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Belt-Shaped Cyclophanes via Photodimerization of Phenanthro-Condensed [18]Annulenes

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A novel cyclophane type can be obtained by photocyclodimerization reactions of condensed [18]annulenes. Quantitative yields in pure columnar liquid crystalline phases and high yields in 10^{-6} M solution raise the inquiry about the unusual dimerization mechanism in this process. Concentration-dependent measurements of the emission and excitation spectra and the fluorescence lifetimes reveal a ground state aggregation in solution even at very low concentrations.

Introduction

Recently we reported briefly on the synthesis of a new class of cyclophanes called "*belt cyclophanes*".[1] They were formed from disk-shaped [18]annulenes which are condensed symmetrically (C_3) with three phenanthrene units. Two main types of systems could be realized. They differ in the phenanthrene anellation. The investigated [18]annulenes fused with phenanthrenes in the 1,9-position (**1a**–**e**) or in the 2,10-position (**2a**–**i**) are shown in Chart 1. The syntheses of **1a**–**c**,[2] **1d**,[3] and **2a**–**c**,**e**,**g**,**h**[3] were described in previous papers.[2,3]

Here, we report (1) a detailed description of the synthesis of **1e** which differs in some steps from that of other compounds **1**, the isolation of a [24]annulene (**13**), and the experimental data of **2d**,**f** and of the deuterated compound **2i**; (2) the structural study of the new compounds and their mesogenic properties; and (3) the photodimerization of **1e** and **2a**,**e**,**i** together with a photophysical investigation of **2e**.

Synthesis of Phenanthro-Condensed [18]Annulenes

The synthesis of **1e** is outlined in Scheme 1. The starting material 3,4,5-tris(dodecyloxy)benzaldehyde (**3**)[4] gave the alcohol **4** in an almost quantitative yield using a Grignard reaction. The phosphonium salt **5** could be obtained by treatment of **4** with triphenylphosphonium hydrobromide. Wittig reaction of **5** with commercially available 2-bromobenzaldehyde (**6**) resulted in the formation of the substituted stilbene **7** as an *E*/*Z* mixture. The pure isomers could be separated by repeated crystallization; however, that was not necessary, because the following oxidative photocyclization[5] is accompanied by a photochemical *E*/*Z* interconversion. In principle, the cyclization of (*Z*)-**7** could lead to two different phenanthrene systems, **8** and **9**; however, a highly regioselective process, (*Z*)-**7** → **8** was observed. The resulting bromophenanthrene **8** was converted to the aldehyde **10** by treatment with BuLi and DMF. After the quantitative formation of the Schiff base **12**, a cyclocondensation reaction (Siegrist reaction[6]) led directly to the expected [18]annulene **1e**. Linear oligomers were formed as the main side products. Due to their polar end groups, they could be easily removed by chromatography on a short column. Nevertheless, the ^{1}H NMR spectrum of the eluted product revealed two sets of signals. Since no methyl and phenylimino end groups could be detected, we concluded that two types of cyclic oligomers were generated, the *trimeric* [18]annulene **1e** and the *tetrameric* [24]annulene **13**. Actually, the two cyclic oligomers could be separated by repeated column chromatography. The second fraction, isolated in 39% yield, was characterized as the expected [18]annulene **1e**. The first fraction (3%) was identified as tetrafold phenanthro-anellated [24]annulene **13**; the structure was assigned by using NMR and FD-MS (field desorption mass spectroscopy) techniques.

Structural Study

The larger π-system of **13** shows a UV/visible spectrum that is not significantly shifted in comparison to the spectrum of **1e**. Although $\lambda_{\max}$ values of **13** and **1e** are to 352 and 338 nm, respectively, both absorptions end at 450 nm, and this is in contrast with the known spectrum of [18]annulene. Obviously, the conjugation of **1e** and **13** is impaired.[7] As shown in a previous paper, annelated [18]annulenes of type **1e** are characterized by nonplanar ground state conformations.[2] As a consequence of fast equilibration between C_3 and C_1 conformations, the molecules show C_{3h} symmetry on average. This result is in accordance with force field calculations[2,3] and is supported by the ^{1}H NMR spectra; particularly noticeable is the chemical equivalence of the geminal protons of the OCH_2 groups. The [24]annulene **13** exhibits a lower symmetry, as exemplified by the diastereomeric

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) Meier, H.; Müller, K. *Angew. Chem.* **1995**, *107*, 1598; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1437.

(2) Meier, H.; Kretzschmann, H.; Kolshorn, H. *J. Org. Chem.* **1992**, *57*, 6847.

(3) Kretzschmann, H.; Müller, K.; Kolshorn, H.; Schollmeyer, D.; Meier, H. *Chem. Ber.* **1994**, *127*, 1735.

(4) Kosteyn, F.; Zerban, G.; Meier, H. *Chem. Ber.* **1992**, *125*, 893.

(5) *Excited States in Organic Chemistry*; Barltrop J. A., Coyle J. D., Eds.; Wiley: London, 1975; pp 246–287. Mallory F. B.; Mallory C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 1.

(6) Siegrist, A. E. *Helv. Chim. Acta* **1981**, *64*, 662 and references therein.

(7) The UV/vis spectra of **1e** and **13** resemble the spectrum of 9-(2-phenyl ethenyl)phenanthrene. See also: Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705 and references therein.

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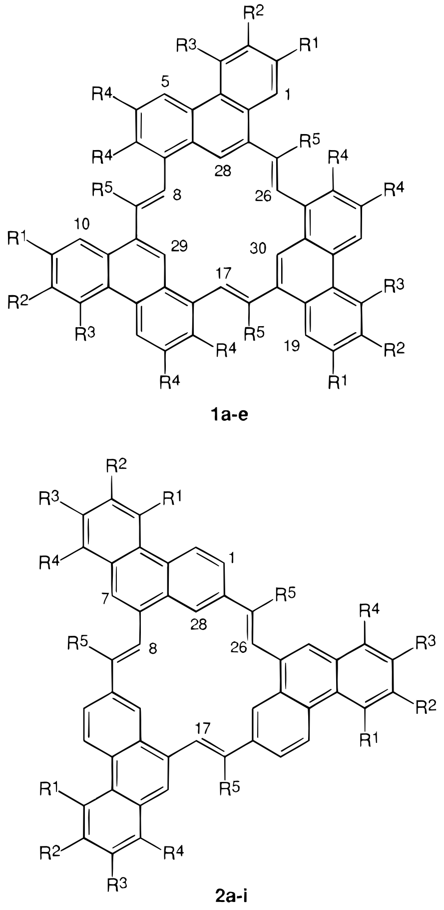
Chart 1

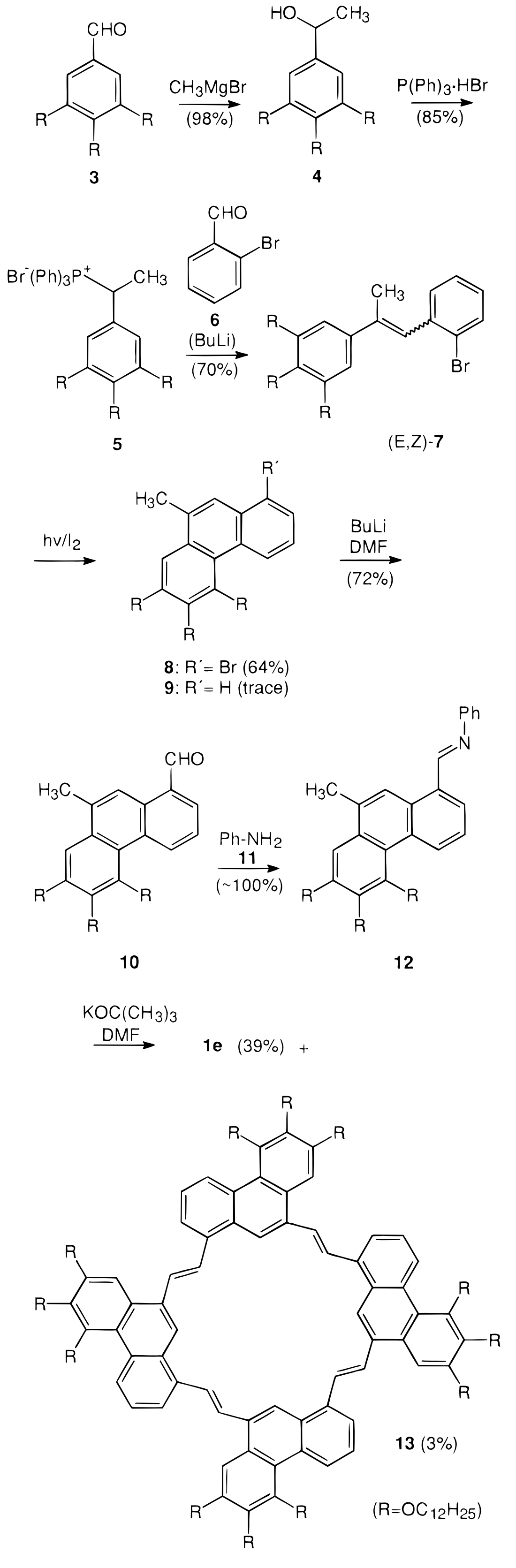


1a-e

2a-i

	R^1	R^2	R^3	R^4	R^5
1a	H	H	H	OCH_3	H
1b	H	H	H	OCH_3	D
1c	H	H	H	OC_6H_{13}	H
1d	H	OC_6H_{13}	H	OC_6H_{13}	H
1e	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	H
2a	H	OC_6H_{13}	H	H	H
2b	H	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	H
2c	H	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	H
2d	OCH_3	OCH_3	OCH_3	H	H
2e	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	H	H
2f	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	H	H
2g	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	H
2h	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	H
2i	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	D

Scheme 1



OCH_2 protons in the ^1H NMR spectrum; indeed, six signals for three different CH_2 groups are consistent with C_4 or S_4 symmetry. More information about the conformational behavior of **13** could be obtained from force field calculations (MMX, Serena, PCM Version 4) of a model compound in which the outer six-membered rings with the side chains were neglected. According to the calculation, the tetrafold-anellated [24]annulenes should exist in a highly twisted boat conformation, S_4.

The boat form can undergo simultaneous or consecutive torsions around the single bonds linked with the olefinic bonds. This process involves a compression (c) and a stretching (s) in directions which are perpendicular to each other and to the S_4 axis. Thus, energetically close-lying local minima belonging to the point groups C_2 or C_1 could be considered. The optimized geometry (ΔH_f = 215.3 kcal/mol) is shown in Figure 1. The fast equilibration between these conformations induces ^1H NMR signals of a symmetrical species, but the lack of planarity results in diastereomeric OCH_2 protons.

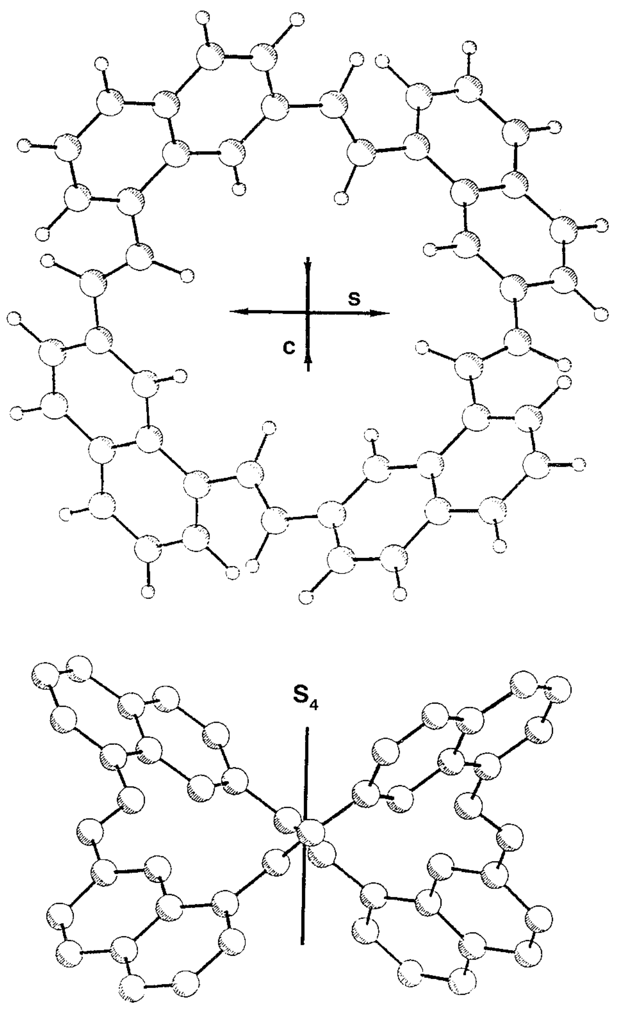


Figure 1. Boat conformation (S_4) of [24]annulene condensed with four naphthalene units (calculated by applying the force field program MMX, Serena, PCM Version 4). Illustration of the molecular dynamics: compression, c; stretching, s.

Liquid Crystal Properties

Previous investigations[2,3] on the possible mesogenic properties of this family of molecules have shown that **1c** and **2c**,**e**−**i** generate mesophases; **1a**,**b** and **2a**,**d** have too short or too few side chains. The reason why the nonakis(hexyloxy)-substituted system **1d** and the hexakis(dodecyloxy)-substituted system **2b** do not form liquid crystalline (LC) phases has not been established. Except for the nematic discotic phase (N_D) generated by molecular pairs of **1c**,[3] we found hexagonal columnar phases in all LC systems. In contrast to the on average planar [18]annulene **1e**, the nonplanar [24]annulene **13** was found not to form an LC phase; the molecular geometry seems to be at the origin of this behavior. The temperature intervals of the LC phases are very broad;[1] **1e**, for example, shows a D_{hd} phase between −4 and 266 °C in the heating curve of the differential scanning calorimetry and between 250 and −20 °C in the corresponding cooling curve. The characterization of the phases was performed by using polarization microscopy and small-angle X-ray measurements. The intense (100) reflection at $2\Theta = 3.02°$ corresponds to an intercolumnar distance of 2.93 nm. Due to the flip of the central 18-membered ring, there is no regular distance within the columns. A macroscopic orientation of the columns can be achieved by the application of a high magnetic field.[8]

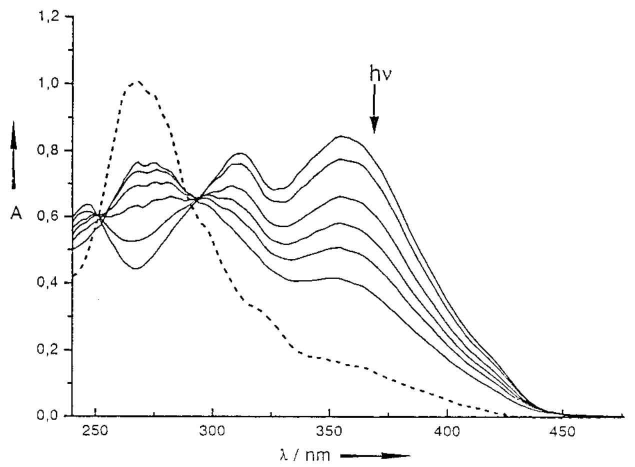


Figure 2. UV/vis spectra of the monochromatic irradiation ($\lambda = 366$ nm) of degassed samples of **2e** (—) (10^{-6} M solution in CH_2Cl_2) and of the pure dimer **15e** (- - -). Due to small amounts of side products, the curve of **15e** does not exactly fit the isosbestic points.

Photochemistry in Solution and in the Mesophase. (1) Formation of Photodimers. The anellated annulenes **1** and **2** exhibit remarkable photochemical properties. The behavior in isotropic highly diluted solution is illustrated for **2e**, which, during irradiation of a dichloromethane solution (10^{-6} M) at 366 nm undergoes typical spectral modifications (Figure 2). The gradual decrease in intensity of the strong absorption band peaking at 360 nm is accompanied by the emergence of a new band ($\lambda_{max} \approx 260$ nm); the presence of two isosbestic points at 253 and 293 nm is in favor of the formation of a single photoproduct. The strong green fluorescence emission of the starting material disappeared after the irradiation. The other annulenes behaved similarly. The samples should be degassed prior to irradiation; otherwise, the starting materials undergo partial oxidative degradation.

To identify the photoproduct, degassed (inert gas bubbling) benzenic solutions (10^{-4} M) of **1c**,**e** and **2a**,**e**,**i** were irradiated with a Hanovia 450 W medium-pressure mercury immersion lamp through a Duran glass filter ($\lambda \geq 280$ nm). The course of the reaction was monitored using UV/vis as well as ^{1}H NMR spectroscopy. The UV/vis spectrum of the photoproduct of **2e** was found to be identical to that recorded for the 10^{-6} M solution, which demonstrated the occurrence of the same photochemical process at both concentrations. In all cases, except for **1c**, the photoproducts were identified as photodimers (Scheme 2) by NMR and mass spectra (see Experimental Section); they are constructed through a threefold regio- and stereospecific $[2\pi + 2\pi]$ cyclodimerization and have a *belt cyclophane* shape. Moreover, *Z* configurations of **1** and **2** could not be observed by NMR spectroscopy, probably because of an unfavorable stereochemistry. **1c** proved to be photochemically inert under these conditions.

Irradiation of thin LC films of **1c**,**e** and **2e**,**i** at room temperature did not yield any photoproduct; only when temperatures close to the clearing point were reached did photodimerization leading to the cyclophanes occur. The process induced a fast breakdown of the LC phases. Compound **2i**, for example, yielded quantitatively **15i** at 230 °C. The olefinic double bonds as reactive centers are

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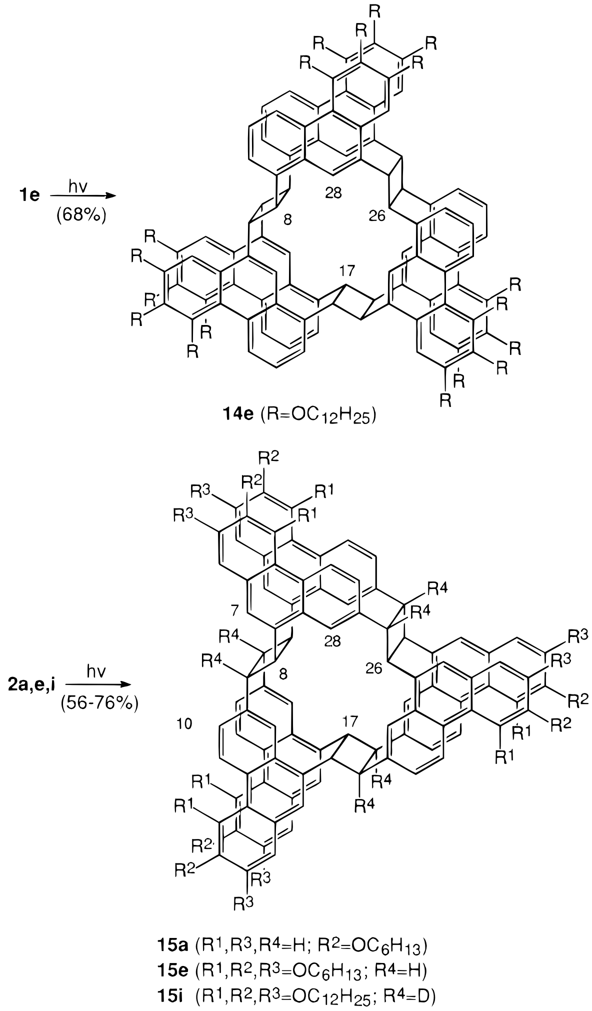
(8) A detailed publication of this effect is in preparation.

Scheme 2



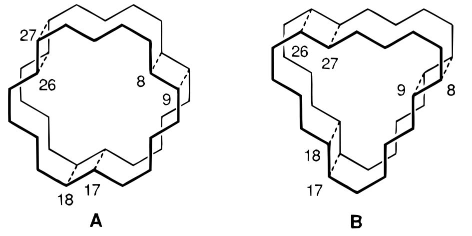
14e (R=OC$_{12}$H$_{25}$)

15a (R^1,R^3,R^4=H; R^2=OC$_6$H$_{13}$)
15e (R^1,R^2,R^3=OC$_6$H$_{13}$; R^4=H)
15i (R^1,R^2,R^3=OC$_{12}$H$_{25}$; R^4=D)

presumably too far away from each other in the columnar arrangement to form an activated complex within the lifetime of the excited state. When the LC phase is sufficiently heated, the columnar rotation increases and enhances, therefore, the probability for a π-bond interaction. Compound **1c** is again an exception; it is photostable in the LC phase as well as in solution.

(2) ^{1}H NMR Study of the Belt Cyclophanes. The flexibility of the [18]annulenes **1** and **2** disappears after the threefold cycloaddition, since the belt cyclophanes have a rigid skeleton. A priori, two distinct photodimers (**14** and **15**) could be formed: besides the preferred[2] conformation, another possible conformation containing a C_3 axis should be considered (Chart 2); although B has a higher enthalpy of formation, ΔH_f, its intermediacy could not be excluded with the result that the inner and outer protons 8-H/9-H, 17-H/18-H, and 26-H/27-H would have exchanged their places. The symmetry of the belt cyclophane in both cases is C_{3h}. To distinguish between these two possible structures, a nuclear overhauser effect (NOE) study was undertaken, for which the isotope-labeled 9-D, 18-D, 27-D compounds **2i**/**15i** were prepared. The labeling permits an unambiguous assignment of the olefinic signals. Irradiation of the ^{1}H NMR signal of 8-H in the undeuterated systems gave a positive NOE for 28-H, whereas irradiation of 9-H in the undeuterated system gave a positive NOE for 10-H and 7-H (Scheme 2). These results indicate that the preferred conformation of **2i** is retained in **15i**; consequently, the structure **B** (Chart 2) can be ruled out.

Chart 2



Other important features of the ^{1}H NMR regard some chemical shifts and coupling constants: the inner protons of **1** and **2**, 8-H, 17-H, and 26-H, lead to a doublet at δ 8.00 ± 0.25, whereas the outer protons 9-H, 18-H, and 27-H are characterized by a doublet at δ 7.45 ± 0.40; the olefin coupling constants were found to be 16.0 ± 0.5 Hz. The resonance of the inner protons at lower field rules out a diamagnetic current in the 18-membered rings; these annulenes have thus the character of aromatic "islands" linked by olefinic bridges with *E* configurations. A macrocyclic diatropicity cannot be detected. The photocyclodimerization transforms the olefinic double bonds to four-membered rings, in which the inner protons also resonate at lower field than the outer protons: δ 6.84 ± 0.05 versus δ 5.80 ± 0.30. Another significant change in the ^{1}H NMR shifts during the dimerization was observed for the inner aromatic protons 28-H, 29-H, and 30-H: steric compression in the annulene center induces a downfield shift from δ 8.65 ± 0.20 to δ 9.65 ± 0.25.

(3) Further Investigation of the Photochemical Properties of 2e. In view of the usual photochemical behavior of stilbenoid compounds,[9] which readily undergo cis–trans isomerization or oxidative cycloisomerization and require much higher concentrations to photodimerize,[9,10] it is possible to observe the efficient photodimerization of these phenanthro[18]annulenes at concentrations as low as 10^{-6} M. A short-lifetime singlet state reaction could be considered if aggregates are present in the ground state. This is supported by the tendency of these compounds to form molecular stacks and columnar discotic LC phases. Evidence of the aggregation process is given by the observed high-field shift ($\Delta\delta = 1$ ppm) of the aromatic and olefinic protons in NMR spectra when the concentration increases from 10^{-3} to 3×10^{-2} M.

The *fluorescence* emission techniques were used to cover the concentration range below 10^{-3} M, especially in the case of **2e**. The solutions are strongly fluorescent in the visible range. The fluorescence emission quantum yield of a degassed solution of **2e** in cyclohexane ($\sim 10^{-6}$ M) was found to be $\phi_F = 0.56$. The fluorescence decay was also studied by the *single-photon timing* technique at three concentrations: 10^{-6}, 10^{-4}, and 10^{-3} M. At very low concentration (10^{-6} M), the decay curve was reasonably fitted with a single-exponential function. Three different observation wavelengths ($\lambda = 450, 500, 550$ nm) were used (Table 1). The lifetime is ~5.4 ns at room temperature, a value in the range of those found for stilbenoid compounds.[9,10] The radiative lifetime $\tau_0 = \tau_F/\phi_F$ amounts to 9.8 ns. At 10^{-4} M, the fluorescence decays are no longer single exponential, and a sum of two exponentials is necessary to give the best fit for the fluorescence profiles, indicating the coexistence of two

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(9) Meier, H. *Angew. Chem.* **1992**, *104*, 1447; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399 and references therein.

(10) See also: Meier, H.; Zertani, R.; Noller, K.; Oelkrug, D.; Krabicheler, G. *Chem. Ber.* **1986**, *119*, 1716.

Table 1. Fluorescence Decay Data of Compound 2e in Cyclohexane at Different Concentrations, Obtained by the Single-Photon Timing Technique at Room Temperature[a]

concn (M)	λ_{obs} (nm)	A_1	λ_1^{-1} (ns)	A_2	λ_2^{-1} (ns)	χ^2
10^{-6}	450	1.12	5.25			1.15
	500	1.25	5.40			1.21
	550	0.32	5.66			1.17
10^{-4}	450	0.77	3.24	0.34	6.42	1.16
	500	0.75	3.33	0.36	7.42	1.09
	550	0.25	2.59	0.25	7.13	1.30
10^{-3}	450	0.94	2.97	0.22	6.60	1.11
	500	0.73	2.57	0.26	8.08	1.05
	550	0.68	3.72	0.33	9.80	1.16

[a] The fluorescence emission was monitored at a right angle for the lowest concentration (10^{-6} M) and by front-face illumination for higher concentrations (10^{-4} and 10^{-3} M). The decay curves fit equations such as $A_1 \exp(-1/\lambda_1 t) + A_2 \exp(-1/\lambda_2 t)$; at 10^{-6} M, $A_2 = 0$. Statistical tests (other than χ^2), i.e., autocorrelation function, weighted residuals, Durbin−Watson parameters, were found to be satisfactory (accuracy, ±10%).

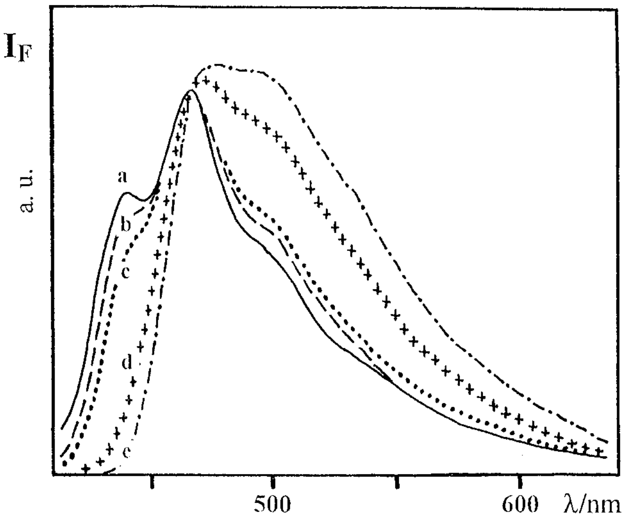

Figure 3. Fluorescence emission spectra of **2e** ($\lambda_{exc} = 350$ nm) measured at room temperature in cyclohexane for different concentrations: (a) 10^{-5}, (b) 5×10^{-5}, (c) 10^{-4}, (d) 5×10^{-4}, and (e) 1×10^{-3} M.

emitting species, whose associated kinetic parameters were found to be ~3 and 7 ns, respectively. Changing the concentration to 10^{-3} M induced small additional alterations to the lifetimes (see Table 1).

Such a clear modification of the S_1 lifetimes is reflected in the stationary state fluorescence spectra, which were recorded in cyclohexane in the concentration range 10^{-5}–10^{-3} M (Figure 3). As the concentration increases, the fine structure attenuates, with the clear disappearance of the 460 nm band (reabsorption) and the stepwise growing and widening of the 510 nm vibronic band. Similar observations can be made on the excitation spectra (recorded at 440 and 500 nm) with the ~415 nm absorption vibronic band (Figure 4). Those observations are consistent with the occurrence of at least two ground state species (monomer, dimer, and possibly higher aggregates) whose ratio alters with the concentration change. The association probably rests on dispersion forces between the large disk-like molecules.

Still unanswered are the difficult questions of the aggregation numbers and the assignment of the lifetimes to certain species of these *polychromophoric macrocyclic compounds*. Further experimental studies involving concentration, temperature, and wavelengths effects in both the isotropic phases and the mesophases are desirable to unravel these problems.

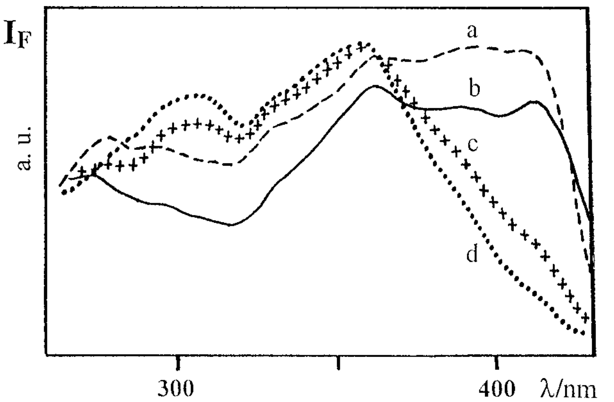

Figure 4. Fluorescence excitation spectra of **2e** ($\lambda_{obs} = 440$ nm) measured at room temperature in cyclohexane for different concentrations: (a) 10^{-3}, (b) 5×10^{-4}, (c) 10^{-4}, and (d) 5×10^{-5} M.

A related, although in several respects different, type of photochemical reaction has been performed on photoreactive diskotic mesophases forming molecules such as hexacyclenehexacinnamates.[11] In this case, the chromophores can undergo *cis−trans isomerization* and $[2\pi + 2\pi]$ *cycloaddition*; UV irradiation of thin films led to only small amounts of oligomeric products. But in cyclohexane, columnar aggregates seemed to be formed, which led progressively to photodimers, trimers, and oligomers under irradiation at 300 nm.

Summary and Conclusions

A series of new (*abc*)phenanthro-condensed [18]annulenes has been synthesized and found to have the properties of phenanthrene islands linked together by olefinic bridges with *E* configuration, i.e., stilbenoid compounds; substitution by alkoxy groups with long aliphatic side chains was shown to confer mesogenic properties and enhance the solubility of the hydrocarbons. These compounds exhibit interesting photochemical properties which contrast with those of most stilbene derivatives: they photocyclodimerize (neither *E*/*Z* isomerization nor cycloisomerization) even at very low concentration. The structure of these novel *belt cyclophanes* was established from NMR and mass spectra measurements. Stationary state and transient kinetic fluorescent studies at room temperature are consistent with the occurrence of *aggregation in the ground state*, which allows the threefold photocyclodimerization.

The trend to self-assemble of LC or micelles or vesicules forming molecules in solution generates a local high concentration of reactive centers favorable to *intermolecular photoreactions* even at very low overall concentration.

The case in point is an illustration of this supramolecular effect conducive to a regio- and stereospecific photocycloaddition, a sort of topochemical reaction in solution and in the mesophase.[12]

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(11) Cabrera, I.; Engel, M.; Häussling, L.; Mertesdorf, C.; Ringsdorf, H. In *Frontiers in Supramolecular Chemistry and Photochemistry*; Schneider, H. J., Dürr, H., Eds.; VCH: Weinheim, 1991; pp 311−336.

(12) Greiving, H.; Hopf, H.; Jones, P. G.; Bubenitschek, P.; Desvergne, J. P.; Bouas-Laurent, H. *Liebigs Ann.* **1995**, 1949.

Experimental Section

General. Melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively. The fluorescence spectra were corrected for emission and excitation. The fluorescence quantum yields and the lifetime measurements were performed on samples degassed by the freeze and thaw technique as described elsewhere;[13] the latter measurements were determined with an accuracy of approximately 10%. The fluorescence decay curves were fitted with the DECAN 1.0 program,[14] kindly provided by F. De Schryver. The investigation of the LC phases was performed with a polarization microscope and with small-angle X-ray scattering. The samples used for the photophysical studies were purified by repeated column chromatography on SiO_2, and their purity was controlled by HPLC (reversed phase, Sperisorb C_{18}; eluent, methanol). In the mass spectra (MSFD), the *m/e* values of the molecular ions represent the highest peak in the pattern of the unprotonated species, taking the isotopic contribution into account.

Preparation of the Annulenes 1 and 2. Compounds **1a**–**c**[2] and **1d,** and **2a**–**c,e,g,h**[3] were synthesized according to the literature methods. Nearly the same procedure[3] was used for **2d,f,i**.

(8*E*,17*E*,26*E*)-3,4,5,12,13,14,21,22,23-Nonakis(methoxy)-triphenanthro[7,8,9-*abc*:7,8,9-*ghi*:7,8,9-*mno*]cyclooctadecene (2d): yield 22%, yellow needles, mp 300 °C dec; ^{1}H NMR δ 3.96 (s, 9H), 3.99 (s, 9H), 4.04 (s, 9H), 6.86 (s, 3H), 7.15/7.88 (d, ^3J = 15.9 Hz, 6H), 7.32 (d, 3H), 7.68 (s, 3H), 8.55 (br s, 3H), 9.34 (d, 3H); ^{13}C NMR δ 55.8, 60.2, 61.2, 105.4, 118.5, 118.7, 123.3, 125.3, 127.2, 127.2, 129.6, 129.8, 130.3, 131.9, 134.9, 130.2, 142.8, 152.1, 152.4; MS (FD) *m/e* (relative intensity) 876 ($M^{\bullet+}$, 100). Anal. Calcd for $C_{57}H_{48}O_9$ (876.3): C, 78.06; H, 5.52. Found: C, 78.14; H, 5.63.

(8*E*,17*E*,26*E*)-3,4,5,12,13,14,21,22,23-Nonakis(octyloxy)-triphenanthro[7,8,9-*abc*:7,8,9-*ghi*:7,8,9-*mno*]cyclooctadecene (2f): yield 16%, clearing point 292 °C; ^{1}H NMR δ 0.92 (t, 27H), 1.34 (m, 54H), 1.38 (m, 18H), 1.58 (m, 18H), 1.93 (m, 18H), 4.09 (m, 12H), 4.14 (t, 6H), 6.96 (s, 3H), 7.32/8.08 (d, ^3J = 15.9 Hz, 6H), 7.46 (d, 3H), 7.84 (br s, 3H), 8.74 (br s, 3H), 9.61 (d, 3H); ^{13}C NMR δ 13.9, 22.6–31.8 (54C), 68.3, 73.4, 74.0, 105.9, 118.4, 118.8, 123.3, 125.4, 126.8, 127.3, 129.6, 129.8, 130.2, 131.5, 134.7, 130.0, 142.3, 151.4, 152.3; MS (FD) *m/e* (relative intensity) 1760 ($M^{\bullet+}$, 100). Anal. Calcd for $C_{120}H_{174}O_9$ (1759.3): C, 81.86; H, 9.96. Found: C, 81.71; H, 9.88.

(8*E*,17*E*,26*E*)-9,18,27-Trideuterio-3,4,5,12,13,14,21,22,23-nonakis(dodecyloxy)triphenanthro[7,8,9-*abc*:7,8,9-*ghi*:7,8,9-*mno*]cyclooctadecene (2i). The synthesis of **2i** was realized like the synthesis of **2h**.[3] The deuterium was incorporated by replacing the DMF involved in the formylation of the corresponding bromophenanthrene with DMF-d_6: yield 50%, yellow solid, clearing point 230 °C; ^{1}H NMR δ 0.87 (t, 27H), 1.29 (m, 144H), 1.58 (m, 18H), 1.96 (m, 18H), 4.14 (m, 18H), 6.98 (s, 3H), 7.49 (d, 3H), 7.87 (s, 3H), 8.13 (s, 3H), 8.79 (br s, 3H), 9.59 (d, 3H); ^{13}C NMR δ 14.1, 22.7–32.0 (90C), 68.6, 73.6, 74.2, 106.1, 118.6, 119.0, 123.6, 125.7, 126.9, 127.6, 129.8, 130.0, 130.4, 131.7, 134.9, 142.5, 151.6, 152.6; MS (FD) *m/e* (relative intensity) 2268 ($M^{\bullet+}$, 100).

Preparation of 1e and 13. 1-[3,4,5-Tris(dodecyloxy)-phenyl]ethanol (4). A solution of CH_3MgCl (31 mL, 90 mmol, 22% in THF) was added to a stirred solution of **3** (50.0 g, 76 mmol) in ether (100 mL) at 0 °C over a period of 30 min. After the mixture was refluxed for 1 h and the reaction carefully quenched with water (100 mL), the mixture was neutralized with HCl (10%). The aqueous portion was extracted twice with diethyl ether. The combined organic layers were washed with water. After drying over Na_2SO_4 and removal of the solvent, 50.19 g (98%) of a pale yellow solid, mp 41 °C, was obtained: ^{1}H NMR δ 0.86 (t, 9H), 1.24 (m, 48H), 1.41 (m, 6H), 1.43 (d, 3H), 1.75 (m, 6H), 3.88 (t, 2H), 3.94 (t, 4H), 4.75 (q, 1H), 6.52 (s, 2H); ^{13}C NMR δ 14.1, 25.1, 22.7–31.9, 69.2, 70.6, 73.4, 104.0, 137.6, 141.4, 153.2. Anal. Calcd for $C_{44}H_{82}O_4$ (674.6): C, 78.28; H, 12.24. Found: C, 78.36; H, 12.38.

{1-[3,4,5-Tris(dodecyloxy)phenyl]ethyl}triphenylphosphonium Bromide (5). A mixture of **4** (50.0 g, 74 mmol) and $Ph_3P{\cdot}HBr$ (25.32 g, 74 mmol) was refluxed for 3 h in 250 mL of $CHCl_3$. The generated water was continuously removed by an extractor. After evaporation of the solvent, the residue was recrystallized from diethyl ether to yield 62.92 g (85%) of a colorless powder, mp 64 °C: ^{1}H NMR δ 0.82 (t, 9H), 1.21 (m, 48H), 1.35 (m, 6H), 1.60 (m, 6H), 1.77 (dd, 3H), 3.54 (m, 4H), 3.84 (m, 2H), 6.21 (d, 2H), 6.44 (m, 1H), 7.59 (m, 6H), 7.69 (m, 9H); ^{13}C NMR δ 14.0, 17.2, 22.6–31.9 (30C), 35.4, 35.8, 68.9, 73.4, 108.7, 117.6, 118.4, 128.0, 128.1, 130.0, 130.1, 134.7, 134.8, 134.9, 138.1, 153.1.

(*E*,*Z*)-1-(2-Bromophenyl)-2-[3,4,5-tris(dodecyloxy)-phenyl]propene (7). A solution of BuLi (13.1 mL, 21 mmol, 1.6 M in hexane) was added to a solution of **5** (20.0 g, 20 mmol) in dry THF (150 mL) at 0 °C over a period of 15 min. After it was stirred for 10 min at 25 °C, a solution of 2-bromobenzaldehyde (**6**, 3.89 g, 21 mmol) in THF (50 mL) was added, and the mixture was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in diethyl ether. After the organic layer was washed with water and dried over $MgSO_4$ and the solvent evaporated, the residue was purified by chromatography (silica gel, toluene, 15 × 10 cm). The first fraction contained 11.56 g (70%) of the *E*/*Z* mixture of **7**. Pure (*E*)-**7**, mp 35 °C, could be obtained by repeated crystallization from petroleum ether (40–70 °C): ^{1}H NMR δ 0.89 (t, 9H), 1.28 (m, 48H), 1.49 (m, 6H), 1.82 (m, 6H), 2.12 (d, 3H), 3.99 (t, 2H), 4.03 (t, 4H), 6.78 (s, 2H), 6.80 (br s, 1H), 7.11 (m, 1H), 7.30 (m, 2H), 7.62 (m, 1H); ^{13}C NMR δ 14.1, 17.4, 22.7–31.9 (30C), 69.4, 73.5, 105.5, 126.5, 126.9, 128.1, 130.9, 132.6, 134.7, 138.3, 138.5, 138.5, 138.6, 153.0. For (*Z*)-**7**: ^{1}H NMR δ 0.89 (t, 9H), 1.28 (m, 48H), 1.49 (m, 6H), 1.82 (m, 6H), 2.12 (d, 3H), 3.73 (t, 4H), 3.90 (t, 2H), 6.28 (s, 2H), 6.47 (br s, 1H), 6.80 (m, 1H), 6.92 (m, 2H), 7.48 (m, 1H); Anal. Calcd for $C_{51}H_{85}BrO_3$ (824.6): C, 74.15; H, 10.37; Br 9.67. Found: C, 74.08; H, 10.56; Br, 9.96.

1-Bromo-5,6,7-tris(dodecyloxy)-9-methylphenanthrene (8). An *E*/*Z* mixture of **7** (4.96 g, 6 mmol), iodine (1.65 g, 6.5 mmol), and propylene oxide (50 mL) in 2 L of cyclohexane was irradiated for 48 h as described in a previous paper.[3] After 1.5 L of the solvent was removed in vacuo and the remainder was washed with 15% $Na_2S_2O_3$ and water, the solution was dried over Na_2SO_4. Chromatography of the residue (silica 4 × 30 cm; petroleum ether/toluene 2/1) and recrystallization from petroleum ether (40–70 °C) yielded 3.17 g (64%) **8** as colorless crystals, mp 34 °C: ^{1}H NMR δ 0.89 (t, 9H), 1.27 (m, 48H), 1.54 (m, 6H), 1.90 (m, 6H), 2.70 (s, 3H), 4.05 (t, 2H), 4.15 (m, 4H), 7.19 (s, 1H), 7.34 (m, 1H), 7.78 (d, 1H), 8.02 (s, 1H), 9.65 (d, 1H); ^{13}C NMR δ 14.1, 21.0, 22.7–31.9 (30C), 68.6, 73.8, 74.2, 102.3, 119.3, 122.3, 125.3, 125.7, 126.6, 129.7, 129.9, 130.0, 131.2, 133.4, 142.7, 152.2, 152.8. Anal. Calcd for $C_{51}H_{83}BrO_3$ (822.6): C, 74.33; H, 10.15. Found: C, 74.25, H, 10.34. Traces of **9** can be detected in the ^{1}H NMR spectrum of the raw product.

5,6,7-Tris(dodecyloxy)-9-methyl-1-phenanthrenecarboxaldehyde (10). To a stirred solution of **8** (3.00 g, 3.6 mmol) in dry diethyl ether (30 mL) was added *n*-BuLi (3.8 mL, 1.6 M in hexane). The mixture was stirred for 30 min at room temperature, and 1.5 mL of dry DMF was added quickly. After 2 h, the solution was treated with 10% HCl (10 mL). The organic phase was washed with water, dried over $MgSO_4$, and concentrated in vacuo. Recrystallization from petroleum ether (40–70 °C) gave 2.02 g (72%) of **8** as pale yellow needles, mp 30 °C: ^{1}H NMR δ 0.88 (t, 9H), 1.25 (m, 48H), 1.55 (m, 6H), 1.90 (m, 6H), 2.76 (s, 3H), 4.06 (t, 2H), 4.17 (m, 4H), 7.22 (s, 1H), 7.66 (dd, 1H), 7.95 (d, 1H), 9.03 (s, 1H), 9.98 (d, 1H), 10.47 (s, 1H); ^{13}C NMR δ 14.0, 21.3, 22.6–31.9 (30C), 68.6, 73.8, 74.1, 102.1, 119.0, 122.0, 124.4, 133.5, 134.2, 129.6, 130.0, 130.2, 130.4, 135.4, 142.7, 152.0, 152.8, 193.7. Anal. Calcd for $C_{52}H_{84}O_4$ (772.6): C, 80.77; H, 10.95. Found: C, 80.58; H, 10.81.

(*E*)-5,6,7-Tris(dodecyloxy)-9-methyl-*N*-phenyl-1-phenanthrenecarbaldimine (12). A mixture of **10** (1.40 g, 1.8 mmol)

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and aniline (340 mg, 3.7 mmol) was stirred at 75 °C for 3 h. During that period, the water generated was removed in vacuo (15 Torr). The excess aniline was distilled under reduced pressure; the residue contained 1.54 g (100%) of **12** as a yellow solid, mp 48 °C: ^{1}H NMR δ 0.89 (t, 9H), 1.28 (m, 48H), 1.56 (m, 6H), 1.90 (m, 6H), 2.72 (s, 3H), 4.08 (t, 2H), 4.16 (t, 2H), 4.18 (t, 2H), 7.22 (s, 1H), 7.28 (m, 1H), 7.33 (m, 2H), 7.45 (m, 2H), 7.63 (dd, 1H), 8.19 (d, 1H), 8.48 (s, 1H), 9.24 (s, 1H), 9.84 (d, 1H); ^{13}C NMR δ 14.1, 21.3, 22.7−31.9 (30C), 68.6, 73.7, 74.1, 102.2, 119.6, 121.0, 121.5, 124.9, 125.7, 127.4, 130.4, 129.1, 129.5, 130.0, 130.4, 130.7, 133.2, 142.6, 152.2, 152.5, 153.0, 160.1. Anal. Calcd for $C_{58}H_{89}NO_3$ (847.7): C, 82.11; H, 10.57; N, 1.65. Found: C, 82.13; H, 10.36; N, 1.75.

[18]Annulene 1e and [24]Annulene 13. A solution of **12** (1.10 g, 1.3 mmol) in dry DMF (300 mL) was heated under argon to 85 °C. Under stirring, a large excess of $KOC(CH_3)_3$ (1.12 g, 10 mmol) was added in one portion. After 2 h at 85 °C, the reaction mixture was cooled to room temperature and quenched with water (300 mL). The brown precipitate, which was separated by suction, was purified by short chromatography on silica (10 × 5 cm, CH_2Cl_2). The eluate contained a mixture of **1e** and **13**, which could be separated by repeated chromatography (silica, 50 × 2 cm; petroleum ether/CH_2Cl_2 3/1). The first, blue fluorescing fraction contained 29 mg (3%) of **13** as yellow solid, mp 100 °C. The second, green fluorescing fraction yielded 382 mg (39%) of **1e**, clearing point 266 °C.

(8*E*,17*E*,26*E*)-2,3,4,11,12,13,20,21,22-Nonakis(dodecyloxy)triphenanthro[8,9,10-*abc*:8,9,10-*ghi*:8,9,10-*mno*]cyclooctadecene (1e): ^{1}H NMR δ 0.87 (t, 27H), 1.27 (m, 144H), 1.55 (m, 18H), 1.98 (m, 18H), 4.10 (t, 6H), 4.20 (t, 6H), 4.28 (t, 6H), 7.57 (s, 3H), 7.65 (dd, 3H), 7.83/8.07 (AB, ^3J = 15.6 Hz, 6H), 7.92 (d, 3H), 8.47 (s, 3H), 9.70 (d, 3H); ^{13}C NMR δ 14.1, 22.7−31.9 (30C), 68.8, 73.9, 74.3, 102.4, 120.1, 120.1, 124.2, 125.9, 127.1, 130.4, 130.6, 128.6, 129.3, 130.6, 133.8, 135.6), 142.9, 152.4, 152.6; MS (FD) *m*/*e* (relative intensity) 2265 ($M^{\bullet+}$, 100). Anal. Calcd for $C_{156}H_{246}O_9$: C, 82.70; H, 10.94. Found: C, 82.72; H, 10.64.

(8*E*,17*E*,26*E*,35*E*)-2,3,4,11,12,13,20,21,22,29,30,31-Dodecakis(dodecyloxy)tetraphenanthro[8,9,10-*abc*:8,9,10-*ghi*:8,9,10-*mno*:8,9,10-*stu*]cyclotetraeicosane (13): ^{1}H NMR δ 0.85 (t, 36H), 1.24 (m, 192H), 1.50 (m, 24H), 1.88 (m, 24H), 4.01−4.15 (m, 24H), 7.34 (s, 4H), 7.54 (m, 4H), 7.75/8.10 (AB, $^3J_{HH}$ = 15.0 Hz, 8H), 7.78 (d, 4H), 8.31 (s, 4H), 9.65 (d, 4H); ^{13}C NMR δ 14.1, 22.7−32.0, 68.8, 73.7, 74.2, 102.2, 119.8, 120.9, 124.2, 125.9, 127.3, 129.7, 131.1, 128.6, 129.5, 130.5, 134.8, 135.1, 142.7, 152.3, 152.6; MS (FD) *m*/*e* (relative intensity) 3021 ($M^{\bullet+}$, 100).

General Procedure for Photodimerizations. The photoreactor was a cylindrical glass vessel with a branched gas inlet tube and a magnetic stirrer. The solutions of the corresponding [18]annulenes in benzene were degassed by repeated freeze−pump−thaw technique or, alternatively, by bubbling nitrogen through the solutions for about 30 min. The irradiation was realized with a water-cooled Hanovia 450 W medium-pressure Hg vapor lamp. The light was filtered by water and a Duran glass filter. The course of the reaction was monitored by either ^{1}H NMR analyses of the crude material or UV/vis spectroscopy.

Cyclophane 14e. A solution of **1e** (31 mg) in benzene (30 mL, 4.6 × 10^{-4} M) was irradiated for 4 h. After removal of the solvent and chromatography on silica (CH_2Cl_2/petroleum ether 1/2), 21 mg (68%) of **14e** was obtained as a yellow oil: ^{1}H NMR δ 0.86 (m, 9H), 1.15−1.37 (m, 48H), 1.50 (m, 6H), 1.60−2.05 (m, 6H), 3.63 (m, 1H) 3.90, 4.03 (m, 1H), 4.13 (m, 1H), 4.30 (m, 2H, OCH_2), 6.10 (m, 1H), 6.81 (m, 1H), 7.37 (t, 1H), 7.49 (s, 1H), 7.96 (d, 1H), 9.02 (d, 1H), 9.48 (br s,1H);^{13}C NMR (100 MHz) δ 14.0, 22.7−31.8, 40.8, 43.9, 69.3, 73.6, 74.0, 101.6, 120.2, 123.9, 124.5, 125.2, 125.6, 128.5, 128.7, 129.2, 130.9, 134.3, 142.2, 151.7, 151.8; MS (FD) *m*/*e* (relative intensity) 4531 ($M^{\bullet+}$, 10). Anal. Calcd for $C_{312}H_{492}O_{18}$: C, 82.70; H, 10.94. Found: C, 82.70; H, 10.94.

Cyclophane 15a. A solution of **1a** (70 mg) in benzene (180 mL, 4.3 × 10^{-4} M) was irradiated for 20 min. After removal of the solvent and recrystallization from petroleum ether (40−70 °C), 53 mg (76%) of **15e** was obtained as a brown amorphous solid, mp 120 °C: ^{1}H NMR δ 0.89 (t, 3H), 1.32 (m, 4H), 1.45 (m, 2H), 1.78 (m, 2H), 4.00 (t, 2H), 5.50 (m, 1H), 6.88 (m, 1H), 7.05 (dd, 1H), 7.28 (d, 1H), 7.63 (d, 1H), 7.73 (d, 1H), 7.91 (s, 1H), 8.07 (d, 1H), 9.87 (s, 1H); ^{13}C NMR δ 14.0, 22.6, 25.8, 29.7, 31.6, 43.5, 45.7, 68.1, 104.6, 116.5, 122.7, 125.1, 127.3, 127.6, 129.6, 126.0, 128.7, 130.1, 130.5, 130.5, 136.2, 157.6; MS (FD) *m*/*e* (relative intensity) 1814 ($M^{\bullet+}$, 21), 907 (100). Anal. Calcd for $C_{132}H_{132}O_6$: C, 87.38; H, 7.33. Found: C, 87.34; H, 7.25.

Cyclophane 15e. A solution of **2e** (200 mg) in benzene (180 mL, 7.4 × 10^{-4} M) was irradiated for 30 min. After removal of the solvent and chromatography on silica (CH_2Cl_2/petroleum ether 1/2), 120 mg (60%) of **15e** was obtained as a pale yellow oil: ^{1}H NMR δ 0.83 (t, 3H), 0.88 (t, 3H), 0.94 (t, 3H), 1.23−1.50 (m, 18H), 1.63−1.92 (m, 6H), 3.71 (m, 1H), 3.80 (m, 1H), 3.97 (m, 1H), 4.04 (m, 1H), 4.11 (m, 2H), 5.42 (m, 1H), 6.82 (m, 1H), 7.07 (s, 1H), 7.16 (d, 1H), 7.83 (s, 1H), 9.01 (d, 1H), 9.81 (br s, 1H); ^{13}C NMR δ 14.0, 22.6, 22.7, 22.7, 25.7, 25.8, 25.9, 29.4, 29.7, 30.3, 30.5, 31.7, 31.8, 43.5, 45.7, 68.7, 73.2, 74.1, 106.2, 118.3, 125.5, 126.4, 126.8, 127.7, 128.8, 129.4, 129.6, 132.9, 135.0, 142.0, 151.2, 151.9; MS (FD) *m*/*e* (relative intensity) 3016 ($M^{\bullet+}$, 62), 1508 (100). Anal. Calcd for $C_{204}H_{276}O_{18}$ (3014.1): C, 81.23; H, 9.22. Found: C, 81.00; H, 9.31.

Cyclophane 15i. A solution of **2i** (210 mg) in benzene (180 mL, 5.1 × 10^{-4} M) was irradiated for 30 min. After removal of the solvent and purification by HPLC (silica Si60, 10n, 250 × 20.5 mm; hexane/$CHCl_3$ 5/1, 4 mL/min), 118 mg (56%) of **15e** was obtained as a pale yellow glass: ^{1}H NMR δ 0.86 (m, 9H), 1.15−1.31 (m, 48H), 1.50 (m, 6H), 1.60−1.95 (m, 6H), 3.71 (m, 1H), 3.80 (m, 1H), 3.97 (m, 1H), 4.04 (m, 1H), 4.11 (m, 2H), 6.79 (m, 1H), 7.05 (s, 1H), 7.14 (d, 1H), 7.79 (s, 1H), 9.00 (d, 1H), 9.79 (br s, 1H); ^{13}C NMR δ 14.0, 22.7−31.8, 43.4, 45.2, 68.6, 73.2, 74.0, 106.1, 118.2, 125.5, 126.4, 126.7, 127.6, 128.8, 129.3, 129.6, 132.8, 134.9, 142.0, 151.2, 151.9; MS (FD) *m*/*e* (relative intensity) 4537 ($M^{\bullet+}$, 18), 3401 (25), 2268 (100). Anal. Calcd for $C_{412}H_{486}D_6O_{18}$ (4533.8): C, 82.59; H(D), 11.06. Found: C, 82.57; H, 11.05.

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