

Tetraindeno-Fused Cyclooctatetraene and Oligomeric Biindenyls by Oxidative Coupling of 2,2'-Biindenyl

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Lithiated biindenyls **2** and **4**, prepared by deprotonation of 2,2'-biindenyl (**1**) and 10,11-dihydrodiindenyl[1,2-*b*:2',1'-*d*]thiophene (**3**) with *n*-butyllithium, are oxidatively coupled to give

oligomeric biindenyls (**17**) as well as tetraindeno-fused eight-membered rings (**16**, **19**, **24**).

We have recently reported that the biindenyl species **1** and **7** as well as the diindenyl-fused thiophenes **3** and **5** are readily available from 1- and 2-indanone^[1], respectively. These compounds can be transformed into the dianions **2**, **4**, **6**, and **8** by deprotonation of the indenyl units. The synthesis of the thiophenes **3** and **5** is a particularly useful example of 1,4-diketone formation by oxidative coupling of ketoenolates^[1]. A closely related process is the oxidative dimerization of carboxylic esters^[2], nitriles^[3], dithianes^[4], and

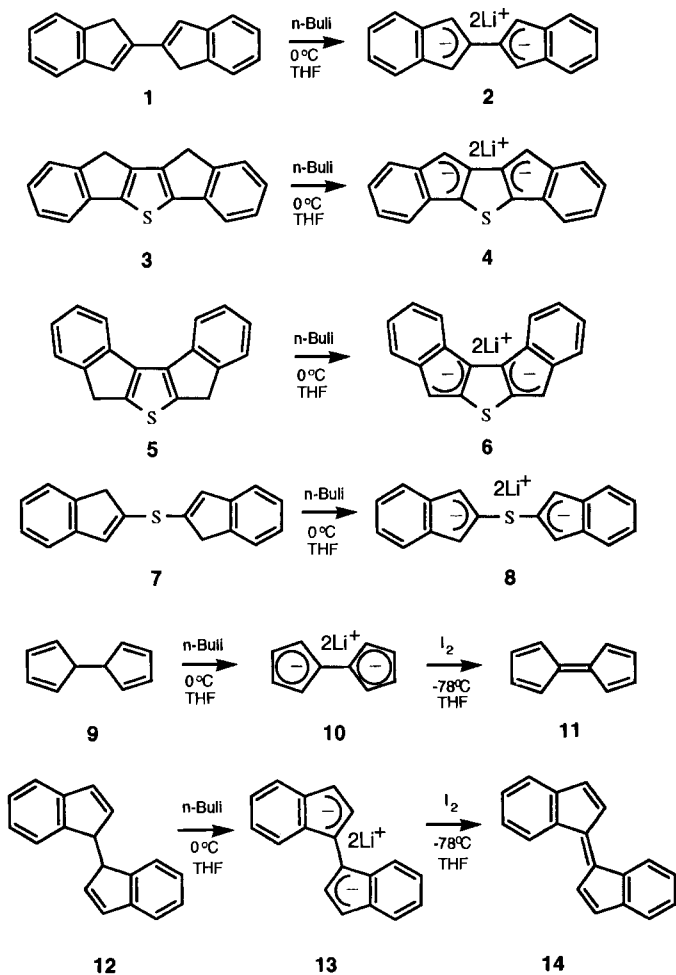
cyclopentadienide^[5] species; the coupling products such as **9** and **12** are known as precursors of the pentafulvalenes^[6,7] **11** and the dibenzopentafulvalene^[7] **14**, respectively, which can be obtained by chemical oxidation of the corresponding dianions **10** and **13**.

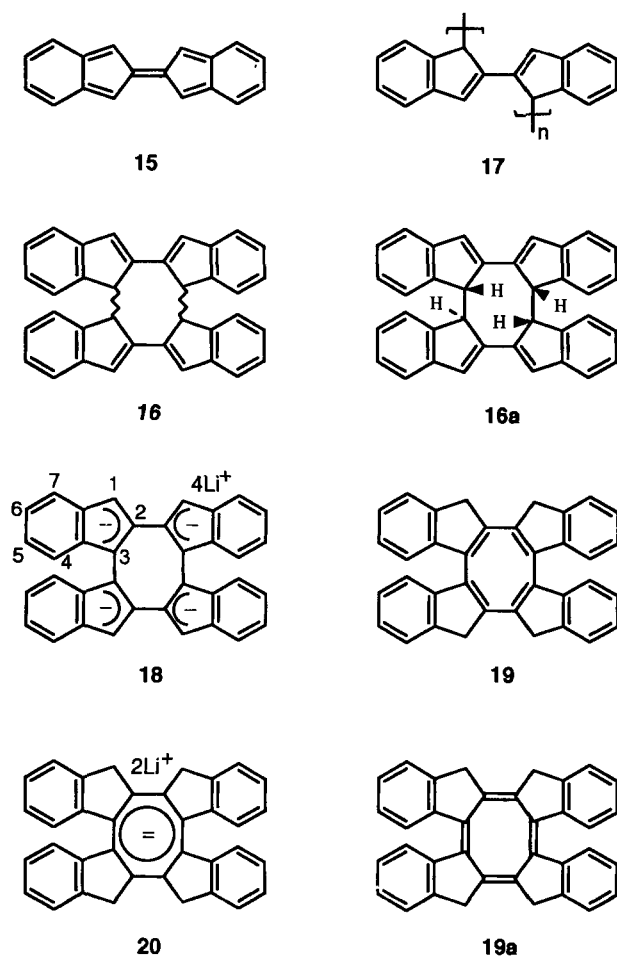
Herein, we describe the oxidative coupling of related 2,3-benzo-fused dicyclopentadienes **1** and **3**, which provides novel cyclodimerization products such as **16** in addition to linear oligomeric biindenyls **17**.

Results

The doubly charged species **2** and **4** were generated quantitatively by the addition of two equivalents of *n*-butyllithium to a solution of **1** and **3**, respectively, in tetrahydrofuran (THF) at 0°C. Evidence for complete deprotonation was obtained from the ¹H- and ¹³C-NMR spectroscopic detection of the dianions **2** and **4** and from the formation of quenching products^[1].

Treatment of **2** with iodine in THF (0.01 mol/l) at -78°C afforded the cyclic dimers **16** (one stereoisomer was formed preferentially, see discussion) in 15% and oligomeric material in 37% yield. In order to obtain appropriate model systems for a comprehensive characterization of the oligomers, the monoanion **21**^[8] was oxidized with iodine to afford the dimeric and trimeric compounds **22** and **23** in 44 and 7% yield, respectively. The diastereomeric mixture of **22a**, **22b** and the two isomeric trimers of **23** (the absolute configurations are not known) were separated by column chromatography and the ratio of **22a**/**22b** determined to be *meso*:*d/l* = 3:1. The dimers **22a** and **22b** were characterized by ¹H- and ¹³C-NMR spectroscopy, mass spectrometry, and elemental analysis (see discussion). The ¹H- and ¹³C-NMR spectra of the trimeric products were much more complex than those of the dimers due to the increasing number of asymmetric carbon centers. A comparison of ¹H- and ¹³C-NMR data with those of the dimers (**22a**, **22b**), along with the results of mass spectrometry (*M*⁺ *m/z* = 686) and chromatographic methods (TLC, GPC), however, leave no doubt about the structure of **23**. Unfortunately, it was not possible to determine either the absolute configurations of the sep-





arated trimers, or to decide whether both trimer fractions were mixtures of further stereoisomers.

According to an NMR, UV, and IR spectroscopic comparison with dimer **22** and trimer **23**, structure **17** can safely be assigned to the oligomeric fraction. When the concentration of **2** in THF was increased, the yield of the linear oligomers increased, while that of **16** decreased slightly. The highest yields of oligomerization products (48%) were observed at a 0.2 molar concentration of dianion **2** in THF. Under these conditions **16** was obtained in 11% yield. Oxidation of **2** in more dilute solutions did not favor the formation of **16**, but resulted in a decrease of the total amount of products. The oligomers can be separated by successive precipitation in a mixture of dichloromethane/methanol with increasing methanol concentration.

Analysis of all oligomer fractions **17** by gel permeation chromatography (GPC) using a polystyrene calibration showed an unimodal molecular mass distribution with a M_n/M_w ratio of 1.08–1.99; the M_n values observed were slightly lower than those obtained upon calibration with the well-defined reference systems **22a/22b** and **23**. The second oligomer sample (fraction B, see Experimental), which showed an average molecular mass of 1700 g/mol by GPC analysis, was subjected to an absolute M_n determination by means of vapor pressure osmometry in toluene giving a value of $M_n = 2400$ g/mol. A comparable result was obtained by the absolute M_n determination of the oligomer sample generated

by oxidation of **2** in dilute solution. When trichloromethane was used as solvent, the M_n was determined to be 2300 g/mol.

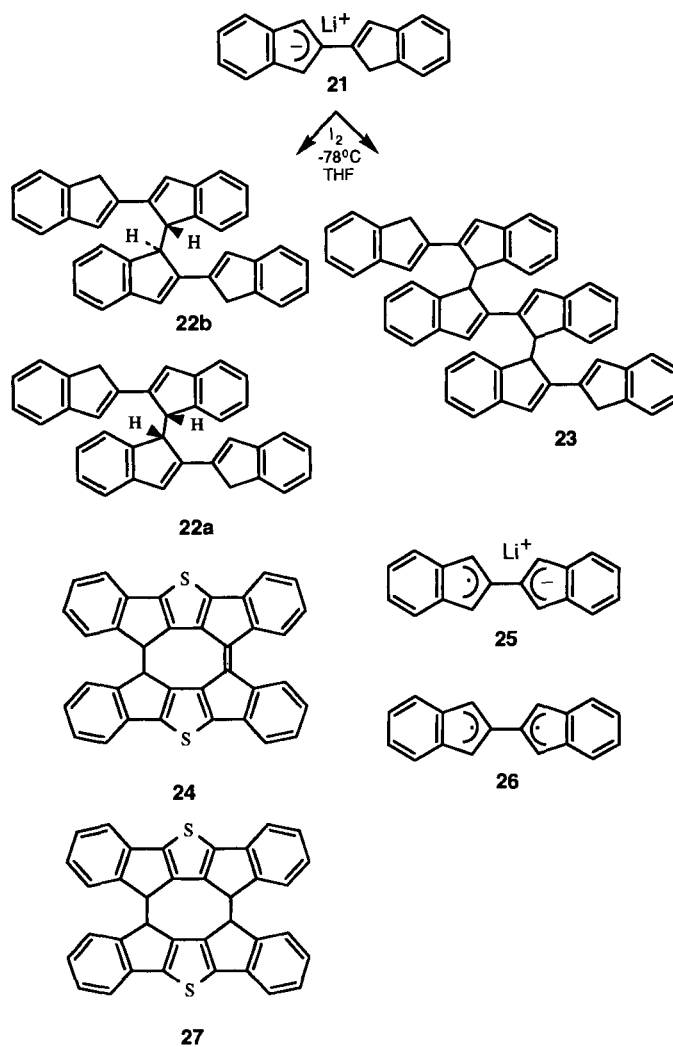
Treatment of the sulfur-bridged dianion **4** with iodine (THF, -78°C) gave an unsaturated cyclic dimer **24** in 7% yield after twofold purification by column chromatography.

Deprotonation of **16** with *n*-butyllithium (THF) led to the tetraanion **18**, which was characterized by ^1H - and ^{13}C -NMR spectroscopy. Treatment of **18** with methanol yielded the tetraindenyl-fused cyclooctatetraene **19** in 15% yield after purification by column chromatography. The structural assignment of **19**, in particular the position of the double bonds, is based on ^1H - and ^{13}C -NMR data.

Cyclovoltammetric studies in THF and DMF showed that the hydrocarbon **19** can be reduced directly to the dianion **20** in a reversible two-electron process ($E_{1/2} = -1.94$ V). The exclusive formation of **18** by the reaction of **19** potassium was documented by NMR spectroscopy.

Discussion

The oxidative bis-dehydrodimerization^[9] of **1** and **3** constitutes a facile route to the hitherto unknown polycycles **16**, **19** and **24**. The synthesis of **16** goes along with the for-



mation of four asymmetric centers. An analysis of the ^1H - and ^{13}C -NMR spectrum of the cyclodimerization product reveals that one stereoisomer, namely **16a**, is formed preferentially. Evidence for the cyclic structure comes from a ^{13}C -NMR spin echo experiment, in which only tertiary benzylic carbon centers can be detected. While the ^1H -NMR spectrum supports the formation of the asymmetric stereoisomer **16a**, the number of signals in the ^{13}C -NMR spectrum indicate the existence of more than one isomer. Nevertheless, four benzylic absorptions ($\delta = 40\text{--}60$) have a significantly higher intensity (by a factor of 2) than the other two ($\delta = 55.6, 58.9$).

Treatment of all stereoisomers of **16** with *n*-butyllithium in THF results in their quantitative conversion into the stable tetraanion **18**. This species shows the expected simplification of the NMR spectra due to the higher symmetry of the molecule. The ^{13}C -NMR chemical shifts of C-1, C-3 (assignments according to numbering in formula of **18**) and of the aromatic carbons of tetraanion **18** are very similar to those of the parent 2,2'-biindenide **2** and of the lithium indenide^[10], but the signals of C-1 and of all quaternary centers exhibit a slight line broadening (see Experimental).

Quite remarkably, treatment of the tetralithio compound with protic solvents such as water or methanol does not lead to the expected mixture of stereoisomers like **16a**, but results in the exclusive formation of cyclooctatetraene **19**. Attempts to increase the poor yield of **19** (15%) have been unsuccessful. The analysis of the ^1H - and ^{13}C -NMR spectra of the reaction product confirms the structure **19**, which gives rise to 9 carbon signals and a characteristic AB system of the benzylic protons (^1H -NMR spectrum). The alternative structure **19a** can be excluded, since the chemical shift of the neighboring *ortho*-protons of the benzene rings fail to indicate a "van der Waals" interaction. Precedence for such a "van der Waals" interaction comes from the ^1H -NMR spectrum of heterocycle **24**, in which two indene moieties are linked by a double bond. The resonances of the *ortho*-protons appear below $\delta = 8$ as a result of strong steric interaction. Compound **24** is characterized by ^{13}C -NMR and mass spectrometry. Its formation might be due to a twofold deprotonation followed by oxidation of an intermediate **27** or by a spontaneous dehydrogenation of **27** by iodine. The main products obtained upon oxidation of **4** with iodine are oligomers, which have not been further investigated.

The attempted chemical reduction of **19** by potassium leads to the tetraanion **18** instead of to the expected dianion **20**. Obviously, metalation of the four CH-acidic indene moieties in the periphery is more favorable than reduction of the central eight-membered ring. The dianion of **20** can be generated electrochemically^[11]. Compared to the known 1,3,5,7-tetraphenylcyclooctatetraene^[12] ($E_{1/2} = -1.71$) the reduction potential of **19** is more negative. This is due to the stronger steric interaction between the fixed benzene rings which renders a planarization more difficult.

A comparison of the ^1H -NMR spectra of dimers **22a** and **22b** at room temperature reveals a remarkable difference. While **22b** gives a well-resolved spectrum, **22a** exhibits line-broadened absorptions. When raising the temperature to

120°C, however, a singlet is observed for the tertiary benzylic protons and an AB system for the other benzylic protons, similar to the spectrum of **22b** at room temperature. The geminal coupling constants are comparable (**22a**: $^2J = 22.5$, **22b**: $^2J = 21$ Hz); at -30°C a doubling of all signals is observed in the proton spectrum of **22a**. Obviously, this behavior is due to a hindered rotation about the σ bond linking the biindenyl units **22a**. At 120°C (solvent $\text{C}_2\text{D}_2\text{Cl}_4$) free rotation about the σ bond is possible, giving rise to well-resolved signals. The diastereomers **22a** (*d/l*) and **22b** (*meso*) can be distinguished by inspecting the intensities and chemical shifts of the absorptions^[13] at lowest field. Molecular models show that the benzene protons strongly approach each other upon rotation about the linking σ bond in **22a**, but not in **22b**.

The formation of trimers **23** can be rationalized by considering that the generation of **21**^[8] is accompanied by a small amount of the dianion **2**, which can couple oxidatively with two equivalents of **21**. The ^{13}C -NMR resonances of the trimeric products **23** closely resemble those of the dimers, but intensities are doubled or tripled. The characteristic absorptions of the two different benzylic centers confirm that all three biindenyl moieties are linked by saturated carbons. Dynamic effects and the multitude of possible stereoisomers prevent a detailed assignment of signals in the proton spectra of **23**. Signal integration, however, indicates the correct ratio of benzylic to aromatic/olefinic protons.

The characterization of the oligomer **17** by an NMR spectroscopic comparison with the dimers and trimers is complemented by gel permeation chromatography (GPC), vapor pressure osmometry as well as UV and IR spectroscopy. The ^1H -NMR spectrum of **17** shows two very broad absorptions ($\delta = 6\text{--}8$ and $3\text{--}5.5$) as a result of the multitude of possible stereoisomers and the polydisperse character. Additionally, a line-broadening effect can result from the restricted conformational mobility of linked biindenyl units. The ^{13}C -NMR spectrum of **17** displays broad absorptions of the aromatic and olefinic carbons in the same range as observed for the dimers and trimers, but only one broadened signal at $\delta = 52$ (tertiary benzylic centers). The absence of resonances at $\delta = 38\text{--}42$ is due to the iodine substitution at the end groups. This is verified by elemental analysis. An oligomer sample, produced by oxidation of **2** in dilute solution, with an average molecular mass of 2300 g/mol contains approximately 4% iodine.

The elemental analyses of the three oligomer fractions obtained in concentrated solution (second procedure, see Experimental) reveal an increasing iodine content with decreasing average molecular mass. Obviously, the chain length of the linear oligomers is closely related to the nature of the end groups (incorporation of iodine).

The UV spectroscopic data of oligomers, trimers, and dimers show a close correspondence to those of 2,2'-biindenyl^[14] (**1**). This finding indicates that the biindenyl moieties are electronically independent; the absence of extended π conjugation can also be deduced from the ^{13}C -NMR spectra, which show that the bridgehead centers are tertiary benzylic carbons.

Attempts to increase the molecular mass by changing the oxidant [CuCl_2 , $\text{Cu}(\text{OTf})_2$] or the concentration of dianion **2** have been unsuccessful. Nevertheless, the total amount of oligomer increases with increasing concentration of **2** (up to 0.2 mol/l in THF), even though the main portion of the dilithio compound **2** precipitates at -78°C .

The detailed mechanism of the oxidative coupling of **1** to yield oligomerization and cyclodimerization products is not known. In principle, one can invoke the intermediacy of a radical anion **25** or a diradical **26**. Experiments directed toward an ESR spectroscopic detection of the primary oxidation products are under way.

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Experimental

4b, 4c, 14b, 14c-Tetrahydrocycloocta[1,2-a:4,3-a':5,6-a'':8,7-a''']-tetraindene (16) by Oxidative Coupling of 2,2'-Biindenyl (**1**): To a solution of **1** (0.46 g, 2 mmol) in THF (200 ml) at 0°C under argon was added dropwise 2.8 ml (4.48 mmol) of *n*-butyllithium (1.6 M in hexane). After stirring for 15 min at 0°C the solution of the resulting dianion **2** was cooled to -78°C in an acetone/dry ice bath. Iodine (0.51 g, 2 mmol), dissolved in 30 ml THF, was added over 15 min. The mixture was stirred for another 1.5 h and then allowed to stand at room temp. for about 5 h. After quenching of the reaction with methanol (1 ml) the solvent was removed under reduced pressure. Dichloromethane (100 ml) and a saturated solution of sodium thiosulfate were added to the residue. This mixture was shaken for 5 min, the organic phase separated and washed three times with water, dried (MgSO_4) and concentrated. Chromatography of the crude product (silica gel, hexane/ CH_2Cl_2 , 5:1) yielded **16** (70 mg, 15%), m.p. 221°C . — ^1H NMR (CD_2Cl_2): $\delta = 3.58\text{--}4.22$ (AB, 2H, benzyl., $J = 5.15$ Hz), 4.29–4.56 (AB, 2H, benzyl., $J = 5$ Hz), 6.12–6.15 (d, 1H, olefin.), 6.42 (s, 1H, olefin.), 6.47 (s, 1H, olefin.), 6.57 (s, 1H, olefin.), 6.69–6.73 (t, 1H, arom. H), 7.08–7.18 (m, 2H, arom. H), 7.25–7.40 (m, 9H, arom. H), 7.51–7.55 (m, 1H, arom. H), 7.79–7.83 (m, 1H, arom. H), 7.93–8.01 (m, 2H, arom. H). — ^{13}C NMR (CDCl_3): $\delta = 50.0$ (weak), 53.6, 54.2, 55.6 (weak), 57.6 (tert. benzyl. C); 120.8, 121.0, 121.2, 121.3, 123.0, 123.2, 123.6, 124.0, 124.3, 124.4, 124.8, 125.1, 125.9 (weak), 126.9, 127.0, 127.3, 127.5, 127.9, 128.5, 129.1, 130.2, 131.4 (tert. arom./olefin. C); 143.1, 144.6, 144.8, 145.7, 148.8, 150.4 (quat. arom./olefin. C). — MS (70 eV), m/z (%): 456 (100) [M^+], 341 (40) [$\text{M}^+ - \text{Indenyl}$], 228 (17) [$\frac{1}{2} \text{M}^+$]. — UV (CH_2Cl_2): λ_{max} (lg ϵ) = 233 nm (4.265), 325 (4.365).

$\text{C}_{36}\text{H}_{24}$ (456.6) Calcd. C 94.70 H 5.29
Found C 94.48 H 5.26

The silica gel used was exhaustively extracted with dichloromethane, and the resulting red-brown solution was concentrated to 15 ml. This solution was added dropwise to methanol (85 ml) with stirring. The precipitated oligomer **17** (200 mg, 37%) was washed with methanol and dried in vacuo (oil pump).

$(\text{C}_{18}\text{H}_{12})_n$ Calcd. C 94.70 H 5.30 (ideal Oligomer)
Found C 88.66* H 4.90 I 3.82

* The reduced carbon content of the oligomer samples is due to the end groups, which are mainly iodine, but partly contain oxygen (hydroxy- or ketone-functionalized).

GPC analysis (calibration: polystyrene): $M_n = 1449$, $M_w = 2514$, $M_z = 4063$. — Vapor pressure osmometry (Knaur osmometer, solvent: trichloromethane): $M_n = 2300$ (± 200) g/mol. — UV (CH_2Cl_2): λ_{max} (lg ϵ) = 249 nm (4.348), 343 (4.433), 352 (4.428), 371

(shoulder) (4.235). — ^1H -NMR (CDCl_3): $\delta = 2.9\text{--}5.5$ (s, broad, benzyl., H), 5.5–8.5 (s, broad, arom./olef. H). — ^{13}C NMR (CDCl_3): $\delta = 50\text{--}54$ (broad) (tert. benzyl. C), 121.2, 123.1, 124.6, 127.1, 130.5 (all broad) (tert. arom./olef. C), 143–145, 146 (broad, quart. arom./olef. C).

Preparation of Oligomer 17 by Using a High Concentration of the Dianion 2: To a suspension of **1** (0.46 g, 2 mmol) in THF (9 ml) at 0°C under argon was added dropwise 1.76 ml (4.4 mmol) of *n*-butyllithium (2.5 M in hexane). After stirring for 30 min at 0°C the solution of the resulting dianion **2** was cooled to -78°C in an acetone/dry ice bath (the dianion **2** precipitated). Iodine (0.51 g, 2 mmol) was added in one portion. The mixture was vigorously stirred for another 2 h and then allowed to stand at room temp. for about 5 h. After quenching of the reaction with methanol (0.2 ml) the solvent was removed under reduced pressure. Dichloromethane (100 ml) and a saturated solution of sodium thiosulfate were added to the residue. This mixture was shaken for 5 min, the organic phase separated and washed three times with water, dried (MgSO_4) and concentrated to 10 ml. Methanol (150 ml) was added to the residue, the precipitate separated and dried in vacuo. The crude product (600 mg) was dissolved in dichloromethane (40 ml) and precipitated again with methanol (20 ml). After 1 h the first precipitated fraction was separated and dried in vacuo. This procedure was repeated three times with the mother solution by adding successively methanol (10 ml) and separating each fraction. The fifth fraction was obtained by adding 30 ml of methanol. Removal of the solvent from the residue afforded the sixth fraction. While the first three fractions were again dissolved in dichloromethane (2 ml) and precipitated with an excess of methanol, the latter fractions were chromatographed (silica gel, hexane/ CH_2Cl_2 , 5:1) to yield compound **16** (50 mg, 11%). Drying of the oligomer fractions afforded three samples of **17** in the order of decreasing molecular mass (A: 122 mg, B: 65 mg, C: 35 mg, $\Sigma = 48\%$). GPC analysis of the three fractions in the order of decreasing molecular mass: *Fraction A*: $M_n = 2028$, $M_w = 5012$, $M_z = 7531$; *fraction B*: $M_n = 1667$, $M_w = 2906$, $M_z = 3905$; *fraction C*: $M_n = 1370$, $M_w = 2041$, $M_z = 2617$. — GPC-Analysis of the dimer **22b** ($\text{M}^+ m/z = 458$) and the trimer **23** ($\text{M}^+ m/z = 686$): *Dimer 22b*: $M_n = 296$, $M_w = 330$, $M_z = 364$; *trimer 23*: $M_n = 488$, $M_w = 533$, $M_z = 576$.

$(\text{C}_{18}\text{H}_{12})_n$ Calcd. C 94.70 H 5.30 (ideal Oligomer)

Fraction A: Found C 87.83* H 5.38 I 4.35

Fraction B: Found C 87.38* H 5.29 I 5.02

Fraction C: Found C 87.35* H 5.33 I 5.73

* See above.

1,1'-Bi(2,2'-biindenyl) (22) by Oxidative Coupling of 2,2'-Biindenyl (**1**): To a solution of **1** (0.23 g, 1 mmol) in THF (50 ml) at 0°C under argon was added 0.36 ml (0.9 mmol) of *n*-butyllithium (2.5 M in hexane) by means of a syringe. After stirring for 15 min at 0°C , the orange-red solution of the anion **21** was cooled to -78°C , and 254 mg (1 mmol) of iodine was added in one portion. The mixture was stirred for 1.5 h at -78°C , then allowed to slowly warm to room temp., and the reaction was quenched with methanol (1 ml). The solvent was removed under reduced pressure. A solution of the residue in dichloromethane (100 ml) was washed three times with a saturated solution of sodium thiosulfate, then with water and twice with brine. The organic layer was dried (MgSO_4) and concentrated to give a crude mixture of dimeric and trimeric isomers. Both dimers were separated by chromatography (silica gel, hexane/ CH_2Cl_2 , 5:1). Further chromatography with a more polar solvent mixture (silica gel, hexane/ CH_2Cl_2 , 2:1) yielded the two trimers. Each of the chromatographed dimers (*meso/d,l*) was recrystallized from toluene. This procedure yielded **22a** (24 mg, 10%), m.p. 227°C ;

22b (77 mg, 34%), m.p. 264 °C; **23** (trimer A) (20 mg, 6%), m.p. 200–225 °C; **23** (trimer B) (5 mg, 1%), m.p. 208–220 °C.

22a: UV (CH₂Cl₂): λ_{max} (lg ε) = 249 nm (4.245), 337 (4.557), 352 (4.575), 370 (4.370). — ¹H NMR (C₂D₂Cl₄, 120 °C): δ = 3.13–3.69 (AB, 4H, benzyl. H, *J* = 22.5 Hz), 4.61 (s, 2H, tert. benzyl. H), 6.59 (s, 2H, olefin. H), 6.73 (s, 2H, olefin. H), 6.82–6.87 (m, 2H, arom. H), 7.01–7.23 (m, 12H, arom. H), 7.32–7.35 (d, 2H, arom. H). — ¹H NMR (CDCl₃, –30 °C): δ = 2.70–3.48 (AB, 2H, benzyl. H, *J* = 27.5 Hz), 3.66–3.96 (AB, 2H, benzyl. H, *J* = 22.5 Hz), 4.48 (s, 1H, tert. benzyl. H), 4.71 (s, 1H, tert. benzyl. H), 5.78–5.82 (d, 1H, olefin. H), 6.23 (s, 1H, olefin. H), 6.55 (s, 1H, olefin. H), 6.68 (s, 1H, olefin. H), 6.78–6.83 (m, 1H, arom. H), 7.04–7.17 (m, 4H, arom. H), 7.21–7.23 (d, 2H, arom. H), 7.29 (s, broad, 2H, arom. H), 7.40 (s, broad, 4H, arom. H), 7.53–7.62 (m, 2H, arom. H), 7.80–7.86 (m, 1H, arom. H). — ¹³C NMR (CDCl₃): δ = 39.3 (sec. benzyl. C); 51.5 (tert. benzyl. C); 120.8, 121.0, 122.8, 123.5, 124.9, 125.0, 126.6, 127.1, 128.9, 142.6, 142.8, 144.2 (broad), 145.1 (broad), 145.3 (arom./olefin. C). — MS (70 eV), *m/z* (%): 458 (48.7) [M⁺], 229 (100) [$\frac{1}{2}$ M⁺].

C₃₆H₂₆ (458.6) Calcd. C 94.28 H 5.71
Found C 94.02 H 5.90

22b: UV (CH₂Cl₂): λ_{max} (lg ε) = 250 nm (4.289), 338 (4.549), 352 (4.624), 371 (4.493). — ¹H NMR (CD₂Cl₂): δ = 3.94–4.15 (AB, 4H, benzyl. H, *J* = 21 Hz), 4.65 (s, 2H, tert. benzyl. H), 6.78–6.82 (t, 2H, arom. H), 6.92–6.94 (d, 2H, arom. H), 6.99–7.03 (t, 2H, arom. H), 7.14 (s, 1H, olefin. H), 7.16 (s, 1H, olefin. H), 7.22–7.25 (t, 2H, arom. H), 7.29–7.33 (t, 2H, arom. H), 7.36 (s, 2H, arom. H), 7.50–7.52 (t, 2H, arom. H), 7.55–7.57 (d, 2H, arom. H). — ¹³C NMR (CD₂Cl₂): δ = 40.2 (sec. benzyl. C); 51.0 (tert. benzyl. C); 121.1, 121.6, 123.5, 124.1, 124.7, 125.6, 127.22, 127.27, 128.8, 130.6 (tert. C); 142.7, 143.3, 144.1, 144.5, 145.7, 145.9 (quat. C). — MS (70 eV), *m/z* (%): 458 (53) [M⁺], 229 (100) [$\frac{1}{2}$ M⁺].

C₃₆H₂₆ (458.6) Calcd. C 94.28 H 5.71
Found C 93.98 H 5.82

23: Trimer A: UV (CH₂Cl₂): λ_{max} (lg ε) = 250 nm (4.504), 341 (4.749), 352 (4.769), 371 (4.615). — ¹H NMR (CDCl₃): δ = 3.3–5.0 (m, broad, 8H, benzyl. H), 6.3–7.6 (m, broad, 30H, arom./olef. H). — MS (70 eV), *m/z* (%): 686 (20) [M⁺], 457 (26.4) [$\frac{2}{3}$ M⁺], 228 (13), 229 (17) [$\frac{1}{3}$ M⁺].

Trimer B: ¹H NMR (CD₂Cl₂): δ = 3.9–4.3 (m, 4H, benzyl. H), 4.7–4.9 (m, 4H, benzyl. H), 6.6–7.7 (m, broad, 30H, arom./olefin. H). — MS (70 eV), *m/z* (%): 686 (4) [M⁺], 457 (8) [$\frac{2}{3}$ M⁺], 228 (13), 229 (17) [$\frac{1}{3}$ M⁺].

Synthesis of 24 by Oxidative Coupling of 10,11-Dihydrodiindenyl[1,2-b:2',1'-d]thiophene (3): In a procedure analogous to that described for the preparation of **16** from **1**, a solution of **4**, prepared by the addition of 1.4 ml (2 mmol) of BuLi (1.6 M in hexane) to a solution of 0.52 g (2 mmol) of **3** in THF (400 ml), was treated with iodine (0.51 g, 2 mmol) in THF (30 ml) at –78 °C. Twofold chromatography of the crude product on silica gel with hexane/CH₂Cl₂ (5:1) as eluant gave **24** (38 mg, 7%), m.p. 273–276 °C (dec.). — ¹H NMR (C₂D₂Cl₄): δ = 3.53 (s, 2H, benzyl. H), 7.0–7.01 (d, 2H, arom. H), 7.05–7.12 (q, 4H, arom. H), 7.18–7.22 (t, 2H, arom. H), 7.28–7.35 (m, 4H, arom. H), 7.44–7.46 (d, 2H, arom. H), 8.28–8.30 (d, 2H, arom. H). — ¹³C NMR (C₂D₂Cl₄): δ = 48.7 (tert. benzyl. C); 118.7, 119.3, 124.5, 125.7, 127.8, 128.3, 129.0, 129.8 (tert. arom./olefin. C); 133.3, 138.91, 138.98, 139.4, 144.7, 145.2, 146.0, 148.5 (quat. arom./olefin. C).

C₃₆H₁₈S₂ Calcd. 514.0850 Found 514.0849 (MS)

9,10,19,20-Tetrahydrocycloocta[1,2-a:4,3-a':5,6-a'':8,7-a''']tetraindene (19): To a stirred solution of **16** (31 mg, 0.068 mmol) in

THF (40 ml) was added under argon at 0 °C 0.14 ml (0.28 mmol) of *n*-butyllithium (2 M in hexane) by means of a syringe. After stirring for 15 min the resulting tetraanion **18** was reprotonated with 1 ml of methanol. The solvent was removed under reduced pressure and the residue purified by column chromatography (silica gel, hexane/CH₂Cl₂, 5:1) to yield yellow-red crystals (4.6 mg, 15%), m.p. 260 °C. — UV (CH₂Cl₂): λ_{max} (lg ε) = 238 nm (3.973), 317 (4.404), 374 (shoulder) (3.342). — ¹H NMR (CD₂Cl₂): δ = 3.55–3.88 (AB system, 8H, benzyl. H, *J* = 23 Hz), 6.98–7.01 (m, 4H, arom. H), 7.14–7.20 (m, 8H, arom. H), 7.49–7.51 (m, 4H, arom. H). — ¹³C NMR (CD₂Cl₂): δ = 42.3 (sec. benzyl. C); 122.0, 123.9, 125.1, 126.3 (tert. arom. C); 138.5, 144.7, 145.1, 145.3 (quat. arom./olefin. C). — MS (70 eV), *m/z* (%): 456 (100) [M⁺], 341 (19) [M⁺ – indenyl], 228 (10) [$\frac{1}{2}$ M⁺].

NMR-Spectroscopic Data of Tetraanion 18: ¹H NMR ([D₈]THF): δ = 6.16 (s, 4H, five-membered ring H), 6.30–6.38 (m, 8H, arom. H), 7.14–7.22 (m, 8H, arom. H). — ¹³C NMR ([D₈]THF; assignments according to numbering in formula of **18**): δ = 95.3 (broad, C-1), 103.3 (broad, C-3), 112.0, 113.4, 118.5, 120.8 (C-4 to C-7), 128.2–128.9 (broad), 131.4–132.1 (broad, C-2, –7a, –3a).

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^[8] We assume that the monoanion **21** is generated by adding only one equivalent of *n*-butyllithium to a solution of **1** in tetrahydrofuran. In view of the fact that the first and the second pK_a value of **1** differ only slightly (0.5)^[15], a quantitative generation of **21** is not possible because of the formation of an equilibrium between hydrocarbon **1**, monoanion **21** and dianion **2**. This assumption is supported by the formation of trimers.

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