Ring-Chain Equilibrium between an [18]Cyclacene Derivative and a Ladder Oligomer

Oliver Kintzel[a], Peter Luger[b], Manuela Weber[b], and A.-Dieter Schlüter*[a]

Freie Universität Berlin, Institut für Organische Chemie[a],
Takustraße 3, D-14195 Berlin, Germany
Fax: (internat.) + 49(0)30/838-3357
E-mail: adschlue@chemie.fu-berlin.de

Freie Universität Berlin, Institut für Kristallographie[b],
Takustraße 6, D-14195 Berlin, Germany
Fax: (internat.) + 49(0)30/838-3464
E-mail: luger@chemie.fu-berlin.de

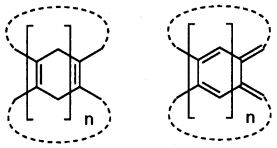
Received August 9, 1997

Keywords: Ladder polymers / Macrocycles / Cycloadditions / Retro Diels-Alder reaction / Benzo[*c*]furan

The synthesis of the AB-type Diels-Alder (DA) monomer **12** is reported whose self-condensation leads to the formation of the linear ladder oligomer **17** and its cyclic congener **18**. **18** is the largest [*n*]cyclacene derivative known ($n = 18$) and can be obtained by thermal treatment of **17** in yields of up to 45% utilizing the reversibility of the DA cyclization involved. **17** can be considered a "storage form" for **18**.

Introduction

The synthesis of ladder polymers by repetitive Diels-Alder (DA) reaction[1] is occasionally accompanied by an inadverted formation of cyclic oligomers.[2] These cycles have a double-stranded, belt-like structure and gained considerable interest not only because they can act as conformationally rigid guest molecules in inclusion complexes but also because they are potential precursors for their partially or fully unsaturated counterparts, the [*n*]beltenes **1** and [*n*]cyclacenes **2**. The latter ones are specifically exciting compounds, because they resemble the infinite polyacene, and interesting physical properties were postulated for them including superconductivity.[3][4] Some precursors of **1** and **2** have been synthesized.[2] The transformation into the targets, however, is still waiting to be accomplished. One reason for this may be the strain implemented by this sp^3-sp^2 conversion. The detrimental effect of a (small) ring size has recently again been shown by Cory et al.[2e] using an [8]cyclacene derivative. We here report on the synthesis of the multicyclic compound **11** whose thermal treatment liberates the AB-type DA monomer **12** which then reacts further to a mixture of predominantly DA ladder polymer **17** and some of the [18]cyclacene derivative **18**. Furthermore it is described how a ring-chain equilibrium between these two structures can be shifted to the ring side, thus providing a surprisingly facile access to **18** which makes this compound available in yields of up to 45%.



1 **2**

Results and Discussion

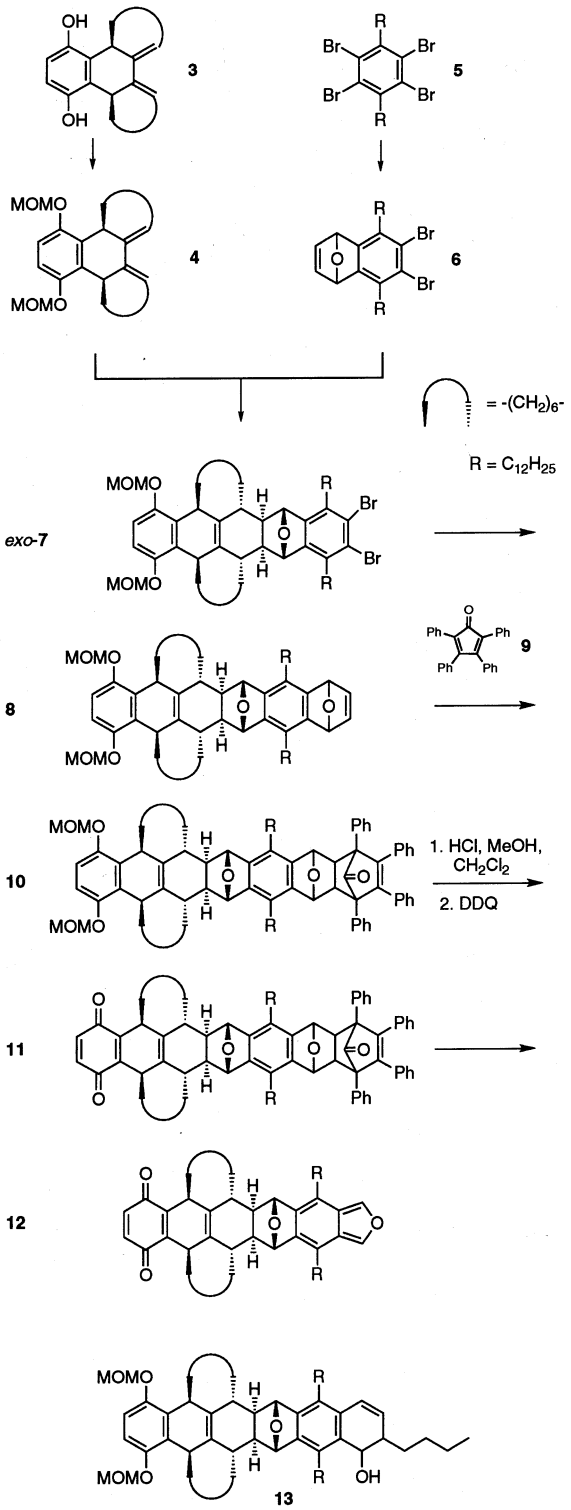
Synthesis of Precursor 11

The sequence starts with the DA addition of protected hydroquinone **4** and 1,4-epoxide **6** to give the corresponding 1:1 adduct **7** (Scheme 1). The former was easily obtained in gram quantities from the corresponding hydroquinone **3**[5] and the latter was prepared in analogy to Hart et al.[6] by adding furan to an intermediately formed dehydrobenzene derivative of **5**. Compound **7** was obtained as a mixture of the *exo* and *endo*-diastereomers in a ratio of exo:endo = 4:1. The isomers were separated by column chromatography and *exo*-**7** was isolated in 73% yield. For the stereochemical assignment see below. Its treatment with BuLi in the presence of furan gave **8** as a mixture of two isomers (by NMR spectroscopy, *cis* and *trans* with respect to the oxygen bridges) in 65% yield. No efforts were undertaken to separate them as this stereochemical information is lost anyhow during formation of monomer **12**. Synthesis of **8** was accompanied by the formation of a small amount of side product **13** which stems from the addition of BuLi to already formed **8** with opening of the oxygen bridge.[7] Compound **13** could not be completely removed from **8** by column chromatography and was thus carried through one step further. In the next step, tetracyclone (**9**) was added to **8** to give **10,** which was isolated and separated from all side products by precipitating it into ethanol. Finally, the MOM protective group was removed cleanly with hydrochloric acid and the resulting hydroquinone oxidized to give mono-

  1434–193X/98/0101–0099 $ 17.50+.50/0

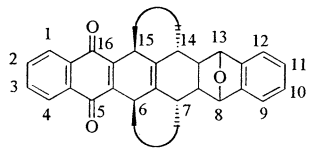
mer precursor **11** as a mixture of two diastereomers (^{1}H NMR) on the gram scale in a yield of 87%.

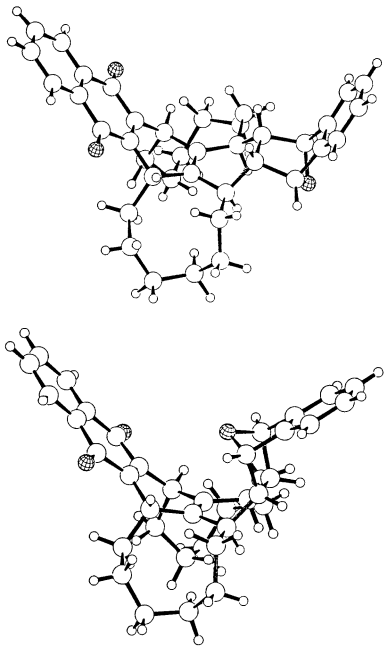
Scheme 1



The DA reaction between **4** and **6** can in principal lead to eight different stereoisomers only two of which were formed. Inspection of the ^{1}H-NMR spectrum of crude **7** helped to reduce this number to four. The signals of the hydrogen atoms in β-position to the oxygen bridges appear as sharp singlets which shows that they are positioned at the *endo* side of the oxanorbornene moiety. A further assignment, however, was not possible because none of the diastereomers could be grown as single crystals. Compound **16** which closely resembles the critical part of **7** was therefore prepared from diene **14** and dienophile **15**. The two diastereomers formed (ratio approx. 1:1) were separated, single crystals of both isomers grown, and their structure determined by X-ray diffraction. Figure 1 shows the crystal structures of *exo*-**16** and *endo*-**16**. The cyclohexene ring in both adopts a boat-like conformation. With these structures at hand the NMR spectra of **16** could be assigned and this assignment was then used in turn to establish the structures of *exo*-**7** and *endo*-**7**. This assignment is consistent with the fact that oxanorbornenes (like **6**) tend to add dienes from the oxygen side[8] and dienes of type **4** prefer to add dienophiles from the less crowded side with respect to the hexamethylene loop.[9]

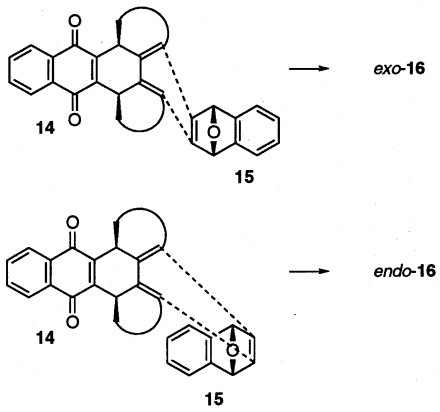
Figure 1. Molecular structures of *exo*- (top) and *endo*-**16** (bottom) in the crystal (SCHAKAL representation)





A further question of interest was the spatial shape of *exo*-**16** in solution.[10] Since this shape to a good part reflects that of monomer **12**, an assessment of it should help to gain some insight into geometrical features of the oligomers formed during the first steps of growth of **12**. The dihedral angles 7-H/7a-H and 13a-H/14-H of *exo*-**16** in the crystal are 165° and 172°, respectively.[11] These large angles seem to be more or less retained also in solution since large coupling constants are observed in the ^{1}H-NMR spectrum

Scheme 2



(7a-H: J = 10; 13a-H: J = 12 Hz).[12] With stick-and-ball models the dihedral angles in other conformations of *exo*-**16** were studied qualitatively and found to be smaller. For example, the conformation in which the cyclohexene boat is inverted, the angles lie only around some 60° which ought to result in a small coupling constant. This conformation resembles very closely that of *endo*-**16** in the crystal in which the dihedral angles are 56 and 60°. The assumption that the favored conformation of *exo*-**16** in the crystal and in solution are similar to one another is reasonable since the hexylene loops are pseudo-equatorial at C-7 and C-14, which is energetically favored, and pseudo-axial[13] at C-6 and C-15 which helps to avoid *peri* interactions with the carbonyl group.

Oligomerization

The oligomerization was performed by refluxing monomer precursor **11** in toluene for 60 h, during which time monomer **12** is generated in situ and its self-addition takes place. Size exclusion chromatography (SEC) versus polystyrene standard of the raw material obtained reveals a bimodal distribution[14] for which the individual peaks correspond to average degrees of oligomerization of P_n = 7−14 (6100 < M_n < 12200) and P_n = 3 (M_n = 2700). The two fractions were separated by preparative SEC and the material with P_n = 3 was further purified by preparative HPLC (yield: 6%). The open-chain structure **17** and the cyclic trimer **18** were tentatively assigned to these fractions. The structure of oligomer **17** was established by elemental analysis and NMR spectroscopy (Figure 2). The MALDI-TOF mass spectrum (matrix: dihydroxyanthracene) of the presumed cycle gave m/z = 2616 which corresponds to a protonated trimer plus two hydrogen atoms of the most abundant isotopomer. This assumption is reasonable because transhydrogenation from the matrix may be particulary easy under laser irridiation.[15] The proof that trimer **18** is actually a cycle could be unequivocally brought about by the following NMR evidence:

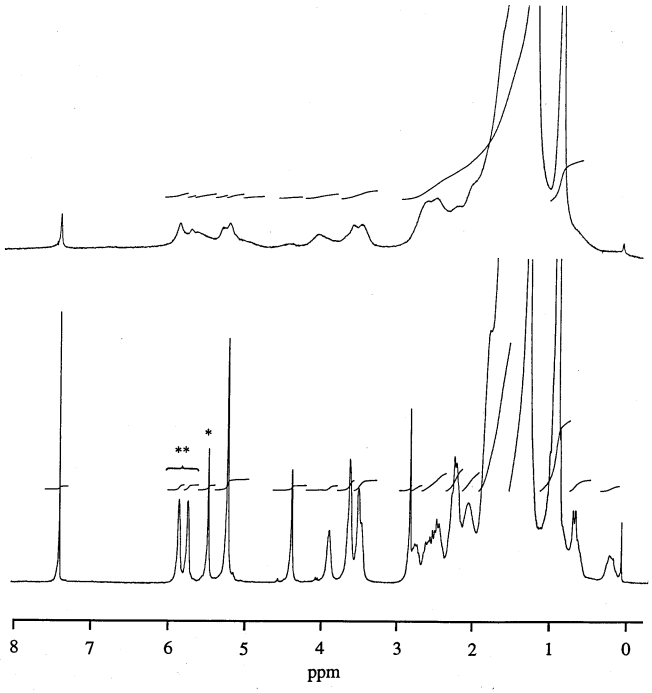
(a) The ^{1}H-NMR spectrum of **18** (Figure 2) shows no quinoid end group[16], whose signal would be expected at δ ≈ 6.7.

(b) For the protons H^a which are directly involved in the DA cyclization (Scheme 3) three (and not two) signals are observed at δ = 5.3−5.8. Because of the multiplicity and the intensity of these signals it can be decuced that one *exo* and two (stereochemically different) *endo* connections between the monomer units exist.

(c) The ^{13}C-NMR spectrum shows three sets of three signals each for C^b, C^d, and C^e (and not less).

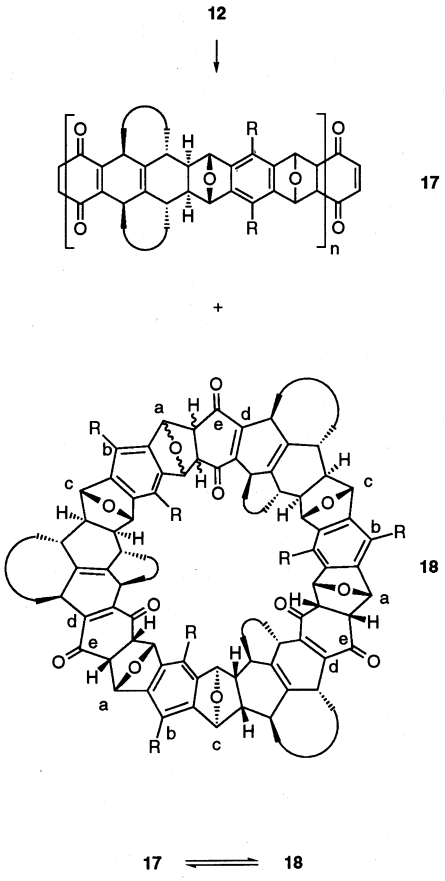
(d) The carbon atoms C^a and C^c give rise to a group of six signals (and not five) at δ = 81.1−84.2.

Figure 2. ^{1}H-NMR spectra of linear oligomer **17** (P_n = 7) (top) and [18]cyclacene derivative **18** (bottom) in $CDCl_3$ at 20°C with an assignment of the protons H^a at the *exo* (*) and *endo* linkages (**)



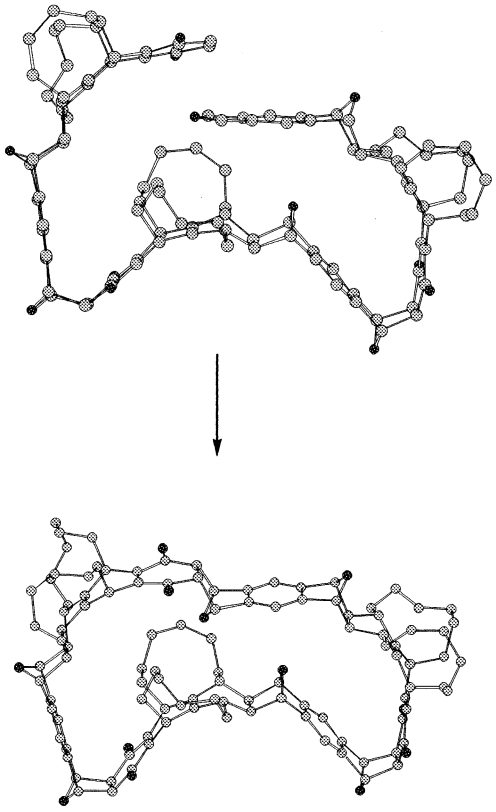
The stereochemistry of ring **18** is complex. The proposed stereochemistry is based on the NMR-spectroscopically detected one *exo*- and two *endo*-configurated linkages and the following geometrical consideration. Several precursors for **18** which differed in the respective stereochemistry at the two *endo* linkages were constructed (Chem3D and X-ray data of *exo*-**16**) in which only the final cyclization step was missing. The *endo* linkages of the only low-strained precursor in which the termini are in close contact and allow for an *exo* linkage to occur are *endo(syn)-trans* and *endo(anti)-cis* (Figure 3).[17] Figure 3 suggests the *exo* linkage to be *exo(anti)-trans*. This geometrical consideration, however, is only valid if monomer **12** does not undergo the conformational flip of the cyclohexene moiety as discussed for *exo*-**16**. This flip is unlikely to occur because the ^{1}H-NMR spectra of *exo*-**16** even at 100°C (reaction temp.: 110°C) still show almost unchanged coupling constants (see above). Crystals of **18** could be obtained from dichloromethane. X-ray diffraction using synchroton radiation, however, showed that they have a layered structure with lateral order but with no periodicity across the layers.

Scheme 3

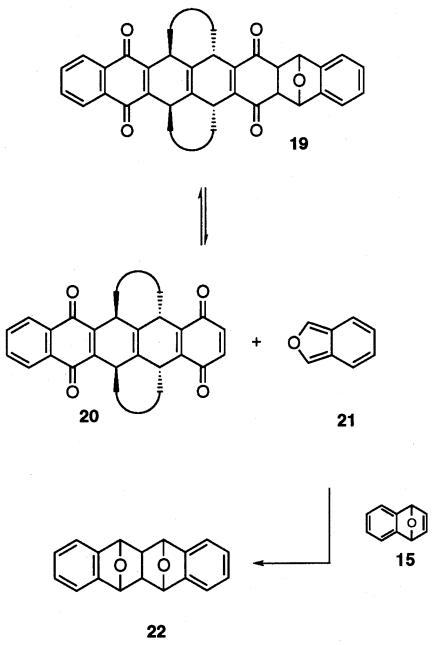


The DA polyaddition of **12** is reversible in contrast to most other reactions of this kind leading to ladder polymers. This is advantageous and disadvantageous at the same time. The advantage is that simple refluxing of oligomer **17** in decalin[18] until the equilibrium is reached furnishes macrocycle **18** in a maximum yield of 45% (^{1}H NMR). After separation of the macrocycle, subjection of the remaining oligomer provides additional macrocycle, so that, in principle, the linear **17** can be completely converted into macrocycle **18**. The disadvantage is, of course, the limited achievable molecular weight of **17**, a situation which is reminiscent of the ceiling phenomenon in chain polymerizations. The reversibility of some DA reactions of furans is well-known[19] as is that of quinone adducts with phenyl-substituted benzofuran. They may even proceed at room temperature.[20] The reversibilty of the DA reaction under consideration was further established with the help of compound **19**[21] which also contains the critical structural motif. All four diastereomers of **19** were separated by HPLC and individually heated in refluxing decalin. In each case the same mixture of diastereomers was obtained as in the original preparation. Heating of one of the diastereomers in the presence of two equivalents of **15** gave the same mixtures of diastereomers but also 5−10% of the well-characterized compound **22**, which is stable against cycloreversion.[22] These results clearly establish that the DA reaction is in equilibrium with the retro DA reaction even at 110°C.

Figure 3. Chem3D-generated structure of the precursor to **18** (top) and the final cycle **18** (bottom); for a discussion of the stereochemical features, see text



Scheme 4



This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We are greatful to Dr. *Lamer* and his crew for doing all SEC and HPLC separations and to Dr. *Franke* for carrying out the MALDI-TOF experiment. We thank one of the referees for valuable comments.

Experimental Section

General: Starting materials were either prepared acording to literature procedures or purchased from Fluka, Aldrich or Acros and used without further purification. All solvents were purified and dried by standard methods. All reactions were carried out under N_2. – ^{1}H-NMR spectra: Bruker AM 270 spectrometer (270 MHz) ($CDCl_3$ at δ = 7.24 as internal standard). – ^{13}C-NMR spectra: Bruker AM 270 spectrometer (67.9 MHz) ($CDCl_3$ at 77.0 as internal standard). – MS: Varian MAT 711 spectrometer. – Elemental analyses: Perkin Elmer EA 240.

rel-(1R,4S)-1,2:4,3-Di(1-heptanyl-7-yliden)-5,8-bis(methoxymethoxy)-1,4-dihydronaphthalene (**4**): Hydroquinone **3** (2.7 g, 7.67 mmol) was dissolved in 150 ml of degassed acetone. Then KO*t*Bu (2.06 g, 16.86 mmol) was added and the dark solution was stirred for 15 min before chloromethyl methyl ether (1.23 g, 15.33 mmol) was added in one portion. Then the mixture was refluxed for 3 h. The cooled solution was quenched with water, concentrated and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and concentrated again. Ethanol was added and the mixture was left standing for 2 d. The light brown precipitate was filtered and dried to give 2.18 g (4.95 mmol, 65%) of **4**. – ^{1}H NMR: δ = 1.4–1.8 (m, 20 H, CH_2), 2.15 (m, 2 H, C=C–CH_2), 2.55 (m, 2 H, C=C–CH_2), 3.49 (s, 6 H, OCH_3), 4.30 (m, 2 H, 1-, 4-H), 5.18 (AB system, 4 H, OCH_2), 5.99 (dd, J_1 = 7 Hz, J_2 = 11 Hz, 2 H, C=C-H). – ^{13}C NMR: δ = 24.09, 26.91, 27.29, 27.41, 27.97, 35.31, 37.04, 55.86, 94.84, 111.38, 122.90, 133.25, 140.56, 148.17. – $C_{28}H_{40}O_4$ (440.6): calcd. C 76.32, H 9.15; found C 76.39, H 9.07.

rel-(1R,4S)-6,7-Dibromo-5,8-didodecyl-1,4-epoxynaphthalene (**6**): 1,2,4,5-Tetrabromo-3,6-didodecylbenzene **5** (10.32 g, 14.13 mmol) was dissolved in 200 ml of dry toluene and 30 ml of dry furan. The solution was cooled to −30°C and 11 ml of BuLi (1.3 M, 14.3 mmol), diluted with 150 ml of dry hexane, was slowly added over a period of 3 h. The reaction mixture was allowed to warm up to room temperature before being quenched with 200 ml of water. The organic phase was separated, dried with $MgSO_4$ and concentrated. Then the mixture was separated by chromatography (silica gel, hexane) to remove unreacted starting material. The eluent was changed to toluene/hexane (1:2) to give a yellow oil after concentration. Ethanol (20 ml) was added and the mixture was left standing overnight. The white precipitate was filtered and dried to furnish 3.89 g (6.09 mmol, 43%) of **6**. – ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 6 H, CH_3), 1.10–1.65 (m, 40 H, CH_2), 2.79 (t, 7.2 Hz, 4 H, Bn), 5.75 (s, 2 H, 1-, 4-H), 7.0 (s, 2 H, 2-, 3-H). – ^{13}C ($CDCl_3$): δ = 14.10, 22.68, 29.34, 29.43, 29.56, 29.63, 29.84, 31.91, 34.79, 81.80, 124.52, 134.92, 142.69, 147.59. – $C_{34}H_{54}Br_2O$ (638.6): calcd. C 63.95, H, 8.52; found C 63.91, H 8.41.

rel-(5R,6S,6aS,7R,12S,12aR,13R,14S)-9,10-Dibromo-8,11-didodecyl-1,4-bis(methoxymethoxy)-5,6,6a,7,12,12a,13,14-octahydro-7,12-epoxy-5,6:13,14-dihexanopentacene (*exo*-**7**) *and rel-(5R,6S,6aR,7S,12R,12aS,13R,14S)-9,10-dibromo-8,11-didodecyl-1,4-bis(methoxymethoxy)-5,6,6a,7,12,12a,13,14-octahydro-7,12-epoxy-5,6:13,14-dihexanopentacene* (*endo*-**7**): Diene **4** (2.68 g, 6.09 mmol) and epoxide **6** (3.89 g, 6.09 mmol) were refluxed in 80 ml of toluene for 2 d. After removal of the solvent, the mixture was separated by chromatography [silica gel, hexane/AcOEt (20:1)] to give 4.77 g (73%) of *exo*-**7** as white solid and 1.11 g (17%) of *endo*-**7** as light yellow oil which solidified after some days.

exo-**7**: ^{1}H NMR ($CDCl_3$): δ = 0.9 (t, J = 7.2 Hz, 6 H, CH_3), 1.18–1.93 (m, 62 H, CH_2, 6a-, 12a-H), 2.08 (m, 4 H, CH_2), 2.50 (m, 2 H, 6-, 13-H), 2.70 (m, 4 H, Bn), 3.47 (s, 6 H, OCH_3), 4.20 (m, 2 H, 5-, 14-H), 5.12 (AB system, 4 H, OCH_2), 5.24 (s, 2 H, 7-, 12-H), 6.79 (s, 2 H, 2-, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 14.115, 22.69, 25.43, 26.11, 27.36, 28.77, 29.35, 29.59, 29.68, 29.80, 29.88, 31.58, 31.93, 34.52, 35.08, 39.38, 43.32, 52.00, 55.91, 83.63, 94.89, 110.88, 125.36, 133.52, 134.62, 139.63, 144.63, 147.98. – $C_{62}H_{94}Br_2O_5$ (1079.2): calcd. C 69.00, H 8.78; found C 69.06, H 8.59.

endo-**7**: ^{1}H NMR($CDCl_3$): δ = 0.9 (t, J = 7.2 Hz, 6 H, CH_3), 1.1–1.9 (m, 60 H, CH_2), 1.93 (s, 2 H, 6a-, 12a-H), 2.0 (m, 2 H, CH_2), 2.35 (m, 2 H, CH_2), 2.53 (m, 2 H, 6-, 13-H), 2.65 (m, 4 H, Bn), 3.50 (s, 6 H, OCH_3), 4.13 (m, 2 H, 5-, 14-H), 4.85 (s, 2 H, 7-, 12-H), 5.16 (AB system, 4 H, OCH_2), 6.75 (s, 2 H, 2-, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 14.11, 22.69, 25.45, 26.00, 27.91, 28.63, 29.35, 29.41, 29.59, 29.67, 29.71, 29.85, 30.26, 31.93, 35.01, 35.99, 39.60, 43.06, 50.59, 56.01, 95.15, 111.05, 125.03, 132.90, 134.90, 136.90, 145.98, 148.00. – $C_{62}H_{94}Br_2O_5$ (1079.2): calcd. C 69.00, H 8.78; found C 69.31, H 8.71.

8,13-Didodecyl-1,4-bis(methoxymethoxy)-5,6,6a,7,9,12,14,14a,15,16-decahydro-7,14:9,12-diepoxy-5,6:15,16-dihexanohexacene (**8**) *and 10-Butyl-8,13-didodecyl-9-hydroxy-1,4-bis(methoxymethoxy)-5,6,6a,7,9,10,14,14a,15,16-decahydro-7,14-epoxy-5,6:15,16-dihexanohexacene* (**13**): *exo*-**7** (4.63 g, 4.28 mmol) was dissolved in 60 ml of dry toluene and 40 ml of dry furan, before being cooled to −60°C. Then BuLi (4.8 mmol in 40 ml of dry hexane) was added slowly. The mixture was allowed to warm up to room temperature before being quenched with 50 ml of water. The organic layer was separated and dried with $MgSO_4$. The solvent was removed and the residue purified by column chromatography [silica gel, hexane/AcOEt (20:1)] to give 2.73 g (65%) of **8** as a white solid and 240 mg (5%) of the alcohol **13**.

8: ^{1}H NMR ($CDCl_3$): δ = 0.9 (t, J = 7.2 Hz, 6 H, CH_3), 1.1–2.2 (m, 66 H, CH_2, 6a-, 14a-H), 2.55 (m, 6 H, Bn, 6-, 15-H), 3.48 (s, 6 H, OCH_3), 4.15 (m, 2 H, 5-, 16-H), 5.10 (AB system, 4 H, OCH_2), 5.14, 5.17 (2 s, 2 H, 7-, 14-H), 5.57, 5.59 (2 s, 2 H, 9-, 12-H), 6.73, 6.76 (2 s, 2 H, 10-, 11-H), 6.80, 6.85 (2 s, 2 H, 2-, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 14.07, 22.65, 25.42, 26.09, 27.41, 28.73, 28.80, 29.31, 29.43, 29.54, 29.62, 29.84, 30.19, 30.25, 31.14, 31.26, 31.89, 34.47, 39.39, 43.51, 52.06, 52.39, 55.81, 55,87, 80.96, 81.09, 82.71, 82.85, 94.85, 110.84, 124.98, 125.16, 134.74, 134.78, 139.65, 139.89, 142.35, 142.42, 143.00, 143.07, 146.29, 146.42, 147.95. – HRMS; *m/z* [M^+, $C_{66}H_{98}O_6$]: calcd. 986.7363, found 986.7363.

13: ^{1}H NMR ($CDCl_3$): δ = 0.9 (t, J = 7.6 Hz, 6 H, $C_{11}H_{22}$–CH_3), 0.95 (t, J = 7.2 Hz, 3 H, C_3H_6–CH_3), 1.1–2.2 (m, 73 H, CH_2, OH, 6a, 14a-H), 2.25 (m, 1 H, 10-H), 2.42–2.80 (m, 6 H, Bn, 6-, 15-H), 3.42 (s, 6 H, OCH_3), 4.21 (m, 2 H, 5-, 16-H), 4.61 (m, 1 H, 9-H), 5.12 (AB system, 4 H, OCH_2), 5.16, 5,18 (2 s, 2 H, 7-, 14-H), 5.72 (d, J = 9.9 Hz, 1 H, 11-H), 6.68 (dd, J_1 = 9.9 Hz, J_2 = 1.0 Hz, 1 H, 12-H), 6.75 (s, 2 H, 2-, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 14.10, 22.67, 22.84, 25.42, 26.13, 27.42, 28.76, 29.35, 29.39, 29.67, 30.00, 30.97, 31.91, 34.52, 39.39, 40.21, 40.37, 43.46, 52.37, 55.83, 65.93, 83.21, 94.82, 110.82, 123.85, 127.97, 228.86, 129.01, 129.51, 129.70, 133.56, 134.75, 139.69, 144.23, 144.64, 147.92. – HRMS ($C_{70}H_{108}O_6$): calcd. 1044.81459, found 1044.81500.

10,13-Carboxy-8,15-didodecyl-1,4-bis(methoxymethoxy)-10,11,12,13-tetraphenyl-5,6,6a,7,9,9a,10,13,13a,14,16,16a,17,18-tetradecahydro-7,16:9,14-diepoxy-5,6:17,18-dihexanoheptacene (**10**): Compound **8** (2.03 g, 2.06 mmol) and tetraphenylcyclopentadienone (0.79 g, 2.06 mmol) were stirred in 80 ml of toluene at 70°C for 2 d, during which time the deep purple color of the solution almost disappeared. The solution was concentrated and ethanol (50 ml) was added. A white precipitate formed which was filtered and dried (1.83 g, 65%). – ^{1}H NMR ($CDCl_3$): δ = 0.85 (t, J = 7.2 Hz, 6 H, CH_3), 1.0–2.1 (m, 66 H, CH_2, 6a-, 16a-H),

2.50−2.90 (m, 6 H, Bn, 6-, 17-H), 2.96, 2.99 (2 s, 2 H, 9a-, 13a-H), 3.41, 3.46 (2 s, 6 H, OCH_3), 4.21 (m, 2 H, 5-, 18-H), 5.12 (m, 4 H, OCH_2), 5.29 (s, 2 H, 7-, 16-H), 5.76 (s, 2 H, 9-, 14-H), 6.73, 6.79 (2 s, 2 H, 2-, 3-H), 6.80−7.04 (m, 10 H, Ph), 7.24−7.50 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 14.11, 22.67, 25.42, 26.15, 27.32, 28.78, 29.34, 29.45, 29.66, 30.05, 30.27, 30.89, 31.20, 31.64, 31.91, 34.45, 39.40, 43.54, 46.83, 46.96, 51.98, 55.81, 55.90, 64.20, 64.27, 79.95, 80.06, 82.85, 94.77, 110.78, 123.57, 123.75, 126.62, 127.27, 127.44, 128.19, 129.41, 129.87, 134.67, 135.13, 135.66, 138.48, 139.59, 139.75, 144.13, 144.23, 144.40, 147.88, 147.97, 196.67. − $C_{95}H_{118}O_7$ (1372.0): calcd. C 83.17, H 8.67; found C 82.71, H 8.67.

10,13-Carboxy-8,15-didodecyl-10,11,12,13-tetraphenyl-5,6,6a,7,9,9a,10,13,13a,14,16,16a,17,18-tetradecahydro-7,16:9,14-diepoxy-5,6:17,18-dihexano-1,4-heptacenedione (**11**): Compound **10** (1.24 g, 0.90 mmol) was stirred with 120 ml of MeOH, 30 ml of CH_2Cl_2 and 2 ml of 24% HCl at 60°C for 1d. The mixture was concentrated and extracted with CH_2Cl_2. The organic layer was separated and dried with $MgSO_4$. After addition of DDQ (205 mg, 0.90 mmol), the solution was stirred for 30 min. The solution was concentrated and the product precipitated with EtOH. The bright yellow solid was filtered and dried (1.00 g, 87%). − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.5 Hz, 6 H, CH_3), 1.0−2.2 (m, 66 H, CH_2, 6a-, 13a-H), 2.40−2.87 (m, 6 H, Bn, 6-, 17-H), 2.94, 2.98 (2 s, 2 H, 9a-, 13a-H), 3.90 (m, 2 H, 5-, 18-H), 5.26 (s, 2 H, 7-, 16-H), 5.74 (s, 2 H, 9-, 14-H), 6.59, 6.63 (2 s, 2 H, 2-, 3-H), 6.80−7.10 (m, 10 H, Ph), 7.25−7.55 (m, 10 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 14.12, 22.69, 25.20, 25.94, 26.42, 28.58, 29.18, 29.34, 29.51, 29.68, 30.09, 30.36, 30.90, 31.21, 31.54, 31.73, 31.93, 33.73, 38.37, 43.21, 46.88, 47.05, 52.12, 64.24, 79.99, 82.62, 123.75, 123.92, 126.65, 127.33, 127.47, 128.23, 129.43, 129.90, 135.19, 135.66, 135.98, 138.53, 138.98, 144.13, 144.29, 146.75, 186.98. − $C_{91}H_{108}O_5$ (1281.9): calcd. C 85.27, H 8.49; found C 84.58, H 8.51.

Polyaddition of Monomer **11**: Monomer **11** (907 mg, 0.71 mmol) was refluxed in 10 ml of dry toluene for 60 h. After reducing the temperature to 50°C, the solution was stirred overnight. The product was precipitated in methanol and freeze-dried in benzene to give 620 mg of a light yellow solid. This was purified by preparative SEC (Nucleosil 50-5, THF) to give 282 mg (45%) of polymer **17** and 216 mg (35%) of a low molecular weight fraction. The latter was further purified by HPLC (Eurosphere 100/Si, 5 μ) to furnish 35 mg (6%) of the [18]cyclacene derivative **18**.

Polymer **17**: $[C_{60}H_{86}O_4]_n$ ([871.3]$_n$): calcd. C 82.71, H 9.95; found C 82.12, H 9.95.

rel-(1R,4S,4aS,6R,7S,7aS,8R,10S,10aR,12R,13S,14R,16S,16aS,18S,19R,19aR,20S,23R,23aS,24S,25R,26aR,27R,29S,29aR,30R,31S,32aS,33R,35S,35aR,36R,37S,38aR)-9,15,28,34-Tetradodecyl-1,4,4a,6,7,7a,8,10,10a,12,13,13a,14,16,16a,18,19,19a,20,23,23a,24,25,26a,27,29,29a,30,31,32a,33,35,35a,36,37,38a,-hexatriacontahydro-1,4:8,35:10,33:14,29:16,27:20,23-hexaepoxy-6,7:12,13:18,19:24,25:30,31:36,37-hexahexano-2,22:3,21-bis(dodecylmetheno)-5,11,17,26,32,38-heptadecacenehexone (**18**): ^{1}H NMR ($CDCl_3$): δ = 0.19 (m, 2 H, CH_2), 0.67 (t, 4 H, CH_2), 0.90 (t, *J* = 6.5 Hz, 18 H, CH_3), 1.1−2.1 (m, 192 H, CH_2, 7a-, 13a-, 19a-, 23a-, 29a-, 35a-H), 2.20−2.70 (m, 18 H, Bn, 7-, 13-, 19-, 24-, 30-, 36-H), 2.77 (s, 2 H, 10a-, 32a-H), 3.42, 3.54, 3.80 (3 m, 10 H, 4a-, 6-, 12-, 16a-,18-,25-, 26a-, 31-, 37-, 38a-H), 4.28 (s, 2 H, 20-, 23-H), 5.11 (s, 4 H, 8-, 14-, 29-, 35-H), 5.36 (s, 2 H, 16-, 27-H), 5.60 (m, 2 H, 4a-, 38a-H or 16a-, 26a-H), 5.73 (m, 2 H, 4a-, 38a-H or 16a-, 26a-H). − ^{13}C NMR ($CDCl_3$): δ = 14.12, 22.71, 25.14, 25.35, 25.89, 26.38, 26.52, 28.39, 28.91, 29.39, 29.74, 30.20, 30.32, 30.64, 30.98, 31.55, 31.92, 31.97, 33.79, 34.65, 37.34, 38.19, 42.61, 42.75, 48.14, 49.11, 51.19, 51.63, 52.21, 81.15, 81.39, 82.09, 82.46, 82.65, 84.18, 123.56, 124.08, 124.67, 137.13, 138.12, 139.41, 140.43, 141.83, 143.84, 144.45, 144.69, 151.41, 151.72, 153.38, 194.28, 194.54, 196.37. − $C_{180}H_{258}O_{12}$ (2614.0): calcd. C 82.71, H 9.95; found C 81.57, H 9.62.

rel-(6R,7S,7aS,8R,13S,13aR,14R,15S)-6,7,7a,8,13,13a,14,15-Octahydro-8,13-diepoxy-6,7:14,15-dihexano-5,16-hexacenedione (*exo*-**16**) *and rel-(6R,7S,7aR,8S,13R,13aS,14R,15S)-6,7,7a,8,13,13a,14,15-Octahydro-8,13-diepoxy-6,7:14,15-dihexano-5,16-hexacenedione* (*endo*-**16**): Diene **12** (802 mg, 2.00 mmol) and naphthalene epoxide (289 mmol, 2.00 mmol) were refluxed in 20 ml of toluene for 2 d under exclusion of light. The solvent was removed and the two diastereomers separated by silica gel column chromatography [toluene/hexane (3:1)] to give 520 mg (48%) of *exo*-**16** and 442 mg (41%) of *endo*-**16** both as bright yellow solids. Single crystals were obtained from CH_2Cl_2/EtOH (*exo*-**16**) and CH_2Cl_2/hexane (*endo*-**16**).

exo-**16**: ^{1}H NMR ($CDCl_3$): δ = 1.36 (m, 2 H, 7a-, 13a-H), 1.45−2.17 (m, 22 H, CH_2), 2.51 (m, 2 H, 7-, 14-H), 4.11 (m, 2 H, 6-, 15-H), 5.21 (s, 2 H, 8-, 13-H), 7.04 (m, 2 H, 10-, 11-H), 7.15 (m, 2 H, 9-, 12-H), 7.64 (m, 4 H, 2-, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 25.21, 25.83, 26.64, 28.59, 29.20, 34.26, 38.40, 43.13, 52.26, 83.94, 118.63, 126.03, 126.34, 132.13, 133.30, 138.95, 145.87, 149.22, 184.36. − $C_{38}H_{40}O_3$ (544.7): calcd. C 83.79, H 7.40; found C 83.31, H 7.13.

endo-**16**: ^{1}H NMR ($CDCl_3$): δ = 1.4−2.15 (m, 22 H, CH_2, 1.99 (s, 2 H, 7a-, 13a-H), 2.35 (m, 2 H, CH_2), 2.51 (m, 2 H, 7-, 14-H), 4.10 (m, 2 H, 6-, 15-H), 5.87 (s, 2 H, 8-, 13-H), 7.00 (m, 4 H, 9-, 10-, 11-, 12-H), 7.62 (m, 2 H, 2-, 3-H), 8.02 (m, 2 H, 1-, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 25.24, 25.73, 27.09, 28.34, 29.64, 35.76, 38.45, 43.04, 50.62, 80.60, 118.07, 125.98, 132.47, 133.08, 136.27, 147.14, 149.37, 184.73. − $C_{38}H_{40}O_3$ (544.7): calcd. C 83.79, H 7.40; found C 83.44, H 7.26.

Crystal-Structure Analysis of exo-**16**: Crystal data: $C_{38}H_{40}O_3$; M_r = 544.70; triclinic; space group $P\bar{1}$; *a* = 1129.7(2), *b* = 1184.3(2), *c* = 1263.5(2) pm; α = 106.93(1), β = 89.82(1), γ = 115.84(1)°; *V* = 1.4404 nm^3; *Z* = 2; D_x = 1.256 Mgm^{-3}; λ(Mo-K_α) = 71.068 pm; μ = 0.078 mm^{-1}; *T* = 293 K. Data collection and reduction: A pale yellow quadratic prism 0.8 × 0.6 × 0.4 mm was used for all X-ray experiments executed on a Siemens four-circle diffractometer. 6970 reflection intensities (6632 unique, R_{int} = 0.012) were collected until $2\Theta_{max}$ = 55° with the ω/2Θ-scan technique. Cell constants were obtained from centering of 102 high-order reflections. Lorenz and polarization correction, but no absorption correction were applied. Structure solution and refinement: The structure was solved by direct methods (program SHELX586)[23] and refined anisotropically on F^2 using the program SHELXL-93.[24] Hydrogen atoms from difference syntheses refined isotropically. The final $wR(F^2)$ was 0.143 for 530 parameters, conventional $R(F)$ = 0.048 [$F > 4\sigma(F)$]; *S* = 1.05, $\delta/\sigma < 0.002$, $\Delta\sigma_{max}$ = 290 e nm^{-3}.

Crystal-Structure Analysis of endo-**16**: Crystal data: $C_{38}H_{40}O_3$; M_r = 544.70; monoclinic; space group $P2_1/a$; *a* = 2038.0(3), *b* = 1516.3(2), *c* = 961.7(2) pm; β = 102.05(2)°; *V* = 2.9064 nm^3; *Z* = 4; D_x = 1.245 Mgm^{-3}; λ(Cu-K_α) = 154.18 pm; μ = 0.599 mm^{-1}; *T* = 293 K. Data collection and reduction: A pale yellow quadratic prism 0.38 × 0.25 × 0.18 mm was used for all X-ray experiments executed on a Stoe four-circle diffractometer. 4808 reflection intensities (4510 unique, R_{int} = 0.012) were collected until $2\Theta_{max}$ = 125° with the ω/2Θ-scan technique. Cell constants were obtained from centering of 66 high-order reflections. Lorenz and polarization correction, but no absorption correction were applied. Structure solution and refinement: As for *exo*-**16**. The final $wR(F^2)$ was 0.077 for

531 parameters, conventional $R(F) = 0.034$ [$F > 4\sigma(F)$]; $S = 1.09$, $\delta/\sigma < 0.004$, $\Delta\sigma_{max} = 163$ e nm^{-3}.

Additional material to this paper can be ordered refering to the depostion numbers CSD-407495 and -407496, the names of the authors and the journal citation from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany.

[1] [1a] A.-D. Schlüter, *Adv. Mater.* **1991**, *3*, 282. – [1b] A.-D. Schlüter, M. Löffler, A. Godt, K. Blatter "Perfect Diels-Alder Ladder Polymers: Precursors for Extended π-Conjugation" in *Desk Reference of Functional Polymers*, R. Arshady (Ed.), ACS, Washington, DC, **1997**, p. 73.

[2] [2a] A. Godt, V. Enkelmann, A.-D. Schlüter, *Angew. Chem.* **1989**, *101*, 1704; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1680. – [2b] P. R. Ashton, G. R. Brown, N. S. Isaacs, D. Giuffrida, F. H. Kohnke, J. P. Mathias, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 6330. – [2c] S. Wegener, K. Müllen, *Macromolecules* **1993**, *26*, 3037. – [2d] J Benkhoff, R. Boese, F.-G. Klärner, *Tetrahedron Lett.* **1994**, *35*, 73. – [2e] R. M. Cory, C. L. McPhail, A. J. Dikmans, J. J. Vittal, *Tetrahedron Lett.* **1996**, *37*, **1983. –** [2f] O. Kintzel, A.-D. Schlüter, *Acta Polym.* **1997**, *48*, 212.

[3] [3a] R. W. Alder, R. B. Session, *J. Chem. Soc, Perkin Trans. 2* **1985**, 1849. – [3b] R. O. Angus, Jr., R. P. Johnson, *J. Org. Chem.* **1988**, *53*, 314. – [3c] F. Vögtle, *Top. Curr. Chem.* **1983**, *115*, 157. – [3d] F. Vögtle, *Top. Curr. Chem.* **1994**, *172*, 179.

[4] S. Kvielson, O. L. Chapman, *Phys. Rev.* **1983**, *B28*, 7236.

[5] A. Godt, A.-D. Schlüter, *Chem. Ber.* **1991**, *124*, 149.

[6] H. Hart, C. Lai, N. Chukuemeka, S. Shamouilian, *Tetrahedron* **1987**, *43*, 5203. See also: H. Meier, B. Rose, *Liebigs Ann.* **1997**, 663.

[7] G. Wittig, L. Pohmer, *Chem. Ber.* **1956**, *89*, 1334.

[8] A. W. McCulloch, D. G. Smith, A. G. McInnes, *Can. J. Chem.* **1973**, *51*, 4125.

[9] A. Godt, V. Enkelmann, A.-D. Schlüter, *Chem. Ber.* **1992**, *125*, 433.

[10] Since there are only two of the possible four diastereomers formed we refer to them as *exo*- and *endo*-**16** for clarity.

[11] The fact that the angles are not identical reflects a slightly disortion of **16** towards a half-chair conformation.

[12] The coupling constants were determined by simulation of the signal for 7a-H and 13a-H.

[13] P. W. Rabideau, *Acc. Chem. Res.* **1978**, *11*, 141.

[14] The elution curve also shows a signal for tetraphenylbenzene, a by-product of the formation of **16**.

[15] There is an additional peak at $m/z = 2826$ Da which stems from an adduct of **18** and the matrix dihydroxyanthracene. The width at half height of all peaks is approximately 50 Da. Peaks are also observed at $m/z = 1745$ and 1368 which stem from fragmentation in the matrix (retro DA).

[16] The top spectrum in Figure 2 shows some indication for an end group "signal" at $\delta \approx 6.7$. The intensity of this "signal" does not correspond to the measured $P_n = 7$. It should be mentioned that GPC determination of the molecular weight of ladder polymers tends to underestimate the actual molecular weight. For example, see: A. Godt, A.-D. Schlüter, *Makromol. Chem.* **1992**, *193*, 501.

[17] The prefix *syn*/*anti* refers to the relative orientation of the oxygen bridges at C^a to the adjacent hexamethylene loop; the prefix *cis*/*trans* describes the relative orientation of two adjacent oxygen bridges. Since the hexamethylene loops are always orientated *trans* to one another a descriptor referring to this is omitted for clarity.

[18] In toluene the equilibration is too slow for preparative purposes.

[19] A. S. Onishenko, *Diene Synthesis*, Israel Program for Scientific Translation, Jerusalem, **1964**.

[20] W. C. Christopfel, L. L. Miller, *J. Org. Chem.* **1986**, *51*, 4169.

[21] O. Kintzel, W. Münch, A.-D. Schlüter, A. Godt *J. Org. Chem.* **1996**, *61*, 7304.

[22] M. Löffler, R. Packe, A.-D. Schlüter, *Macromolecules* **1992**, *25*, 4213.

[23] G. M. Sheldrick, C. Krüger, R. Goddard, *Crystallographic Computing 3*, Oxford University Press, **1985**, pp. 175–189.

[24] G. M. Sheldrick, *SHELXL, A Program for Refinement of Structures*, University of Göttingen, **1995**.

[97251]