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MP2 and DFT Calculations on Circulenes and an Attempt to Prepare the Second Lowest Benzolog, [4]Circulene

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Dedicated to Professor Klaus Hafner on the occasion of his 80th birthday

Abstract: MP2 and DFT calculations have been carried out for [*n*]circulenes for $n=3$ to 20 in order to predict the strain energy and topology of these cyclically condensed aromatic systems. To synthesise [4]circulene (**2**), 1,5,7,8-tetrakis(bromomethyl)biphenylene (**14**) was prepared from the corresponding tetramethyl derivative (**8**) and subjected to various dehalogenation reactions; all attempts to obtain [2.2]biphenylenophane (**7**) as a precursor for **2** by this route failed. Treatment of **14** with sodium sulfide furnished the thiaphanes **16** and **17**, thermal and photochemical desulfurization of which also failed to provide **7**. In a second approach [2.2]paracyclophane was converted to the pseudo-geminal dithiol **23**, which was subsequently bridged to the thiaphanes **22** and **24**. On flash vacuum pyrolysis at 800 °C these were converted exclusively into phenanthrene (**30**). An approach to dehydrochlorinate the commercial product PARYLENE C® to the tetrahydro[4]-circulene **7** led only to polymerisation. The X-ray structures of the intermediates **8**, **14**, **17**, **23**, **24**, **26**, and **35** are reported.

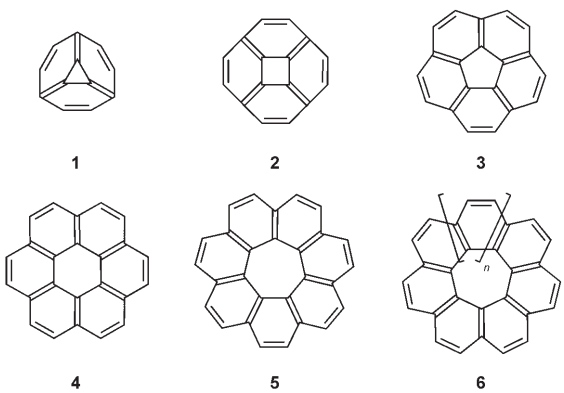
Keywords: circulenes · density functional calculations · pyrolysis · structure elucidation · thiols

Introduction

[*n*]Circulenes are cyclic aromatic compounds that can formally be derived from the alicyclic [*n*]radialenes[1,2] by connecting the termini of the semicyclic double bonds by etheno bridges. The simplest circulene is hence [3]circulene (**1**), the next higher benzolog is [4]circulene (**2**) and so on (Scheme 1).

From this homologous series of compounds only three have been prepared so far: [5]circulene (**3**, corannulene),[3–5] [6]circulene (**4**, coronene),[5–7] and [7]circulene (**5**, pleiadannulene).[5,8–10]

On proceeding from **3** to **5** the geometry of these hydrocarbons changes from a cuplike structure through a flat arrangement to a saddle-shaped geometry. Although various attempts to prepare the four-membered derivative **2** (see below) and a [7.7]circulene (in which ten contiguous benzene rings are fused around a central bicyclo[5.5.0]dodecane



Scheme 1. The lower members of the circulene family.

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core[11]) have been reported in the literature, the circulene family so far consists only of the above-mentioned three members. These are the hydrocarbons for which not only structural and computational work but also reactivity studies have been performed. This limitation is not really surprising in view of the formidable preparative problems that have to be solved to prepare either lower or higher benzologs of **3**–**5**; these involve overcoming severe problems of strain, the availability of suitable starting materials and the development of (novel) bridge-forming reactions. In order to initiate synthetic efforts in this area we have 1) carried out extensive calculations on the structures and energies of the circulene series and 2) worked on preparative routes towards [4]circulene. We report the first results of these studies in the present publication.

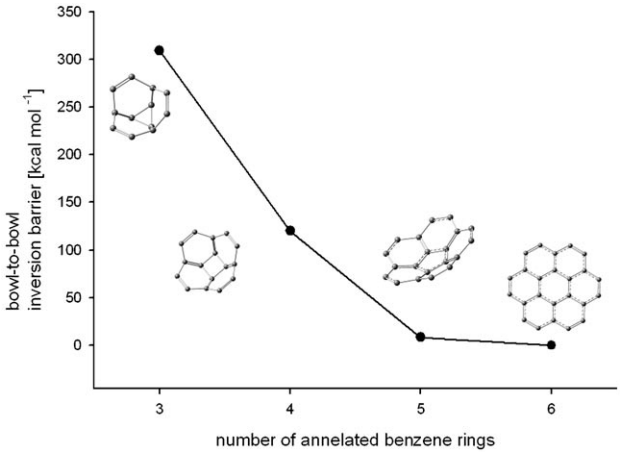


Figure 1. Calculated barrier for bowl-to-bowl inversion of the small circulenes **1**–**4** at the MP2/cc-pvtz level of theory.

Results and Discussion

Calculations on the [*n*]circulenes 1–4: In a first step we systematically studied the "smaller" circulenes **1**–**4** in order to get an impression of the amount of strain that has to be overcome during synthesis.

Starting with the known [6]circulene (**4**, coronene), using its planar structure within D_{6h} symmetry as a "strain-free" reference point, we performed energy minimizations including electron correlation at the MP2 level of theory[12] and a triple-zeta basis (cc-pvtz). We used the barrier for the bowl-to-bowl inversion for circulenes **1**–**3** as a first descriptor of the overall strain in each system.[13] Though this is only an indirect assessment, this procedure allows a comparison of the rigidity in the smaller circulene family members. While the barrier height in **3** rises moderately (8.6 kcal mol^{-1}) when leaving the plane, the next smaller circulene, our title compound [4]circulene (**2**), shows a barrier of 120.2 kcal mol^{-1}. Due to its extreme rigidity, the smallest family member [3]circulene (**1**) exhibits a huge energy barrier for the inversion of 309.2 kcal mol^{-1}. Figure 1 displays the results of these calculations in graphical form.

Calculations on the higher [*n*]circulenes: In a second step, we additionally performed DFT calculations using the B3LYP hybrid functional[14] for the series of the higher circulenes from [7]circulene (**5**) up to [20]circulene (**6**, $n=14$). While selected higher circulenes have been studied theoretically before (for example the [8]circulene (**6**, $n=2$),[15] to the best of our knowledge this is the first systematic calculation on higher circulenes. Figure 2 shows the optimised structures of all circulenes studied: from [3]circulene (**1**) to [20]circulene (**6**, $n=14$).

According to our calculations, one can distinguish between three types of non-planar circulene topographies:

1) Bowl topography: [3]circulene (**1**) to [5]circulene (**3**).
2) Saddle topography: [7]circulene (**5**) to [16]circulene (**6**, $n=10$).
3) Helical topography: [17]circulene ($n=11$) and higher.

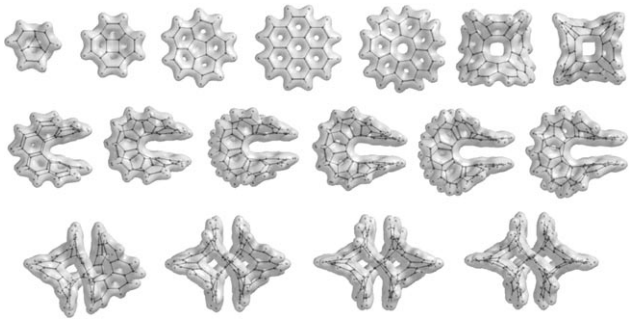


Figure 2. From [3]circulene (**1**) to [20]circulene (**6**, $n=14$): Calculated structures at the B3LYP/6–31G(d) level of theory.

As mentioned above, the bowl-to-bowl barrier is only a rough measure for the overall strain in circulenes. Furthermore, it is not possible to include the higher circulenes exhibiting a saddle or helical topography in such a comparison. We therefore used the calculated total energy for the $-[C_4H_2]-$ increment (153.64964 hartree at the B3LYP/dz level of theory), obtained for [6]circulene as a strain-free reference increment. Figure 3 shows the results. Starting from coronene (**4**) and proceeding to the larger members of the circulene family, the strain rises quickly up to $\approx$17 kcal mol^{-1} for [9]circulene (**6**, $n=3$). After this sharp increase, practically no additional strain (well below 20 kcal mol^{-1}) is added for the circulenes from [9]- up to about [14]circulene. The saddle topography is able to accommodate each additional $-[C_4H_2]-$ increment, as the two wings of the saddle for example (Figure 2, middle row) come increasingly closer. Beginning with [16]circulene (**6**, $n=10$) the strain rises again, because the two wings of the saddle come very close (2.81 Å), which forces the higher circulenes to adopt a kind of twisted saddle or helical (C_2 symmetric) topography (see Figure 4). Again, this new topography is able to include more and more increments without too much additional strain ($\approx$30 kcal mol^{-1}).

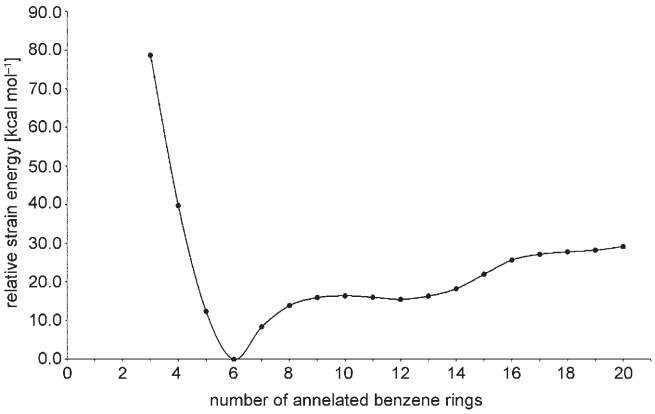


Figure 3. Calculated strain energies (relative to coronene, **4**) for [3]circulene (**1**) to [20]circulene (**6**, $n=14$) at the B3LYP/6–31G(d) level of theory.

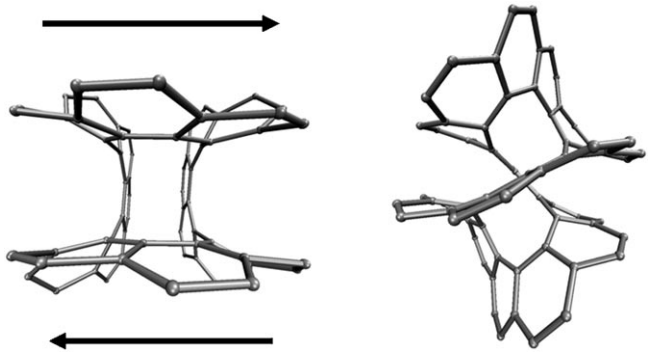
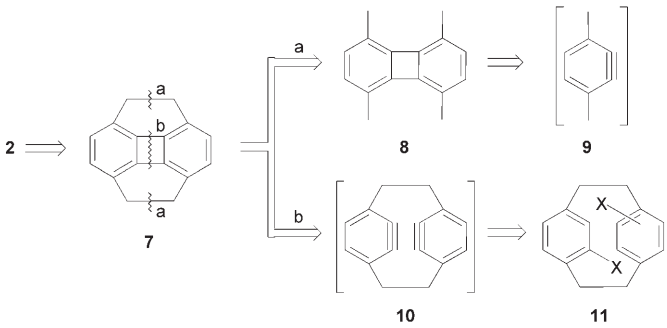


Figure 4. The higher circulenes: Transition from saddle to helical topology.

Though the increase of the strain is more pronounced for the smaller circulenes, namely, ≈10, ≈40 and ≈80 kcal mol^{-1} for [5]circulene (**3**), [4]circulene (**2**) and [3]circulene (**1**), respectively, the route to **2** does not seem to be so steep as to make an approach hopeless from the very beginning. We therefore decided to embark on an attempt to synthesise this lower benzolog of corannulene.

Attempts to prepare [4]circulene (2): Two simple retrosynthetic routes leading to readily available substrates for the preparation of **2** are summarised in Scheme 2.

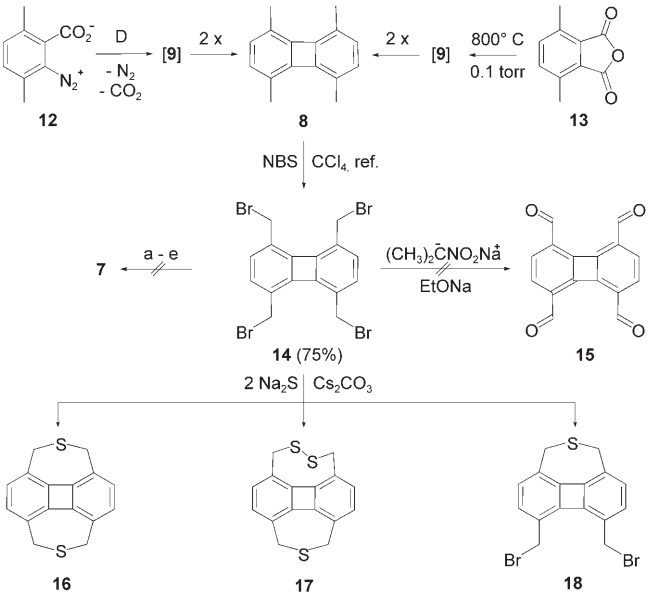
The formal hydrogenation of two opposing "etheno bridges" of **2** results in the doubly-bridged biphenylene derivative **7** ([2.2]biphenylenophane), which may be further degraded by two different routes. If the saturated bridges are disconnected (route a) 1,5,7,8-tetramethylbiphenylene (**8**) results, for which the dehydro-*p*-xylene **9** could be a suitable precursor. Bridge formation from **8** to **7** could be accomplished by methods such as Wurtz coupling, sulfone pyrolysis, decarbonylation or any of the numerous protocols that have been developed and optimised in cyclophane chemistry[16] starting with appropriately functionalised derivatives of **8**. These precursors, and those for **9**, should be available by standard preparative transformations.



Scheme 2. Retrosynthetic analysis for the preparation of [4]circulene (**2**).

If, on the other hand, the saturated bridges are left intact and the central four-membered ring of **7** is cleaved, as depicted in route b, the bis dehydrobenzene **10** would be generated. This is a double "cyclophyne"[17] for which either a pseudo-geminal or pseudo-*ortho* disubstituted cyclophane **11** could serve as precursors; both substitution types are known.[18]

Synthetic efforts starting from tetramethylbiphenylene (8; route a): The reaction sequence depicted in Scheme 3 has been studied independently by three groups (Hopf/Christoph; Maier/Scholtissek; Vögtle/Saitmacher) and is predominantly described in various PhD theses.[19–22] In the first two laboratories the goal was specifically set on the elaboration of strategies to synthesise [4]circulene (**2**). From the very beginning, the attention paid to this molecule originated from the assumption that this species might shed some light on



Scheme 3. Transformations in the biphenylene series. a) −78 °C, $TiCl_4$/Zn, THF; b) −78 °C, $TiCl_4$/$LiAlH_4$, THF; c) 0 °C, $Me_3SiSnBu_3$, CsF, DMF; d) 80 °C, Na, benzene; e) 600–1000 °C, 0.1 torr.

the cyclobutadiene problem.[22] Nowadays the interest is mainly focused on the question of how molecular strain influences the peculiar structural features of **2**, and whether the theoretical predictions (see above) can be confirmed by experiment.

Direct coupling: A very simple way of transforming tetramethylbiphenylene (**8**) into [4]circulene (**2**) via its tetrahydro derivative **7** as an intermediate would be halogen elimination from tetrabromide **14**.

The diazonium dicarboxylate **12** was prepared from 3,5-dimethyl anthranilic acid[23] according to a modified procedure (see Experimental Section) by Wilcox and Farley;[24] its thermal decomposition in boiling 1,2-dichloroethane subsequently provided **8** in an acceptable 21% yield, the dehydrobenzene **9** presumably being formed en route. Alternatively, **8** was prepared by flash vacuum pyrolysis of the readily available[25] 3,6-dimethylphthalic anhydride (**13**). However, with an approximate 11% yield, this procedure, which probably also proceeds via **9**,[26] cannot compete with the route starting from **12**. Although the spectroscopic data of **8** have been reported several times,[19–21] its X-ray structural analysis, which gives insight into the critical distance between the carbon atoms of the methyl substituents, was not available. Fortunately, single crystals of sufficient quality could be obtained by recrystallisation from methanol, and the crystal structure of **8** is shown in Figure 5 (top).

The molecule displays crystallographic inversion symmetry; its bond lengths in the six-membered ring alternate between shorter and longer (≈1.38 and 1.42 Å), whereby the bond fused to the four-membered ring belongs to the longer set, as was noted for the parent hydrocarbon, unsubstituted biphenylene.[27] The ring angles at C1 and C4, the carbon atoms bearing the methyl substituents, are very narrow (113.6° and 113.7°), whereas the other ring angles are all about 123°. The distance between the methyl carbon atoms, C9···C10#1, is 3.881(2) Å. The molecular packing (Figure 5, bottom) involves a herring-bone pattern in which neighbouring molecules are connected in the *y* direction by short C–H···π contacts (C9–H9A···Cg 2.60 Å, 160° and C10–C10A···Cg 2.61 Å, 154°; Cg = ring centroid; C–H bond lengths are normalised throughout to 1.08 Å).[28]

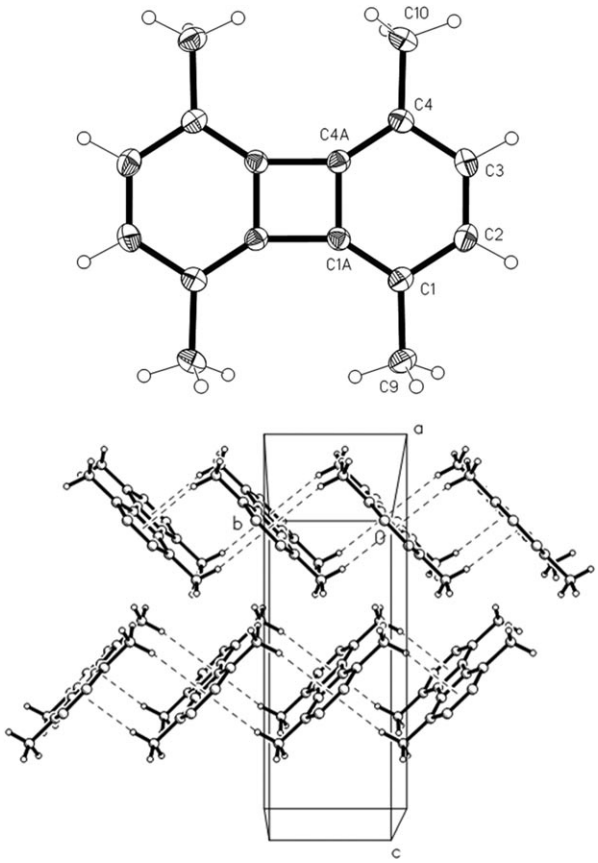


Figure 5. Top: The molecule of compound **8** in the crystal. Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered. Selected bond lengths (Å) and angles (°): C1–C1A 1.372(2), C1–C2 1.424(2), C2–C3 1.384(2), C3–C4 1.425(2), C4–C4A 1.375(2), C1A–C4A 1.424((2), C1A–C4A#1 1.523(2); C4-C4A-C1A#1 146.9(1), C1-C1A-C4A#1 146.4(1). Symmetry operator #1: $-x,1-y,1-z$. Bottom: packing diagram of compound **8**; dashed lines indicate C–H···π interactions.

Functionalisation of **8** was accomplished by slowly adding portions of *N*-bromosuccinimide to a solution of the hydrocarbon in carbon tetrachloride heated under reflux, again following a protocol of Wilcox and Farley.[24] 1,4,5,8-Tetrakis(bromomethyl)biphenylene (**14**) was obtained in a gratifying 75% yield and characterised by its spectroscopic data.[19–21] On standing in deuteriochloroform it crystallised in the form of lemon yellow plates that were suitable for X-ray structural analysis; the structural data are shown Figure 6.

Compound **14** crystallises with imposed 2*m* symmetry (Figure 6, top), so that the asymmetric unit is composed of a quarter molecule. Bond lengths alternate shorter/longer as for compound **8**, and the bond length pattern is also similar. The molecular packing is largely determined by Br···Br contacts; the independent bromine atom is involved in five such interactions, with Br···Br distances of 3.771(1) (×2; second atom at $x,-\frac{1}{2}+y,\frac{1}{2}-z$ and $x,\frac{1}{2}+y,\frac{1}{2}-z$), 3.8570(5) (×2; $\frac{1}{2}-x,-\frac{1}{2}+y,z$ and $\frac{1}{2}-x,\frac{1}{2}+y,z$) and 3.881(1) Å ($\frac{1}{2}-x,y,\frac{1}{2}-z$). All these contacts are slightly longer than double the van der Waals radius (3.70 Å), but the significant net effect is to form columns of bromine atoms parallel to the *y* axis (Figure 6, bottom). Within the columns, a contact C9–H9B···Br (not shown in Figure 6) with H···Br 2.92 Å, angle 162°, operator $x,-1+y,z$, presumably acts as an additional stabilising factor. A similar contact H9A···Br is observed intramolecularly, with dimensions 2.92 Å, 153°, operator $x,1-y,1-z$.

We subjected **14** to various dehalogenation reactions. As shown in Scheme 3, none of these was successful. In all cases (besides unreacted starting material) intractable product mixtures were produced and there was no indication, for example, by mass spectrometric or ^{1}H NMR analysis, that **7** had been produced. In addition, tetraiodide **15a**, prepared from **14** by Br/I exchange with potassium iodide in acetonitrile, was tested as a potential precursor for **7**, but again

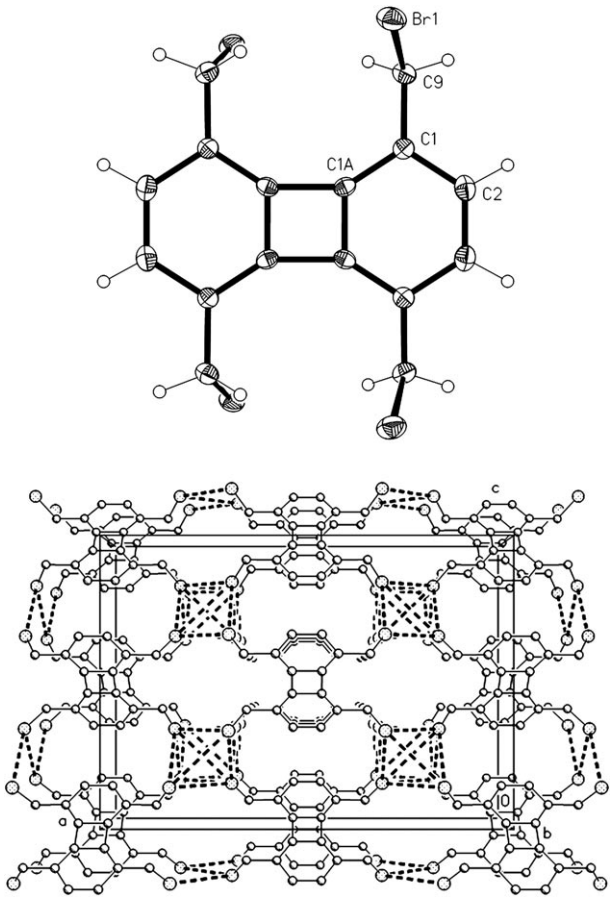


Figure 6. Top: The molecule of compound **14** in the crystal. Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered. Selected bond lengths (Å): C1A–C1A#1 1.417(5), C1–C1A 1.377(4), C1–C2 1.427(4), C2–C2#1 1.375(6), C1A–C1A#2 1.523(2). Symmetry operators #1: $1-x,y,z$ (mirror plane horizontal in the plane of the paper), #2 $x,1-y,1-z$ (twofold axis vertical in the plane of the paper). Bottom: packing diagram of compound **14**; dashed lines indicate Br···Br interactions. H atoms are omitted.

without success. The tetraiodide is stable at room temperature. However, on heating in substance to 250°C iodine was eliminated and a black solid (polymer) was formed. Definite products could not be detected. Due to the insolubility of **15a** in standard solvents photochemical iodine elimination was not possible. An attempt to convert **14** to the tetraaldehyde **15b** by treatment with 2-nitropropane/sodium ethoxide, a known and usually reliable method of converting bromomethyl into formyl groups,[29] also met with failure. On the other hand, derivative **15b** had been obtained in low yield, by converting **14** into the corresponding tetraacetate **15c**, its subsequent hydrolysis to the tetraalcohol **15d** (hydrolysis of **14** with methanol/water leads mainly to the tetraether **15e**), and pyridinium dichromate oxidation of the latter;[19] unfortunately, there was never enough material available to subject it to coupling processes such as the McMurry coupling.

Bridge formation with subsequent ring contraction: Since, evidently, the direct connection of the substituent carbon atoms in **14** and related compounds is not possible, we decided to employ an approach that has proved its worth countless times in cyclophane chemistry: the construction of phane precursors with longer bridges followed by ring contraction processes. The rationale behind this strategy is the step-wise build-up of strain, rather than one sudden step as would be required for **14**. One can expect that the doubly S-bridged biphenylene **16** would be an ideal candidate for the synthesis of the tetrahydro derivative **7**, and logically also for [4]circulene (**2**).

Treating **14** with sodium sulfide in the presence of caesium sulfate ("caesium effect")[30] in a mixture of toluene/ethanol heated to reflux and to which a small amount of water had been added, under high dilution conditions, yielded the dithiaphane **16** in 27% yield and the trisulfur derivative **17** in 6% yield, and none of the "mono-cyclised" product **18** was formed. On replacing the toluene by benzene, but keeping the other reaction conditions unchanged, the amount of **16** is greatly increased (51%), whereas the yield of **17** drops to a meager 2.6%. In a final experiment in toluene/ethanol, the amount of added water was tripled, causing a drastic reduction in the yield of **16** (9%) but a doubling of that of **17** to 14%; under these conditions traces of the mono-closed dibromide **18** were also isolated, as shown by mass spectrometric analysis. Although the interpretation of these trends is highly speculative,[22] they clearly show that the product distribution is strongly influenced by the cyclisation conditions and that there is room for optimisation. Dithiaphane **16** is an unstable compound that decomposes with sulfur extrusion on attempted recrystallisation. The derivative **17**, on the other hand, crystallised from deuteriochloroform on standing at room temperature in the form of colourless plates, which were suitable for X-ray structural analysis.

Compound **17** is shown in Figure 7. The bond length pattern in the six-membered rings is very similar to that in **8** and **14**, and the carbon skeleton is essentially planar (mean deviation 0.06 Å). The strain imposed by the sulfur link (S1) between C9 and C10, forming the seven-membered ring and reducing the distance between these atoms to 2.988(3) Å, can be recognised in terms of several altered molecular dimensions, as follows:

1) The six-membered rings are exactly parallel by symmetry in **8** and **14**, but the corresponding angle between vectors C1···C4 and C5···C8 in **17** is 7°.
2) The angles $C_{four}\cdots C\cdots C_{methyl}$ in **8**, in which C_{four} represents the relevant atom of the four-membered ring, are approximately 125°, but the corresponding angles in **17**, in the seven-membered ring, narrow greatly to around 118°.
3) The angles at the junction of the four- and six-membered rings alter appreciably. The necessarily wide exocyclic angles of ≈147° in **8** narrow to 141° in the seven-membered ring of **17** (but widen further to 150° in the eight-membered ring with its two sulfur atoms). The four angles of 123° in the six-membered rings of **8** widen still

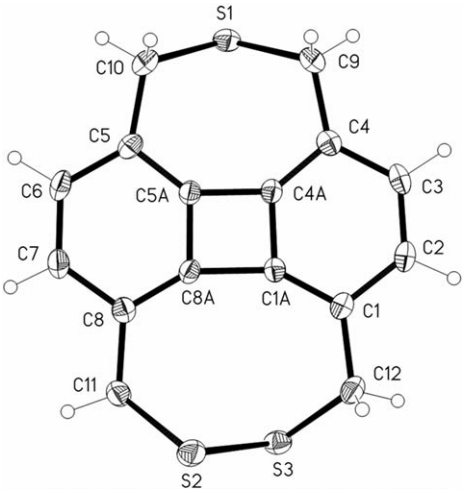
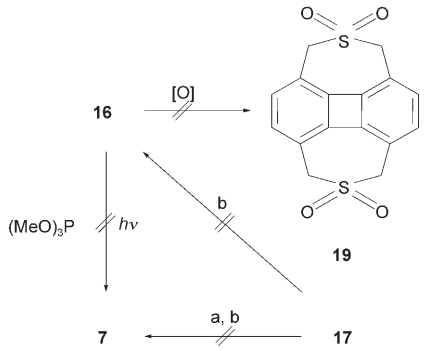


Figure 7. The molecule of compound **17** in the crystal. Ellipsoids represent 50% probability levels. Selected bond lengths (Å): S2–S3 2.052(1), C4A–C5A 1.469(3), C1A–C8A 1.534(3); for other averaged values see text.



Scheme 4. Failed attempts to convert the dithia[2.2]paracyclophane **16**. a) $(MeO)_3P$, $CDCl_3$, *hν*; b) $(Et_2N)_3P$, benzene, DT.

further to 128° in the seven-membered ring of **17** (C1A-C4A-C4 and C8A-C5A-C5), but narrow to 121° in the eight-membered rings (C1-C1A-C4A and C8-C8A-C5A).

4) The formally single bonds in the four-membered ring, equal by symmetry in **8** at 1.513 Å, differ appreciably in **17**, in which the bond common to the seven-membered ring shortens to 1.469 Å, whereas that common to the eight-membered ring lengthens to 1.534 Å.

The packing of compound **17** involves no markedly short contacts and is not presented here; a list of borderline C–H···S contacts is included in the supplementary crystallographic data (see below). There is also a sulfur contact S3···S3 (3.443(1) Å) with operator $1-x,1-y,-z$.

Since the sulfur bridges indeed brought the methylene carbon atoms in **16** and **17** closer together, we were eager to desulfurise these compounds either directly or via sulfone intermediates, the latter route being attractive since they can either be subjected to sulfone pyrolysis or ring contractions such as the Ramberg-Bäcklund process. Unfortunately, we were unable to oxidise **16** to the bissulfone **19**, although many different reactions and conditions that are usually successful in this transformation were tried (hydrogen peroxide in acetic acid, *m*-chloroperbenzoic acid in dichloromethane, Oxone in chloroform, etc.; Scheme 4); similar observations have been made by Saitmacher.[20]

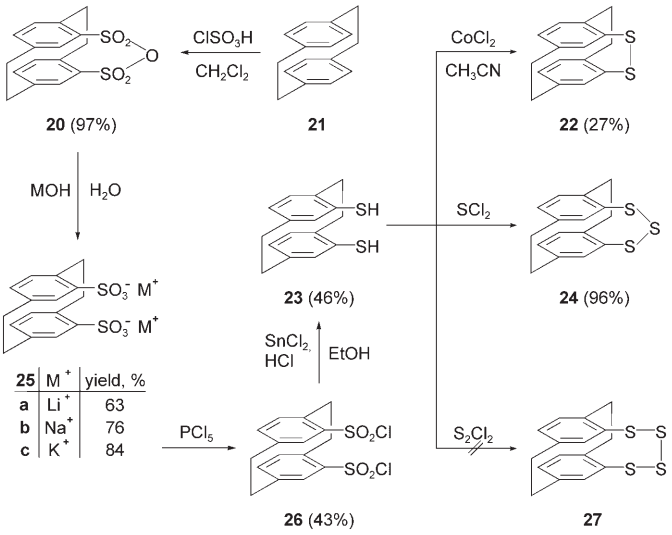
Sato and co-workers have successfully used photodesulfuration in the presence of trimethyl phosphite for the preparation of various sulfur-bridged biphenylenophane dimers and biphenylenonaphthalenophanes.[31] However, when applied to **16** and **17** (150 W medium pressure mercury lamp, trimethyl phosphite in deuteriochloroform, RT) only decomposition to indefinable products was observed (^{1}H NMR and GC/MS analysis). In another successful desulfurisation experiment, various thiaphanes were treated with tris(diethylamino)phosphane in benzene,[32] the method also having been used for the "shortening" of a disulfide to a thioether bridge. However, subjecting **16** and **17** to these conditions again gave only negative results, whereby not even the conversion of the latter to the former could be observed.

Last but not least, removal of the sulfur bridges in **17** and identification of the products by applying matrix isolation techniques was attempted.[33] A combination of flash pyrolysis at 800 °C with isolation of the products at 10 K and subsequent irradiation (254, 310 nm) led to unspecific decomposition of **17**. Only traces of CS_2 could be identified. Direct photochemical excitation of **17** in an argon matrix with different wavelengths (254, 366, and 385 nm) showed no effect.

Tetrabromide **14** was also the starting molecule in our search for additional variations in applying the bridging/ring contraction principle. For instance, one can envisage an entry to O-bridged systems (compounds of type **16**, in which S has been replaced by O) either by dehydration of tetraalcohol **15d** or by transformation of tetraacid **15f** into the corresponding cyclic bisanhydride. All attempts to eliminate water from **15d** failed. Similarly disappointing were the results with the tetraacid **15f**. In this case tetraalcohol **15d** was oxidised with potassium permanganate and the resulting reaction mixture treated with diazomethane. This procedure yielded tetraester **15g**, which could be easily purified by chromatography. Hydrolysis with KOH/H_2O gave tetraacid **15f**. Again, ring closure could not be achieved. Reaction of **15f** with thionyl chloride did not furnish the desired bis anhydride, but the tetra(acyl chloride) **15h**.

Dieckmann condensation of tetranitrile **15i** or tetraester **15j** was believed to be a reasonable procedure for the construction of CO-bridged analogues of disulfide **2**. Tetranitrile **15i** was isolated in low yield only, when tetrabromide **14** was treated with sodium cyanide. Tetraester **15j** has been prepared by reaction of **14** with $CO/Co_2(CO)_8$/TEBA in a two-phase system (benzene/aq. sodium hydroxide) and addition of diazomethane to the crude reaction product. Unfortunately **15j** showed no indication of any ring formation under the conditions normally applied for Dieckmann condensations.

Synthetic efforts starting from [2.2]paracyclophanes (route b): Because of all these failures we next turned our attention to the cyclophane route discussed in Scheme 1 (route b). To introduce the pseudo-geminal substitution pattern, [2.2]paracyclophane (**11**, X = H) was treated with chlorosulfonic acid according to the procedure of van Lindert et al. to provide [2.2]paracyclophane-4,15-disulfonic acid anhydride (**20**) in nearly quantitative yield (97%, Scheme 5).[34,35] Ring-opening of **20** with an aqueous base



Scheme 5. Preparation of different sulfur derivatives of [2.2]paracyclophane.

took place readily, with the yield of the transformation depending on the alkali counterion: whereas lithium hydroxide furnished **25a** in 63% yield, potassium hydroxide gave 84% of **25c**, with sodium hydroxide providing the intermediate **25b** in 76% yield. Treatment of **25c** with phosphorus pentachloride gave the pseudo-*gem*-disulfonyl chloride **26**, which was characterised by its spectroscopic data (see Experimental Section) and X-ray structural analysis (see below). The reduction of **23** with tin dichloride[36] in ethanol furnished the oxygen-sensitive dithiol **23**, which was also crystallised and investigated by X-ray structural analysis (see below).

Upon oxidation of **23** with anhydrous cobalt dichloride in acetonitrile,[37] the dithiaphane **22** is formed in low yield (27%, Scheme 5). Although this cyclophane, which is the second one with a two-atom bridge consisting of heteroatoms only (the first is the corresponding azo compound),[38] could be recrystallised from, for example, ethanol, the structure was disordered, preventing a reliable X-ray structural determination. An extension of this heteroorganic bridge is possible, as was revealed when **23** was treated with sulfur dichloride: the trithiaphane **24** was formed in near quantitative yield (96%), and this time recrystallisation (from cyclohecxane) provided yellow needles that were suitable for an X-ray structure determination. In the hope of adding another sulfur atom to the bridge (to produce the tetrasulfur derivative **27**), we treated **23** with disulfur dichloride. The only product that could be isolated, in 84% yield, was again the trisulfide **24**. Evidently sulfur had been split off during the bridging process, a suspicion that was supported by the generation of an amorphous precipitate (sulfur) during the reaction.

The structure of the dithiol **23** is shown in Figure 8 (top). The poor quality of the data is reflected in the rather irregular ellipsoids. The refined hydrogen positions of the thiol

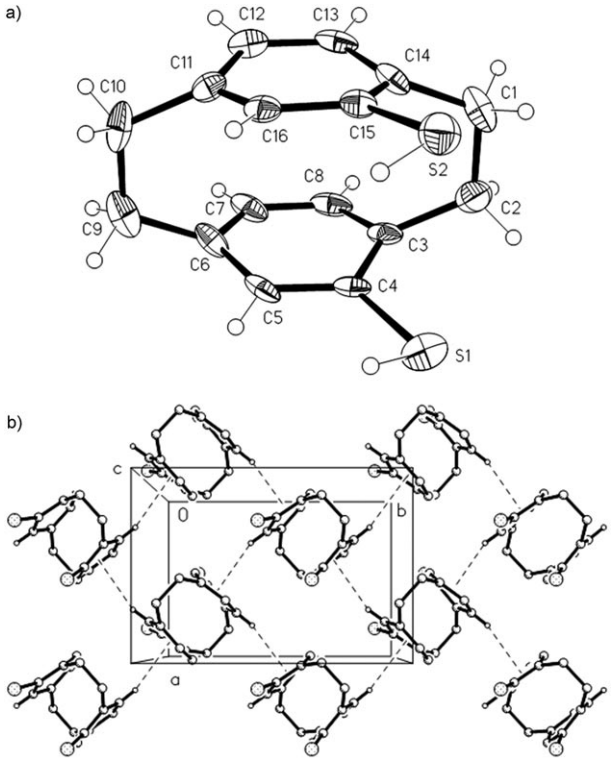


Figure 8. Top: the molecule of compound **23** in the crystal. Ellipsoids represent 30% probability levels. Bottom: packing diagram of compound **23**; dashed lines indicate C–H···π interactions.

groups should be regarded as tentative, but display reasonable bond angles and torsion angles, and make no impossibly short contacts. There is no evidence for weak hydrogen bonds of the form S–H···S or C–H···S. There are two short S···S contacts, intramolecular (3.651(3) Å) and intermolecular S1···S2 (3.467(3) Å), operator $1-x,1-y,1-z$, but the thiol hydrogen atoms do not appear to mediate these. The molecular packing involves two C–H···π interactions, from C8–H8 to the centroid of C12,13,15,16 (2.81 Å, 159°, $-x,{}^1/_2+y,{}^1/_2-z$] and from C16–H16 to the centroid of C4,5,7,8 (2.74 Å, 160°, $1-x,-{}^1/_2+y,{}^1/_2-z$]. The net effect is to form layers of molecules parallel to the *xy* plane (Figure 8, bottom). We have already noted[39] that many simple cyclophanes pack with this layer pattern, often leading to cell constants of 7 and 11 Å parallel to the layer.

The structure of thiaphane **24**, with its additional S_3 bridge, is shown in Figure 9. The standard [2.2]para-

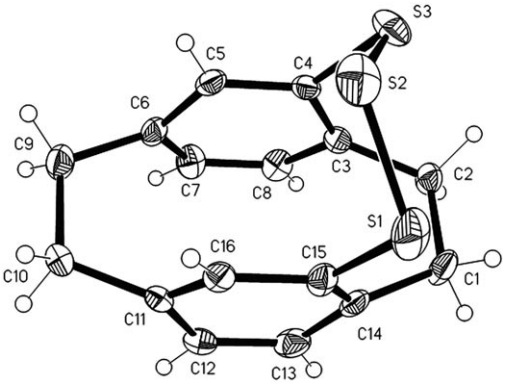


Figure 9. The molecule of compound **24** in the crystal. Ellipsoids represent 30% probability levels. Selected bond lengths (Å): S1–S2 2.055(2), S2–S3 2.054(2).

cyclophane geometry is scarcely altered by the introduction of the extra bridge; the rings retain their flattened boat geometries, whereby the bridgehead atoms (referring to the $(CH_2)_2$ bridges) lie approximately 0.16–0.17 Å out of the plane of the other four atoms, and are parallel. The bridge C–C bonds are lengthened to C1–C2 1.574(4) and C9–C10 1.592(4) Å; the bridge C–C–C angles are widened to 113°, and the angles in the six-membered rings at the bridgehead atoms are narrowed to 116–117°. The packing presents no striking features; some borderline C–H···S contacts are listed in the supplementary crystallographic data. There are no short S···S or C–H···π contacts.

The pseudo-geminal-bis(sulfonyl chloride) derivative **26** crystallises with two molecules in the asymmetric unit, of which one is shown in Figure 10 (top); the second molecule is numbered analogously but with primes. The two molecules differ most in the orientation of the sulfonyl chloride groups; the $C_{bridgehead}$–C–S–Cl torsion angles are −83, 96, −67 and 110° for Cl1, Cl1′, Cl2, Cl2′, respectively. A least-squares fit of the two molecules in terms of the C and S atoms gives a root-mean-square deviation of 0.13 Å. The molecules show the usual cyclophane features (see above), which will not be further commented upon. A superficial inspection of the molecular packing reveals three hydrogen bonds of the form C–H···Cl and five of the form C–H···O (see the supplementary crystallographic data), but all are long. More relevant structurally may be three Cl···O interactions [1) Cl2···O1 3.093(3) Å, S–Cl···O 152.0(1)°, operator $-x,-{}^1\!/_2+y,1{}^1\!/_2-z$; 2) Cl2′···O2 3.118(3) Å, S–Cl···O 134.4(1)°, operator $x,1{}^1\!/_2-y,-{}^1\!/_2+z$; 3) Cl1′···O3 3.350(3) Å, S–Cl···O 157.7(1)°, operator $1+x,y,z$], which combine to form layers of molecules parallel to the plane $(\bar{1}02)$ (Figure 10, bottom).

To learn about the possibility of bond formation between the two aromatic rings of **22** and **24**, respectively, we subjected these precursors to flash vacuum pyrolysis at 800 °C and 0.1 torr. It is not impossible that hydrocarbon **7** would be produced during this process, since it requires, besides the sulfur removal, only the loss of hydrogen, either in molecular or radical form, which is a definite possibility at these high temperatures. As it turned out, the only pyrolysis product we could identify in small yields (10–14%) was phenanthrene (**30**, Scheme 6).

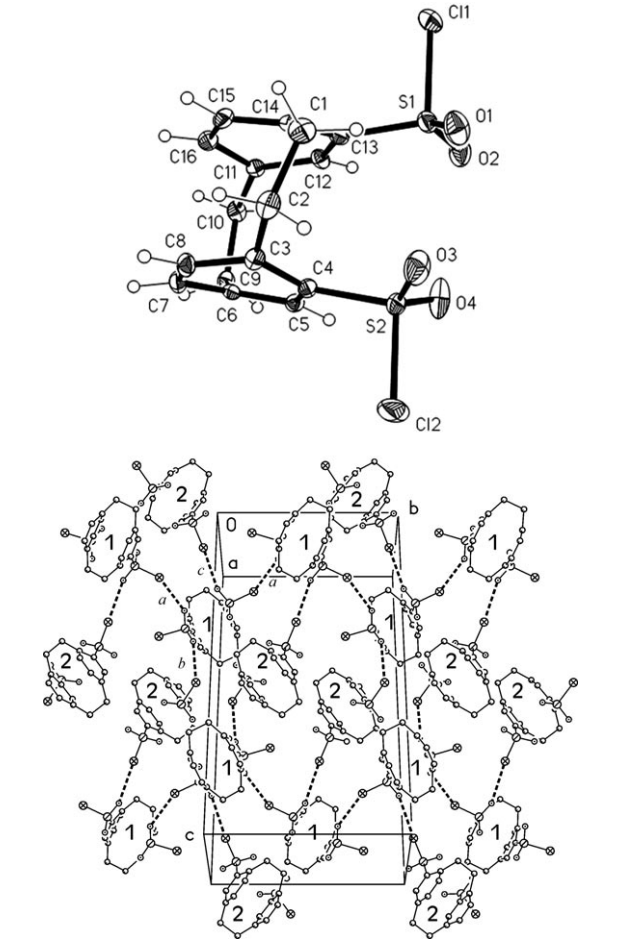
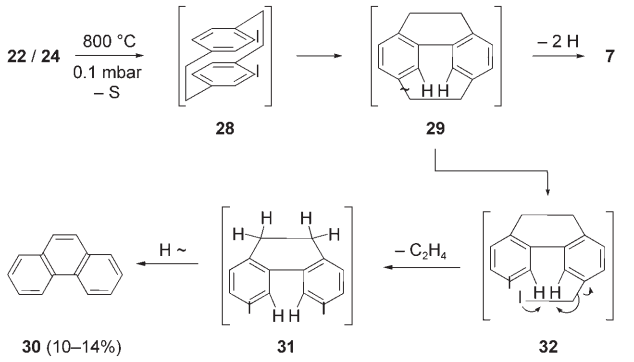


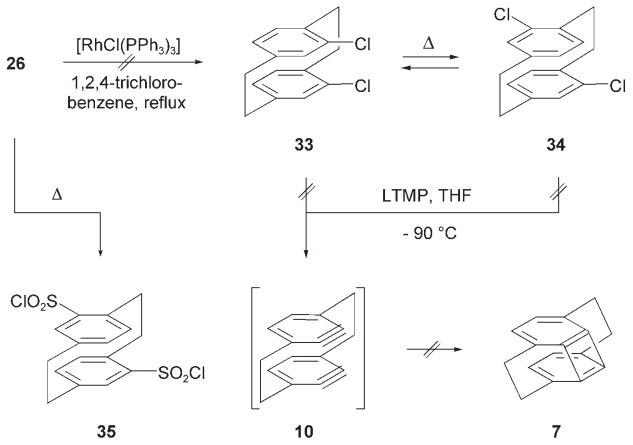
Figure 10. Top: one of the two independent molecules of compound **26** in the crystal. Ellipsoids represent 30% probability levels. Bottom: packing diagram of compound **26**. Boldface numerals indicate independent molecules 1 and 2. Dashed lines and italic letters (the latter indicate the contacts formed by one molecule, see text) indicate Cl···O interactions. H atoms are omitted.



Scheme 6. Flash vacuum pyrolysis of the thiaphanes **22** and **24**.

To rationalise this fragmentation, we propose that sulfur ejection indeed provides the diradical **28** initially. This subsequently closes by intra-annular bond formation to the highly strained intermediate **29**. Rather than losing hydrogen to **7**, rupture of one of the ethano bridges takes place, furnishing the diradical **32**, which, by splitting off ethylene, is converted into the phenanthrenyl diradical **31**. The final stabilisation (formally a symproportionation) could then take place by two 1,5-hydrogen migration reactions.

Exploratory steps to reach **7** via the bisdehydrobenzene intermediate **10** were undertaken last. As already mentioned (Scheme 1) pseudo-*ortho* or pseudo-geminally disubstituted [2.2]paracyclophanes, **11**, could serve as precursors for this cyclophyne. One such derivative is the dichloride **33**, which we hoped to obtain by desulfurisation of the pseudo-geminal bis(sulfonyl chloride) **26** according to a procedure described by Blum and Scharf.[39] These authors have shown that numerous aromatic sulfonyl halides readily undergo SO_2-extrusion when heated in 1,2,4-trichlorobenzene in the presence of various Wilkinson catalysts such as $[RhCl(PPh_3)_3]$. When these conditions were applied to **26** a reaction did indeed take place; however, it did not provide the desired **33** but instead the pseudo-*meta*-isomer **35** of the substrate (Scheme 7). The structure of this cyclophane derivative was



Scheme 7. Attempts to prepare dichloro[2.2]paracyclophanes and to dehydrochlorinate them.

proved by its spectroscopic data and by an X-ray structural analysis (see below). Thermal isomerisations of this type have long been known in cyclophane chemistry;[40,41] they proceed via the diradical formed by homolytic cleavage of an ethano bridge, rotation of the now more flexible intermediate and reclosure of the rotated diradical to the thermodynamically more stable phane isomer. In principle, **35** could also undergo sulfur dioxide loss to the pseudo-*meta*-dichloride **34**. There was, however, no evidence that this product, which could also be generated from **33** by a subsequent thermal process, is part of the product mixture.

The structure of the pseudo-*meta* isomer **35** is shown in Figure 11 (top). The orientations of the sulfonyl chloride

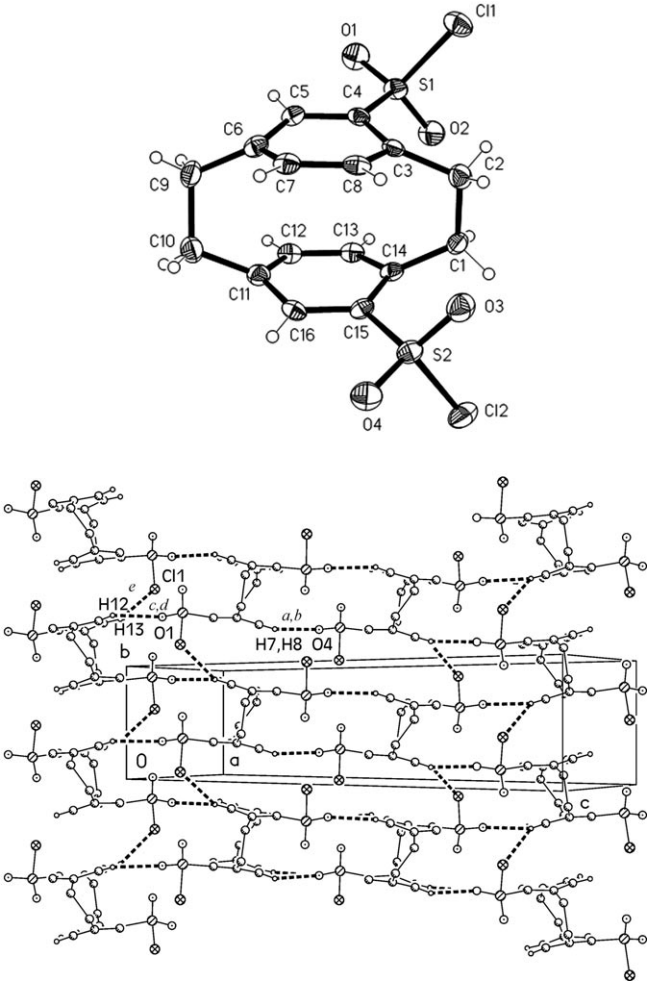


Figure 11. Top: the molecule of compound **35** in the crystal. Ellipsoids represent 50% probability levels. Bottom: packing diagram of compound **35**. Dashed lines and italic letters (see text) indicate C–H···*X* interactions (*X* = O, Cl). H atoms not involved in hydrogen bonds are omitted. Note that the bifurcated systems (see text) are seen edge on, so that the two components almost exactly overlap.

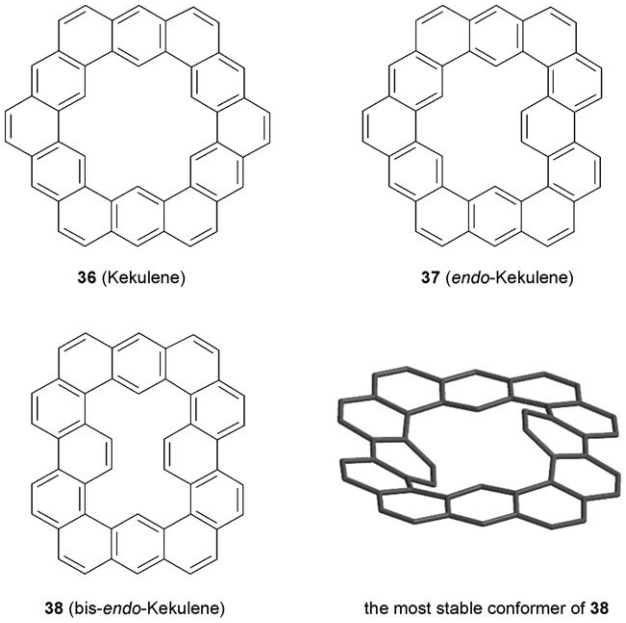
groups are given by the torsion angles (as defined above for **26**) −61° and −63° for Cl1 and Cl2, respectively. The molecular packing is completely different from that of **26**. There are no significant Cl···O contacts, but instead two bifurcated hydrogen bond systems [a,b) (C7–H7, C8–H8)···O4, with H···O 2.60, 2.47 Å, C–H···O 117, 123°, operator $2-x,1-y,1-z$; c,d) (C12–H12, C13–H13)···O1, with H···O 2.54, 2.59 Å, C–H···O 121, 119°, operator $1-x,{}^1/_2+y,{}^1/_2-z$] and a C–H···Cl contact from one of the same hydrogen atoms [e) C13–H13···Cl1, with H···Cl 2.77 Å, C–H···Cl 152°, operator $x,1+y,z$]. The net effect of these is to form layers of molecules parallel to the plane $(\bar{1}02)$ (Figure 11, bottom).

In a final, now rather desperate attempt, we took the commercial product PARYLENE C®, a mixture of chlorine derivatives of [2.2]paracyclophane (**11**, X = Cl) of for us unknown composition, and treated it with lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF at −90 °C. Since it is

known that chloro-*p*-xylene under these conditions provides small amounts of 1,4,5,8-tetramethyl-biphenylene (**8**) via 3,6-dimethyl-dehydrobenzene (**9**),[42] the hope was that **10** should be produced analogously, provided that the substrate mixture contained at least some **33** or its pseudo-*ortho* isomer. On work-up, the PARYLENE C® had vanished completely, but unfortunately again no defined products could be isolated. A bisdehydrobenzene intermediate, of course, has other possibilities for reaction than to yield **7**; it could, for example, polymerise, an option that would become even more pronounced if it had the "wrong" stereochemistry, namely, *anti*-orientation of the two "triple" bonds. Since, in the meantime, we have developed a selective route to the pseudo-geminal-dichloride **33**,[43] we are planning to repeat these elimination reactions under more controlled conditions.

Addendum:[43] The circulenes discussed above formally are constructed from phenanthrene moieties, that is, they all contain the smallest angularly annelated aromatic ring system as the repeating unit. In principle, however, linearly fused and other condensed aromatic systems may also form a section of a circulene ring. Thus, Staab's celebrated kekulene (**36**)[44] may formally be regarded as a [12]circulene that is constructed out of two phenanthrene and two anthracene units, respectively. The phenanthrene moieties, however, are not necessarily be annelated in *exo*,*exo*-fashion as in **36**, but in principle can also assume different orientations as shown in **37** ("*endo*-kekulene") and **38** ("bis-*endo*-kekulene", Scheme 8).

Whereas **36** is a well-investigated hydrocarbon,[45] its two isomers shown in Scheme 8 are so far unknown. As far as their geometries are concerned, **38** should be especially interesting. In kekulene the interior hydrogen atoms are evidently accommodated well by the "hole" inside the molecule, because, according to X-ray structural analysis,[46] the hydrocarbon possesses a nearly perfect planar geometry. However, as shown by B3LYP calculations[14] its bis-*endo*-isomer **38** displays the C_{2h}-symmetric curved structure shown in **39**. Numerous other circular arrangements of benzene rings are conceivable and it remains to be seen which of these become reality.



Scheme 8.

Experimental Section

General remarks: Column chromatography: Silica gel 60 (70–230 mesh, Merck); aluminium oxide, activity II–III (Woelm). Melting points: Kofler hot stage (uncorrected). NMR: Bruker AC 200 (^{1}H: 200 MHz; ^{13}C: 50.3 MHz); Bruker AM 300 (^{1}H: 300 MHz; ^{13}C: 75.5 MHz); Bruker WM 400 and Bruker AM 400 (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) in $CDCl_3$, TMS as internal standard. IR: Perkin–Elmer 1420 as KBr pellets. MS: Finnigan MAT 84530 (70 eV, EI). UV: Beckman UV 5230.

1,4,5,8-Tetramethylbiphenylene (8): A solution of 3,6-dimethylanthranilic acid (48.07 g, 0.29 mol)[23,24] in anhydrous THF (360 mL) was cooled to −10 °C, and trifluoracetic acid (7.7 mL, 10 mmol) was added at this temperature. After stirring for 15 min, *i*-amyl nitrite (60 mL, 0.45 mol) was added over a period of 1 h, and the reaction mixture was stirred for a further 15 min. The diazonium carboxylate **12** precipitated, and was removed by filtration through a teflon Büchner funnel. The salt was washed first with cold THF (≈50 mL, −20 °C), and subsequently with cold 1,2-dichloroethane, taking care that the product never became dry or warmed to RT. According to our experience under these conditions the salt is stable for at least 0.5 h. The suspension was added in portions to boiling 1,2-dichloromethane (3 L), keeping the gas evolution moderate. After 1 h at reflux temperature, the solvent was concentrated by rotary evaporation leading to the crystallisation of **8**. After washing the product with ice-cold methanol and drying it in vacuo, **8** (6.31 g, 21 %) was obtained as colourless prisms. The spectroscopic and analytical data agree with those given in the literature;[37] for the X-ray diffraction study see below.

Pyrolysis of 3,6-dimethylphthalic anhydride (13): A sample of **13** (0.88 g, 5.0 mmol)[25] was pyrolysed in a quartz apparatus at 820 °C at a pressure of 0.1 torr. The pyrolysate, condensed in a cold trap, was dissolved in toluene/chloroform (1:1, v/v) and subjected to chromatography on silica gel with cyclohexane: 115 mg (11 %) of **8** was found, identical to the authentic material (see above). In the pyrolysate no substrate could be detected.

1,4,5,8-Tetrakis(bromomethyl)biphenylene (14): Five portions of *N*-bromosuccinimide (NBS; 4.45 g, 25 mmol) were added to a boiling solution of **8** (6.31 g, 30.0 mmol) in anhydrous carbon tetrachloride (2 L), each portion followed by addition of dibenzoyl peroxide (20 mg). To complete the bromination (the degree of which was monitored by ^{1}H NMR analysis) a final portion of NBS (1.78 g, 10 mmol) plus the peroxide (20 mg) was added, and the reaction mixture was refluxed overnight. The solvent was removed completely and the solid residue washed with cold acetone to remove the succinimide. The parent solution was concentrated to a third of its volume and the precipitated crystals were united with the above solid residue. Recrystallisation of these bromination products from cold acetone yielded **14** (11.85 g, 75 %), identical in its spectroscopic and analytical data with those reported;[19–21,24] for the X-ray diffraction study see below.

2,2′-Dithia[3^{1,8}.3^{4,5}]biphenylenophane (16) and 2,3-dithia[4^{1,8}]-2′-thia-[3^{4,5}]biphenylenophane (17): Toluene (1 L), ethanol (575 mL), and water (175 mL) were placed in a 4 L three-necked flask with a mechanical stirrer. Caesium carbonate (3.00 g, 9.20 mmol) was added to the solvent mixture. A solution of tetrabromide **14** (2.24 g, 4.28 mmol) in toluene (1 L) and sodium sulfide nonahydrate (1.04 g, 4.33 mmol) in ethanol (400 mL) and water (100 mL) were added simultaneously to the boiling solution over a period of 20 h and under nitrogen protection. When the addition

Table 1. Crystallographic data for compounds **8**, **14**, **17**, **23**, **24**, **26**, and **35**.

	8	**14**	**17**	**23**	**24**	**26**	**35**
formula	$C_{16}H_{16}$	$C_{16}H_{12}Br_4$	$C_{16}H_{12}S_3$	$C_{16}H_{16}S_2$	$C_{16}H_{14}S_3$	$C_{16}H_{14}Cl_2O_4S_2$	$C_{16}H_{14}Cl_2O_4S_2$
M_r	208.29	523.90	812.40	272.41	302.45	405.29	405.29
habit	colourless tablet	pale yellow prism	pale yellow plate	yellow plate	yellow tablet	colourless tablet	colourless needle
crystal size [mm]	$0.8\times0.4\times0.2$	$0.4\times0.2\times0.14$	$0.22\times0.14\times0.06$	$0.45\times0.4\times0.02$	$0.4\times0.4\times0.2$	$0.8\times0.3\times0.16$	$0.5\times0.15\times0.15$
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$Cmca$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a [Å]	8.8330(8)	20.461(2)	18.586(8)	7.681(3)	8.7986(12)	8.6377(18)	9.390(2)
b [Å]	5.0262(6)	5.2978(6)	7.687(4)	11.002(3)	9.1506(14)	13.9829(16)	6.3659(15)
c [Å]	13.2209(12)	14.536(2)	9.359(5)	15.928(4)	16.852(2)	27.854(3)	27.336(7)
α [°]	90	90	90	90	90	90	90
β [°]	105.158(6)	90	97.32(4)	92.01(2)	90	91.869(10)	93.72(2)
γ [°]	90	90	90	90	90	90	90
V [Å^3]	566.54(10)	1575.7(3)	1326.1(11)	1345.1(7)	1356.8(3)	3362.4(9)	1630.6(7)
Z	2	4	4	4	4	8	4
ρ_{calcd} [Mg m^{-3}]	1.221	2.208	1.505	1.345	1.481	1.601	1.651
μ [mm^{-1}]	0.07	10.2	0.54	0.37	0.53	0.65	0.67
$F(000)$	224	992	624	576	632	1664	832
T [°C]	−100	−100	−130	−100	−100	−100	−130
$2\theta_{max}$	55	55	56.2	50	55	50	55
reflns measured	2599	2984	9731	2543	3402	6353	3840
independent reflns	1301	932	3369	2358	3123	5907	3759
transmission	–	0.60–0.98	–	–	0.85–0.93	0.86–0.91	0.86–0.88
R_{int}	0.012	0.038	0.061	0.071	0.020	0.031	0.036
parameters	76	47	172	169	172	433	217
restraints	0	0	0	157	0	0	0
$wR(F^2$, all reflns)	0.141	0.040	0.106	0.210	0.098	0.103	0.130
$R[F>4\sigma(F)]$	0.044	0.023	0.042	0.075	0.043	0.044	0.058
S	1.14	0.82	0.96	0.79	0.92	0.89	1.06
max $\Delta\rho$ [e Å^{-3}]	0.27	0.47	0.77	0.70	0.46	0.55	0.38

was complete, the reaction mixture was heated to reflux for 2 h, and, after cooling to RT, the solvents were removed completely. The solid residue was dissolved in cyclohexane/chloroform (3:2, v/v) and separated by column chromatography on silica gel using the same solvent mixture providing the following fractions: fraction 1: several milligrams of monocyclised thioether **18**; fraction 2: 180 mg (14%) of **17**; fraction 3: 107 mg (9%) of **16**. The majority of the product mixture consisted of polymeric compounds that were not identified. In a second cyclisation experiment (benzene 1.6 L; ethanol 1.15 L; water 50 mL; caesium carbonate 3.00 g) the bromide **9a** (1.12 g, 2.14 mmol) in benzene (500 mL) was coupled with sodium sulfide nonahydrate (1.02 g, 4.25 mmol) in ethanol (200 mL) and water (50 mL). In this case two fractions were obtained after silica gel chromatography: **17** (17 mg, 2.6%) and **16** (292 mg, 51%).

*Fraction 1—4,5-bis(bromomethyl)-2-thia[3^{1,8}]biphenylenophane (**18**)*: M.p. 112°C; MS (EI, 70 eV): *m/z* (%): 398 (20), 396 (39), 394 (26), [M^+], 317 (100), 315 (93), 235 (56), 220 (34), 202 (38), 189 (49).

*Fraction 2—2,3-dithia[4^{1,8}]-2′-thia[3^{4,5}]biphenylenophane (**17**)*: M.p. 108°C (decomp); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta=3.49$ (d, $J=17.3$ Hz, 2H; 9-, 12-H), 3.74 (s, 4H; 13-, 15-H), 3.88 (d, $J=17.4$ Hz, 2H; 9-, 12-H), 6.37 (d, $J=8.3$ Hz, 2H; 2-, 7-H), 6.50 ppm (d, $J=8.3$ Hz, 2H; 3-, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=36.8$ (t, C-13, C-15), 38.8 (t, C-9, C-12), 126.5 (d, C-3, C-6), 127.9 (d, C-2, C-7), 128.4 (s, C-1, C-8), 129.7 (s, C-4, C-5), 146.0 (s, C-8a, C-8b), 149.8 ppm (s, C-4a, C-4b); IR (KBr): $\tilde{\nu}=3443$ (s), 2926 (m–s), 1396 (vs), 1350 (vs), 1216 (m), 1195 (w–m), 1163 (s), 1134 (m), 1109 (m), 897 (m–s), 842 (m), 838 (m), 784 (s), 771 (s), 762 cm^{-1} (m); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 264 (sh, 4.39), 270 (4.45), 292 (3.45), 330 (3.03), 346 (3.30), 364 nm (3.32); MS (EI, 70 eV): *m/z* (%): 302 (15), 301 (20), 300 (100) [M^+], 237 (18), 236 (89), 235 (48), 234 (20), 221 (21), 208 (14), 202 (21), 189 (21); elemental analysis calcd (%) for $C_{16}H_{12}S_3$: C 64.00, H 4.03, S 31.97; found: C 64.05, H 4.01, S 31.77; X-ray structural analysis: see below, Table 1.

*Fraction 3: 2,2′-Dithia[3^{1,8}.3^{4,5}]biphenylenophane (**16**)*: M.p. 208°C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta=3.80$ (s, 8H; 9-, 11-, 12-, 14-H), 6.62 ppm (s, 4H; 2-, 3-, 6-, 7-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=37.2$ (t, C-9, C-11, C-12, C-14), 128.5 (s, C-1, C-4, C-5, C-8), 129.3 (d, C-2, C-3, C-6, C-7), 144.7 ppm (s, C-4a, C-4b, C-8a, C-8b); IR (KBr): $\tilde{\nu}=3031$ (vw), 2908 (m–s), 2898 (m–s), 1448 (m), 1444 (m), 1412 (m–s), 1352 (m), 879 (m), 800 (vs), 698 (s), 661 (s), 602 cm^{-1} (vs); UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 382 (3.07), 366 (3.11), 308 (sh, 3.35), 280 (4.29), 232 nm (4.03); MS (EI, 70 eV): *m/z* (%): 270 (10), 269 (20), 268 (100) [M^+], 236 (10), 234 (13), 222 (14), 208 (12), 189 (12); elemental analysis calcd (%) for $C_{16}H_{12}S_2$: C 71.60, H 4.51, S 23.89; found: C 71.42, H 4.51, S 23.64.

Dipotassium salt of [2.2]paracyclophane-4,15-disulfonic acid (25c): Compound **20** (60.0 g, 0.17 mol),[34,35] was added in portions to a 10 N aqueous potassium hydroxide solution (100 mL). The reaction mixture was heated to reflux for 1.5 h, cooled with an ice-bath, and the resulting precipitate removed by filtration through a Büchner funnel. The filter cake was washed with ice-water, and subsequently dried in a desiccator over phosphorus pentoxide to give **25c** (63.5 g, 84%) as a beige amorphous mass, m.p. 219°C (decomp). When a solution of **25c** (6.35 g, 14 mmol) in water was acidified with dilute hydrochloric acid and the organic material dissolved in dichloromethane, 4.52 g (86%) of the free acid was obtained after work-up. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta=3.00$–3.35 (m, 6H; ethano bridges), 4.04–4.12 (m, 2H; ethano bridges), 6.81–6.94 ppm (overlapping multiplets, 6H; arom. H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=35.0$ (t, C-1, C-2), 36.0 (t, C-9, C-10), 128.5 (d, C-5, C-16), 136.0 (d, C-8, C-13), 137.0 (s, C-3, C-14), 137.5 (d, C-7, C-12), 141.0 (s, C-6, C-11), 141.5 ppm (s, C-4, C-15); IR (KBr): $\tilde{\nu}=3447$ (w), 2931 (m), 1450 (w), 1435 (w), 1231 (s), 1217 (s), 1177 (s), 1084 (s), 1032 (s), 1026 (s), 719 (m), 708 (s), 639 cm^{-1} (s); UV (water): λ_{max} ($\log\varepsilon$) = 298 (3.04), 260 (3.45), 230 nm (4.16).

[2.2]Paracyclophane-4,15-disulfonylchloride (26): Compound **25c** (50.0 g, 0.11 mol) was carefully added to phosphorus oxychloride (40 mL), and, after phosphorus pentachloride (100 g, 0.48 mol) had been added, the stirred reaction mixture was heated for 3 h under reflux. The $POCl_3$ and the excess PCl_5 were distilled off under vacuum, and toluene was added to the resulting residue. After crystallisation from that solvent, **26** (19.5 g, 43%) was obtained as pale yellow prisms. M.p. 207°C; ^{1}H NMR

(400.1 MHz, $CDCl_3$): $\delta = 3.21$–3.32 (m, 6H; ethano bridges), 4.32–4.37 (m, 2H; ethano bridges), 6.89–6.90 (m, 2H; 8-, 13-H), 6.98 (dd, $J_1 = 7.8$, $J_2 = 1.8$ Hz, 2H; 7-, 12-H), 7.30 ppm (d, $J = 1.8$ Hz, 2H; 5-, 16-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 33.7$ (t, C-9, C-10), 34.3 (t, C-1, C-2), 130.5 (d, C-5, C-16), 137.5 (s, C-3, C-14), 138.1 (d, C-8, C-13), 139.4 (d, C-7, C-12), 141.7 (s, C-6, C-11), 142.6 ppm (s, C-4, C-15); IR (KBr): $\tilde{\nu} =$ 3445 (w), 2858 (w), 1398 (w), 1047 (w), 684 (m), 616 (m), 587 (s), 573 cm^{-1} (s); UV (acetonitrile): λ_{max} ($\log \varepsilon$) = 310 (3.48), 262 (3.87), 230 (sh, 4.02), 220 (sh, 4.22), 212 nm (sh, 4.34); MS (EI, 70 eV): *m*/*z* (%): 407/405/403 (0.15/0.64/0.94) [M^+−H], 371/369 (9/22) [M^+−Cl], 241 (15), 205 (13), 189 (10), 150 (14), 140 (32), 139 (16), 138 (100), 103 (30), 77 (21); elemental analysis calcd (%) for $C_{16}H_{14}Cl_2O_4S_2$: C 47.41, H 3.48, S 15.82; found: C 47.24, H 3.49, S 15.59; X-ray structural analysis: see below.

[2.2]Paracyclophane-4,15-dithiol (23): Tin dichloride dihydrate (175.0 g, 0.71 mol) was added to a mixture of ethanol (250 mL) and concentrated hydrochloric acid (250 mL), followed by **26** (19.0 g, 47.0 mmol). The reaction mixture was heated to reflux overnight; after cooling, water (750 mL) was added and the ethanol distilled off. The precipitate was removed by filtration, and the aqueous phase was extracted thoroughly with dichloromethane and diethyl ether. The organic phases were combined, dried (sodium sulfate), and the solvents were removed in vacuo. The resulting residue was combined with the above precipitate and the raw dithiol was recrystallised from ethanol to give **23** (5.9 g 46%) as yellow needles. M.p. 208 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 2.91$–3.08 (m, 6H; ethano bridges), 3.56 (s, 2H; -SH), 3.76–3.84 (m, 2H; ethano bridges), 6.39–6.52 (m, 4H; 7-, 8-, 12-, 13-H), 6.60 ppm (d, $J = 1.6$ Hz, 2H; 5-, 16-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 33.5$ (t, C-1, C-2), 34.7 (t, C-9, C-10), 129.8 (s, C-4, C-15), 132.0 (d, C-7, C-12), 134.6 (d, C-8, C-13), 135.9 (d, C-5, C-16), 139.5 (s, C-3, C-14), 139.6 ppm (s, C-6, C-11); IR (KBr): $\tilde{\nu} = 3024$ (w), 2952 (m), 2927 (s), 2889 (m), 2851 (m–s), 1581 (m), 1476 (m), 1394 (s), 1056 (m), 910 (m), 866 (m), 838 (m), 711 cm^{-1} (vs); UV (acetonitrile): λ_{max} ($\log \varepsilon$) = 310 (3.03), 282 (sh, 3.40), 252 (sh, 3.92), 214 nm (4.37); MS (EI, 70 eV): *m*/*z* (%): 274 (6), 273 (10), 272 (50) [M^+], 240 (18), 239 (90), 238 (13), 137 (34), 136 (100), 135 (43), 121 (15), 93 (32), 92 (27); elemental analysis calcd (%) for $C_{16}H_{16}S_2$: C 70.57, H 5.93, S 23.50; found: C 70.47, H 5.87, S 23.62; X-ray structural analysis: see below.

[2.2]Paracyclophane-4,15-disulfide (22): Anhydrous cobalt dichloride (97 mg, 0.74 mmol) was added to a solution of **23** (1.39 g, 5.1 mmol) in anhydrous acetonitrile (300 mL), and the mixture heated to reflux under nitrogen overnight. The orange precipitate formed after cooling to RT was removed by filtration and recrystallised from ethanol to give **22** (0.38 g, 27%) as orange needles. M.p. 185 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.21$–3.32 (m, 6H; ethano bridges), 4.32–4.37 (m, 2H; ethano bridges), 6.35 (d, $J = 7.9$ Hz, 2H; 8-, 13-H), 6.49 (d, $J = 1.9$ Hz, 2H; 5-, 16-H), 6.85 ppm (dd, $J_1 = 7.9$, $J_2 = 1.9$ Hz, 2H; 7-, 12-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 33.6$ (t, C-1, C-2), 35.2 (t, C-9, C-10), 132.7 (s, C-4, C-15), 133.0 (d, C-7, C-12), 133.9 (d, C-8, C-13), 139.8 (s, C-6, C-11), 148.2 (d, C-5, C-16), 148.9 ppm (s, C-3, C-14); IR (KBr): $\tilde{\nu} = 3030$ (w), 2925 (s), 2890 (m), 1469 (s), 1446 (m), 1435 (m), 1428 (m), 1386 (m), 918 (vs), 904 (m), 888 (m), 839 (m), 723 (vs), 698 (s), 654 cm^{-1} (s); UV (acetonitrile): λ_{max} ($\log \varepsilon$) = 312 (3.40), 286 (sh, 3.72), 256 (sh, 3.97), 218 nm (4.33); MS (EI, 70 eV): *m*/*z* (%): 272 (9), 271 (17), 270 (100) [M^+], 269 (16), 155 (14), 238 (12), 237 (54), 222 (13), 205 (14), 147 (30), 135 (14); elemental analysis calcd (%) for $C_{16}H_{14}S_2$: C 71.10, H 5.22, S 23.68; found: C 71.17, H 5.23, S 23.57.

[2.2]Paracyclophane-4,15-trisulfide (24): Freshly distilled sulfur dichloride (0.1 mL, 1.6 mmol) in diethyl ether (10 mL) was added to a solution of **23** (0.272 g, 1 mmol) in anhydrous diethyl ether (20 mL), and the reaction mixture heated to reflux for 5 h. The solvent was removed and the remaining residue was subjected to chromatography on silica gel with cyclohexane to give **24** (0.291 g, 96%) as yellow crystals. M.p. 165 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.16$–3.20 (m, 4H; ethano bridges), 3.22–3.26 (m, 2H; ethano bridges), 4.09–4.13 (m, 2H; ethano bridges), 6.44 (dd, $J_1 = 7.9$, $J_2 = 1.9$ Hz, 2H; 7-, 12-H), 6.69 (d, $J = 7.9$ Hz, 2H; 8-, 13-H), 7.47 ppm (d, $J = 1.8$ Hz, 2H; 5-, 16-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 34.8$ (t, C-9, C-10), 35.1 (t, C-1, C-2), 130.1 (s, C-4, C-15), 135.0 (d, C-7, C-12), 135.5 (d, C-8, C-13), 138.1 (d, C-5, C-16), 141.3 (s, C-6, C-11), 143.6 ppm (s, C-3, C-14); IR (KBr): $\tilde{\nu} = 2954$ (w), 2928 (vs), 2886 (m), 1470 (s), 1444 (m), 1393 (s), 911 (s), 875 (s), 716 cm^{-1} (vs); UV (acetonitrile): λ_{max} ($\log \varepsilon$) = 312 (3.37), 244 (sh, 3.96), 206 nm (sh, 4.41); MS (EI, 70 eV): *m*/*z* (%): 304 (8), 303 (9), 302 (53) [M^+], 167 (20), 166 (100), 134 (7), 91 (17); elemental analysis calcd (%) for $C_{16}H_{14}S_3$: C 63.57, H 4.67, S 31.76; found: C 63.21, H 4.57, S 31.70; X-ray structural analysis: see below.

When the experiment was repeated with disulfur dichloride (0.1 mL, 1.2 mmol) under otherwise identical conditions, 254 mg (84%) of **24** was obtained. The amounts of a second compound giving the correct mass spectrum for the tetrasulfide **27** (EI, 70 eV: *m*/*z* (%) = 334 (3) [M^+], 302 (46), 166 (100)) were so minute that no spectroscopic data could be obtained.

Pyrolysis of 22 and 24: Either **22** (270 mg, 1 mmol) or **24** (302 mg, 1 mmol) was placed in a 25 mL round-bottomed flask and the flask connected and placed in the preheating (evaporation) zone of a pyrolysis apparatus (quartz tube, $l = 60$, o.d. = 3.5 cm). At the other end of the pyrolysis tube a cold trap was placed, and cooled with liquid nitrogen. The evaporation zone was heated to 130–150 °C, and the pyrolysis oven to 800 °C, and the whole apparatus was evacuated to ≈0.1 torr. The brown pyrolysate that formed over 12 h was dissolved in a small amount of chloroform/toluene and the solution subjected to chromatography on silica gel with cyclohexane/chloroform (3:1, v/v). As the only organic product phenanthrene (**30**) was isolated and identified by comparison with an authentic sample; yield: 18 mg (10%) from **22** and 25 mg (14%) from **24**.

Attempted catalytic desulfonylation of [2.2]paracycylophane-4,15-disulfonylchloride (26): Chlorotris(triphenylphosphine)rhodium(I) (61 mg, 0.17 mmol) was added to a solution of **26** (3.0 g, 7.4 mmol) in 1,2,4-trichlorobenzene (30 mL). The reaction mixture was heated to reflux for 30 min with stirring. After cooling to RT the solvent was removed in vacuo and the obtained residue chromatographed on silica gel with cyclohexane/dichloromethane (1:1, v/v). Besides substrate **26** (0.52 g 25%), [2.2]paracyclophane-4,13-disulfonylchloride (**35**; 1.90 g, 63%) was isolated as colourless needles (toluene). M.p. 206 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.09$–3.17 (m, 2H; ethano bridges), 3.33–3.48 (m, 4H; ethano bridges), 3.98–4.06 (m, 2H; ethano bridges), 6.73 (dd, $J_1 = 7.9$, $J_2 = 1.8$ Hz, 2H; 7-, 16-H), 6.97 (d, $J = 7.9$ Hz, 2H; 8-, 15-H), 7.33 ppm (d, $J = 1.8$ Hz, 2H; 5-, 12-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 34.1$ (t, C-1, C-2), 34.3 (t, C-9, C-10), 130.7 (d, C-5, C-12), 137.0 (d, C-8, C-15), 139.1 (d, C-7, C-16), 139.2 (s, C-3, C-14), 141.7 (s, C-6, C-11), 143.2 ppm (s, C-4, C-13); IR (KBr): $\tilde{\nu} = 2983$ (w), 2957 (m), 2928 (m), 1479 (m), 1395 (s), 1366 (vs), 1195 (s), 1170 (vs), 922 (s), 705 cm^{-1} (s); UV (acetonitrile): λ_{max} ($\log \varepsilon$) = 302 (3.23), 274 (3.79), 234 nm (sh, 3.94); MS (EI, 70 eV): *m*/*z* (%): 407/406/405/404/403 (0.19/0.20/0.53/0.37/054) [M^+], 371 (9), 369 (21), 241 (15), 189 (10), 150 (14), 140 (31), 139 (16), 138 (100), 103 (30), 102 (12), 77 (31); elemental analysis calcd (%) for $C_{16}H_{14}Cl_2O_4S_2$: C 47.41, H 3.48, S 15.82; found: C 47.48, H 3.47, S 15.67; X-ray structural analysis: see below.

X-ray structure determinations: Numerical details are presented in Table 1.

Data collection and reduction: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**17**: Bruker SMART 1000 CCD; **35**: Stoe STADI-4; others: Siemens P4, with appropriate low temperature attachments). Measurements were performed with monochromated $Mo_{K\alpha}$ radiation. Absorption corrections were performed on the basis of ψ-scans for **14**, **24**, **26**, and **35**.

Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97, G.M. Sheldrick, University of Göttingen). Hydrogen atoms were included as rigid methyl groups or with a riding model.

Exceptions/special features of refinement: An extinction correction was performed for compounds **8** and **14**. The data for compound **23** were of poor quality (weakly diffracting thin plate); restraints on the displacement factor components were employed to improve refinement stability. Hydrogen atoms of the SH groups were identified tentatively in difference syntheses and refined with constrained S–H distances and fixed *U*

values; the positions are structurally reasonable (no impossibly short contacts) but should be interpreted with caution. For compound **24**, the Flack parameter refined to −0.07(11); the compound crystallises by chance in a chiral space group.

CCDC-631107 (**8**), 631108 (**14**), 631109 (**17**), 631110 (**23**), 631111 (**24**), 631112 (**26**), 631113 (**35**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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