Intramolecular excimer formation in short- and long-chainlength di(9-anthryl) bichromophoric compounds and relation to ground state properties†

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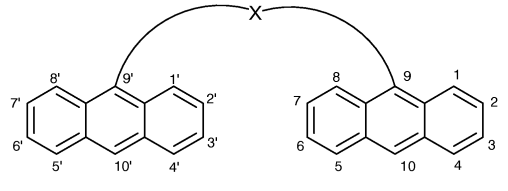
The ground state conformational, UV absorption and fluorescence spectral as well as decay time data for a series of polymethylene- and one polyoxyethylene-linked di(9-anthracenes) in solution are compared, for chainlengths varying from $n = 0$ (directly linked system A0A, 9,9′-bianthryl) to $n = \infty$ (A∞, reference system 9-decylanthracene). ^{1}H NMR spectroscopy of A2A to A11A shows that there is no clearly preferred ground state conformation of the anthracene moieties. The crystal structure of A2A was solved and the *anti* conformation of the anthracene units was established. The UV spectra show a redshift interpreted within the Förster exciton model (predominance of extended conformations). Fluorescence spectra for $(CH_2)_n$-bridged systems show no clear excimer band for short-chain systems but redshifted excimer emission for A4A to A9A. Loss of structure and fluorescence band shape changes as well as biexponential decay times allow the conclusion that excimer formation occurs in all chained systems. For a related polyoxyethylene-chained system, the excimer band is substantial, probably a consequence of the increased flexibility of the chain and moderate photoreactivity. Solvent polarity changes are strong for A0A [formation of a twisted intramolecular charge transfer (TICT) state] but also significant in the systems A1A and A2A. This is rationalized by the possiblity for competitive formation of an excimer-type (parallel but tilted chromophore arrangement) and a TICT-type (near perpendicular) conformation. For AnA ($n > 2$) the solvent polarity was found to have virtually no influence.

Polycyclic aromatic hydrocarbons are known to easily form excimers that are 1 : 1 complexes which are stable in the excited state but dissociative in the ground state. These are detected by their redshifted structureless fluorescence emission, which has no corresponding absorption spectrum.[1] Intramolecular excimers, generated from two aromatic nuclei linked together by a polymethylene chain, reveal the molecular dynamics of the chain and can be used as sensors for conformational changes in molecular assemblies[2] and polymers.[3] This has led to intense research activity in stationary fluorescence spectroscopy and transient kinetic analysis of 1,n-diarylalkanes where the aryl groups are phenyl and biphenyl,[4] 1- and 2-naphthyl,[2c,5] 1-pyrenyl,[2d,6] 9-carbazolyl,[2a] 1-,2-, and 9-anthryl,[7] *etc.*

Dianthryls, hereafter denoted A*n*A, (Scheme 1) are of special interest because a photochemical reaction, the intramolecular photocycloaddition[8] (Scheme 2), competes with excimer fluorescence emission. The 9 and 10 positions being more reactive, the 9-anthryl derivatives are generally readily synthesized and therefore have been more extensively investigated.[8,9] However, the preceding studies seem to have omitted *the systematic study of the solvent polarity influence* with the exception of some excellent work on A2A.[10,11] Moreover, it is noteworthy that the emission spectrum of the first member, 9,9′-dianthryl (A0A), is strongly sensitive to solvent polarity. The mechanism (Scheme 3) is well-established:[12] two excited state conformers (termed DE and TICT) are formed. In the first state that is not dipolar, the π electrons of the two rings undergo some overlap (delocalized excitation, DE) and the



A*n*A X = $-(CH_2)_n-$
A6(O$_3$)A X = $-CH_2(OCH_2CH_2)_2OCH_2-$

Scheme 1 (*i*) 1,*n*-Di(9-anthryl)alkanes [$X = (CH_2)_n$]; in this study, the following derivatives are considered: $n = 0,1,2,3,4,5,6,9,11,\infty$ denoted as A0A, A1A, A2A, A3A, ... A11A, A∞. A∞ is represented by 9-decylanthracene. (*ii*) 1,9-Di-(9-anthryl)-2,5,8-trioxanonane is denoted as A6(O$_3$)A.

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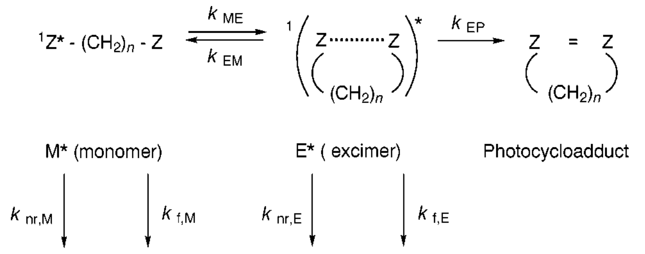
† Supplementary material available: tables of positional parameters and torsion angles for A2A. Available from BLDSC (No. SUP 57498, 4 pp.). See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).



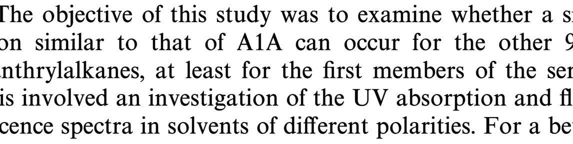
Scheme 2 Kinetic scheme of 1,*n*-diarylalkanes (Z = aryl group) in the excited state. M* = "monomer" or LE = locally excited state. E* = excimer (several configurations are possible). $k_{nr,M}$, $k_{f,M}$, k_{ME}, k_{EM}, $k_{nr,E}$, $k_{f,E}$, k_{EP} = rate constants for monomer nonradiative deactivation, fluorescence, excimer formation, excimer dissociation, excimer nonradiative deactivation, excimer fluorescence, excimer reaction, respectively.

twist angle is around 70°,[13] whereas in the second conformer the overlap is minimal with a strong dipolar character that is borne out by a strong solvent-polarity-induced redshift of the fluorescence spectrum.

Fluorescence spectra can give evidence of excimer formation but also of the population of a charge transfer (CT) state, different from the excimer, such as previously shown for the directly linked system A0A, which is able to undergo solvent-induced symmetry breaking to a luminescent charge transfer (CT) state.[12,14–27] This results in a strong redshift of the fluorescence spectra with increasing solvent polarity. On the other hand, for excimer formation in more flexible systems such as di(2-anthryl)ethane, the excimer fluorescence component is virtually solvent independent,[12,28] indicating that the electronic wavefunction of the emitting state is not symmetry-broken, although in the very early stages of excimer formation, nonluminescent charge-separated species have also been reported.[29] Whether or not symmetry breaking in the luminescent state can occur is a question of the size of the coupling matrix element *V* between the excitonic anthracene-type state ["locally excited" or better yet, delocalized excited state (DE) emitting the structured short-wavelength fluorescence band] and the CT state.[12,18,22] As the CT state is forbidden, any observed emission intensity derives from an admixture of the DE-type wavefunction to this state through *V*. For sandwich-type excimers, *V* is large and the solvent fluctuations cannot break the symmetry of the wavefunction; therefore the mixing between DE and CT states involves equal amounts of forward and backward CT [so-called charge resonance (CR) states], resulting in zero dipole moments. There are cases with intermediate coupling *V*, such as in A1A, which should be investigated.

The objective of this study was to examine whether a situation similar to that of A1A can occur for the other 9,9′-dianthrylalkanes, at least for the first members of the series. This involved an investigation of the UV absorption and fluorescence spectra in solvents of different polarities. For a better understanding of the conformational interconversion, the ground state structure, in solution and in the crystal state, have also been studied and in one case an X-ray structure analysis has been carried out.

The entire A*n*A family is included in this study but of special significance are short-chain bichromophores (A0A to A3A), which are compared with the medium- and long-chain representatives (A5A to A11A) and, eventually, with the compound A∞, represented by 9-decylanthracene, in which the rings are at infinite distance from each other (and, therefore, undergo no mutual interaction). Moreover, it seemed interesting to compare the behaviour of a polymethylene chain with that of a more flexible polyoxyethylene link[30] in examining 1,9-di(9-anthryl)-2,5,8-trioxanonane [denoted A6(O_3)A]. The following points are successively dealt with: (*i*) general considerations on different methods of preparation of the A*n*A, (*ii*) the ground state structure and (*iii*) the excited state properties with emphasis on the solvent polarity effect on the fluorescence emission spectra.



Scheme 3 Formation of two excited state conformers for 9,9′-bianthryl (A0A). DE = delocalized excited state. TICT = twisted intramolecular charge transfer state.

Experimental

Absorption spectra were measured on Cary 17 and 219 spectrometers, corrected fluorescence spectra on a Perkin-Elmer 650-60 or MPF44 fluorimeter. Fluorescence decay curves were determined using a time-correlated single-photon-counting setup described in detail elsewhere[31] and with BESSY synchrotron radiation as excitation source. NMR spectra have been recorded on a Bruker AC200 spectrometer.

The structure of the compounds studied and their abbreviations are represented in Scheme 1. Synthetic details for some of the compounds have been reported before.[32a,30] The compounds were recrystallized and showed only one TLC and HPLC trace. Moreover, the excitation spectra were found to correspond to the UV spectra. Solvents were of spectroscopic quality.

Syntheses

9,9′,10,10′-Tetrahydro-1,3-di(9-anthryl)propane (THA3A).[7d] 9,10-Dihydroanthracene (DHA, 5.4 g, 30 mmol) was dissolved in THF (100 ml) in a three-neck round-bottom flask equipped with a stirrer, under a stream of argon and maintained at −40 °C; a solution of BuLi in hexane (30 mmol) was then added dropwise. The medium turned red and the agitation was continued for 0.5 h to complete formation of the DHA carbanion. A solution of 1,3-dibromopropane (3 g 150 mmol) in THF (40 ml) was then added slowly under continuous stirring and the temperature was allowed to rise up to *ca.* 25 °C. After usual workup, the mixture was chromatographed on alumina (II-III standard) using successively pentane and pentane–benzene (1 : 1 vol/vol) as eluents for the separation of DHA, anthracene and a mixture of THA3A and anthracene, respectively. Anthracene was separated from the last fraction by treatment with maleic anhydride in refluxing xylene for 3 h. After workup, the tetrahydroderivative (THA3A) was crystallized from a benzene–methanol mixture (colourless crystals, m.p. 143 °C, 0.72 g, 12%). ^1H NMR ($CDCl_3$) δ 1.2–1.8 (m, 6H), 3.4–4.2 (t, 2H; AB, 4H), 6.8–7.2 (m, 16H); MS *m/z* 400 (M^+); anal. calc. for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.77; H, 6.97%.

1,3-Di(9-anthryl)propane (A3A).[7d] A benzene solution of THA3A (0.300 g, 0.75 mmol) was gently refluxed for 20 h in the presence of 2 molar equiv. of dichlorodicyanobenzoquinone (DDQ, 0.340 g). After usual workup, the product was chromatographed on silica gel (eluent: light petroleum ether) and crystallized from a benzene–pentane mixture; A3A was isolated as pale yellow crystals (m.p. 195–196 °C, 0.223 g, 75%). ^1H NMR ($CDCl_3$) δ 2.1–2.7 (m, 2H), 3.8 (t, 4H), 7.2–8.3 (m, 18H); MS *m/z* 396 (M^+), 205, 191; anal. calc. for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 93.86; H, 6.23%. Overall yield from DHA: 9%. A sample of A3A, so prepared, was found to be spectroscopically pure and used for an extensive photophysical study in the solid state.[7q]

9-Decylanthracene (A∞). 9-Decylanthracene (A∞) was prepared using the Krollpfeiffer procedure[32d] and purified by column chromatography (silica gel, eluent: pentane), mp 44 °C, white crystals. ^1H NMR (CCl_4) δ 0.85–0.95 [t, 3H, A-$(CH_2)_{10}CH_3$]; 1.25–1.5 (m, 2H), 1.7–1.85 [m, 14H, A-$(CH_2)_2$-

$(CH_2)_7CH_3$]; 3.5–3.6 [m, 2H, benzylic: A-$CH_2(CH_2)_8CH_3$], 7.35–7.45 (m, 4H, aryl), 7.85–7.95 (m, 2H, aryl), 8.15–8.25 (m, 3H, aryl); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3), 22.9, 28.3, 29.6, 29.8, 29.9, 30.6, 31.6, 32.1 [-$(CH_2)_9$-], 124.6, 124.9, 125.4, 125.6, 129.4 (C_{Ar}-H), 129.7, 131.8, 135.6 (quat. C); HRMS (AutoSpecEQ FAB$^+$) $C_{24}H_{30}$ calc.: 318.234751, found: 318.234305.

Synthetic methods

Because of the wide interest in compounds A*n*A, a brief survey of the different ways of preparing them now appears appropriate (Scheme 4). Two general methods [eqn. (1) and (2)] apply to medium- and long-chain dianthryls whereas specific preparations are outlined in eqn. (3)–(7).

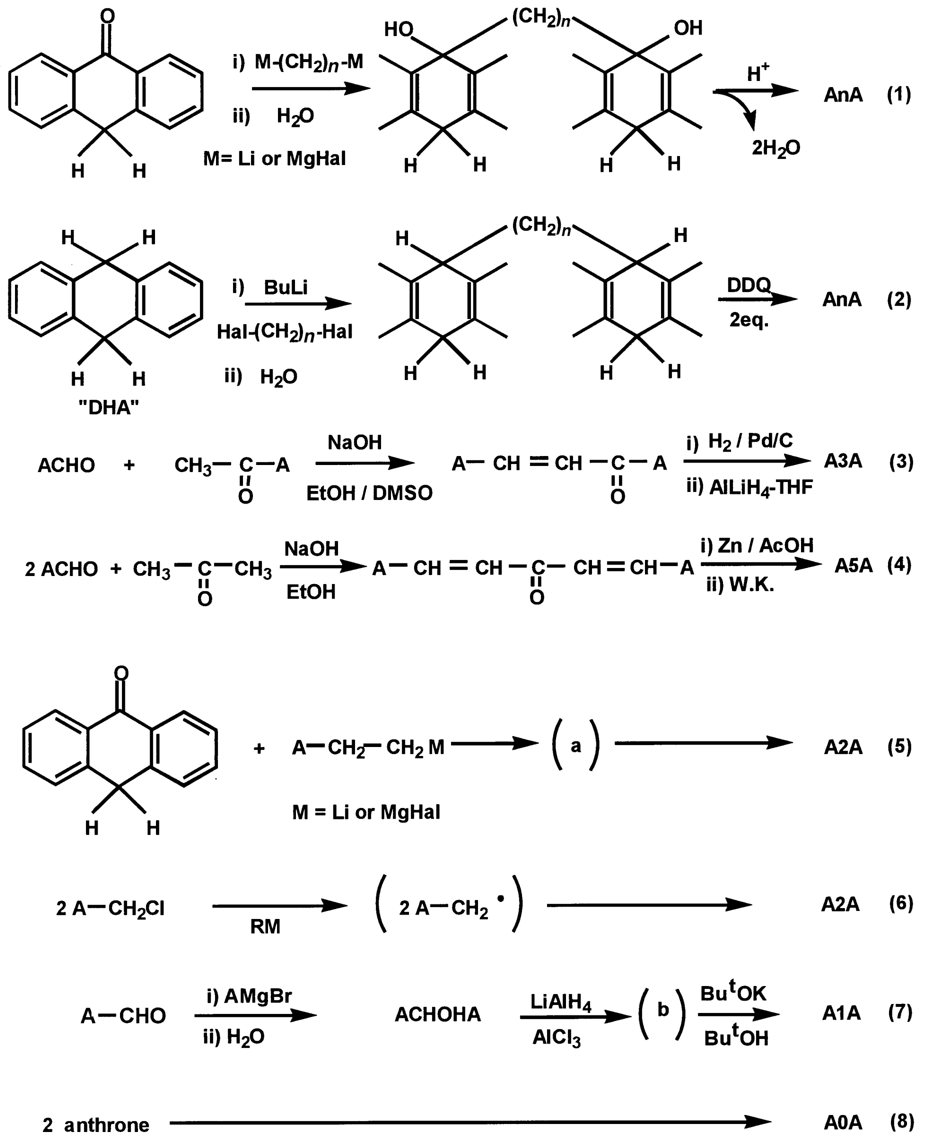
Medium-chainlength compounds have been obtained using the reaction of bis-α,ω-organolithium or magnesium reagents upon anthrone followed by a facile aromatizing dehydration [eqn. (1)]; the organometallic reagents have to be employed in excess because their reactivity as bases competes with the nucleophilic action.[33] An alternative pathway is outlined in eqn. (2). This is a two-step reaction, with isolation of the tetrahydro intermediate[34,35] that, especially in the case of A3A, led to a very pure sample; the procedure is described in detail in the Experimental section.

A third preparation of A3A relies on the intermediacy of the anthrylchalcone [eqn. (3)] but the successive reduction of the double bond and the carbonyl group may affect the side rings, generating byproducts which may be difficult to separate.[7q] This method has also been used by Ikeda *et al.*[7o] for the preparation of A5A [eqn. (4)]. The regular preparation of A2A occurs according to eqn. (5).[36,37] A2A can also be obtained by head-to-head coupling of the anthrylmethyl radical generated by single-electron transfer from a Grignard reagent to 9-anthrylmethyl chloride.[38] A1A is synthesized from 9-anthraldehyde by the three-step procedure outlined in eqn. (7)[39] and A0A can be obtained by the reductive dimerization of anthrone [eqn. (8)].[40] A11A was prepared from 9,10-dihydroanthracene and undecyleneditoluene sulfonate as described previously,[7d,32a–c,34,35] and A6A analogously.

Results and discussion

Ground state structure of A*n*A

^1H NMR spectroscopy, crystal structure analysis and UV absorption spectrometry allow an examination of the ground state conformational properties of AnA.



Scheme 4 Outline of the different methods of preparation of 1,*n*-di(9-anthryl)alkanes (A*n*A) (see refs 33–40). DDQ = 2,3-dichloro-5,6-dicyano-benzoquinone. W.K. = Wolff–Kishner. A = 9-anthryl, DHA = 9,10-dihydroanthracene. (a) alcohol intermediate. (b) 9-(9-anthrylmethylidene)-9,10-dihydroanthracene.

Table 1 ^1H NMR chemical shifts of mono- and dianthryl compounds (200 MHz, 0.05 molar in $CDCl_3$) at room temperature. The numbering of the H atoms follows that of the C atoms in Scheme 1

Position	A∞	A[2,2]A	A1A	A2A	A3A	A6A	A11A
1	8.35	7.73	8.29	8.34	8.22	8.26	8.30
2	7.53	6.83	7.39	7.47	7.46	7.46	7.52
3	7.53	6.83	7.39	7.44	7.44	7.46	7.48
4	8.05	7.73	8.01	7.97	7.98	7.99	7.95
10	8.40		8.41	8.33	8.35	8.32	8.35
C_α	3.68	4.16	5.98	4.10	4.10	3.61	3.60

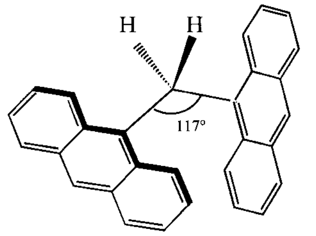


Fig. 1 Conformation of A1A in the solid state according to ref 9*c*.

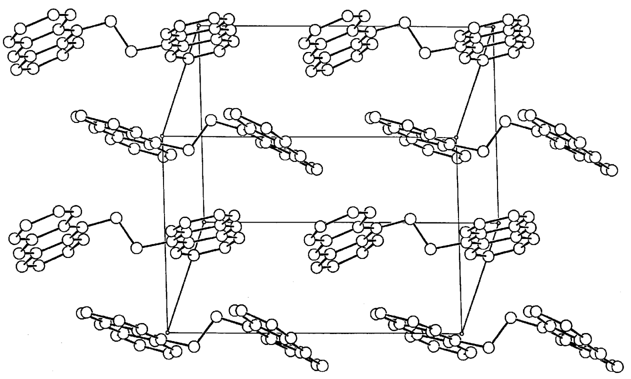


Fig. 2 Unit cell of A2A as determined by crystal structure analysis.

Table 2 Crystallographic data for A2A

Chemical formula	$C_{30}H_{22}$
Formula weight	382.48
Crystal system	Monoclinic
Space group	*Pc*
μ/mm^{-1}	0.071
R	$R_1 = 0.047$, $R_2 = 0.046$
a/Å	10.0957(9)
b/Å	12.6244(8)
c/Å	8.3296(6)
β/°	107.263(10)
U/Å^3	1013.8
D_{calc}/g cm^3	1.253
Z	2
T/K	293
Measured reflections	1868
Independent reflections	1708
R(int)	0.02

Table 3 Selected torsion and bond angles of A2A as determined by X-ray analysis. For definition of atoms, see Scheme 1 (the aliphatic carbon is labelled C_α)

Atom 1	Atom 2	Atom 3	Atom 4	Angle/°
C9	C_α	C'_α	C9′	179.1
C1	C9	C_α	C'_α	84.9
C_α	C'_α	C9′	C1′	96.3
C9	C_α	C'_α		108.1
C_α	C'_α	C9′		112.2

^1H NMR spectroscopy. The degree of interaction between the anthryl groups depends on the conformations (*anti*, *gauche*) along the oligomethylene chain and the torsion angle about the bond connecting the aromatic unit and the α-methylene carbon. As the ^1H chemical shifts depend upon the mutual anisotropic ring current effects between the aromatic units, the spectra of A1A, A2A, A3A, A6A, A11A[9,10] and [2.2]anthracenophane (A[2.2]A)[41] have been recorded and compared with those of A∞ (no interaction between anthryl groups) and collected in Table 1. For the protons H^2 and H^3, one observes a difference of chemical shift $\Delta\delta_{max} = 0.7$ between A∞ (δ 7.53) and A[2.2]A (δ 6.83: maximum shielding between the two anthracene moieties forced to be in a quasi *syn* conformation). It is thus apparent that for A2A to A11A the systems show no preference for a *syn* conformation in solution. *One has to be aware, however, that these data reflect the average of several sets of conformers in equilibrium at room temperature.* In the case of A1A, the chemical shifts for H^2 and H^3 exhibit significant shielding ($\Delta\delta = 0.14$), contrasting with the absence of effect for H^{10}; this suggests that, at least in $CDCl_3$, the average conformation of A1A is in agreement with that of the crystal (*vide infra*).

X-Ray structure analysis. In the crystalline state of A1A (Fig. 1), the dihedral angle between the two anthracene rings was found by Becker *et al.*[9c] to be 88°; the tetrahedral angle about the A—CH_2—A linkage is 117° and the aromatic systems deviate markedly from planarity. According to the authors, the CH_2 group between the two A rings increases the steric interaction as compared to A0A; this should result in a π–π intramolecular interaction (see UV spectroscopy section below).

The crystal structure of A2A is described below; a projection of the unit cell is represented in Fig. 2.

The crystal data is given in Table 2 and selected structural parameters are listed in Table 3. The data clearly reveal an *anti* conformation with respect to the ethane bond and a more-or-less parallel arrangement of the anthracene moieties in the crystal. The crystal structure provides a snapshot that often reflects the most favourable conformation in solution, but packing effects have to be taken into account and a quantitative comparison is not possible. Similar observations were made by Becker and co-workers for 1,2-di(10-acetoxy-9-anthryl)ethane.[42] Besides, from fluorescence studies at low temperature, an *anti* conformation was also proposed for di(10-phenyl-9-anthryl)ethane.[7m]

UV absorption spectroscopy. The shape and wavelengths of the UV absorption spectrum may reveal ground state inter-

Table 4 Wavelength (λ/nm) of the 0–0 peak of the first electronic absorption band (^1L_a) of A*n*A and the reference compound A∞. A0A has not been included because A∞ is not the proper reference compound

Solvent	A1A	A2A	A3A	A4A	A5A	A6A	A7A	A8A	A9A	A10A	A∞
MCH	395[a] 396[b]	392	389	388	388	387	387	387	388	387	387
EtOH	394[c]	391 391[c]	389	388	387	387	387	387	387	387	387

[a] In benzene.[7b] [b] In CH_2Cl_2.[9c] [c] In CH_3CN (this work).

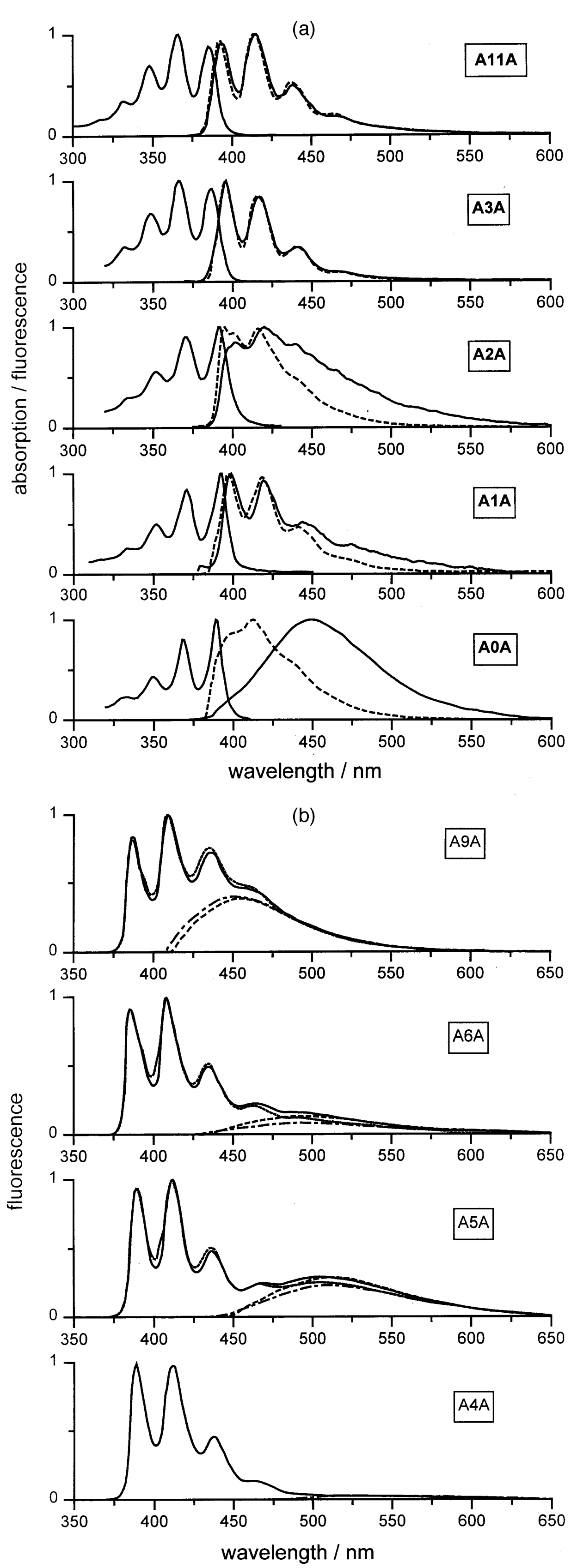


Fig. 3 (*a*) Absorption and corrected fluorescence spectra of A*n*A ($n = 0,1,2,3,11$) in nondegassed acetonitrile (———) at room temperature. For comparison, the fluorescence spectra in *n*-hexane (– – – –) are also shown. All spectra are normalized to the band maximum. (*b*) Corrected fluorescence spectra of A*n*A ($n = 4,5,6,9$) in degassed ethanol (———) and methylcyclohexane (MCH) (– – – –). Excimer spectra (—·—·— in MCH and – – – – in ethanol) were drawn by subtracting the reference spectrum of A∞ (not shown here) from the A*n*A spectra. A*n*A ($n = 7,8$) spectra, not shown, also exhibit excimer bands.

actions between the aromatic moieties. One salient feature is that the first electronic transition (^1L_a) shows *a clear vibronic structure* for the whole series of A*n*A, resembling that of A∞; this implies that there is *no strong π–π interaction* between the two anthracene rings in solution. Nevertheless, when one considers the onset of the ^1L_a transition (Table 4), a bathochromic shift is noted from A3A to A1A, which indicates some degree of interaction between the rings for short-chain bichromophores (the maximum shift is 600 cm^{-1} for A1A in CH_2Cl_2). Moreover, this absorption transition does not appear to be very sensitive to the solvent polarity (Table 4). The redshift can be understood within Förster exciton theory[43] by the interaction of the ^1L_a transition moments on the two anthracene moieties.

In summary, the 9,9′-dianthryls A*n*A do not appear to exhibit significant intramolecular interactions between the two aromatic halves in the ground state conformation, except for the *short-chain compounds* A2A to A0A for which absorption redshifts point to weak inter-ring interactions.

Excited state properties

Chainlength effects on absorption and fluorescence. The absorption and fluorescence spectra of A*n*A are displayed in Fig. 3 in nonpolar *n*-hexane and polar acetonitrile where polarity-induced effects are strong. The absorption bandshape is highly structured and largely solvent independent, except for the above-discussed small redshifts. Also, the fluorescence bandshape barely changes for A11A and A3A, indicating that the excimer contribution to the spectra is small. For $n = 1$ and 2, the spectral shape starts to deviate markedly, which is indicative of additional fluorescing components. For $n = 0$, a strongly redshifted and structureless CT band is found, with only a minor fraction of structured DE fluorescence at the short-wavelength end. In this case, sandwich-type excimer formation is not possible, and the solvatochromic redshift in solvents of different polarities[14,18,23] clearly identifies the CT character of the band.

The deviations observed for $n = 1$ and 2, which are connected with a loss of structure of the fluorescence spectrum,[44] can be understood as the result of the overlapping emissions from (*i*) a structured DE component, (*ii*) an unstructured excimer, and (*iii*) an unstructured CT component. The question arises whether these additional components are predominantly of the excimer- or CT-type. The three components have been shown to be simultaneously present in a derivative of A1A.[45]

The absorption spectra do not show this loss of vibrational structure, which indicates that the unstructured component of the fluorescence spectra cannot be populated by the absorption process (electronic motion only, Franck–Condon principle) but only by a subsequent nuclear rearrangement in the excited state.

The very similar fluorescence bandshapes for A3A and A11A in acetonitrile suggest the question whether intramolecular excimer formation occurs at all in compounds A3A to A11A. Fig. 3(*b*) displays the fluorescence spectra of A*n*A with intermediate chainlengths $n = 4$ to 9 in nonpolar and polar solvents. In these cases, an excimer band redshifted with respect to the anthracene band is clearly observed, but the relative intensities strongly depend on the length of the linking chain. This figure also shows that the excimer component is largely insensitive to solvent polarity, both in spectral position and relative intensity. This behaviour is in contrast to the polarity-induced enhancement of unstructured spectral components for A0A, A1A and A2A [Fig. 3(*a*)].

Weak excimer components can also be detected by inspecting the fluorescence decay traces. For A∞, only monoexponential fluorescence behaviour is observed, whereas A1A to A3A and even A11A all exhibit biexponential behaviour.

Table 5 Decay components for A*n*A, for the reference compound A∞, and for A6(O_3)A, measured at room temperature in *nondegassed solutions* within the short-wavelength band (400–420 nm)

	A∞	A11A	A3A	A2A	A1A	A0A	A6(O_3)A
In hexane							
$\tau_1{}^a$/ns	—	1.7	1.7^b	0.5	0.9	—	0.3^c
τ_2/ns	4.8^d	4.7	2.9	1.7^d	3.4	4.1	8.7
In acetonitrile							
τ_1/ns	—	1.6	—	0.9	1.1	—	0.3^c
τ_2/ns	7.3	5.1	4.3	2.3^d	4.4	12.5	10.4

[a] With large weight: relative pre-exponential factor $\alpha_1 = 0.5$–0.8 (for $\Sigma\alpha_i = 1$) except where indicated otherwise. [b] Very small weight ($\alpha_1 = 0.1$). [c] $\alpha_1 = 0.99$ at 400 nm. [d] Slightly longer lifetimes (factor *ca.* 1.5) have been determined in degassed solvents in ref. 7*j*.

The decay times determined are collected in Table 5. The relative contribution of τ_1 changes somewhat with emission wavelength, but both τ values are wavelength independent. This is consistent with an excited state equilibrium between an excimer and a DE state, after an initial equilibration phase (τ_1). The absence of fluorescence spectral broadening in the case of A11A and A3A indicates that these excimer contributions are minor, at least in nondegassed acetonitrile.

If we make the assumption that the short decay component τ_1 reflects the inverse of the excimer formation rate constant, one observes in Table 5 that for $n = 11$, the formation is slowest, consistent with the requirement of large structural rearrangements necessary to arrive from the extended to the sandwich-type excimer conformation. Interestingly, the excimer formation rate for A1A also appears to be slower than for A2A, suggesting that A1A requires a more important rearrangement process than A2A.

The longer decay component τ_2 is essentially connected with deactivation of the excimer E*. Possible photochemical reactions originating at E* should thus shorten τ_2. Such a shortening is especially observed for A2A and may indicate a particularly efficient dimerization channel, in agreement with the increased photocyclomerization quantum yield for A2A.[7g,7j]

For comparison with the $(CH_2)_n$-bridged systems, Fig. 4 shows the fluorescence spectra of A6(O_3)A in nonpolar and polar solvents. In contrast to A3A and A11A but similar to A5A and A9A, a strong excimer band is present, which does not show a redshift with increasing solvent polarity. Although the chainlength in A6(O_3)A is not much different from that in A9A and A11A, these compounds show a significant difference with respect to excimer formation tendency. In A11A, the excimer band is virtually absent, and in A9A, it is strongly blueshifted in comparison to the excimer band of A6(O_3)A. A likely reason is the increased chain flexibility together with the accessibility of *gauche* conformations in A6(O_3)A due to the ether oxygens, which allows a more stable sandwich-type structure to be reached in the excimer state. The lack of a solvent-polarity-induced redshift in A6(O_3)A is indicative of an emissive state without charge separation with a large-overlap sandwich-type excimer structure that precludes symmetry breaking (large excited-state interaction matrix element V^{12}).

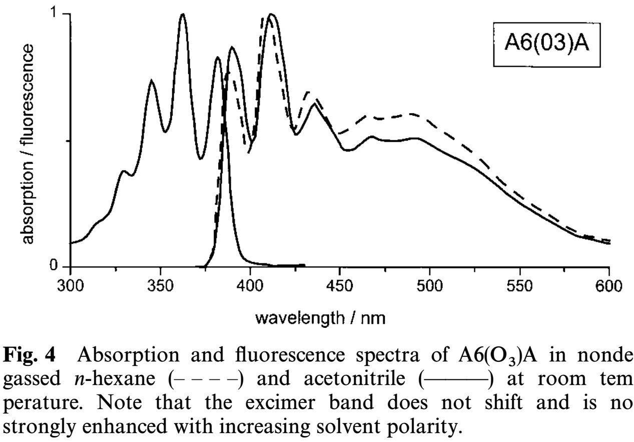


Fig. 4 Absorption and fluorescence spectra of A6(O_3)A in nondegassed *n*-hexane (– – – –) and acetonitrile (———) at room temperature. Note that the excimer band does not shift and is not strongly enhanced with increasing solvent polarity.

The increased chain flexibility is also reflected in the shorter decay component τ_1 (0.3 ns) for A6(O_3)A with respect to A11A (1.7 ns). The presence of rise times (negative pre-exponential factors for τ_1) within the excimer band and the constancy of the lifetimes throughout the dual fluorescence clearly establish the precursor-successor $DE^* \rightleftharpoons E^*$ equilibration mechanism.

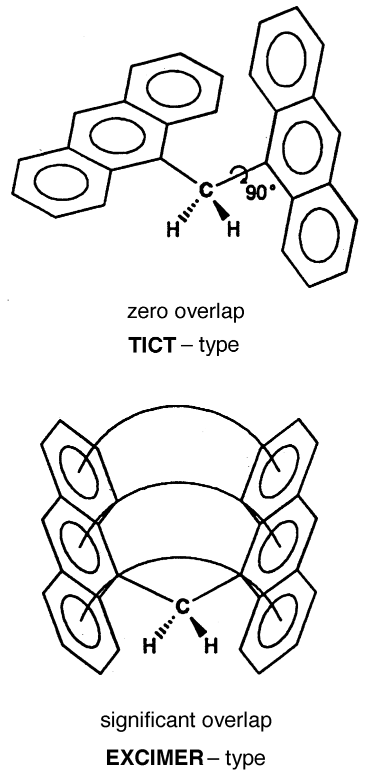
Solvent polarity effects and dual fluorescence. Table 6 gives an analysis of the fluorescence spectra of Fig. 3, in terms of the structuring factor S[44] defined in the footnote of this table and in terms of the intensity ratio r of the first to the second vibronic band. As the chain is shortened, the spectra lose structure (Fig. 3), which is expressed in a decrease of S, and is even present for A11A as compared to A∞. This closer analysis thus shows some spectral evidence of excimer formation. This can also be seen by the value r, which indicates a change of the Franck–Condon bandshape for different chainlengths.

From the particularly low value of S for A2A, a relatively large excimer component can be assigned, in agreement with literature.[7p] This is different from previous studies of chainlength effects where a maximum for the excimer band was found for $n = 3$ (diphenylalkanes[4a] and dipyrenylalkanes[6a]). Here, the excimer component for A3A is clearly less than for A2A.

Table 6 Shape and structuring of the fluorescence spectra of A*n*A

	A∞	A11A	A3A	A2A	A1A	A0A
In hexane						
r^a	0.94	0.94	1.19	1.02	1.04	—
S^b	0.72	0.62	0.64	0.19	0.43	<0
In acetonitrile						
r^a	—	0.92	1.20	0.85	1.08	—
S^b	—	0.55	0.58	0.14	0.42	<0

[a] Intensity ratio of the first to second vibronic peak I_1/I_2. [b] Structure factor $S = 1 - 2\,I_v/(I_1 + I_2)$, where I_v is the intensity in the valley between peaks 1 and 2.



Scheme 5 Two possible adiabatically formed excited species with smaller and larger π-overlap relevant for the photophysics of A1A.

A1A also shows spectral broadening (reduced S values), although an excimer with strong π-overlap is not possible in this short-chainlength system. We can, however, conceive of an excimer-type conformation with partial overlap of the anthracene π-systems (Scheme 5).

Both A2A and A1A show significant enhancement of the red spectral tail with increasing solvent polarity. This suggests a polarity-dependent redshifted component[45] in the spectra of A1A and A2A.

For A0A, these polarity dependences are strongly enhanced (Fig. 3) and in this case have been interpreted as solvent-induced symmetry-breaking [formation of a twisted intramolecular charge transfer (TICT) state],[12,17,18] which becomes possible due to the small overlap (90° twisted ground state) conformation.[13,46,47] A similar conformer is also possible for A1A and actually corresponds to the preferred ground state conformation in the crystal,[9c] and we therefore propose in Scheme 5 the competition of two excited state conformations for this compound, a large-overlap one giving the possibility of excimer formation (no solvent-induced redshifts, large interaction V), and a small-overlap perpendicular one (TICT-type conformation, small V). The latter is thought to be responsible for the polarity-induced redshifts. A third structured fluorescence component should arise from the DE state. This three-state kinetic scheme has been verified for a hydroxy derivative of A1A by multiple spectra and a detailed analysis of fluorescence decay traces at low temperature where three lifetimes are found.[45]

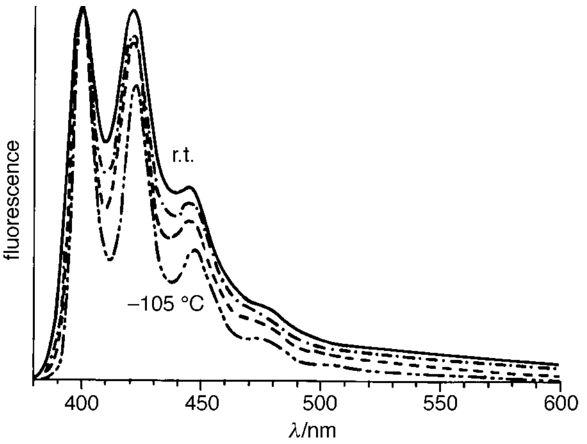


Fig. 5 Temperature effect on the fluorescence spectrum of A1A in ethanol. The spectra are normalized at the first band.

As supporting evidence for the dual fluorescence nature of A1A in Fig. 3, Fig. 5 shows the temperature dependence of the fluorescence of A1A in ethanol. It can be seen that the red component is gradually enhanced with increasing temperature. At low temperature, the full structure of the typical DE fluorescence is restored, thus TICT and excimer components are frozen out.

Conclusions

The comparison of a large variety of 1,n-di(9-anthryl)alkanes with NMR, X-ray, UV absorption and fluorescence methods allows us to draw several conclusions that can be summarized as follows:

(*i*) There are only weak ground state interactions consistent with preferred extended conformations in solution.

(*ii*) A2A populates the *anti* conformation in the crystal.

(*iii*) Fluorescence decay analysis yields evidence for excited state photoactivity in all cases.

(*iv*) Further emission components are evident in the spectra of A1A and A2A, but are unexpectedly weak for A3A.

(*v*) These additional fluorescence components show a strong solvent polarity dependence consistent with charge separation. This is explained with a model involving two fluorescent product species, an excimer-type (larger overlap and π-interaction) and a TICT-type (near perpendicular chromophore arrangement).

(*vi*) With a more flexible linking chain as in A6(O_3)A, large excimer bands are also observed for long chains. Their polarity independence in this case testifies to their weakly polar nature consistent with a large sandwich-type overlap.

(*vii*) For polymethylene $(CH_2)_n$ chains longer than $n = 2$, the solvent polarity was found to have no influence on the intramolecular excimer formation.

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