Studies on Aromatic Trichromophore Systems Incorporating Anthracene Moieties. Part 1. Synthesis, Fluorescence and Photoreactivity

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Trichromophoric molecules (A_2A, A_2Pyr, A_2Phen), incorporating two anthryl moieties, linked by a three-membered chain, and a third chromophore (anthracene, pyrene and phenanthrene) attached by a longer ester chain, have been synthesized. Their electronic absorption spectra and their fluorescence emission were studied in very dilute solution at room temperature in comparison with models representing the different absorbing parts of the trichromophore. Careful examination of their photophysical properties has shown the existence of triple complexes in the ground and excited states. The photochemistry of these molecules is governed by the '$4\pi + 4\pi'$' cyclomerization of the bisanthracene part linked by the three-membered chain. The involvement of the excited complex on the pathway of the cyclomerization is not readily explainable.

Polycyclic aromatic hydrocarbons (PAH) are highly suited to the study of interactions between chromophores. They are generally highly luminescent and their electronic absorption spectra, due to $\pi\pi^*$ transitions, are localized in a convenient wavelength range. Most often PAH fluorescence is sensitive to the mutual orientation of their aromatic rings; new bands in the long wavelength side of the spectrum are observed and attributed to the formation of excited complexes (excimers or exciplexes).[1]

Linking chromophores by a flexible, UV-transparent chain facilitates the study of PAH interactions in very dilute solution.[2] Thus, different kinds of excimer fluorescence and photoreactivity have been revealed in symmetrical bisaromatic systems (anthracene, pyrene, naphthalene) in relation to the length and conformational properties of the chain.[3] Excimer fluorescence in bis-anthracenes has been correlated with the formation of the photocyclomer *via* a pericyclic minimum.[2] As observed for the formation of excited complexes, an efficient photocyclomerization occurs when two 9-anthryl groups are linked by a three-membered chain (φ_r = 0.14 for $[CH_2]_3$;[4] 0.32 for CH_2OCH_2[5] and 0.36 for OCH_2O.[6] Moreover, the CH_2OCH_2 linkage has also been shown to be very useful in the discovery at new fluorescent exciplexes of anthracene with phenanthrene or pyrene.[7]

Triply excited complexes (exterplexes) have mainly been studied for strong electron donor–acceptor systems.[8] Some involved quenching of bichromophores by a donor–acceptor monomer,[9] some were formed in trichromophoric molecules.[10] Excimer-type interactions (low polarity) in linked tris-aromatic hydrocarbons, have mainly been described by Otsubo *et al.*[11] in multilayered cyclophanes. They observed a bathochromic shift, hyperchromism and broadening in the electronic absorption spectra when the number of layers was increased; no exterplex fluorescence was mentioned in the article.

We describe herein the syntheses, photoreactivity, electronic absorption, and room-temperature steady-state fluorescence studies of three trichromophoric molecules which incorporate (*i*) two 9-anthryl moieties linked by a three-carbon unit (2-hydroxypropane-1,3-diyl) chain, (*ii*) a third aromatic chromophore [anthracene (A_2A), phenanthrene (A_2Phen), and pyrene (A_2Pyr)] fixed to the short chain by a diester linkage (eight-membered). These molecules are very suitable for studies in very dilute solutions of the influence of non-polar alternant hydrocarbons on the photophysical and photochemical properties of the 1,3-di(9-anthryl)propane system. For comparison, two anthracene bichromophoric molecules containing short (A_2SC) and long chains (A_2LC) were studied as models. X-Ray structure determination was performed on A_2Phen for which suitable crystals were obtained and showed the preferential orientations of the aromatic rings for maximum interactions in the solid.[12]

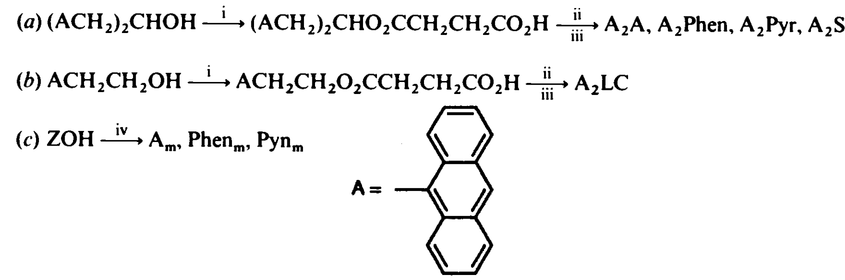
Table 1 Chemical yields and m.p.s of the trichromophores and bichromophores studied

Compound	Yield (%)	M.p./°C
A_2A	27	169
A_2Phen	39	169
A_2Pyr	29	189
A_2SC	79	194
A_2LC	61	156

Results and Discussion

Synthesis.—The route chosen for the syntheses of the trichromophores A_2A, A_2Phen, A_2Pyr, the bichromophores A_2SC, A_2LC and the reference monomers A_m, Phen$_m$ and Pyr$_m$ is outlined in Scheme 1. The basic bichromophore in these syntheses was 1,3-di(9-anthryl)propan-2-ol, obtained according to Becker[13] from 9-anthryllithium and epichlorhydrin. The aromatic 2-substituted ethanols (9-anthryl, 9-phenanthryl, and pyren-1-yl) were prepared by reacting ethylene oxide with the appropriate aryllithium in diethyl ether. 9-Anthrylmethanol was obtained by $NaBH_4$ reduction of 9-anthraldehyde.[7] The tri- and bi-chromophores and the reference compounds were purified by column chromatography (silica gel) and recrystallized. The purity of the compounds was checked by HPLC (NH_2 column). The yields (not optimized) of the last step of each synthesis are listed in Table 1 together with the melting points of the products. The molecular structures were established by ^{1}H NMR, UV and mass spectra and were supported by elemental analyses. The structure of A_2Phen was also established by X-ray diffraction.[12]

Electronic Absorption Spectra.—UV absorption spectra are



Scheme 1 *Reagents:* i, succinic anhydride–4-dimethylamino pyridine (DMAP)–triethylamine–methylene chloride; ii, oxalyl chloride–benzene; iii, ZOH–tetrahydrofuran–pyridine [(*a*) Z = 2-(9-anthryl)ethyl (A_2A); Z – 2-(9-phenanthryl)ethyl (A_2Phen); Z = 2-(pyren-1-yl)ethyl (A_2Pyr); Z = Me (A_2SC); (*b*) Z = (9-anthryl)methyl]; iv, acetic anhydride–DMAP–methylene chloride (see Fig. 1).

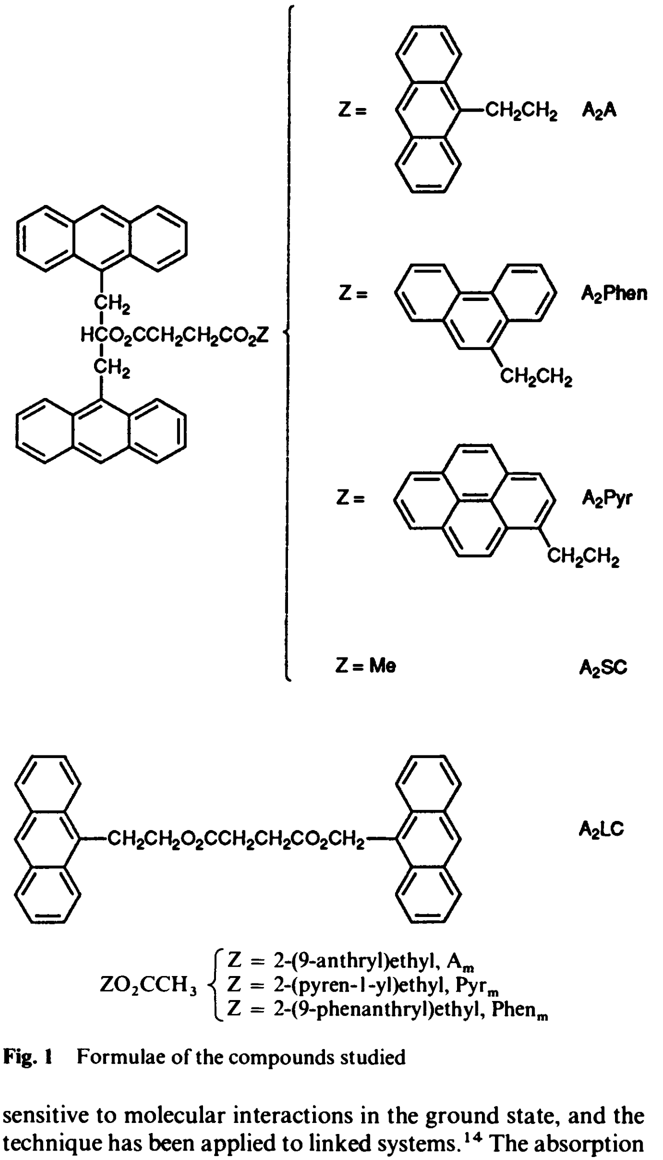


Fig. 1 Formulae of the compounds studied

sensitive to molecular interactions in the ground state, and the technique has been applied to linked systems.[14] The absorption spectra of the bichromophores A_2SC and A_2LC in *tert*-butyl methyl ether are similar in shape to that of the reference monoanthracene derivative A_m; however, some modifications should be noted in both electronic transitions, *e.g.*, $^1L_a \leftarrow A_1$ and $^1B_b \leftarrow A_1$ [Fig. 2(*a*), (*b*)]. For A_2SC, the $^1L_a \leftarrow A_1$ transition presents a marked bathochromic shift (3 nm) and hyperchromic effect compared with the reference compound A_m; in addition, the $^1B_b \leftarrow A_1$ transition is even more perturbed, the intensity of the O–O component being decreased compared with the 0–1 vibronic band. Taking into account some recent results on anthracenophanes,[15] these spectral changes can be attributed to intramolecular interactions between the aromatic nuclei in the ground state, where the long axes of the anthracenic rings experience some degree of parallelism and the two anthracene moieties some overlap. Much weaker interactions are also noted for A_2LC; this contrasts with the fluorescence emission spectra in solution.

The absorption spectra of the trichromophores A_2A, A_2Phen and A_2Pyr, presented in Fig. 2(*c*)–(*e*), and compared with the sum of the absorption of A_2SC and of the reference monomer compounds (A_m, Phen_m and Pyr_m, respectively), reveal weak interactions between the aromatic moiety linked by the long chain with the bisanthracenic part. These interactions suggest the likely formation of weak thermonuclear complexes in the ground state in A_2A and A_2Phen.

Room Temperature Fluorescence.—The bichromophore A_2SC does not exhibit excited complex fluorescence (*ca.* 5×10^{-6} mol dm^{-3}, room temperature, MeOBu^t), however, interactions in the excited singlet state between the two anthracene halves are revealed by a bathochromic shift and a change in relative intensity in the vibronic structure compared with the reference compound A_m (Fig. 3). The fluorescence quantum yield of A_2SC (Table 2) is similar to that of 1,3-di(9-anthryl)propan-2-ol measured by Becker,[13] but much higher than for the reference compound, A_m. Some quenching of the anthracene singlet state by the oxygen lone-pair in A_m might be responsible for this low value (Table 2) as has already been observed for 9-(methoxymethyl)anthracene.[7a]

The fluorescence spectra of A_2A exhibit dual fluorescence: a structured part and a red-shifted, broad, structureless band [Fig. 4(*a*)]. The excitation spectra scanned on the structured and structureless part were found to be similar, pointing to the common origin of the two emissions. The A_2SC bichromophore appears to be a better reference compound than A_m to describe the structure emission maxima of A_2A [Fig. 4(*b*)]. The structureless band, which represents the major part of the emission (Table 2), might be due to a triple excited complex and/or a doubly excited complex between the anthracene part of the long chain and one anthracene chromophore of the three-membered chain.

The interaction between the two anthracenes linked by the long chain in A_2A was approached by studying compound A_2LC. This compound was designed in order to replace one hydrogen of the methyl ester in A_m by a 9-anthryl group. As observed for α,ω-bis(9-anthryl)alkanes (octane to decane)[4] and bis[2-(9-anthryl)ethyl] glutarate,[16] compound A_2LC displays ($\approx 5 \times 10^{-6}$ mol dm^{-3}, room temperature, MeOBu^t) dual fluorescence with a high contribution of excimer emission (Fig. 5 and Table 2).

The photophysical behaviour of A_2LC compared with A_2SC must be related to the α,ω-bis(9-anthryl)alkane series, in which no fluorescent excimer was observed for the propane chain in contrast with the nonane chain.[4] The absence of excimer fluorescence in bis-9-anthryl bichromophores linked by three

Table 2 Fluorescence quantum yield (Φ_f) and photocyclomerization quantum yield (Φ_r) of the studied compounds

	Fluorescence[a]				Disappearance quantum yield[b]	
Compound	λ_{ex}/nm	Φ_f(total)	Monomer (%)	Excited complex (%)	c/mol dm^{-3}	Φ_r
A_m	366	0.21	100	0		
Pyr_m	340	0.64	100	0		
$Phen_m$	297	0.53	100	0		
A_2SC	366	0.41	100	0	3.8×10^{-5}	0.30
A_2LC	366	0.45	15	85	3×10^{-5}	<0.003
A_2A	366	0.59	27	73	4×10^{-5}	0.06
A_2Pyr	366	0.46	76	24	4.5×10^{-5}	0.14
A_2Phen	366	0.33	87	13	4×10^{-5}	0.13

[a] Concentration $\approx 5 \times 10^{-6}$ mol dm^{-3}; room temperature; solvent: MeOBu^t; percentage of the excited complex fluorescence calculated by subtraction of the normalized spectrum of the bi- or tri-chromophore from the selected reference compound (bichromophore or monomer). [b] High-pressure mercury lamp filtered through a glass filter which selects 366 nm light emission; the disappearance of the starting compound is measured by UV absorption, the conversion rate being limited to 10% conversion; solvent: MeOBu^t; light intensity measured using ferrioxalate actinometry as previously described.[14b]

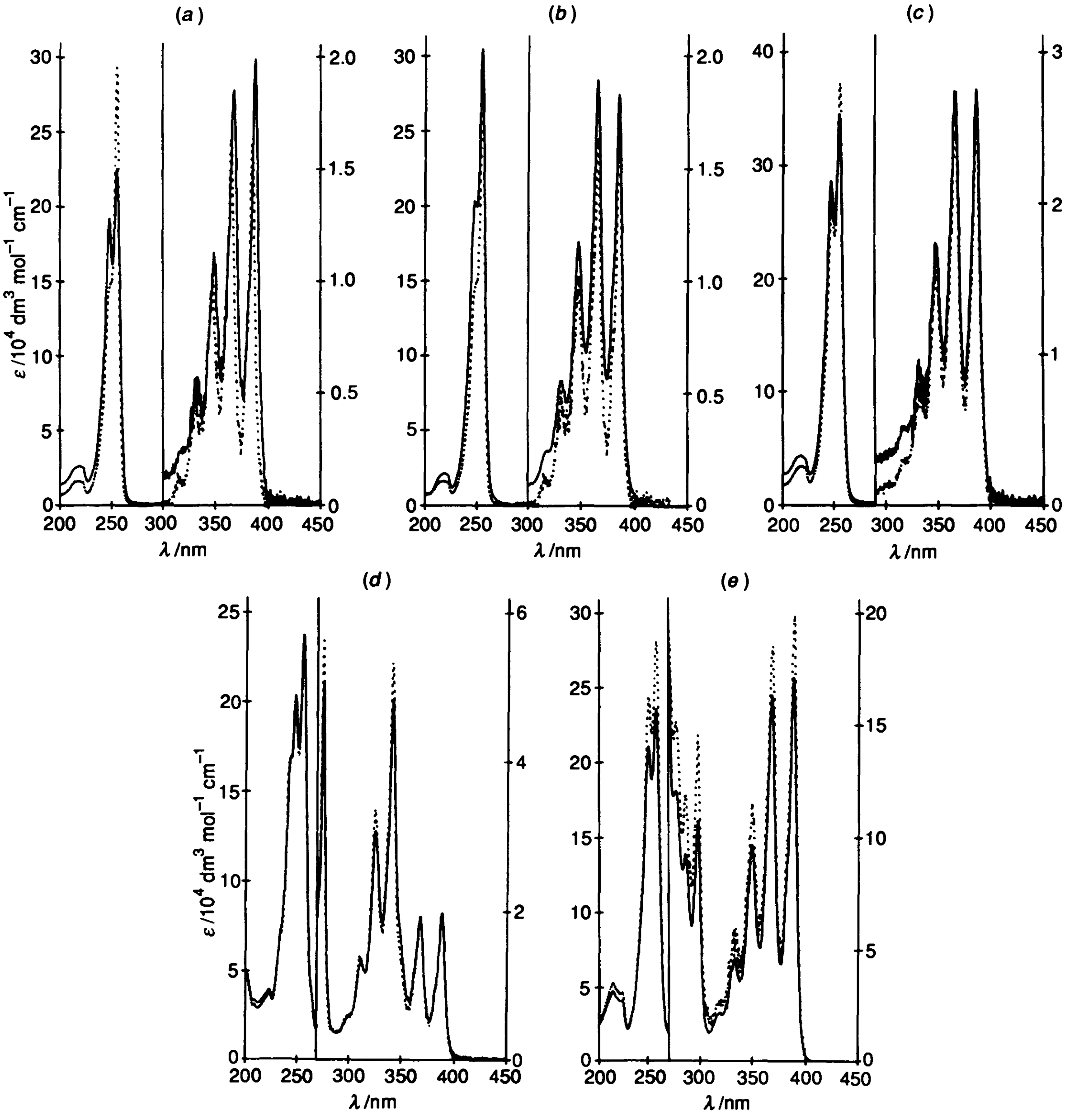


Fig. 2 UV absorption spectra in MeOBu^t at room temperature of bi- and tri-chromophores compared with models of the different moieties: (*a*) A_2SC (——), A_m (- - - -) ($\varepsilon \times 2$); (*b*) A_2LC (——), A_m (- - - -) ($\varepsilon \times 2$); (*c*) A_2A (——), A_2SC (ε) + A_m (ε) (- - - -); (*d*) A_2Pyr (——), A_2SC (ε) + Pyr_m (ε) (- - - -); (*e*) A_2Phen (——), A_2SC (ε) + $Phen_m$ (ε) (- - - -)

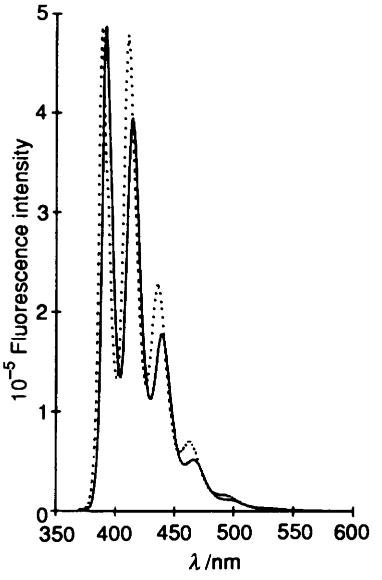


Fig. 3 Corrected fluorescence spectra (normalized at the first vibronic band) in MeOBu^t at room temperature (conc. < 10^{-5} mol dm^{-3}, λ_{exc} = 366 nm) of compounds A_2SC (——) and A_m (– – – –)

atoms was attributed to a fast non-radiative deactivation process to a pericyclic minimum.[6] The excited complex emission in A_2A probably involves a strong intramolecular interaction between the anthracene of the long chain and one anthracene of the propane chain, the latter interacting more or less with the third anthracenic part, as suggested by the electronic absorption spectrum.

The trichromophore A_2Pyr displays different emission spectra when excited in the anthracene absorption band (366 nm) and in the pyrene absorption band (340 nm) [Fig. 6(*a*), (*b*)]. Nevertheless, when the spectra are compared with the emission spectrum of A_2SC (λ_{ex} = 366 nm) and to that of Pyr_m (λ_{ex} = 340 nm) an excited complex emission, very similar in both cases, can be seen [Fig. 6(*a*), (*b*)]. This emission might be attributed to an excited loose triple complex in which the pyrene moiety interacts with one anthracene chromophore, the latter interacting with the other anthracene entity, as suggested by the similarity of the vibronic aspect of the $^1B_b \leftarrow A_1$ anthracene absorption bands and that of A_2SC [Fig. 2(*d*)]. The structured pyrene- and anthracene-type emissions in A_2Pyr spectra are due to the locally excited monomer contributions.

With regard to A_2Pyr, the fluorescence emission of A_2Phen (λ_{ex} = 366 nm) reveals the presence of an excited complex when the spectrum is compared with that of A_2SC [Fig. 7(*a*)]. Excitation of the phenanthrene chromophore (λ_{ex} = 297 nm) does not induce emission of the excited complex [Fig. 7(*b*)] but reveals efficient energy transfer to the anthracenic parts. Similar energy transfer has been observed for 9-anthrylmethyl 1-naphthylmethyl ether.[17] The difference observed between A_2Phen and A_2Pyr where no or limited energy transfer was observed is presently difficult to understand, however, new fluorescence experiments under dynamic conditions at various temperatures, giving access to the thermodynamic parameters, should give clues to this problem.

There is an inverse correlation between the fluorescence quantum yields of trichromophores and their ability to exhibit excited complex fluorescence emission. This correlation might be due to different contributions to the stability of the fluorescent complex by exciton resonance energy ($^1L_a \leftarrow A_1$ band) brought by the third chromophore. If we consider the intensity of the transition and the difference in energy with the anthracenes moieties in the dianthrylpropane part (see Fig. 2), the exciton energy should be in the decreasing order anthracene < pyrene < phenanthrene.[1]

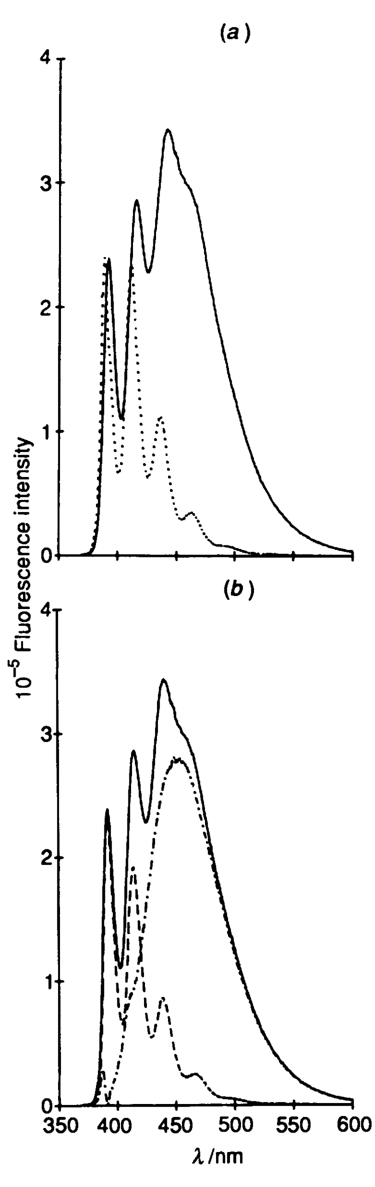
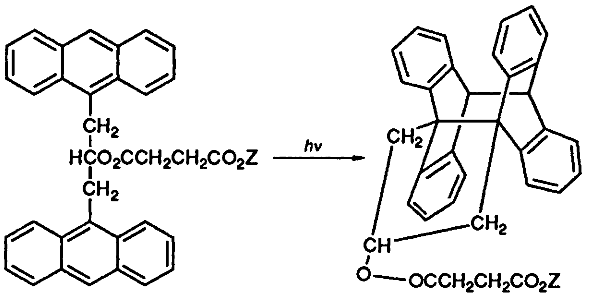


Fig. 4 Corrected fluorescence spectra in MeOBu^t (room temperature, conc. < 10^{-5} mol dm^{-3}, λ_{exc} = 366 nm) of compounds: (*a*) A_2A (——) and A_m (– – – –); (*b*) A_2A (——) and A_2SC (– – – –). The excited complex emission spectrum (–·–·–) was deduced by difference spectra of A_2A and A_2SC.

Photochemistry.—Irradiation of A_2SC, A_2A, A_2Pyr and A_2Phen in diethyl ether resulted in isomerization by $4\pi + 4\pi$ cycloaddition in the 1,3-di(9-anthryl)propan-2-ol part to give the corresponding photoproducts (Scheme 2). Their structures are supported by their ^1H NMR spectra (see Fig. 8 as an example for A_2Phen), their mass spectra, and the UV absorption spectra obtained after irradiation of the trichromophoric solution where the disappearance of the 1,3-di(9-anthryl)propan-2-ol part is clearly seen. Chemical yields of the isolated products generally ranged between 80 and 95%. No cyclomerization involving the 2(9-anthryl)ethyl part was found for A_2A.

The photocyclomerization quantum yields Φ_r were found in the decreasing order A_2SC < A_2Phen < A_2Pyr < A_2A < A_2LC. This order is an indication of the existence of a quenching of the 1,3-di(9-anthryl)propan-2-ol part by the third chromophore which is not conducive to the formation of the photoproduct. The value found for A_2LC is comparable to that found for bis[2-(9-anthryl)ethyl] glutarate.[16]



Z = 2-(9-anthryl)ethyl
Z = 2-(pyren-1-yl)ethyl
Z = 2-(9-phenanthryl)ethyl
Z = Me

Scheme 2 Photocyclomerization of A_2SC, A_2A, A_2Pyr, A_2Phen

X-Ray Structure Determination of A_2Phen.—Only the A_2Phen molecule gave crystals suitable for X-ray diffraction study. The crystals were grown by slow evaporation of an heptane–methylene chloride mixture. Although a detailed description of the molecular and crystal structure will be published elsewhere,[12] some salient features are described here. The crystal belongs to the monoclinic system, with $C2/c$ (Z = 8) space group with the following cell parameters: $a = 39.471$, $b = 9.1782$, $c = 19.924$ and $\beta = 97.813°$. The ORTEP drawing of the molecule with the atomic numbering is presented in Fig. 9, and the projection of the structure along the b axis is given in Fig. 10. In the isolated molecule, the anthracenic parts A_1 (C1 to C14), A_2 (C21 to C34) and the phenanthrenic moiety Phen have mean planes which are not parallel and make the following angles: $A_1/A_2 = 74°$, $Phen/A_1 = 70°$ and $Phen/A_2 = 35°$. This spatial arrangement in the crystal indicates that almost no or very little intramolecular overlapping between the aromatic parts occurs in the molecule. In contrast, there are intermolecular π interactions between the anthracenic moiety A_1 of one molecule (x, y, z) and its homologous A'_1 ($1 - x, y, 1 - z$) of another molecule. These interactions induce overlapping (π stacking) between the aromatic A_1 rings with a distance between the main planes close to 3.49 Å. In addition, there are also Van der Waals interactions between the phenanthrenic parts of two adjacent molecules (x, y, z and $\frac{1}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$), but the two phenanthrenic mean planes display an angle of 74.4°.

Conclusion

This work represents the first investigation, in linked systems, of the effect of an alternant aromatic hydrocarbon (anthracene, pyrene and phenanthrene) on the photophysical and photochemical properties of the bis-9-anthryl three-membered-linked bichromophore, able to display both fluorescence and photocyclomerization. Careful examination of the absorption and fluorescence spectra in comparison with selected reference compounds has shown the existence of triple complexes in the ground and singlet states; the interactions between the chromophores in the ground state and the excited state are revealed to be different. The involvement of these complexes in

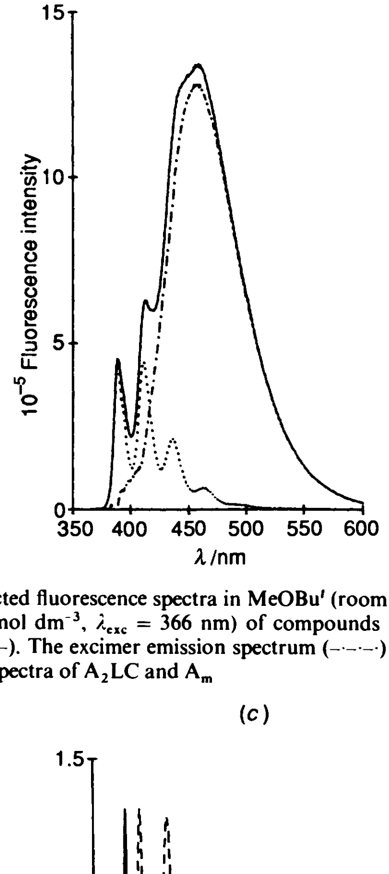


Fig. 5 Corrected fluorescence spectra in MeOBu^t (room temperature, conc. < 10^{-5} mol dm^{-3}, λ_{exc} = 366 nm) of compounds A_2LC (——) and A_m (- - - -). The excimer emission spectrum (–·–·–) was deduced by difference spectra of A_2LC and A_m

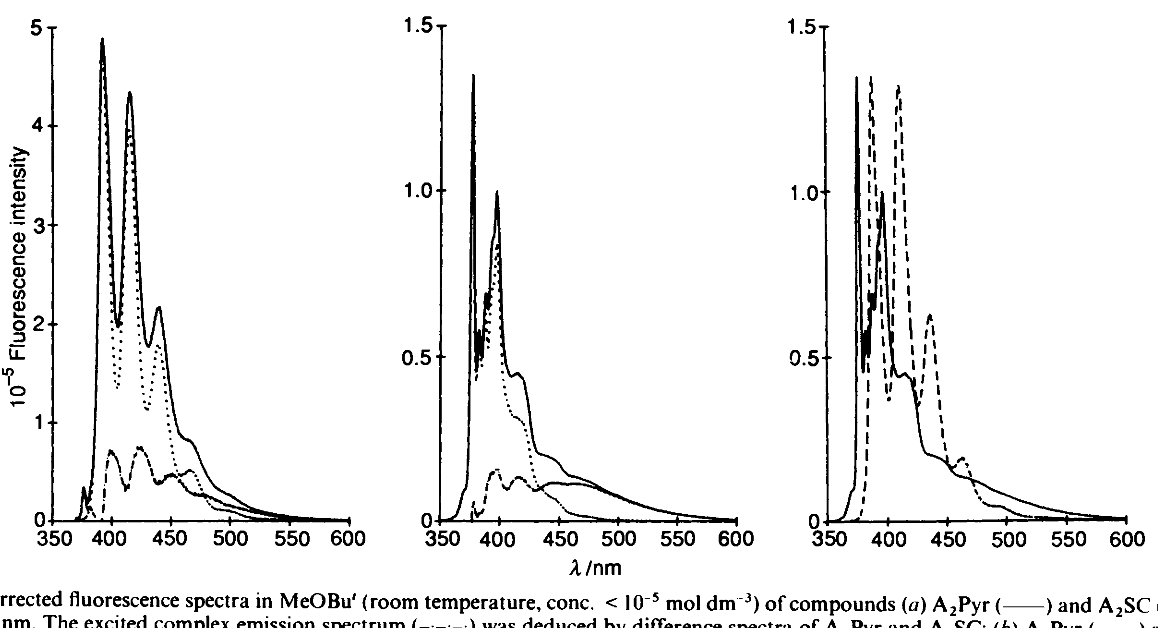


Fig. 6 Corrected fluorescence spectra in MeOBu^t (room temperature, conc. < 10^{-5} mol dm^{-3}) of compounds (*a*) A_2Pyr (——) and A_2SC (- - - -), λ_{exc} = 366 nm. The excited complex emission spectrum (–·–·–) was deduced by difference spectra of A_2Pyr and A_2SC; (*b*) A_2Pyr (——) and Pyr_m (- - - -), λ_{exc} = 340 nm. The excited complex emission spectrum (–·–·–) was deduced by difference spectra of A_2Pyr and Pyr_m; (*c*) A_2Pyr (——) and A_m (- - - -), λ_{exc} = 340 nm.

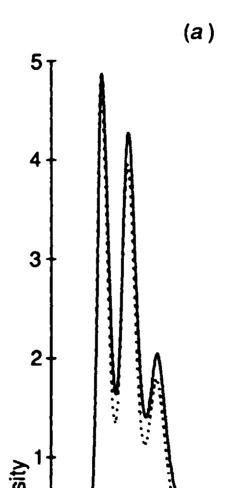


Fig. 7 Corrected emission fluorescence spectra in MeOBu^t (room temperature, conc. < 10^{-5} mol dm^{-3}) of compounds: (*a*) A_2Phen (——) and A_2SC (- - - -), λ_{exc} = 366 nm. The excited complex emission spectrum (-·-·-·) was deduced by difference spectra of A_2Phen and A_2SC; (*b*) A_2Phen (——), Phen$_m$ (· · · ·) and A_m (- - - -), λ_{exc} = 297 nm.

the pathway of the cyclomerization is not clear. Steady-state and dynamic fluorescence studies of these systems at low and high temperatures, which are underway in this laboratory, should give new information about the thermodynamic parameters of these new exterplexes.

Experimental

General and Physical Methods.—M.p.s were taken with a heating microscope (Reichter) and are uncorrected. A microbalance (Mettler ME 30, sensitivity 1 µg) was used to weigh the samples for spectrometric measurements. NMR spectra were recorded on Hitachi R1200 (60 MHz), Bruker WH 90 (FT 90 MHz) and Bruker AC 250 (FT 250 MHz) spectrometers (reference Me_4Si, solvent $CDCl_3$). IR and electronic absorption spectra were run on Perkin-Elmer 412 and Cary 219 instruments. Mass spectra were obtained using VG Micromass 16F and VG autospec Q spectrometers. The fluorescence spectra were recorded with a Spex Fluorolog fluorimeter. The fluorescence quantum yields were determined by comparison with quinine sulfate in 0.5 mol dm^{-3} sulfuric acid.[18] The determination of the reaction quantum yields was performed in MeOBu^t, with degassed samples at 366 nm as previously described.[5] Deoxygenation of irradiated solutions was carried out by the freeze–thaw technique under vacuum (10^{-6} Torr). Pyrex vessels and a medium-pressure mercury lamp (Mazda 400 W) surrounded by water-cooled Pyrex jacket were used for preparative irradiation (solvent diethyl ether). The purity of all new compounds and of the photocyclomers was checked by TLC (silica gel) and HPLC (Lichrosorb NH2, 5 µm, length 25 cm, eluent CH_2Cl_2). Elemental analyses were carried out at the CNRS microanalysis centre (Lyon).

All compounds synthesized were purified by careful column chromatography on silica with appropriate eluents. The solid products were crystallized from CH_2Cl_2–heptane mixtures after column chromatography. Commercial starting materials were obtained from Aldrich, and solvents (chromatographic and/or spectrometric quality), from SDS (*Solvants-Documentation-Synthèses*, Marseille) and Aldrich. No fluorescent impurities in the solvents were detected under our experimental conditions before fluorescence measurements.

1,3-*Di*(9-*anthryl*)-2-*propyl Hydrogen Succinate.*—A mixture of 1,3-di(9-anthryl)propan-2-ol (1 g, 2.43 mmol) prepared according to Becker,[13] 4-dimethylaminopyridine (DMAP) (80 mg, 0.65 mmol), triethylamine (3.63 g, 35.9 mmol) and succinic anhydride (0.48 g, 4.86 mmol) in methylene chloride (100 cm^3) was refluxed for 18 h. After being washed with HCl (2%) and water, the organic phase was dried over sodium sulfate, filtered and evaporated under reduced pressure. Column chromatography of the solid residue gave 1 g of 1,3-di(9-anthryl)-2-propyl hydrogen succinate (80%), m.p. 221 °C, δ($CDCl_3$; 60 MHz) 2.2 (4 H, s), 3.85 (4 H, m), 5.7 (1 H, m) and 6.8–8.5 (19 H, m); ν_{max}(KBr)/cm^{-1} 3080, 3040, 1730, 1710, 1620, 1520, 1490, 1445, 1410, 1380, 1345, 1230, 1160, 1030, 1000, 980, 940, 870, 830, 775 and 720.

1,3-*Di*(9-*anthryl*)-2-*propyl Methyl Succinate* (A_2SC).—To a stirred solution of 1,3-di(9-anthryl)-2-propyl hydrogen succinate (0.2 g, 0.39 mmol) in degassed anhydrous benzene (30 cm^3) was added dropwise oxalyl chloride (5.9 g, 46.6 mmol). The mixture was stirred for 5 h under reflux. The solution was then evaporated to give the acid chloride A_2SuCl (0.2 g, 0.39 mmol) as a brown solid. The compound was used without further purification.

To the preceding acid chloride was added, under a nitrogen atmosphere, methanol (30 cm^3) and pyridine (0.04 g, 5 mmol). The mixture was refluxed for 5 h and, after evaporation of the solvent, the residue was dissolved in CH_2Cl_2; the solution was washed with water, dried (sodium sulfate) and evaporated. Chromatography of the residue (silica; eluent CH_2Cl_2–light petroleum 9:1) gave A_2SC (0.165 g, 79%), m.p. 194 °C, δ($CDCl_3$; 250 MHz) 2.24 (4 H, s), 3.47 (3 H, s), 3.71 (2 H, m), 4.06 (2 H, m), 5.66 (1 H, m) and 7.15–8.38 (18 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2920, 2840, 1720, 1620, 1520, 1490, 1440, 1415, 1340, 1315, 1260, 1150, 1090, 1030, 1010, 1000, 980, 940, 870, 830, 790, 770, 720, 690 and 650; *m*/*z* 526 (14%, $M^{\cdot+}$), 394 (21), 191 (100) and 115 (89); λ_{max}(MeOBu^t)/nm 388.5 (ε/dm^3 mol^{-1} cm^{-1} 18 920), 368 (17 880), 349.5 (10 600), 332 (4990), 256 (226 600) and 248 (193 350) (Found: C, 81.95; H, 5.6; O, 12.1. $C_{36}H_{30}O_4$ requires C, 82.13; H, 5.70; O, 12.17%).

2-(9-*Anthryl*)*ethanol*, 2-(*Pyren*-1-*yl*)*ethanol and* 2-(9-*Phenanthryl*)*ethanol.*—The alcohols were synthesized by bubbling ethylene oxide in excess through a dry diethyl ether solution (50 cm^3, 0 °C) of the organolithium aromatic hydrocarbon prepared from the bromo derivative (8 mmol) and *n*-butyl-

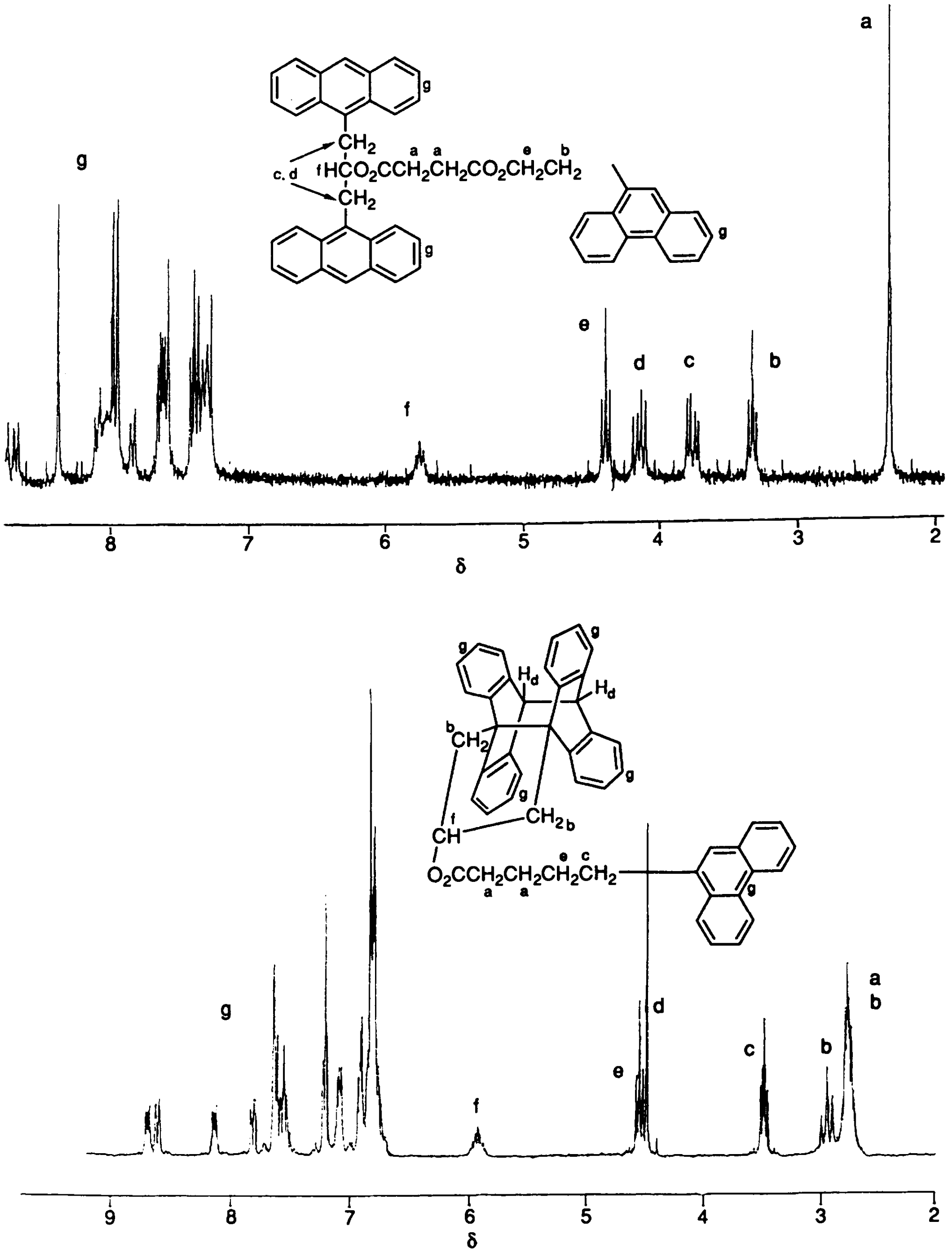


Fig. 8 250 MHz ^1H NMR spectra of A_2Phen and its photocyclomer ($CDCl_3$, room temperature)

lithium (9 mmol). After usual work-up, the compounds were purified by column chromatography (silica; eluent CH_2Cl_2) and crystallized from CH_2Cl_2–heptane (4/1). 2-(9-Anthryl)ethanol (76%), m.p. 107 °C (lit.,[19] 106.5–107.5 °C), δ($CDCl_3$; 60 MHz) 1.6 (1 H, br s), 3.96 (4 H, m) and 7–8.5 (9 H, m); 2-(pyren-1-yl) ethanol (67%), m.p. 94 °C (lit.,[20] 57–59 °C), δ($CDCl_3$; 60 MHz) 1.73 (1 H, br s), 3.53 (2 H, t), 4.00 (2 H, t) and 7.5–8.3 (9 H, m); 2-(9-phenanthryl)ethanol (69%), m.p. 102 °C (lit.,[21] 92 °C), δ($CDCl_3$; 60 MHz) 2.8 (1 H, br s), 3.30 (2 H, t), 3.95 (2 H, t) and 7.2–8.9 (9 H, m).

2-(9-Anthryl)ethyl, 2-(Pyren-1-yl)ethyl and 2-(9-Phenanthryl)ethyl Acetates: (A_m, Pyr_m, $Phen_m$).—A mixture of the 2-arylethanols (0.45 mmol), 4-dimethylaminopyridine (DMAP) (0.16 mmol), triethylamine (14.4 mmol) and acetic anhydride (21.2 mmol) in methylene chloride (30 cm^3) was refluxed for 4 h. The solution was washed with HCl (2%) and water and the organic phase was dried over sodium sulfate, filtered and evaporated under reduced pressure. Column chromatography (silica; eluent CH_2Cl_2) of the solid gave the corresponding acetates, 2-(9-Anthryl)ethyl acetate (A_m) (95%), m.p. 87 °C, δ($CDCl_3$; 60 MHz) 1.9 (3 H, s), 3.77 (2 H, t), 4.27 (2 H, t) and 6.93–8.26 (9 H, m); ν_{max}(KBr)/cm^{-1} 3050, 2960, 1735, 1690, 1620, 1450, 1390, 1365, 1300, 1260, 1245, 1100, 1045, 1030, 980, 960, 875, 850, 790, 750, 730 and 700; *m*/*z* 264 (31%, $M^{•+}$), 204 (100) and 191 (93); λ_{max}($MeOBu^t$)/nm 385.5 (ε/dm^3 mol^{-1} cm^{-1} 8090), 366 (7960), 348 (4750), 331 (2310) and 255.5 (148 200); 2-(pyren-1-yl)ethyl acetate (Pyr_m) (96%), m.p. 56 °C, δ($CDCl_3$; 60 MHz) 1.83 (3 H, s), 3.37 (2 H, t), 4.20 (2 H, t) and 7.33–8.50 (9 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2960, 1725, 1605, 1590, 1475, 1435, 1420, 1390, 1370, 1250, 1185, 1100, 1030, 980, 950, 900, 830, 790, 750, 720 and 700; *m*/*z* 288 (21%, $M^{•+}$), 228 (100), 215 (73) and 149 (15); λ_{max}($MeOBu^t$)/nm 375 (ε/dm^3 mol^{-1} cm^{-1} 490), 341 (48 600), 325 (30 600), 310 (12 240), 275 (55 260), 264 (26 900), 242.5 (80 400) and 233.5 (42 660); 2-(9-Phenanthryl)ethyl acetate ($Phen_m$) (90%), m.p. 94 °C, δ($CDCl_3$; 60 MHz) 1.93

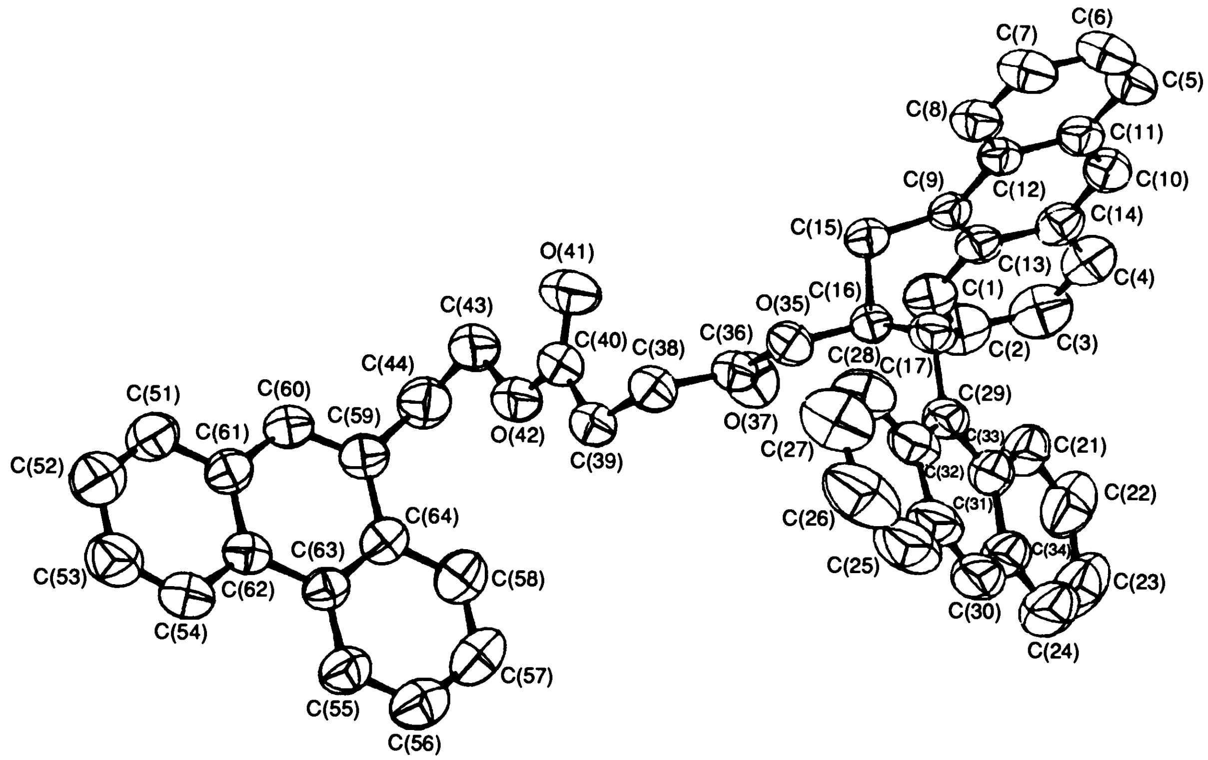


Fig. 9 X-Ray structure of A$_2$Phen with atomic numbering (see the Discussion)

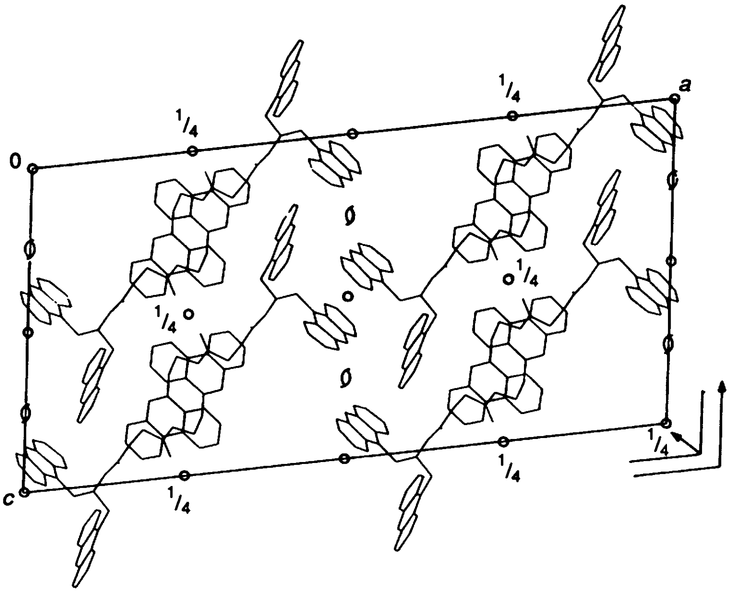


Fig. 10 Projection of A$_2$Phen in the crystal along the *b* axis

(3 H, s), 3.30 (2 H, t), 4.37 (2 H, t) and 7.10–8.90 (9 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2960, 1725, 1605, 1585, 1475, 1435, 1390, 1370, 1250, 1185, 1035, 985, 950, 900, 860, 835, 820, 750, 720 and 700; *m/z* 264 (13.5%, M$^{\cdot+}$), 204 (100) and 191 (32); λ_{max}(MeOBu^t)/nm 348.5 (ε/dm^3 mol^{-1} cm^{-1} 264), 340 (215), 332 (297), 297 (12 290), 285 (10 300) and 253.5 (63 950).

2-(9-*Anthryl*)*ethyl* (9-*Anthryl*)*methyl Succinate* (A$_2$LC).—A mixture of 2-(9-anthryl)ethanol (0.3 g, 1.35 mmol), DMAP (0.05 g, 0.41 mmol), triethylamine (2.18 g, 21.5 mmol) and succinic anhydride (0.27 g, 2.7 mmol) in methylene chloride (60 cm^3) was refluxed for 18 h. After being washed with HCl (2%) and water, the organic solution was dried over sodium sulfate, filtered and evaporated under reduced pressure. Column chromatography (silica; eluent Et$_2$O) of the solid gave the expected acid ester (0.41 g, 94%), m.p. 196 °C, δ(CDCl$_3$; 60 MHz) 2.55 (4 H, s), 3.36 (2 H, t), 4.43 (2 H, t) and 7–9 (10 H, m); ν_{max}(KBr)/cm^{-1} 3500–2500br, 1720br, 1600, 1495, 1475, 1415, 1390, 1360, 1260, 1235, 1190, 1070, 1045, 1020, 995, 975, 880, 855, 830, 780, 760 and 740.

Oxalyl chloride (7.4 g, 58.3 mmol) was added dropwise to a stirred solution of the preceding acid ester (0.2 g, 0.62 mmol) in degassed anhydrous benzene (40 cm^3). The mixture was stirred for 5 h under reflux. The solution was then evaporated, to give the acid chloride which was used without further purification for the next step. To the preceding acid chloride in THF (50 cm^3) were added, under a nitrogen atmosphere, 9-anthrylmethanol[5] (0.15 g, 0.72 mmol) and pyridine (0.05, 0.63 mmol). The mixture was refluxed for 18 h and, after evaporation of the solvent, the residue was dissolved in CH$_2$Cl$_2$. The solution was washed with water, dried (sodium sulfate) and evaporated. Chromatography of the residue (silica; eluent CH_2Cl_2) gave A_2LC (0.194 g, 61%), m.p. 156 °C, δ($CDCl_3$; 90 MHz) 2.11 (4 H, s), 3.24 (2 H, t), 3.82 (2 H, t), 5.55 (2 H, s) and 6.50–7.80 (18 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2920, 1720, 1620, 1445, 1420, 1375, 1335, 1310, 1150, 985, 960, 875, 825, 775 and 720; *m/z* 512 (9%, $M^{\bullet +}$), 222 (12), 204 (39) and 191 (100); λ_{max}($MeOBu^t$)/nm 385.5 (ε/dm^3 mol^{-1} cm^{-1} 18 500), 366 (18 870), 348 (11 700), 331 (5660), 255.5 (305 660) and 248 (203 780) (Found: C, 82.25; H, 5.4; O, 12.35. $C_{35}H_{28}O_4$ requires C, 82.03; H, 5.46; O, 12.50%).

1,3-*Di*(9-*anthryl*)-2-*propyl* 2-(9-*Anthryl*)*ethyl Succinate* (A_2A).—To 2-(9-anthryl)ethanol (0.1 g, 0.45 mmol) dissolved in THF (40 cm^3) was added pyridine (40 mg, 0.5 mmol) and A_2SuCl (0.22 g, 0.39 mmol), the mixture was then refluxed for 18 h. After completion, 100 cm^3 of CH_2Cl_2 were added to the solution and the organic phase was washed with distilled water, dried over sodium sulfate and evaporated. The solid residue was purified by chromatography (silica; eluent CH_2Cl_2) to give A_2A (0.074 g, 27%), m.p. 169 °C, δ($CDCl_3$; 250 MHz) 2.33 (4 H, m), 3.79, (2 H, m), 3.85 (2 H, m), 4.14 (2 H, m), 4.39 (2 H, m), 5.76 (1 H, m) and 7.26–8.38 (27 H, m); ν_{max}(KBr)/cm^{-1} 3050, 2960, 1730, 1620, 1520, 1490, 1450, 1410, 1380, 1350, 1260, 1160, 1100, 1030, 980, 940, 870, 830, 790, 720 and 700; *m/z* 716 (22%, $M^{\bullet +}$), 394 (39), 215 (11), 205 (36) and 191 (100); λ_{max}($MeOBu^t$)/nm 387.5 (ε/dm^3 mol^{-1} cm^{-1} 27 000), 367 (27 560), 348.5 (17 330), 332 (8240), 255.5 (349 500) and 247.5 (286 950) (Found: C, 85.3; H, 5.4; O, 8.95. $C_{51}H_{30}O_4$ requires C, 85.47; H, 5.59; O, 8.94%).

1,3-*Di*(9-*Anthryl*)-2-*propyl* 2-(*Pyren*-1-*yl*)*ethyl Succinate* (A_2Pyr).—Using the same procedure as for the preparation of A_2A, the trichromophore A_2Pyr was synthesized from 1-(2-hydroxyethyl)pyrene and A_2SuCl (29%), m.p. 189 °C, δ($CDCl_3$; 250 MHz) 2.31 (4 H, s), 3.55 (2 H, m), 3.73 (2 H, m), 4.07 (2 H, m), 4.43 (2 H, m), 5.73 (1 H, m) and 7.26–8.34 (27 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2960, 1740, 1625, 1600, 1450, 1420, 1315, 1260, 1210, 1170, 1100, 1030, 980, 870, 830, 790, 750, 725 and 700; *m/z* 740 (8%, $M^{\bullet +}$), 394 (52), 346 (12), 215 (91) and 191 (100); λ_{max}($MeOBu^t$) 388.5 (ε/dm^3 mol^{-1} cm^{-1} 18 990), 368 (18 480), 341.5 (47 460), 325.5 (30 510), 275.5 (50 850), 255.5 (239 000) and 248 (201 700) [Found: C, 83.85; H, 5.2. $C_{53}H_{40}O_4$ (with 0.25 mol CH_2Cl_2) requires C, 83.96; H, 5.32%].

1,3-*Di*(9-*anthryl*)-2-*propyl* 2-(9-*Phenanthryl*)*ethyl Succinate* (A_2Phen).—Using the same procedure as for the preparation of A_2A, the trichromophore A_2Phen was synthesized from 9-(2-hydroxyethyl)phenanthrene and A_2SuCl (39%), m.p. 167 °C, δ($CDCl_3$; 250 MHz) 2.33 (4 H, s), 3.32 (2 H, m), 3.77 (2 H, m), 4.13 (2 H, m), 4.39 (2 H, m), 5.75 (1 H, m) and 7.26–8.74 (27 H, m); ν_{max}(KBr)/cm^{-1} 3040, 2940, 1725, 1620, 1440, 1350, 1205, 1160, 1000, 980, 870, 825, 770 and 720; *m/z* 716 (30%, $M^{\bullet +}$), 394 (25), 205 (53) and 191 (100); λ_{max}($MeOBu^t$)/nm 388.5 (ε/dm^3 mol^{-1} cm^{-1} 16 220), 368 (15 200), 349.5 (9120), 297 (11 490), 255.5 (233 100), 247.5 (212 900) [Found: C, 83.25; H, 5.25; O, 8.55. $C_{51}H_{40}O_4$ (with 0.25 mol CH_2Cl_2) requires C, 83.44; H, 5.49; O, 8.68%].

Preparative Irradiations of A_2SC, A_2Phen, A_2Pyr *and* A_2A.—*Compound* A_2Phen. A degassed solution (diethyl ether, 100 cm^3) of the trichromophore (20 mg, 2.8×10^{-4} mol dm^{-3}) was irradiated in a Pyrex vessel equipped with a quartz cell to follow the progress of the photocyclomerization. The photochemical reaction was completed within 25 min. After removal of the solvent, the solid was chromatographed (silica; eluent CH_2Cl_2) to give the 9,9′,10,10′-anthracenic photocyclomer (10 mg, 95%), m.p. 248 °C, δ($CDCl_3$; 250 MHz) 2.76 (6 H, m), 2.93 (2 H, m), 3.46 (2 H, m), 4.46 (2 H, s), 4.53 (2 H, m), 5.90 (1 H, m) and 6.60–8.80 (25 H, m); *m/z* 716 (100%, $M^{\bullet +}$), 530 (17), 394 (41), 307 (38) and 289 (38); λ_{max}($MeOBu^t$)/nm 297.5 (ε/dm^3 mol^{-1} cm^{-1} 10 100), 286 (8950), 276 (10 400) and 254 (47 100).

Compound A_2Pyr. Under the above irradiation conditions and work-up, A_2Pyr (2.7×10^{-4} mol dm^{-3}) gave the 9,9′,10,10′-anthracenic photocyclomer (94%), m.p. 229 °C, δ($CDCl_3$, 250 MHz) 2.82 (6 H, m), 2.99 (2 H, m), 3.76 (2 H, m), 4.54 (2 H, m), 4.63 (2 H, m), 5.97 (1 H, m) and 6.70–8.50 (25 H, m); *m/z* 740 (28%, $M^{\bullet +}$), 394 (13), 391 (15), 229 (100) and 215 (31); λ_{max}($MeOBu^t$)/nm 341 (ε/dm^3 mol cm^{-1} 27 000), 326 (18 500), 312 (9300), 275.5 (37 000), 265 (24 000) and 242.5 (51 000).

Compound A_2A. Under the above irradiation conditions and work-up, A_2A (2.7×10^{-4} mol dm^{-3}) gave the 9,9′,10,10′-anthracenic photocyclomer (80%), m.p. 232 °C, δ($CDCl_3$; 250 MHz) 2.76 (6 H, m), 2.94 (2 H, m), 3.99 (2 H, m), 4.47 (2 H, m), 4.54 (2 H, m), 5.92 (1 H, m) and 6.70–8.50 (25 H, m); *m/z* 716 (9%, $M^{\bullet +}$), 394 (8), 391 (100) and 279 (16); λ_{max}($MeOBu^t$)/nm 386 (ε/dm^3 mol^{-1} cm^{-1} 7150), 366 (7150), 348 (4300), 282 (1612), 272 (2500) and 256 (140 000).

Compound A_2SC. Under the preceding irradiation conditions and work-up, A_2SC (3.8×10^{-4} mol dm^{-3}) gave the 9,9′,10,10′-anthracenic photocyclomer (95%), m.p. 199 °C, δ($CDCl_3$; 250 MHz) 2.76 (6 H, m), 2.92 (2 H, m), 3.72 (3 H, s), 4.50 (2 H, s), 5.90 (1 H, m) and 6.50–7.40 (16 H, m); *m/z* 526 (24%, $M^{\bullet +}$), 394 (29), 191 (100) and 115 (72); λ_{max}($MeOBu^t$)/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 1300) and 273 (1450).

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