Macrocyclic Hydrocarbons with Rigid and Flexible Building Blocks

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Abstract. We report the synthesis of a series of new hydrocarbon macrocycles. Following the dithia-phane route, four large rings **3**–**6** of the cyclophane type containing different numbers of ring atoms were prepared confirming the general applicability of this route compared to alternative macrocyclizations. Cycle **3** is the hydrocarbon analogue to the tetralactam and the sulfone amide macrocycles **1** and **2** used in many rotaxane syntheses. The macrocycles synthesized here are supposed to be uselful as wheels in the *slipping* approach to rotaxanes to further establish a reference system for the cavity size of cyclic compounds by comparing them to certain complemenatry blocking groups. The x-ray data obtained of the macrocycles **3**, **5**, and **6** reveal the cavity shape and size in solid state.

Besides by *clipping* [1], *threading* [2], and recently also by *trapping* [3] a wide range of rotaxanes has been obtained *via* the *slipping* method [4, 5]. As no templating interactions are required for a thermally promoted *slipping* of the wheels onto the axle, only the steric compatibility of the macrocyclic cavity and the size of the blocking group (stopper) is vital for a successful rotaxane synthesis. Hence, rotaxanes with pure hydrocarbon axles [4e, 5b,d,e] have become accessible by means of this method. Particularly simple and still very effective is the *slipping* procedure in the melt [5], in which the preformed components – axle and wheel – are heated to about 350 °C for one minute. Therefore, this method has been employed to examine the size complementarity of several pairs of macrocycles and stoppers [5b–d]. *Slipping* and subsequent *deslipping* experiments allowed to determine sterically matching pairs of wheels and blocking groups and, thus, to infer the actual size of the macrocyclic cavity. Although modern computer calculations have very much improved during the last years, predictions of the compatibility of certain elements still seem to be difficult due to the size and complexity of supramolecular structures. Even the effective cavity size and shape depends on many factors, such as the constitution of the ring-forming elements [4f–g, 6], the conformation at a specific temperature [4c,d] the solvation, and other effects [2d], so that it is hard to prognosticate. Thus, reliable data on the cavity size still have to be obtained from experimental studies, such as *slipping-deslipping* investigations. The first to carry out systematic studies was *Harrison* in 1972 who employed cycloalkanes of different sizes as wheels [4a,b]. The results from these investigations can be used as a reference system for comparing macrocycles of different structures by rotaxaning them and relating the matching blocking group to the corresponding cycloalkane [5a]. When employed in *slipping* syntheses, new hydrocarbon macrocycles will help to study size complementarities as well as the effect of small changes in more detail and, thus, enhance the reference system. Furthermore, hydrocarbons have the advantage over amide-based macrocycles of being more stable to oxidation processes which can occur during the slipping in the melt.

Remarkably, hydrocarbon macrocycles which fulfill the above mentioned requirements for being used as rotaxane wheels can rarely be found in the literature, i.e., wheel type macrocycles with around 32 ring member atoms – partly rigid and partly flexible – are not well known hitherto.

Results and Discussion

Since the tetralactam macrocycle **1** was found to be complementary to the 3,5-di-*tert*-butylbenzene stopper, whereas the corresponding sulfonamide cycle **2** needs the larger blocking group *p*-tritylbenzene to form ro-

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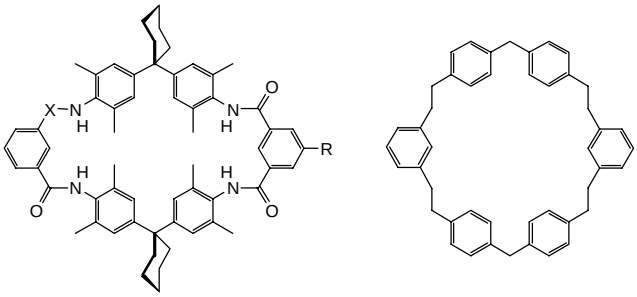
taxanes stable towards deslipping at room temperature, we developed a hydrocarbon macrocycle **3** which is an analogue to those cycles (Fig. 1), i.e. it possesses the same number of carbon ring members (32) as **1** and **2**, and contains rigid phenylene units as well as flexible alkyl bridges units.

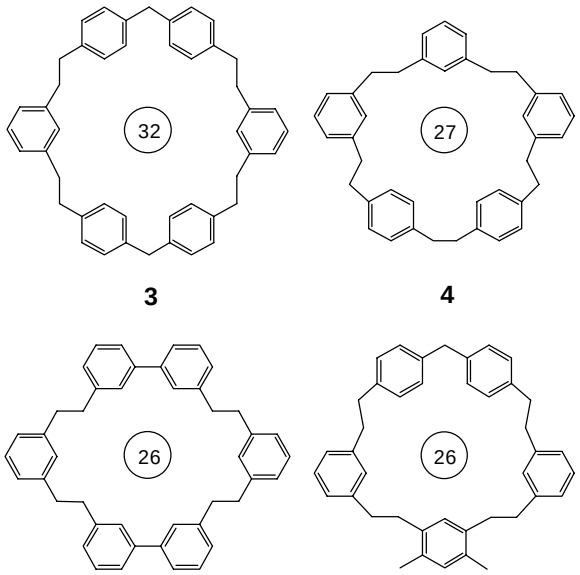


1: R = $C(CH_3)_3$, X = CO

2: R = H, X = SO_2

3

Fig. 1 The tetralactame and sulfonamide macrocycles **1** and **2** and their hydrocarbon analogue **3**



3 **4** **5** **6**

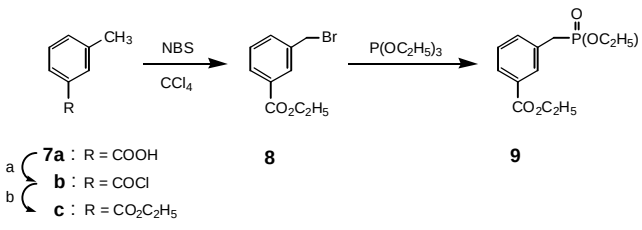
Fig. 2 New hydrocarbon macrocycles **3**–**6** prepared by the same synthetic route. The numbers given in the centers of the molecules indicate the number of ring members which describe the cavity.

Furthermore, cyclophane macrocycles of smaller and larger ring size should be synthesized in order to cover a wider range of cavity sizes. Thus, a synthetic route is preferred which gives the possibility of obtaining many macrocycles by an analogous way. Like in the preparation of the tetralactam cycle according to Hunter [7] and Vögtle [2h], it seemed favorable to synthesize an elongated building block first and to couple it with another unit to give the cyclic molecule, rather than trying a one-step cyclization which generally leads to various cyclic and acyclic by-products. As the macrocyclization reaction is the most limiting factor in the course of the synthesis, the well-known sulfide cyclization [8] was chosen which was introduced and very often applied in cyclophane chemistry [9] and usually lead to even strained products in good yields. In this S_N reaction, two bromomethyl functions are attached to two thiol functions in the presence of an alkali metal base resulting in the macrocyclic dithia compound.

Hence, by reacting the same elongated bromide building block with different thiols different macrocycles can be formed. If varied elongated bromides are employed, a whole range of cyclic products can be obtained.

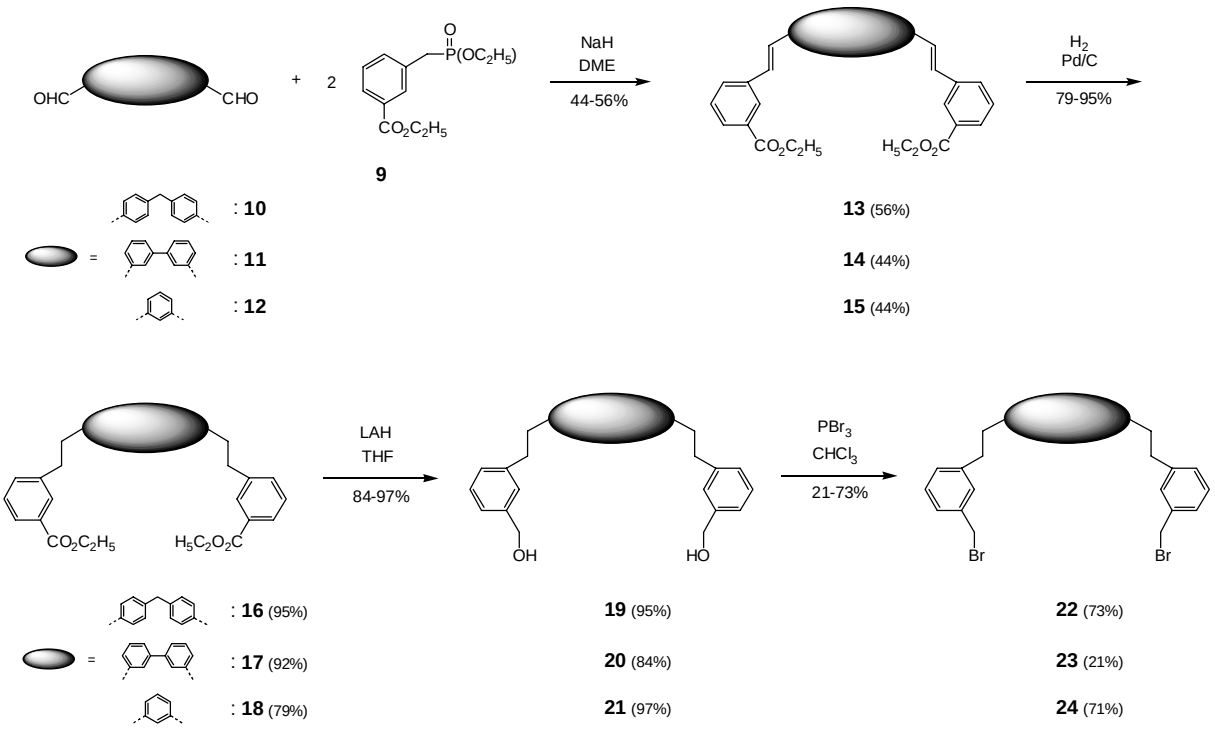
Here, we describe the synthesis of four hydrocarbon macrocycles **3**–**6**, which have been prepared following the same synthetic route. These cyclic compounds **3**–**6** depicted in Fig. 2 can be regarded as examples for a series of cyclophane-type macrocycles – and hence hydrocarbon wheels – and prove the general applicability of this synthetic route.

The ethyl phosphonate component **9** was the same in all *Wadsworth-Emmons* reactions performed here and provided with an ester function which can easily be transformed into a bromide function required for a sulfide cyclization. It was prepared in 68% yield starting from 3-methylbenzoic acid (**7a**) *via* **7b** and **7c**, subsequent NBS bromination to give the bromomethyl compound **8** and treatment with triethylphosphonate (Scheme 1).



Scheme 1 Preparation of intermediates a: $SOCl_2$; b: C_2H_5OH

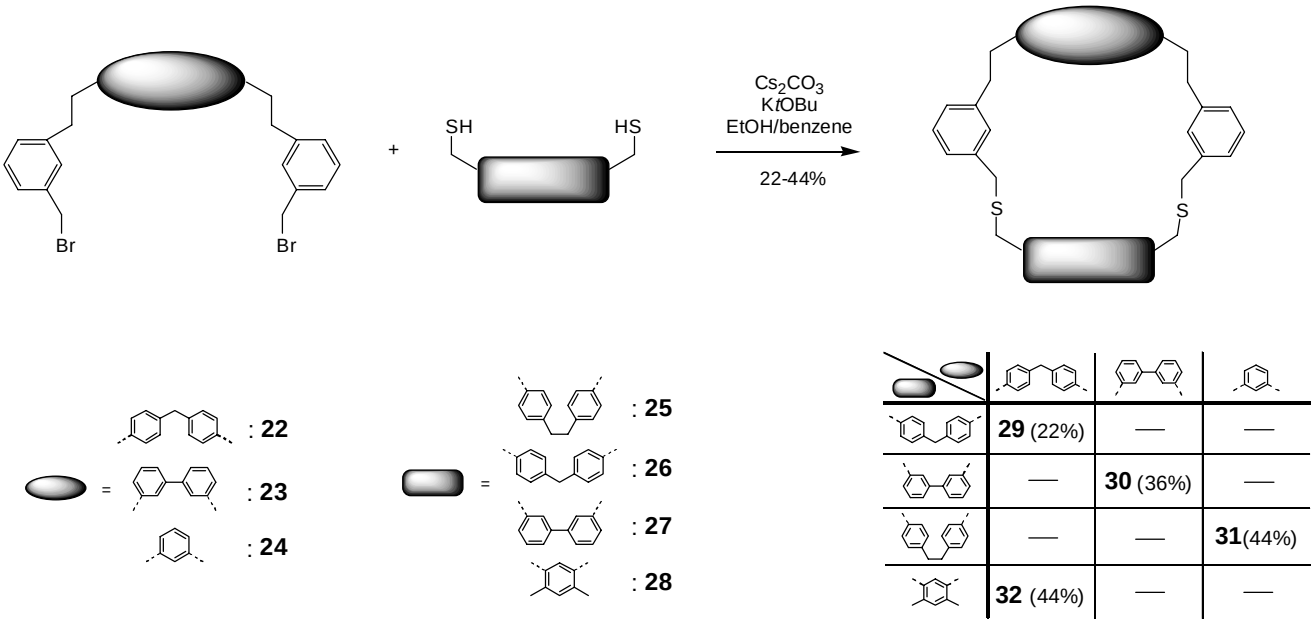
The aldehydes **10**–**12** were coupled to the phosphonate yielding the elongated ester-functionalized building blocks **13**–**15** (Scheme 2). After catalytically hydrogenation of the double bonds, which were found to be disturbing in the course of the synthesis [10], to give



Scheme 2 Synthesis and functionalization of the elongated building blocks **22**–**24**

the compounds **16**–**18** in 79–95% yield, the ester groups were reduced to hydroxymethyl moieties using lithium aluminium hydride (LAH) to yield compounds **19**–**21** (84–97%). Bromination with phosphorous tribromide afforded the corresponding bromomethyl compounds **22**–**24** (yield 21–73%). In contrast, a different route for converting diesters into bromides *via* the bis(acetoxymethyl) compound [11] led to lower yields and less pure bromides.

In the sulfide cyclization reaction, several combinations of the bromomethyl compounds **22**–**24** and the thioles **25**–**28** were reacted in the presence of caesium carbonate [12] and potassium *tert*-butoxide under dilution conditions [13]. After column-chromatographic



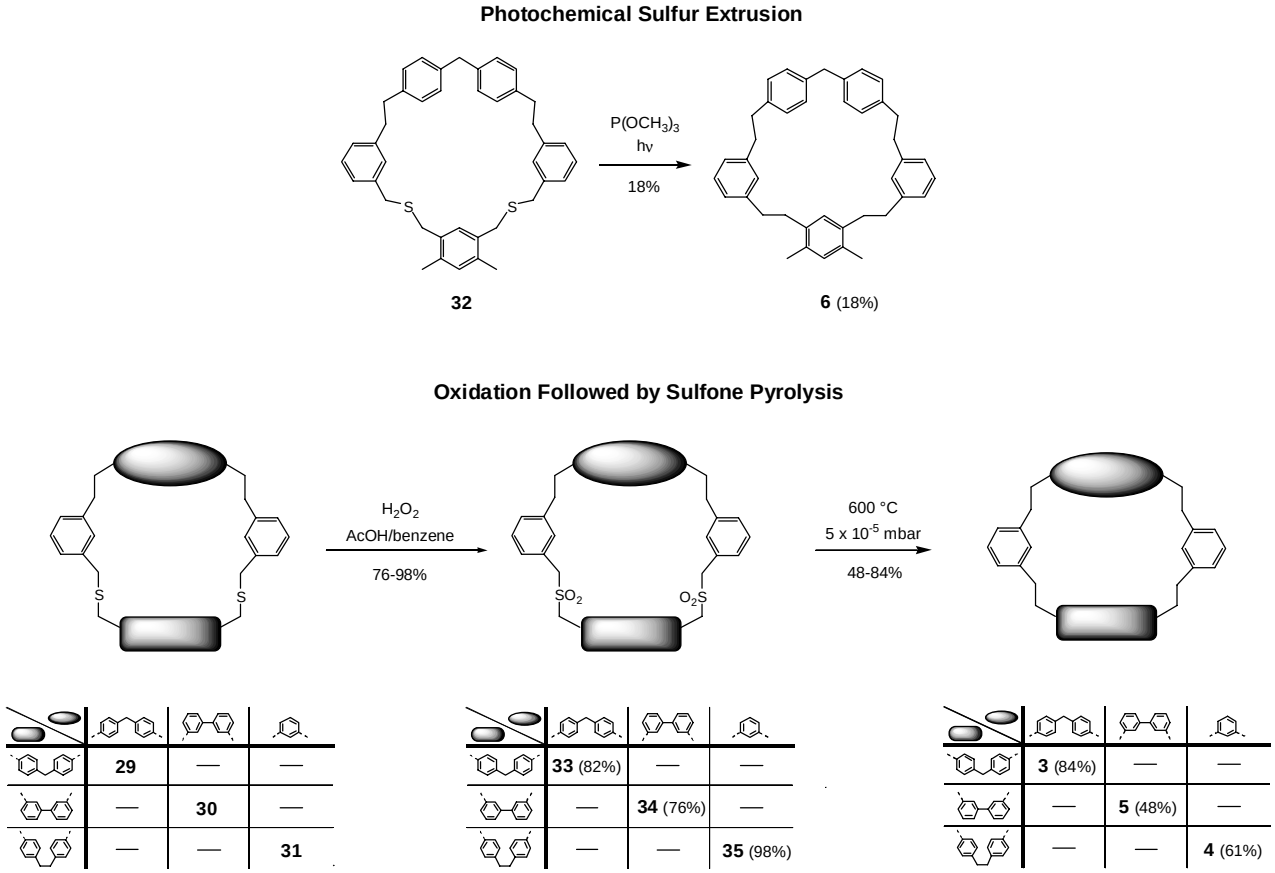
Scheme 3 Macrocyclization reactions

work-up, the resulting dithia compounds **29**–**32** could be isolated in yields between 22–44% (Scheme 3).

To remove the sulfur atoms from dithia cycles several reactions have proven to be useful [14], two of which were employed in the course of these syntheses (scheme 4). Photochemical sulfur extrusion discovered by Corey and Block [15] was applied to dithia compounds **29**–**33**. While **32** was successfully converted into hydrocarbon macrocycle **6** in 18% yield by irradiating a solution of the substance in trimethylphosphite with UV light for 20 hours, the equivalent desulfurization of the other ones did not succeed. Synthesizing various [2.2]cyclophanes Misumi *et al*. also observed that for some cyclophanes the photochemical pathway failed, whereas the pyrolysis method afforded the desired hydrocarbons [16]. Similarly, the hydrocarbon **3** as well as **4** and **5** could be achieved by sulfone pyrolysis [8a, 17] of the corresponding sulfones **33**–**35**. During the oxidation of dithia cycle **32** many side products were, however, formed preventing a subsequent pyrolysis, as all sulfones are very difficult to purify owing to their poor solubility. Amounts of up to 0.1 mmol of the sulfone substances were pyrolysed using a ring oven apparatus [17c,d] at 600 °C and $4-5\times10^{-5}$ mbar. Although involving one additional step, the oxidation of the dithia compounds with hydrogenperoxide in glacial acetic acid and benzene [18] the overall yield of desulfurization (oxidation followed by pyrolysis) was 69, 37, and 60% for the dithia compounds **29**, **30**, and **31**, respectively, and hence, higher as compared to that of the photochemical sulfur extrusion reaction of compound **32**.

The x-ray crystal structures [19] could be solved for three of the macrocycles. Single crystals of **3** and **5** were grown by solvent diffusion of methanol into dichloromethane, the ones of **6** by slow evaporation of trichloromethane. The crystallographic data are given in Table 1.

The crystal strucure of macrocycle **3** reveals a large cavity which is not – unlike the cavities of tetralactame macrocycles [7, 20] – of a regular shape (Fig. 3). While in vertical direction it is narrow (smallest C–C distance: 4.4 Å), in horizontal direction is comparatively broad (longest C–C distance: 15.6 Å). This is probably due to the missing cyclohexylidene moieties which in the



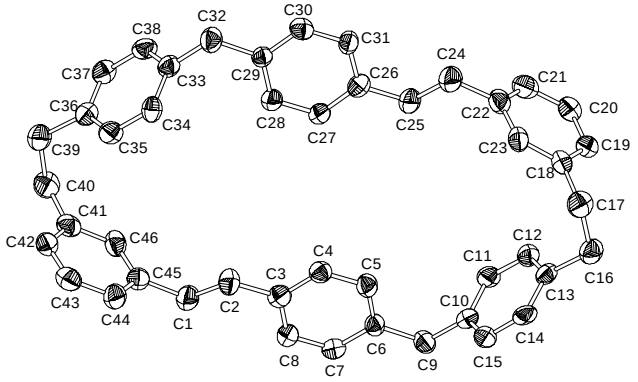
Scheme 4 Desulfurization reactions

Table 1 X-ray data of the macrocycles **3**, **5**, and **6**

Compound	**3**	**5**	**6**
Empirical formula	$C_{46}H_{44}$	$C_{44}H_{40}$	$C_{41}H_{42}$
Molecular weight	596.81	568.76	534.75
Wavelenght/Å	0.71073 (MoKα)	0.71073 (MoKα)	0.71073 (MoKα)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (No.19)	P 2_1/c (No. 14)	$P2_1$ (No. 4)
a/Å	6.1265(4)	14.9078(5)	13.2137(3)
b/Å	18.8806(16)	16.9439(5)	17.1741(6)
c/Å	28.773(3)	6.2211(2)	14.6429(5)
β/°	β = 90°	99.562(2)	111.072(2)
Volume/Å^3	3328.2(5)	1549.59(9)	3100.75(17)
Z	4	2	4
$D_{calc.}$/mg m^{-3}	1.191	1.219	1.145
μ/mm^{-1}	0.067	0.069	0.064
F(000)	1280	608	1152
Crystal size/mm	0.25 × 0.05 × 0.03	0.30 × 0.10 × 0.05	0.40 × 0.30 × 0.20
θ range for data collection/°	1.78 to 25.00	2.77 – 28.26	2.85 – 28.32
Limiting indices	$-7 \le h \le 5$, $-14 \le k \le 22$, $-34 \le l \le 27$	$-19 \le h \le 19$, $-22 \le k \le 22$, $-8 \le l \le 8$	$-17 \le h \le 17$, $-22 \le k \le 22$, $-19 \le l \le 19$
Reflections collected	13473	30575	57673
R_{int}	0.1620	0.0369	0.0553
No. of unique reflections	5637	3831	15262
Absortion correction	none	none	none
Data/restraints/parameters:	5637/0/415	3831/0/199	15262/1/743
Goodness-of-fit on F^2	0.896	1.082	0.909
Final R indices [I > 2σ(I)]	R_1 = 0.0840, wR_2 = 0.1413	R_1 = 0.0379, wR_2 = 0.0999	R_1 = 0.0430, wR_2 = 0.0711
R indices (all data)	R_1 = 0.2004, wR_2 = 0.1788	R_1 = 0.0503, wR_2 = 0.1051	R_1 = 0.0775, wR_2 = 0.0776
Largest diff. peak and hole/eA^{-3}	0.250 and – 0.250	0.224 and – 0.191	0.145 and – 0.207

tetralactam cycle **1** force the diphenylmethylane units to take up a different conformation resulting in a more rigid, "open" cavity.

Comparing the crystal structures of **5** and **6** it must be noted that the cavity shape and size can differ tremendously, even if both macrocycles are constructed from similar building blocks and contain the same number of ring atoms, in this case **26** (Fig. 3). While cycle **5** puts up a cavity which is relatively large and well accessible – at least in solid state –, the effective cavity of macrocycle **6** turns out to be much smaller, because of the methyl-substituted phenylene unit folded into the cycle. These observations will certainly have to be taken into account intending to use such rings as wheels for rotaxanes.



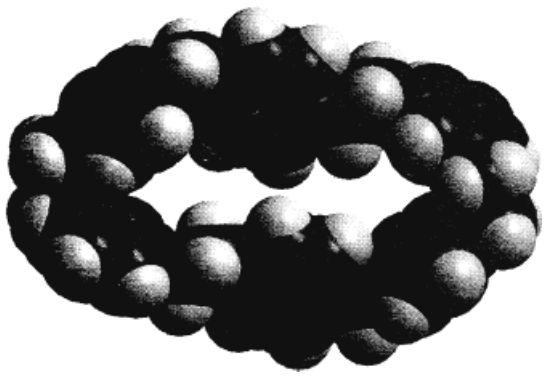


Fig. 3 Crystal-structure analysis of **3**

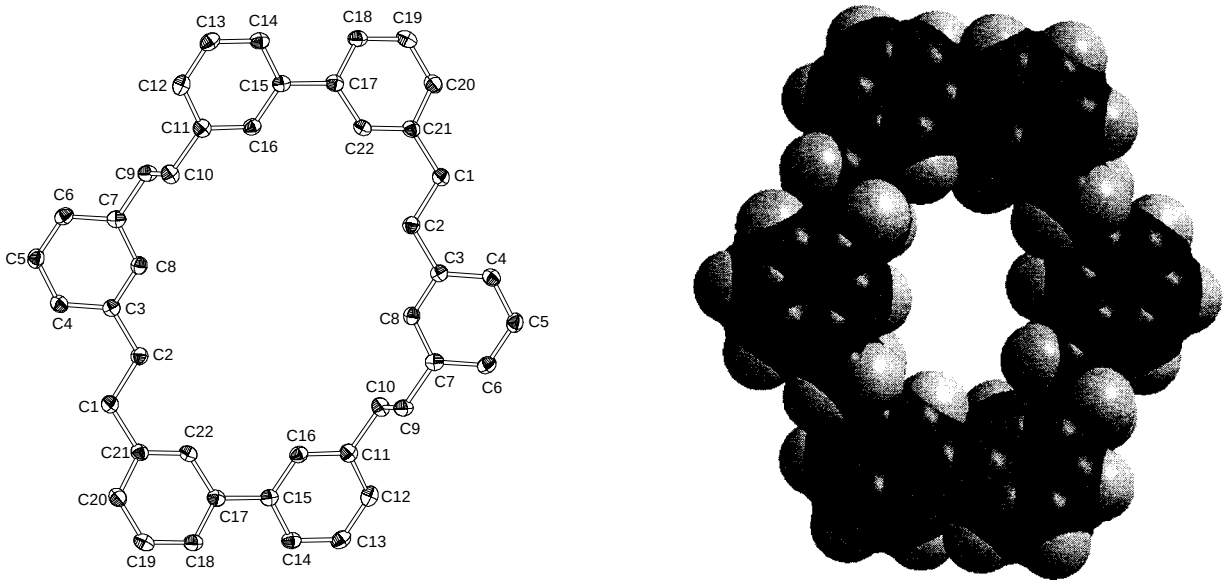


Fig. 4 Crystal-structure analysis of **5**

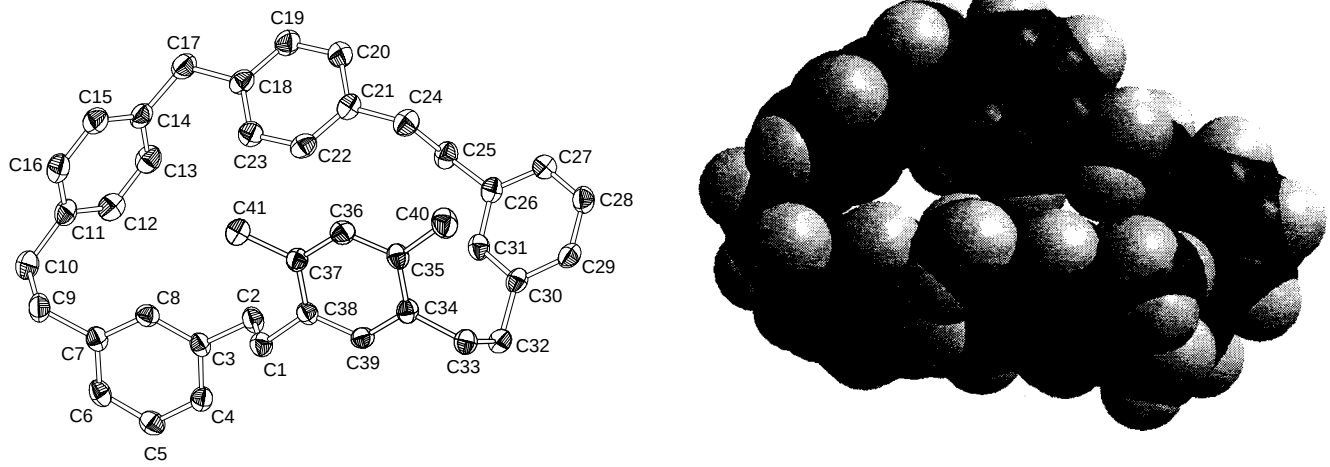


Fig. 5 Crystal-structure analysis of **6**

Historically, medium-sized and many-membered hydrocarbon rings have always been considered as being difficult to obtain. This work demonstrates that macrocyclic hydrocarbons suitable for wheels are well accessible in reasonable yields.

Although first orientational experiments to form rotaxanes by melting the macrocycles **3**–**6** in the presence of hydrocarbon axles with blocking groups of different sizes have not led to sufficient amounts of the corresponding rotaxanes so far, we will continue to search for matching blocking groups in order to enhance the reference system for cavity and complementary stopper sizes.

We would like to thank E. Kujala and Dr. M. Lämsä for preparative work as well as Dr. C. Reuter and Dr. C. Schalley for helpful discussion.

Experimental

General: Solvents were purified by standard methods and dried if necessary. Reagents were used in commercial quality. TLC: Merck silica gel 60 F_{254}; visualization by UV light. HPTLC: Merck silica gel 60 F_{254}; visualization by UV light. Column chromatography: Merck silica gel 60 (40–63 µm, 63–100 µm). Melting points: Kofler hot stage (Reichert); uncorrected. ^{1}H and ^{13}C NMR: AM-250 (^{1}H: 250 MHz, ^{13}C: 62.9 MHz) and AM-400 (^{1}H: 400 MHz, ^{13}C: 100.64 MHz) of Bruker Analytische Meßtechnik GmbH, Karlsruhe, Germany, with solvent signals as reference. EI-MS: A.E.I. MS-50, Manchester, Great Britain. FAB-MS: Concept 1H, Kratos Analytical Ltd., Manchester, Great Britain; matrix: *m*-nitrobenzyl alcohol (*m*-NBA). MALDI-TOF-MS: MALDI-Tof-Spec-E, Micromass, Manchester, Great Britain; matrix: 9-nitroanthracene (9-NA) or 2,5-dihydroxybenzoic acid (2,5-DHB). X-ray structure analyses: Nonius-KappaCCD, Delft,

The Netherlands. Elemental analyses were performed by the Microanalytical Department of the Kekulé-Institut für Organische Chemie und Biochemie, University of Bonn.
The following compounds were prepared according to the literature methods cited: aldehydes 10 [21, 22], 11 [19], thioles 25–28 [23].

3-Methyl ethyl benzoate (**7c**)

A mixture of 3-methylbenzoic acid (**7a**) (44.9 g, 0.33 mol), thionyl chloride (80 mL, 164.0 g, 1.28 mol) and a few drops of *N*,*N*-dimethyl formamide are heated under reflux for 2h. After cooling to room temperature, the excess thionyl chloride is removed *in vacuo* and the acid chloride is purified by distillation (GC-MS (EI): *m/z* (%) = 156/154 ([M]$^+$, 5/12), 119 ([M–Cl$^-$]$^+$, 100), 91 (86), 65 (35)). Under ice cooling ethanol (200 mL) is added to 3-methylbenzoic acid chloride (**7b**) (49.6 g, 0.32 mol), and it is refluxed for three hours. Then the excess alcohol is distilled off. Yield 51.5 g (95%), colourless liquid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.38 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_2CH_3), 2.39 (s, 3H, Ar–CH_3), 4.36 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2), 7.30 (pt, $^3J_{HH}$ = 6.5 Hz, 1H, 5-H_{ar}); 7.31 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 4-H_{ar}), 7.84 (d, $^3J_{HH}$ = 6.6 Hz, 1H, 6-H_{ar}), 7.85 (s, 1H, 2-H_{ar}). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 14.30 (CH_2CH_3), 21.23 (Ar–CH_3), 60.84 (OCH_2), 126.62 (6-C), 128.17 (5-C), 130.01 (2-C), 130.36 (1-C), 133.52 (4-C), 138.04 (3-C), 166.80 ($COOCH_2$). – GC-MS (EI): R_t = 4.20 min; *m/z* (%) = 164 ([M]$^+$, 19), 149 ([M–CH_3]$^+$, 7), 136 ([M–C_2H_4]$^+$, 15), 119 ([M–C_2H_5O]$^+$, 100), 91(64), 65 (17). $C_{10}H_{12}O_2$ (164.20).

(3-Methylene diethyl phosphonate)ethyl benzoate (**9**)

After the addition of *N*-bromosuccinimide (7.48 g, 42 mmol) and a spatula-point of azobisisobutyronitrile to a solution of 3-methyl ethyl benzoate (**7c**) (6.59 g, 40mmol) in tetrachloromethane (100 mL) the mixture is heated under reflux and irradiation by a 500 W lamp for 2h. It is cooled to room temperature and the solid is filtered. The solvent is removed from the filtrate under reduced pressure. A brown oil remains which is used without any further purification (GC-MS (EI): *m/z* (%) = 242/244 ([M]$^+$, 7/8), 197/199 ([M–C_2H_5O]$^+$, 12/10), 169/171 ([M–$COOC_2H_5$]$^+$, 5/5), 163 ([M–Br]$^+$, 100), 135 ([M–Br–C_2H_4]$^+$, 18), 119 (29), 90 (21), 89 (18), 63 (8)). The crude 3-bromomethyl ethyl benzoate (**8**) (3.58 g) and triethylphosphite (5.2 mL, 30 mmol) are heated under reflux for four hours. Then the excess triethylphosphite is removed by distillation under reduced pressure. The remaining brown oil is purified by column chromatography (silica gel 60, dichloromethane/methanol = 30/1). Yield 17.3 g (72%), yellowish oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, $POCH_2CH_3$), 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $COCH_2CH_3$), 3.17 (d, $^2J_{PH}$ = 21.5 Hz, 2H, PCH_2), 4.00 (dq, $^3J_{PH}$ = 7.3 Hz, $^3J_{HH}$ = 7.4 Hz, 4H, $POCH_2CH_3$), 4.34 (q, $^3J_{HH}$ = 7.1 Hz, 2H, $COCH_2CH_3$), 7.36 (pt, $^3J_{HH}$ = 7.6 Hz, 1H, 5-H_{ar}), 7.49 (d, $^3J_{HH}$ = 6.4 Hz, 1H, 4-H_{ar}), 7.91 (d, $^3J_{HH}$ = 7.7 Hz, 1H, 6-H_{ar}), 7.93 (s, 1H, 2-H_{ar}. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 14.43 (s, $COCH_2CH_3$), 16.45 (d, $^3J_{CP}$ = 5.9 Hz, $POCH_2CH_3$), 33.69 (d, $^1J_{CP}$ = 138.8 Hz, PCH_2), 61.14 ($COCH_2CH_3$), 62.35 (d, $^2J_{CP}$ = 6.9 Hz, $POCH_2CH_3$), 128.24 (d, $^3J_{CP}$ = 2.9 Hz, C_{ar}), 128.68 (d, $^3J_{CP}$ = 2.9 Hz, C_{ar}), 130.86 (d, $^4J_{CP}$ = 1.9 Hz, C_{ar}), 130.94 (d, $^4J_{CP}$ = 1.9 Hz, C_{ar}), 132.24 (d, $^2J_{CP}$ = 9.8 Hz, C_q, 3-C_{ar}), 134.29 (d, $^5J_{CP}$ = 5.9 Hz, C_{ar}), 166.49 (s, C=O). – MS (EI): *m/z* (%) = 300 ([M]$^+$, 70), 271 ([M–C_2H_5]$^+$, 18), 255 ([M–OC_2H_5]$^+$, 59), 226 (74), 198 (30), 164 ([M–$PO(OC_2H_5)_2$]$^+$, 53), 135 (31), 118 (100), 90 (49), 65 (7).
$C_{14}H_{21}O_5P$ (300.29).

Wadsworth-Emmons Reaction (General Procedure)

(3-Methylene diethyl phosphonate)ethyl benzoate (**9**) (6.01 g, 20 mmol), sodium hydride (60% in oil) (0.84 g, 21 mmol), and bisaldehyde **10**–**12** (2.24 g, 10 mmol) were added to dry 1,2-dimethoxyethane (40 mL). The mixture is heated slowly to 85 °C with stirring. At 75–85 °C the evolution of hydrogen and the appearance of a brown, semi-solid precipitate is observed. The solution is refluxed for half an hour, cooled to room temperature and taken up in a large excess of water yielding a light brown precipitate. The reaction mixture is extracted with dichloromethane several times until the solid is dissolved. After drying of the combined organic layers over magnesium sulfate, the solvent is evaporated.

4,4'-Bis[3-(E)-(ethoxycarbonyl)phenyl-2-ethenyl] diphenylmethane (**13**)

Purification of the residue by column chromatography (silica gel 60, trichloromethane/petroleum ether = 10/1). Yield 2.90 g (56%), colourless solid, *m.p.* 115 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.42 (t, $^3J_{HH}$ = 7.14 Hz, 6H, CH_2CH_3), 4.01 (s, 2H, $ArCH_2Ar$), 4.41 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2CH_3), 7.09 (d, $^3J_{HH}$ = 16.3 Hz, 2H, H_{olef}), 7.18 (d, $^3J_{HH}$ = 16.3, 2H, H_{olef}), 7.21 (d, $^3J_{HH}$ = 8.1 Hz, 4H, A-H_{ar}, A'-H_{ar}), 7.42 (pt, $^3J_{HH}$ = 7.7 Hz, 2H, H_{ar}), 7.47 (d, $^3J_{HH}$ = 8.1 Hz, 4H, B-H_{ar}, B'-H_{ar}), 7.67 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 7.92 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 8.19 (s, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 14.40 (CH_2CH_3), 41.48 ($ArCH_2Ar$), 61.12 (CH_2CH_3), 126.85 (B–C_{ar}, B'-C_{ar}), 127.14, 127.45, 128.43 (C_{ar}), 128.71, 129.36 (C_{olef}), 129.60, 130.62 (C_{ar}), 130.95, 135.01, 137.72, 140.87 ($C_{q,ar}$), 166.61 (C=O). – MS (EI): *m/z* (%) = 516 ([M]$^+$, 100), 487 ([M–C_2H_5]$^+$, 12), 471 ([M–OC_2H_5]$^+$, 6), 442 (3), 370 (5), 258 (6). $C_{35}H_{32}O_4$ (516.63).

4,4'-Bis[3-(E)-(ethoxycarbonyl)phenyl-2-ethenyl] biphenyl (**14**)

Purification of the residue by column chromatography (silica gel 60, trichloromethane/petroleum ether = 6/1). Yield 2.21 g (44%), colourless solid, *m.p.* 97 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.44 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2CH_3), 4.42 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2CH_3), 7.22 (d, $^3J_{HH}$ = 16.3 Hz, 2H, H_{olef}), 7.29 (d, $^3J_{HH}$ = 16.3 Hz, 2H, H_{olef}), 7.42–7.51 (m, 4H, H_{ar}), 7.55 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_{ar}), 7.56 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_{ar}), 7.72 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.78 (s, 2H, H_{ar}), 7.96 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H_{ar}), 8.24 (s, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 14.41 (CH_2CH_3), 61.13 (CH_2CH_3), 125.58, 125.71, 126.87, 127.58, 128.10, 128.65 (C_{ar}), 128.77, 129.24 (C_{olef}), 129.71, 130.75 (C_{ar}), 131.03, 137.53, 137.57, 141.56 ($C_{q,ar}$), 166.65 (C=O). – MS (EI): *m/z* (%) = 502 ([M]$^+$, 52), 457 ([M–OC_2H_5]$^+$, 4), 412 ([M–$2OC_2H_5$]$^+$, 4), 400 (45), 386 (88), 342 (18), 311 (100), 265 (16), 253 (35), 239 (20). $C_{34}H_{30}O_4$ (502.60).

1,3-Bis[3-(E)-(ethoxycarbonyl)phenyl-2-ethenyl] benzene (**15**)

Purification of the residue by column chromatography (silica gel 60, dichloromethane/cyclohexane = 5/1). Yield 1.87 g (44%), colourless solid, *m.p.* 81–83 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.44 (t, $^3J_{HH}$ = 7.11 Hz, 6H, CH_2CH_3), 4.43 (q, $^3J_{HH}$ = 7.2 Hz, 4H, CH_2CH_3), 7.21 (s, 4H, H_{olef}), 7.35–7.50 (m, 3H, H_{ar}), 7.45 (pt, $^3J_{HH}$ = 7.6, 2H, H_{ar}), 7.69 (s, 1H, H_{ar}), 7.72 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H), 7.96 (d, $^3J_{HH}$ = 7.3, 2H, H_{ar}), 8.23 (s, 2H, H_{ar}). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 14.53 (CH_2CH_3), 61.09 (CH_2CH_3), 125.04, 126.25, 127.66, 128.17, 128.74 (C_{ar}), 128.85, 129.22 (C_{olef}), 129.66 (C_{ar}), 130.80, 131.10, 137.52, 137.61 ($C_{q,ar}$), 166.64 (C=O). – MS (EI): *m/z* (%) = 426 ([M]$^+$, 100), 381 ([M–OC_2H_5]$^+$, 14), 351 (16), 279 (20), 203 (22). $C_{28}H_{26}O_4$ (426.50).

Catalytic Hydrogenation (General Procedure)

The palladium catalyst (10% Pd on activated carbon) (0.90 g) was added to a solution of the ethenyl derivative **13**–**15** (3 mmol) in toluene (150 mL) in a hydrogenation flask and shaken under hydrogen atmosphere (4–4.5 bar) at 40 °C for 7 h. Then the catalyst was removed by filtration over celite and the solvent was evaporated *in vacuo*.

4,4'-Bis[3-(ethoxycarbonyl)phenyl-2-ethanyl] diphenylmethane (**16**)

Yield 1.48 g (95%), first colourless oil, turned into a solid after a few days, *m.p.* 46–48 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.41 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2CH_3), 2.87–3.01 (m, 8H, $ArCH_2CH_2Ar$), 3.94 (s, 2H, $ArCH_2Ar$), 4.39 (q, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 7.12 (s, 8H, A-H_{ar}, A'-H_{ar}, B-H_{ar}, B'-H_{ar}), 7.32–7.37 (m, 4H, H_{ar}), 7.87–7.93 (m, 4H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 14.40 (CH_2CH_3), 37.41, 37.77 ($ArCH_2CH_2Ar$), 41.17 ($ArCH_2Ar$), 60.97 (CH_2CH_3), 127.24, 128.34, 128.54, 128.95, 129.52 (C_{ar}), 130.57 ($C_{q,ar}$), 133.08 (C_{ar}), 138.99, 139.08, 142.11 ($C_{q,ar}$), 166.82 (C=O). – MS (EI): *m/z* (%) = 521 ([M+H]$^+$, 46), 475 ([M–OC_2H_5]$^+$, 100), 429 ([M–2 OC_2H_5]$^+$, 20), 313 (48), 223 (83), 193 (49). $C_{35}H_{36}O_4$ (520.66).

3,3'-Bis[3-(ethoxycarbonyl)phenyl-2-ethanyl] biphenyl (**17**)

Yield 1.39 g (92%), colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.41 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2CH_3), 3.03 (s, 8H, $ArCH_2CH_2Ar$), 4.39 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2CH_3), 7.18 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.34–7.40 (m, 6H, H_{ar}), 7.39 (s, 2H, H_{ar}), 7.42 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H_{ar}), 7.92 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H_{ar}), 7.95 (s, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 14.39 (CH_2CH_3), 37.83, 37.93 ($ArCH_2CH_2Ar$), 60.98 (CH_2CH_3), 125.00, 127.31, 127.42, 127.47, 128.39, 128.83, 129.62 (C_{ar}), 130.63 ($C_{q,ar}$), 133.12 (C_{ar}), 141.40, 141.81 , 141.99 ($C_{q,ar}$), 166 80 (C=O). – MS (EI): *m/z* (%) = 506 ([M]$^+$, 48), 460 ([M+H–OC_2H_5]$^+$, 100), 415 (9), 299 (85), 180 (15). $C_{34}H_{34}O_4$ (506.63).

1,3-Bis[3-(ethoxycarbonyl)phenyl-2-ethanyl] benzene (**18**)

Yield 1.02 g (79%), colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 1.40 (t, $^3J_{HH}$ = 7.11 Hz, 6H, CH_2CH_3), 2.84–3.00 (s, br, 8H, $ArCH_2CH_2Ar$), 4.38 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2CH_3), 6.97 (s, 1H, H_{ar}), 7.02 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_{ar}), 7.21 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H_{ar}), 7.30–7.39 (m, 4H, H_{ar}), 7.85–7.94 (m, 4H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 14.48 (CH_2CH_3), 37.89 ($ArCH_2CH_2Ar$), 61.04 (CH_2CH_3), 126.29, 127.32, 128.41, 128.55, 128.83 (C_{ar}), 129.22 ($C_{q,ar}$), 129.64, 133.19 (C_{ar}), 141.52, 142.13 ($C_{q,ar}$), 166.89 (C=O). $C_{28}H_{30}O_4$ (430.54).

Reduction (General Procedure)

Lithium aluminium hydride (0.52 g, 13.25 mmol) is suspended in dry tetrahydrofurane (50 mL). The bis(ethoxycarbonyl) compound **16**–**18** (5.0 mmol) is dissolved in dry tetrahydrofurane (50 mL) and added dropwise to the suspension within 15 min. The mixture is stirred at room temperature for 1 h, then heated under reflux for 7 h, cooled to room temperature and stirred over night. After the addition of water (0.5 mL) it is stirred for 1 h, then again water (5 mL) is added. A fine precipitate is formed by a lithium–aluminium salt. Some drops of an aqueous sodium hydroxide solution (15%) are added, then the reaction mixture is filtered and washed with tetrahydrofurane. The filtrate is dried over magnesium sulfate and the solvent removed under reduced pressure. The product was used without any further purification.

4,4'-Bis[3-(hydroxymethyl)phenyl-2-ethanyl] diphenylmethane (**19**)

Yield 2.07 g (95%), colourless solid, *m.p.* 94–96 °C. – ^{1}H NMR (250 MHz, C_4D_8O): δ/ppm = 2.86 (s, br, 8H, $ArCH_2CH_2Ar$), 3.89 (s, 2H, $ArCH_2Ar$), 4.09 (t, $^3J_{HH}$ = 5.7 Hz, 2H, OH), 4.53 (d, $^3J_{HH}$ = 5.7 Hz, 4H, CH_2OH), 6.98–7.25 (m, 16H, all H_{ar}). – ^{13}C NMR (62.9 MHz, C_4D_8O): δ/ppm = 38.79, 39.24 ($ArCH_2CH_2Ar$), 42.07 ($ArCH_2Ar$), 65.09 (CH_2OH), 124.94, 127.47, 127.69, 128.89 (C_{ar}), 129.35 (B–C_{ar}, B'–C_{ar}), 129.77 (A–C_{ar}, A'–C_{ar}), 140.13, 140.62, 142.78, 144.08 ($C_{q,ar}$). – MS (FAB): *m/z* (%) = 435 ([M–H]$^+$, 43), 418 ([M–H_2O]$^+$, 63), 401 (88), 193 (100). $C_{31}H_{32}O_2$ (436.58).

3,3'-Bis[3-(hydroxymethyl)phenyl-2-ethanyl] biphenyl (**20**)

Yield 1.77 g (84%), colourless solid, *m.p.* 75–76 °C. – ^{1}H NMR (400 MHz, C_4D_8O): δ/ppm = 2.95 (s, br, 8H, $ArCH_2CH_2Ar$), 4.16 (t, $^3J_{HH}$ = 5.8 Hz, 2H, OH), 4.55 (d, $^3J_{HH}$ = 5.4 Hz, 4H, CH_2OH), 7.1 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H_{ar}), 7.14–7.19 (m, 6H, H_{ar}), 7.21 (pt, $^3J_{HH}$ = 7.3 Hz, 2H, H_{ar}), 7.30 (pt, $^3J_{HH}$ = 8.2 Hz, 2H, H_{ar}), 7.40 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_{ar}), 7.41 (s, 2H, H_{ar}). – ^{13}C NMR (100 MHz, C_4D_8O): δ/ppm = 39.11, 39.13 ($ArCH_2CH_2Ar$), 64.92 (CH_2OH), 124.84, 125.41, 127.40, 127.65, 128.08, 128.11, 128.78, 129.40 (C_{ar}), 142.27, 142.55, 143.30, 143.95 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 422 ([M]$^+$, 8), 404 ([M–H_2O]$^+$, 100), 386 ([M–$2H_2O$]$^+$, 13), 299 (72), 181 (29), 165 (16), 121 (27), 105 (51), 91 (11). $C_{30}H_{30}O_2$ (422.56).

1,3-Bis[3-(hydroxymethyl)phenyl-2-ethanyl] benzene (**21**)

Yield 1.68 g (97%), colourless solid, *m.p.* 45–48 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.93 (br, 8H, $ArCH_2CH_2Ar$), 4.71 (s, 4H, CH_2OH), 7.02 (s, 2H, H_{ar}), 7.05 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.16 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.20–7.27 (m, 5H, H_{ar}), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_{ar}). –

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 37.89, 37.95 ($ArCH_2CH_2Ar$), 65.37 (CH_2OH), 124.61, 126.09, 127.16, 127.81, 128.33, 128.58, 128.75 (C_{ar}), 140.91, 141.72, 142.22 ($C_{q,ar}$). – MS (FAB): *m/z* (%) = 347 ($[M+H]^+$, 9), 328 ($[M–H_2O]^+$, 47), 311 ($[M–H_2O–OH]^+$, 100), 289 (65), 223 (22), 205 (26), 178 (41). $C_{24}H_{26}O_2$ (346.46).

Bromination (General Procedure)

To the hydroxymethyl compound **19**–**21** (3.0 mmol), suspended in dry trichloromethane (150 mL), phosphorus tribromide (1.45 mL, 15 mmol) is added. The mixture is stirred at room temperature for 4 d. After the addition of water (7 mL) it is stirred for 1 h to hydrolyse excessive phosphorus tribromide. The organic layer is separated and washed two times with a saturated sodium bicarbonate solution and water. After drying over magnesium sulfate the solvent is removed.

4,4'-Bis[3-(bromomethyl)phenyl-2-ethanyl] diphenylmethane (**22**)

Yield 1.23 g (73%), colourless solid, *m.p.* 98 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.89 (s, br, 8H, $ArCH_2CH_2Ar$), 3.93 (s, 2H, $ArCH_2Ar$), 4.46 (s, 4H, CH_2Br), 7.06–7.15 (m, 10H, A-H_{ar}, A'-H_{ar}, B-H_{ar}, B'-H_{ar}, 4'-H_{ar}), 7.18 (s, 2H, H_{ar}), 7.20–7.29 (m, 4H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 33.75 (CH_2Br), 37.38, 37.82 ($ArCH_2CH_2Ar$), 41.18 ($ArCH_2Ar$), 126.65, 128.55 (C_{ar}), 128.64 (B-C_{ar}, B'-C_{ar}), 128.80, 128.91 (C_{ar}), 129.21 (A-C_{ar}, A'-C_{ar}), 137.73, 139.00, 139.18, 142.48 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 560/562/564 ($[M]^+$, 52/100/55), 481/483 ($[M–Br]^+$, 18/16), 401 ($[M–2Br-H]^+$, 35), 379 (22), 297 (98), 207 (42) 193 (85), 179 (38), 105 (40), 91 (8). $C_{31}H_{30}Br_2$ (562.38).

3,3'-Bis[3-(bromomethyl)phenyl-2-ethanyl] biphenyl (**23**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). Yield 0.41 g (21%), colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.94 (s, br, 8H, $ArCH_2CH_2Ar$), 4.44 (s, 4H, CH_2Br), 7.11 (d, $^3J_{HH}$ = 7.1 Hz, 2H, H_{ar}), 7.13 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.18–7.27 (m, 6H, H_{ar}), 7.29 (s, 2H, H_{ar}), 7.31 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}), 7.37 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 33.75 (CH_2Br), 37.88, 37.90 ($ArCH_2CH_2Ar$), 124.97, 126.73, 127.39, 127.47, 128.74, 128.80, 128.87, 129.26(C_{ar}), 137.85, 141.37, 141.93, 142.39 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 546/548/550 ($[M]^+$, 52/100/54), 468/470 ($[M–HBr]^+$, 7/6), 387 ($[M–2Br]^+$, 48), 363/365 (12/11), 283 (12), 194 (34), 179 (20), 165 (14), 119 (32), 105 (34), 91 (8), 80 (10). $C_{30}H_{28}Br_2$ (548.35).

1,3-Bis[3-(bromomethyl)phenyl-2-ethanyl] benzene (**24**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). – Yield 1.01 g (71%), colourless solid, *m.p.* 54 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.91 (s, br, 8H, $ArCH_2CH_2Ar$), 4.49 (s, 4H, CH_2Br), 6.98 (s, 1H, H_{ar}), 7.04 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, H_{ar}), 7.13 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, H_{ar}), 7.20–7.31 (m, 7H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 33.80 (CH_2Br), 37.78, 37.85 ($ArCH_2CH_2Ar$), 126.16, 126.69, 128.46, 128.71, 128.77, 128.83, 129.23 (C_{ar}), 137.80, 141.59, 142.50 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 470/472/474 ($[M]^+$, 11/20/10), 391/393 ($[M–Br]^+$, 6/7), 311 ($[M–2Br]^+$, 100), 287/289 (92/86), 207 ($[C_{16}H_{14}]^+$, 26), 183/185 (14/13), 156 (19) 119 (22), 104 (37). $C_{24}H_{24}Br_2$ (472.26).

Sulfide Cyclization (General Procedure)

The bis(bromomethyl) compound **22**–**24** (3.0 mmol) and the bis(mercaptomethyl) compound **25**–**28** (3.0 mmol) are dissolved in a 1/1-mixture of ethanol/benzene (in 250 mL each). Under inertgas atmosphere both solutions are added simultaneously to a refluxing suspension of caesium carbonate (3.90 g, 12.0 mmol) and potassium *tert*-butoxide (0.78 g, 6.9 mmol) in ethanol/benzene (1/1) (600 mL) by means of a 2C-VP apparatus [17d] over a period of 8 h. After the addition being completed, it is refluxed for another 12 h. Then the reaction mixture is allowed to cool to room temperature, and the solvent is evaporated. The residue is taken up in trichloromethane. The suspension is washed with water several times to remove the inorganic salts. After drying of the organic layer over magnesium sulfate, the solvent is evaporated under reduced pressure.

[15,27]-Dithiaheptacyclo[34.2.2.2^{3,6}.2^{17,20}.2^{22,25}.1^{9,13}.1^{29,33}] octatetraconta[3,5,9,11,13(46),17,19,22,24,29,31,33(41), 36,38,39,42,44,47]octadecaene (**29**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). Yield 0.43 g (22%), colourless solid, *m.p.* 137 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.89 (s, 8H, $ArCH_2CH_2Ar$), 3.30 (s, 4H, $ArCH_2S$), 3.47 (s, 4H, $ArCH_2S$), 3.56 (s, 2H, $ArCH_2Ar$), 3.94 (s, 2H, $ArCH_2Ar$), 6.74 (s, 2H, H_{ar}), 6.91 (s, 8H, H_{ar}), 7.03 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H_{ar}), 7.08 (d, $^3J_{HH}$ = 8.2 Hz, 6H, H_{ar}), 7.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.25 (pt, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 34.47, 35.21 ($ArCH_2CH_2Ar$), 36.87, 37.23 ($ArCH_2S$), 40.90, 41.14 ($ArCH_2Ar$), 126.50, 127.07, 128.63, 128.68, 129.00, 129.08, 129.18, 129.87 (C_{ar}), 135.92, 137.86, 138.79, 138.84, 139.78, 141.33 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 660 ($[M]^+$, 85), 465 (62), 433 (100), 329 (15), 226 (22), 194 (77), 179 (30), 119 (7), 105 (33). $C_{46}H_{44}S_2$ (660.97).

[15,28]-Dithiaheptacyclo[35.3.1.1^{2,6}.1^{9,13}.1^{17,21}.1^{22,26}.1^{30,34}] hexatetraconta[1(40),2,4,6(46), 9,11,13(45),17,19,21(44), 22,24,26(43)30,32,34(42),37,39]octadecaene (**30**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). – Yield 0.68 g (36%), colourless solid, *m.p.* 130–133 °C. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.92 (s, 8H, $ArCH_2CH_2Ar$), 3.41 (s, 4H, $ArCH_2S$), 3.52 (s, 4H, $ArCH_2S$), 6.93 (s, 2H, H_{ar}), 7.04 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.14 (pt, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 7.18 (s, 2H, H_{ar}), 7.24 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.27–7.38 (m, 8H, H_{ar}), 7.41 (s, 2H, H_{ar}), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 34.80, 35.02 ($ArCH_2CH_2Ar$), 38.02, 38.07 ($ArCH_2S$) , 124.97, 125.73, 126.83, 127.27, 127.56, 127.65, 127.94, 128.28, 128.82, 128.89, 128.99, 129.82 (C_{ar}), 138.06, 138.92, 141.04, 141.28, 141.59, 142.03 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 632 ($[M]^+$, 100), 599 ($[M–HS]^+$, 9), 451 (32), 419 (38), 388 (27), 315

(10), 283 (8), 212 (20), 180 (30), 167 (19), 119 (13), 105 (30). $C_{44}H_{40}S_2$ (632.92).

[10,23]-Dithiaheptacyclo[30.3.1.2^{12,15}.2^{18,21}.1^{4,8}.1^{17,21}.1^{25,29}]dotetraconta[1(36),4,6,8(42),12,14,18,20,25,7,29(37),32,34,38,40]pentadecaene (**31**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). Yield 0.65 g (44%), colourless solid, *m.p.* 124 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.86 (s, 8H, $ArCH_2CH_2Ar$), 2.98 (s, 4H, $ArCH_2CH_2Ar$), 3.49 (s, 4H, $ArCH_2S$), 3.55 (s, 4H, $ArCH_2S$), 6.79 (s, 2H, H_{ar}), 6.89 (s, 1H, H_{ar}), 6.99 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H_{ar}), 7.03 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, H_{ar}), 7.09 (d, $^3J_{HH}$ = 7.9 Hz, 6H, H_{ar}), 7.23 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, H_{ar}), 7.28 (pt, $^3J_{HH}$ = 7.5 Hz, 3H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 34.95, 35.27 ($ArCH_2CH_2Ar$), 37.32 , 37.80 ($ArCH_2S$), 126.14, 126.56, 127.08, 128.46, 128.61, 128.86, 128.90, 128.97, 129.57 (C_{ar}), 135.44, 138.07, 139.90, 141.51 ($C_{q,ar}$) (two signals have the same δ). – MS (EI): *m/z* (%) = 584 ([M]$^+$, 32), 551 ([M–HS]$^+$, 19), 519 (66), 375 (28), 343 (46), 311 (29), 207 (19), 136 (27), 119 (20), 104 (100), 91 (25). $C_{40}H_{40}S_2$ (584.88).

18,20-Dimethyl-[15,23]-dithiahexacyclo[30.2.2.2^{3,6}.1^{9,13}.1^{17,21}.1^{25,29}]untetraconta[3,5,9,11,13(39),17,19,21(38),25,27,29(37),32,34,35,40]pentadecaene (**32**)

Purification of the residue by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). Yield 0.80 g (44%), colourless solid, *m.p.* 172–172 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.19 (s, 6H, CH_3), 2.93 (s, br, 8H, $ArCH_2CH_2Ar$), 3.29 (s, 4H, $ArCH_2S$), 3.37 (s, 4H, $ArCH_2S$), 3.73 (s, 2H, $ArCH_2Ar$), 6.58 (s, 2H, H_{ar}), 6.77 (s, 1H, H_{ar}), 6.87–6.99 (m, 9H, H_{ar}), 7.12 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_{ar}), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 7.28 (pt, $^3J_{HH}$ = 7.3 Hz, 2H, H_{ar}). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 18.64 (CH_3), 32.83, 35.79 ($ArCH_2S$), 37.64, 37.93 ($ArCH_2CH_2Ar$), 41.14 ($ArCH_2Ar$), 126.43, 127.17, 128.62, 128.71, 129.04, 130.66, 131.69, 132.75, 133.11 (C_{ar}), 135.81, 137.92 ($C_{q,ar}$), 138.90 (C_{ar}), 139.27, 141.24 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 598 ([M]$^+$, 44), 583 ([M–CH_3]$^+$, 3), 565 ([M–S]$^+$, 19), 533 ([M–2S]$^+$, 10), 465 (74), 433 (35), 400 (11), 193 (48), 178 (18), 163 (34), 133 (100), 119 (44), 105 (63), 91 (35). $C_{41}H_{42}S_2$ (598.90).

Photochemical Sulfur Extrusion

17,19-Dimethyl-hexacyclo[28.2.2.2^{3,6}.1^{9,13}.1^{16,20}.1^{23,27}]nonatriconta[3,5,9,11,13(37),16,18,20(36),23,25,27(35),30,32,33,38]pentadecaene (**6**)

Under inertgas atmosphere the dithiacycle **32** (299 mg, 0.5 mmol) is dissolved in trimethylphosphite (350 mL) and irradiated by a high-pressure mercury arc lamp (150 W) for 20 h. Then the trimethylphosphite is removed under reduced pressure, and the residue is purified by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1). Yield 48 mg (18%), colourless solid, *m.p.* 143–145 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.24 (s, 6H, CH_3), 2.84 (s, 8H, $ArCH_2CH_2Ar$), 2.87–3.05 (m, 8H, $ArCH_2CH_2Ar$), 4.02 (s, 2H, $ArCH_2Ar$), 6.57 (s, 2H, H_{ar}), 6.89 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H_{ar}), 6.99 (s, 1H, H_{ar}), 7.05 (d, $^3J_{HH}$ = 7.6 Hz, 6H, H_{ar}), 7.12 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.13 (pt, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.41 (s, 1H, H_{ar}). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 34.99, 36.84, 37.17, 37.61 ($ArCH_2CH_2Ar$), 40.92 ($ArCH_2Ar$), 126.00, 126.30, 128.09, 128.69, 129.02, 129.85, 130.49, 132.17, 133.68 (C_{ar}), 137.28, 138.65, 139.06, 141.23, 141.35 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 534 ([M]$^+$, 60), 279 (17), 193 (18), 167 (41), 149 (100), 133 (60), 119 (20), 105 (25), 71 (28), 57 (39).

$C_{41}H_{42} \cdot 0.5H_2O$	Calcd.:	C 90.56	H 7.97
(534.77)	Found:	C 90.91	H 7.80.

Oxidation (General Procedure)

The dithiacycle (**29**–**31**, 0.3 mmol) is dissolved or suspended in benzene (1.5 mL) and glacial acetic acid (3.0 mL). 35% Hydrogen peroxide (1.0 mL) is added and heated to 60–80 °C for 6 h. Then water (5 mL) is added and the mixture stored at 4 °C overnight. The solid is filtered, washed with water several times, dried *in vacuo* and used without any further purification.

[15,27]-Tetraoxo-15,27-dithiaheptacyclo[34.2.2. 2^{3,6}.2^{17,20}.2^{22,25}.1^{9,13}.1^{29,33}]octatetraconta[3,5,9,11,13(46),17,19,22,24,29,31,33(41),36,38,39,42,44,47]octadecaene (**33**)

Yield 178 mg (82%), colourless solid, *m.p.* 288 °C. – ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ/ppm = 2.80–3.00 (m, 8H, $ArCH_2CH_2Ar$), 3.42 (s, 2H, $ArCH_2Ar$), 3.79 (s, 4H, $ArCH_2SO_2$), 3.93 (s, 2H, $ArCH_2Ar$), 4.32 (s, 4H, $ArCH_2SO_2$), 6.70 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 6.89 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H_{ar}), 7.02 (s, 2H, H_{ar}), 7.18 (d, $^3J_{HH}$ = 7.0 Hz, 2H, H_{ar}), 7.23 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H_{ar}), 7.26 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 7.30 (pt, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ/ppm = 35.33, 35.47 ($ArCH_2CH_2Ar$), 40.68 ($ArCH_2Ar$), 55.46, 58.36 ($ArCH_2SO_2$), 125.23 ($C_{q,ar}$), 128.31, 128.32, 128.61, 128.81, 128.87, 128.91 (C_{ar}), 131.27 ($C_{q,ar}$), 131.49 (C_{ar}), 138.02, 139.13, 141.44, 141.74 ($C_{q,ar}$). – MS (MALDI): *m/z* (%) = 763 ([M+K]$^+$, 8), 747 ([M+Na]$^+$, 100). $C_{46}H_{44}S_2O_4$ (724.97).

[15,28]-Tetraoxo-15,28-dithiaheptacyclo[35.3.1.1^{2,6}.1^{9,13}.1^{17,21}.1^{22,26}.1^{30,34}]hexatetraconta [1(40),2,4,6(46),9,11,13(45),17,19,21(44),22,24,26(43)30,32,34(42),37,39]octadecaene (**34**)

Yield 159 mg (76%), slightly yellow solid, *m.p.* 244 °C. – ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ/ppm = 2.89 (s, 8H, $ArCH_2CH_2Ar$), 4.48 (s, 4H, $ArCH_2SO_2$), 4.58 (s, 4H, $ArCH_2SO_2$), 7.25 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 7.29 (s, 2H, H_{ar}), 7.34 (pt, $^3J_{HH}$ = 7.4 Hz, 4H, H_{ar}), 7.36 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.42 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 7.52 (pt, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.59 (s, 2H, H_{ar}), 7.63 (s, 2H, H_{ar}), 7.70 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ/ppm = 37.24, 37.39 ($ArCH_2CH_2Ar$), 57.44, 57.91 ($ArCH_2SO_2$), 124.24, 126.74, 126.86, 127.39 (C_{ar}), 127.61 ($C_{q,ar}$), 128.48, 128.55, 128.81, 129.00 (C_{ar}), 129.03 ($C_{q,ar}$), 129.26, 129.51, 130.46, 131.22 (C_{ar}), 139.79, 140.15, 141.97, 142.20 ($C_{q,ar}$). – MS (FAB): *m/z* (%) = 735 ([M+K]$^+$, 1), 719 ([M+Na]$^+$, 3), 697 ([M+H]$^+$, 5), 569 ([M–2SO_2]$^+$, 2). $C_{44}H_{40}S_2O_4$ (696.92).

[10,23]-Tetraoxo-10,23-dithiaheptacyclo[30.3.1.2^{12,15}.2^{18,21}.1^{4,8}.1^{17,21}.1^{25,29}]dotetraconta[1(36),4,6,8(42),12,14,18,20,25,27,29(37),32,34,38,40]pentadecaene (**35**)

Yield 191 mg (98%), slightly yellow solid, *m.p.* 238–240 °C. – ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ/ppm = 2.73–2.87 (m, 8H, $ArCH_2CH_2Ar$), 3.00 (s, 4H, $ArCH_2CH_2Ar$), 4.17 (s, 4H, $ArCH_2SO_2$), 4.30 (s, 4H, $ArCH_2SO_2$), 6.89 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}), 7.05 (s, 2H, H_{ar}), 7.06 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H_{ar}), 7.07 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 7.13 (d, $^3J_{HH}$ = 8.4 Hz, 4H, H_{ar}), 7.20 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.23 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.30 (pt, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}), 7.37 (s, 1H, H_{ar}). – ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ/ppm = 35.26, 36.73, 36.80 ($ArCH_2CH_2Ar$), 56.62, 57.53 ($ArCH_2SO_2$), 125.45 ($C_{q,ar}$), 125.85, 127.90, 128.24 (C_{ar}), 128.33 ($C_{q,ar}$), 128.38, 128.50, 128.60, 128.76, 130.65, 130.81 (C_{ar}), 140.85, 140.97, 141.59 ($C_{q,ar}$). – MS (FAB): *m/z* (%) = 649 ([M+H]$^+$, 100), 520 ([M–2SO$_2$]$^+$, 38). $C_{40}H_{40}S_2O_4$ (648.88).

Pyrolysis (General Procedure) [17c]

The dithiatetroxide cycle **33**–**35** (0.1 mmol), placed at the bottom of a quartz tube (inside diameter 0.5cm), is sublimated at 250–350 °C and 5×10^{-5} mbar through a 600 °C pyrolysis zone. The product condenses at the glass wall behind the pyrolysis zone. The crude product is extracted with dichloromethane and purified by column chromatography (silica gel 60, cyclohexane/dichloromethane = 2/1).

Heptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene (**3**)

Yield 50 mg (84%), colourless product, *m.p.* 139–141°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.62–6.87 (m, 16H, $ArCH_2CH_2Ar$), 3.88 (s, 4H, $ArCH_2Ar$), 6.33 (s, 2H, H_{ar}), 6.87 (d, $^3J_{HH}$ = 8.2 Hz, 8H, H_{ar}), 7.01 (d, $^3J_{HH}$ = 8.2 Hz, 12H, H_{ar}), 7.21 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 37.50, 37.82 ($ArCH_2CH_2Ar$), 41.03 ($ArCH_2Ar$), 126.05, 128.24, 128.62, 128.85, 129.81 (C_{ar}), 138.61, 139.09, 141.05 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 596 ([M]$^+$, 100), 492 (5), 402 (9), 388 (4), 297 (8), 246 (10), 193 15), 179 (5), 105 (7).

$C_{46}H_{44} \cdot 0.5H_2O$	Calcd.:	C 91.19	H 7.48
(596.84)	Found:	C 91.84	H 7.37.

Heptacyclo[33.3.1.1^{2,6}.1^{9,13}.1^{16,20}.1^{21,25}.1^{28,32}]tetratetraconta[1(39),2,4,6(44),9,11,13(43),16,18,20(42),21,23,25(41),28,30,32(40),35,37]octadecaene (**4**)

Yield 27 mg (48%), colourless solid, *m.p.* 229 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.84–2.98 (s, br, 16H, $ArCH_2CH_2Ar$), 6.99 (s, 2H, H_{ar}), 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 4H, H_{ar}), 7.17 (d, $^3J_{HH}$ = 7.4 Hz, 4H, H_{ar}), 7.23 (s, 4H, H_{ar}), 7.28 (pt, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.34 (t, $^3J_{HH}$ = 7.5 Hz, 4H, H_{ar}), 7.41 (d, $^3J_{HH}$ = 7.63 Hz, 4H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 38.57, 38.73 ($ArCH_2CH_2Ar$), 124.66, 126.24, 127.40, 127.61, 128.51, 128.77, 129.38 (C_{ar}), 141.06, 141.72, 142.20 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 568 ([M]$^+$, 100), 463 (2), 387 (3), 283 (8), 269 (6), 179 (11), 165 (6), 119 (6), 105 (12), 56 (6).

$C_{44}H_{40} \cdot 0.5H_2O$	Calcd.:	C 91.46	H 7.15
(568.79)	Found	C 91.36	H 7.36.

Hexacyclo[28.3.1.2^{11,14}.2^{17,20}.1^{4,8}.1^{23,27}]nonatriconta[1(33),4,6,8(39),11,13,17,19,23,25,27(34),30,32,35,37]pentadecaene (**5**)

Yield 32 mg (61%), colourless solid, *m.p.* 147–149 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 2.58–2.66 (m, 4H, $ArCH_2CH_2Ar$), 2.68–2.77 (m, 4H, $ArCH_2CH_2Ar$), 2.87 (s, br, 8H, $ArCH_2CH_2Ar$), 2.89 (s, br, 4H, $ArCH_2CH_2Ar$), 6.26 (s, 2H, H_{ar}), 6.83 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H_{ar}), 7.00 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H_{ar}), 7.01 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H_{ar}), 7.04–7.13 (m, 5H, H_{ar}), 7.24 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H_{ar}), 7.25 (pt, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 37.14, 37.52, 37.64, 37.89, 38.61 ($ArCH_2CH_2Ar$), 125.38, 125.79, 126.14, 128.18, 128.21, 128.44, 128.83, 129.18, 129.90 (C_{ar}), 138.54, 139.17, 141.00, 141.91 ($C_{q,ar}$). – MS (EI): *m/z* (%) = 520 ([M]$^+$, 100), 415 (18), 311 (24), 207 (27), 119 (17), 105 (41), 91 (10).

$C_{40}H_{40}$	Calcd.:	C 92.26	H 7.74
(520.75)	Found	C 92.00	H 7.30.

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