From four-fold functionalised [3.3]cyclophanes to belt-shaped and multibridged molecules

Stefan Breidenbach,[a] Jörg Harren,[a] Susanne Neumann,[a] Martin Nieger,[b] Kari Rissanen[c] and Fritz Vögtle*,[a]

[a] *Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany*
[b] *Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany*
[c] *University of Jyväskylä, Department of Chemistry, FIN-40351 Jyväskylä, Finland*

Reaction of the four-fold functionalised cyclophane 7 with tetrafunctionalised aromatic building blocks such as 9 and 10 afforded the new belt-shaped molecules 3 and 4, respectively. The new four-fold bridged cyclophane 8 was synthesised by cyclisation of 7 with tosylamide monosodium salt. The macropolycycle 5, the structure of which has been confirmed by single crystal X-ray analysis, was obtained by cyclisation of the first tetrafunctionalised biphenylophane 15 with the tetrathiol 16. The constitution and conformation of compounds 3, 5 and 8 were examined by VT-NMR studies and HH-NOE experiments. Crystallisation of 8 from two different solvents leads to guest-dependent conformational changes revealed by X-ray analysis. The results described demonstrate that molecular belts and tubes of different type and size are accessible by varying the building blocks within our synthetic strategy.

In organic chemistry, routes to 'extraordinary' compounds have been sought for a long time. Therefore, molecular architectures, minimising common macroscopic structures and functions are an important field of interest in supramolecular chemistry.[1] Up to now many molecules or supramolecules have been designed, to carry out macroscopic functions and act for example as cages,[2] wires[3] or sensors.[4] It is valuable to examine such substances in order to understand the connection between macroscopic properties and microscopic structure.[5] Due to their unique molecular architecture and their promising properties, tube- and belt-shaped molecules have also aroused considerable interest.[6] These macropolycyclic substances include a cavity built up by aromatic spacer units, which allows complexation of small guests by various types of interactions. As possible model substances for membrane pores,[6a,7] molecular tubes are interesting for biochemical studies. Moreover, the spherical arrangement of the possibly bent aromatic rings might lead to an enhanced understanding of aromaticity, π-π- and CH-π-interactions. Hypothetic macrocyclic condensed hydrocarbons like **1**[8] can be considered as an ultimate future aim in this area. Their synthesis could be achieved by extrusion of all heteroatoms out of a macrocyclic framework. In earlier work we have established a repetitive synthetic strategy leading from tetrafunctionalised two- or multi-layered [3.3]metacyclophanes to tube-shaped molecules like **2**.[9]

In this contribution we report on new small belt-shaped molecules **3** and **4** having heteroatom-free cyclophane subunits in their framework. Extended tube-lengths compared to all belt-shaped molecules synthesised so far were achieved from the macropolycycle **5**. Additionally, a remarkable complexation of toluene by the tosyl groups of cyclophane **8** in analogy to further observations offers an interesting side aspect of this substance class as model substances for the investigation of CH-π-interactions.

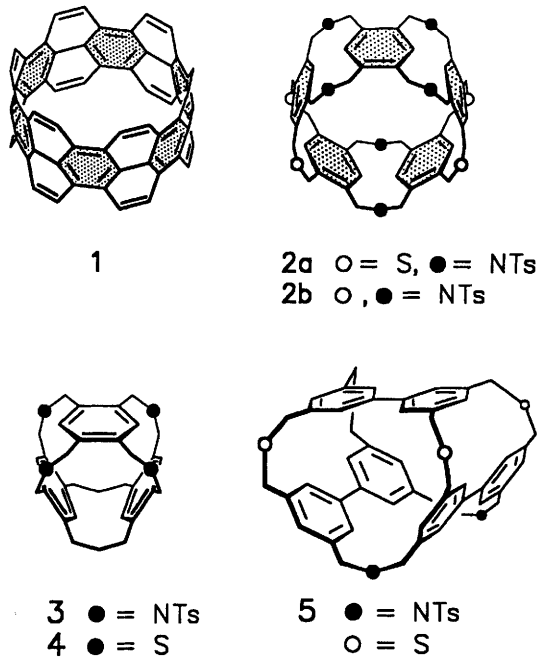


Fig. 1 Belt-shaped molecules

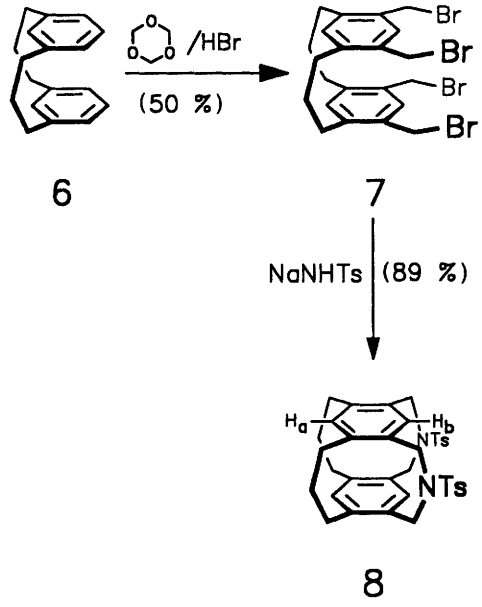
1. Four-fold bridged cyclophane 8

The synthesis of the key cyclisation precursor, the four-fold functionalised [3.3]metacyclophane **7** was improved by a three-step procedure.[10] The introduction of four bromomethyl functions into the non-substituted [3.3]metacyclophane **6** was carried out under comparatively mild phase-transfer conditions[11] and supplied 5,7,14,16-tetrakis(bromomethyl)[3.3]-metacyclophane **7** in 50% yield.

The single-crystal X-ray structure of **7** as well as the ^{1}H NMR data exhibit the typical *syn*-conformation of the cyclophane although the molecule is substituted with four bromomethyl groups.[12] The conformation of the propylene bridges is chair-chair. Two of the bromomethyl groups project into the niche of the cyclophane, which may be caused by crystal packing effects. Furthermore, there are intermolecular bromine–bromine interactions (distance: 384–414 pm) leading to a zig-zag-arrangement of the cyclophanes in the crystal structure.

The functionalised cyclophane **7** can be used for the

preparation of new belt-shaped compounds and multilayered [3.3]metacyclophanes. Furthermore, intramolecular ring closure reactions lead to fourfold bridged cyclophanes.[10] Reaction of **7** with toluene-4-sulfonamide monosodium salt afforded the diaza[3.3.3.3](1,2,4,5)cyclophane **8** in analogy to our earlier observations in a remarkably high yield (89%, Scheme 1).[13]



Scheme 1 Synthesis of the four-fold bridged molecule **8**

The ^{1}H NMR spectrum of **8** shows a simple pattern of the arene protons and multiplets for the propylene bridges. The protons of the two aza bridges indicate the staple character of the molecule (AB system centred at δ 3.53, 5.03). NOE experiments at 20 °C revealed the most stable conformation of the propylene bridges to be boat-boat.[12a]

Dynamic ^{1}H NMR spectroscopy at low temperatures showed only a broadening of the H_a proton signal (see Scheme 1). A rapid conformational motion of the propylene bridges even at low temperatures is most probable, whereas the H_b signal is sharp down to −80 °C. Crystals of **8** for a single-crystal X-ray structure determination could be obtained by crystallisation from trichloromethane and from toluene. Structure **8a** contains one molecule of trichloromethane per host molecule forming a hydrogen bond to a sulfonyl group (distance: H–O: 237 pm, C–O: 323 pm, angle O–H–C: 169°, Fig. 3). Another weak interaction is observed between the tosyl group forming the *H-bond* and a second tosyl group of an adjacent molecule **8**. The conformation of the propylene bridges is boat-boat, as well as the nitrogen-containing bridge which forms the hydrogen bond, whereas the second aza bridge is chair-shaped with a tosyl group being arranged orthogonally to the cyclophane skeleton. Crystals obtained from a toluene solution (**8b**) enclose two solvent molecules per host molecule (Fig. 4). One toluene molecule is bound in a similar way as reported in a previous paper dealing with a clathrate of a three-layered cyclophane.[13] The toluene molecule seems to be additionally fixed by CH-π-interaction: The toluene acts as a two-fold π-acceptor (CH-acid) and the tosyl groups, complexing the guest like tweezers, constitute the corresponding π-donors. The distances of this edge-to-face arrangement are 296 and 329 pm, respectively (distance of the toluene-hydrogen to the tosyl ring centre). The distance of the centres of interaction calculated for benzene dimers is 519 pm (ideal T-stacking; distance between the centre of one benzene ring to the nearest carbon atom of the next ring).[14] In our case the distances are very close to those calculated (529 and 533 pm). A second molecule of toluene is clathrated without evident additional binding. It is placed between two crystal layers and exhibits weak interactions to a

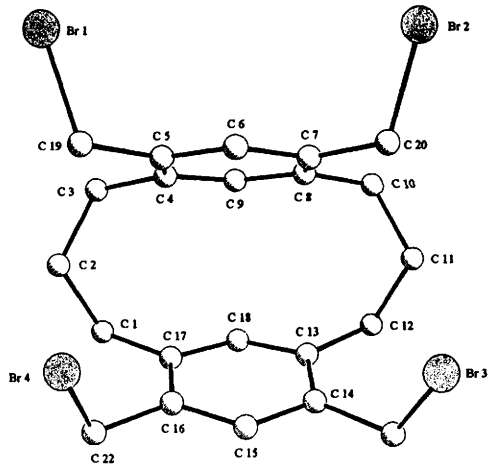


Fig. 2 X-Ray structure of **7**

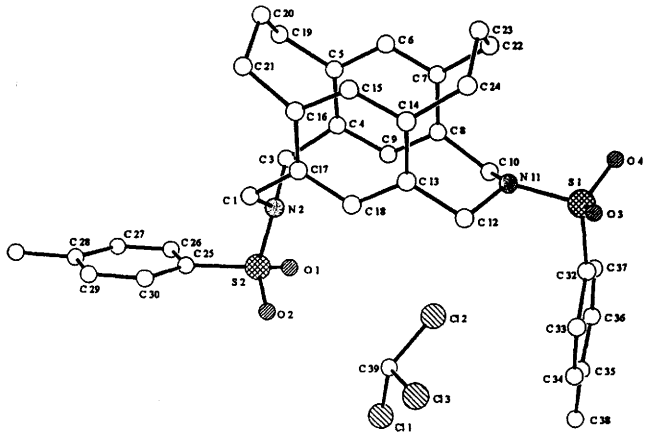


Fig. 3 X-Ray structure of **8a** containing trichloromethane

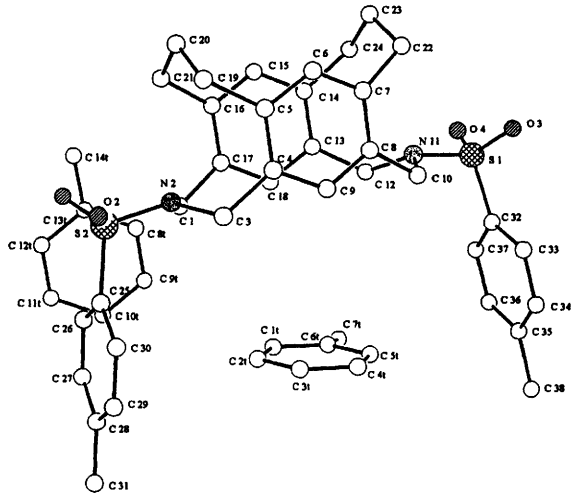


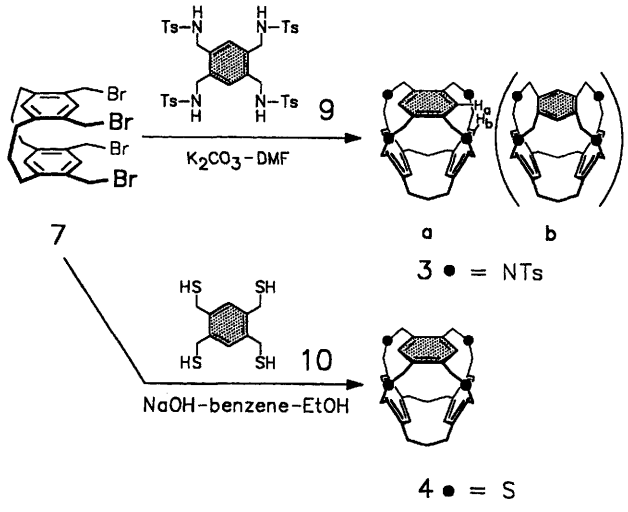
Fig. 4 X-Ray structure of **8b** containing toluene

cyclophane molecule of each layer. The only important conformational difference between trichloromethane and toluene containing crystals is the change in the geometry of one tosylaza bridge, which moves from boat to chair conformation with an accompanying symmetry change approximately from C_s in **8a** to C_{2v} in **8b**. Unlike the nearly identical host–guest arrangement we reported previously,[13a] we here encounter a guest-induced conformational change of supramolecular structure depending on varying weak host–guest interactions.[15]

2. Belt-shaped molecules 3 and 4 by four-fold bridging of 7

Cyclophane **7** is an ideal building block for the preparation of belt-shaped molecules. The single-crystal X-ray structure analysis and the NMR data display the typical *syn* conformation. So the reactive centres of tetrakis(bromomethyl)cyclophane **7** are all directed to the same side and favour a four-fold bond connection with appropriate reactants like **9** and **10**.[13,16]

Cyclisation of the cyclophane **7** with 1,2,4,5-tetrakis[(4-tolylsulfonylamino)methyl]benzene **9** in DMF and K_2CO_3 as base afforded the macropolycycle **3** in 23% yield. The 250 MHz ^{1}H NMR spectrum of **3** at room temperature shows the expected four AB systems for the azamethylene bridges (δ 3.22–5.24) and three broad signals for the propylene bridges (centred at δ 2.25, 2.95, 3.40). As expected, there are three singlets in the arene region for the aromatic protons situated on the belt skeleton [δ 7.39, 7.35 (H_a), 7.04 (H_b)]. The tosyl groups are spectroscopically different, indicated by two AB systems in the aromatic region and two signals for the tosylmethyl groups (δ 2.45, 2.51). At higher temperatures the spectrum is simplified with broadening of the signals. At 138 °C the azamethylene bridges show only one broad signal centred at δ 4.63 and the tosyl groups are equivalent (AB system at δ 7.49 and 7.88). For the determination of the exact constitution of belt molecule **3** a HH-NOE experiment at this temperature was necessary. The only NOE effect between the protons H_a and H_b revealed the constitution to be linear (**3a**, see Scheme 2). The possible crossed isomer **3b** has not been detected yet.

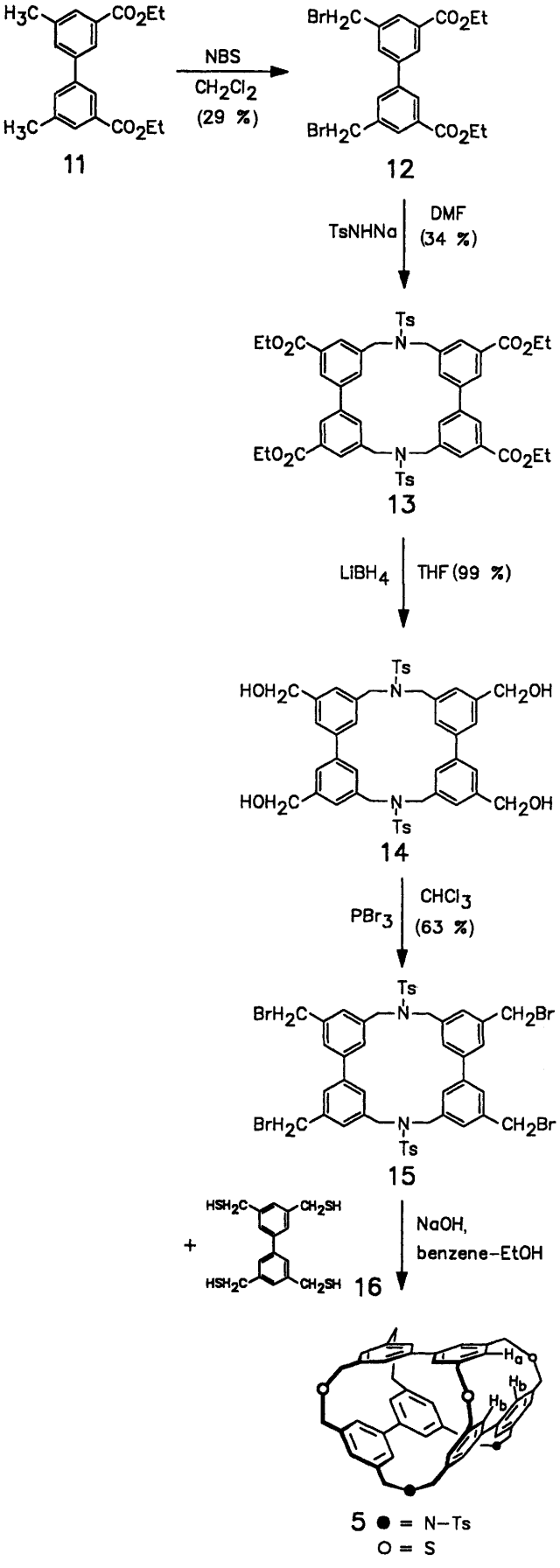


Scheme 2 New belt-shaped molecules **3** and **4**

Species with a hydrocarbon skeleton are an even greater challenge than the heterocyclic ribbon molecules. Various attempts to replace the tosyl groups in molecules like **3** and subsequent nitrogen extrusion by different methods have failed up to now,[17] probably due to steric hindrance. A second route to obtain hydrocarbon tubes or belts is cyclisation by means of sulfur bridges. Extrusion of sulfur by pyrolytic or photochemical methods is well established and should lead to the appropriate ring-contracted hydrocarbons.[18] Cyclisation of **7** and 1,2,4,5-tetrakis(mercaptomethyl)benzene **10** in benzene–ethanol and sodium hydroxide as base provided the desired thiamacropolycycle **4** in 7% yield. The high-resolution mass spectrum verifies the successful cyclisation. Unfortunately, the strained molecule **4** is insoluble in all common solvents, which prevented a complete NMR analysis. For the same reason, the following reactions turned out to be more difficult.[19]

3. Length-extended molecular tubes by cyclisation of biphenylophanes

An extension of the length of the belt skeleton can be achieved by cyclisation of suitable tetra-functionalised biphenyls: reaction of **12** with toluenesulfonamide monosodium salt leads to the diazabiphenylophane **13** in 34% yield (Scheme 3).



Scheme 3 Tube-shaped biphenylophane by two-component cyclisation strategy

Standard derivatisation afforded the tetrakis(bromomethyl) compound **15**. This biphenylophane was converted with tetrakis(mercaptomethyl)biphenyl **16** into the macropolycycle **5**. The crossed isomer of two possible reaction products formed solely. The molecular structure was confirmed by an HH-NOESY experiment at 50 °C (cross signals of the protons H_a and H_b, see Scheme 3) and single crystal X-ray structure determination.

The crystal-structure analysis of **5** reveals a T-shaped cavity (T-dimensions: height: 725 pm; width bottom: 386 pm; width top: 725 pm).[20] One trichloromethane molecule is placed outside the cavity and builds a three-centred hydrogen bond to one sulfonyl group [distances H–O(1): 268 pm; C–O(1): 359; H–O(2): 267 pm; C–O(2): 349 pm; H–O–C angles: 158°, 145°, resp.]. In the solid state the two tosyl groups are placed in the same tweezer formation as in **8b** with both aromatic rings in a face-to-face conformation and the aza bridges forming a chair-chair arrangement. Complexation experiments with suitable guests (*e.g.* naphthalene) are topic of current research.

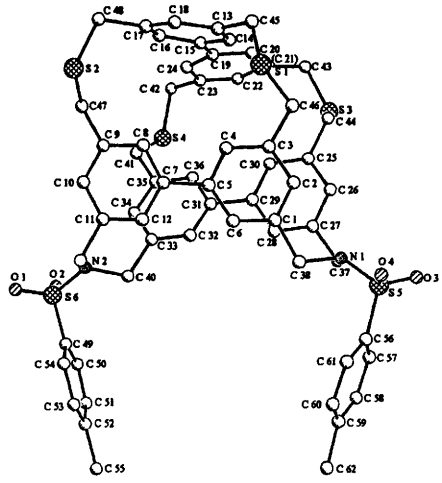


Fig. 5 X-Ray structure of **5**

4. Conclusions

In this paper the syntheses of new belt- and tube-shaped molecules (**3**, **4** and **5**) are described. Our strategy for the preparation of molecular belts from [3.3]cyclophanes makes use of various tetrafunctionalised building blocks. The now extended syntheses lead to macropolycycles in which the aza/thia-bridges are partly replaced by propylene bridges as a further step on the way to tube-shaped hydrocarbons. Successful cyclisation of new biphenylophane building blocks to extended tubes emphasises the variability of this synthetic concept.

Experimental

Solvents were purified by standard methods and dried if necessary. Reagents were used in commercial quality. Column chromatography: silica gel 60 (40–63 μm, Merck). Thin layer chromatography: silica gel 60 F 254 (Merck). Melting points were determined on a Kofler Mikroskop Heiztisch, Reichert and are not corrected. Microanalyses: Mikroanalytische Abteilung des Instituts für Organische Chemie der Universität Bonn. ^{1}H and ^{13}C NMR: WP 60 (60 MHz), WM 250 (^{1}H: 250 MHz, ^{13}C: 62.9 MHz) and AM 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz), Bruker Physik AG. The NMR signals were assigned by the aid of HH-COSY and DEPT 135 experiments when necessary. MS: MS 50, A.E.I. (EI, 70 eV) and Concept 1 H, Kratos Analytical Ltd. (FAB). *J* Values are recorded in Hz.

5,7,14,16-Tetrakis(bromomethyl)[3.3]metacyclophane 7

A mixture of [3.3]metacyclophane[10b] **6** (400 mg, 1.7 mmol), 1,3,5-trioxane (406 mg, 4.5 mmol), hydrobromic acid (48%; 10 ml) and tetradecyltrimethylammonium bromide (200 mg, 0.6 mmol) as phase-transfer catalyst was dissolved in glacial acetic acid (30 ml) and heated at 75 °C for 12 h. After cooling, the reaction was quenched by addition of saturated aqueous $NaHCO_3$. The neutral solution was extracted with dichloromethane (3 × 100 ml). Work-up followed by purification of the resulting light brown solid by column chromatography afforded tetrabromide 7 as a colourless powder (512 mg, 50%), R_F(silica gel; hexane–acetone = 15:1) = 0.29 [Found (HRMS, EI): *m/z* 605.8598. Calc. for $C_{22}H_{24}Br_4$: 605.8595]. The other analytical data are in agreement with the data reported by Shinmyozu *et al.*[10a]

2,11-Bis(4-tolylsulfonyl)-2,11-diaza[3.3.3.3](1,2,4,5)cyclophane 8

Toluene-4-sulfonamide monosodium salt (595 mg, 3.1 mmol) was suspended in dry DMF (15 ml) under an argon atmosphere and heated to 60 °C. A solution of the metacyclophane **7** (47 mg, 0.08 mmol) in dry DMF (50 ml) was added dropwise within 8 h. After continued stirring for 2 h at 60 °C the solvent was evaporated under reduced pressure. The residue was suspended in methanol to remove the unreacted toluene-4-sulfonamide monosodium salt. The resulting colourless solid was filtered off and washed with methanol and dried *in vacuo* (43 mg, 89%). R_F(silica gel; $CHCl_3$–methanol = 100:1) = 0.13, mp 189 °C; δ_H(250 MHz, CD_2Cl_2) 2.1–2.35 (m, 4 H, CH_2), 2.47 (s, 6 H, $ArCH_3$), 2.64 (dt, $^2J_{HH}$ 13.8, $^3J_{HH}$ 3.7, 4 H, CH_2-arene), 3.40 (dt, $^2J_{HH}$ 13.8, $^3J_{HH}$ 3.7, 4 H, CH_2-arene), 3.53 (d, $^2J_{HH}$ 22.4, 4 H, CH_2N), 5.03 (d, $^2J_{HH}$ 22.4, 4 H, CH_2N), 6.48 (s, 2 H, ArH, H_a), 7.05 (s, 2 H, ArH, H_b), 7.42 (d, $^3J_{HH}$ 8, 4 H, ArH) and 7.72 (d, $^3J_{HH}$ 8, 4 H, ArH); δ_C(62.89 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 29.7 (CH_2), 30.6 ($ArCH_2$), 53.0 (NCH_2), 127.5 (ArCH), 130.0 (ArCH), 130.7 (Cq), 133.5 (ArCH), 133.9 (Cq), 137.6 (ArCH), 141.0 (Cq) and 143.8 (Cq); *m/z* (FAB, matrix mNBA) (%) 627.2 (30) $[M + H]^+$ and 471.2 (10) $[M + H - Tos]^+$ (Found: C, 67.81; H, 6.27; N, 4.70. Calc. for $C_{36}H_{38}N_2O_4S_2 \cdot 0.5H_2O$: C, 68.00; H, 6.18; N, 4.40%).

2,11,20,29-Tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3]-(1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(4,6)benzeno⟨3⟩phane 3[21]

To a gas-free suspension of powdered potassium carbonate (180 mg, 1.31 mmol) in dry DMF (30 ml) solutions of 1,2,4,5-tetrakis[4-toluenesulfonylamino)methyl]benzene **9**[13a] (73 mg, 0.090 mmol) and 5,7,14,16-tetrakis(bromomethyl)[3.3]meta-cyclophane **7** (50 mg, 0.082 mmol), each dissolved in DMF (30 ml) were added dropwise and synchronously. After addition (10 h) the reaction was stirred for 24 h. The solvent was then evaporated *in vacuo*. The residue was dissolved in water–trichloromethane and after phase separation the organic layer was dried (Na_2SO_4). The remaining white solid was subjected to column chromatography on silica gel and yielded **3** (21 mg, 23%); R_F = 0.44 ($CHCl_3$–acetone = 40:1); mp > 300 °C; δ_H(250 MHz, $CDCl_3$) 2.25 (br, 4 H, CH_2), 2.45 (s, 6 H, $ArCH_3$), 2.51 (s, 6 H, $ArCH_3$), 2.95 (br, 4 H, $ArCH_2$), 3.22 (d, $^2J_{HH}$ 13.6, 2 H, CH_2N), 3.30 (d, $^2J_{HH}$ 13.3, 2 H, CH_2N), 3.4 (br, 4 H, $ArCH_2$), 3.77 (d, $^2J_{HH}$ 15.6, 2 H, CH_2N), 4.48 (d, $^2J_{HH}$ 17.2, 2 H, CH_2N), 4.74 (d, $^2J_{HH}$ 15.6, 2 H, CH_2N), 4.93 (d, $^2J_{HH}$ 13.6, 2 H, CH_2N), 5.10 (d, $^2J_{HH}$ 17.2, 2 H, CH_2N), 5.24 (d, $^2J_{HH}$ 13.3, 2 H, CH_2N), 7.04 (s, 2 H, ArH), 7.37–7.44 (m, 12 H, ArH) and 7.75–7.82 (m, 8 H, ArH); δ_C(62.89 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 29.5 (CH_2), 30.4 ($ArCH_2$), 51.1 ($ArCH_2N$), 51.5 ($ArCH_2N$), 55.5 ($ArCH_2N$), 57.0 ($ArCH_2N$), 126.8 (ArCH), 127.8 (ArCH), 128.7 (Cq), 130.1 (ArCH), 130.2 (ArCH), 135.4 (Cq), 135.7 (Cq), 136.6 (Cq), 137.1 (ArCH), 143.6 (Cq) and 144.4 (Cq); *m/z* (FAB, matrix mNBA) (%) 1095.4 (10) $[M + H]^+$ and 940.4 (15) $[M + H - Tos]^+$ (Found: C, 66.03; H, 5.92; N, 5.42. Calc. for $C_{60}H_{62}N_4O_8S_4$: C, 65.79, H, 5.70; N, 5.11%).

2,11,20,29-Tetrathia[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)-(4,6)benzeno⟨3⟩phane 4

A suspension of caesium carbonate (25 mg, 0.13 mmol) in benzene–ethanol (1:1; 1200 ml) was refluxed in a two-component dilution apparatus[22] under an argon atmosphere and oxygen-free conditions. Solutions of 5,7,14,16-tetrakis(bromomethyl)[3.3](1,3)metacyclophane **7** (394 mg, 0.65 mmol) in oxygen-free benzene (50 ml) (dilution-knee 1), sodium hydroxide (104 mg, 2.60 mmol) in degassed ethanol–water (95:5; 50 ml) and of 1,2,4,5-tetrakis(mercaptomethyl)-benzene **10** (171 mg, 0.65 mmol) in degassed benzene (50 ml) (both dilution-knee 2) were synchronously added dropwise within 10 h. After 3 h of additional reflux the solvents were evaporated under reduced pressure. The residue was heated to reflux with trichloromethane (200 ml) and filtered over silica gel. The filtrate was concentrated and subjected to column chromatography to yield **4** (25 mg, 7%), R_F = 0.22 $CHCl_3$–light petroleum = 3:1); mp 270 °C. The resulting colourless solid was insoluble in all common solvents and, therefore, an NMR analysis was not possible; *m/z* (EI) (%) 546 (36) $[M]^+$, 514 (10) $[M - S]^+$ and 482 (5) $[M - 2S]^+$ [Found (HRMS, EI): *m/z* 546.1544. Calc. for $C_{32}H_{34}S_4$ 546.1544].

Diethyl 5,5′-bis(bromomethyl)biphenyl-3,3′-dicarboxylate 12

Diethyl 5,5′-dimethylbiphenyl-3,3′-dicarboxylate **11** (1.14 g, 3.49 mmol), NBS (0.62 g, 3.50 mmol) and a catalytic amount of AIBN were dissolved in dichloromethane (50 ml) and illuminated by a 200 W lamp. After 2 h under reflux, a second portion of NBS (0.62 g, 3.5 mmol) was added and the reaction mixture was illuminated for an additional 2 h. After cooling, the crude solution was washed with aq. $NaHCO_3$ and water, dried and evaporated. The remaining solid was subjected to column chromatography on silica gel to yield **12** (0.48 g, 29%) as colourless crystals; R_F = 0.17 (cyclohexane–ethyl acetate = 25:1); mp 165 °C; δ_H(60 MHz, $CDCl_3$) 1.3 (t, $^3J_{HH}$ 7.0, 6 H, CH_3), 4.33 (q, $^3J_{HH}$ 7.0, 4 H, OCH_2), 4.46 (s, 4 H, CH_2Br), 7.73 (s, 2 H, ArH), 8.03 (s, 2 H, ArH) and 8.16 (s, 2 H, ArH); δ_C(62.89 MHz, $CDCl_3$) 14.46 (CH_3), 32.33 (OCH_2), 61.57 (CH_2Br), 128.34 (ArCH), 129.58 (ArCH), 132.02 (Cq), 132.10 (ArCH), 139.11 (Cq), 140.68 (Cq) and 165.89 (CO); *m/z* (EI) 484 (100%) $[M]^+$ [Found (HRMS, EI): *m/z* 481.9731. Calc. for $C_{20}H_{20}Br_2O_4$: 481.9729].

6,12,21,27-Tetrakis(ethoxycarbonyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza[3.3](3,3′)(3,3′)biphenylophane 13

To a gas-free suspension of toluene-4-sulfonamide monosodium salt (1.15 g, 6.0 mmol) in dry DMF was added within 1 h a solution of the ester **12** (2.91 g, 6.0 mmol), dissolved in DMF–dichloromethane (2:3; 50 ml) under argon at 80 °C. After 1 h, additional toluene-4-sulfonamide monosodium salt (1.15 g, 6.0 mmol) was added to the reaction mixture which was then heated for a further 4 h before evaporation *in vacuo*. The residue was dissolved in dichloromethane and the solution washed with water and dried ($MgSO_4$). The oily residue was recrystallised from ethyl acetate to give **13** (1.05 g) as a colourless powder (35%); R_F = 0.06 (silica gel, $CHCl_3$–acetone = 100:1); mp 253 °C; δ_H(250 MHz, $CDCl_3$) 1.40 (t, $^3J_{HH}$ 7.4, 12 H, CH_3), 2.48 (s, 6 H, Ts-CH_3), 4.35 (q, $^3J_{HH}$ 7.4, 8 H, CH_2O), 4.36 (s, 8 H, CH_2N), 7.31 (s, 4 H, ArH), 7.43 (d, $^3J_{HH}$ 8.1, 4 H, ArH), 7.64 (s, 4 H, ArH), 7.76 (s, 4 H, ArH) and 7.84 (d, $^3J_{HH}$ 8.1, 4 H, ArH); δ_C(62.89 MHz, $CDCl_3$) 14.41 (CH_3), 21.69 (Ts-CH_3), 53.78 (OCH_2), 61.27 (NCH_2), 127.46 (TsArCH, ArCH), 129.09 (ArCH), 130.23 (ArCH), 131.19 (Cq), 131.95 (ArCH), 135.57 (Cq), 136.92 (Cq), 139.72 (Cq), 144.14 (Cq) and 165.71 (CO); *m/z* (FAB, matrix mNBA) 987.3 (35%) $[M]^+$, 941.3 (100) $[M - C_2H_5O]^+$ (Found: C, 65.89; H, 5.55; N, 3.06. Calc. for $C_{54}H_{54}N_2O_{12}S_2$: C, 65.70; H, 5.51; N, 2.84%).

6,12,21,27-Tetrakis(bromomethyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza[3.3](3,3′)(3,3′)biphenylophane 15

To a suspension of lithium borohydride (1.16 g, 55.2 mmol) in abs. tetrahydrofuran (200 ml) under argon the biphenylophane **13** (2.29 g, 2.31 mmol) was added in one portion. The reaction mixture was stirred at room temp. for 1 h and then under reflux for a further 3 h. After cooling, the mixture was diluted with water (50 ml) and stirred for 1 h. It was then evaporated *in vacuo* to afford a colourless solid which was washed with water and dried. The resulting 6,12,21,27-tetrakis(hydroxymethyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza-[3.3](3,3′)(3,3′)biphenylophane **14** (1.87 g, 99%) was used for the next reaction without further purification. To a stirred solution of **14** (1.87 g, 2.28 mmol) in trichloromethane (200 ml) phosphorus tribromide (8.10 g, 30 mmol) was added under an argon atmosphere. The solution was heated under reflux for 4 h to provide a yellow precipitate. After cooling, the reaction mixture was poured into ice–water. The organic layer was separated, washed with aq. $NaHCO_3$ and water, dried ($MgSO_4$) and evaporated. The resulting colourless solid was purified by heating with dichloromethane (15 ml) and subsequent filtration to give **15** (1.5 g, 63%); R_F(silica gel, $CHCl_3$) = 0.19; mp 275 °C; δ_H(400 MHz, [$^2H_6$]DMSO) 2.45 (s, 6 H, CH_3), 4.29 (s, 8 H, CH_2N), 4.58 (s, 8 H, CH_2Br), 7.06 (s, 4 H, ArH), 7.13 (s, 4 H, ArH), 7.21 (s, 4 H, ArH), 7.51 (d, $^3J_{HH}$ 8.1, 4 H, Ts-ArH) and 7.88 (d, $^3J_{HH}$ 8.1, 4 H, Ts-ArH); δ_C(100 MHz, [$^2H_6$]-DMSO) 21.03 (CH_3), 34.12 (CH_2Br), 52.54 (CH_2N), 126.35 (ArCH), 127.16 (ArCH), 127.64 (ArCH), 128.43 (ArCH), 130.10 (ArCH), 135.68 (Cq), 137.28 (Cq), 138.15 (Cq), 139.18 (Cq) and 143.56 (Cq); *m/z* (FAB, matrix mNBA) 1069.7 (25%) $[M]^+$.

2,17-Bis(4-tolylsulfonyl)-2,17-diaza-32,47,50,53-tetrathia[3.3]-(3,3′)(3,3′)[3.3](5,5′)(3,5)[3.3](3′,5′)(5,5′)biphenylo⟨3⟩phane 5

A mixture of ethanol and benzene (1:1; 1000 ml) was heated to reflux under an argon atmosphere and oxygen-free conditions in a two-component-dilution apparatus. Solutions of the biphenylophane **15** (1.06 g, 1 mmol) in DMF (200 ml) (dilution-knee 1), 3,3′,5,5′-tetrakis(mercaptomethyl)biphenyl **16**[23] (0.33 g, 1 mmol) in DMF (200 ml) and sodium hydroxide (0.16 mg, 4 mmol) in ethanol–water (95:5; 100 ml) (both dilution-knee 2) were synchronously added dropwise within 9 h. After an additional 4 h of reflux the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (1000 ml), washed with brine and water (500 ml) and dried ($MgSO_4$). The organic solution was concentrated and subjected to column chromatography to **5** (15 mg, 1.4%); R_F = 0.18 (silica gel, $CHCl_3$–acetone = 150:1); mp > 300 °C; δ_H(250 MHz, CD_2Cl_2) 2.43 (s, 6 H, CH_3), 3.70 (d, $^2J_{HH}$ 14.8, 4 H, CH_2S), 3.74 (d, $^2J_{HH}$ 14.8, 4 H, CH_2S), 3.91 (d, $^2J_{HH}$ 15.4, 4 H, CH_2S), 3.94 (d, $^2J_{HH}$ 15.4, 4 H, CH_2S), 4.14 (d, $^2J_{HH}$ 14.1, 4 H, CH_2N), 4.25 (d, $^2J_{HH}$ 14.1, 4 H, CH_2N), 6.42 (s, 4 H, ArH, H_b), 6.83 (s, 4 H, ArH), 7.24 (s, 4 H, ArH), 7.33 (s, 4 H, ArH), 7.39 (d, $^3J_{HH}$ 8.1, 4 H, TsArH), 7.56 (s, 2 H, ArH, H_a) and 7.77 (d, $^3J_{HH}$ 8.1, 4 H, TsArH); δ_C(100.62 MHz, CD_2Cl_2) 21.55 (CH_3), 37.24 (CH_2S), 39.28 (CH_2S), 54.80 (CH_2N), 123.73 (ArCH), 124.06 (ArCH), 125.84 (ArCH), 127.43 (ArCH), 127.54 (ArCH), 128.52 (ArCH), 130.25 (ArCH), 135.77 (Cq), 136.51 (Cq), 137.38 (Cq), 138.20 (Cq), 139.92 (Cq), 142.32 (Cq) and 144.16 (Cq); *m/z* (+FAB, matrix mNBA) 1085.4 (100%) $[M + H]^+$. The purity of **5** was proved by HPLC (column: analytical Lichrosorb).

X-Ray analysis

Single-crystal X-ray structures of **5**, **7** and **8**: Crystals of **7** were obtained by slow diffusion of hexane into a trichloromethane solution of the cyclophane. The crystals of **8** were obtained by slow crystallisation from solutions of **8** in $CHCl_3$ (**8a**) and toluene (**8b**), respectively. Crystals of **5** were formed through slow crystallisation from a $CHCl_3$–tetrachloroethane solution. The determination of the lattice constants and reflex intensities

Table 1 Crystallographic data of the compounds **5**, **7**, **8a** and **8b**

Compound	**5**	**7**	**8a**	**8b**
Crystal parameters				
Empirical formula	$C_{62}H_{56}N_2O_4S_6 \cdot 2CHCl_3$	$C_{22}H_{24}Br_4$	$C_{36}H_{38}N_2O_4S_2 \cdot CHCl_3$	$C_{36}H_{38}N_2O_4S_2 \cdot 2$toluene
Formula weight	1324.3	608.1	746.2	811.1
Crystal colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.10 × 0.06 × 0.05	0.55 × 0.50 × 0.30	0.40 × 0.35 × 0.10	0.50 × 0.40 × 0.25
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	15.064(3)	11.477(3)	11.653(1)	11.928(3)
b (Å)	14.774(3)	14.629(5)	13.140(1)	13.018(2)
c (Å)	28.961(7)	15.239(5)	22.962(1)	15.814(3)
α (°)	90	115.98(2)	90	78.91(2)
β (°)	101.09(8)	91.68(3)	91.97(1)	70.69(2)
γ (°)	90	105.87(3)	90	68.06(2)
V (Å^3)	6325(1)	2179(1)	3513.9(4)	2142.9(8)
Z	4	4	4	2
ρ (calc.) [g cm^{-3}]	1.39	1.85	1.41	1.26
μ (mm^{-1})	4.75	7.39	3.82	0.17
F(000)	2744	1184	1560	864

were carried out by a Nicolet R3m-diffractometer (**7**, **8b**) and an Enraf-Nonius-CAD4-diffractometer (**8a**) with graphite-monochromator, respectively. The structures were solved by direct methods (SHELXTL-PLUS).[24] Non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-93).[24] The hydrogen atoms were located by difference electron density determination and refined using a riding-model. An empirical absorption correction on the basis of Ψ-scans were applied to **7** and **8a**.

The data of **5** were collected on a Rigaku R-AXIS IIC area detector using graphite monochromated Cu-Kλ_α-radiation produced by a Rigaku RU200HB rotating anode (50 kV, 180 mA) to a resolution of 1.17 Å ($2\theta_{max}$ = 82.62°, completeness of data 73.8%), crystal to detector distance 65.6 mm, detector two theta angle −25°, 36 frames, 10° oscillation. The area detector data were processed using RAXIS IIC software. No absorption correction was applied. The structure of **5** was solved by direct methods (SHELXS-86)[25] and subjected to partial full-matrix refinement on F (CRYSTALS).[25] The structure solution revealed disorder in one of the two sulfur bridges and in one of the trichloromethane solvents (treated as in two orientations with occupancy 0.5). The phenyl rings were restrained to their ideal value (1.39 Å and 120°) during the isotropic phase and refined as rigid groups in the final anisotropic refinement. Solvent molecules and sulfur bridges were restrained to chemical bond distances and angles. The hydrogen atoms were calculated to their idealised positions with fixed isotropic temperature factors (U = 0.10 Å^2), included in the final structure factor calculations but were not refined. The crystallographic data are listed in Table 1.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue No. 1. Any request to the CCDC for this data should quote the full literature citation and the reference number 207/35.

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