repulsions, which can be a powerful brake in the last step of the build up of cycloadduct.

The linkage of two chromophores K and L by a non-absorbing and flexible chain is of great value in the study of bimolecular interactions between K and L in dilute solution. Moreover, the kinetics and thermodynamics of the systems in the excited state can provide information on the conformational dynamics of the chain.[2]

As they can display both dual fluorescence emission (monomer and excimer) and intramolecular photocycloaddition, bisanthracenes have been extensively investigated.[1,3] In these systems, the role of the chain in the photochemical and photophysical processes has been examined using several types of link; it was observed that replacing a CH_2 group by an oxygen atom brings about more flexibility, thus driving the systems more efficiently towards overlap between the two terminal anthryl rings to generate excimers and photocyclomers.[3,4] But, to our knowledge, no systematic study has so far been made of bichromophoric compounds incorporating different chains with the same number of linkages between two identical terminal groups.

Therefore, in order to optimize the characteristics of the chain, we studied bis-9-anthryls where the terminal groups are bonded by a four-link chain composed, respectively, of four methylene groups [$A(CH_2)_4A$, I_{CC}] (A = 9-anthryl), three methylene groups and one oxygen atom [$AO(CH_2)_3A$, I_{O1}; $ACH_2O(CH_2)_2A$, I_{O2}], or two methylene groups and two oxygen atoms [$AO(CH_2)_2OA$, I_{OO}]. *Contrary to oxygen, the* $SiMe_2$ group was expected to restrict conformational mobility because of steric crowding; this is the reason why a 1,2-bis-(dimethylsilyl)ethyl chain [$ASiMe_2(CH_2)_2SiMe_2A$, I_{SiC}] was used in contrast with the other members of the series.

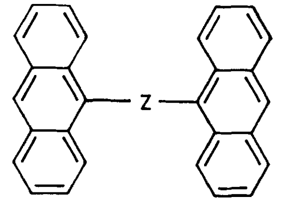
We report (a) the synthesis and characterization of the new compounds I_{XX}, (b) the photochemistry, and (c) a photophysical study (absorption and fluorescence emission, the latter as a function of temperature).

Results and Discussion

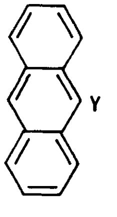
(I) *Synthesis and Characterization of the Bichromophores.*— Compound I_{cc} was prepared by a two-step procedure from 9,10-dihydroanthracene (DHA), already described[5a] and outlined in equation (a).

$$\text{DHA} \xrightarrow{\text{i, ii}} (\text{9DHA-CH}_2\text{CH}_2)_2 \xrightarrow{\text{iii}} \text{I}_{cc} \qquad \text{(a)}$$

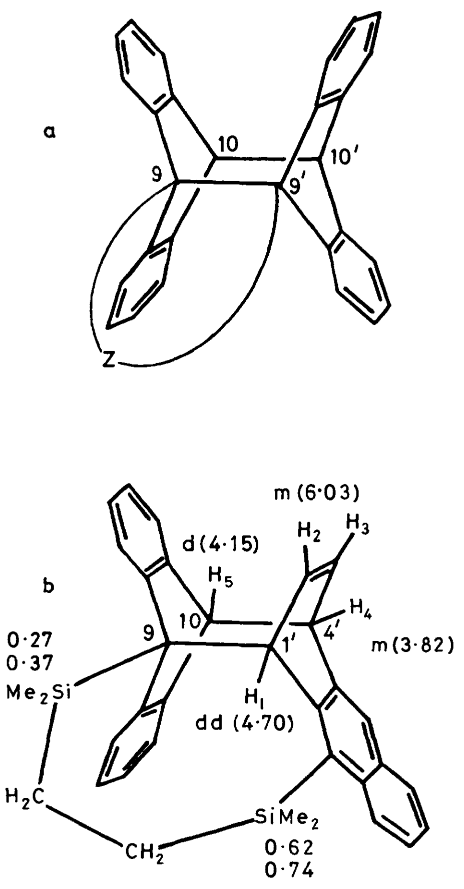
Reagents: i, Bu^nLi, THF; ii, $Br(CH_2)_4Br$; iii, DDQ, benzene



I_{CC} Z = $(\text{CH}_2)_4$
I_{OO} Z = $\text{O(CH}_2)_2\text{O}$
I_{O1} Z = $\text{O(CH}_2)_3$
I_{O2} Z = $\text{CH}_2\text{O(CH}_2)_2$
I_{SiC} Z = $\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2$



R_{CC} Y = n-$\text{C}_{10}\text{H}_{21}$
R_{OO} Y = OCH_3
R_{CO} Y = CH_2OCH_3
R_{SiC} Y = SiMe_3



Scheme 1. a, Molecular structure. b, Typical n.m.r. chemical shifts

Compound I_{OO} was synthesized from anthrone and 1,2-dibromoethane, using phase-transfer catalysis [equation (b)]. It was more satisfactory to proceed in two steps.

$$\text{Anthrone} + \text{Br(CH}_2)_2\text{Br} \xrightarrow{\text{i}} \text{AO(CH}_2)_2\text{Br} \xrightarrow{\text{i, ii}} \text{I}_{\text{OO}} \tag{b}$$

Reagents: i, NaOH, H_2O, CH_2Cl_2, $\text{Bu}^n{}_4\text{NI}$; ii, anthrone

The synthesis of I_{O1} is described by equations (c) and (d); despite the low yield, the one-pot preparation of 9-(γ-hydroxypropyl)anthracene from commercially available 3-chloropropanol, using a sacrificial Grignard reagent,[6] was very convenient.

$$\text{Cl(CH}_2)_3\text{OH} \xrightarrow{\text{i--iii}} \text{A(CH}_2)_3\text{OH} \tag{c}$$

$$\text{A(CH}_2)_3\text{OH} \xrightarrow{\text{iv}} \text{A(CH}_2)_3\text{Br} \xrightarrow{\text{v}} \text{I}_{\text{O1}} \tag{d}$$

Reagents: i, EtMgBr–THF; ii, Mg; iii, anthrone; iv, PBr_3–CHCl_3; v, anthrone–KOH–H_2O–THF

Compound I_{O2} was obtained in a straightforward manner by alkylation of 9-(β-hydroxyethyl)anthracene[7] with 9-chloromethylanthracene[8] using NaH in THF and a catalytic amount of crown ether [equation (e)].

$$\text{A(CH}_2)_2\text{OH} \xrightarrow{\text{i, ii}} \text{I}_{\text{O2}} \tag{e}$$

Reagents: i, NaH, THF; ii, ACH_2Cl

The Harvey method[9] for synthesis of 9-trimethylsilylanthracene was adapted to the preparation of I_{SiC} [equation (f)]. The monocarbanion of 9,10-dihydroanthracene was reacted with 1,2-bis(chlorodimethylsilyl)ethane to obtain the tetrahydro intermediate which was converted into I_{SiC} through its tetra-anion.

$$\text{DHA} \xrightarrow{\text{i, ii}} (\text{9DHASiMe}_2\text{CH}_2)_2 \xrightarrow{\text{iii, iv}} \text{I}_{\text{SiC}} \tag{f}$$

Reagents: i, Bu^nLi–THF; ii, $(\text{ClSiMe}_2\text{CH}_2)_2$; iii, Bu^nLi–TMEDA–cyclohexane; iv, CdCl_2

The bichromophores were purified by column chromatography (silica gel) (except I_{SiC}) and recrystallized. After purification, they were stored in the dark under an inert atmosphere (nitrogen or argon). The yields (not optimized) of the last step of each synthesis are listed in Table 1 together with some physical characteristics. The molecular structures were established essentially by ^1H n.m.r., u.v., and mass spectra and supported by elemental analyses.

The monochromophoric reference compounds R_{CC}, R_{OO}, R_{CO}, and R_{SiC} were prepared according to published procedures (see Experimental section).

(II) *Photochemistry of Bichromophores.*—(1) *General.* In degassed diethyl ether or methylcyclohexane (MCH) solution, irradiation of each compound I_{XX} (10^{-5}—10^{-4}M) at room temperature, with a high-pressure mercury lamp through Pyrex and a liquid filter ($\lambda \geq 335$ nm) gave, quantitatively, a single photoproduct, P_{XX}; the latter was isolated (except P_{SiC}) and identified by u.v. and ^1H n.m.r. spectrometry and its ability to thermally revert to the starting open form I_{XX}. Melting points and photocyclomerization quantum yields (at 365 nm) are collected in Table 1.

(2) *Photocyclomers* P_{CC}, P_{OO}, P_{O1}, P_{O2}. The u.v. spectra are similar to that of a 9,10-dihydroanthracene derivative, showing no absorption at wavelengths longer than 300 nm; this points to the formation of new σ bonds between the 9,9′ and 10,10′ positions (Scheme 1). The n.m.r. spectra agree with this structure, the classical arrangement of the anthracene photodimer[3] where no naphthalene or vinylic protons are detected

Table 1. Chemical yields and m.p.s of the bichromophoric systems I_{XX}; m.p. (decomp.) of the photocyclomers (P_{XX}); the photocycloisomerization chemical yield in degassed methylcyclohexane (MCH) was quantitative.

I_{XX}	Overall yield (%)	M.p. (°C)	P_{XX}	M.p. (°C) (decomp.)
I_{CC}	13	255—256	P_{CC}	200
I_{OO}	27	215—216	P_{OO}	300
I_{O1}	3	192—194	P_{O1}	230—235
I_{O2}	51‡	182—183	P_{O2}	210
I_{SiC}	33	160—162	P_{SiC}	*

* Not isolated. ‡ Yield of last step.

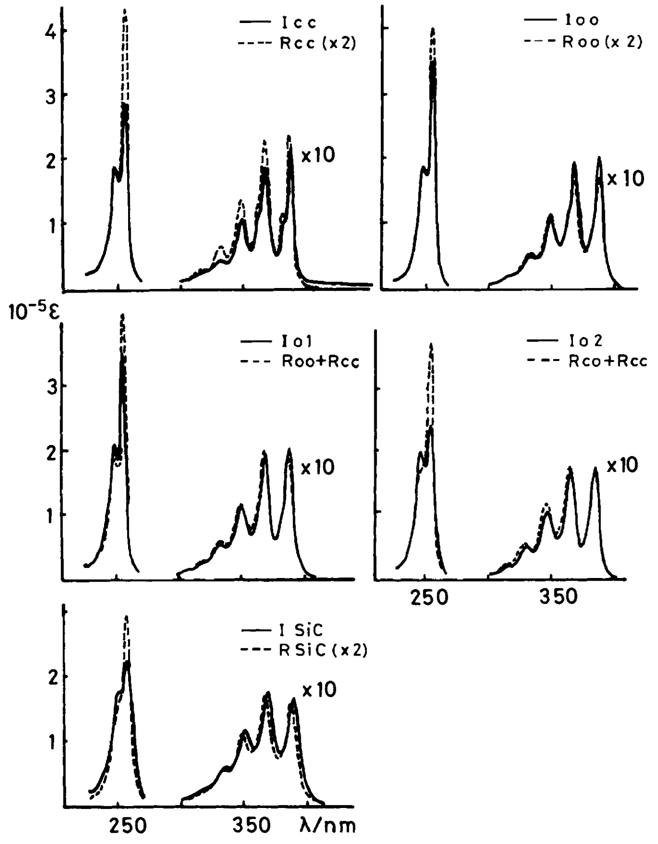


Figure 1. U.v. absorption spectra in MCH at room temperature of compounds I_{XX} compared with those of reference compounds R_{XX}

(see Experimental section). The four photoproducts are thermally stable at room temperature[10] but revert to the open form on heating (temperature ≥150 °C).

(3) *Photocyclomer* P_{SiC}. In contrast to the preceding compounds, P_{SiC} was found to have a dissymmetrical structure (Scheme 1). Its u.v. spectrum exhibits a naphthalene pattern which implies that the cycloaddition must occur between the 9,10 positions of one ring and the 1′,4′ positions of the other.[11] The structure is fully confirmed by the ^1H n.m.r. spectrum detailed in the Experimental section. It was directly recorded on an irradiated and highly dilute (*ca.* 10^{-4}M) C_6D_6 solution of I_{SiC} and more than 3 000 scans were necessary. The signals were assigned unambiguously by using first-order or AB pattern analysis. The four methyl groups are non-equivalent at δ 0.27, 0.37, 0.62, and 0.72 the latter pair being tentatively attributed to the methyl groups borne by the silicon linked to the naphthalene ring;[11a] 1-H which is coupled to 2- and 3-H gives a doublet of doublet centred at δ 4.7, 5-H a doublet at δ 4.15, and 4-H a multiplet centred at δ 3.82. The ethylene protons display a multiplet centred at δ 6.03. Owing to the background noise, it was not possible to analyse with precision the proton signals of the ethane chain linking the two silicon atoms.

(III) *Spectroscopic and Photophysical Study*.—(1) *Electronic absorption spectra*. U.v. absorption spectra are sensitive to molecular interactions in the ground state. The technique has been applied with success to bichromophoric systems.[3,11b,12,13] The absorption spectra of compounds I_{XX} in methylcyclohexane (MCH) are similar in shape to those of the monoanthracene (reference) compounds R_{XX}. However, some modifications are to be noted in the relative intensities of the vibronic bands in both electronic transitions ($^1L_a \longleftarrow A_1$ and $^1B_b \longleftarrow A_1$) as well as slight bathochromic shifts, especially for the long-wavelength absorption of I_{SiC}.

The $^1B_b \longleftarrow A_1$ transition is more perturbed where the intensity of the less energetic component is decreased compared with the other (see Figure 1). Taking into account our recent results on cation-complexing anthracenophanes[13b] these spectral changes can be attributed to moderate intramolecular interactions between the rings with some degree of parallelism between their long axes.

Absorption spectrum of I_{CC}. A weak (ε *ca.* 600 l mol^{-1} cm^{-1} in MCH) long-wavelength absorption (420 nm), extending to 460 nm, is noticeable in MCH as well as in EtOH. It is not apparently very sensitive to the polarity of the solvent and survived repeated attempts to purify the sample; however, the presence of an impurity cannot be ruled out as none of the spectra of the other 1,*n*-di-(9-anthryl)alkanes (*n* = 2—10) exhibits this long-wavelength absorption.[3] This point should be cleared up before suggesting a bonding interaction between the anthryl rings through space or *via* σ-bonds.[14]

(2) *Fluorescence emission and its temperature dependence*. (a) *General*. The temperature-dependent fluorescence study of the bichromophores I_{XX} can provide an insight into the knowledge of the photophysical processes occurring from the excited singlet state which is known to be responsible for photocyclomerization.[3] In order to assess the specific bichromophoric interactions, a comparison has been made between I_{XX} and the reference molecules R_{XX} (see Figure 2).

The fluorescence emission quantum yields of R_{XX} in MCH, at room temperature, listed in Table 2, are in the range normally found for 9-alkylanthracenes[15] except for R_{CO} whose quantum yield (0.09) appears anomalously low; non-radiative deactivation, as discussed elsewhere,[4c] might be associated with partially hindered rotation of the CH_3 group about the CH_2–O bond. Thus R_{CO} is not a good reference molecule for I_{O2} where the non-radiative channels should be different.

The quantum yields of R_{CC} and R_{OO} were also measured as a function of temperature (Figure 3); assuming that k_F is temperature independent, it is possible to determine the activation parameters for the non-radiative processes:

$$\varphi_{nr} = 1 - \varphi_F; \quad k_{nr}\tau = 1 - \varphi_F; \quad \tau = \varphi_F/k_F$$

$$1 - \varphi_F = \varphi_F \cdot k_{nr}/k_F; \quad 1/\varphi_F - 1 = k_{nr}/k_F$$

$$k_{nr} = k^{\circ}_{nr} \exp(-E_a/RT)$$

$$\ln(1/\varphi_F - 1) = \ln(k^{\circ}_{nr}/k_F) - E_a/RT \quad (1)$$

A plot of $\ln(1/\varphi_F - 1)$ *versus* $1/T$ (Figure 3) allowed the determination of the rate parameters for R_{CC} (Table 2). The values for R_{SiC}, determined elsewhere,[16] are also listed in the same table for comparison. The rate parameters are in the range of those determined by Dreeskamp[17] for 9-n-butylanthracene in a mixture of dimethylbutane and pentane and compatible

Table 2. Singlet excited-state lifetime, fluorescence data, and non-radiative rate parameters for reference compounds in MCH at 20 °C. Compare with k°_{nr} 2.0 × 10^{10} s^{-1}, E_a 8.7 kJ mol^{-1} for 9-butylanthracene[17]

	τ_F/ns	φ_F	$10^{-7}\,k_F/s^{-1}$	$10^{-7}\,k_{nr}/s^{-1}$	k°_{nr}/s^{-1}	E/kJ mol^{-1}
R_{CC}	6.3	0.4	6.35	$\simeq$9.1	3 × 10^{10}	14.2
R_{SiC}	12	0.67	5.5	$\simeq$2.8	10^9	8.8
R_{OO}	4.9	0.29				
R_{CO}	1.2	0.09				

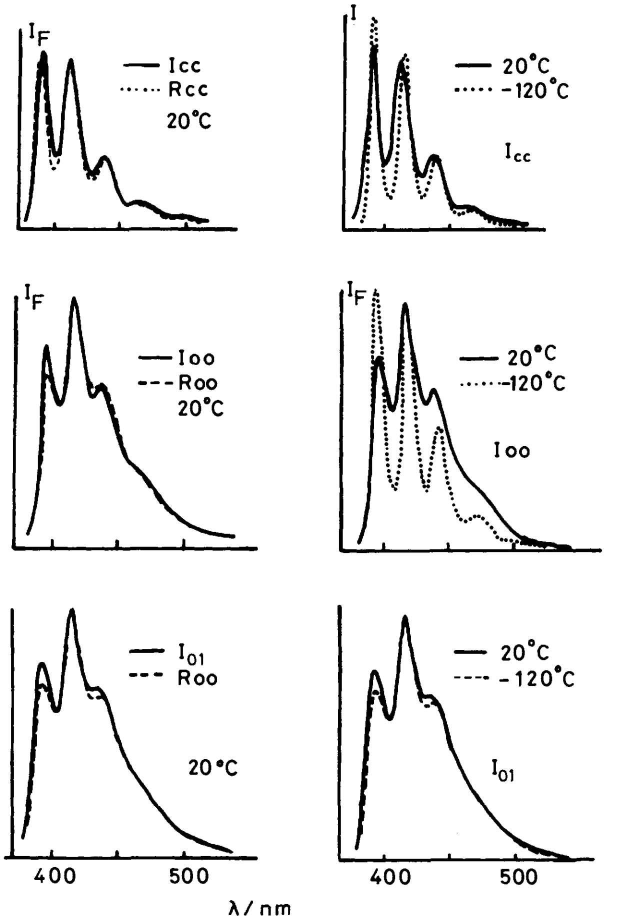


Figure 2. Fluorescence spectra (normalized at the second vibronic band) in MCH ($\lambda_{exc.}$ 380 nm) of I_{XX} and R_{XX} at 20 °C, and I_{XX} at 20 and −120 °C

with the intersystem crossing process.[18] However, by plotting ln $(1/\varphi_F - 1)$ *versus* $1/T$, R_{OO} was found not to give a straight line (Figure 3) which should reflect, as already reported for other anthracene derivatives,[19] the simultaneous occurrence of intersystem crossing and another non-radiative process, presumably the rotation of the methyl group about the C_{Ar}–O bond.

The bichromophores will be divided in two groups according to their fluorescence: those which exhibit a 'monomer fluorescence' and those with a dual ('monomer' and 'excimer') fluorescence.

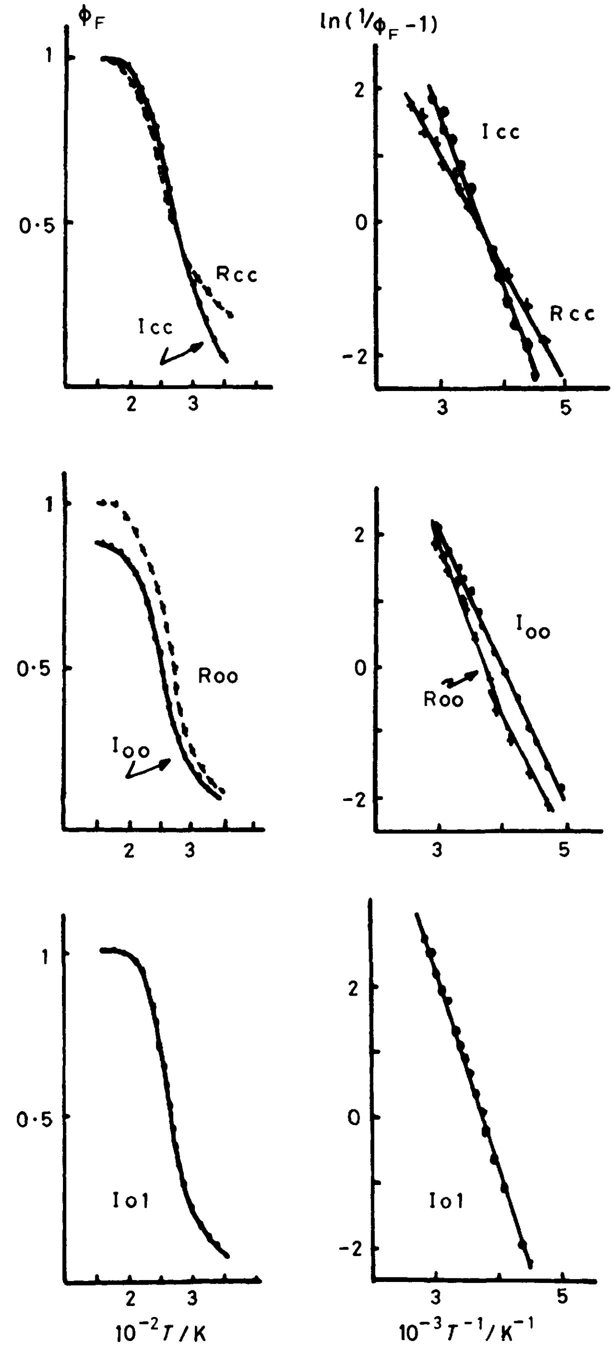


Figure 3. Temperature dependence of fluorescence quantum yields (φ_F) of compounds I_{XX} and relation between ln $(1/\varphi_F - 1)$ and T^{-1} in MCH

(b) *Bichromophores with non-emitting intramolecular excimers* (I_{CC}, I_{OO}, *and* I_{O1}). The fluorescence emission spectra of these compounds* are represented in Figure 2 and compared with those of the corresponding reference compounds. R_{OO} was found to be a suitable model for I_{O1} as their respective spectra are very similar, in contrast to that of R_{CC}. The emission of I_{O1} occurs mainly from the R-O-(9-anthryl) moiety which has the singlet excited state of lowest energy. As expected, the vibronic components sharpened as the temperature decreased in connection with an increase of the fluorescence quantum yield which reached a plateau at *ca.* 200 K (Figure 3). It is noticeable that the fluorescence spectra of these bichromophores I_{CC}, I_{OO}, and I_{O1} look like those of the reference compounds (Figure 2). The fluorescence decays of these bichromophores were found by single-photon counting to be exponential (Table 3). The plots of ln $(1/\varphi_F - 1)$ *versus* $1/T$ gave straight lines (Figure 3). This means that there is a unique (or at least major) deactivation channel. Using equation (1), it was possible to derive the Arrhenius rate parameters (k_{nr} and E_a) for non-radiative

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* Contrary to a previous report,[15b] no intramolecular excimer could be detected for I_{CC}.

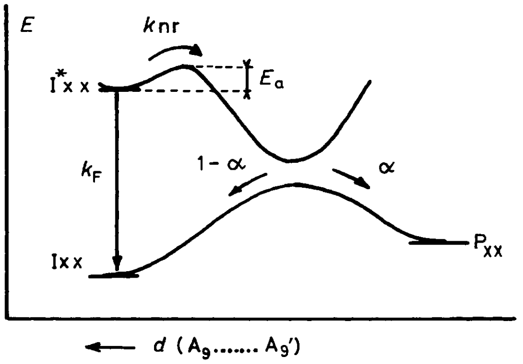


Figure 4. Simplified energy profile (not scaled) for the singlet-state deactivation of bichromophores I_{XX} (I_{CC}, I_{OO}, and I_{O1}); the intersystem crossing quantum yield has been found to be $\leqslant 0.1$ and was neglected; then $\varphi_{nr} = 1 - \varphi_F$ and φ_R (photoproduct quantum yield) $= \alpha \cdot \varphi_{nr}$

deactivation, k_F being calculated from φ_F and τ_F (experimental data, Table 3).

Energy profile. The values of the pre-exponential factors (2×10^{11}—7.5×10^{12} s^{-1}), higher than that of R_{CC}, are indicative[20] of a spin-allowed process (singlet–singlet), probably associated with conformational reorganization. Indeed similar behaviour was already observed with di-(9-anthryl)-ethanes[21] where the fluorescence quenching was shown to be due to a transition from *anti* to *gauche* conformer, the rate parameters being k°_{nr} 4.5×10^{12} s^{-1}; E_a *ca.* 23 kJ mol^{-1}. This activation energy is in the same range as those required for intramolecular excimer formation in bisanthracenes[22] as well as those for the non-radiative process of I_{XX} (Table 3). There is little doubt that the same mechanism applies in all the above cases. It was checked by flash photolysis that, for I_{OO}, intersystem crossing makes a minor contribution ($\varphi_{ST} < 0.10$ at 20 °C whereas φ_{nr} 0.78) and this is also assumed for I_{CC} and I_{O1}. Finally, an energy diagram can be drawn (Figure 4) representing competition between radiative and non-radiative processes. The formation of photoproducts is related to the latter; as the reaction quantum yields (φ_R) are lower than φ_{nr}, a partition coefficient ($\alpha = \varphi_R/\varphi_{nr}$) was calculated (Table 3); it indicates the efficiency with which the 'biradicaloid' intermediates in the funnel (according to Michl's model[23]) can generate intramolecular cycloadducts. The absence of excimer fluorescence could be attributed to a high degree of symmetry of the complex (then k_F must be low[24]) and efficient reactivity. The partition coefficients are in the range found by Bergmark and Jones with the assumption, not proved, that fluorescence quenching goes through a single channel.[25]

(c) *Bichromophores with excimer fluorescence* (I_{O2} *and* I_{SiC}). (i) *Excimer emission.* The fluorescence emission spectra of I_{O2} and I_{SiC} were recorded at various temperatures and are represented in Figure 5; they exhibit a structured part attributed to the locally excited ('monomer') species and a red-shifted, broad, structureless band ascribable to an excimer.[2,3,26] The spectrum and maximum of this emission can be determined from difference spectra (see Figure 5). Indeed, the excitation spectra, scanned at the monomer and excimer wavelengths, were found to be similar, pointing to the common origin of the two emissions. Moreover, the relative amount of monomer and excimer intensities show the temperature dependence depicted in Figure 6.

A sharpening of the 'monomer' vibronic components was also observed on cooling as with I_{CC}, I_{OO}, and I_{O1}. Finally, the existence of the second component of the fluorescence emission was confirmed by transient kinetic analysis[15] at room temperature; the fluorescence decay, recorded in the 'monomer' region (the excimer emission was not intense enough to be measured under our experimental conditions) was fitted by the sum of two exponentials (see Table 4):

$$i_M(t) \propto B_1 \exp(-\lambda_1 t) + B_2 \exp(-\lambda_2 t)$$

We put forward the kinetic Scheme 2 adapted from Birks[15a] that has been already postulated in similar cases;[2,15b] it rests on the demonstration of the intermediacy of an excimer in several examples of photodimerization of the anthracene ring.[27] The possibility that the dissymmetrical photocyclomer of I_{SiC} is formed through a conformer which is not conducive to a fluorescence-emitting excimer cannot be excluded; the weak excimer emission prevented deeper analysis. Nevertheless,

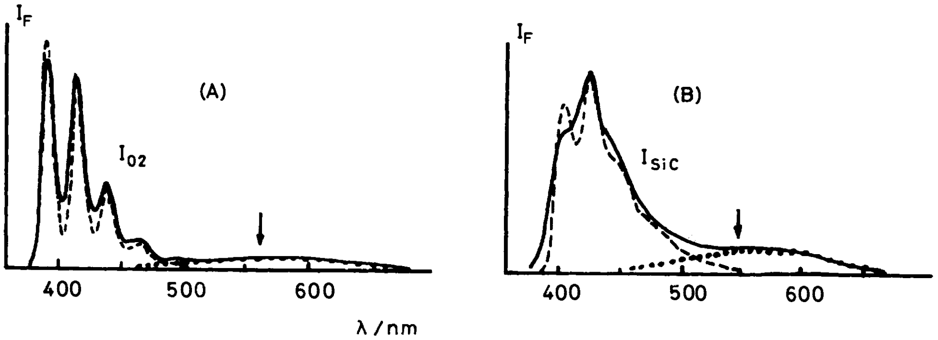
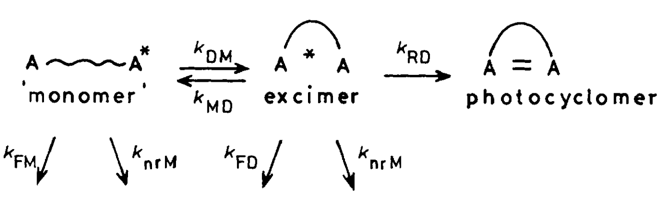


Figure 5. Corrected emission fluorescence spectra of compounds I_{O2} (A) and I_{SiC} (B) in MCH at 20 (——) and −125 °C (– – – –). The excimer spectra (· · · ·) were deduced by difference spectra at r.t. and low temperature after normalization

Table 3. Singlet excited-state lifetime, fluorescence, non-radiative rate parameters, and cyclomerization quantum yields for bisanthracenes I_{CC}, I_{OO}, and I_{O1} which do not exhibit excimer fluorescence. Solvent MCH; 20 °C. The partition coefficient α is derived from the equation $\varphi_R = \alpha \cdot \varphi_{nr}$ (see Figure 4)

	τ_F/ns	φ_F	10^{-7} k_F/s^{-1}	φ_{nr}	k°_{nr}/s^{-1}	E_a/kJ mol^{-1}	φ_R	α	10^{-8} k_{nr} (20 °C)/s^{-1}	10^{-7} k_R (20 °C)/s^{-1}
I_{CC}	4.6	0.37	8.04	0.63	6.5×10^{11}	20.9	0.08_4	0.13	1.42	1.7
I_{OO}	3.8_3	0.22	5.74	0.78	1.9×10^{11}	16.7	0.22	0.28	2.04	5.74
I_{O1}	3.9_5	0.25	6.33	0.75	7.5×10^{12}	25.9	0.20	0.27	1.9	5.06



Scheme 2. k_{FM}, k_{FD}, fluorescence rate constants of monomer and excimer emissions. k_{nrM}, k_{nrD}, non-radiative deactivation rate constants for monomer and excimer. k_{RD}, photocyclomerization rate constant. $k_D = k_{FD} + k_{nrD} + k_{RD}$

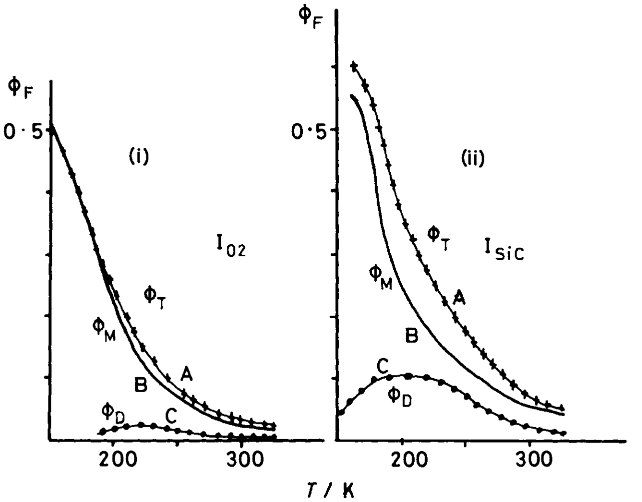


Figure 6. Total φ_T (A), monomer φ_M (B), and excimer φ_D (C) fluorescence quantum yields of I_{O2} (i) and I_{SiC} (ii) *versus* temperature in MCH

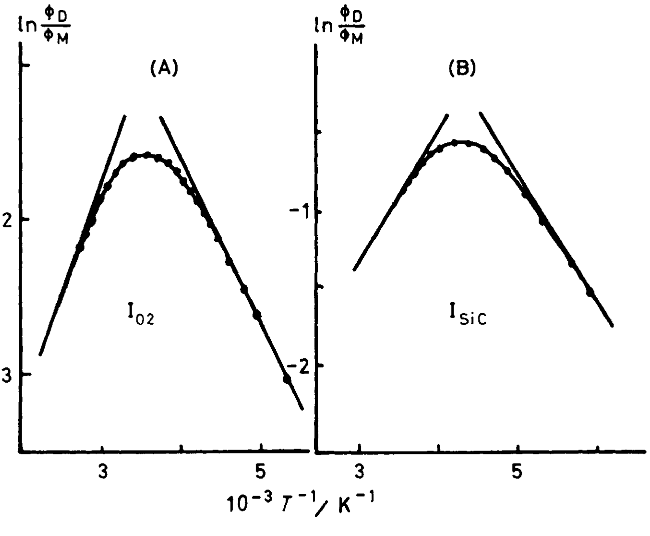


Figure 7. Stevens–Ban plots of the logarithm of the excimer–monomer fluorescence quantum yield ratio *versus* $1/T$. (A) I_{O2}, ΔE 8.8 kJ mol^{-1} (tentative value). (B) I_{SiC}, ΔE 6.7 kJ mol^{-1}; the 'high' temperature slope does not reflect ΔH in a simple way

from molecular models, the formation of a symmetrical excimer appears more likely.

(ii) *Determination of thermodynamic parameters.* By analysis of the behaviour of excimer fluorescence *versus* temperature, Stevens showed[28] that, provided there is an interconversion between 'monomer' and excimer fluorescence, the following approximations follows:

at 'low' temperature ($k_{MD} \ll k_D$)

$$d \ln (\varphi_{FD}/\varphi_{FM})/d(1/T) = -(E_{DM} - E_D)/R$$

(usually E_D is assumed to be much smaller than E_{DM})

at 'high' temperature ($k_{MD} \gg k_D$)

$$d \ln (\varphi_{FD}/\varphi_{FM})/d(1/T) = -\Delta H/R$$

The so-called Stevens–Ban plots for I_{O2} and I_{SiC} are represented in Figure 7. The tangent at the curve at 'low' temperature allows the calculation of the activation energy for excimer formation ($\Delta E \equiv \Delta E_{DM}$) and that for the 'high' temperature curve similarly gives the enthalpy of excimer formation (ΔH). Despite the approximations made and the experimental errors, the present data (Table 4) compare well for I_{O2} with those determined for other bisarenes;[4c,22] thus, for bis-[9-(10-phenylanthrylmethoxy)]methane[22] in methylcyclohexane (MCH), ΔE was 14 kJ mol^{-1} and ΔH -22 kJ mol^{-1}. The activation energies are to be compared with those found by Chandross[29] for 1,3-di-α-naphthylpropane (13.8) and 1,3-di-β-naphthylpropane (16.8 kJ mol^{-1}) in MCH–isopentane; this was for a trimethylene chain. The ΔH value must be taken with caution as the assumption $k_{MD} \gg k_D$ is probably not valid because k_{RD} should be high (φ_R 0.28). Concerning I_{SiC}, $k_{MD} \approx k_D$ and ΔH could not be derived as shown by the single-photon counting technique. Moreover, it has been found that the Stevens–Ban approximation is not valid because of the temperature dependence of k_{FD}.[26] It affects the Stevens–Ban parameters which include the excimer fluorescence activation energy E_{FD}. Therefore, ΔE values should be considered as *very approximate* and taken as accurate within an order of magnitude.

The striking feature of Table 4 is that the activation energies for excimer formation seem rather low, I_{SiC} 6.7 and I_{O2} 8.8 kJ mol^{-1}; however, they compare well with those of 1,4-di-(1-naphthyl)-2-oxabutane (6.3)[30] and 1,3-di(pyren-1-yl)propane (12.1 kJ mol^{-1}).[31a] This suggests that the ground state and excimer conformations are close to each other.

Finally, energy profiles are presented in Figure 8a, b with an excimer on the reaction pathway.

(iii) *Determination of kinetic parameters.* From transient kinetic analysis by use of the single-photon counting technique and quantum yield data (Table 4) it is possible to derive the rate constants of Scheme 2 (which may be average values for the different rotamers[31]), provided there is a suitable reference molecule for the 'monomer' part of the bichromophore.[1,3,15,22] For I_{O2}, neither R_{CC} nor R_{CO} were convenient. I_{SiC} is a symmetrical bichromophore and R_{SiC} was taken as the reference [φ_{FM} 0.67, τ_M 12 ns (k_{FM} 5.5 × 10^7 s^{-1}) in MCH at +20 °C, its lifetime[16] is virtually independent of temperature]. The results are listed in Table 4. A test of the validity of these values consists in using them to calculate the fluorescence quantum yields to be compared with the experimental values;[15b] they were found to be in good agreement: φ_{FM} experimental *ca.* 0.085, φ_{FM} calculated 0.100; φ_{FD} experimental *ca.* 0.025, φ_{FD} calculated 0.024.

The high value of k_{DM} (10^9 s^{-1}) of excimer formation is in accord with the low activation energy required. It is in contrast with the low reactivity (k_R *ca.* 10^5 s^{-1}) of the excimer compared with known data[1,32] (k_R *ca.* 3 × 10^7 s^{-1}); however, such data were already encountered[15b] in some 1,*n*-di-9-anthrylalkanes [*n* 5—10; k_R *ca.* (0.5—3) × 10^5 s^{-1}] ascribable to steric hindrance. Moreover, one observes a low value for k_{FD} which points to some degree of symmetry and a large width for the excimer spectrum (FWHH) (Table 4) indicative of low stabilization energy.[22] It is thus proposed that the symmetrical excimer cannot yield the classical 9-9′, 10-10′ photocyclomer for steric reasons but has to overcome an important energy barrier $\Delta E'$ to form the unsymmetric photoproduct (see Figure 8b).

Table 4. Fluorescence and reaction quantum yields, thermodynamic and kinetic parameters for I_{O2} and I_{SiC} at 20 °C in MCH. ΔE activation energy for excimer formation (from Stevens–Ban plots see text). λ_1, λ_2, B_1, and B_2 were determined by single-photon counting by analysing the 'monomer' fluorescence decay at 400 nm, $i_M(t) \approx B_1 \exp(-\lambda_1 t) + B_2 \exp(-\lambda_2 t)$; for other symbols, see Scheme 2; k_{nrD} 1.0×10^8 s^{-1}; k_D 1.03×10^8 s^{-1}. FWHH, full width at half height. φ_{ST} (unknown) is included in φ_{nr}; α values are only tentative for comparison with those in Table 3

	φ_{FM}	φ_{FE}	φ_{nr}	φ_R	(α)	λ_1^{-1}/ns λ_2^{-1}/ns	B_1 B_2	ΔE/kJ mol^{-1}	10^{-9} k_{DM}/s^{-1}	10^{-7} k_{MD}/s^{-1}	10^{-6} k_{FD}/s^{-1}	10^{-5} k_{RD}/s^{-1}	Excimer $\lambda_{max.}$/nm FWHH (cm^{-1})
I_{O2}	0.03	0.006	0.97	0.28	(0.29)	0.8 4.6	1.24 0.064	8.8					≃560 ≃3 600
I_{SiC}	0.085	0.025	0.915	0.0008	(0.0009)	1.8 9.3	1.54 0.13	6.7	1	8.7	3	1	≃540 ≃5 600

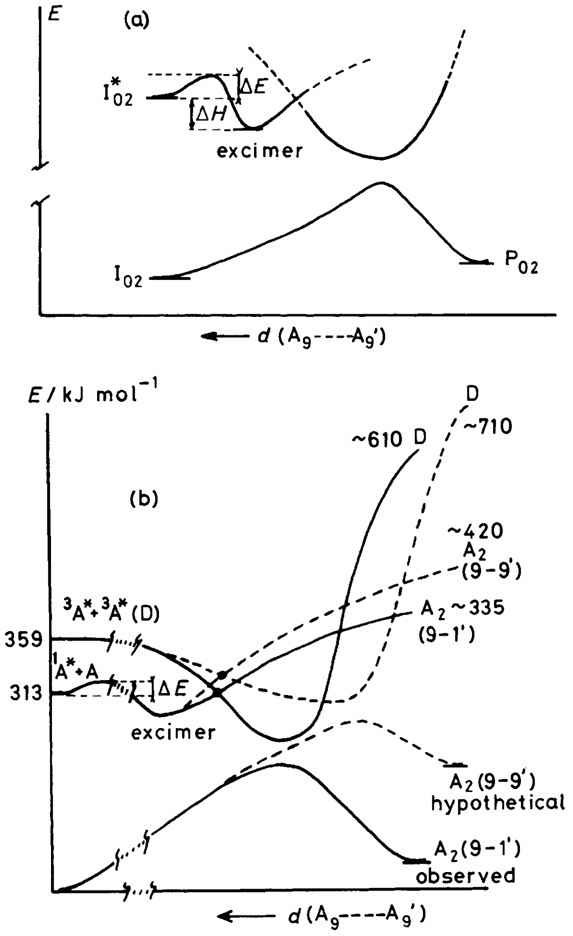


Figure 8. (*a*) Energy profile *versus* inter-ring distance for the photocyclomerisation of I_{O2}. (*b*) Hypothetical energy profile for the photocyclomerization of I_{SiC} (≡ ^1A). The reaction co-ordinate is the distance between position 9 and 9′ of the two rings. As far as the photochemical reaction proceeds it goes from left (large distances) to right (short distances). In the actually observed cyclomer, the 9... 9′ distance is longer than in the hypothetical 9–9′ photoproduct: steric hindrance moves the ground state and excited state surfaces to high energies and enhances the activation energy from the excimer to the doubly excited (D) surface. For the theoretical treatment of the pericyclic minimum on the doubly excited surface see ref. 33 and the experimental evidence of its role in photodimerization see ref. 34. Some thermodynamic data are arbitrary and the short distances are enlarged. ΔE *ca.* 7 kJ mol^{-1} (see Table 4). The energy values given for the doubly excited surface (D) were estimated from the triplet level of single chromophores.

(IV) *Conclusions.*— As expected, the replacement of one CH_2 group by one oxygen atom increases the reaction quantum yield (at room temperature) by a factor of *ca.* 3. A second replacement (I_{OO}) was not found significantly to improve the photocyclization efficiency, at least for the compounds examined. The other possible isomers [A–O–CH_2–O–CH_2–A and A–CH_2–O–O–CH_2–A (A = 9-anthryl)] cannot be synthesized. A thermodynamic study showed that the non-radiative deactivation from the singlet state of I_{CC}, I_{OO}, and I_{O1} leads to partition between photoproduct and starting material. This allowed the derivation of the rate constants (k_{nr}) and partition coefficients (α) (Table 3); these are the two hurdles to overcome on the way to the photocyclomer. It appears that the best position for the oxygen atom is the middle of the chain (I_{O2}) but a direct comparison with the above bichromophores is not possible because the excimer has to be taken into account. The fact that little (if at all) improvement was found with a second oxygen atom could be due to the presence of two hydrogens in the *peri* position[35] which contribute to eclipsed conformations generating energy barriers and low partition factors. The results of the study of the excimer luminescence from I_{O2} and I_{SiC} suggest that there is little molecular rearrangement between the ground and the excimer state, even if the latter adopts a symmetrical conformation. For I_{O2} the reaction quantum yield is limited by the partition in the pericyclic minimum, α *ca.* 0.29 (tentative value); I_{SiC} is too strongly hindered to meet the geometric requirements in the doubly excited state and, presumably also, at the partitioning state as suggested by molecular models. The kinetic data indicate that the main deactivating channels from the excimer are non-radiative deactivation and return to the local excited ('monomer') state.

The best cyclization quantum yield of bisanthracenes are thus to be expected for the most flexible chains (minimum eclipsed interactions) to reach a sandwich conformer (best overlap) and the most favourable partitioning factor (little steric strain and maximum bonding between the reacting centres in the pericyclic minimum).

To sum up, in the bisanthracenes with a four-membered chain, the introduction of an oxygen atom enhanced the reaction quantum yield; however, a second oxygen did not show any further improvement. The presence of bulky $SiMe_2$ groups helped to reach the excimer state smoothly but strongly hindered the formation of a photocyclomer.

Experimental

Physical Methods.—M.p.s were determined with a Kofler block and are uncorrected. A microbalance (Mettler ME 30, sensitivity 10^{-6} g) was used for spectroscopic measurements. I.r. spectra were recorded on a Perkin-Elmer model 412 instru-

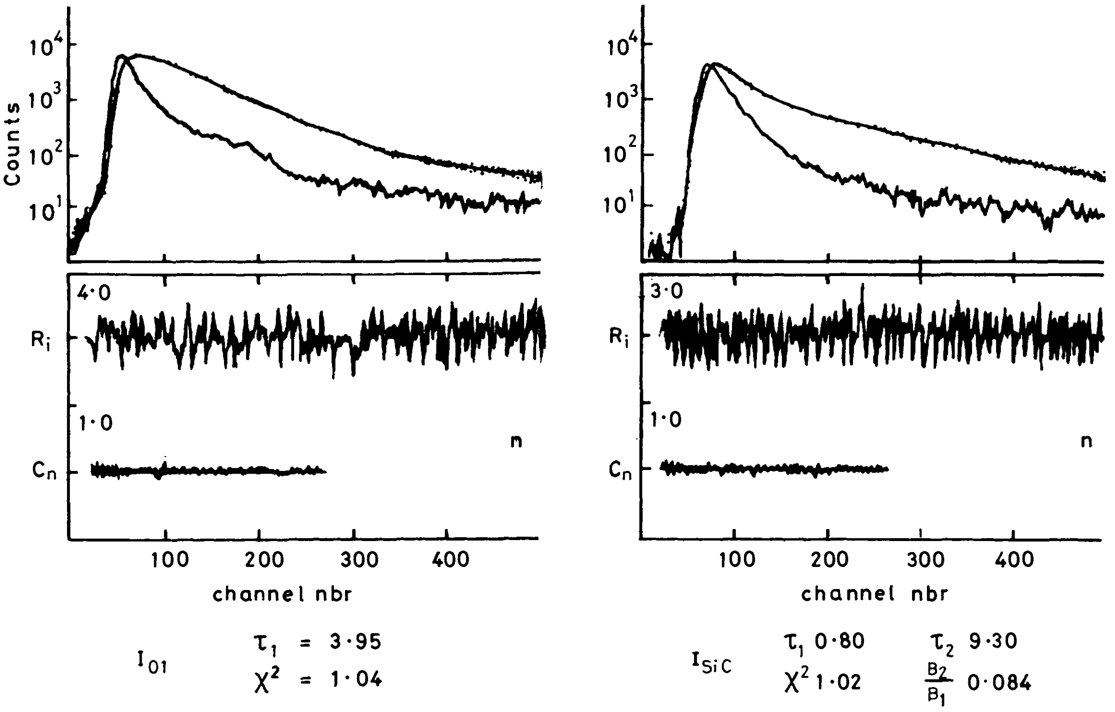


Figure 9. Decays of the fluorescence emission of I_{01} and I_{SiC} in MCH at 20 °C monitored at 400 nm. Channel width 0.1 ns. $\lambda_{exc.}$ 370 nm

ment with KBr pellets. Electronic absorption spectra were recorded on a Cary 219 spectrophotometer. ^1H N.m.r. spectra were obtained using Perkin-Elmer R-12 and R-24B (60 MHz) and Bruker AC 200 (200 MHz) instruments with Me_4Si as standard. Mass spectra were recorded using a VG Micromass 70/70 instrument. The purity of all new compounds was checked by t.l.c. (silica gel) and reverse-phase h.p.l.c. [S_5 octadecylsilane, SiC_{18} Spherisorb (eluent methanol)].

The fluorescence spectra were recorded as described elsewhere[11b] with a Hitachi–Perkin-Elmer MPF 44 fluorimeter corrected for emission and excitation. The sample vessels were degassed by several freeze–pump–thaw cycles on a high-vacuum line and sealed. The fluorescence quantum yields were determinated by comparison with quinine sulphate in N-sulphuric acid or 9,10-diphenylanthracene[36] and the fluorescence lifetimes were measured by single-photon counting, using an Applied Photophysics apparatus as already depicted.[21] Examples of single and double exponential decays with typical statistical tests are given in Figure 9. The determination of the reaction quantum yields was performed with degassed samples at 365 nm, using a Parker actinometer, as previously described.[11b]

Solvents.—Methylcyclohexane (MCH) (Prolabo Paris, or Solvants-Documentation Synthèses, Marseille; u.v. spectroscopic grade) was used without further purification. No fluorescent impurities were detected under our experimental conditions.

Starting Materials.—9-Hydroxymethylanthracene[8] was prepared by smooth reduction of 9-anthraldehyde previously obtained from anthracene by the Vilsmeier–Haack method.[37] 1,2-Bis-(chlorodimethylsilyl)ethane was kindly provided by Dow Corning (Barry).

Syntheses.—Monochromophoric reference materials were prepared according to published procedures. 9-n-Decyl-(R_{CC}),[15b] 9-methoxy-(R_{OO}),[38] 9-methoxymethyl-(R_{CO}),[8] and 9-trimethylsilyl-(R_{SiC})[9] anthracenes were purified by column chromatography (silica gel; ligroin) followed by h.p.l.c.

1,2-Bis-(9-anthryloxy)ethane I_{OO}. The compound was prepared in two steps. (a) To a stirred solution of anthrone (2 g, 10^{-2} mol) in CH_2Cl_2 (50 ml) were added 1,2-dibromoethane (19 g, 10^{-1} mol), tetrabutylammonium iodide (0.1 g, 2.7×10^{-4} mol), and a solution of NaOH (2 g, 5×10^{-2} mol) in water (25 ml. The orange mixture was refluxed for 11 days. After cooling to room temperature the solution was extracted with CH_2Cl_2 (2 × 100 ml). The organic layer was washed, then dried over magnesium sulphate. A brown oil was obtained after removing the solvent. Chromatography on silica column (ligroin–diethyl ether) gave 1-bromo-2-(9-anthryloxy)ethane as a yellow solid (2 g, 67%), m.p. 126 °C, $\delta(CCl_4)$ 3.6 (2 H, t), 4.3 (2 H, t), and 7.0—8.1 (9 H, m).

(b) By the same procedure, from anthrone (0.68 g, 3.5×10^{-3} mol), 1-bromo-2-(9-anthryloxy)ethane (1 g, 3.3×10^{-3} mol), tetrabutylammonium iodide (0.1 g, 2.7×10^{-4} mol), I_{OO} was obtained as yellow crystals (0.6 g, 41%), m.p. 250 °C, $\delta(CDCl_3)$ 4.8 (4 H, s) and 7.4—8.9 (18 H, m), $\nu_{max.}$(KBr) 3 030, 3 015, 2 900, 2 860, 1 935, 1 915, 1 900, 1 810, 1 790, 1 610, 1 540, 1 460, 1 430, 1 400, 1 350, 1 310, 1 270, 1 160, 1 100, 1 000, 990, 950, 840, 800, 790, 740, 700, and 660 cm^{-1}, $\lambda_{max.}$(MCH) 389 (log ε 4.32), 379 (4.26), 350 (4.06), 333 (3.73), 256 (5.56), and 248 nm (5.28), *m/z* 414 ($M^{+\cdot}$) (Found: C, 86.9; H, 5.5; O, 7.6. $C_{30}H_{22}O_2$ requires C, 87.0; H, 5.3; O, 7.7%).

1-(9-Anthryl)-3-(9-anthryloxy)propane I_{O1}. The starting material 9-(3-hydroxypropyl)anthracene was prepared in a one-pot procedure as described by Umio[6] for other compounds.

(a) To an EtMgBr solution [prepared from ethyl bromide (24 g, 0.22 mol), magnesium (4.8 g, 0.2 g atom), and THF (100 ml)] cooled in an ice-bath, 1-chloropropanol (0.25 mol, 24 g) was added dropwise with stirring. After addition was complete, this mixture was stirred for 0.5 h and further magnesium (4.8 g, 0.2 g atom) was added. The stirring was continued at 60 °C until the magnesium nearly completely disappeared. To this mixture, cooled at 0 °C, anthrone (19.4 g, 0.1 mol) was added in portions. The solution was then refluxed for 3 h with stirring. The mixture was cooled in an ice-bath and hydrolysed with saturated aqueous NH_4Cl. After extraction with diethyl ether and usual work-up, a crude solid was obtained which gave, after chromatography on a silica column (ligroin–diethyl ether) and crystallization in CH_2Cl_2, pure 9-(3-hydroxypropyl)anthracene (2.5 g, 11%), m.p. 98—99 °C (lit.,[8] 97.5—98.5 °C), $\delta(CDCl_3)$ 2.2—2.5 (2 H, t), 3.8—4.2 (4 H, m), and 7.0—8.5 (9 H, m).

(b) To a stirred solution of 9-(3-hydroxypropyl)anthracene (1.4 g, 6×10^{-3} mol) in dry chloroform (50 ml) cooled in an ice-bath was added dropwise phosphorus tribromide (4 g, 1.5×10^{-2} mol). Stirring was continued at 0 °C for 12 h. The mixture was extracted with diethyl ether, the organic layer washed with water, and the solvent removed under reduced pressure. The crude oil was chromatographed on a silica column (ligroin). 9-(3-Bromopropyl)anthracene (1.33 g, 75%) was obtained as pale green crystals, m.p. 88 °C (lit.,[39] 85 °C), $\delta(CDCl_3)$ 2.5 (2 H, s), 3.8—4.0 (4 H, m), and 7.5—8.5 (9 H, m).

(c) To a stirred solution of anthrone (4.6 g, 2.4×10^{-2} mol) in THF was added dropwise under stirring a solution of KOH (1.5 g, 2.7×10^{-2} mol) in water (5 ml). Stirring was continued at room temperature for 20 min and the solution turned red. A solution of 9-(3-bromopropyl)anthracene (1.9 g, 6.35×10^{-3} mol) in THF (100 ml) was then added dropwise and the mixture was refluxed for 4 h. After cooling to room temperature, the reacting medium was acidified by addition of dilute hydrochloric acid. The usual work-up was followed by chromatography on silica column (ligroin–diethyl ether) and I_{O1} was obtained (1 g, 38%) as pale *crystals*, m.p. 194 °C, $\delta(CDCl_3)$ 2.0—2.5 (2 H, m), 3.8—4.6 (4 H, m), and 7.1—8.5 (18 H, m), $\nu_{max.}$(KBr) 3 050, 3 010, 2 900, 2 850, 1 610, 1 540, 1 440, 1 410, 1 340, 1 160, 1 150, 1 100, 1 010, 960, 950, 880, 840, 790, 730, and 650 cm^{-1}, $\lambda_{max.}$(MCH) 389 (log ε 4.3), 368.5 (4.29), 349.5 (4.06), 333 (3.73), 266.5 (5.55), and 248.5 nm (5.32) (Found: C, 89.9; H, 5.75. $C_{31}H_{24}O$ requires C, 90.3; H, 5.8%).

1,4-*Bis-(9-anthryl)-2-oxabutane* I_{O2}. Under argon, sodium hydride (0.03 g, 1.1×10^{-3} mol) was suspended in dry THF (150 ml). 15-Crown-5 (0.02 g, *ca.* 10^{-4} mol) was added and the mixture vigorously stirred for 5 min. A solution of 9-(2-hydroxyethyl)anthracene[7] (0.222 g, 10^{-3} mol) in THF (20 ml) was added slowly and the resulting mixture was stirred for 15 min at room temperature. An orange colour was observed. A solution of 9-chloromethylanthracene[8] (226.5 mg, 10^{-3} mol) in THF (15 ml) was added slowly. An orange solution was obtained which turned brown after 5 min. The mixture was stirred at room temperature for 17 h. The solution was hydrolysed with water (100 ml) and the resulting aqueous mixture was extracted with CH_2Cl_2 (3 × 100 ml). The combined extracts gave a solid residue after the usual work-up. Purification by column chromatography (silica; ligroin–diethyl ether) and subsequent crystallization from the same solvent mixture gave I_{O2} as pale yellow needles (0.21 g, 51%), m.p. 182 °C, $\delta(CDCl_3)$ 4.2 (4 H, t), 5.7 (2 H, s), and 7.4—8.7 (18 H, m), $\nu_{max.}$(KBr) 3 025, 3 020, 2 815, 1 630, 1 455, 1 385, 1 350, 1 190, 1 170, 1 095, 1 050, 1 005, 900, 880, 850, 800, 740, 735, and 540 cm^{-1}, $\lambda_{max.}$(MCH) 387 (log ε 4.23), 367 (4.23), 348.5 (4.03), 332 (3.72), 256 (5.35), and 248.5 nm (5.28), *m/z* 412 ($M^{+\cdot}$). (Found: C, 90.0; H, 5.8; O, 3.9. $C_{31}H_{24}O$ requires C, 90.3; H, 5.8; O, 3.9%).

1,2-*Bis(dimethyl-9-anthrylsilyl)ethane* I_{SiC}. (a) *Preparation of the dihydro derivative*. Under argon, to a stirred solution (cooled at −15 °C) of 9,10-dihydroanthracene (9 g, 5×10^{-2} mol) in dry THF (200 ml) was added Bu^{n}Li (5.6×10^{-2} mol) in hexane. The mixture turned red. Bis-1,2-(chlorodimethylsilyl)-ethane (5.7 g, 2.65×10^{-2} mol), b.p. 198 °C at 737 mmHg, in THF (100 ml) was added dropwise. The stirring was continued at room temperature for 2 h. The mixture was hydrolysed with water and successively extracted with diethyl ether (200 ml) and toluene (200 ml). An insoluble solid, isolated by filtration and recrystallized in benzene (6 g, 64%), m.p. 212—213 °C, was 1,2-bis(dimethyl-9,10-dihydro-9-anthrylsilyl)ethane, $\delta(CDCl_3)$ 0.20 (12 H, s), 0.33 (4 H, s), 3.66 (2 H, s), 3.9 (4 H, s), and 7.1—7.5 (12 H, m), $\nu_{max.}$(KBr) 3 040, 3 000, 2 960, 2 920, 1 590, 1 560, 1 470, 1 245, 1 240, 900, and 810 cm^{-1}, *m/z* 323 ($M^{+\cdot}$ − anthryl), the molecular peak was not observed (Found: C, 80.55; H, 7.6. $C_{34}H_{38}Si_2$ requires C, 81.1; H, 7.6%).

(b) *Preparation of* I_{SiC}. To a stirred solution of 1,2-bis-(dimethyl-9,10-dihydro-9-anthrylsilyl)ethane (1 g, 2×10^{-3} mol) in tetramethylethylenediamine (TMEDA) (30 ml) and cyclohexane (80 ml) a solution of Bu^{n}Li (32×10^{-3} mol) in hexane was added dropwise. The red solution was refluxed for 1 h and turned purple. At room temperature $CdCl_2$ (3.6 g, 2×10^{-2} mol) was added after being dried under vacuum at 100 °C. The mixture was refluxed for 2 h, cooled at room temperature, and hydrolysed. After usual work-up, a solid residue was obtained which, after chromatography (silica column; ligroin–diethyl ether) and crystallization in diethyl ether–ligroin–benzene (1:15:2) solution, gave a mixture of two kinds of crystals which were separated using tweezers. The white material corresponded to the starting dihydro derivative whereas the bright yellow crystals were identified as I_{SiC} (0.5 g, 51%), m.p. 160 °C, $\delta(CDCl_3)$ 0.7 (12 H, s), 1.2 (4 H, s), and 7.3—8.5 (18 H, m), $\nu_{max.}$(KBr) 3 010, 2 990, 2 900, 2 860, 1 610, 1 500, 1 440, 1 400, 1 250, 1 120, 1 050, 1 010, 940, 840, and 820 cm^{-1}, *m/z* 498 ($M^{+\cdot}$), $\nu_{max.}$(MCH) 389.3 (log ε 4.22), 379 (4.25), 351 (4.10), 335 (3.77), 258 (5.35), and 251 nm (5.24) (Found: C, 81.6; H, 6.9; Si, 11.7. $C_{34}H_{34}Si_2$ requires C, 81.9; H, 6.8; Si, 11.2%).

Preparation of the photocyclomers P_{XX}. *Compound* P_{CC}. A degassed solution of I_{CC} (4 mg, *ca.* 10^{-4}M) in diethyl ether (100 ml) was irradiated in a Pyrex vessel at λ > 335 nm [liquid filter; lead acetate (7 g)–sodium bromide (540 g)–water (1 l)] with a high-pressure mercury lamp (Philips SP 500) for 12 h. After solvent removal, P_{CC} was obtained as a powder (4 mg, 100%), m.p. 200 °C (decomp.). It thermally decomposed to regenerate I_{CC}, $\nu_{max.}$(KBr) 3 040, 2 910, 1 475, 1 460, 1 440, 1 280, 1 150, 1 040, 990, 930, 760, 690, and 620 cm^{-1}, $\lambda_{max.}$(diethyl ether) 281.5 (log ε 2.98), 272.5 (3.11), and 220 nm (4.46).

Compound P_{OO}. Under the preceding irradiation conditions, I_{OO} (4 mg, *ca.* 10^{-4}M) in degassed diethyl ether (100 ml) yielded P_{OO} as a solid (100%), m.p. 300 °C. It reverted to I_{OO} at ≥215 °C, $\delta(CDCl_3)$ 4.6 (2 H, s), 4.8 (4 H, s), and 6.8—7.6 (18 H, m), $\nu_{max.}$(KBr) 3 060, 3 010, 2 960, 2 860, 1 480, 1 470, 1 450, 1 280, 1 190, 1 160, 1 130, 1 100, 1 000, 960, 940, 780, 700, 650, and 600 cm^{-1}, $\lambda_{max.}$(MCH) 283 (log ε 2.91), 272.5 (3.19), and 217 nm (4.68).

Compound P_{O1}. I_{O1} (3 mg, *ca.* 10^{-4}M) gave P_{O1} as a solid (100%), m.p. 230—235 °C. It thermally decomposed into I_{O1}, $\delta(CDCl_3)$ 2.5 (2 H, m), 4.5—4.8 (6 H, m), and 6.8—7.5 (18 H, m), $\nu_{max.}$(KBr) 3 060, 3 020, 3 000, 2 920, 1 460, 1 445, 1 100, 1 000, 770, and 700 cm^{-1}, $\lambda_{max.}$(MCH) 284 (log ε 2.98), 274 (3.15), 266 (3.12), and 215 nm (3.32).

Compound P_{O2}. I_{O2} (3 mg, *ca.* 10^{-4}M) gave P_{O2} as crystals (100%), m.p. 210 °C. It thermally reverted to I_{O2}, $\delta(CDCl_3)$ 2.90 (2 H, t, *J* 6.6 Hz), 4.51 (2 H, s), 4.62 (2 H, s), 4.67 (2 H, t, *J* 6.6 Hz), and 6.75—7.45 (16 H, m), $\nu_{max.}$ 3 030, 2 950, 1 460, 1 115, and 690 cm^{-1}, $\lambda_{max.}$(MCH) 292 (log ε 2.91), 272 (3.09), and 210 nm (4.62).

Compound P_{SiC}. The photoproduct (P_{SiC}) was not isolated. Its n.m.r. spectrum was directly recorded (5 h scanning) for a C_6D_6 solution (*ca.* 10^{-4}M) after irradiation in a sealed n.m.r. tube; the protons of the ethane bridge were not clearly detected, $\delta(C_6D_6)$ 0.25 (3 H, s), 0.37 (3 H, s), 0.62 (3 H, s), 0.74 (3 H, s), 3.82 (1 H, m), 4.15 (1 H, d), 4.70 (1 H, dd), 6.03 (2 H, m), and 6.35—8.4 (13 H, m). The u.v. spectrum was recorded for an irradiated solution of I_{SiC} (≤10^{-4}M) in MCH, $\lambda_{max.}$ 331 (log ε 3.09), 317

(3.14), 300 (3.70), 289 (3.89), 279 (3.95), 270 (3.97), 249 (4.51), and 223 nm (4.70).

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