Small Hydrocarbon Cyclophanes: Synthesis, X-ray Analysis and Molecular Modelling

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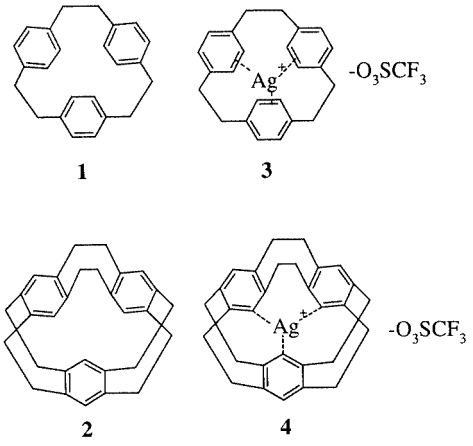
Small hydrocarbon cyclophanes, such as [2.2.0]*m*,*m*,*m*-cyclophane (**20**) and [2.2.0]*p*,*m*,*m*-cyclophane (**21**), are strained analogues of the well-known π-prismand [2.2.2]*p*,*p*,*p*-cyclophane (**1**). The synthetic route to these molecules is based on well-established cyclophane methodology which offers a general access to a whole family of hydrocarbon cyclophanes. Single crystal X-ray analysis and molecular modelling showed that the reduction of the ring size from 18-membered (**1**) to 14-membered (**21**) or 13-membered (**20**) has a substantial effect on the size and the shape of the cyclophane's cavity, thus blocking its ability to complex Ag^+ ions.

Introduction

Cyclophanes play a significant role in supramolecular chemistry, which is one of the fastest developing areas in modern chemistry.[1] Supramolecular chemistry is based on weak, often reversible, noncovalent interactions, holding together supramolecular complexes.[2] Among these interactions are hydrogen bonding, ion pairing, metal-to-ligand attractions, π-acid to π-base interactions, van der Waals attractions and cation-π interactions. The very same interactions control the molecular recognition processes in biological systems.[3]

Some π-systems containing hydrocarbon cyclophanes can complex certain metal cations by interacting with the π-electron system of the hydrocarbon. This complexation is based on electron transfer between the aromatic moiety and positively charged metal cation.[4] Hydrocarbon cyclophanes like [2.2.2]*p*,*p*,*p*-cyclophane (**1**) which can form crystalline silver cation complexes are known as π-prismands.[5]

[2.2.2]*p*,*p*,*p*-Cyclophane (**1**), the first known π-prismand, forms an extraordinarily stable 1:1 complex **3** (Figure 1) with silver triflate where the Ag^+ ion is located on the threefold axis, 0.23 Å outside of the π-prismand cavity.[6] Another very interesting π-prismand was synthesised by Bokelheide et al.[6] They studied gas-phase dimerization of benzocyclobutenes in a stream of nitrogen and found that increasing the concentration of benzo[1,2:4,5]dicyclobutene in the hot zone of the pyrolysis tube produced [2_6](1,2,4,5)cyclophane (**2**) named by the authors as deltaphane (Figure 1).[6,7] The rigid geometry of deltaphane, with its internal cavity surrounded by three benzene rings, seemed ideal for metal ion complexation of the π-prismand type. Although deltaphane itself is essentially insoluble in tetrahydrofuran, it rapidly dissolves in tetrahydrofuran in the presence of silver triflate to form complex **4** (Figure 1). In both hydrocarbons **1** and **2** all three benzene rings are arranged with face-to-face symmetry giving the structure which is considered as an ideal π-prismand.[6,7]



1 **3** **2** **4**

Figure 1. [2.2.2]*p*,*p*,*p*-Cyclophane (**1**), [2_6](1,2,4,5)cyclophane (**2**) and their silver complexes **3** and **4**

Concave hydrocarbon cyclophanes have been shown to be able to extract certain metal ions from the aqueous phase into a nonpolar phase.[8] A number of spherical hydrocarbons have been tested, and among these the concave hydrocarbon [2.2.2]*p*,*p*,*p*-cyclophane (**1**) was found to extract Ag^+ to a much greater extent than alkali metal ions, Tl^+ or Hg^{2+}. This complexation selectivity could be used in applications such as ion-selective electrodes.[8]

Previously, we have reported the synthesis of a family of small hydrocarbon cyclophanes which are either isomeric

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structures or strained analogues of the well-known [2.2.2]*p*,*p*,*p*-cyclophane (**1**). Our aim is to study how strained a molecule can be and still act as a π-prismand and form a stable complex with silver cation.[9−11]

Sulfone pyrolysis was selected as a suitable synthetic method due to the unsymmetrical nature of these hydrocarbon cyclophanes. This procedure is one of the most important applications in cyclophane chemistry as it offers access to a large diversity of macrocycles.[12,13]

Figure 2 presents the two isomeric structures of [2.2.2]*p*,*p*,*p*-cyclophane (**1**) namely, [2.2.2]*m*,*m*,*p*-cyclophane (**5**) and [2.2.2]*m*,*p*,*p*-cyclophane (**6**) and the two slightly strained analogues, namely [2.2.1]*m*,*p*,*p*-cyclophane (**7**) and [2.2.1]*p*,*p*,*p*-cyclophane (**8**), prepared by us.[9−11]

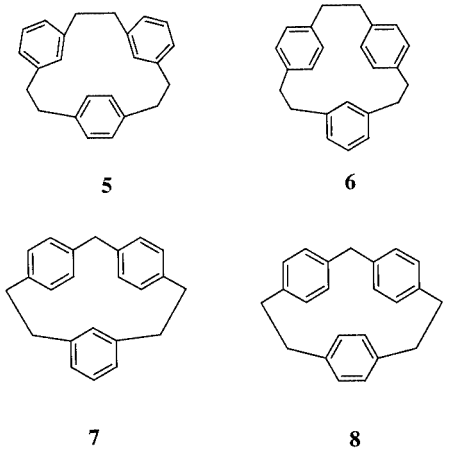


Figure 2. [2.2.2]*m*,*m*,*p*-Cyclophane (**5**), [2.2.2]*m*,*p*,*p*-cyclophane (**6**), [2.2.1]*m*,*p*,*p*-cyclophane (**7**) and [2.2.1]*p*,*p*,*p*-cyclophane (**8**)

We have surveyed the complexation abilities of the hydrocarbon cyclophanes **5**, **6**, **7** and **8** by using the same procedure that Pierre et al.[5] used for the parent [2.2.2]*p*,*p*,*p*-cyclophane (**1**). All [2.2.2]cyclophanes and [2.2.1]cyclophanes presented in Figure 2 are able to complex silver triflate due to electron transfer between their double bonds and the positively charged metal cation, producing π-prismand complexes (Figure 3). The single crystal X-ray analysis of cyclophane complexes **9**, **10**, **11** and **12** showed that the silver cation is located outside of the π-prismand cavity, as in the known [2.2.2]*p*,*p*,*p*-cyclophane- (**3**) and deltaphane-Ag^+ complexes (**4**).[9−11]

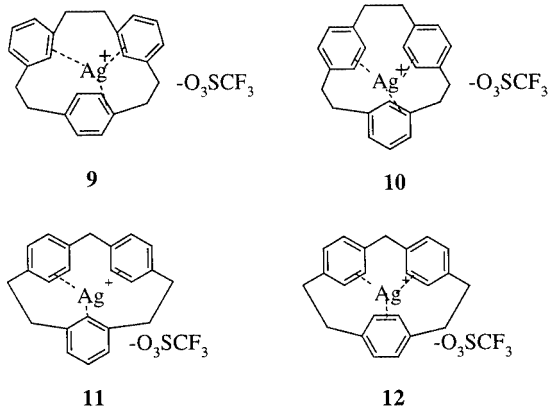


Figure 3. Ag-triflate complexes **9**, **10**, **11** and **12**

We were also interested to study if the cyclophane hydrocarbons could act as ionophores. Four structurally similar cyclophanes, i.e. [2.2.2]*p*,*p*,*p*-cyclophane (**1**), [2.2.2]*m*,*p*,*p*-cyclophane (**6**), [2.2.1]*m*,*p*,*p*-cyclophane (**7**) and [2.2.1]*p*,*p*,*p*-cyclophane (**8**) were studied as π-coordinating ionophores in solvent membrane-based ion-selective electrodes (ISEs).[14,15] The selectivity of the ISEs to Ag^+ was found to depend on both the symmetry and the formal ring size of the cyclophanes, indicating that the cation-π interactions involved are very sensitive to the spatial organisation of the π-coordinating benzene rings in the ionophores. Thus, ISEs based on *p*,*p*,*p*-cyclophanes **1** and **8** showed a significantly higher selectivity for Ag^+ than the corresponding *m*,*p*,*p*-cyclophanes **6** and **7**. The structure of the [2.2.2]*p*,*p*,*p*-cyclophane (**1**) ionophore seems to be particularly favourable for Ag^+-π interactions, resulting in ISEs with the best Ag^+ selectivity among the cyclophanes studied.[14,15]

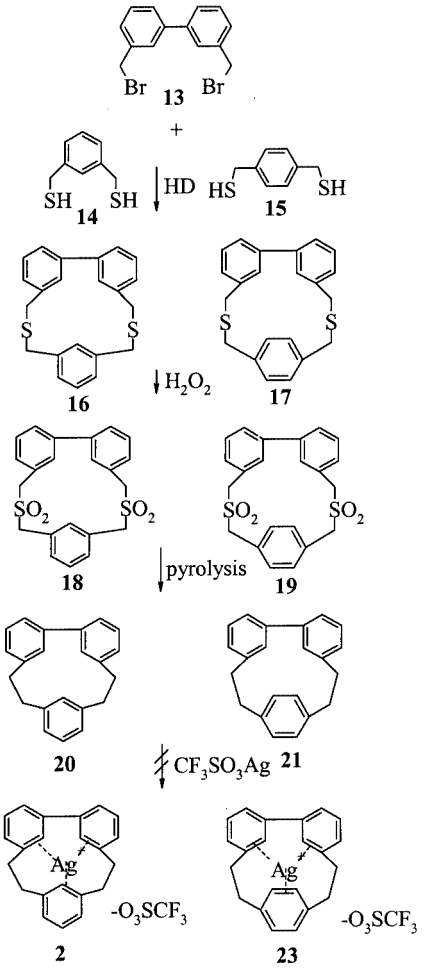
The nature of the bonding in π-prismands and the conformations of [2.2.2]cyclophanes and [2.2.1]cyclophanes has been estimated by ab initio Hartree−Fock (HF) and DFT MO calculations.[16,17] These calculations indicated that [2.2.2]cyclophanes are flexible and the ethane bridges allow twisting, meaning that [2.2.2]cyclophanes are capable of adopting various conformations when complexed with Ag^+. In comparison to [2.2.2]cyclophanes the [2.2.1]cyclophanes possess a more strained structure and are capable of fewer conformations. However, despite this increased rigidity of [2.2.1]cyclophanes they still have only small energy differences between the different conformations and thus are capable of varying their conformation when complexing with metal ions.[16,17]

Following the syntheses and testing of [2.2.1]cyclophanes, we were extremely interested to study even smaller and more strained hydrocarbon cyclophanes, i.e. [2.2.0]*m*,*m*,*m*-cyclophane (**20**)[18] and [2.2.0]*p*,*m*,*m*-cyclophane (**21**)[19] to see if even more rigid and distorted cyclophanes than [2.2.1]cyclophanes can act as π-prismands. In this work we report the synthesis of [2.2.0]*m*,*m*,*m*-cyclophane (**20**)[18] and [2.2.0]*p*,*m*,*m*-cyclophane (**21**)[19] and five new crystal structures, including sulfides **16** and **17**, sulfone **18**, hydrocarbon **21** and from the [2.2.2]cyclophane hydrocarbon family the [2.2.2]*m*,*p*,*p*-cyclophane **5** (Figure 2). We also report molecular orbital calculations on hydrocarbons [2.2.0]*m*,*m*,*m*-cyclophane (**20**) and [2.2.0]*p*,*m*,*m*-cyclophane (**21**).

Results and Discussion

Synthesis

The three step synthesis (Scheme 1) of [2.2.0]*m*,*m*,*m*-cyclophane (**20**)[18] and [2.2.0]*p*,*m*,*m*-cyclophane (**21**)[19] is based on well-known cyclophane methodology, where a sulfide cyclisation is performed under high dilution conditions followed by oxidation and sulfone pyrolysis.[12,13]



Scheme 1

The high-dilution cyclisations to form 1,10-dithia-[3.3.0]*m*,*m*,*m*-cyclophane (**16**; 69% yield) and 1,10-dithia-[3.3.0]*p*,*m*,*m*-cyclophane (**17**; 66% yield) were performed starting from 3,3′-bis(bromomethyl)-1,1′-biphenyl (**13**) and either (1,3-phenylene)bis(methanethiol) (**14**) or (1,4-phenylene)bis(methanethiol) (**15**), with toluene as solvent. The cyclic disulfides **16** and **17** were oxidized by H_2O_2 under reflux to 1,10-dithiatetroxide[3.3.0]*m*,*m*,*m*-cyclophane (**18**; 37%) and 1,10-dithiatetroxide[3.3.0]*p*,*m*,*m*-cyclophane (**19**; 38%), respectively. The disulfides were identified by IR spectroscopy which showed strong adsorption in the SO_2 region (1100−1330 cm^{-1}). The disulfones **18** and **19** were pyrolysed to the hydrocarbons [2.2.0]*m*,*m*,*m*-cyclophane (**20**) and [2.2.0]*p*,*m*,*m*-cyclophane (**21**), respetively, with a ring oven pyrolysis apparatus at 600−620 °C and 2×10^{-5}−8×10^{-6} mbar. The yield after isolation was 50% for **20** and 58% for **21**. To study the complexation ability of ligands **20** and **21**, equimolar amounts of free ligand and silver triflate were mixed using the same procedure as Pierre et al.[5] No complexation was detected.

X-ray Crystallography and Molecular Modelling

After extensive attempts to grow crystals of all the synthesised molecules five new X-ray structures were obtained. A member of the earlier reported family of hydrocarbon [2.2.2]cyclophanes,[9,10] namely [2.2.2]*m*,*m*,*p*-cyclophane (**5**) formed crystals by slow evaporation of a 1:1 dichloromethane/hexane mixture. Colourless crystals of the disulfides (**16** and **17**) were obtained by dissolving the crude products in dichloromethane and allowing the solvent to evaporate very slowly from each solution at room temperature, to give small well-diffracting crystals of **16** and **17**. Disulfone cyclophanes are typically highly insoluble in any solvents, thus getting a crystal structure of those is very difficult. However, fortunately a small amount of disulfone **18** present as an impurity in an NMR tube (in $CDCl_3$) containing hydrocarbon **20** crystallised out. Crystals of hydrocarbon cyclophane **21** were obtained by slow evaporation of a dichloromethane solution. The crystal data and refinement details of all these compounds are given in Table 1.

The hydrocarbon [2.2.2]*m*,*m*,*p*-cyclophane (**5**) crystallises in an acentric monoclinic space group ($P2_1$) with two slightly different molecules (one of them highly disordered) in the asymmetric unit. The X-ray structure (Figure 4) shows a very similar conformation to that present in the earlier hydrocarbon [2.2.2]cyclophanes.[5,9,10] The X-ray structure of its π-prismand Ag^+ complex **9** has been reported earlier.[9,10] X-ray structures of similar cyclophane silver complexes have been reported by Hopf et al.[20−23]

Disulfides **16** and **17** crystallise in a monoclinic space group ($P2_1/n$). The structures are strained and forced almost planar due to the very strained diphenyl parts of the molecules (Figure 5 and 6). Disulfone **18** (Figure 7) crystallises in a monoclinic space group ($P2_1/c$), and shows only a slight conformational change from the disulfide **16**. The target hydrocarbon cyclophane **21** (Figure 8) crystallises in a triclinic space group ($P\bar{1}$). The structure of hydrocarbon **21** is highly strained due to the biphenyl part of the molecule. The angles in [2.2.0]*p*,*m*,*m*-cyclophane (**21**) for the best least-squares planes through the aromatic rings are 161.6(1)°, 50.8(1)° and 53.1(1)°. The same angles in [2.2.2]*p*,*p*,*p*-cyclophane (**1**) are 61.2(1)°, 61.5(1)° and 60.4(1)° indicating an almost ideal π-prismand geometry and a triangular shape. In [2.2.0]*p*,*m*,*m*-cyclophane (**21**) the typical π-prismand face-to-face structure is forced to collapse and the flexibility between the aromatic rings that makes it possible to adapt various conformations is lost.

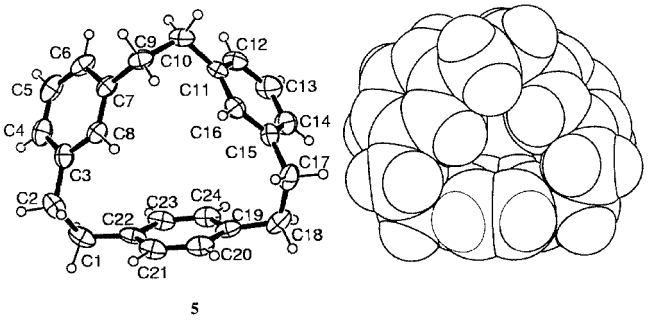
Molecular Orbital Calculations

The starting geometries of [2.2.0] *m*,*m*,*m*-cyclophane (**20**) and [2.2.0] *p*,*m*,*m*-cyclophane (**21**) were fully optimized at the semi-empirical PM3[24] level on a Silicon Graphics O2 workstation by using SPARTAN software.[25] Geometry optimisations were then continued on an AlphaServer ES-40 workstation at the ab initio HF/6−31G* and density functional B3LYP/6−31G* levels with Gaussian98 software.[26]

Both of the methods used, B3LYP/6−31G* and HF/6−31G*, give almost identical optimised structures. Some selected bond and torsion angles of the most stable conformations of the B3LYP-optimised cyclophanes are shown with the experimental values obtained from X-ray analysis in Table 2. These calculated bond parameters agree well

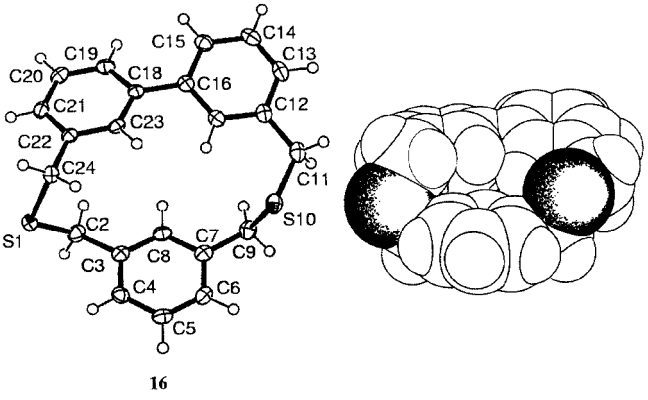
Table 1. Crystal data and experimental details for **5**, **16**, **17**, **18** and **21**

Compound	5	16	17	18	21
Formula	$C_{24}H_{24}$	$C_{22}H_{20}S_2$	$C_{22}H_{20}S_2$	$C_{22}H_{20}S_2O_4$	$C_{22}H_{20}$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
M_r	312.4	348.5	348.5	412.5	284.4
a (Å)	10.3419(4)	12.7237(5)	16.5290(5)	10.6792(3)	8.6888(9)
b (Å)	10.8827(4)	6.9382(5)	5.3933(2)	8.6973(2)	9.3445(9)
c (Å)	16.0015(5)	19.8146(12)	21.2731(8)	21.1205(7)	10.3214(12)
α (°)	90	90	90	90	77.888(7)
β (°)	90.914(1)	100.691(4)	111.503(1)	104.5285(12)	73.150(6)
γ (°)	90	90	90	90	77.694(7)
V (Å^3)	1800.7(1)	1718.9(2)	1764.4(1)	1898.8(2)	773.7(1)
Z	4	4	4	4	2
D_c (Mg·m^{-3})	1.152	1.347	1.312	1.443	1.221
μ (mm^{-1})	0.065	0.309	0.301	0.307	0.069
Refl. Measured/unique	8775/5688	7967/3034	9214/3326	9824/3357	5842/2686
Refl. used in refinement [$I > 2\sigma(I)$]	5208	2422	2383	2252	1972
R_{int}	0.021	0.046	0.075	0.078	0.048
R [$I > 2\sigma(I)$]	0.039	0.043	0.079	0.049	0.046
wR^2 [$I > 2\sigma(I)$]	0.089	0.084	0.163	0.091	0.100



5

Figure 4. The X-ray structure of **5**

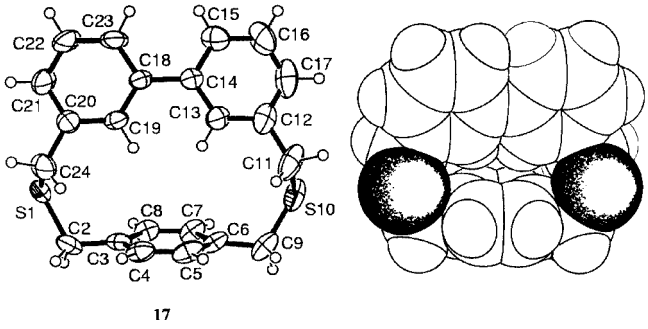


16

Figure 5. X-ray structure of **16**

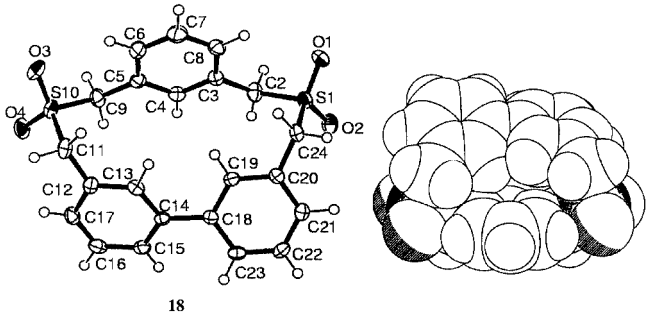
with previously reported values in similar cyclophanes,[16,17] and are also in very good agreement with experimental X-ray values.

Based on the very good agreement between the calculated structure and the X-ray structure for **21**, the calculated structure presented here for [2.2.0] *m*,*m*,*m*-cyclophane (**20**) (Figure 9) can be accepted as a good model of its structure,



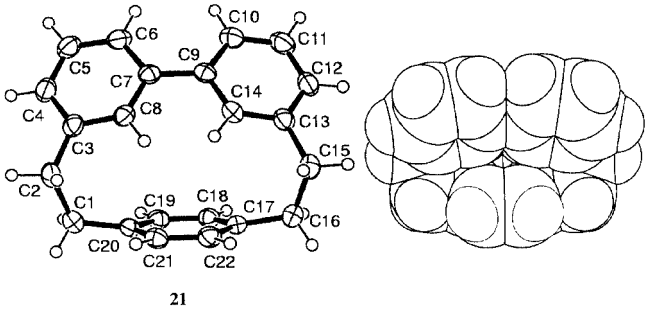
17

Figure 6. X-ray Structure of **17**



18

Figure 7. X-ray Structure of **18**



21

Figure 8. X-ray Structure of **21**

Table 2. Selected bond and torsion angles [°]

Atoms[a]	**20**	**21**	**21**, exp. (X-ray)
C2−C1−C20	114.3	114.0	114.9
C1−C2−C3	112.4	113.4	115.0
C15−C16−C18	114.3	−	−
C15−C16−C17	−	114.0	114.6
C13−C15−C16	112.4	113.4	115.3
C17−C16−C15−C13	−78.5	−56.9	−54.9
C13−C15−C16−C18	78.5	−	−
C3−C2−C1−C20	−	56.9	56.2
C8−C7−C9−C14	−0.1	−0.1	−2.4
C15−C16−C17−C22	−68.9	−67.0	−68.4
C16−C15−C13−C12	−116.7	−105.7	−111.2
C1−C2−C3−C4	116.7	105.7	113.8
C2−C1−C20−C21	68.9	−	−

[a] Numbering according to Figure 8.

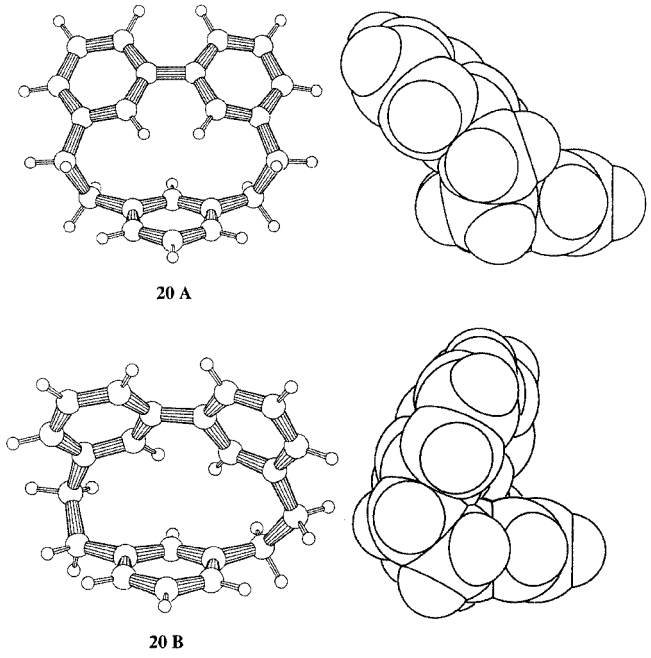


Figure 9. The calculated (B3LYP/6−31G*) structures for **20**

the experimental structure of which is not available. The calculations result in two different conformations for the [2.2.0] *m*,*m*,*m*-cyclophane (**20**) and come from the different orientation of the *meta*-substituted benzene ring. The energy difference between these conformers is about 7 kcal/mol (Figure 9), the A conformer being the more favoured.

Figure 10 shows the most stable calculated structure for [2.2.0] *p*,*m*,*m*-cyclophane (**21**). In this structure the orientation of the benzene rings is similar and agrees very well with the experimental X-ray structure. In all the calculated structures for **20** and **21**, the π-prismand cavity is too small to complex metal ions or small molecules, differing substantially from the π-prismand [2.2.2]- and [2.2.1]cyclophanes.[9−11] This difference originates from the structure of [2.2.0]cyclophane itself. In the [2.2.2]cyclophanes all the aromatic rings are connected together via ethane bridges, whereas in [2.2.0]cyclophanes two out of the three aromatic

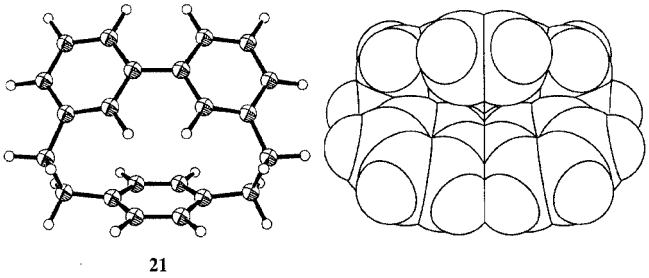


Figure 10. The calculated (B3LYP/6−31G*) structure for **21**

rings are part of a much more rigid biphenylene moiety resulting in a collapsed and rigid structure incapable of acting as a π-prismand.

Conclusion

We have recently synthesised and tested a group of hydrocarbon cyclophanes namely [2.2.2]-, [2.2.1]- and [2.2.0]cyclophanes in order to survey the limits of π-prismand behaviour and compared those to known π-prismands such as [2.2.2]*p*,*p*,*p*-cyclophane (**1**) and deltaphane (**2**). The reduction of the ring size from [2.2.2]cyclophanes to [2.2.0]cyclophanes and the *para*/*meta* coupling of the phenyl rings seems to have a considerable impact on the complexing ability. In particular, in the [2.2.2]cyclophanes, which have a larger ring size than [2.2.1]cyclophanes, the spatial organisation of the benzene rings influences the selectivity of the cyclophanes.

In the case of the [2.2.0]cyclophanes **20** and **21**, in all the calculated structures — this is confirmed by the X-ray structure of **21** — the π-prismand cavity is too small to complex metal atoms or small molecules and differs in this way from [2.2.2]- and [2.2.1]cyclophanes. Although [2.2.1]cyclophanes are more strained than [2.2.2]cyclophanes they still have only a small energy difference between the conformations and thus are capable of adopting different conformations when complexing with metal ions. In the structures of [2.2.0]cyclophanes the inability to complex Ag^+ ions originates from the structure of the cyclophane. The [2.2.2]cyclophane structures have a triangular orientation of three perpendicular benzene rings and a large enough cavity for the complexation. In the [2.2.0]cyclophanes the structure is too collapsed, due to the biphenyldiyl moiety, and the adoption of a suitable conformation for the cation π-interactions needed for the π-prismand behaviour is not possible.

Experimental Section

1,10-Dithia[3.3.0]*m*,*m*,*m*-cyclophane (16):[18] A solution of 3,3′-bis(bromomethyl)-1,1′-biphenyl (**13**) (255.0 mg, 0.750 mmol) and 1,3-di(thiomethyl)benzene (**14**) (125.0 mg, 0.750 mmol) in 100 mL of toluene and a solution of 113.0 mg of KOH in 100 mL of abs. ethanol were added dropwise to 250 mL of refluxing toluene under an inert gas atmosphere in a period of 4 h. After the addition the

mixture was refluxed for an additional 3 h and then cooled to room temperature. The inorganic solid material was filtered and the solvent was evaporated off. The residue was dissolved in a small amount of chloroform and filtered through silica gel. The solvent was evaporated to yield a pale yellow solid product. For the X-ray analysis the crude product was recrystallised from dichloromethane yielding colourless needles. Yield 181.0 mg (69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.51 (s, 4 H), 3.71 (s, 4 H), 6.99−7.42 (m, 12 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.72, 34.89, 123.25, 125.88, 126.48, 127.35, 128.07, 128.15, 128.90, 137.28, 137.95, 138.34 ppm. GC-MS (EI) $C_{22}H_{20}S_2$ (348.5): *m*/*z* (%) = 348 (55).

1,10-Dithia[3.3.0]*p,m,m*-cyclophane (17):[19] A solution of 3,3′-bis-(bromomethyl)-1,1′-biphenyl (**13**) (255.0 mg, 0.750 mmol) and 1,3-di(thiomethyl)benzene (**15**) (125.0 mg, 0.750 mmol) in 100 mL of toluene and a solution of 113.0 mg of KOH in 100 mL of abs. ethanol were added dropwise to 250 mL of refluxing toluene under an inert gas atmosphere in a period of 4 h. After that the mixture was refluxed for an additional 2 h and then cooled to room temperature. The inorganic solid material was filtered and the solvent was evaporated off. The residue was dissolved in a small amount of chloroform and filtered through silica gel. The solvent was evaporated to yield a pale yellow solid product. For the X-ray analysis the crude product was recrystallised from dichloromethane yielding colourless needles. Yield 173.0 mg (66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 4 H), 3.91 (s, 4 H), 6.51 (s, 2 H), 7.09−7.42 (m, 10 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 37.17, 38.50, 124.82, 127.02, 128.02, 128.33, 129.08, 138.78, 139.64, 140.56 ppm. GC-MS (EI) $C_{22}H_{20}S_2$ (348.5): *m*/*z* (%) = 348 (71%).

1,10-Dithiatetroxide[3.3.0]*m,m,m*-cyclophane (18):[18] 1,10-Dithia-[3.3.0]*m,m,m*-cyclophane (**16**) (300.0 mg, 0.860 mmol), 16 mL of glacial acetic acid and 8 mL of toluene were mixed together and heated to reflux. After that 2 mL of 35% H_2O_2 was added and refluxed for an additional hour. The addition of H_2O_2 and 1 h refluxing was repeated three times. After cooling to room temperature the mixture was filtered and the white solid material was washed a few times with glacial acetic acid. The product was used for the following reaction without any further purification. Yield 132.0 mg (37%). IR (KBr): $\tilde{\nu}$ = 1300−1100 cm^{-1} (SO_2). GC-MS (EI) $C_{22}H_{20}S_2O_4$ (412.5): *m*/*z* (%) = 412 (47%).

1,10-Dithiatetroxide[3.3.0]*p,m,m*-cyclophane (19):[19] 1,10-Dithia-[3.3.0]*p,m,m*-cyclophane (**17**) (200.0 mg, 0.570 mmol), 11 mL of glacial acetic acid and 5 mL of toluene were mixed together and heated to reflux. After that 1 mL of 35% H_2O_2 was added and refluxed for an additional hour. The addition of H_2O_2 and 1 h refluxing was repeated three times. After cooling to room temperature the mixture was filtered and the white solid material was washed a few times with glacial acetic acid. The product was used for the following reaction without any further purification. Yield 89.0 mg (38%). IR (KBr): $\tilde{\nu}$ = 1300−1100 cm^{-1} (SO_2). GC-MS (EI) $C_{22}H_{20}S_2O_4$ (412.5): *m*/*z* (%) = 412 (18%).

[2.2.0]*m,m,m*-Cyclophane (20):[18] 1,10-Dithiatetraoxide[3.3.0]-*m,m,m*-cyclophane (**18**) (50.0 mg, 0.121 mmol) was placed in a quartz tube and heated to 600 °C under high vacuum (7.64 × 10^{-6} mbar) in a pyrolysis apparatus. During the heating the product condensed at the other end of the tube. After 5 h the tube was left to cool to room temperature and the pale yellow product was then extracted from the tube with dichloromethane. The solvent was evaporated to yield a pale yellow solid product. Yield 17.4 mg (50%), m.p.: 100−101 °C (ref.[18] 100−101 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.77−3.35 (m, 8 H), 6.93 (s, 2 H), 7.09 (d, 2 H), 7.16 (s, 1 H), 7.22 (d, 2 H), 7.24 (t, 2 H), 7.30 (d, 2 H), 7.34 (t, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.53, 35.26, 122.23, 125.71, 126.82, 127.79, 129.82, 132.69, 135.88, 140.85, 141.86, 142.43 ppm. HRMS: *m*/*z* (M^+, $C_{22}H_{20}$): calcd: 284.156501; found 284.156338.

[2.2.0]*p,m,m*-Cyclophane (21):[19] 1,10-Dithiatetraoxide[3.3.0]*p,m,m*-cyclophane (**19**) (50.9 mg, 0.123 mmol) was placed in a quartz tube and heated to 600 °C under high vacuum (1.46 × 10^{-5} mbar) in a pyrolysis apparatus. During the heating the product condensed at the other end of the tube. After 3 h the tube was left to cool to room temperature and the white product was then extracted from the tube with dichloromethane. The solvent was evaporated to yield a white solid product. The product was recrystallised from dichloromethane yielding well diffracting colourless needles. Yield 20.3 mg (58%), m.p.: 150−151 °C (ref.[19] 165−166 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.87−2.97 (m, 8 H), 6.23 (s, 2 H), 6.85 (s, 4 H), 7.03 (d, 2 H), 7.23 (t, 2 H), 7.41 (d, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 36.95, 37.40, 121.96, 126.24, 128.28, 130.29, 130.81, 137.39, 139.65, 139.68 ppm. HRMS *m*/*z* (M^+, $C_{22}H_{20}$): calcd: 284.156501; found 284.156444.

[2.2.0]*m,m,m*-Cyclophane-Ag-triflate (22): A solution of [2.2.0]*m,m,m*-cyclophane (**20**) (11.6 mg, 0.041 mmol) in dichloromethane was added to solution a of silver triflate (10.5 mg, 0.041 mmol) in THF. The mixture was stirred and allowed to evaporate very slowly to dryness in darkness at room temperature to give a brown solid product. No complexation was detected.

[2.2.0]*p,m,m*-Cyclophane-Ag-triflate (23): A solution of [2.2.0]*p,m,m*-cyclophane (**21**) (11.6 mg, 0.041 mmol) in dichloromethane was added to a solution of silver triflate (10.5 mg, 0.041 mmol) in THF. The mixture was stirred and allowed to evaporate very slowly to dryness in darkness at room temperature to give a whitish crystalline powder. No complexation was detected.

Crystal Structure Analysis: Data were recorded with a Nonius Kappa CCD diffractometer using graphite monochromatised Mo-K_α (λ = 0.71073 Å) radiation, T = 173.0(1) K. The data were processed with *Denzo* (Z. Otwinowski and W. Minor, Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p.307−326, 1997, C. W. Carter Jr. & R. M. Sweet, Eds., Academic Press). Lorentz-polarisation corrections were applied. Structure solutions were performed by direct methods (G. M. Sheldrick, SHELXS-97: *A Program for Automatic Solution of Crystal Structures.*, University of Göttingen, Germany, 1997) and refinements[25] on F^2 (G. M. Sheldrick, SHELXL-97: A *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997). The hydrogen atoms were either calculated at their idealised positions with isotropic temp. factors (1.2- or 1.5-times the C temp. factor) and refined as riding atoms (the structures of **5** and **17**) or found from the electron density map and refined isotropically (**16**, **18** and **21**). In the case of structure **5** two crystallographically independent molecules were found in the asymmetric unit. In one of the molecules two aromatic rings and five bridging CH_2 groups are disordered over two positions with occupancies of 0.45 and 0.55.

CCDC-181698 (**5**), -181699 (**16**), -181700 (**17**), -181701 (**18**) and -181702 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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