Synthesis and X-ray structures of new concave π-prismand hydrocarbon [2.2.1]*m*,*p*,*p*- and [2.2.1]*p*,*p*,*p*-cyclophanes

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The synthesis of the smaller analogues of the well-known [2.2.2]*p*,*p*,*p*-cyclophane (**1**) π-prismand were performed *via* a well-established pyrolysis route from the corresponding disulfones. In spite of their smaller size and increased rigidity, these cyclophanes showed remarkably similar complexation behaviour with Ag^+ ions compared to [2.2.2]*p*,*p*,*p*-cyclophane. X-Ray crystal structure determinations showed the bis-sulfide **12** (1,10-dithia[3.3.1]*m*,*p*,*p*-cyclophane) to be helically chiral. The single crystal X-ray analysis showed that the reduction of the ring size from 17-membered hydrocarbon **17** to 16-membered hydrocarbon **16** has only a slight effect on the size and shape of the cavity. In the Ag^+ complex of [2.2.1]*m*,*p*,*p*-cyclophane (**18**) the interaction between silver and hydrocarbon is accomplished by the coordination of silver to one double bond in two phenyl rings and to only one carbon of the third phenyl ring. However, in the case of [2.2.1]*p*,*p*,*p*-cyclophane–Ag^+ triflate (**19**), silver is bonded to one of the double bonds in each phenyl ring. Similarly to larger [2.2.2]cyclophanes the conformations of the parent [2.2.1]*m*,*p*,*p*- (**16**) and [2.2.1]*p*,*p*,*p*-cyclophanes (**17**) do not change dramatically upon the complexation with the Ag^+ ion.

It is known that certain metal cations can interact with aromatic hydrocarbons to form π-complexes. Bonding in these π-complexes is due to electron transfer between the aromatic moiety and positively charged metal cation.[1] Taylor *et al.*[2] have studied the mechanism of the π-bonding between the aromatic ring and the silver ion in the case of bis(*m*-xylene)–Ag^+ perchlorate. The conclusion was that in the case of electron donation from the aromatic to the metal acceptor orbitals the ideal position for the metal ion would be at the point of highest π-electron density, above one of the carbon atoms of the aromatic ring. On the other hand, the best overlap between the filled metal d orbitals and the antibonding π-MOs of the aromatic moiety for electron back-donation from the metal to the aromatic moiety is achieved when the metal ion is located equidistant between two carbon atoms.[1,2]

This kind of complexation is especially effective for [2.2.2]-*p*,*p*,*p*-cyclophane (**1**), which is the first member of the [2.2.2]cyclophane π-prismands.[3] Its structural isomers [2.2.2]*m*,*m*,*p*- (**2**), [2.2.2]*m*,*p*,*p*-cyclophane (**3**) and other similar structures (Scheme 1) that possess π-electron-rich cavities have been shown to have similar complexing abilities with Ag^+ ions.[4–6]

Previous complexation studies by ^1H NMR showed that silver triflate and [2.2.2]*p*,*p*,*p*-cyclophane (**1**) form an extraordinarily stable 1 : 1 complex where Ag^+ should be located inside of the cyclophane cavity formed by the three benzene rings.[3] Later the X-ray crystal structure analysis verified that the silver ion in the [2.2.2]*p*,*p*,*p*-cyclophane–Ag^+ triflate (**5**) complex is located on the three-fold axis, 0.23 Å outside of the π-prismand cavity.[6] Another very interesting π-prismand was synthesised by Boekelheide *et al.*[6,7] They studied gas-phase dimerisation 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 (deltaphane, **4**). The structure of deltaphane was determined by single crystal X-ray analysis, which showed that the benzene rings in this rigid cyclic hydrocarbon are arranged in a face-to-face geometry and are close enough to render π-delocalisation among all three rings possible, thus making deltaphane an almost ideal π-prismand.[6]

More information about the nature of the bonding in π-prismands has been gathered by calculations using *ab initio* Hartree–Fock and DFT MO methods to study the conformations of [2.2.2]cyclophane π-prismands and the formation of π-complexes with silver ions.[8] The computational results obtained were compared to available X-ray crystal structures. Natural bond orbital (NBO) analysis[9] showed that when Ag^+ is bonded to the cyclophane cavity the formation of bonds is achieved by σ-donation and d–π* back-donation between the silver ion and the hydrocarbon skeleton, which results in hexahapto ($3 \times \eta^2$) overall π-bonding.[8] This is in agreement with the well-known "bonding–back-bonding" scheme in transition metal carbonyl complexes.[10,11] The σ-donation from the hydrocarbon to the silver ion is the main component of the metal–cyclophane bonding.[8] One dihapto (η^2) bonding to one aromatic ring equates in strength to a single strong hydrogen bond, which can be up to 100 kJ mol^{-1}, thus the strength of this $3 \times \eta^2$ bonding in these [2.2.2]cyclophane π-prismands can be compared to three simultaneous strong hydrogen bonds.[10] The same calculations showed that [2.2.2]cyclophanes are flexible and the ethane bridges will allow twisting, thus [2.2.2]cyclophanes are capable of adopting various conformations when complexed with Ag^+.

Concave hydrocarbon cyclophanes have been shown to be able to extract certain metal ions from aqueous phase into non-polar phase.[12] The complexation selectivity of the hydrocarbon cyclophanes could be used in applications such as ion-selective electrodes. A number of cyclophanes were tested as ionophores and PVC–[2.2.2]*p*,*p*,*p*-cyclophane membrane showed selectivity towards silver over alkali metal, alkaline earth metal and thallanium ions.[12] All-solid-state ion-selective electrodes (ISEs) based on two hydrocarbon ionophores, [2.2.2]*p*,*p*,*p*-cyclophane (**1**) and [2.2.2]*m*,*p*,*p*-cyclophane (**3**),

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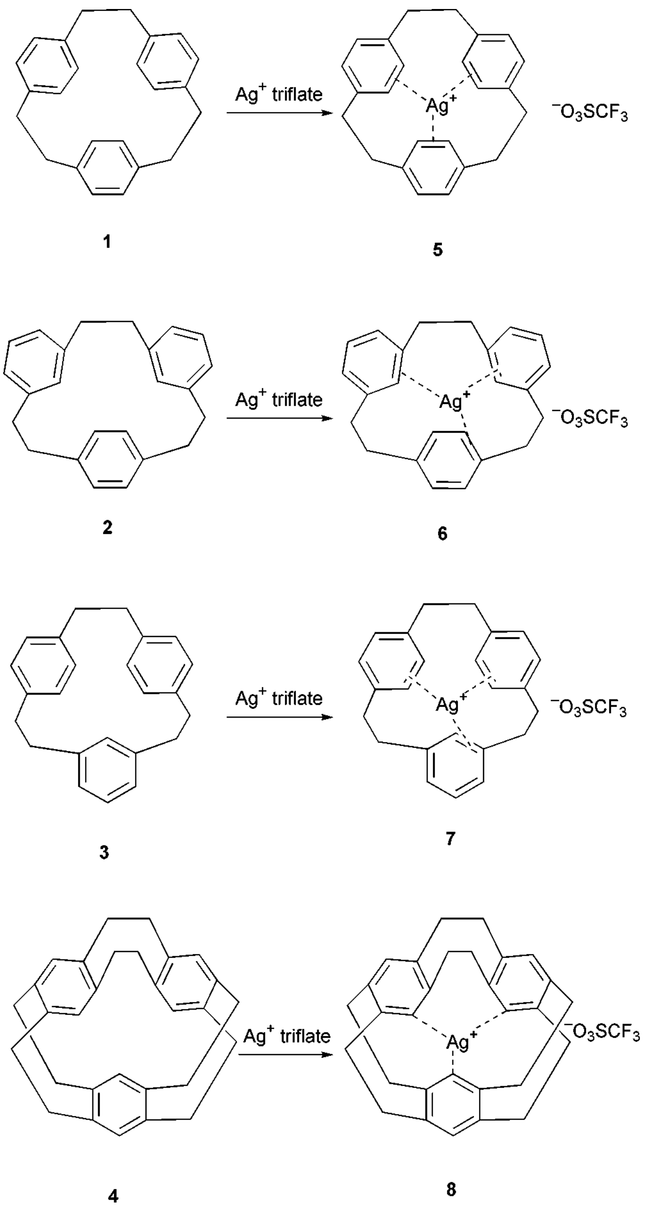


Scheme 1

have recently been reported by us.[13] The selectivities of the two cyclophanes were studied and [2.2.2]*p*,*p*,*p*-cyclophane (**1**) showed superior selectivity for Ag^+ in comparison to the closely related [2.2.2]*m*,*p*,*p*-cyclophane (**3**).

After the synthesis of the first cyclophane ([2.2]-metacyclophane) by Wurtz coupling of 1,3-bis(bromomethyl)benzene in 1899, several different kinds of synthetic methods have been used to produce cyclophanes.[14] The first π-prismand, [2.2.2]*p*,*p*,*p*-cyclophane (**1**), was also prepared by using a modified Wurtz reaction from 1,4-bis(bromomethyl)-benzene.[3] The Wurtz reaction is a very convenient method whenever symmetrical hydrocarbon skeletons are to be constructed. Deltaphane **4** was made by gas-phase dimerisation of benzo[1,2,4,5]dicyclobutene in a stream of nitrogen. It has a very rigid 14-membered hydrocarbon [2.2.2]*m*,*m*,*m*-cyclophane skeleton.[6]

The above-mentioned routes could not be used for the synthesis of [2.2.2]*m*,*m*,*p*-cyclophane (**2**) and [2.2.2]*m*,*p*,*p*-cyclophane (**3**) due to the unsymmetrical nature of these hydrocarbon cyclophanes. By changing the spatial connections of the three benzene rings the 18-membered ring of [2.2.2]*p*,*p*,*p*-cyclophane (**1**) is reduced to the 17-membered ring of [2.2.2]*m*,*p*,*p*-cyclophane (**3**) and to the 16-membered ring of [2.2.2]*m*,*m*,*p*-cyclophane (**2**).[4,5] To achieve the ring closure in the synthesis of these unsymmetrical cyclophanes, a well-known high dilution principle[15] was used. To obtain cyclic structures from suitable cyclic sulfide precursors, a useful synthetic tool, namely sulfone pyrolysis, was developed in the late 1960's and has been tremendously helpful in preparing highly strained (macro)cyclic compounds.[16,17]

After synthesising [2.2.2]*m*,*m*,*p*- and -*p*,*p*,*p*-cyclophanes **2** and **3** we were interested to modify the size of the hydrocarbon cyclophane cavity and to see if other small and strained hydrocarbon structures can act as π-prismands. In this work we report the synthesis of two new π-prismands, which are slightly smaller and more strained analogues of the well-known [2.2.2]*p*,*p*,*p*-cyclophane (**1**). We also report six new crystal structures, including dithiaphanes **12** and **13**, precursors of the hydrocarbons **16** and **17**, which are the ligands for the complexes **18** and **19**.

Results and discussion

Synthesis

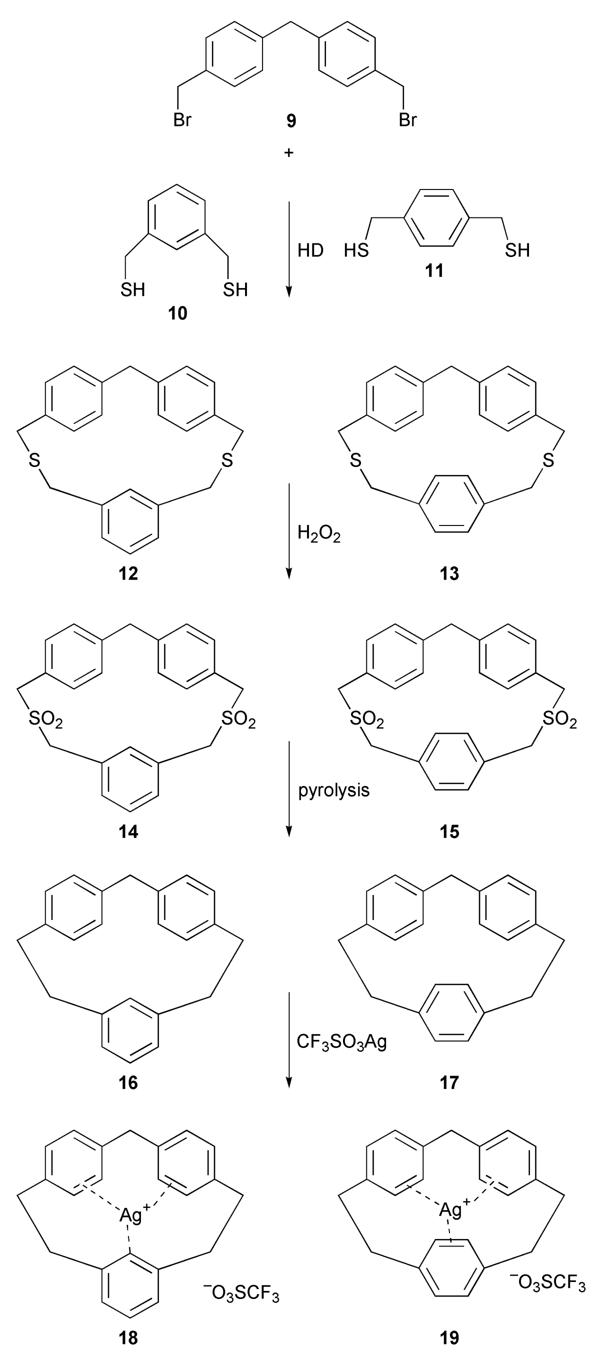
The three-step synthesis (Scheme 2) of [2.2.1]*m*,*p*,*p*-cyclophane (**16**) and [2.2.1]*p*,*p*,*p*-cyclophane (**17**) is based on well-known cyclophane methodology where a sulfide cyclisation is carried out under high dilution conditions, followed by oxidation and sulfone pyrolysis.[15–19]

High dilution cyclisations to form 1,10-dithia[3.3.1]*m*,*p*,*p*-cyclophane (**12**) and 1,10-dithia[3.3.1]*p*,*p*,*p*-cyclophane (**13**) were performed in 62% yield for **12** and 58% for **13**, starting from 4,4′-bis(bromomethyl)diphenylmethane (**9**, *via* bromomethylation[20]) and 1,3-di(thiomethyl)benzene (**10**) or 1,4-di(thiomethyl)benzene (**11**), using toluene as solvent. The cyclic disulfides **12** and **13** were then oxidised by H_2O_2 under reflux to 1,10-dithiatetroxide[3.3.1]*m*,*p*,*p*-cyclophane (**14**) and to 1,10-dithiatetroxide[3.3.1]*p*,*p*,*p*-cyclophane (**15**). **14** and **15** were identified by IR spectroscopy, which revealed strong adsorptions in the $-SO_2-$ region (1100–1330 cm^{-1}). The oxidations gave **14** in 82% and **15** in 69% yields. Disulfones **14** and **15** were pyrolysed to hydrocarbons [2.2.1]*m*,*p*,*p*-cyclophane (**16**) and [2.2.1]*p*,*p*,*p*-cyclophane (**17**) by using a ring oven pyrolysis apparatus operating at 620 °C and $2–4 \times 10^{-5}$ mbar.[5] The yields after isolation were 83% for **16** and 60% for **17**. To study the complexation ability of ligands **16** and **17**, equimolecular amounts of free ligand and silver triflate were mixed using the same procedure as employed by Pierre *et al.*[3] The ^1H NMR spectrum showed a very strong dynamic effect for the complexes **18** and **19**.

X-Ray crystallography

After extensive trials to grow crystals of all the compounds **12**–**19** suitable for X-ray structural analysis, we finally managed to obtain good quality crystals for the bis-sulfides **12** and **13**, hydrocarbons **16** and **17** and hydrocarbon–Ag^+ triflate complexes **18** and **19**. Interestingly, as compounds **12** and **13** are the precursors of hydrocarbons **16** and **17**, which are the free ligands of complexes **18** and **19**, the conformational changes along the synthesis route can be followed. Colourless crystals of the disulfides were obtained by dissolving the crude product **12** in dichloromethane–chloroform (1 : 3) and **13** in CH_2Cl_2. Both solutions were allowed to evaporate very slowly at room temperature, to give small well-diffracting crystals. Crystals of hydrocarbon cyclophane **16** were obtained by slow evaporation of an ethyl acetate solution and those of **17** by slow evaporation of a CH_2Cl_2 solution. The crude complex **18** was recrystallised from dichloromethane–CCl_4 (1 : 1) and crude complex **19** from dichloromethane–ethyl acetate (1 : 1). Both solutions were allowed to evaporate very slowly in the dark at room temperature, to give nicely defined small well-diffracting colourless crystals.

The molecular structures with numbering schemes of **12**, **13** and **16**–**19** are shown in Fig. 1–3. The crystal data and the



Scheme 2

experimental details are given in Table 1 and in the Experimental section.

Disulfide **12** crystallised in an orthorhombic space group (*Pnca*) and **13** in a monoclinic space group ($P2_1/n$) (Fig. 1). In both cases, the bond distances and angles do not show any abnormal values. The two $-CH_2-S-CH_2-$ bridges cause **12** to

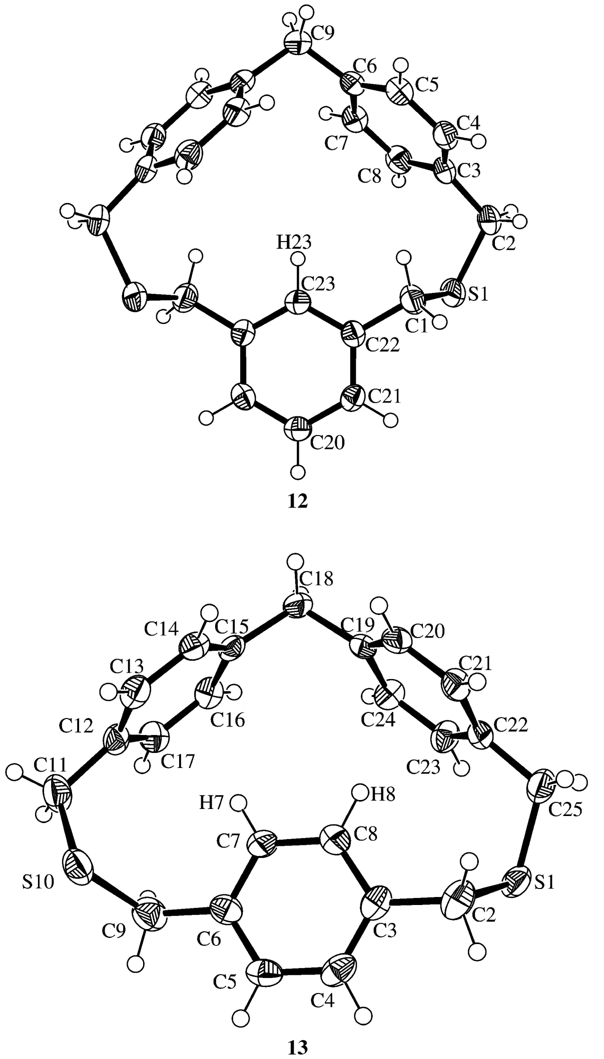


Fig. 1 An ORTEP plot of disulfides **12** and **13** with the numbering scheme. The thermal ellipsoids are shown at the 50% probability level.

Table 1 Crystallographic data for **12**, **13** and **16**–**19**

	12	13	16	17	18	19
Formula	$C_{23}H_{22}S_2$	$C_{23}H_{22}S_2$	$C_{23}H_{22}$	$C_{23}H_{22}$	$C_{23}H_{22}AgCF_3SO_3$	$3C_{23}H_{22}AgCF_3SO_3 \cdot C_{23}H_{22}OAg^+ \cdot CF_3SO_3 \cdot 3C$
M_r	362.53	362.53	298.41	298.41	555.35	2273.41
a/Å	10.3346(3)	10.9684(7)	10.2631(8)	9.6690(6)	11.7142(6)	10.8557(3)
b/Å	10.5105(3)	10.2645(6)	10.4883(5)	9.6690(6)	13.7436(5)	55.1676(18)
c/Å	17.3351(4)	16.6081(10)	15.9213(12)	18.4244(9)	13.8602(6)	15.8584(4)
β/°		91.045(3)				90.312(1)
U/Å^3	1883.0(1)	1869.5(2)	1713.8(2)	1722.5(2)	2231.43(2)	9497.2(5)
Z	4	4	4	4	4	4
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Tetragonal	Orthorhombic	Monoclinic
Space group	*Pnca*	$P2_1/n$	$P2_1nb$	$P4_1$	$P2_12_12_1$	*Cc*
μ/mm^{-1}	0.285	0.287	0.065	0.065	1.046	0.986
Refl. measured/unique	17 140/2219	8351/3234	6372/2556	4592/2672	12 265/3938	22 844/15 280
Refl. used in refinement [$I > 2\sigma(I)$]	1972	2601	2188	2365	3322	13 818
R_{int}	0.035	0.047	0.039	0.039	0.070	0.027
R [$I > 2\sigma(I)$]	0.037	0.063	0.037	0.039	0.044	0.062
wR^2 [$I > 2\sigma(I)$]	0.098	0.125	0.066	0.079	0.063	0.156

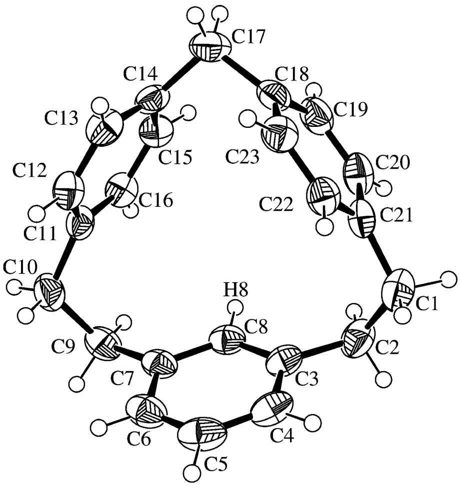
have a conformation in which the *meta*-substituted benzene ring is forced to enter (self-include) the cleft created by the two *para*-substituted benzene rings. The phenylic H23 is located in the center of the cleft and is strongly shielded by the π-electrons of the benzene rings, as can be seen in the ^{1}H NMR spectrum, in which the chemical shift of H23 is 5.31 ppm, showing an upfield shift. The screw-like conformation of the benzene rings makes **12** helically chiral, in the crystalline state it possesses a crystallographic 2-fold symmetry axis, thus showing that this is the *meso* form.

In compound **13**, all the aromatic rings are 1,4-substituted, which leads to a slightly more strained conformation than in the case of **12**. The hydrogen atoms H7 and H8 (Fig. 1) are, in the solid state, located near to the center of the cleft with short non-bonded contacts of 2.57(1) and 2.56(1) Å to the centroids of the *para*-substituted benzene rings. These short contacts observed in the crystal structure can be explained by the packing forces. In the ^{1}H NMR spectrum of **13**, the protons H7 and H8 are slightly less shielded by the π-electrons of the benzene rings than in compound **12**. Due to the dynamic flipping of the benzene ring in solution the four protons show a singlet at δ 5.96.

Hydrocarbon cyclophane **16** crystallised in an orthorhombic space group ($P2_1nb$) and **17** in a tetragonal space group ($P4_1$). A shielding effect by the π-electrons of the benzene rings, similar to but weaker than that discovered in the case of the precursor **12**, can also be seen in the ^{1}H NMR spectrum of **16**. The ^{1}H NMR chemical shift of the H8 resonance is 5.81 ppm and the non-bonded contacts to the centroids of the benzene rings are 3.89(1) and 4.00(1) Å (Fig. 2).

Hydrocarbon **17** is rigid and highly symmetrical like deltaphane **4**.[6] The distances between the centroids of the benzene rings in **17** are 4.19(1), 4.20(1) and 4.20(1) Å, the same distances in deltaphane are 4.06(1), 4.06(1) and 4.11(1) Å. Thus, the structure of **17** is closer to that of deltaphane **4** than to that of [2.2.2]*p,p,p*-cyclophane **1**, where the corresponding distances are 4.34(1), 4.36(1) and 4.37(1) Å. The overall structure of all of these compounds is close to an equilateral triangle.

The structures of the hydrocarbons and the corresponding silver triflate complexes are remarkably similar in both cases (**16** → **18** and **17** → **19**). [2.2.1]*m,p,p*-Cyclophane–Ag$^+$ triflate



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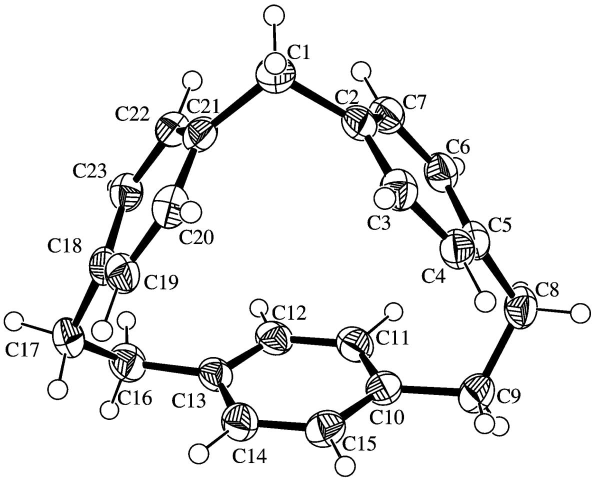


17

Fig. 2 An ORTEP plot of hydrocarbon cyclophanes **16** and **17** with the numbering scheme. The thermal ellipsoids are shown at the 50% probability level.

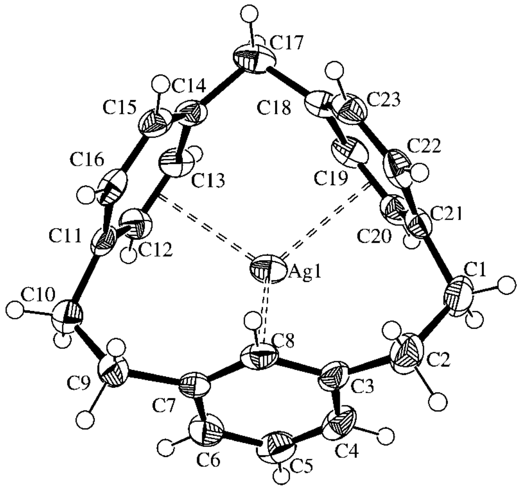
Table 2 Selected non-bonded contacts (Å) and angles (°)

	5	**8**	**18**	**19a**	**19b**	**19c**	**19d**
Ag1–O1	2.32(1)	2.49(1)	2.37(1)	—	2.45(1)	2.53(1)	2.42(1)
Ag1–O10	—	—	—	2.38(1)	—	—	—
Ag1–C4	—	2.48(1)	—	—	—	—	—
Ag1–C8	—	—	2.55(1)	—	—	—	—
Ag1–C13	—	2.41(1)	—	—	—	—	—
Ag1–C20	—	2.41(1)	—	—	—	—	—
Ag1–Cb1	2.50(1)[a]	—	2.56(1)[b]	2.46(1)[c]	2.51(1)[c]	2.48(1)[c]	2.47(1)[c]
Ag1–Cb2	2.53(1)[a]	—	2.52(1)[b]	2.43(1)[c]	2.42(1)[c]	2.40(1)[c]	2.40(1)[c]
Ag1–Cb3	2.53(1)[a]	—	—	2.51(1)[c]	2.56(1)[c]	2.47(1)[c]	2.50(1)[c]
O1–Ag1–C4	—	88.9(1)	—	—	—	—	—
O1–Ag1–C8	—	—	127.6(1)	—	—	—	—
O1–Ag1–C13	—	110.6(1)	—	—	—	—	—
O1–Ag1–C20	—	86.5(1)	—	—	—	—	—
O1–Ag1–Cb1	96.2(1)[a]	—	85.3(1)[b]	96.6(1)[c]	84.1(1)[c]	76.2(1)[c]	98.6(1)[c]
O1–Ag1–Cb2	103.9(1)[a]	—	100.3(1)[b]	100.6(1)[c]	106.3(1)[c]	103.0(1)[c]	99.7(1)[c]
O1–Ag1–Cb3	84.7(1)[a]	—	—	97.7(1)[c]	104.0(1)[c]	112.7(1)[c]	92.6(1)[c]
C4–Ag1–C13	—	120.1(1)	—	—	—	—	—
C4–Ag1–C20	—	119.7(1)	—	—	—	—	—
C13–Ag2–C20	—	117.7(1)	—	—	—	—	—
C8–Ag1–Cb1	—	—	114.4(1)[b]	—	—	—	—
C8–Ag1–Cb2	—	—	118.3(1)[b]	—	—	—	—
Cb1–Ag1–Cb2	122.3(1)[a]	—	104.7(1)[b]	114.5(1)[c]	114.9(1)[c]	126.4(1)[c]	119.1(1)[c]
Cb1–Ag1–Cb3	121.3(1)[a]	—	—	112.7(1)[c]	112.2(1)[c]	111.4(1)[c]	113.8(1)[c]
Cb2–Ag1–Cb3	114.2(1)[a]	—	—	126.4(1)[c]	125.6(1)[c]	117.5(1)[c]	122.6(1)[c]

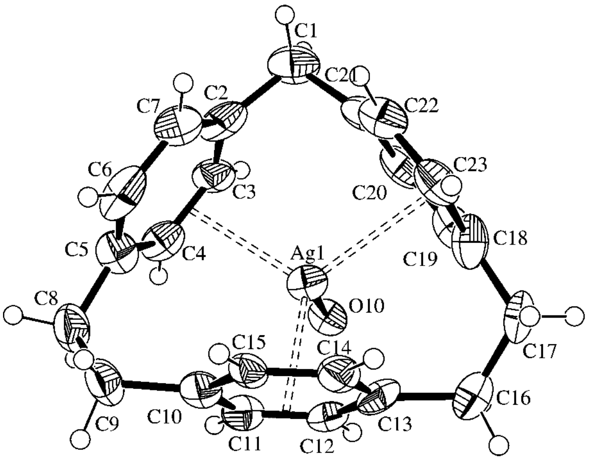
[a] Cb1 = C4–C5, Cb2 = C15–C16, Cb3 = C23–C24. [b] Cb1 = C12–C13, Cb2 = C19–C20. [c] Cb1 = C3–C4, Cb2 = C11–C12, Cb3 = C19–C20.

(**18**) crystallises in an orthorhombic space group ($P2_12_12_1$) and [2.2.1]*p,p,p*-cyclophane–Ag$^+$ triflate (**19**) in a monoclinic space group (*Cc*).

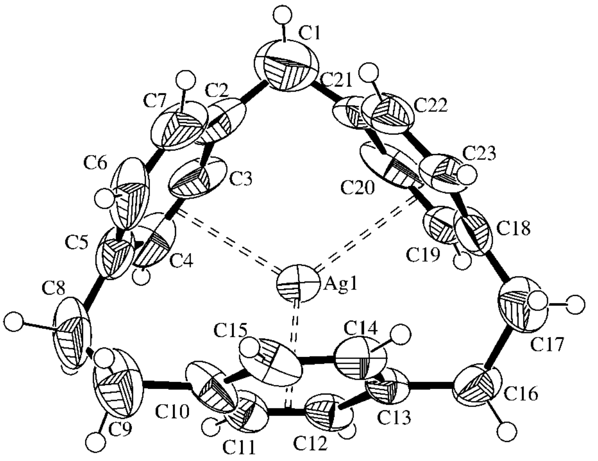
Interestingly, in the case of **18**, the interaction between Ag$^+$ and the cyclophane is accomplished by π-bonding with one of the double bonds in each of the two *para*-substituted phenyl rings and with one carbon atom in the *meta*-substituted phenyl ring (Fig. 3). A similar kind of interaction between Ag$^+$ and one carbon atom in each benzene ring can be found in the deltaphane–Ag$^+$ complex (**8**) where the silver ion lies an average distance of 2.43 Å from the three nearest carbon atoms.[6] So the Ag–C interaction in both **18** and **8** involves primarily the π-electron systems located around one carbon atom of the benzene ring. This is somewhat different from the usual cases, in which coordination is directed to the double bonds of the aromatic systems, as unambiguously shown by the X-ray analyses of arene–silver complexes.[21,22] In [2.2.1]-*p,p,p*-cyclophane–Ag$^+$ triflate (**19**), the silver ion is coordinated to a double bond from each of the benzene rings (Fig. 3) as in [2.2.2]*p,p,p*-cyclophane–Ag complex (**5**) (Table 2). The bonding distances and angles around silver in *para*-connected **19** are surprisingly similar to those of **5**, even though the ring size of the former is reduced by one carbon atom compared to the latter.



18



19a



19b

Fig. 3 An ORTEP plot of Ag complexes **18** and **19** with the numbering scheme. The thermal ellipsoids are shown at the 50% probability level. The triflate anions are omitted for clarity. In the case of **19**, one molecule in which silver is coordinated to water (**19a**) and one of three molecules in which silver is coordinated to triflate (**19b**) are shown.

The coordination sphere around the silver ion in **18** and **19** is supplemented by the O atom of the triflate anion with Ag–O bond lengths equal or slightly shorter than the Ag–C interactions (Table 2). The geometry around the silver ion in **18** and **19**, as in the previously reported **5**–**8**, is a distorted tetrahedron formed by three Ag–π interactions (or Ag–C bonds, as in deltaphane complex **8** and complex **18**) of the cyclophanes and the Ag–O bond to the triflate. Exceptionally, in one of the four crystallographically independent molecules of complex **19**, water is coordinated to the silver ion (Fig. 3). However, all four molecules are only slightly conformationally different from each other, in spite of the water coordination. The bond distances and angles agree extremely well with those of all the reported cyclophane–Ag$^+$ complexes (Table 2 and ref. 5). This rendering of tetrahedral coordination with nearly equal bond distances and angles is very surprising due to the change in the connectivities of the benzene rings, the ring size reduction and flexibility of the ligand cyclophanes. When the ring size is reduced enough (as in deltaphane) or the the benzene rings cannot adopt a suitable orientation (as in **16**), the bonding to the Ag$^+$ ion is accomplished *via* one carbon only instead of the double bond. The general requirement for complexation is that the cavity size of the hydrocarbon cyclophane must be big enough to allow the Ag$^+$ ion to approach close enough to the bonding π-orbitals of the carbon atoms.

Conclusion

The well-known [2.2.2]*p,p,p*-cyclophane (**1**) has an 18-membered ring structure, its isomeric cyclophanes [2.2.2]*m,m,p*- (**2**) and -*p,p,p*-cyclophane (**3**) have 16 and 17 membered rings, respectively, while deltaphane (**4**) (also a [2.2.2]cyclophane) has only 14 members, all are known π-prismands. The new π-prismands [2.2.1]*m,p,p*- (**16**) and -*p,p,p*-cyclophane (**17**) have a different number of carbons in the bridges between the benzene rings. Reduction of an ethylene to a methylene bridge between two of the benzene rings reduces the flexibility of the cyclophane hydrocarbons and makes them more strained, however the ring size is comparable to the [2.2.2]cyclophane π-prismands, the number of carbons in the structures being 16 in **16** and 17 in **17**.

In spite of the less flexible structures of the cyclophanes **16** and **17** the π-basic cavity formed inside these compounds is big enough and suitable for complexing Ag$^+$ ions, since relatively stable complexes with silver triflate were formed and could be isolated in crystalline form. The X-ray structures of the parent hydrocarbons and their Ag$^+$ triflate complexes showed virtually no change in the overall conformation of the cyclophane skeleton during the complexation, which indicates that the short connections between the benzene rings pre-organised the structures for complexation. The pre-organisation coupled with sufficient spatial flexibility and the correct size of the π-basic cavity makes hydrocarbon [2.2.2]- and [2.2.1]-cyclophanes suitable for Ag$^+$ complexation. This

π-prismand behaviour is quite unique and has been shown to be useful in the construction of selective materials[12,13] (*e.g.* electrodes, extracting agents, *etc.*).

We are currently focusing on the syntheses and structural elucidation of even smaller and more strained hydrocarbon cyclophanes in order to survey the limits of π-prismand behaviour.

Experimental

Synthesis

1,10-Dithia[3.3.1]*m,p,p*-cyclophane (12). To 500 ml of refluxing toluene was added dropwise solutions of 530 mg (1.5 mmol) di[4-(bromomethyl)phenyl]methane (**9**) and 250 mg (1.5 mmol) 1,3-di(thiomethyl)benzene (**10**) in 125 ml toluene and 225 mg of KOH in 125 ml abs. ethanol under an inert gas atmosphere over a period of 5.5 h. After that, the mixture was refluxed for an additional 1 h and then cooled to room temperature. The solid inorganic material was filtered off and solvent evaporated. The residue was dissolved in a small amount of chloroform and filtered over silica gel. The solvent was evaporated to yield a pale yellow solid. The crude product was recrystallised from dichloromethane–chloroform (1 : 3) yielding colourless needles. Yield 338 mg (62%). M.p.: 228–229 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.15 (s, 4H), 3.62 (s, 4H), 3.92 (s, 2H) 5.31 (s, 1H), 6.93–7.26 (m, 11H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 34.79, 38.43, 44.11, 128.58, 129.43, 129.76, 131.20, 131.51, 137.75, 140.26, 143.44. GC-MS (EI): *m*/*z* (%) 362 (85).

1,10-Dithia[3.3.1]*p,p,p*-cyclophane (13). To 500 ml of refluxing toluene was added dropwise solutions of 530 mg (1.5 mmol) di[4-(bromomethyl)phenyl]methane (**9**) and 250 mg (1.5 mmol) 1,4-di(thiomethyl)benzene (**11**) in 125 ml toluene and 225 mg of KOH in 125 ml abs. ethanol under an inert gas atmosphere over a period of 6 h. After that, the mixture was refluxed for an additional 2 h and then cooled to room temperature. The solid inorganic material was filtered off and solvent evaporated. The residue was dissolved in a small amount of chloroform and filtered over silica gel. The solvent was evaporated to yield a pale yellow solid. The crude product was recrystallised from dichloromethane yielding colourless needles. Yield 315 mg (58%). M.p.: 110–111 °C ^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.57 (s, 4H), 3.75 (s, 4H), 3.85 (s, 2H), 5.96 (s, 4H), 7.09–7.23 (m, 8H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 36.57, 40.02, 42.98, 127.85, 128.66, 130.00, 138.30, 138.52, 142.24. GC-MS (EI): *m*/*z* (%) 362 (92).

1,10-Dithiatetroxide[3.3.1]*m,p,p*-cyclophane (14). 1,10-Dithia[3.3.1]*m,p,p*-cyclophane (**12**, 300 mg, 0.83 mmol), 16.2 ml glacial acetic acid and 8.1 ml toluene were mixed together and heated to reflux. After that, 1.6 ml 30% H_2O_2 was added and the solution refluxed for an additional 1 h. Addition of H_2O_2 and 1 h refluxing was repeated 3 times. After cooling to room temperature, the mixture was filtered and the white solid product was washed a few times with glacial acetic acid. The crude product was used for the subsequent reaction without any further purification. Yield 288 mg (82%). IR (KBr): ν/cm^{-1} 1300–1100 (SO_2). GC-MS (EI): *m*/*z* (%) 426 (7).

1,10-Dithiatetroxide[3.3.1]*p,p,p*-cyclophane (15). 1,10-Dithia[3.3.1]*p,p,p*-cyclophane (**13**, 300 mg, 0.83 mmol), 16.2 ml glacial acetic acid and 8.1 ml toluene were mixed together and heated to reflux. After that, 1.6 ml 30% H_2O_2 was added and the solution refluxed for an additional 1 h. Addition of H_2O_2 and 1 h refluxing was repeated 3 times. After cooling to room temperature, the mixture was filtered and the white solid product was washed a few times with glacial acetic acid. The crude product was used for the subsequent reaction without any further purification. Yield 243 mg (69%). IR (KBr): ν/cm^{-1} 1300–1100 (SO_2). GC-MS (EI): *m*/*z* (%) 426 (6).

[2.2.1]*m,p,p*-Cyclophane (16). 1,10-Dithiatetraoxide[3.3.1] *m,p,p*-cyclophane (**14**, 50.7 mg, 0.119 mmol) was placed in a quartz tube. The tube was heated to 620 °C under high vacuum (1.23×10^{-5} mbar) using pyrolysis apparatus. During the heating, the product condensed at the other end of the tube. After 2.5 h, the tube was allowed to cool to room temperature and the white product was extracted from the tube with dichloromethane. The solvent was evaporated to yield a white solid. The crude product was recrystallised from ethyl acetate yielding colourless needles. Yield 29.3 mg (83%) M.p.: 129–130 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.63–2.65 (m, 4H), 2.85–2.88 (m, 4H), 3.66 (s, 2H), 5.81 (s, 1H), 6.69–6.71 (m, 4H), 6.80–6.82 (m, 4H), 6.92 (dd, 2H), 7.11 (t, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 35.31, 37.65, 43.13, 124.96, 127.31, 127.41, 128.74, 132.27, 137.83, 139.65, 142.66. HRMS: *m*/*z* (M^+, $C_{23}H_{22}$) calc. 298.171 768; found: 298.172 151.

[2.2.1]*p,p,p*-Cyclophane (17). 1,10-Dithiatetraoxide[3.3.1]-*p,p,p*-cyclophane (**15**, 50.2 mg, 0.118 mmol) was placed in a quartz tube. The tube was heated to 620 °C under high vacuum (3.5×10^{-5} mbar) using pyrolysis apparatus. During the heating the product condensed at the other end of the tube. After 3.5 h the tube was allowed to cool to room temperature and the white product was extracted from the tube with dicloromethane. The solvent was evaporated to yield a white solid. The crude product was recrystallised from dichloromethane yielding colourless needles. Yield 21.2 mg (60%); M.p.: 102–102.5 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.83–2.89 (m, 4H), 2.95–2.98 (m, 4H), 3.60 (s, 2H), 6.54 (s, 4H), 6.73–6.78 (m, 8H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 32.93, 34.50, 42.86, 126.64, 128.27, 129.39, 135.90, 137.44, 141.61. HRMS: *m*/*z* (M^+, $C_{23}H_{22}$) calc. 298.172 067; found: 298.172 151.

[2.2.1]*m,p,p*-Cyclophane–Ag triflate (18). Into a solution of 13.8 mg (0.054 mmol) silver triflate in THF was added a solution of 16.0 mg (0.054 mmol) [2.2.1]*m,p,p*-cyclophane (**16**) in dichloromethane. The mixture was stirred and then allowed to evaporate very slowly to dryness in darkness at room temperature to give a stoichiometric amount of the 1 : 1 silver triflate complex as a whitish crystalline powder. The crude complex was recrystallised from dichloromethane–carbontetrachloride to give small colourless crystals. Crystals were analysed by X-ray diffraction and NMR. ^{1}H-NMR showed a very strong dynamic effect.

[2.2.1]*p,p,p*-Cyclophane–Ag triflate (19). Into a solution of 8.6 mg (0.033 mmol) silver triflate in THF was added a solution of 10.0 mg (0.034 mmol) [2.2.1]*p,p,p*-cyclophane (**17**) in dichloromethane. The mixture was stirred and then allowed to evaporate very slowly to dryness in darkness at room temperature to give a stoichiometric amount of the 1 : 1 silver triflate complex as a whitish crystalline powder. The crude complex was dissolved in dichloromethane–ethyl acetate and allowed to evaporate very slowly in the dark to give small colourless crystals. Crystals were analysed by X-ray diffraction and NMR. ^{1}H-NMR showed a very strong dynamic effect.

X-Ray diffraction

Data were recorded with a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) radiation, $T = 173.0(1)$ K. The data were processed with Denzo.[23] Lp corrections were applied. Structure solutions were done by direct methods[24] and refinements[25] on F^2. The hydrogen atoms were either calculated to be in their idealised positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms (structures of **12**, **18** and **19**) or found from the electron density map and refined isotropically (**13**, **16** and **17**). In the case of **19** there are four crystallographically independent molecules in one asymmetric unit: in three of them a triflate anion is coordinated to silver, while in one molecule the coordination of silver was completed by a water oxygen. Eleven geometrical DFIX restraints were needed to make two of the cyclophane molecules and one triflate anion chemically reasonable. Altogether, 13 temperature factors were equalised. The residual electron density was modelled as six positionally disordered carbon atoms (all of them with an occupancy of 0.5), because any reliable model for probable, but badly disordered ethyl acetate solvent, was impossible to accomplish. However in the end, the convergence of the structure refinement was good (shift/error < 0.01).

CCDC reference numbers 160113–160118. See http://www.rsc.org/suppdata/nj/b1/b102725p/ for crystallographic data in CIF or other electronic format.

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