New Ladder Polymers via Repetitive Diels–Alder Reaction under High Pressure

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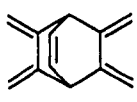
ABSTRACT: The synthesis of a new ladder-type polymer by repetitive Diels–Alder reaction is described. The "bis-diene" 1 was treated with 1,4:5,8-bisepoxy-9,10-dihexyl-1,4:5,8-tetrahydroanthracene (2) at high pressure (7–8 kbar). Under these conditions the formation of polymer 5 was obtained. The influence of concentration, solvent, and temperature on the polymer-forming reaction is discussed. The polymer was characterized by size-exclusion chromatography, by NMR spectroscopy, and by DSC and thermogravimetric methods. An attempt is made to solve the complex stereochemistry by the preparation of model compounds 7a and 7b.

Introduction

In 1928 Diels and Alder discovered the cycloaddition of cyclopentadiene and *p*-benzoquinone.[1] Since then, the Diels–Alder reaction has been one of the most useful tools in organic synthesis and utilized for the synthesis of many six-membered carbocycles and heterocycles. Often the Diels–Alder reaction is unsuccessful because of the low reactivity of the reaction system. In these cases, the reaction can sometimes be accelerated by changing the reaction conditions, e.g., reaction temperature, Lewis acid catalysts,[2] solvent, additives,[3] or pressure.[4] The increase of the temperature usually accelerates cycloreversion more than cycloaddition, thereby bringing the equilibrium toward the starting materials and causing side reactions which are also obtained by Lewis acids.

Normally, Diels–Alder reactions possess highly negative activation volumes.[5] Consequently, high pressures may accelerate the rates of these reactions without the disadvantage of raising the temperature. This entropic effect leads to an increase in the reaction rate by a factor of 10–1000.[6] In our case the increase of the reaction rate is so large that a repetitive reaction to a polymer becomes possible with components which show only low reactivity at normal pressure.

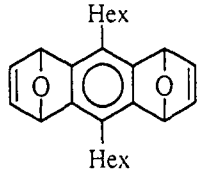
In contrast to the usual polymer-forming reactions (e.g., radical, anionic, or cationic polymerization), the repetitive Diels–Alder reaction, due to its concerted reaction mechanism, offers the possibility of constructing defect-free band-type structures leading directly to a two-dimensional framework. In our search for new ribbon structures via repetitive Diels–Alder reaction, we successfully used *exo*-5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene (1).[7]



1

1 was first prepared by Vogel et al.[7] for investigations on the reaction rate with strong dienophiles such as tetracyanoethylene or dimethyl acetylenedicarboxylate,[8] but only monofunctional dienophiles have been employed thus far.

To carry out a repetitive Diels–Alder reaction a bifunctional dienophile is required. In this context, we report on the reaction of 1 with 1,4:5,8-bisepoxy-9,10-dihexyl-1,4:5,8-tetrahydroanthracene (2).[9]



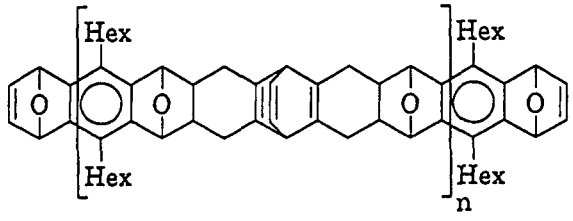
2

Results and Discussion

Heating of the starting materials 1 and 2 (1:1, 110 °C, 24 h) in toluene provided only the 1:1, 2:1, or 1:2 adducts. No oligomeric or polymeric material could be detected under normal pressure.

In a previous publication[10] the same effect was obtained for the reaction of 1 with unsubstituted 1,4:5,8-bisepoxy-1,4:5,8-tetrahydroanthracene (3)[11] (1:1 stoichiometry, 7.5 kbar, dichloromethane, 55 °C, 3 days). In this case the oligomers 4a–c (Scheme I) could be isolated if the reaction was carried out under high pressure (7.5 kbar).

Because of this result we expected that by use of the dialkylated "bis-dienophile" 2 under similar conditions polymeric material could be obtained, and, indeed, we isolated polymer 5, which is soluble in most common



5

solvents (e.g., chloroform, THF, and acetone) and could therefore be characterized by NMR spectroscopy in solution. Comparison of the ^{1}H- and ^{13}C-NMR spectra with a model compound (n = 1) showed no detectable structural defects (Figure 1). Surprisingly, both spectra possess only signals of epoxy groups as an end group. No resonances of the exocyclic double bonds as an end group from monomer 1 were found. Up to now we cannot explain this phenomenon. From our experimental results we exclude the possibility of the precipitation of 1 under high pressure using monomer concentrations of 0.45 mol/L.

The appearance of these end-group signals makes it possible to determine the molecular weight of 5 by NMR. Comparison of the integral for the bridgehead protons of the end group and the integral of the bridgehead protons of the epoxy groups of the repeating unit indicated a M_n of 9000. Size-exclusion chromatography (Figure 2) (PS/THF) was in very good agreement (M_n of 8800) with the

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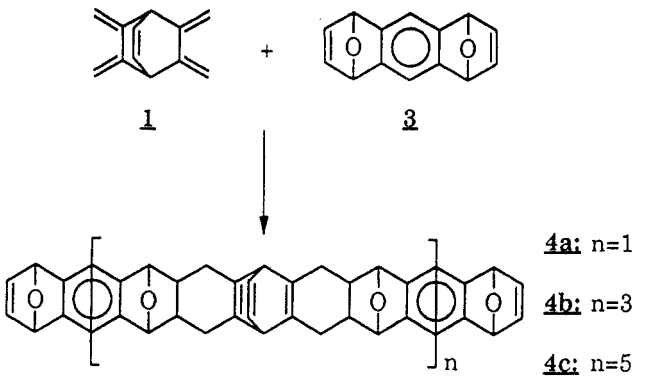
Scheme I



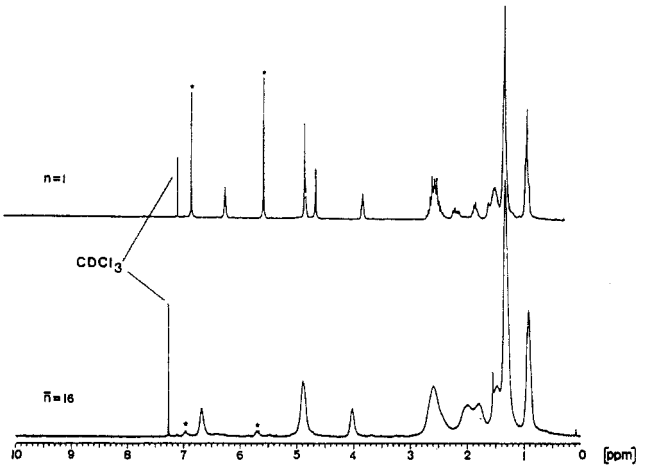


Figure 1. ^{1}H-NMR spectra of the model compound with n = 1 (upper spectrum) and polymer **5**. The asterisks indicate an end group.

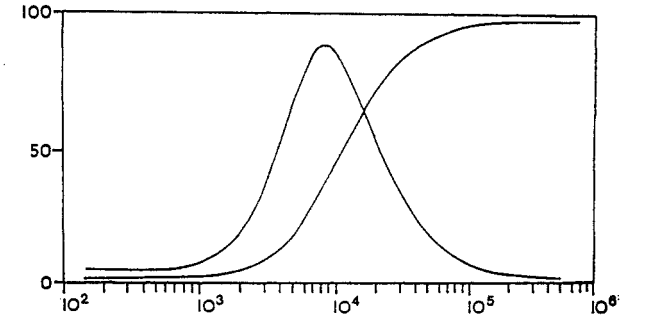


Figure 2. GPC diagram of **5**.

value detected by NMR. M_w is about 27 200. For nearly all synthesized polymer samples M_w/M_n was in the range of 2.8–3.15.

To investigate the reaction behavior under high pressure the reaction conditions (temperature, concentration, and solvent) were varied.

Influence of Concentration. A 0.3 M solution leads to a M_n of 7700. Monomer concentrations between 0.45 and the maximal concentration 0.65 mol/L (saturated solution) resulted in a mean molecular weight of 9000. This is probably affected by the precipitation of the starting materials at higher concentrations (>0.45 mol/L) caused by the decreasing solubility under high pressure.

Influence of the Solvent. Dichloromethane seems to be the best solvent for this reaction. Many solvents and solvent mixtures have been tested but the highest molecular weights have been reached with CH_2Cl_2. The relatively low M_n of 5500 for 2-MTHF, which is often used in high-pressure reactions, is probably caused by the lower concentration as a result of the limited solubility of **2** in this solvent. Table I shows a few examples.[12]

Table I

solvent	M_n	c (mol/L)
CH_2Cl_2	9000	0.45
2-MTHF	5500	0.30
CBr_2CF_2	7700	0.45
hexane/CH_2Cl_2	5700	0.45
toluene	8400	0.50

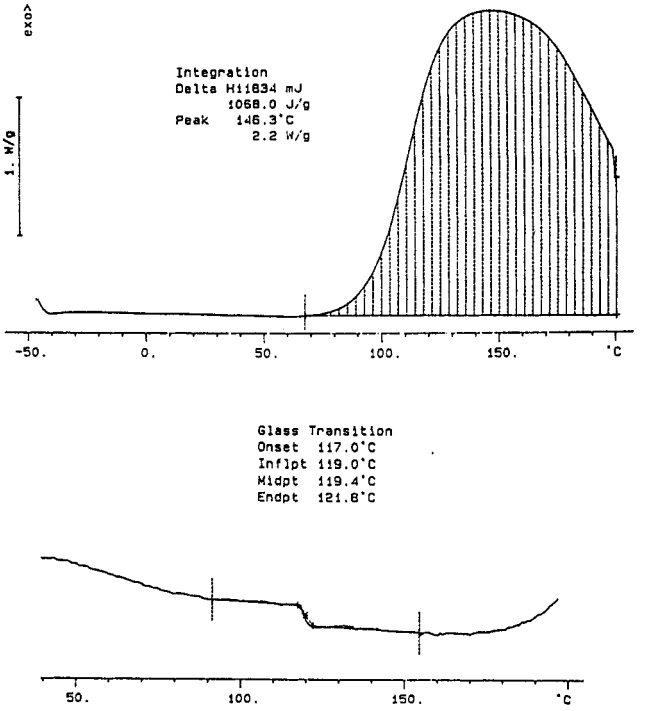


Figure 3. DSC of polymer **5** (upper DSC) and the DSC after cooling again to −50 °C and second heating.

Influence of the Temperature. There is no detectable influence of the temperature on the molecular weight of **5**. Normally, the reactions were carried out at 65 °C. If the temperature was raised to 85 °C, M_n was still 9000. At a reaction temperature of 100 °C an insoluble material was observed. From the FT-IR spectra we suppose that a thermally induced ring opening of the epoxy groups occurs because OH absorptions were detected and the intensity of the aromatic absorptions increased strongly. As shown below, TGA and DSC experiments confirmed this statement.

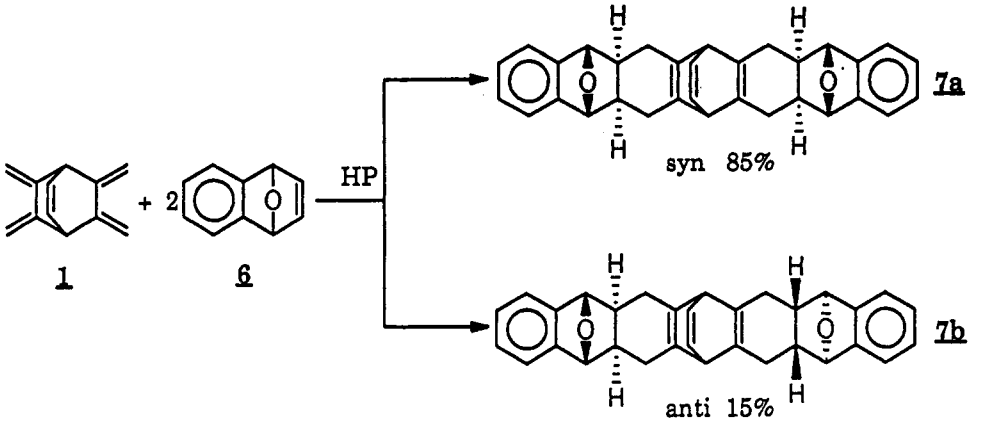
Thermogravimetric Investigations. Thermogravimetric analysis of polymer **5** showed low thermal stability. There is no loss of weight up to 200 °C. At higher temperatures decomposition occurs. The two detectable steps cannot be related to the loss of water but the second step (−48.6%, 300–500 °C) corresponds to the loss of the hexyl chains.

DSC reveals no glass transition in the range of −190 to +95 °C. At higher temperatures an exothermic reaction occurs, and the already-mentioned insoluble material is obtained.

Because there is no loss of weight up to 200 °C, the molecular composition must still be the same so that only the formation of phenols or probably the formation of a network is possible. DSC was carried out up to 200 °C. After cooling again to −50 °C, the new product shows a glass point at 119 °C (Figure 3). Investigations on the structure of this material are in progress.

Stereochemical Aspects. The Diels–Alder reaction normally prefers the endo attack of the dienophile.[13] This effect is caused by secondary orbital interactions. Because in most cases the transition state of the endo attack has

Scheme II



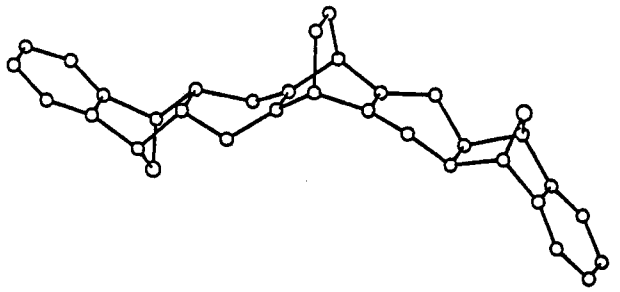
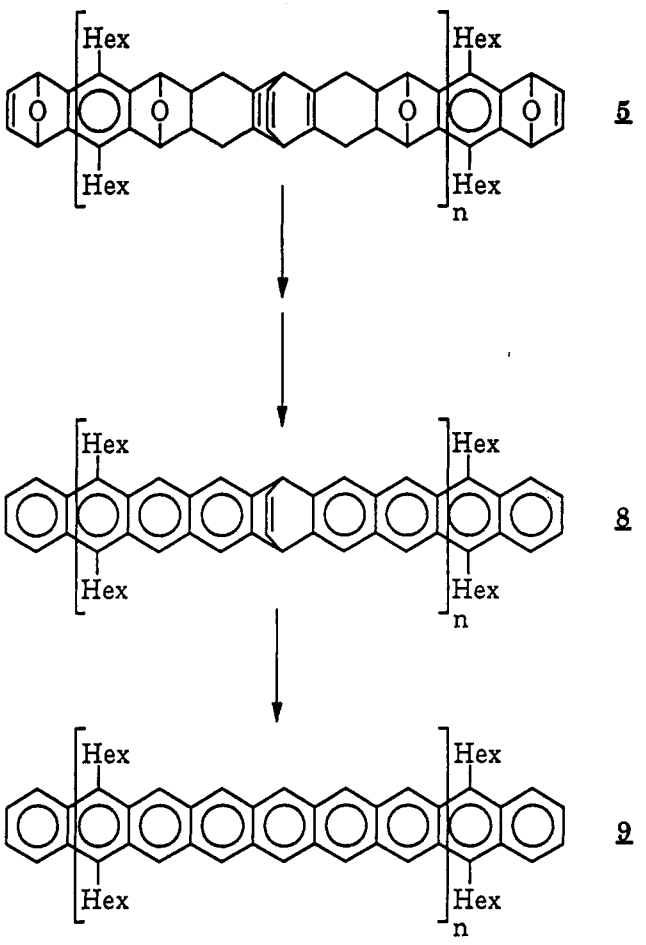


Figure 4. X-ray crystal structure of **7b**.

a more negative activation volume than the transition state of the exo attack, high-pressure conditions favor the endo product additionally. To solve the complex stereochemistry, model compounds were prepared. For this purpose **1** was reacted with 1,4-dihydro-1,4-epoxynaphthalene (**6**) (Scheme II). In this reaction, the formation of only two isomers, **7a** and **7b**, was observed, which could be separated by column chromatography as described in ref 10. The structure of the two isomers was solved by NMR spectroscopy (^1H, ^{13}C, and SFD experiments) and by X-ray crystallography (Figure 4). The ratio of the endo–endo adduct **7a** ("syn" related to the oxygen atoms) to the exo–endo adduct ("anti") is 4.1/1. This means that more than 90% of all attacks occur at the endo side of the "bis-diene" **1**. One should therefore expect cyclic material or a helical structured polymer because of the concave structure of the monomers. However, the stereochemistry is more complex because the "bis-dienophile" **2** consists of two isomers ("syn" and "anti" related to the oxygen bridges) itself.[14] Cyclic material can only be formed by use of the pure "syn" isomer or in case of the isomer mixture as a byproduct. However, cage-type molecules were never isolated even at high dilution conditions. The influence of the neighboring epoxy group on the stereochemistry is not solved at the moment, but the already-mentioned oligomers **4a–c** show a much more complicated stereochemistry than expected. No cyclic material could be obtained neither in this case nor in the case if the more easily available pure "syn" isomer of **3** was used.[10]

Chemical Transformations. Regardless of the complex stereochemistry polymer **5** should give the opportunity for chemical modifications. In an aromatization sequence (Scheme III) we tried to generate the fully aromatic system **8** interrupted by ethylene bridges by treatment of **5** with TMSI/NEt_3/CH_3CN followed by aromatization with tetrachloro-*p*-benzoquinone. At the moment this sequence does not work quantitatively as is required for a polymer analogous reaction. This material would offer the possibility of casting films and afterward preparing polyacene **9** via a retro-Diels–Alder reaction in the solid state. Higher

Scheme III



acenes are known to be very unstable in solution but they are often stable to air for weeks in the solid state.[15] Therefore we decided to generate the acene in an immobilized film. This totally new concept to polyacenes is partially presented in two other publications.[16,17]

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 and Bruker AM-400 spectrometers. Chemical shifts were measured relative to Me_4Si as internal standard. FT-IR spectra were obtained on a Nicolet 5 DXC FT-IR spectrometer. TGA and DSC were conducted on Mettler TA 3000 and Mettler TG 50 systems, and GPC was performed on a Waters 150-C ALC/GPC (UV detection, 254 nm; standard, PS). High-pressure experiments were conducted on a Nova Swiss 10-kbar high-pressure autoclave.

X-ray Crystallography. The X-ray diffraction measurement was performed on an Enraf-Nonius CAD4 diffractometer with

graphite-monochromated Cu Kα radiation. The structure was solved by direct methods (MULTAN). Lattice parameters were determined by least squares refinement of diffraction angles with $\Theta > 20°$ from 25 centered reflections. The intensities were measured by δ–2δ scans and corrected for Lorentz and polarization factors and for absorption. Carbon and oxygen atoms were refined with anisotropic temperature factors, and hydrogen atoms were refined in the "riding mode" with isotropic temperature factors.

Sample Preparation for High-Pressure Experiments. Both components were dissolved in the solvent and placed in a one-side-closed Teflon shrinking tube with a diameter of 0.5 in. The tube was sealed and placed in the high-pressure autoclave, which was filled with kerosene as a pressure medium.

1,4:6,21:10,17:12,15-Tetraepoxy-8,19-etheno-1,4,6,6a,7,8,9,-9a,10,12,15,17,17a,18,19,20,20a,21-octadecahydrononacene (4a). "Bis-diene" 1 (250 mg, 1.6 mmol) and 2 (815 mg, 3.9 mmol) were dissolved in 10 mL of methylene chloride and heated to 40 °C for 2 days under high pressure (7.5 kbar). The solvent was removed in vacuo and the residue chromatographed on silica gel (hexane/ethyl acetate (2/1)): yield 920 mg (84.4%) as a colorless powder; mp 165 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.90–7.11 (m, 8 H, CH arom and H2, H3, H13, H14), 6.61–6.71 (m, 2 H, CH), 5.62 (m, 4 H, H1, H4, H12, H15), 4.81 (m, 4 H, H6, H10, H17, H21), 4.04 (m, 2 H, H8, H19), 2.51–2.74 (m, 4 H, CH_2), 1.85–2.11 (m, 4 H, CH_2), 1.68–1.90 (m, 4 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.37, 144.05, 143.84, 143.75, 140.42, 140.33, 114.53, 114.29, 112.65, 112.37, 85.75, 85.51, 82.87, 82.78, 56.85, 42.92, 42.45, 42.06; FAB-MS 576.2 [M$^+$]. Anal. Calcd for $C_{40}H_{32}O_4$ (576.3): C, 83.30; H, 5.55. Found: C, 82.94; H, 5.05.

Cycloaddition Products (4b,c). **4a** (88 mg, 0.15 mmol) and 1 (24 mg, 0.15 mmol) were dissolved in 8 mL of chloroform and heated to 45 °C under high pressure (7.5 kbar) for 3 days. The reaction product was chromatographed on silica gel. First, hexane/ethyl acetate (2/1) eluted unreacted material, then oligomer **4b** was eluted with chloroform, and finally **4c** was eluted with methanol/chloroform (1/1). The workup yielded 21 mg of **4b** (21.4%) and 18 mg of **4c** (17.6%) referred to **4a**.

4b: mp 171 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) (all signals very broad) δ = 6.85–7.10 (m, 12 H), 6.55–6.74 (m, 6 H), 5.56–5.66 (m, 4 H), 4.70–4.91 (m, 12 H), 4.02 (s, br, 6 H), 2.42–2.76 (m, 12 H), 1.57–2.13 (m, 24 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 149.01, 145.51, 144.45 (3), 143.71 (3), 140.15 (3), 112.40 (3), 110.51 (3), 85.69 (2), 82.81 (2), 56.63, 42.61 (8), 31.62 (2); FAB-MS 1308.5 [M$^+$]. Anal. Calcd for $C_{92}H_{72}O_8$ (1308.60): C, 84.37; H, 5.81. Found: C, 84.06; H, 5.77.

4c: mp 178 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) (all signals very broad) δ = 6.83–7.13 (m, 16 H), 6.50–6.85 (m, 10 H), 5.55–5.68 (m, 4 H), 4.64–4.93 (m, 20 H), 4.03 (s, br, 10 H), 2.38–2.80 (m, 20 H), 1.50–2.15 (m, 40 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 149.05, 145.59, 145.08, 144.4 (6), 143.65 (4), 140.28 (3), 112.43 (3), 110.45 (3), 85.59 (3), 82.84 (3) 56.99, 56.82, 43.25 (3), 42.50 (8), 31.50 (3); FAB MS 2040.9 [M$^+$]. Anal. Calcd for $C_{144}H_{120}O_{12}$ (2040.95): C, 84.67; H, 5.88. Found: C, 84.19; H, 5.52.

Polymer (5). 1 (624 mg, 4 mmol) and 2 (1.51 g, 4 mmol) were dissolved in 10 mL of solvent (indicated in Table I). The tube was placed in the high-pressure autoclave and heated (see Table I for temperature and reaction time) under 7.5 kbar. After the reaction was finished the tube was removed, and the solution was added dropwise to 150 mL of diethyl ether to precipitate the polymer. Depending on the solvent used, the yields for the polyreaction ranged between 35 and 75%. Methanol cannot be used for the precipitation because even the monomers fall out.

^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.94, 1.32, 1.46, 1.78, 2.00, 2.11, 4.01, 4.87, 5.69, 6.68, 6.96 (all signals very broad and nonstructured); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.8, 23.2, 29.7, 30.8, 31.6, 32.1, 33.5, 43.1, 56.8, 83.9, 119.4, 124.0, 144.1, 146.1; IR (KBr) ν 3070, 2930, 2860, 1610, 1460, 1265, 1000, 905, 865, 745 cm^{-1}; UV (film) λ 216, 280 nm.

5,18:9,14-Bisepoxy-7,16-etheno-5,5a,6,8,8a,9,14,14a,15,17,-17a,18-dodecahydroheptacene (7). "Bis-diene" 1 (156 mg, 1 mmol) and 1,4-dihydro-1,4-epoxynaphthalene (6) (400 mg, 2.8 mmol) were dissolved in 6 mL of methylene chloride and heated to 50 °C for 2 days under high pressure (7.5 kbar). The solvent was removed by evaporation and the residue chromatographed on silica gel (hexane/ethyl acetate (10/1)). The workup yielded 200 mg of **7a** (45.5%) and 51 mg of **7b** (11.1%) as colorless powders.

7a: mp 190 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.03–7.18 (m, 8 H, CH arom), 6.71 (t, 2 H, CH), 4.92 (s, 4 H, CH), 4.09 (t, 2 H, CH), 2.56–2.77 (m, 4 H, CH_2), 1.98–2.16 (m, 4 H, CH_2), 1.73–1.84 (m, 4 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.24, 144.30, 140.24, 127.10, 119.18, 85.77 (C5, C9, C14, C18), 57.01, 42.79, 31.81; EI-MS *m/e* (relative intensity (%)) 444.2 (M$^+$, 10.2), 326.0 (12.7), 180.0 (10.8), 165.1 (14.9), 155.0 (10.9), 145.0 (10.7), 118.2 (100). Anal. Calcd for $C_{32}H_{28}O_2$ (444.2): C, 86.49; H, 6.31. Found: C, 86.06; H, 6.14.

7b: mp 226 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.05–7.18 (m, 8 H, CH arom), 6.71 (t, 2 H, CH), 4.98 (s, 2 H, CH), 4.92 (s, 2 H, CH), 4.09 (t, 2 H, CH), 2.60–2.82 (m, 4 H, CH_2), 1.96–2.18 (m, 4 H, CH_2), 1.83–2.04 (m, 4 H, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.27, 146.21, 144.07, 143.92, 126.92, 126.86, 119.17, 119.13, 85.76 (C5, C18), 85.68 (C9, C14), 56.92, 42.72, 42.46, 31.64; EI-MS, similar to **5a**. Anal. Calcd for $C_{32}H_{28}O_2$ (444.2: C, 86.49; H, 6.31. Found: C, 86.16; H, 6.33. Crystal data and data collection parameters of **7b** are given in Table II.

Table II

formula	$C_{32}H_{28}O_2$
solvent	$CHCl_3$
lattice type	orthorhombic ($\alpha = \beta = \gamma = 90°$)
space group	*Pbca*
T (K)	298
cell dimensions	
a, b, c (Å)	20.172(3), 32.460(3), 8.243(1)
V (Å^3)	5397(2)
D_c (g cm^{-3})	1.388
Z	8
no. of unique reflections measd (obsd)	3886 (2204)
no. of variables	459
R	0.051
R_w	0.054

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **7b** (7 pages). Ordering information is given on any current masthead page.

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