Aggregation and Photodimerization of Areno-Condensed Annulenes

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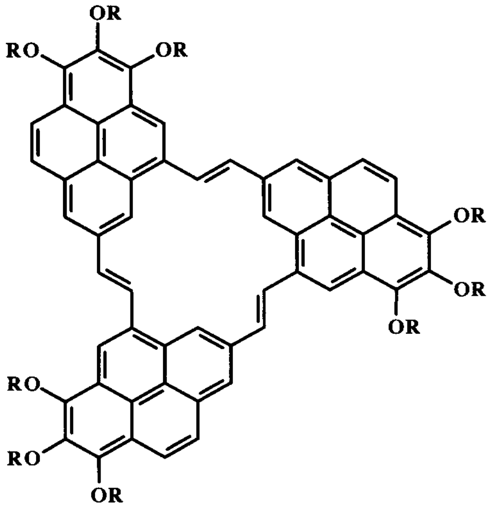
Dedicated to Prof. *André M. Braun* on the occasion of his 60th birthday

[18]- and [24]Annulenes condensed with three pyrene or phenanthrene ring systems show, in solution, especially in apolar solvents, a strong aggregation evidenced, for example, by concentration-dependent ^{1}H-NMR spectra. However, the fluorescence bands and the fluorescence lifetimes of these compounds depend only to a minor extent on the concentration and correspond essentially to the measurements obtained for the monomer. Among several models discussed, one is favored in which aggregates can be excited, but the emission is due to an almost undisturbed monomer. Even for the pyrene system, an excimer fluorescence cannot be detected. Nevertheless, short-lived excimers are responsible for the regio- and stereoselective photodimerization to belt cyclophanes.

1. Introduction. – Areno-condensed annulenes [1–10] represent an interesting class of compounds in materials science because these disc-like systems form nematic or columnar discotic mesophases [1][2][5–10]. The liquid-crystalline (LC) phases $\mathrm{Col_h}$ show, at room temperature, an appreciably high photoconductivity. At temperatures above 150° in the LC phases, irreversible photoreactions take place that lead to regular belt cyclophanes or to a nonspecific crosslinking of the discs [3–7]. The photodimerization in solution does not exhibit a thermal activation barrier and works even in highly diluted solutions [6]. Thus, aggregation is obviously a decisive factor in solution as well as in the LC phases. The crucial question for the present work was, how does the aggregation affect the photophysical and photochemical properties.

2. Results and discussion. – The recently synthesized compound **1**, a tripyreno[2,3,4-*abc*:2,3,4-*ghi*:2,3,4-*mno*][18]annulene with nine hexyloxy chains [1], represents an excellent example for this study. Apart from the $\pi\pi$ interactions, the long alkoxy chains should enhance the aggregation and, moreover, guarantee a reasonably good solubility.

Förster and *Kasper* [11] were the first to observe a strong influence of the concentration on the fluorescence of pyrene. A classical excimer-generating mechanism was postulated for the rationalization of the dual fluorescence [11][12]. According to this mechanism, a pyrene molecule in the excited singlet state can meet by diffusion a ground-state molecule and form an excimer, which can enter an adiabatic or a nonadiabatic dissociation. The latter process is either radiationless or promotes a fluorescence different from the monomer fluorescence. Later, the model was extended by the incorporation of encounter complexes (*Van der Waals* complexes) [13–15]. A similar excimer fluorescence was found in pyrene crystals, pyrene absorbed on silica gel, pyrene included in vesicles, micelles, membranes, *etc.* [16–20].



1 ($R = C_6H_{13}$)

Our measurement of **1** in cyclohexane revealed only a very small dependence of the fluorescence emission spectra on the concentration (*Fig. 1*). The excitation spectrum of a 10^{-6} M solution corresponds to the absorbance spectrum; but, in the concentration range of 10^{-5} to 10^{-4} M, the excitation spectra change completely.

The effect of concentration on the emission of the parent system pyrene is strong; moreover, time-resolved measurements revealed that the excimer fluorescence in

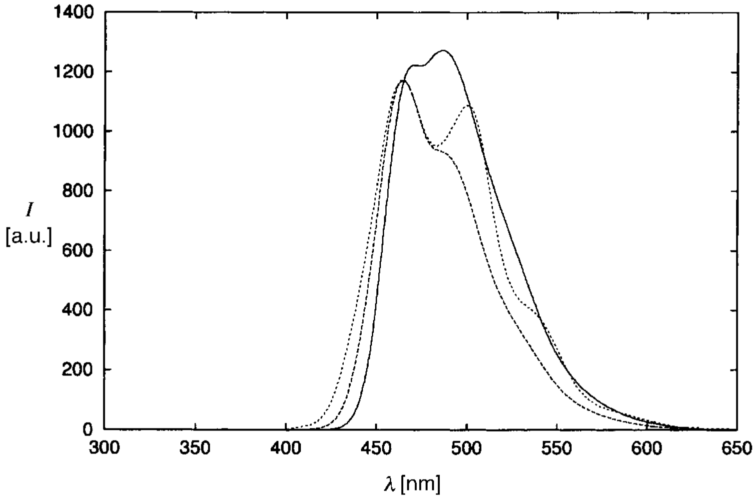


Fig. 1. *Steady-state fluorescence spectra of* **1** *at* 10^{-4} M (——), 10^{-5} M (– – –), *and* 10^{-6} M (- - - -) *in cyclohexane* (excitation at 337 nm).

concentrated solutions of pyrene develops on a ns time scale after the excitation pulse and corresponds, after *ca.* 100 ns, to the steady-state fluorescence [21]. The delay in the excimer emission is due to the diffusion of an excited molecule to a ground-state molecule and to the geometrical change of the encounter complex to the excimer. The latter is characterized by a parallel arrangement of the molecular planes in a distance of 3.0–3.5 Å [22].

The emission of compound **1** does not change after the excitation; the fluorescence spectrum measured 2 ns after the pulse corresponds to the spectrum under steady-state conditions.

Further important information can be obtained from the fluorescence lifetime of **1** dissolved in cyclohexane. The fluorescence decay curves of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} M solutions can be fit very well to monoexponential functions and reveal average lifetimes of 7.3, 8.2, 8.2, and 8.0 ns, respectively. Despite the strong tendency to aggregate, there is virtually only one emitting species. An excimer – like in the case of the unsubstituted pyrene – would not only exhibit fluorescence shifted to longer wavelengths, it would also show significantly longer average lifetimes [22]. It is reasonable to attribute the emission to loose aggregates of two (or more) monomers. The small differences in the fluorescence spectra depicted in *Fig. 1* may be due to different vibrational activations (*Franck-Condon* factors) in different aggregates.

To determine whether the results obtained for the pyrene system **1** are also valid for other areno-condensed annulenes, we studied the triphenanthro-condensed [18]annulenes **2a**,**b** [5][8] and the triphenanthro-condensed [24]annulenes **3a**,**b** [23].

The *Table* summarizes the results obtained for the fluorescence decay of the compounds **1**, **2a**,**b**, and **3a**,**b**. In most cases, the decay curves can be fitted by monoexponential functions ($1.0 < \chi^2 < 3.0$); two exponentials are needed only for the higher concentrations of **2a**,**b** in cyclohexane[1]). On the whole, the average lifetimes τ do not depend significantly on the concentration in the range of 10^{-3} to 10^{-6} M in cyclohexane solution. This result can be explained on the assumption that there is vitrually only one emitting species that is influenced to some extent by the neighboring molecules in aggregates.

Normally, the aggregation tendency of the areno-condensed annulenes is high in apolar solvents like cyclohexane and lower in solvents like $CHCl_3$ that show very good solvation of the alkoxy-substituted electron-rich ring systems. The highest aggregation tendency in the series **1–3** was found for **3a**. *Fig. 2* shows the effect of concentration – even in $CDCl_3$ – on the ^1H-NMR spectrum of **3a**. The broadening of the signals promoted by aggregation has several grounds: exchange of molecules between aggregates, restricted mobility of the whole aggregate (in comparison to single molecules), and restricted mobility of molecular segments.

Irradiation of a degassed solution of **1** in benzene with a mercury medium-pressure lamp and a *Duran* glass filter leads to the belt cyclophane **4**. A stepwise threefold photocycloaddition occurs, which is comparable to processes observed earlier in the series of the triphenanthro[18]annulenes [5–7]. Conformer **1a** in *Scheme 1* represents

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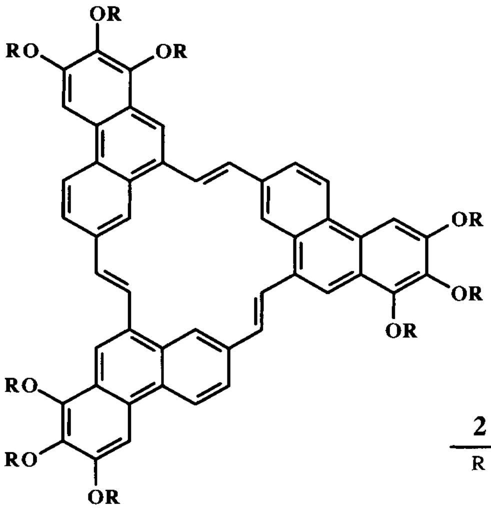
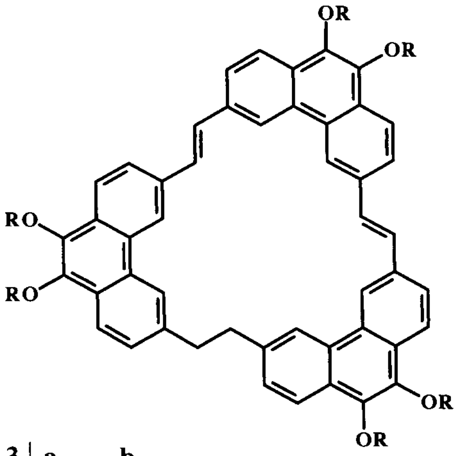
[1]) A reasonably good fit of the decay curves of the 10^{-4} and 10^{-3} M solutions of **2a**,**b** takes into account a species with $\tau \approx 4$ ns, also found at lower concentration, and a shorter-lived species of unknown nature with $\tau \approx 1$ ns.



2	**a**	**b**
R	C_6H_{13}	$C_{12}H_{25}$



3	**a**	**b**
R	C_6H_{13}	$C_{12}H_{25}$

the *energetically preferred conformation* of the 18-membered ring [8][10]. The higher steric hindrance of the six inner H-atoms makes conformation **1b** less likely – neither **1a** nor **1b** should be planar. The NMR spectra of **1a** reveal a fast inversion of the central ring[2]). The photodimerization of **1a** and **1b** would lead to different rigid *configurations* of belt cyclophanes; however, only **4a**, the dimer of **1a** can be obtained in reasonably good yields. Compound **4a** exhibits in cyclohexane a structureless emission band with a maximum at 471 nm. This corresponds nearly to the maximum of the excimer emission of pyrene, but one should consider that the pyrene units in **4a** do not have a face-to-face

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[2]) An inversion that is slow on the NMR time scale would lead to diastereotopic oxymethylene protons (see [1]).

Table. *Fluorescence Decay of* **1**, **2a**,**b** *and* **3a**,**b** *in Cyclohexane at 25°: Average Lifetimes* τ [ns], *Preexponential Factors A, Correlation factors* χ^2

Compound		Concentration [M]			
		10^{-6}	10^{-5}	10^{-4}	10^{-3}
1	τ	7.3	8.2	8.2	8.0
	A	0.024	0.032	0.036	0.036
	χ^2	1.47	1.61	2.05	1.80
2a	τ_1	3.8	4.5	5.6	5.8
	A_1	0.018	0.024	0.031	0.025
	τ_2			1.4	1.1
	A_2			0.017	0.026
	χ^2	2.63	2.70	2.01	2.02
2b	τ_1	3.7	3.9	4.4	4.3
	A_1	0.018	0.031	0.025	0.023
	τ_2			1.1	1.1
	A_2			0.011	0.015
	χ^2	1.97	2.20	1.21	1.34
3a	τ	11.2	16.0	13.3	13.3
	A	0.032	0.044	0.024	0.026
	χ^2	1.42	1.18	2.92	2.92
3b	τ	7.5	8.0	9.1	12.8
	A	0.026	0.043	0.042	0.043
	χ^2	1.39	1.56	1.38	2.32

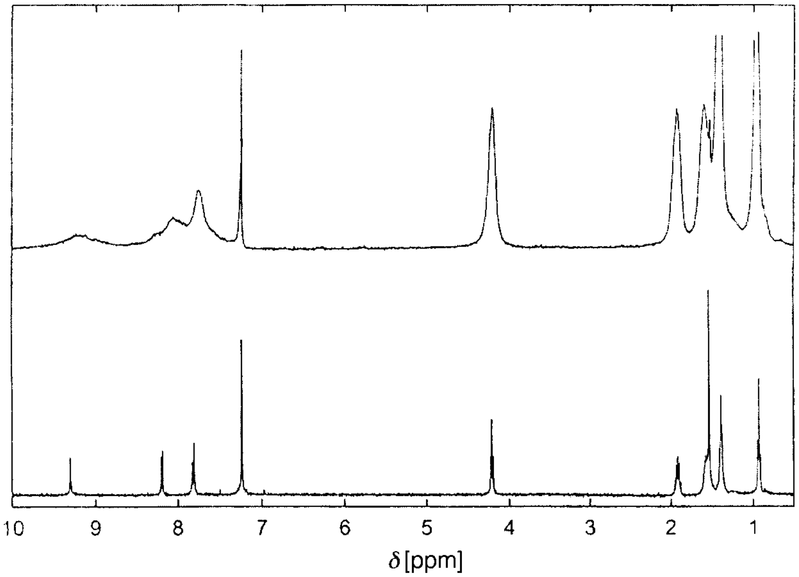
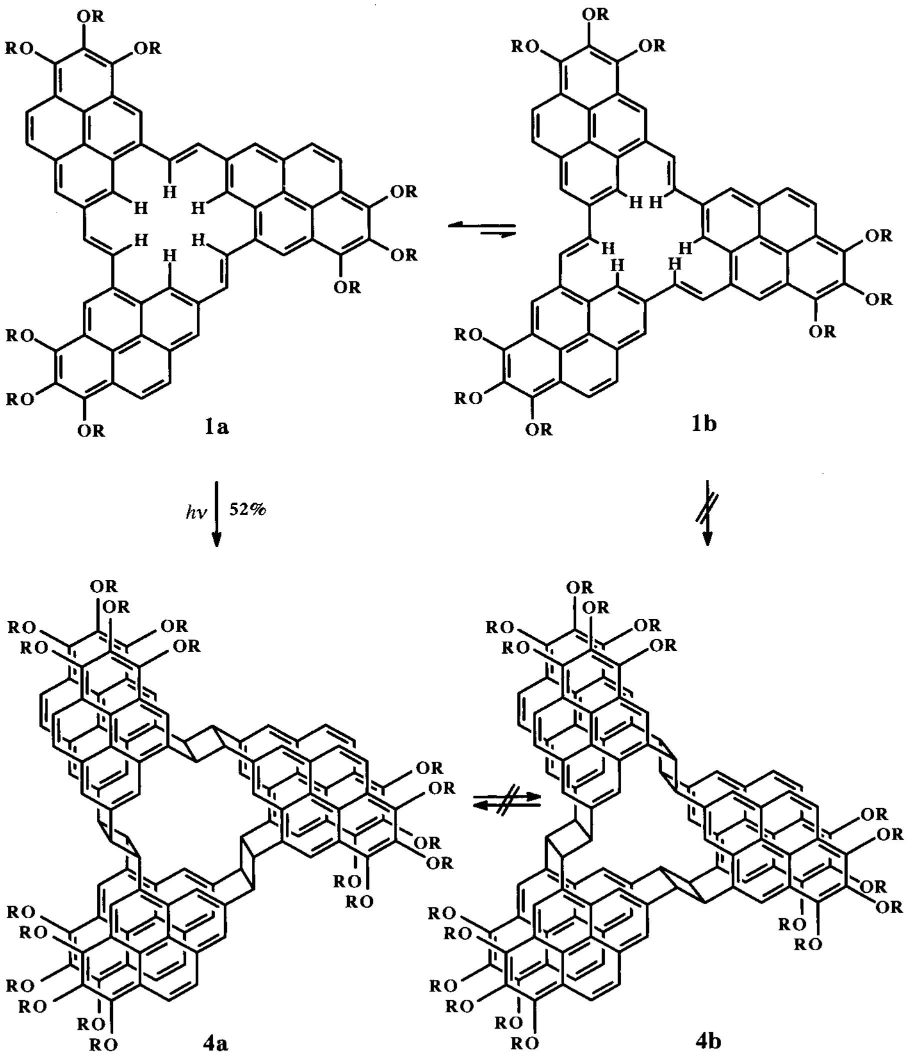


Fig. 2. *400-MHz* ^{1}*H-NMR spectra of* **3a** *in* $CDCl_3$; bottom: $6.0 \cdot 10^{-4}$ M, top: $6.0 - 10^{-3}$ M (the signals with $9.5 > \delta > 7.5$ belong to the aromatic *ABX* spin system, the signal at $\delta = 4.3$ to the OCH_2 groups, the signals at $2.0 > \delta > 1.5$ to the other CH_2 groups and the signal at $\delta = 0.9$ to the CH_3 groups)

Scheme 1



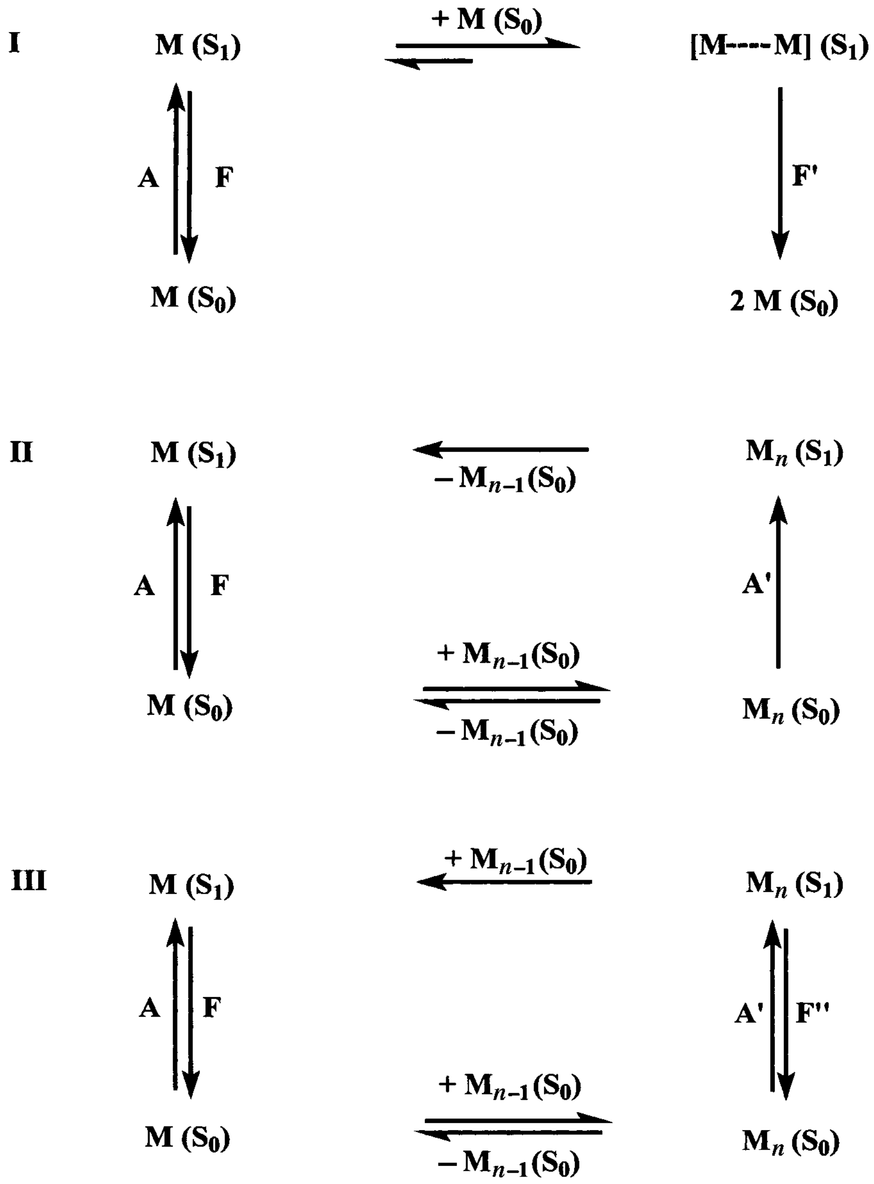
R = n-C_6H_{13}

orientation. Due to the geometry of the four-membered rings, the planes of opposite pyrene units form an angle of *ca.* 135°.

The photochemical C–C bond formation of stilbenoid compounds can also lead to polymers and cross-linked systems [9]. Whereas the latter route is only a minor process for **1** and **2a**,**b**, it is the prevailing process for the [24]annulenes **3a**,**b**. Surprisingly, both photoreactions work also in highly diluted solutions in cyclohexane. Since the average lifetimes of the S_1 states are not long enough to form an encounter complex (or an excimer) S_1S_0 by diffusion in 10^{-6} M solutions, one has to assume aggregation even at such low concentrations.

Conclusions. – *Scheme 2* summarizes three models for the fluorescence of aggregating compounds. The upper model I represents the classical case for the formation of singlet excimers $[M \cdots M]$ (S_1) that show a fluorescence F′ different from

Scheme 2



the monomer fluorescence F; the deactivation F′ leads to a slope area in the energy hypersurface of the ground state S_0 and, therefore, dissociation to 2 M (S_0) occurs.

On the contrary, the models II and III are characterized by ground-state minima for the aggregates M_n (S_0) ($n = 2,3,..$). Irrespective of the excitation of M (S_0) or M_n (S_0) in model I, a single fluorescence F can be observed that corresponds principally to the monomer fluorescence. Slight modifications of F are likely due to the influence of the neighboring molecules in the aggregate. An adiabatic process $M_n (S_1) \rightarrow M (S_1)$ might be included.

Model III is distinguished by a dual fluorescence F and F″, but F″ does not lead to dissociation like F′ in model I.

Despite the existence of some ground-state aggregates [24], pyrene obeys model I. The pyreno-condensed compound **1** and the other annulenes **2a**,**b** and **3a**,**b** obey model II. Of course, one can also imagine a combination of the models I–III; especially an adiabatic process seems to be interesting, in which a dimer aggregate M_2 (S_1) is transformed to an excimer [M ⋯ M] (S_1). The regular geometry of excimers appears to be a good precondition for the formation of highly symmetrical belt cyclophanes, like in the photodimerization **1a** → **4a**. The lack of an excimer fluorescence could be due to a fast collapse to the dimer. Moreover, the absence of excimers should lead to a nonspecific photopolymerization as observed for the [24]annulenes **3a**,**b**.

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Experimental Part

1. *General*. The continuous-wave excitation and emission spectra: *Hitachi* fluorescence spectrometer in degassed samples in cyclohexane at r.t. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-400* spectrometer-, in $CDCl_3$, with TMS as internal standard; δ in ppm, J in Hz. Field-desorption (FD-) MS: *Finnigan MAT 95*; m/z (%).

2. *Fluorescence Lifetimes*. The fluorescence lifetimes were measured with *Hamamatsu* single-photon-counting instrument including a streak scope [*C 4334* with a N_2 laser ($\lambda = 337$ nm)], a picosecond-lifetime measurement system (*C 4780*) and a computer (*Apple Macintosh*, capture card *U 4790*). The compounds **1** [1], **2a**,**b** [5][8], and **3a**,**b** [23] were freshly recrystallized from petroleum (b.p. 50–80°) into which acetone was dropped until the solns. became turbid. Since **1** is very sensitive towards daylight, it was further purified in a darkroom by HPLC (silica gel, hexane/toluene 85:15). The cyclohexane solns. were degassed. A stream of Ar saturated with cyclohexane was bubbled through the cells just before the start of the measurements. After excitation with the pulsed laser (width 1–1.5 ns), emission spectra were recorded between 5 and 10 ns. A sequence of 1000 laser pulses was accumulated for the registration of the fluorescence-decay curves. The *Hamamatsu* fluorescence software *V 2.43* was used for the evaluation of the average lifetimes.

3. *Photodimerization of* **1** *to the Belt Cyclophane* **4**. A stream of Ar was bubbled through a soln. of 79 mg (0.05 mmol) of **1** [1] in 180 ml benzene. After 30 min of irradiation with a 450-W *Hanovia* lamp equipped with a *Duran* glass filter, the solvent was removed and the residue purified by column chromatography (40 × 3 cm SiO_2, CH_2Cl_2/hexane 1:3). Slightly colored viscous oil (41 mg, 52%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (t, 36 H, Me); 0.94 (t, 18 H, Me); 1.25–1.70 (m, 108 H, CH_2); 1.71–1.95 (m, 36 H, CH_2); 4.05–4.15 (m, 24 H, OCH_2); 4.20–4.36 (m, 12 H, OCH_2); 5.88 (m, 6 outer H, 4-membered rings); 7.55 (m, 6 inner H, 4-membered rings); 7.61 (6 H), 7.92 (AB, 6 H, $^3J = 9.1$, outer arom. H); 7.75 (s, 6 H, outer arom. H); 8.65 (s, 6 H, outer arom. H); 10.56 (s, 6 H, inner arom. H)[3]). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.0 (Me), 14.1 (Me); 22.6, 22.7, 25.8, 26.0, 29.4, 30.4, 30.5,

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[3]) The interior protons of the belt exhibit astonishingly high δ values in the ^{1}H-NMR spectrum of **4**, resulting from the extended ring currents in the three pyrene units; additionally, steric constraints may contribute to this effect. The assignment of the signals is based on a 2D-^{1}H,^{1}H-COSY measurement. The ^{13}C nuclei have δ values in the normal range.

31.8 (CH_2, partly superimposed); 44.8, 46.4 (CH, 4-membered rings); 74.4, 74.9, 75.3 (OCH_2); 121.0, 121.1, 121.3, 124.1, 124.3, 125.5, 125.9, 128.8, 128.9, 130.9, 131.0, 132.8, 135.2, 143.7, 147.1, 147.6 (arom. C). FD-MS: 1581 (100, M^{2+}).

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