Study of Non-conjugated Bichromophoric Systems, the So-called ' Jaw Photochromic Materials '. Part 1. Photocyclomerization and Fluorescence of Bis-9-anthrylmethyl Ethers

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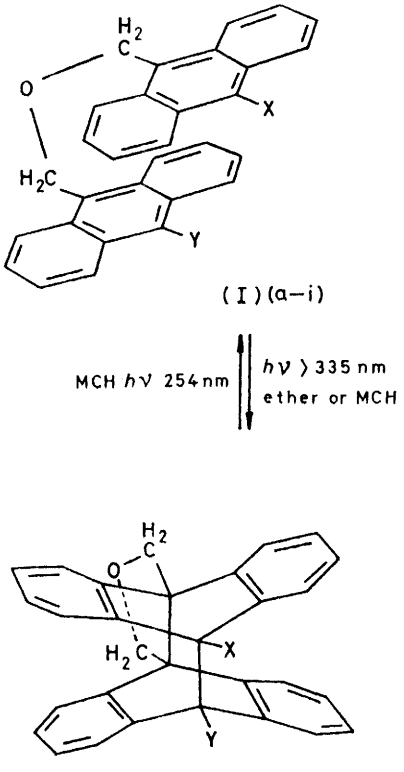
Bis-9-anthrylmethyl ether and eight derivatives of the type $XACH_2OCH_2AY$ (Ia—i) where A is 9,10-anthrylidene and X and Y are substituents have been prepared and investigated. The three-member ether linkage was chosen in order to obtain more easily than with a polymethylene chain the relevant conformations for efficient photocyclomerization. Indeed, the majority of these compounds photocyclomerized in fluid solution at 366 nm with a quantum yield of 0.16—0.50. Photodissociation at 254 nm has also a high efficiency (0.27—0.64). Cyclomerization occurs even for compounds where both X and Y are bulky (CH_3, Br). An increase in the photocyclization quantum yield was noted in acetonitrile relative to methylcyclohexane (MCH). These systems are thus photochromic. A study of the u.v. absorption spectra of (Ia—h) reveals considerable hypochromism relative to those of model compounds and this is consistent with the presence of ground state conformations having a high degree of interaction between the aromatic groups: in contrast (Ii) exhibits hyperchromism with respect to the reference compound and this is ascribable to different conformations arising from steric crowding of the substituents. Excimer fluorescence was recorded in fluid solution at room temperature for the diphenyl derivative (Ii) which does not react and in MCH matrices at 77 K for the cyclomers cleaved at 254 nm by the method of Chandross and Ferguson. Their maximum emission (550—575 nm) points to the presence of strong overlapping conformations.

BIMOLECULAR photochemical interactions can often be studied at very low concentrations by taking advantage of the ability of a short (u.v. transparent) aliphatic chain to keep two chromophores in relative proximity.[1,2] From another point of view, examination of these bichromophoric interactions can provide information about conformational [3a] and dynamic properties [3b] of the chain.



a; X = Y = H
b; X = CH_3, Y = H
c; X = C_6H_5, Y = H
d; X = Br, Y = H
e; X = CH_3, Y = CN
f; X = C_6H_5, Y = CN
g; X = CH_3, Y = Br
h; X = Y = Br
i; X = Y = C_6H_5

SCHEME

One of these systems, bisanthracenes, has photochromic properties.[4] We have investigated compounds (I) where the chromophores are 9-anthryl groups linked by a three-membered chain. These are able to cyclomerize to (II) which can in turn revert to (I) by heating or irradiation (Scheme). The opening and closure of such systems suggest the motion of a jaw; for this reason, we propose to call them ' jaw photochromic materials '.

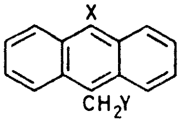
Inspection of models shows that the best overlap of the two aromatic halves is reached with a three-membered chain.[5] This is in keeping with the well known, although questioned, Hirayama rule.[2,6-8] Moreover, the sequence $-CH_2-O-CH_2-$ was chosen in preference to $-CH_2-CH_2-CH_2-$ because we expected the lower rotational barrier about the C–O bonds [9] to facilitate cyclomerization. Indeed, the closure of (Ia) proved simple.[4a,b,5] Therefore, we report the preparation, photocyclomerization, and spectroscopic properties of a series of derivatives of bis-9-anthrylmethyl ether.

RESULTS

Preparation.—The known parent compound (Ia) [4b,5] was prepared by a published method.[4b] The same procedure was applied to the synthesis of the new compounds (Ib—i). The yields vary between 20 and 90% according to the nature of X and Y (see Experimental section). The nitriles (Ie,f) are bright yellow, whereas compounds (Ia—d, g—i) are pale yellow crystals. The spectra are consistent with the proposed structures. Most of the compounds are prone to oxidation at room temperature and are difficult to keep. We also prepared the model compounds 9-methoxymethylanthracene (IIIa) [10] and 9-

methoxymethyl-10-phenylanthracene (IIIb) for spectroscopic measurement.

Photocyclomerization.—According to their photochemical behaviour, compounds (Ia—i) can be divided into three groups. Compounds (Ia—f), the first group, are easily cyclomerized; the second group, the bromo derivatives (Ig, h), undergo C–Br cleavage; the third group comprises compound (Ii) which is photostable under our conditions.



(III)

a; X = H , Y = OCH_3
b; X = C_6H_5 , Y = OCH_3
c; X = H , Y = OH
d; X = H , Y = Cl
e; X = CH_3 , Y = OH
f; X = CH_3 , Y = Cl
g; X = C_6H_5 , Y = OH
h; X = C_6H_5 , Y = Cl
i; X = Br , Y = OH
j; X = Br , Y = Cl

(A) *Compounds* (Ia—f). In degassed fluid solutions [ether or methylcyclohexane (MCH)] irradiation of (Ia—f) (*ca.* 5 × 10^{-5}M; room temperature) with light of wavelength >335 nm gave intramolecular cyclomerization at the 9, 10 and 9′, 10′ positions. The cyclomers (IIa—d) were isolated and characterized by their u.v. absorption spectra and by n.m.r. The u.v. spectra of the products resemble that of 9,10-dihydroanthracene. Irradiation at 254 nm of (IIa—d) (5 × 10^{-5}M; MCH; room temperature) gave back (Ia—d). This cycle could be repeated several times.

Because the photocyclomers of (IIe and f) were thermally unstable, they could not be isolated. After irradiation they revert spontaneously to (Ie and f). They persist sufficiently for the photochemical ring closure and thermal opening to be monitored by u.v. spectroscopy. We have previously observed a similar thermal instability for the crossed head-to-head photodimer of 9-cyano- and 9-methoxy-anthracene.[11]

The quantum yields of the reactions are collected in Table 1.

TABLE 1

Photocyclomerisation ($\phi_{(I) \rightarrow (II)}$) and photoreverse ($\phi_{(II) \rightarrow (I)}$) quantum yields for (Ia—f) and (IIa—d) in MCH at 20 °C

Compounds	10^5 Concentration (mol l^{-1})	$\phi_{(I) \rightarrow (II)}$ λ 366 nm	$\phi_{(II) \rightarrow (I)}$ λ 254 nm
(Ia) $\rightleftarrows$ (IIa)	4.12	0.32	0.64
(Ib) $\rightleftarrows$ (IIb)	4.85	0.32	0.38
(Ic) $\rightleftarrows$ (IIc)	5.11	0.19	0.27
(Id) $\rightleftarrows$ (IId)	3.48	0.18	0.28
(Ie) $\rightleftarrows$ (IIe) *	3.48	0.25	
(If) $\rightleftarrows$ (IIf) *	4.97	0.16	

* The thermal instability of (IIe and f) prevents the determination of $\phi_{(II) \rightarrow (I)}$.

(B) *Compounds* (Ig *and* h). The reactivity of the bromo derivatives (Ig and h) is quite different (Table 2). A second cyclomer appears in ether, resulting from C–Br cleavage followed by hydrogen abstraction, probably from the solvent. In contrast, one observes a single photoproduct in acetonitrile.

Despite its thermal instability, (IIg) was isolated as the single photoproduct in the irradiation of (Ig) in acetonitrile (λ>335 nm) and characterized by n.m.r., i.r., and u.v. The irradiation of (Ig) in ether yields a mixture of (IIg and b) in the ratio 1 : 1 (n.m.r.). Compound (IIh) could not be isolated from the irradiation of (Ih) in acetonitrile (λ >335 nm). In this solvent, however, one can follow by u.v. spectroscopy the photochemical ring closure of (Ih) to (IIh) as well as the thermal opening of (IIh). When a degassed solution of (Ih) (*ca.* 5 × 10^{-5}M) in ether is irradiated (λ>335 nm), n.m.r. analysis of the photoproduct shows the presence of (IIh and d) in the ratio 66 : 34. This ratio is probably not characteristic of the real kinetic proportions of (IIh and d) due to the thermal instability of (IIh). The photocyclomerization quantum yields were measured for (Ig and h) in acetonitrile where only one photoproduct is formed and compared to those of (Ia and d) in the same solvent. The results are collected in Table 3.

(C) *Compound* (Ii). This does not react at 20 °C in degassed MCH when irradiated at a wavelength >335 nm.

Spectroscopy.—(A) *Electronic absorptions.* Table 4 gives the wavelengths (λ_1 and λ_2) and molecular extinction coefficients (ε_1 and ε_2) of the longest wavelength component of the absorption bands for the first ($^1L_a \longleftarrow {}^1A$) and second ($^1B_b \longleftarrow {}^1A$) electronic transitions for (Ia—i) and (IIIa and b). These transitions were assigned by analogy with the well known absorption spectra of anthracene and its derivatives.[12] Table 4 also includes the oscillator strengths of the first electronic transition.

TABLE 2

Photocyclomerization of (Ig and h) in acetonitrile and ether (*ca.* 5 × 10^{-5}M) at room temperature (λ>335 nm)

Starting compound	Solvent	Photoproduct (relative ratio)
(Ig)	CH_3CN	(IIg) (100%)
(Ig)	Ether *	(IIg) (50%) + (IIb) (50%)
(Ih)	CH_3CN †	(IIh)
(Ih)	Ether †	(IIh) + (IId)

* N.m.r. estimation ($CDCl_3$ solution) at 98% conversion rate of the starting material. † See text.

TABLE 3

Photocyclomerization quantum yield ($\phi_{(I) \rightarrow (II)}$) of (Ia, d, g, and h) in acetonitrile at 20 °C

Compounds	10^5 Concentration (mol l^{-1})	$\phi^*_{(I) \rightarrow (II)}$ λ 366 nm
(Ia) $\longrightarrow$ (IIa)	4.72	0.50
(Id) $\longrightarrow$ (IId)	3.52	0.25
(Ig) $\longrightarrow$ (IIg)	4.64	0.26
(Ih) $\longrightarrow$ (IIh)	3.53	0.17

* Accurate measurements of the quantum yield of the photoreverse reaction ($\phi_{(II) \rightarrow (I)}$) is prevented by the thermal instability of (IIg and h).

(a) Comparison of the bichromophores. First electronic transition. It is possible to see four distinct vibrational bands and one shoulder when the two halves are identical (X = Y); otherwise the vibrational structure is blurred. Compared with (Ia), (Ib—i) show a bathochromic effect (6—20 nm) of the same order of magnitude as that found in anthracene derivatives.[12a] Only (Ih) exhibits a noticeable hypochromic effect compared with (Ia). In addition, we observe that the nitriles display an absorption tail which confers their bright yellow colour.

Second electronic transition. The bathochromic shift (Δλ *ca.* 3 nm) is of the same order of magnitude as that one observes for the 9,10-disubstituted anthracenes.[12] One notices a hypochromic effect for (Ih) ($\Delta\varepsilon$ *ca.* 125 000) and (Ie and f) ($\Delta\varepsilon$ *ca.* 110 000) by comparison with (Ia).

(b) Comparison of the bichromophores (Ia, c, and i) with the model compounds (IIIa and b). For the ^1L_a band, we have derived the percentage of hypo (or hyper) chromism (%H) which corresponds to an integrated effect [13] (Table 5).

TABLE 4

Wavelengths (λ_1 and λ_2) and molecular extinction coefficients (ε_1 and ε_2) of the longest wavelength component of the absorption bands for the first ($^1L_a \longleftarrow {}^1A$) and the second ($^1B_b \longleftarrow {}^1A$) electronic transition for (Ia—i) and (IIIa and b) (MCH; 20 °C). f is the oscillator strength of the first electronic transition $^1L_a \longleftarrow {}^1A$.

Compound	f	λ_1/ nm	ε_1/ l mol^{-1} cm^{-1}	λ_2/ nm	ε_2/ l mol^{-1} cm^{-1}
(Ia)	0.24	388	19 500	255	207 400
(Ib)	0.26	397	14 300	256	90 400
(Ic)	0.27	394	15 400	255.3	164 400
(Id)	0.27	400	16 300	256	186 000
(Ie)	0.23	408	11 200	258	96 000
(If)	0.20	408	8 900	258	84 400
(Ig)	0.21	400	16 600	258	141 000
(Ih)	0.12	401	10 000	258	75 000
(Ii)	0.35	397	24 900	258	171 250
(IIIa)	0.17	383	13 300	255	201 000
(IIIb)	0.15	393	12 150	258	153 500

TABLE 5

Oscillator strength f of (Ia, c, and i) and (IIIa and b) for the first electronic absorption $^1L_a \longleftarrow {}^1A$ and hypochromicity of (Ia,c) and hyperchromicity for (Ii) in methylcyclohexane at room temperature

Compound	f	Hypochromicity (%)
(Ia)	0.24_2	+28
(Ic)	0.26_7	+16.5
(Ii)	0.34_8	−14.5
(IIIa)	0.16_8	
(IIIb)	0.15_2	

TABLE 6

Fluorescence quantum yields (ϕ_F) at 20 °C and maxima of the first vibronic band (λ_3) of fluorescence for (Ia—i) and (*IIIa* and b)

Compound	ϕ_F [a]	λ_3/nm
(Ia)	0.03	393
(Ib)	0.07	402
(Ic)	0.093	404
(Id)	0.035	405
(Ie)	0.055	414
(If)	0.050	415
(Ig)	0.045	406
(Ih)	0.050	404
(IIIa)	0.08	389
(IIIb)	0.92	403
(Ii) monomer	0.21	408
(Ii) excimer	0.34	550 [b]

[a] Corrected spectra of samples in degassed MCH solution relative to quinine sulphate. [b] Maximum excimer emission.

In the case of (Ia and c) the results point to an important hypochromic effect, larger than that observed in dinucleotide analogues; [13] this effect suggests there is a high probability of finding the planar anthracene rings parallel in the ground state.[14] The presence of one phenyl ring in (Ic) decreases %H but two phenyl rings as in (Ii) lead to hyperchromism; this is probably related to the noncoplanarity of the benzene and anthracene rings preventing the latter from reaching a parallel conformation in the ground state.

(B) *Fluorescence emission.* (a) Room temperature. Only the diphenyl compound (Ii) shows intramolecular excimer fluorescence (Figure 1) at room temperature. For (Ia—h), we could not detect intramolecular excimer fluorescence at room temperature in methylcyclohexane. The fluorescence quantum yield for (Ia—i), the position of the maximum of the first vibronic band, the excimer fluorescence quantum yield, and the maximum of the excimer band for (Ii) are collected in Table 6. Compounds (Ia—c and h) do not display intramolecular excimer emission at temperatures between 77 and 293 K in MCH.

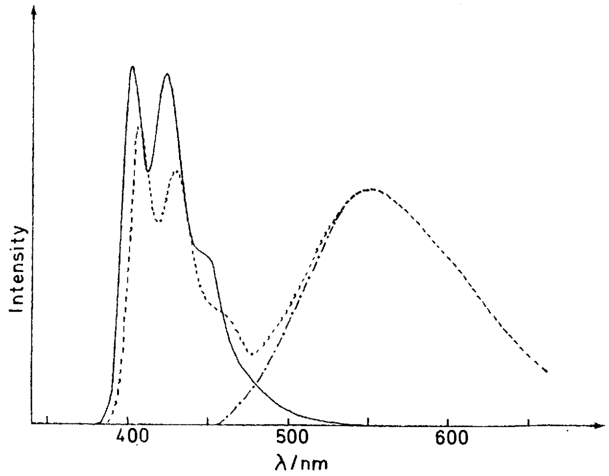


FIGURE 1 Fluorescence spectrum of (Ii) (– – – –) and of (IIIb) (——). Intramolecular excimer fluorescence (— · — · —) difference between emission of (Ii) and (IIIb). Degassed solutions in MCH (20°; 5 × 10^{-5}M). Intensity in arbitrary units. All fluorescence spectra are corrected for monochromator and photomultiplier responses

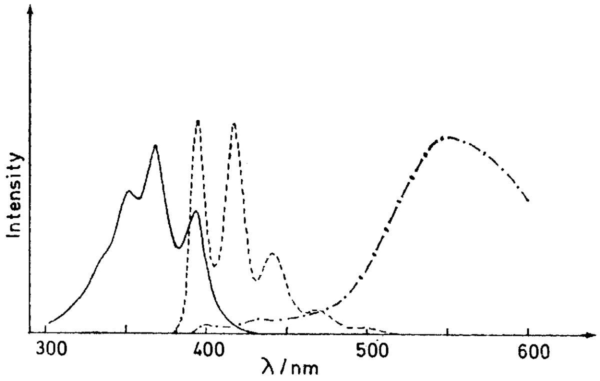


FIGURE 2 Fluorescence spectrum (— —) of the ' cleaved photocyclomer ' of (IIa) in MCH glass at 77 K. Excitation spectrum of the unstructure band (λ *ca.* 500—600 nm) (——). Spectrum obtained (– – – –) after softening the glass and refreezing at 77 K [monomer fluorescence of (Ia)]

(b) ' Broken dimers ' in methylcyclohexane at 77 K. We have generated ' broken dimers ' [15] in MCH matrices at 77 K by irradiating the cyclomers of (IIa—c) at λ 254 nm; these reveal excimer fluorescence (see Figures 2—4). The excimer fluorescence intensity of (Ic) seems stronger than than of (Ia). The excimer emission of (Ib) is difficult to detect. The maximum emissions of the cleaved cyclomers are 550 [(Ia)], 570 [(Ib)], and 565 nm [(Ic)].

In addition to the excimer fluorescence band, one observes a structured emission between 390 and 450 nm in the spectrum of (Ia) (Figure 2). The latter might be ascribed to a relaxed dimer.[16] In (Ib), the emission intensity is very weak and a similar phenomenon could not be detected. Also relevant is the time of irradiation for the photocleavage which is rather long for (IIa) (1 h) and (IIb) (2 h) compared with (IIc) (3 min).

The excitation spectra corresponding to each wavelength of the structureless fluorescence bands are identical to the absorption spectra of the broken dimers; this strongly suggests that such excimers found originate from a single type of conformation.

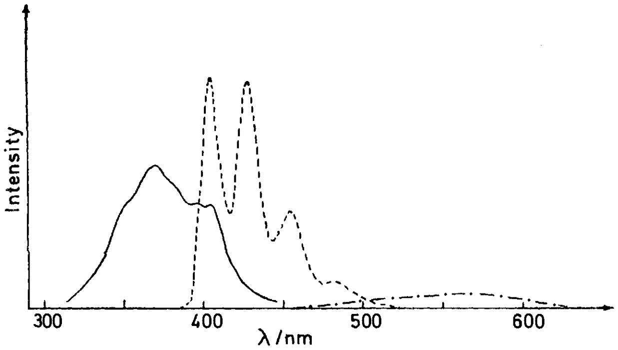


FIGURE 3 Fluorescence spectrum (— · —) of the 'cleaved cyclomer' of (IIb) in MCH glass at 77 K. Excitation spectrum of the unstructured band (——). Spectrum obtained (– – – –) after softening the glass and refreezing at 77 K [monomer fluorescence of (Ib)]

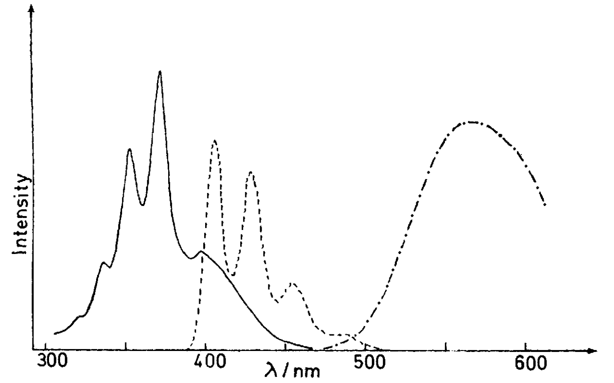


FIGURE 4 Fluorescence spectrum (— · —) of the cleaved cyclomer' of (IIc) in MCH glass at 77 K. Excitation spectrum of the unstructured band (——). Spectra obtained (– – – –) after softening the glass and refreezing at 77 K [monomer fluorescence of (Ic)]

DISCUSSION

Quantum Yields and Reactivity.—As seen in Table 3, compounds (Ia—f) undergo ready photocyclomerization at 366 nm in MCH, the quantum yields being between 0.16 and 0.32. Photodissociation at 254 nm is even more efficient. In degassed fluid solutions, it was possible to achieve several reversible photocyclizations.

It is to be noted that the intramolecular photodimerization of these systems has an efficiency comparable with that of the free monomers in highly concentrated solutions (in benzene, photodimerization quantum yields extrapolated at infinite concentration are 0.34 and 0.30, respectively, for anthracene and 9-methylanthracene).[17]

The photocyclization and the photocleavage quantum yields for (Ia) and (IIa) are similar to those observed by Kaupp[18] for the [2.2]paracyclo(9,10)anthracenophane (0.30 * and 0.60, respectively, in CH_2Cl_2).

Inter- or intra-molecular photodimerization of anthracene may involve the intermediacy of one or several excimers followed by an intermediate having diradical or zwitterionic character.[20-22] A diradical has recently been postulated as intermediate for bisanthracenes connected by a short linkage.[18] With these authors' data[18] and ours for (Ia), it is possible to derive the overall rate constant of cyclomerization k_r (Table 7) from the simple kinetic scheme (1) assuming that the reaction proceeds through the singlet state.[20,23]

TABLE 7

Quantum yields and reaction rate constants of some bisanthracenes

Compounds	Solvent	ϕ_r	ϕ_F	τ_F/ ns	$10^{-8}k_F$/ s^{-1}	$10^{-8}k_r$/ s^{-1} ‡
$A[CH_2]_2A$ [a]	B	0.26	0.16	1.7	0.94	1.53
ACH_2A [a]	B	0.15	0.06	1.1	0.55	1.36
ACH_2OCH_2A	MCH	0.32	0.03	0.9 †	0.33	3.55

[a] Ref. 18; A = 9-anthryl. B = benzene, ϕ_r = cyclomerization quantum yield.

† τ_F Determined by a single photon counting; $k_r = \phi_r \times \tau_F^{-1}$; $\tau_F = 1/(k_F + k_d + k_r)$. ‡ k_r Should be taken as an order of magnitude because of experimental uncertainty in the lifetimes.

$$\mathrm{(Ia)} \underset{k_F,k_d}{\overset{h\nu}{\rightleftarrows}} \mathrm{(Ia^*)} \xrightarrow{k_r} \mathrm{(IIa)} \qquad (1)$$

Although the reactive centres are on average closer in di-9-anthryl-ethane and -methane, these molecules seem less reactive † than (Ia); it is only *with the* CH_2–O–CH_2 linkage that the anthracene groups adopt the parallel conformation known to be necessary for *stable* excimer formation in the intermolecular case; this facile, parallel, mutual orientation is also certainly conducive to cyclomerization.

One can observe photocyclomerization even for compounds where both X and Y are bulky (Ig and h) with high quantum yields in CH_3CN (Table 4). The steric interaction between bulky substituents X and Y is shown by the thermal instability of (IIg and h). While anthracene photodimers are known with 9,9′-dimethyl and 9-methyl-9′-bromo substituents,[24] this is the first time that a dimer with two bromo substituents face-to-face has been reported.

In fluid solution, the photocyclomerization quantum yields of (Ia—h) (Table 1) are high and the excimer fluorescence is not observed; this is in keeping with competition between the two processes; let us note that

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* Others have found a higher value (0.36) in benzene.[19]

† It would be interesting to compare the reactivity of 9-anthrylmethane, 1,2-di-9-anthrylethane and 1,3-di-9-anthrylpropane. Although we have measured Φ_r for the latter [0.07 (MCH)] we cannot derive k_r without knowing τ_F.

(Ii) does not photocyclomerize but emits excimer fluorescence with a high quantum yield (Φ_F *ca.* 0.34).

One might wonder to what extent the two aromatic portions of the bichromophores behave independently and, in particular, whether the values $k_1 = k_F + k_{ISC} + k_d$ of the bichromophore (Ia) is very different from that of the model compound (IIIa). The data on the reactivity of (Ia) (Table 7) allow the determination of k_1 from the expression $\Phi_r = k_r/(k_r + k_1) = 0.32$. One finds $k_1 \simeq 2k_r \simeq 7.1 \times 10^8$ s^{-1} and τ_1 ($1/k_1$), the 'lifetime' of the model compound (IIIa) included in the bichromophore, is found *ca.* 1.4 ns. Such a short lifetime is not unexpected in view of the low fluorescence quantum yield of (IIIa) [ϕ_F 0.08 (Table 6)]. This lifetime can be obtained from another source, considering the relation $\Phi_F = k_F\tau_1$ [for (IIIa)]; a value of k_F [(IIIa)] *ca.* 1.4 × 10^8 s^{-1} can be calculated from the absorption spectrum (*f* 0.17) using an approximate formula. We deduce τ_1 *ca.* 0.6 ns.

There is a discrepancy between the two calculated values, which may be due to the approximations made and the absence of a high accuracy in the measurements of lifetimes of the range of 1 ns.* These uncertainties preclude any conclusion on this matter without further investigations, especially by the picosecond technique.

Solvent Effect.—Comparison of Tables 2 and 4 reveals an increase of the quantum yield with the solvent polarity. This phenomenon had been noticed previously [25] for anthracene and 9-methylanthracene (10^{-2}M-anthracene, $\Phi_{C_6H_6}{}^{365}$ 0.07, $\Phi_{CH_3CN}{}^{365}$ 0.13; 10^{-2}M-9-methylanthracene, $\Phi_{C_6H_6}{}^{365}$ 0.15, $\Phi_{CH_3CN}{}^{365}$ 0.21. At present, any attribution of this polar effect would be speculative.

The fact that the C–Br cleavage is easier for (Ig) than for (Ih) in ether suggests the participation of an intramolecular excimer (stabilized by donor acceptor interaction of the substituents) in the photodecomposition of bromo derivatives as for 1-chloronaphthalene.[26] However acetonitrile seems to inhibit the photodecomposition of (Ig and h); this behaviour is in opposition to the preceding result. A similar observation has been reported for chlorobenzene.[27] Our case is more complicated than the preceding one.[26,27] Because of the competition between C–Br breakage and cyclomerization, we cannot offer a simple rationalisation.

Fluorescence.—The diphenyl derivative (Ii) is the only photostable compound of the series but it displays an intense excimer fluorescence in MCH at room temperature. In anthracenes, this emission usually appears when the photocyclization is inhibited or slowed, the two processes being in competition. The fact that we could not detect any photocyclomerization for (Ii) in our conditions is probably not simply ascribable to the thermal instability of the overcrowded hypothetical photocyclomer (IIi). One must also consider the difficulty to overcome the energy barrier † from the excimer state to the higher excited state potential surfaces.[21] In any event, this question deserves further study.[28]

The absence of excimer fluorescence in MCH at 300 K for (Ia—f) is probably related to their rapid transformation of the excimer into the photocyclomers (IIa—f) (and a predissociation state for the bromo derivatives). It is indeed likely that excimers of various conformations are on the reaction pathway as shown by De Schryver [2a] and Ferguson [16] even if no excimer fluorescence can be detected at room temperature.

Fluorescent excimers are observed at 77 K in a MCH matrix, when they are generated from (IIa—c) by the method of Chandross and Ferguson (Figures 2—4). Their maximum wavelength is *ca.* 550—570 nm. This result suggests that their conformation is close to that of the species denoted type A by Ferguson [16,19] ($\lambda_{max.}$ 580 nm at 10 K) where the aromatic moieties displaced along the long axis, still strongly overlap (Figure 5).

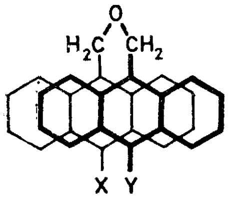

FIGURE 5 Proposed conformation for the cleaved cyclomers obtained by photolysing (IIa—c) at 254 nm in MCH glass at 77 K

Referring to the data in Table 5, it is possible to calculate k_F from the oscillator strength for (Ia) (*f* 0.24 in MCH) using an approximation formula.[29] One finds k_F 2 × 10^8 s^{-1}; this value is appreciably higher than that determined from Φ_F and τ_F together (Table 7); the discrepancy suggests that the Franck–Condon excited state is different from the relaxed emitting state; but, because of possible errors on the approximations made and as the accuracy of τ_F (0.9 ns) is not high in this range of lifetimes, it seems irrelevant to speculate further on this matter.

Bispyrenes [2b] (Py[CH$_2$]$_n$Py) show intense excimer fluorescence for different lengths of the chain; it is noticeable that for *n* 2 and 4—9, a blue shift of the energy of excimer emission maximum relative to *n* 3 is found. Recently Morawetz [30] prepared dibenzyl ether and used its excimer fluorescence to measure the microscopic viscosity of various media; in contrast to monochromophores, this fluorescing probe can be utilized at minute concentrations. Davidson [31] has investigated the fluorescence of a series of bisnaphthalenes. The author observed that the only compounds which undergo intramolecular photocycloaddition reactions are those which exhibit excimer formation, in particular bis-1-naphthylmethyl ether.

These results, obtained for pyrene, benzene, and naphthalene derivatives together with the present data, show the interest of using a three-membered chain, especially

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* An attempt to measure the lifetime of (IIIa) by single photon counting has shown that τ_1 is < 1 ns. We thank Professor F. De Schryver for this determination.

† The excimer seems to be thermodynamically stable.[28]

when it bears an oxygen atom, as a linkage between the fluorescing chromophores.

Conclusions.—We have reported the first synthesis of non-conjugated bisanthracenes linked at the 9,9′-positions by a CH_2-O-CH_2 chain. Several of these molecules are efficient jaw photochromic materials, having high quantum yields of closure and opening ($\Phi_{(I)\rightarrow(II)} \geqslant 0.15$ and $\Phi_{(II)\rightarrow(I)} \geqslant 0.25$). The three-membered ether chain is a useful link to enhance the bichromophoric interactions and study the bimolecular reactivity in very dilute media. This could be easily extended to other chromophores.

EXPERIMENTAL

Solvents.—Methylcyclohexane (Prolabo; u.v. spectrograde) was washed with sulphuric acid and water, dried ($MgSO_4$), and distilled over sodium. Acetonitrile (Prolabo; spectrograde) was used without further purification. Ether was distilled before use.

Physical Methods.—Apparatus. M.p.s were taken with a Kofler block and are uncorrected. Elemental analysis were performed at the CNRS microanalysis centre. Some compounds [(Ib and d—h)] gave incorrect results, the carbon percentage being especially small. Spectral data are consistent with the proposed structures. 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 Beckman DK 2A or Beckman Acta M VI instrument; oscillator strengths ($f = 4.3 \times 10^{-9} \int \varepsilon d\nu$)[12a] were determined by computer integration of the electronic absorption spectra from a cut-off wavelength in the vicinity of the absorption minimum to the point of zero absorption at long wavelength. I.r. spectra were taken with a Perkin-Elmer 412 and mass spectra (70 eV) with an A.E.I. model MS 12 instrument. Fluorescence spectra were obtained with a Hitachi–Perkin-Elmer MPF 44 fluorimeter, corrected for emission. The sample vessels were degassed on a high vacuum line with several freeze–pump–thaw cycles and sealed with high vacuum stopcocks.

Fluorescence quantum yields. The fluorescence quantum yields of compounds (Ia—i) were measured in degassed MCH relative to quinine sulphate in 1N-sulphuric acid as standard (ϕ_F 0.55) by the usual method.[32]

Determination of the reaction quantum yields. Measurements were made with an optical bench equipped with a high pressure mercury lamp (Osram HBO 200 W in a Schoeffel box type 101) and a photomultiplier RCA 1 P-28 which had a micrometric slit attachment and is connected with a recorder. The 366 nm wavelength was selected by using an aqueous solution of $CuSO_4,5H_2O$ (80 g l^{-1}) and an optical filter (MTO A 371 b). A similar set-up was used for the determination of the photodissociation quantum yield with a Philips spectral low pressure mercury lamp and an interferential filter (MTO intervex) to select the 254 nm wavelength.

(a) Cyclomerization ($\phi_{(I)\rightarrow(II)}$). The photocyclomerization quantum yield ($\phi_{(I)\rightarrow(II)}$) was calculated by formula

$$\phi_{(I)\rightarrow(II)} = \frac{V}{2.303l\varepsilon} \times \frac{1}{I_a}\left(\frac{dT}{dt}\right)_{t=0} \times \frac{1}{T_0} \qquad (2)$$

(2). $(dT/dt)_{t=0}$ is equal to the slope at time zero of the transmittance curve for the disappearance of compound (I), which is irradiated with 366 nm light; T_0 is the transmittance at time zero; V is the volume of the irradiated sample (3 ml); ε is the extinction coefficient of (I) at 366 nm and l the optical path length (1 cm); I_a is the intensity of the light absorbed by the sample (3 ml) determined by ferrioxalate actinometry following the procedure outlined by Parker.[33]

(b) Photodissociation. According to Livingston and Sin Wei,[23] we have calculated the quantum yield ($\phi_{(II)\rightarrow(I)}$) at the photostationary equilibrium when a solution of (II) (*ca.* 5×10^{-5}M) is irradiated at 254 nm. Assuming that $\phi_{(I)\rightarrow(II)}$ is the same[23,34] at 366 and 254 nm, we can derive equation (3) where $\varepsilon_{(I)}$ and $\varepsilon_{(II)}$ are the molar

$$\phi_{(II)\rightarrow(I)} = \phi_{(I)\rightarrow(II)} \frac{1 - \exp(-2.303\ \varepsilon_{(I)}C_{(I)}l)}{1 - \exp(-2.303\ \varepsilon_{(II)}C_{(II)}l)} \qquad (3)$$

extinction coefficients for (I) and (II) at 254 nm and $C_{(I)}$ and $C_{(II)}$ are the equilibrium concentration of (I) and (II), respectively.

Photocleavages of the cyclomers in matrices. An e.s.r. quartz tube containing a non-degassed (aerated) 10^{-4}M-methylcyclohexane solution of (IIa—c) was immersed in a quartz Dewar filled with liquid nitrogen and irradiated at 254 nm. The fluorescence spectra were recorded before and after irradiation. The spectra in Figures 2—4 were obtained by subtracting the first spectra from the second ones. The broad red-shifted structureless emission bands are typical of 'broken dimer' excimer fluorescence.[15] The excitation spectra are superimposable on each other whatever the monitoring wavelength of the structureless emission band chosen, and they are similar to the absorption spectrum of the photocleaved cyclomer. When the solutions were allowed to warm to room temperature and re-frozen to 77 K, the fluorescence was that of compounds (Ia—c) at 77 K.

Preparation of Starting Materials.—The starting materials were prepared as described in the literature (Table 8).

TABLE 8

Anthracene derivatives used as starting materials for the preparation of (Ib—i)

Compound	Ref.
(IIIa)	10
(IIIc)	10
(IIId)	10
(IIIe)	*a*
(IIIf)	*b*
(IIIg)	*a*
(IIIh)	*a*
(IIIi)	*c*
(IIIj)	*c*

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Synthesis of the Bichromophores (Ib—i) *and the Model* (IIIb).—The preparation of (Ia) has been described elsewhere.[4b]

Compound (Ib). At room temperature, to a solution of sodium hydride (36 mg, 1.5×10^{-3} mol) in dimethylformamide (DMF) (10 ml), was added dropwise with stirring (IIIc) (312 mg, 1.5×10^{-3} mol) in DMF (30 ml). The solution became orange-red. Stirring was continued for 30 min after the end of addition. A DMF solution (30 ml) of the chlorine derivative (IIIf) (360 mg, 1.5×10^{-3} mol) was then introduced dropwise and stirred for 30 min at room temperature. The solution was hydrolysed with water (150 ml), the precipitate formed was filtered, dried, and chromatographed on an alumina column. Elution with ligroin–benzene (70 : 30) and crystallization in the same solvent mixture gave yellow crystals of (Ib) (195 mg, 32%), m.p. 169—170°, $\nu_{max.}$ (KBr) 3 050, 2 880, 1 620, 1 520, 1 445, 1 380, 1 340, 1 225, 1 180, 1 070, 1 025, 950, 930, 890, 790, 745, 730, and 715 cm^{-1}, δ(CDCl$_3$) 3.02 (3 H, s), 5.56 (4 H, s), 7.20—7.53 (8 H, m), and 7.78—8.49 (9 H, m); $\lambda_{max.}$ (MCH) 397 (log ε 4.15), 387 (4.09), 375.5 (4.15), 367 (4.11), 357 (3.99), 348 (3.92), 256 (4.95), and 249 nm (4.96), *m/e* 412 (M^+).

Compound (Ic). The experimental procedure was as for (Ib). The compounds used were (IIIg) (570 mg, 2 × 10^{-3} mol), (IIId) (450 mg, 2 × 10^{-3} mol), sodium hydride (48 mg, 2 × 10^{-3} mol), and DMF (80 ml). Chromatography on alumina and elution with ligroin–benzene (70 : 30) followed by a crystallization in cyclohexane gave yellow needles of 9-*anthrylmethyl* 10-*phenyl*-9-*anthrylmethyl ether* (470 mg, 50%), m.p. 208—209°, $\nu_{max.}$ (KBr) 3 050, 2 930, 2 890, 1 620, 1 600, 1 520, 1 440, 1 345, 1 175, 1 160, 1 065, 1 030, 950, 930, 890, 775, 765, and 725 cm^{-1}, δ(CDCl$_3$) 5.66 (2 H, s), 5.71 (2 H, s), 7.15—7.71 (15 H, m), 7.87—8.10 (2 H, m), and 8.20—8.53 (5 H, m), $\lambda_{max.}$ (MCH) 394 (log ε 4.19), 3.87 (4.13), 373 (4.18), 367 (4.14), 355 (4.00), 255.3 (5.22), and 248 (5.17), *m/e* 474 (M^+) (Found: C, 90.95; H, 5.65; O, 3.5. $C_{36}H_{26}O$ requires C, 91.15; H, 5.5; O, 3.35%).

Compound (Id). The reactants used were (IIIc) (2 g, 2 × 10^{-2} mol), (IIIj) (3 g, 10^{-2} mol), sodium hydride (0.3 g, 10^{-2} mol), and DMF (150 ml). Following the procedure for (Ic) we obtained compound (Id) as yellow needles (2.5 g, 54%), m.p. 219—220°, $\nu_{max.}$ (KBr) 3 050, 2 910, 2 880, 1 620, 1 440, 1 330, 1 255, 1 170, 1 155, 1 060, 1 020, 985, 930, 900, 890, 755, 745, and 725 cm^{-1}, δ(CDCl$_3$) 5.48 (2 H, s), 5.57 (2 H, s), 7.1—8.4 (16 H, m), and 8.53 (1 H, s), $\lambda_{max.}$ (MCH) 400 (log ε 4.21), 387.5 (410), 379 (4.21), 367.5 (4.10), 360 (4.05), 350 (3.92), 256 (5.21), and 249.5 nm (5.28), *m/e* 476 and 478 (1 : 1, M^+).

Compound (Ig). The reactants used were (IIIi) (427 mg, 1.5 × 10^{-3} mol), (IIIj) (360 mg, 1.5 × 10^{-3} mol), sodium hydride (36 mg, 1.5 × 10^{-3} mol), and DMF (60 ml). Use of the (Ic) provided compound (Ig) as yellow needles, (240 mg, 33%), m.p. 229—230°, $\nu_{max.}$ (KBr) 3 080, 3 040, 2 890, 1 620, 1 550, 1 520, 1 475, 1 440, 1 355, 1 325, 1 255, 1 175, 1 070, 1 025, 930, 900, 885, 850, and 680 cm^{-1}, δ(CDCl$_3$) 3.05 (3 H, s), 5.50 (2 H, s), 5.59 (2 H, s), 7.10—7.58 (8 H, m), and 8.10—8.58 (8 H, m), $\lambda_{max.}$ (MCH) 400 (log ε 4.22), 378 (4.18), 358 (3.94), 340 (3.61), 258 (5.15), and 252 nm (5.14), *m/e* 490 and 492 (1 : 1, M^+).

Compound (Ih). The reactants used were (IIIi) (430 mg, 1.5 × 10^{-3} mol), (IIIj) (455 mg, 1.5 × 10^{-3} mol), sodium hydride (36 mg, 1.5 × 10^{-3} mol), and DMF (70 m). With the procedure used for (Ic), we obtained (Ih) as yellow needles (190 mg, 23%), m.p. 265—266°, $\nu_{max.}$ (Kbr) 3 070, 3 030, 2 890, 1 550, 1 475, 1 440, 1 325, 1 255, 1 170, 1 065, 1 020, 995, 975, 930, 900, 840, and 740 cm^{-1}, δ(CDCl$_3$) 5.54 (4 H, s), 7.15—7.60 (8 H, m), 8.1—8.3 (4 H, m), and 8.4—8.6 (4 H, m), $\lambda_{max.}$ (MCH) 401 (log ε 4.00), 379 (3.95), 359 (3.71), 341 (3.37), 258 (4.87), and 251 nm (4.84), *m/e* 554, 556, 558 (1 : 2 : 1, M^+).

Compound (Ii). The reactants used were (IIIg) (570 mg, 2 × 10^{-3} mol), (IIIh) (604 mg, 2 × 10^{-3} mol), sodium hydride (48 mg, 2.10^{-3} mol), and DMF (70 ml). Use of the procedure for (Ic) provided (Ii) as yellow needles (490 mg, 45%), m.p. 203—204°, $\nu_{max.}$ (KBr) 3 060, 2 910, 1 600, 1 475, 1 445, 1 370, 1 335, 1 150, 1 065, 1 030, 995, 920, 770, 745, and 700 cm^{-1}, δ(CDCl$_3$) 5.77 (4 H, s), 7.15—7.79 (22 H), m), and 8.29—8.58 (4 H, m), $\lambda_{max.}$ (MCH) 397 (log ε 4.40), 376 (4.39), 357 (4.18) 340 (3.87), 258 (5.27), and 253 nm (5.23), *m/e* 550 (M^+) (C, 91.15; H, 5.55; O, 3.45. $C_{42}H_{30}O$ requires C, 91.65; H, 5.45; O, 2.9%).

Compound (Ie). Compound (Ig) (200 mg, 4 × 10^{-4} mol) in *N*-methylpyrrolidone (NMP) (20 ml) with dried copper(I) cyanide (72 mg, 8 × 10^{-4} mol) was heated at 200° for 2 h. Then the hot solution was added to a concentrated aqueous ammonia solution (20 ml), extracted with hot benzene, dried (MgSO$_4$), and chromatographed on alumina. Elution with benzene yielded (Ie), yellow-orange crystals (120 mg, 68%), m.p. 224—225°, $\nu_{max.}$ (KBr) 3 030, 2 880, 2 215, 1 625, 1 530, 1 475, 1 450, 1 375, 1 360, 1 180, 1 085, 1 050, 1 020, 950, 940, 765, 720, and 710 cm^{-1}, δ(CDCl$_3$) 3.05 (3 H, s), 5.45 (2 H, s), 5.64 (2 H, s), and 7.15—8.5 (16 H, m), $\lambda_{max.}$ (MCH) 408 (log ε 3.95), 398 (3.97), 386 (3.98), 377 (3.99), 360 (3.81), 258 (4.93), and 252 nm (4.92), *m/e* 437 (M^+).

Compound (If). Reactants (IIIg) (570 mg, 2 × 10^{-3} mol), (IIIj) (606 mg, 2 × 10^{-3} mol), sodium hydride (48 mg, 2 × 10^{-3} mol), and DMF (80 ml) were used to synthesize 10-bromo-9-anthrylmethyl 10-phenyl-9-anthrylmethyl ether (590 mg, 52%), m.p. 238—240°, $\nu_{max.}$ (KBr) 3 060, 3 040, 2 890, 1 620, 1 450, 1 355, 1 265, 1 185, 1 085, 1 055, 1 025, 950, 935, 885, 855, and 780 cm^{-1}, δ(CDCl$_3$) 5.59 (2 H, s), 5.65 (2 H, s), and 7.1—8.48 (16 H, m).

A mixture of this derivative (225 mg, 5 × 10^{-4} mol) and dried copper cyanide (90 mg, 10^{-3} mol) in NMP, using the procedure for (Ie), provided (If), yellow-orange crystals (175 mg, 70%), m.p. 218—220°, $\nu_{max.}$ (KBr) 3 060, 2 880, 2 210, 1 620, 1 450, 1 375, 1 355, 1 185, 1 085, 1 050, 1 020, 950, 935, 780, 765, and 720 cm^{-1}, δ(CDCl$_3$) 5.60 (2 H, s), 5.70 (2 H, s), 7.10—7.70 (13 H, m), and 8.05—8.50 (8 H, m), $\lambda_{max.}$ (MCH) 408 (log ε 4.05), 399 (4.04), 386 (4.07), 378 (4.07), 370 (3.99), 258 (4.98), and 252 nm (4.99), *m/e* 499 (M^+).

Compound (IIIb). The reactants used were (IIIg) (1.1 g, 4 × 10^{-3} mol), ethyl iodide (568 mg, 4 × 10^{-3} mol), sodium hydride (96 mg, 5 × 10^{-3} mol), and DMF (50 ml), giving (IIIb) as yellow needles, (1 g, 80%), m.p. 130—131°, $\nu_{max.}$ (KBr) 3 030, 2 950, 1 705, 1 555, 1 480, 1 445, 1 365, 1 265, 1 200, 1 165, 1 090, 1 055, 1 020, 965, 935, 875, 860, 790, 770, and 720 cm^{-1}, δ(CDCl$_3$) 3.55 (3 H, s), 5.50 (2 H, s), 7.20—7.80 (11 H, m), and 8.20—8.50 (2 H, m), $\lambda_{max.}$ (MCH) 393 (log ε 4.08), 373 (4.10), 354 (3.88), 338 (3.52), and 258 nm (5.19) (Found: C, 88.0; H, 6.1; O, 5.45. $C_{22}H_{18}O$ requires C, 88.6; H, 6.05; O, 5.45%).

Photochemical Reactions.—(A) *Photocyclomerization of* (Ib—f). Compound (Ib). A degassed solution of (Ib) (25 mg, 6 × 10^{-5} mol) in ether (500 ml) was irradiated at $\lambda > 335$ nm [liquid filter, lead acetate (7 g)–sodium bromide (540 g)–water (1 l)] with a high pressure mercury lamp (Philips SP 500) for 3 h. After concentration, a solid precipitated; this was centrifuged to isolate 10-methyl-9,9′-oxydimethyl-9,10-(9,10-anthrylene)anthracene (IIb) as a powder (21 mg, 85%), m.p. 285° (decomp.), $\nu_{max.}$ (KBr) 3 060, 3 010, 2 890, 1 470, 1 450, 1 370, 1 290, 1 135, 1 075, 1 035, 960, 915, 780, 750, 735, and 705 cm^{-1}, δ(CDCl$_3$) 2.09 (3 H, s), 3.87 (1 H, s), 4.80 (4 H, s), and 6.60—7.36 (16 H, m), $\lambda_{max.}$ (MCH) 290 (log ε 2.88), 275 (3.22), 258 (3.66), and 220 nm (4.45).

Photolysis of (IIb) (9.13 × 10^{-5}M) in degassed MCH at

254 nm for 30 min yielded (Ib) characterized by its u.v. absorption spectra. The photochemical cycle (Ib) $\rightleftarrows$ (IIb) could be repeated several times.

Compound (Ic). By the standard irradiation conditions, (Ic) (25 mg, 5.3 × 10^{-5} mol) in degassed ether (500 ml) after 2 h exposure, yielded (IIc) (23 mg, 92%), m.p. 280° (decomp.), $\nu_{max.}$ (KBr) 3 060, 2 920, 2 900, 2 850, 1 600, 1 470, 1 450, 1 290, 1 260, 1 075, 1 045, 1 030, 960, 900, 800, 780, 740, and 700 cm^{-1}, $\delta(CDCl_3)$ 4.82 (2 H, s), 4.93 (2 H, s), 5.34 (1 H, s), and 6.20—7.80 (21 H, m), $\lambda_{max.}$ (MCH) 305 (log ε 2.62), 270 (3.04), 255 (3.83), and 211 nm (4.80).

The photochemical cycle (Ic) $\rightleftarrows$ (IIc) (4.47 × 10^{-5}M) in degassed MCH could be repeated several times.

Compound (Id). (Id) (24 mg, 5 × 10^{-5} mol) in degassed ether (500 ml) for 4 h provided (IId) (22 mg, 92%), m.p. 270° (decomp.), $\nu_{max.}$ (KBr) 3 040, 2 900, 2 880, 1 475, 1 450, 1 280, 1 155, 1 060, 1 025, 980, 925, 910, 880, 855, 780, 755, 740, and 720 cm^{-1}, $\delta(CDCl_3)$ 4.82 (4 H, s), 5.27 (1 H, s), and 6.75—7.30 (16 H, m), $\lambda_{max.}$ (MCH) 285 (log ε 2.64), 258 (3.94), 250 (4.00) 220 (4.77), and 215 nm (4.84).

The photochemical cycle (Id) $\rightleftarrows$ (IId) (3.69 × 10^{-5}M) in degassed MCH could be repeated several times.

Compound (Ie). A degassed solution of (Ie) (25 mg, 5.7 × 10^{-5} mol) in ether (500 ml) was irradiated at $\lambda > 335$ nm for 3 h. The solvent was evaporated and the solid analysed by t.l.c., u.v., and n.m.r. showing (Ie) : (IIe) 35 : 65, $\delta(CDCl_3)$ 2.31 (3 H, s), 4.79 (2 H, s), 4.81 (2 H, s), and 7.15—8.5 (ArH).

Compound (If). For (If) we used the procedure for (Ie). T.l.c. and n.m.r. analysis of the solid obtained after elimination of the solvent showed that (If) was the only product. However, we could follow the photocyclomerization of (If) into (IIf) and the thermal opening of (IIf) into (If) by electronic absorption spectrometry.

(B) *Irradiation of the bromo derivatives* (Ig *and* h). Compound (Ig) in acetonitrile. A degassed solution of (Ig) (25 mg, 5 × 10^{-5} mol) in acetonitrile (500 ml) was irradiated for 3 h ($\lambda > 335$ nm). Elimination of the solvent after centrifugation provided (IIg) (22 mg, 88%), m.p. 250° (decomp.), $\nu_{max.}$ (KBr) 3 060, 3 000, 2 895, 1 470, 1 450, 1 375, 1 285, 1 155, 1 070, 1 040, 960, 910, 855, 785, 755, 735, and 710 cm^{-1}, $\delta(CDCl_3)$ 2.31 (3 H, s), 4.78 (2 H, s), 4.84 (2 H, s), 6.60—7.30 (14 H, m), 7.75—7.95 (2 H, m), $\lambda_{max.}$ (MCH) 283 (log ε 3.07), 259 (3.83), 249 (3.93), and 220 nm (4.56).

Compound (Ig) in ether. A degassed solution of (Ig) (25 mg, 5 × 10^{-5} mol) in ether (500 ml) was irradiated for 4 h ($\lambda > 335$ nm). The solvent was evaporated and the product analysed by n.m.r., $\delta(CDCl_3)$ 2.09 [s, (IIb)], 2.31 [s, (IIg)], 3.87 [s, (IIb)], 4.80 [s, (IIb)], 4.78 [s, (IIg)], 4.84 [s, (IIg)], 6.60—7.95 [aromatic protons of (IIb and g)]. Integration of the peaks at δ 2.09 and 2.31 gave (IIg) : (IIb) 60 : 40.

Compound (Ih) in acetonitrile. A degassed solution of (Ih) (30 mg, 5.4 × 10^{-5} mol), in acetonitrile (500 ml), was irradiated ($\lambda > 335$ nm) for 3 h. After irradiation the solution was colourless but during evaporation of the solvent it turned yellow. N.m.r. and t.l.c. analysis indicated the presence of only (Ih) in the product. By electronic absorption spectrometry, we could follow the cyclomerization of (Ih) in degassed acetonitrile (3.53 × 10^{-5}M) by disappearance of the 320—400 nm absorption band after irradiation for 1 h. The thermal opening of (IIh) (60°; 30 min) gave back (Ih).

Compound (Ih) in ether. A degassed solution of (Ih) (30 mg, 5.4 × 10^{-5} mol) in ether (500 ml) was irradiated ($\lambda > 335$ nm) for 3 h. After evaporation of the solvent the solid residue was analysed by n.m.r., $\delta(CDCl_3)$ 4.82 [s, (IId)], 4.84 [s, (IIh)], 5.28 [s, (IId)], 5.54 [s, (Ih)], 6.73—8.67 [m, aromatic protons of (Ih) and (IId and h)]. The peaks at δ 4.82 and 4.84 overlap. The absorption at δ 4.84 was attributed to (IIh). Integration of the peaks at δ 4.84 and 5.28 showed (IIh) : (IId) 63 : 34.

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