

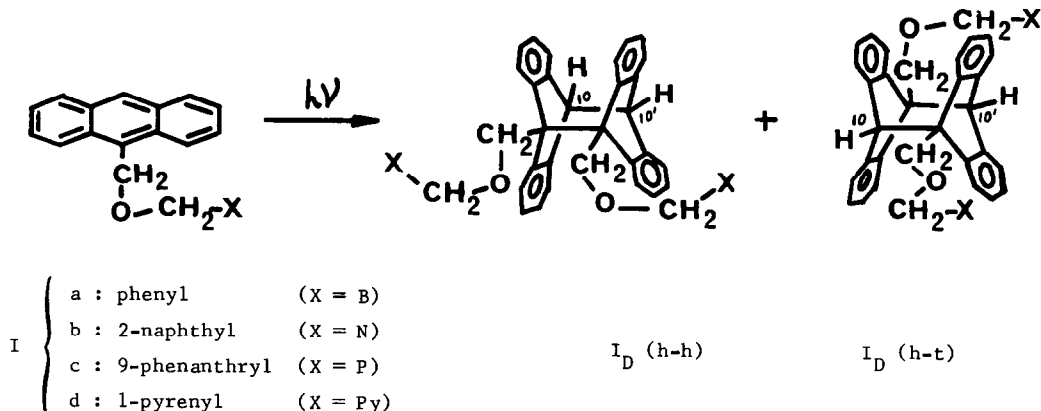
NEW INTRAMOLECULAR EXCIPLEXES BETWEEN POLYNUCLEAR AROMATIC HYDROCARBONS AND HEAD-TO-HEAD VS HEAD-TO-TAIL PHOTODIMERIZATION OF MESOSUBSTITUTED ANTHRACENES.

Jean-Pierre DESVERGNE, Alain CASTELLAN and Henri BOUAS-LAURENT

Laboratoire de Chimie Organique et ERA 167 (Photophysique et Photochimie Moléculaire)
 Université de Bordeaux I, 33405 Talence Cedex, France.

SUMMARY : New dissymmetrical non conjugated bichromophores linked by an oxygenated chain : (9-anthrylmethyloxymethyl)arenes [arenes: benzene (I_a), 2-naphthalene (I_b), 9-phenanthrene (I_c) and 1-pyrene (I_d) and (9-phenanthrylmethyloxymethyl)-1-pyrene (II)] have been prepared. I_{c-d} and II exhibit intramolecular exciplex fluorescence in methylcyclohexane at room temperature. Intramolecular photoadducts were not found but I_{a-d} yield a mixture of head-to-head and head-to-tail anthracenic photodimers.

It is well known that intramolecular reactions are favoured over intermolecular reactions due to smaller entropy changes to form cyclomers than to bring two independent reacting sites in contact. In photochemistry, intramolecular events must occur during the lifetime of excited species¹ so that bichromophoric interactions in non conjugated bichromophores will strongly depend on chain dynamics². As anthracenes can display excimer and photodimer formation, we have studied a number of 9,9'-bisanthracenes where the two terminal groups are connected by polymethylene³, polyoxyethylene⁴ or etheroxide (CH_2-O-CH_2)⁵ links. As expected from Hirayama's first observation⁶ a special reactivity was noted for the three-member chains in particular⁵ CH_2-O-CH_2 . This mode of linking has also been used by others, especially in symmetrical bichromophores⁷.

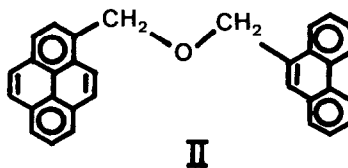


III: A-CH₂-O-CH₃ ; IV: P-CH₂-O-CH₃ ;

V: Py-CH₂-O-CH₃ ;

A = 9-anthryl ; P = 9-phenanthryl ;

Py = 1-pyrenyl .



Photochemical interactions between two different aromatic bichromophores X and Y have been investigated, giving either intermolecular photocycloaddition⁸ or intramolecular interactions in dissymmetrical open chain bichromophores⁹ as well as in cyclophanes¹⁰ ; in the latter cases, the arenes were linked essentially by a polymethylene chain. We thought that a CH₂-O-CH₂ link should be ideally suited to the study of interactions between X and Y on account of the low rotational barrier about a C-O bond¹¹ and easy synthetic access to compounds X-CH₂-O-CH₂-Y. We report preliminary results on the excited state interactions between i) anthracene and other arenes such as benzene, naphthalene, phenanthrene and pyrene in compounds I_{a-d}, ii) phenanthrene and pyrene in compound II.

The new bichromophores (I_{a-d} , II) and the reference compounds (III-V) were prepared by reacting the benzylic alcohols and the appropriate halogenated derivatives with NaH in DMF according to a described procedure^{5,12}; the yields (20-50%) of pale yellow crystallised bichromophores were not optimized. The starting materials and melting points (Kofler bench) are given in table 1. From examination of the UV absorption spectra, I_{a-d} and II seem to undergo

Table 1

	Starting Materials	m.p.(°C)
I _a	(B-CH ₂ Cl + A-CH ₂ OH)	60
I _b	(A-CH ₂ Cl + N-CH ₂ OH)	114-115
I _c	(A-CH ₂ Cl + P-CH ₂ OH)	193-194
I _d	(A-CH ₂ Cl + Py-CH ₂ OH)	155-157
II	(P-CH ₂ Cl + Py-CH ₂ OH)	154

little if any intramolecular interaction in the ground state in methylcyclohexane solution, at room temperature. Under the same conditions and at very low concentration ($\approx 10^{-5}M$), I_{c-d} and II exhibit intramolecular exciplex fluorescence. They are the first examples of exciplexes between respectively, anthracene and phenanthrene, anthracene and pyrene, phenanthrene and pyrene (see fluorescence spectra fig. 1-2 and table 2).

Accepting that $\Delta\bar{\nu}_{o-max}$ gives a rough estimate of the stability, one notes a low stability for the exciplexes of I_c and II and a systematically higher $\Delta\bar{\nu}_{o-max}$ for the corresponding excimers (table 2). A larger contribution of the charge transfer state may account for a pretty good stability of the exciplex of I_d. The matter was first discussed by Chandross^{9a} for the anthracene-naphthalene exciplex.

The non observation of a fluorescing exciplex for I_a must be, for the moment, considered only as an experimental fact. In the case of I_b, the absence of exciplex emission is confirmed by a single exponential decay for the fluorescence; it might be assigned to a weak overlap between the two rings due to geometrical constraints. By contrast, (9-anthrylmethoxy-methyl)-1 naphthalene shows exciplex fluorescence^{4a}. These results are reminiscent of Chandross' observations on bisnaphthylpropanes¹³.

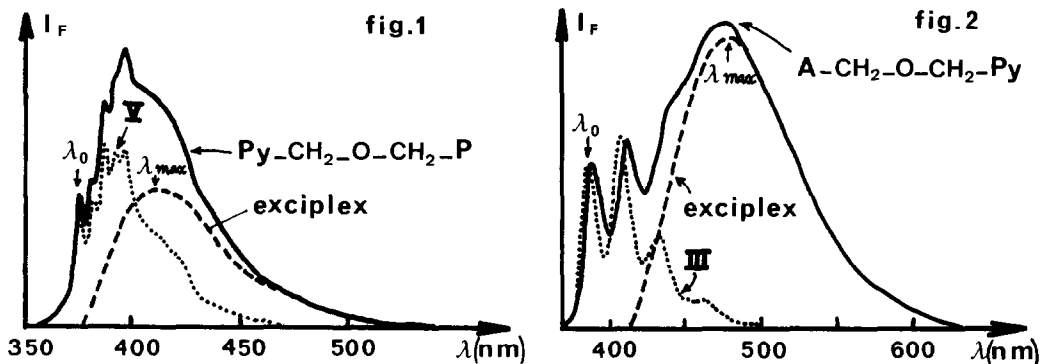
Table 2

Fluorescence (Φ_{FM} and Φ_{FD}) and photoreactivity (Φ_R) quantum yields of bichromophores and reference compounds in methylcyclohexane at room temperature.

Compound		Φ_{FM}	Φ_{FD}	Exciplex λ_{max} (nm)	$\Delta\bar{\nu}_{o-max}$ (cm^{-1})	Φ_R (conc., M)
A-CH ₂ -O-CH ₂ -B	I _a	0.08 ₅	-	-	-	3 x 10 ⁻³ (9x10 ⁻⁶) *
A-CH ₂ -O-CH ₂ -N	I _b	0.10	-	-	-	10 ⁻³ (5x10 ⁻⁵) *
A-CH ₂ -O-CH ₂ -P	I _c	0.07 ₂	0.07 ₈	440	3.000	0.8 x 10 ⁻³ (6x10 ⁻⁶) *
A-CH ₂ -O-CH ₂ -Py	I _d	0.04 ₆	0.15 ₄	478	4.750	0.9 x 10 ⁻³ (7x10 ⁻⁶) *
Py-CH ₂ -O-CH ₂ -P	II	0.20	0.24	410	2.500	0.04x 10 ⁻³ (2x10 ⁻⁶) °
A-CH ₂ -O-CH ₃	III	0.09	-	-	-	1.5 x 10 ⁻³ (\approx 10 ⁻⁵) *
A-CH ₂ -O-CH ₂ -A		0.03	-	550 [▲]	7.450	0.32 * (ref.5)
Py-CH ₂ -O-CH ₂ -Py				505 [□]	6.650(ref.7c)	0.01 x 10 ⁻³ (\approx 10 ⁻⁵)
P-CH ₂ -O-CH ₂ -P		0.019	(0.001)	(430)	(5.500)	0.29 §

* λ_{irr} . 366nm ; ° λ_{irr} . 343nm . Φ_F (IV) : 0.108 . Φ_F (V) : 0.58 . [▲] at 77K [□] in benzene.

• FM refers to monomer fluorescence (locally excited state) and FD to exciplex (excimer) fluorescence. $\Delta\bar{\nu}_{o-max} = \bar{\nu}_{o(max)} - \bar{\nu}_{max}$ (exciplex). § to be published.



Fluorescence spectra in methylcyclohexane (room temperature).

Contrary to bisanthracenes, I_{a-d} and II have a very low photoreactivity when they are irradiated in their first electronic absorption band (table 2). No photocyclomer was characterized but the only photoproducts isolated were the head-to-head (h-h) and head-to-tail (h-t) poorly soluble photodimers I_D of I_{a-d} in a ratio h-h/h-t of about 40/60 or 50/50. The regioisomers were not separated but analyzed by NMR by estimating the signal areas of the 10,10' protons; the chemical shifts found : δ (CDCl₃) H_{10,10'} (h-h) : 4.67-4.73 ; H_{10,10'} (h-t) : 3.44-3.73 are in agreement with the published values¹⁴. One remarks that a mixture of h-h and h-t mesosubstituted anthracene photodimers has been obtained when the substituent is not too polar or bulky.

This lack of intramolecular photoreactivity does not mean that no crossed photoadduct can be obtained : indeed [4+4] photoaddition of benzene to anthracene in a cyclophane^{10a} and of naphthalene to anthracene in 9-anthryl-1 naphthyl-1,3 propane^{9a} have already been found. The absence of photocyclomerization of I_b may again be related essentially to geometrical constraints. Several photoproducts of II were detected in very low yield by thin layer chromatography but not isolated; a splitting of the chain is well possible. Dipyme (1-Py-CH₂-O-CH₂-1-Py) is also not photochemically stable. No [2+2] photocycloaddition between phenanthrene and pyrene was expected according to Caldwell's reactivity algorithm¹⁵.

In conclusion, the first attempts of crossed photoreactivity between anthracene, phenanthrene and pyrene have not led to any efficient intramolecular photocycloaddition. However, due to their weak photoreactivity and high exciplex fluorescence yield, I_{c-d} and II are potential fluorescence probes in polymers or in molecular assemblies.

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