Hexahelicenophanes

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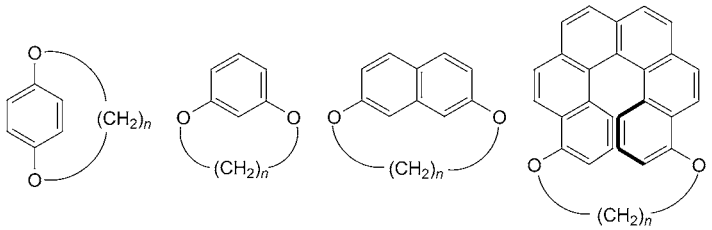
A reaction sequence was studied for the preparation of cyclophanes **12**, which contain 2,7-bis(2-phenylethenyl)naphthalene chromophores and polymethylenedioxy chains of different length. The irradiation of **12** in the presence of I_2 led then, by oxidative cyclization processes, to the hexahelicenophanes **13**, provided that the methylenedioxy chain of **12** is long enough ($n = 8, 10$). As competitive photoreaction, a twofold $[2\pi + 2\pi]$ cyclodimerization occurred, which furnished the belt cyclophanes **14**. The latter process is the only photoreaction for **12** with $n = 6$. The hexahelicenophanes **13** have lower racemization barriers and longer spin–lattice relaxation times compared to those of hexahelicenes.

Introduction. – Due to their physical and chemical properties, cyclophanes are a fascinating class of compounds, which have kept their attractivity over decades [1–12]. The famous '*Ansa Compounds*', obtained by *Lüttringhaus et al.* in 1937, were the first α,ω-dioxa[$n+2$]cyclophanes **1** [13–18] (*Fig. 1*). Apart from the *para*-compounds, *Ziegler* and *Lüttringhaus* studied also the *meta* systems **2** [13][19]. The corresponding naphthalene derivatives **3** were prepared 40 years later by *Mandolini et al.* [20]. In 1998, we started to study hexahelicenophanes **4**, whose terminal benzene rings were linked by a (polymethylene-α,ω-dioxy) chain [21]. Hexahelicenacrowns were obtained by *Nakazaki et al.* [22][23]. Here, we present a full report on the phane type **4** ($n = 8, 10$).



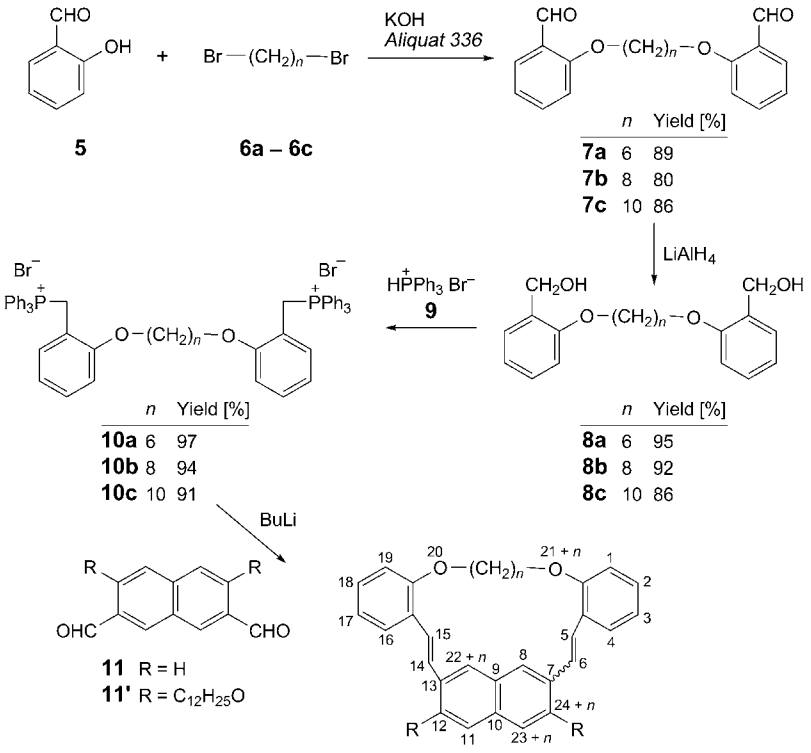
1 ($n \geq 8$) **2** ($n \geq 6$) **3** ($n \geq 12$) **4**

Fig. 1. *α,ω-Dioxa[*n *+ 2]phanes*

Results and Discussion. – In contrast to the usual concept for the synthesis of cyclophanes, we prepared the aromatic part of the hexahelicenophanes **4** in the final step. 2-Hydroxybenzaldehyde (salicylaldehyde; **5**) and α,ω-dibromoalkanes **6a**–**6c** of different length ($n = 6, 8, 10$) were reacted to the dialdehydes **7a**–**7c** by using phase-transfer catalysis (*Scheme 1*). Reduction with $LiAlH_4$ yielded the diols **8a**–**8c**, which

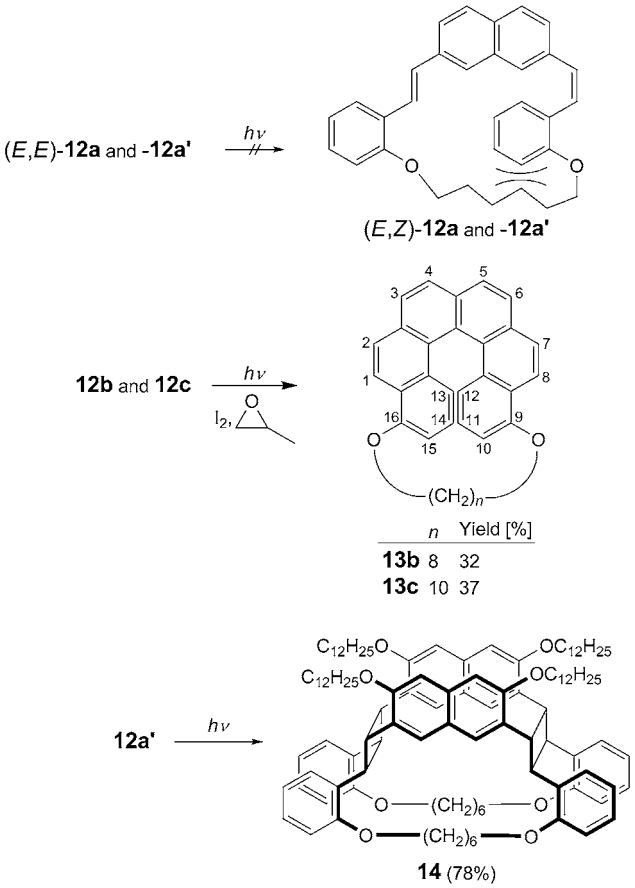
were then transformed with triphenylphosphine hydrobromide (**9**) to the bisphosphonium salts **10a**–**10c**, respectively. Up to this stage, all yields were excellent. The next step, however, becomes problematic, because **10a**–**10c** as well as their reaction partners, the dialdehydes **11** and **11′** [24], respectively, are both bifunctional compounds. To obtain the desired products **12a**, **12a'**, **12b**, and **12c**, the dilution principle had to be applied for the *Wittig* reaction. The ^{1}H-NMR spectra revealed that **12** and **12a'** had (*E*,*E*)-configuration. However, the bigger macrocycles **12b** and **12c** contained *ca.* 20 and 33%, respectively, of the isomers with (*E*,*Z*)-configuration. The (*Z*,*Z*)-isomers were below the detection limit in the ^{1}H-NMR spectra in $CDCl_3$. *Reetz* and *Sostmann*, who applied our reaction sequence for the preparation of 7,8,9,10,11,12,13,14-octahydro-3,5 :16,18-diethenophenanthro[5,4,3-*opqr*][3,12]benzodioxacyclononadecin obtained a mixture of all three isomers (*E*,*E*), (*E*,*Z*), and (*Z*,*Z*), of the corresponding dialkene [25].

Scheme 1



Irradiation of **12b** and **12c** in the presence of I_2 gave the helicenophanes **13b** and **13c**, respectively. Methyloxirane served thereby as scavenger for the generated HI (*Scheme 2*). The shorter chains in **12a** and **12a′** do not allow the initial photochemical generation of (*E*,*Z*)-**12a** and -**12a′**, which is a prerequisite for the cyclization. Obviously, the steric effect in **12a** and **12a′** is the cause of the return of the electronically excited singlet state S_1 to the (*E*,*E*)-configuration. We observed, however, the formation of photodimers [21], whose solubility are low, so that they could be filtered off after irradiation. To study the dimerization process in detail, we used the better soluble **12a′**, which also permitted a higher monomer concentration. Two stereoselective $[2\pi + 2\pi]$ cycloadditions occurred, leading, in high yield, to the belt cyclophane **14**. To avoid this bimolecular photoreaction, the monomolecular electrocyclic processes of **12b** and **12c** were performed in high dilution ($< 2 \times 10^{-4}$ M). Nevertheless, small amounts of photodimers of **12b** and **12c** were still formed under this condition as well. For synthetic purposes, it is not advisable to use concentrations below 10^{-4} M.

Scheme 2



The high yield of photodimer **14** obtained by irradiation of a 3.7×10^{-4} M solution of **12a'** becomes plausible by the aggregation of **12a′** in the ground state. *Fig. 2* shows the concentration-dependent absorption of **12a′** in benzene. The absorption maximum of a 5.6×10^{-6} M solution at *ca.* 335 nm is shifted to 374 nm for a concentration of 8.4×10^{-5} M. This finding hints to an aggregation in the sense of *J* aggregates.

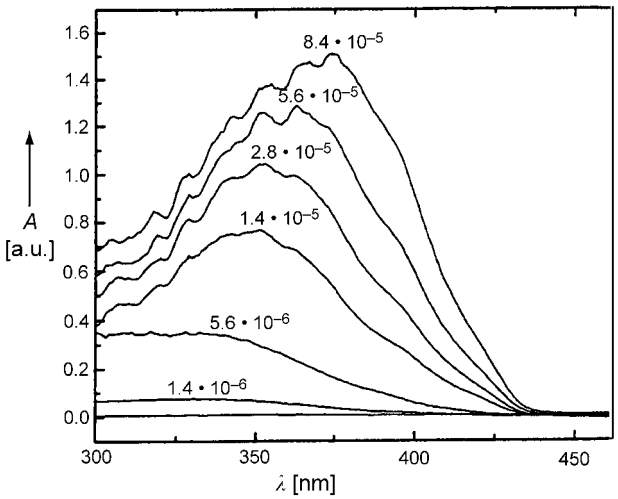


Fig. 2. *Concentration-dependent long-wavelength absorption of* **12a′** *in benzene*

The structure determinations of **13b**, **13c**, and **14** were performed by 1D- and 2D-NMR techniques. *Fig. 3* displays the obtained δ (^{1}H) and δ (^{13}C)) values of **13b** and **13c**, which have C_2 symmetry. In contrast to the precursor cyclophanes **12**, the CH_2 groups in **13** contain diastereotopic H-atoms. The splitting of their resonance signals is clearly visible for the α- and β-positions. Normally, an alkoxy substituent on a benzene ring provokes a strong high-field shift for the signals of the *o*-positioned ^{1}H and ^{13}C nuclei. This was found here for **13b** and **13c** too, but the smallest δ(^{1}H) values were recorded for H–C(11) and H–C(14), the H-atoms in *m*-position to the alkoxy substituents. This is a consequence of the overlapping terminal benzene rings.

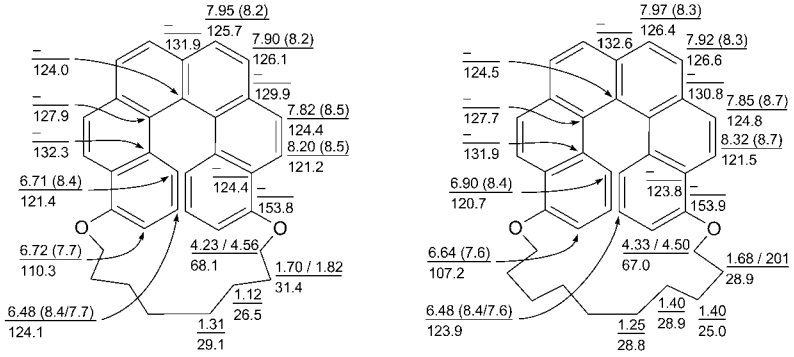


Fig. 3. *NMR Data*, δ (^{1}H) (^3J [Hz])/δ (^{13}C), *of* **13b** *and* **13c** *in* $CDCl_3$ (TMS as internal standard)

The longitudinal or spin–lattice relaxation times $T_1(^{13}C)$ of **13b** and **13c** reflect the special phane structure. The T_1 values of **13b**, **13c**, and 9,16-bis(dodecyloxy)hexahelicene **15** (*Fig. 4*) are compiled in the Table. According to the size of the molecules, **15** has relaxation times in the normal range. We observed, however, a gradual increase of T_1 from **15** to **13b** *via* **13c**. The dipole–dipole relaxation type should predominate in all three molecules. The moment of inertia of the C_2 axis is less than that relative to other axes of rotation. Therefore, the T_1 values of the ^{13}C nuclei close to the C_2 axis should be smaller than those of the more remote ^{13}C nuclei. Here, this is not always valid: C(12d), for example, has, compared to C(2a) a smaller T_1 value in **13b** but not in **13c** and **15**. The neighborhoods of the H-atoms are equivalent in all three molecules. Further studies should reveal whether steric constraints in the phanes **13b** and **13c** play an important role for the relaxation.

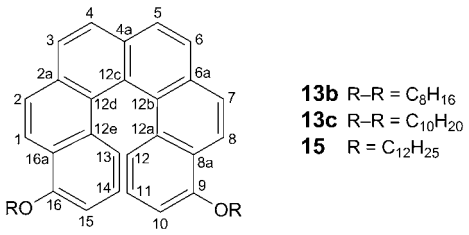


Fig. 4. *C-Atom numbering of the hexahelicenes* **13b**, **13c**, *and* **15**

Table. *Comparison of Spin–Lattice Relaxation Times* $T_1(^{13}C)$ *in s of the Helicenophanes* **13b** ($n=8$) *and* **13c** ($n=10$) *with those of 9,16-Bis(dodecyloxy)hexahelicene* (**15**) *in* $CDCl_3$ *at Room Temperature* (the limits of error of T_1 amount to *ca.* 10%)

	13b	**13c**	**15**
H–C(1), H–C(8)	1.05	0.87	0.33
H–C(2), H–C(7)	1.19	0.88	0.39
H–C(3), H–C(6)	1.04	0.92	0.36
H–C(4), H–C(5)	0.95	0.82	0.41
H–C(10), H–C(15)	0.90	0.82	0.43
H–C(11), H–C(14)	0.96	0.86	0.40
H–C(12), H–C(13)	1.02	0.87	0.33
C(2a), C(6a)	6.23	4.81	2.44
C(12a), C(12e)	7.09	6.16	2.44
C(12b), C(12d)	5.67	5.89	2.53
OCH_2	0.63	0.54	0.35

The C_2-symmetric hexahelicenophanes **13b** and **13c** are chiral. Their enantiomers could be enriched by column chromatography on silica gel doped with the *Newman* reagent, (−)-(*R*)-**16** [26][27]. The (−)-(*M*)-configurated **13b** and **13c** form somewhat weaker charge-transfer complexes with (−)-(*R*)-**16** than those with the (+)-(*P*)-configurations and were eluted first (*Fig. 5*) [28].

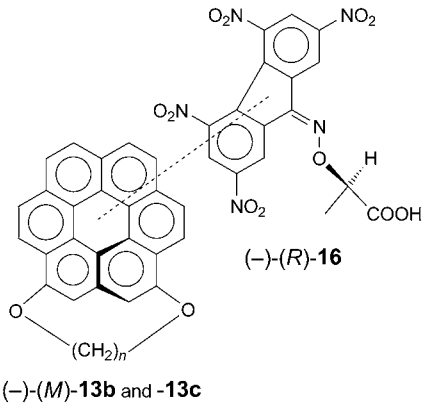


Fig. 5. *Complexation of (–)-(*M*)-***13b*** *and -***13c** *with* Newman *reagent (–)-(*R*)-***16***

The racemization rates were determined by the optical rotation values $[\alpha]_D$ in the temperature range of 120°–200° [21]. The *Arrhenius* plots of the racemization are depicted in *Fig. 6*. The most remarkable result is that the racemization barrier of the phane **13b** with the O–$(CH_2)_8$–O chain is much lower than that of **13c** or of the unsubstituted hexahelicene [29][30]. The half-life time at 200° amounts for **13b** to 48 s, whereas it is for **13c** *ca.* 15 times and for hexahelicene about 132 times longer. An explanation of this steric effect was provided on the basis of the spatial structures in the ground-state and in the transition state of the racemization [21][31].

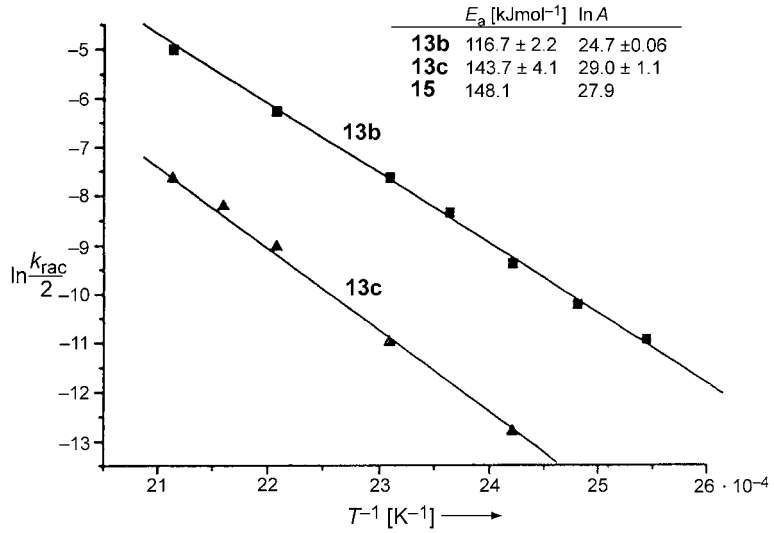


Fig. 6. Arrhenius *plots of the racemization of the hexahelicenophanes* **13a** *and* **13b** *in 1,2,4-trichlorobenzene*

Conclusions. – In the present article, we reported on compounds, which connect helicene and phane structures. The hexahelicenophanes **13** with (polymethylene)-α,ω-dioxy chains O–$(CH_2)_n$–O, could be obtained by photocyclization and oxidation of the precursor cyclophanes **12**, provided that the methylene chain is long enough ($n = 8, 10$). The competitive twofold photocyclodimerization led to belt cyclophanes **14**, a process which was studied for compound **12a′**, which contains solubilizing dodecyloxy substituents. Since **12a′** has a shorter polymethylenedioxy chain ($n = 6$), the cyclodimerization to **14** is the only photoreaction.

The hexahelicenophanes exhibited some unexpected properties. They have relatively low activation barriers, E_a, for the racemization, and the spin–lattice relaxation times T_1 of their ^{13}C nuclei are much longer than those of hexahelicenes without phane structure.

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Experimental Part

General. The dialdehydes **7a**–**7c** were prepared as described in [24] for the alkylation of hydroxymonoaldehydes. M.p.: *Büchi* melting-point apparatus. Optical rotations: in 1,2,4-trichlorobenzene with the *Polarimeter 241* from *Perkin-Elmer*. UV/VIS: *Zeiss MCS 320/340* diode array spectrometer. ^1H- and ^{13}C-NMR spectra: *AM-400* spectrometer from *Bruker*; $CDCl_3$ as solvent, if not otherwise stated, Me_4Si as internal standard; δ in ppm and J in Hz. The spin–lattice relaxation times T_1 were determined at r.t. in oxygen-free $CDCl_3$ solns. by applying the *Bruker Software* for the inversion recovery method. EI- and FD-MS: *Finnigan-MAT-95* spectrometer; 5-kV ionization voltage for FD and 70-eV ionization energy for EI.

2,2′-[Hexane-1,6-diylbis(oxy)]dibenzaldehyde (**7a**). *Salicylaldehyde* (**5**; 5.0 g, 40.9 mmol), *1,6-dibromohexane* (**6a**; 4.9 g, 20.1 mmol), KOH (2.8 g, 49.9 mmol), and 0.5 g *Aliquat 336* in 100 ml of 1,4-dioxane yielded **7a**. The purification was accomplished by column filtration (SiO_2 (5×40 cm); petroleum ether (PE; b.p. 40–70°)/$CHCl_3$ 1:1). The colorless compound (5.8 g, 89%) melted at 80° ([32]: m.p. 80°). The product was identical to an authentic sample [32][33].

2,2′-[Octane-1,8-diylbis(oxy)]dibenzaldehyde (**7b**). Compound **5** (5.0 g, 40.9 mmol), *1,8-dibromooctane* (**6b**; 5.4 g, 19.9 mmol), KOH (2.8 g, 49.9 mmol), and 0.5 g of *Aliquat 336* in 100 ml of 1,4-dioxane gave **7b**. The purification was performed by column filtration (SiO_2 (5×40 cm); PE (b.p. 40–70°)/Et_2O 1:1). Recrystallization from EtOH yielded 5.7 g (80%) colorless **7b**; m.p. 71° ([32]: m.p. 72–73°). The product was identical to an authentic sample [34–36].

2,2′-[Decane-1,10-diylbis(oxy)]dibenzaldehyde (**7c**). Compound **5** (10.2 g, 83.5 mmol), *1,10-dibromodecane* (**6c**; 12.5 g, 41.7 mmol), KOH (5.6 g, 99.8 mmol), and 1.0 g of *Aliquat 336* in 150 ml of 1,4-dioxane gave **7c**. The purification was accomplished by column filtration (SiO_2 (5×60 cm); toluene). The colorless compound (13.8 g, 86%) melted at 66° ([37]: 68–68.5°). The product was identical to an authentic sample [36][37].

The reduction of **7a**–**7c** to the diols **8a**–**8c**, resp., was performed according to the procedure 2-alkoxybenzaldehyde → 2-alkoxybenzylalcohol described in [24].

[Hexane-1,6-diylbis(oxybenzene-2,1-diyl)]dimethanol (**8a**). Compound **7a** (3.0 g, 9.2 mmol) and $LiAlH_4$ (180 mg, 4.7 mmol) gave 2.9 g (95%) of **8a**. Colorless solid. M.p. 59–60°. ^1H-NMR ($CDCl_3$): 1.45–1.60 (m, 2 γ-CH_2); 1.75–1.87 (m, 2 β-CH_2); 3.96 (t, $^3J = 6.4$, 2 CH_2O); 4.65 (s, 2 CH_2OH); 6.83–6.98 (m, 2 H–C(3), 2 H–C(5)); 7.20–7.33 (m, 2 H–C(4), 2 H–C(6)). ^{13}C-NMR ($CDCl_3$): 25.9 (γ-CH_2); 29.2 (β-CH_2); 61.5 (CH_2OH); 67.8 (CH_2O); 111.1 (C(3)); 120.6 (C(5)), 128.5, 128.7 (C(4), C(6)); 129.5 (C(1)); 156.8 (C(2)). EI-MS: 312 (26, $[M - H_2O]^+$), 123 (40), 107 (83), 83 (100). Anal. calc. for $C_{20}H_{26}O_4$ (330.4): C 72.70, H 7.93; found: C 72.92, H 8.02.

[Octane-1,8-diylbis(oxybenzene-2,1-diyl)]dimethanol (**8b**). Compound **7b** (11.4 g, 32.1 mmol) and $LiAlH_4$ (610 mg, 16.1 mmol) gave 10.6 g (92%) of **8b**. Colorless solid. M.p. 68°. ^{1}H-NMR ($CDCl_3$): 1.35–1.50 (*m*, 2 γ-CH_2, 2 δ-CH_2); 1.74–1.88 (*m*, 2 β-CH_2); 4.00 (*t*, ^3J = 6.3, 2 CH_2O); 4.68 (*s*, 2 CH_2OH); 6.84–6.97 (*m*, 2 H–C(3), 2 H–C(5)); 7.20–7.30 (*m*, 2 H–C(4), H–C(6)). ^{13}C-NMR ($CDCl_3$): 26.1(γ-CH_2); 29.2 (β-CH_2, δ-CH_2, superimposed); 62.2 (CH_2OH); 67.8 (CH_2O); 111.0 (C(3)); 120.5 (C(5)); 128.5, 128.8 (C(4); C(6)); 129.1 (C(1)); 156.8 (C(2)). EI-MS: 340 (35, $[M - H_2O]^+$), 123 (36), 107 (100). Anal. calc. for $C_{22}H_{30}O_4$ (358.5): C 73.71, H 8.44; found: C 73.96, H 8.41.

[Decane-1,10-diylbis(oxybenzene-2,1-diyl)]dimethanol (**8c**). Compound **7c** (13.6 g, 35.6 mmol) and $LiAlH_4$ (680 mg, 17.9 mmol) gave 11.8 g (86%) of **8c**. Colorless solid. M.p. 79°. ^{1}H-NMR ($CDCl_3$): 1.30–1.53 (*m*, 2 γ-CH_2, 2 δ-CH_2, 2 ε-CH_2); 1.74–1.88 (*m*, 2 β-CH_2); 4.00 (*t*, ^3J = 6.4, 2 CH_2O); 4.67 (*s*, 2 CH_2OH); 6.83–6.95 (*m*, 2 H–C(3), 2 H–C(5)); 7.20–7.30 (*m*, 2 H–C(4), 2 H–C(6)). ^{13}C-NMR ($CDCl_3$): 26.1 (γ-CH_2); 29.2, 29.4 (β-CH_2, δ-CH_2, ε-CH_2, superimposed); 62.3 (CH_2OH); 67.9 (CH_2O); 111.0 (C(3)); 120.4 (C(5)); 128.6, 128.8 (C(4), C(6)); 129.1 (C(1)); 156.9 (C(2)). EI-MS: 386 (35, M^+), 368 (5, $[M - H_2O]^+$), 124 (100). Anal. calc. for $C_{24}H_{34}O_4$ (386.5): C 74.58, H 8.87; found: C 74.42, H 8.83.

General Procedure for the Preparation of the Bisphosphonium Dibromides **10a**–**10c**. The diols **8a**–**8c** (30 mmol) and $Ph_3P \cdot HBr$ (21.3 g, 62.1 mmol) were heated in 300 ml of dry $CHCl_3$ to reflux. The generated H_2O was continously removed. After *ca.* 12 h, the reaction was complete. The solvent was distilled off, and the residue was recrystallized from EtOH/$CHCl_3$.

[Hexane-1,6-diylbis(oxybenzene-2,1-diylmethanediyl)]bis(triphenylphosphonium) Dibromide (**10a**). Yield: 28.50 g (97%). M.p. 230–231°. ^{1}H-NMR ($CDCl_3$): 1.06–1.18 (*m*, 2 γ-CH_2); 1.18–1.35 (*m*, 2 β-CH_2); 3.40–3.50 (*m*, 2 CH_2O); 4.97 (*d*, ^2J (P,H) = 14.4, 2 PCH_2); 6.76–6.90 (*m*, 4 arom. H); 7.00–7.10 (*m*, 2 arom. H); 7.25–7.35 (*m*, 2 arom. H); 7.50–7.80 (*m*, 24 arom. H); 7.80–7.95 (*m*, 6 arom. H). ^{13}C-NMR ($CDCl_3$): 23.5 (*d*, ^1J (P,C) = 48.0, PCH_2); 25.0, 28.1 (CH_2); 67.4 (CH_2O); 111.9, 117.2, 118.9, 120.5 (arom. CH), 115.4 (C_q, Ph); 130.0, 133.8, 135.0 (CH, Ph); 131.6, 156.7 (arom. C_q). MS: Not recorded. Anal. calc. for $C_{56}H_{54}Br_2O_2P_2$ (980.8): C 68.58, H 5.55; found: C 68.61, H 5.42.

[Octane-1,8-diylbis(oxybenzene-2,1-diylmethanediyl)]bis(triphenylphosphonium) Dibromide (**10b**). Yield: 28.45 g (94%). M.p. 182°. ^{1}H-NMR ($CDCl_3$): 1.10–1.46 (*m*, 2 β-CH_2, 2 γ-CH_2, 2 δ-CH_2); 3.40–3.52 (*m*, 2 CH_2O); 4.92 (*d*, ^2J (P,H) = 14.1, 2 PCH_2); 6.75–6.90 (*m*, 4 arom. H); 7.00–7.10 (*m*, 2 arom. H); 7.25–7.38 (*m*, 2 arom. H); 7.50–7.80 (*m*, 24 arom. H); 7.80–7.95 (*m*, 6 arom. H). ^{13}C-NMR ($CDCl_3$): 24.9 (*d*, ^1J (P,C) = 50.0, PCH_2); 25.7, 28.7, 29.1 (CH_2); 67.4 (CH_2O); 111.1, 117.0, 118.7, 120.8 (arom. CH); 115.1 (C_q, Ph); 129.9, 133.9, 134.9 (CH, Ph); 131.8, 156.6 (arom. C_q). MS: Not recorded. Anal. calc. for $C_{58}H_{58}Br_2O_2P_2$ (1008.9): C 69.05, H 5.79; found: C 69.09, H 5.07.

[Decane-1,10-diylbis(oxybenzene-2,1-diylmethanediyl)]bis(triphenylphosphonium) Dibromide (**10c**). Yield: 28.31 g (91%). M.p. 150°. ^{1}H-NMR ((D$_6$)DMSO): 1.05–1.40 (*m*, 2 β-CH_2, 2 γ-CH_2, 2 δ-CH_2, 2 ε-CH_2); 3.35–3.50 (*m*, 2 CH_2O); 4.94 (*d*, ^2J = 14.4, 2 PCH_2); 6.73–6.90 (*m*, 4 arom. H); 6.95–7.05 (*m*, 2 arom. H); 7.20–7.32 (*m*, 2 arom. H); 7.50–7.80 (*m*, 24 arom. H); 7.80–7.95 (*m*, 6 arom. H). ^{13}C-NMR ((D$_6$)DMSO): 25.7 (*d*, ^1J (P,C) = 49.4, PCH_2); 27.0, 30.0, 30.5, 30.6 (CH_2); 69.0 (OCH_2); 112.9, 118.5, 120.3, 121.8 (arom. CH); 116.5 (C_q, Ph); 131.2, 135.2, 136.3 (CH, Ph); 132.0, 158.5 (arom. C_q). MS: Not recorded. Anal. calc. for $C_{60}H_{62}Br_2O_2P_2$ (1036.9): C 69.50, H 6.03; found: C 69.24, H 5.83.

General Procedure for the Preparation of the Precursor Cyclophanes **12a**, **12a′**, **12b**, **12c**. To compounds **10a**–**10c** (1.1 mmol), dissolved in 500–600 ml of dry THF, a 1.6M soln. of BuLi in hexane (1.4 ml, 2.2 mmol) was slowly added at 0°. The red reaction mixture was stirred for 15 min at r.t., before dialdehyde **11**[1]) or **11′** [24] (1.1 mmol) suspended/dissolved in 70 ml of dry THF was added. The red color disappeared, and a blue fluorescence appeared slowly. After 3–4 h heating to reflux, 50 ml of H_2O and 5 ml of 2M HCl were added. The H_2O layer was extracted (2×) with 50 ml of Et_2O, each. The combined org. phases were neutralized ($NaHCO_3$), dried ($MgSO_4$), and evaporated. The crude product was purified by CC (SiO_2 (3 × 40 cm); PE (b.p. 40–70°)/$CHCl_3$ 1:1) and/or recrystallization.

*(5*E*,14*E*)-21,22,23,24,25,26-Hexahydro-7,10-etheno-9,13-(metheno)dibenzo[*i,v*][1,8]dioxacyclotricosine* (**12a**). Yield: 90 mg (18%). Yellow solid, M.p. 258–260° (recrystallized from acetone). ^{1}H-NMR ($CDCl_3$): 1.80–1.95 (*m*, 2 γ-CH_2); 1.95–2.12 (*m*, 2 β-CH_2); 4.04 (*t*, ^3J = 5.1, 2 CH_2O); 6.91 (*d*, ^3J = 8.0, H–C(1), H–C(19)); 6.99 (*t*, ^3J = 8.0, H–C(3), H–C(17)); 7.14 (*d*, ^3J = 16.5, H–C(5), H–C(15)); 7.18–

[1]) Commercially available.

7.27 (*m*, H–C(2), H–C(18)); 7.37 (*dd*, $^3J = 8.2$, $^4J = 1.6$, H–C(12), H–C(30)); 7.68–7.78 (*m*, H–C(4), H–C(11), H–C(16), H–C(29)); 8.01 (*d*, $^3J = 16.5$, H–C(6), H–C(14)); 8.29 (*s*, H–C(8), H–C(28)). ^{13}C-NMR ($CDCl_3$): 28.0 (γ-CH_2); 31.0 (β-CH_2); 69.7 (OCH_2); 113.5 (C(1), C(19)); 121.1 (C(3), C(17)); 123.9 (C(8), C(28)); 124.7 (C(5), C(15)); 125.2 (C(4), C(16)); 125.9 (C(12), C(30)); 126.6 (C(11), C(29)); 126.6 (C(4a), C(15a)); 127.3 (C(6), C(14)); 128.8 (C(2), C(18)); 132.3 (C(9)); 133.9 (C(10)); 136.5 (C(7), C(13)); 156.9 (C(19a), C(27a)). EI-MS: 446 (100, M^+), 447 (35). Anal. calc. for $C_{32}H_{30}O_2$ (446.6): C 86.06, H 6.77; found: C 86.27, H 6.98.

*(5*E*,14*E*)-12,30-Bis(dodecyloxy)-21,22,23,24,25,26-hexahydro-7,10-etheno-9,13-(metheno)dibenzo[*i,v*][1,8]dioxacyclotricosine* (**12a′**). Yield: 305 mg (34%). Yellow solid. M.p. 190–191°. ^{1}H-NMR ($CDCl_3$): 0.80–0.90 (*m*, 2 Me); 120–1.44 (*m*, 16 CH_2); 1.44–1.58 (*m*, 2 CH_2); 1.80–2.08 (*m*, 6 CH_2); 4.00–4.15 (*m*, 4 CH_2O); 6.89 (*d*, $^3J = 8.0$, H–C(1), H–C(19)); 6.95 (*s*, H–C(11), H–C(29)); 6.99 (*t*, $^3J = 8.0$, H–C(3), H–C(17)); 7.18 (*t*, $^3J = 7.9$, H–C(2), H–C(18)); 7.46 (*d*, $^3J = 16.7$, H–C(6), H–C(14)); 7.73 (*d*, $^3J = 7.6$, H–C(4), H–C(16)); 7.86 (*d*, $^3J = 16.7$, H–C(5), H–C(15)); 8.11 (*s*, H–C(8), H–C(28)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.7, 26.2, 28.0, 29.2, 29.5, 29.7, 30.9, 31.9 (CH_2, partly superimposed); 68.3, 69.5 (OCH_2); 104.6 (C(11), C(29)); 113.3 (C(1), C(19)); 121.1, 121.3, 123.6, 124.8, 125.5, 127.9 (remaining arom. and olefin. CH); 124.0 (C(9)); 127.0, 127.2 (C(4a), C(7), C(13), C(15a)); 134.7 (C(10)); 155.5, 156.6 (C(12), C(19a), C(27a), C(30)). FD-MS: 815 (100, M^+). Anal. calc. for $C_{56}H_{78}O_4$ (815.2): C 82.51, H 9.64; found: C 82.35, H 9.70.

*6,7,8,9,10,11,12,13-Octahydro-21,24-etheno-23,27-(metheno)dibenzo[*k,x*][1,10]dioxacyclopentacosine* (**12b**). Yield: 330 mg (63%). Light yellow solid. M.p. 266°. The ^{1}H-NMR spectrum of the product revealed an (*E*,*E*)/(*E*,*Z*)-ratio of 4:1. Recrystallization from acetone gave pure (*E*,*E*)-**12b**. ^{1}H-NMR ($CDCl_3$): 1.55–1.70 (*m*, 2 δ-CH_2); 1.70–1.83 (*m*, 2 γ-CH_2); 1.83–1.99 (*m*, 2 β-CH_2); 4.03 (*t*, $^3J = 5.2$, 2 CH_2O); 6.86 (*d*, $^3J = 8.3$, H–C(1), H–C(19)); 6.96 (*t*, $^3J = 7.3$, H–C(3), H–C(17)); 7.22 (*t*, $^3J = 7.3$, H–C(2), H–C(18)); 7.33 (*d*, $^3J = 16.6$, H–C(6), H–C(14)); 7.45 (*d*, $^3J = 8.5$, H–C(12), H–C(32)); 7.64 (*d*, $^3J = 7.6$, H–C(4), H–C(16)); 7.74 (*d*, $^3J = 16.6$, H–C(5), H–C(15)); 7.74 (*d*, $^3J = 8.5$, H–C(11), H–C(31)); 8.08 (*s*, H–C(8), H–C(30)). ^{13}C-NMR ($CDCl_3$): 27.9, 30.3, 31.0 (β-CH_2, γ-CH_2, δ-CH_2); 68.5 (CH_2O); 112.1 (C(1), C(19)); 120.6 (C(3), C(17)); 123.6 (C(8), C(30)); 124.2 (C(5), C(15)); 126.1 (C(4a), C(15a)); 126.2 (C(4), C(16)); 126.3 (C(12), C(32)); 127.6 (C(11), C(31)); 128.2 (C(6), C(14)); 128.7 (C(2), C(18)); 132.5 (C(9)); 134.0 (C(10)); 136.1 (C(7), C(13)); 156.9 (C(19a), C(29a)). EI-MS: 474 (100, M^+). Anal. calc. for $C_{34}H_{34}O_2$ (474.7): C 86.04, H 7.22; found: C 86.29, H 7.13.

*6,7,8,9,10,11,12,13,14,15-Decahydro-23,26-etheno-25,29-(metheno)dibenzo[*m,z*][1,12]dioxacycloheptacosine* (**12c**). Yield: 210 mg (38%). Nearly colorless solid. M.p. 211°. The ^{1}H-NMR spectrum of the product revealed an (*E*,*E*)/(*E*,*Z*)-ratio of 2:1. *Data of* (*E*,*E*)-**12c**. ^{1}H-NMR ($CDCl_3$): 1.50–1.64 (*m*, 2 δ-CH_2, 2 ε-CH_2); 1.70–1.84 (*m*, 2 γ-CH_2); 1.84–2.00 (*m*, 2 β-CH_2); 4.07 (*t*, $^3J = 5.3$, 2 CH_2O); 6.90 (*d*, $^3J = 8.0$, H–C(1), H–C(19)); 6.95 (*t*, $^3J = 7.7$, H–C(3), H–C(17)); 7.15–7.28 (*m*, H–C(2), H–C(18)); 7.39–7.60 (*m*, H–C(4), H–C(6), H–C(12), H–C(14), H–C(16), H–C(34)); 7.67 (*d*, $^3J = 16.5$, H–C(5), H–C(15)); 7.77 (*d*, H–C(11), H–C(33)); 7.88 (*s*, H–C(8), H–C(32)). ^{13}C-NMR ($CDCl_3$): 27.2, 29.8, 30.2, 30.2 (β-CH_2, γ-CH_2, δ-CH_2, ε-CH_2); 68.1 (OCH_2); 111.7 (C(1), C(19)); 120.5 (C(3), C(17)); 124.6, 125.2, 125.4, 126.0, 127.9, 128.5, 128.8, 130.2 (arom. and olefin. CH); 132.5 (C(9)); 134.0 (C(10)); 136.1 (C(7), C(13)); 156.9 (C(19a), C(31a)). EI-MS: 502 (100, M^+). Anal. calc. for $C_{36}H_{38}O_2$ (502.7): C 86.02, H 7.60; found: C 85.87, H 7.61.

*9,16-(Epoxyoctanooxy)phenanthro[3,4-*c*]phenanthrene* (*=4,13-(Epoxyoctanooxy)hexahelicene*; **13b**). The soln. of **12b** (100 mg, 0.21 mmol) and I_2 (107 mg, 0.42 mmol) in 2 l benzene was purged with O_2-free N_2 for 30 min. Methyloxiran (1.5 ml, 21 mmol) was added, and the irradiation was started with a *Hanovia-450-W* medium-pressure lamp, equipped with a *Pyrex* filter. The flow of N_2 was reduced but maintained until the reaction was complete, which became visible by the disappearance of the red color (I_2). The soln. was then treated with an aq. soln. of $NaHSO_3$, dried ($MgSO_4$), concentrated, and filtered. CC (3 × 30 cm, alkaline Al_2O_3/Et_2O) gave the desired **13b**. The chromatography was repeated with toluene/PE. Yield: 32 mg (32%). Pale yellow-crystals. M.p. 243°. FD-MS: 470 (100, M^+). Anal. calc. for $C_{34}H_{30}O_2$ (470.6): C 86.78, H 6.43; found: C 86.83, H 6.55.

*9,16-(Epoxydecanooxy)phenanthro[3,4-*c*]phenanthrene* (*=4,13-(Epoxydecanooxy)hexahelicene*; **13c**). Prepared as described for **12b** → **13b**. Yield: 38 mg (37%). Pale-yellow crystals. M.p. 252°. FD-MS: 498 (100, M^+). Anal. calc. for $C_{36}H_{34}O_2$ (498.7): C 86.71, H 6.87; found: C 86.58, H 6.90.

Belt Cyclophane **14** (*=5,9,58,62-Tetrakis(dodecyloxy)-19,26,41,48-tetraoxatridecacyclo[55.5.3.3^{4,10}.0^{2,34}.0^{3,33}.0^{7,67}.0^{11,56}.0^{12,55}.0^{13,18}.0^{27,32}.0^{35,40}.0^{49,54}.0^{60,64}]octahexaconta-1(63),4(68),5,7(67),8,10(66),13,15,17,27,29,31,35,37,39,49,51,53,57(65),58,60(64),61-docosaene*). Compound **12a′** (60 mg, 0.074 mmol) was dissolved in 200 ml of O_2-free benzene, which corresponds to a concentration of 0.37 10^{-3} M . The irradiation with a Hg medium-pressure lamp (*Hanovia-450-W*), equipped with a *Pyrex* filter, was controlled by TLC (SiO_2; $CHCl_3$). When the starting compound was consumed, the solvent was evaporated, and the residue was chromatographed (SiO_2; 2 × 30 cm, $CHCl_3$) to yield. **14** (47 mg, 78%). Colorless solid. M.p. 225°. ^{1}H-NMR ($CDCl_3$): 0.83–0.95 (*m*, 4 Me); 1.20–1.47 (*m*, 40 CH_2); 1.47–1.60 (*m*, 2 CH_2); 1.60–1.70 (*m*, CH_2); 1.70–1.80 (*m*, CH_2); 1.80–1.95 (*m*, 2 CH_2); 2.10–2.20 (*m*, 2 CH_2); 3.68–3.80 (*m*, 8 OCH_2); 4.96, 5.24 (*AA′BB′*, 4 outer H/4 inner H of cyclobutane rings); 6.21 (*s*, 4 H, outer H of naphthalene moiety); 6.64, 6.82, 7.06, 7.31 (*ABCD*, 4 × 4 H, benzene rings); 7.80 (*s*, 4 H, inner H of naphthalene moiety). Inner and outer H-atoms, related to the belt structure, were distinguished by NOE experiments. ^{13}C-NMR ($CDCl_3$): 14.2 (Me); 22.7, 26.4, 26.5, 29.4, 29.5, 29.6, 29.7, 29.8, 29.8, 29.9, 30.1, 32.0 (CH_2); 37.5, 41.5 (CH); 68.1, 68.2 (CH_2O); 103.6, 110.7, 119.5, 126.5, 128.0, 130.1 (arom. CH); 124.4, 126.4, 130.7, 133.1, 155.7, 157 (arom. C_q). FD-MS: 1630 (38, M^+), 815 (100, M^{2+}). Anal. calc. for $C_{112}H_{156}O_8$ (1630.5): C 82.51, H 9.64; found: C 82.49, H 9.46.

The model compound **15** was prepared on the basis of naphthalene-2,7-dicarbaldehyde and [2-(dodecyloxy)benzyl](triphenyl)phosphonium bromide [38][39].

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