5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene as "Bis(diene)" in Repetitive Diels-Alder Reactions[1)]

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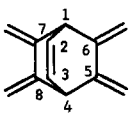
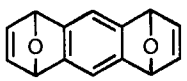
The synthesis of ladder-type oligomers by repetitive Diels-Alder reactions is described. The title compound **1** has been treated with the "bis(dienophile)" **2** at high pressure (7.5 kbar). Under these conditions the formation of oligomers with up to 33 laterally anellated six-membered rings has been achieved. An attempt has been made to analyze the complex stereochemistry of the cycloadditon by using the model compounds **5a**, **5b**.

Conjugated polymers with band- or ladder-type structures have recently been the subject of intensive synthetic and theoretical efforts[2)]. These structures are predicted to have attractive electronic, optical, and magnetic properties as well as high thermostability. The repetitive Diels-Alder reaction[3)] has been a useful method for the synthesis of precursors for band-type systems. In our search for new band structures, we successfully applied 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene (**1**)[4)], first prepared by Vogel et.al., in a repetitive Diels-Alder reaction. The kinetic data for the first and second cycloaddition of **1** with reactive dienophiles such as tetracyanoethylene or dimethyl acetylenedicarboxylate are known[5)], 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 the "bis(diene)" 1,4:5,8-diepoxyanthracene (**2**)[6)].

Scheme 1



1



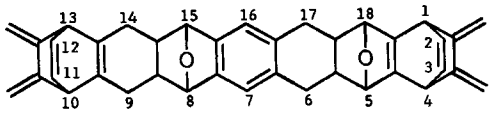
2

Results and Discussion

The "bis(dienophile)" **2** is a mixture of the *syn* and *anti* isomer which may be separated by fractional crystallisation[6)]. The configuration of **2** and the diastereoselectivity of the Diels-Alder reaction are crucial for the type of cycloaddition products; thus the use of the *syn* isomer of **2** and a diastereoselective *endo-endo-syn-syn* (*syn*: oxygen and ethylene bridges on one side of the molecule) Diels-Alder reaction with the "bis(diene)" **1** could afford cyclic ("cage-type") molecules as it is shown with comparable compounds by Stoddart et.al.[7)]. The formation of linear material should be possible as well if at least one of the following requirements is met: (i) *exo* attack, (ii) formation of the *anti* product in the cycloaddition, (iii) use of the *anti* isomer of **2**.

All reactions were carried out with the *syn* isomer, but first the *anti* isomer was applied to study the reactivity and to attain the maximum chain length. In this case the formation of cyclic material can be avoided. Heating of the starting material **1** and the *anti* isomer of **2** (2:1, 110°C, 24 h) in toluene provides the 2:1 adduct **3** in nearly quantitative yield. Surprisingly, even 1:1 stoichiometry of the reactants affords only the 2:1 adduct **3** and unreacted **2**.

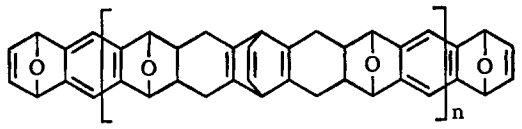
Scheme 2



3

No oligomeric or polymeric material could be detected at normal pressure. Therefore, all the following reactions were carried out at high pressure[8)] (7–10 kbar) and, indeed, under these conditions the synthesis of the linear oligomers **4a**–**4c** has been successful, but no cyclic material could be obtained.

Scheme 3



4a: n=1
4b: n=3
4c: n=5

First, the 2:1 adduct **4a** was prepared (2:1 stoichiometry of **1** and **2**, 7.5 kbar, CH_2Cl_2, 55°C, 3d) and in a subsequent step the higher oligomers **4b** and **4c** by the reaction of the latter with **1**. **4b** and **4c** could also be obtained in a one-step reaction (1:1 stoichiometry, 7.5 kbar, CH_2Cl_2, 55°C, 3d), although in lower yields. It is surprising that even the largest oligomer, which contains 33 laterally anellated six-

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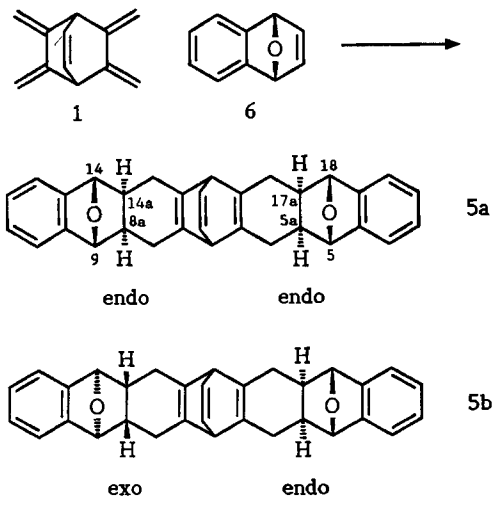
membered rings, is still soluble in common solvents such as $CHCl_3$ or THF. To our knowledge these oligomers are the most extended band-type structures not substituted with solubilizing aromatic or aliphatic side groups.

In 1988, Miller reported on rigid linear molecules with dimensions in the range of 5–10 nm prepared by Diels-Alder reactions[9]. After aromatization the band-type oligomers **4a–4c** should have comparative rigidity and dimensions up to the nm-scale.

The title structures **4a–4c** are monodisperse materials with a defined number of rings, but they exist as mixtures of stereoisomers. Organic reactions under high-pressure conditions are known to depend on the activation and reaction volumes ΔV^{+} and ΔV. If there is a decrease of the activation or reaction volumes, as is usually the case in Diels-Alder reactions, this entropic effect leads to an increase of the reaction rate by a factor of 10–1000[8]. According to the above results in our case the application of high-pressure conditions brings about an increase in the reaction rate and a change of the *exo*-to-*endo* ratio of the "bis(diene)".

It was expected that the sythesis of **4a–4c** would allow the described diastereoselective formation of the *endo* products with the oxygen and the ethylene bridges on one side of the molecule. The ^{13}C-NMR spectra of the cycloadducts reveal several different stereoisomers. It is possible to seperate the oligomers of different size by column chromatography, but we have not yet succeeded in separating the stereoisomers. Due to the small change in chemical shifts, NMR spectra cannot be used to determine the stereochemistry of isomers in the mixture. For a better understanding of the stereochemistry of the cycloaddition, the model compounds **5a** and **5b** have been synthesized by the reaction of **1** with two equivalents of 1,4-dihydro-1,4-epoxynaphthalene (**6**) (CH_2Cl_2, 50°C, 7.5 kbar, 2d). In this reaction, the formation of only two isomers **5a** and **5b** was observed which could be separated by column chromatography [silica gel, hexane/ethylacetate (10:1)].

Scheme 4

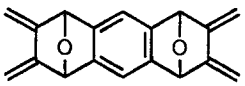


The high-resolution, broadband-decoupled ^{13}C-NMR spectrum of **5a** shows the expected 9 signals while for the isomer **5b** 16 signals should arise because of its C_s symmetry. Experimental data show 15 resonances whereby the missing signal must be explained by an isochronic effect.

In the ^1H-NMR spectra the differences between both isomers can be seen more clearly, in particular, from the resonances of the methine protons at the oxygen and ethylene bridges ($\Delta\delta$ = 0.05; 0.15).

The assignment of the *endo* position of the protons at the connecting carbon atoms of the six-membered rings (C–5a, –8a, –14a, –17a) is possible due to the very small coupling (^3J < 0.5 Hz) with the vicinal protons at the neighboring bridgehead carbons atoms[10] (C–5, –9, –14, –18). The ratio of the isomers **5a** and **5b** deserves a further comment. Stoddart treated the "bis(diene)" **7** in a similar reaction but he only isolated traces of the *endo-exo* adduct[7]. In contrast to this result, we found that the ratio for **5a** (*endo-endo*)/**5b** (*exo-endo*) is 4.1:1. This is astonishing, because the high-pressure conditions are expected to favor the formation of the *endo-endo* product.

Scheme 5



Unfortunately, the results for **5a**, **5b** cannot be applied to a stereochemical analysis of **4a–4c**, because the additional oxygen-bridged ring in **2** changes the entire stereochemical behavior. From the ten theoretical possible stereoisomers of **4a**, at least six were detectable by NMR spectroscopy. As expected, the higher oligomers **4b** and **4c** show much more stereoisomers, and a separation seems to be impossible.

The complicated stereochemical situation, however, should by no means inhibit the synthesis of larger oligomers than **4a–4c** by a proper choice of the high-pressure conditions. It will be shown in a subsequent paper that, regardless of the complex stereoisomerism, the cycloadducts **4** can be used for attractive chemical transformations.

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Experimental

General: Melting (decomposition) points (uncorrected): Büchi capillary apparatus; decomposition goes along with obvious gas evolution. – NMR (^1H, ^{13}C): Varian Gemini 200; chemical shifts were measured relative to Me_4Si as internal standard. – EI-MS: Varian CH 7 A (electron impact at 70 eV). – FAB-MS: Matrix: 3-nitrobenzyl alcohol. – High-pressure experiments: Nova-Swiss 10-kbar high-pressure apparatus. – Column chromatography: Silica gel Merck 60 (70–230 mesh); the eluents are indicated in the text of the individual procedures.

6,17:8,15-Diepoxy-1,4:10,13-bis(methylenethano)-1,4,5,5a,6,8,8a,9,10,13,14,14a,15,17,17a,18-hexadecahydroheptacene (**3**): **1** (40 mg, 0.26 mmol) and **2** (27 mg, 0.13 mmol) were heated under reflux in 20 ml of toluene for 24 h. The solvent was removed in vacuo. Chromatography on silica gel [hexane/ethylacetate (4:1)] yielded 66 mg (98.5%) **3** as a colorless powder, m.p. 170°C (dec.). – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.0 (s, 2H, arom. CH), 6.37 (t, 4H, CH),

4.91 (s, 4H, CH), 4.88 (s, 4H, CH_2), 4.73 (s, 4H, CH_2), 3.87 (t, 4H, CH), 2.42–2.60 (m, 4H, CH_2), 2.02–2.20 (m, 4H, CH_2), 1.72–1.87 (m, 4H, CH). – ^{13}C NMR (40 MHz, $CDCl_3$): δ = 144.65, 137.93, 134.07, 110.74, 101.64, 85.50, 54.06, 43.52, 31.09. – EI-MS: *m/z* (%) = 522.4 (1.34) [M^+], 340.1 (24.7), 182.0 (12.5), 167.0 (16.1), 158.0 (100), 128.0 (14.9), 84.9 (40.5).

$C_{38}H_{34}O_2$ (522.4) Calcd. C 87.36 H 6.51
Found C 87.62 H 6.20

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**): **1** (250 mg, 1.6 mmol) and **2** (815 mg, 3.9 mmol) were dissolved in 10 ml of CH_2Cl_2 and heated to 40°C under high pressure (7.5 kbar) for 2 d. 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, m.p. 165°C (dec.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 6.90–7.11 (m, 8H, arom. CH and 2-, 3-, 13-, 14-H), 6.61–6.71 (m, 2H, CH), 5.62 (m, 4H, 1-, 4-, 12-, 15-H), 4.81 (m, 4H, 6-, 10-, 17-, 21-H), 4.04 (m, 2H, 8-, 19-H), 2.51–2.74 (m, 4H, CH_2), 1.85–2.11 (m, 4H, CH_2), 1.68–1.90 (m, 4H, 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: *m/z* = 576.2 [M^+].

$C_{40}H_{32}O_4$ (576.3) Calcd. C 83.30 H 5.55
Found C 82.94 H 5.05

Cycloaddition Products **4b**, **4c**: **4a** (88 mg, 0.15 mmol) and **1** (14 mg, 0.15 mmol) were dissolved in 8 ml of $CHCl_3$ and heated to 45°C under high pressure (7.5 kbar) for 3 d. The reaction product was chromatographed on silica gel; hexane/ethylacetate (2:1) first eluted unreacted material. Then oligomer **4b** was eluted with $CHCl_3$ and finally **4c** with methanol/chloroform (1:1). The workup yielded 21 mg (21.4%) of **4b** and 18 mg (17.6%) of **4c** (based on **4a**).

4b: M.p. 171°C (dec.). – ^1H NMR (200 MHz, $CDCl_3$, all signals very broad): δ = 6.85–7.10 (m, 12H), 6.55–6.74 (m, 6H), 5.56–5.66 (m, 4H), 4.70–4.91 (m, 12H), 4.02 (br. s, 6H), 2.42–2.76 (m, 12H), 1.57–2.13 (m, 24H). – ^{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: *m/z* = 1308.5 [M^+].

$C_{92}H_{76}O_8$ (1308.60) Calcd. C 84.37 H 5.81
Found C 84.06 H 5.77

4c: M.p. 178°C (dec.). – ^1H NMR (200 MHz, $CDCl_3$, all signals very broad): δ = 6.83–7.13 (m, 16H), 6.50–6.85 (m, 10H), 5.55–5.68 (m, 4H), 4.64–4.93 (m, 20H), 4.03 (br. s, 10H), 2.38–2.80 (m, 20H), 1.50–2.15 (m, 40H). – ^{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: *m/z* = 2040.9 [M^+].

$C_{144}H_{120}O_{12}$ (2040.95) Calcd. C 84.67 H 5.88
Found C 84.19 H 5.52

5,18:9,14-Diepoxy-7,16-etheno-5,5a,6,7,8,8a,9,14,14a,15,16,17,17a,18-tetradecahydroheptacene (**5**): **1** (156 mg, 1 mmol) and **6** (400 mg, 2.8 mmol) were dissolved in 6 ml of CH_2Cl_2 and heated to 50°C under high pressure (7.5 kbar) for 2 d. The solvent was removed by evaporation and the residue chromatographed on silica gel [hexane/ethyl acetate (10:1)]. The workup yielded 200 mg (45.5%) of **5a** and 51 mg (11.1%) of **5b** as colorless powders.

5a: M.p. 190°C (dec.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.03–7.18 (m, 8H, arom. CH), 6.71 (t, 2H, CH), 4.92 (s, 4H, CH), 4.09 (t, 2H, CH), 2.56–2.77 (m, 4H, CH_2), 1.98–2.16 (m, 4H, CH_2), 1.73–1.84 (m, 4H, CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.24, 144.30, 140.24, 127.10, 119.18, 85.77 (C-5, -9, -14, -18), 57.01, 42.79, 31.81. – EI-MS: *m/z* (%) = 444.2 (10.2) [M^+], 326.0 (12.7), 180.0 (10.8), 165.1 (14.9), 155.0 (10.9), 145.0 (10.7), 118.2 (100).

$C_{32}H_{28}O_2$ (444.2) Calcd. C 86.49 H 6.31
Found C 86.08 H 6.14

5b: M.p. 226°C (dec.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.05–7.18 (m, 8H, arom. CH), 6.71 (t, 2H, CH), 4.98 (s, 2H, CH), 4.92 (s, 2H, CH), 4.92 (s, 2H, CH), 4.09 (t, 2H, CH_2), 1.96–2.18 (m, 4H, CH_2), 1.83–2.04 (m, 4H, 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 (C-5, -18), 85.68 (C-9, -14), 56.92, 42.72, 42.46, 31.64. = EI-MS: Similar to that of **5a**.

$C_{32}H_{28}O_2$ (444.2) Calcd. C 86.49 H 6.31
Found C 86.16 H 6.33

CAS Registry Numbers

1: 62234-75-7 / **2**: 87207-46-3 / **3**: 133832-83-4 / **4a**: 133832-84-5 / **4b**: 133850-18-7 / **4c**: 133832-85-6 / **5a**: 133832-86-7 / **5b**: 133906-46-4 / **6**: 573-57-9

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[1] Dedicated to Professor *Kurt Schaffner* on the occasion of his 60th birthday.

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