Concave π-Prismand Hydrocarbon [2.2.2]Cyclophanes and their Crystalline Ag-triflate Complexes

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Abstract. New small concave hydrocarbon cyclophanes were prepared *via* the well-known HD-2SO$_2$-method [2] . The cyclophanes obtained are isomers of the very well-known [2.2.2]*p,p,p*-cyclophane, C$_{24}$H$_{24}$, a π-prismand efficiently complexing Ag$^+$-ion. X-ray crystal structure determinations showed the bis-sulfide **7** (1,10-dithia[3.3.2]*m,p,p*-cyclophane) to be helically chiral and that the conformation of the parent hydrocarbon cyclophane **13** ([2.2.2]*m,p,p*-cyclophane) does not change dramatically upon complexation with the Ag$^+$-ion. The 16- and 17-membered [2.2.2]*m,m,p*- and [2.2.2] *m,p,p*-cyclophane (**15** and **16**) also act as π-prismands and form surprisingly similar crystalline 1:1 Ag-triflate complexes (π-prismates) as the well-known 18-membered *p,p,p*-isomer proved by the X-ray structure analysis.

High dilution principle and its use as a synthetic tool has been widely recognised and was reviewed by Vögtle in 1991 [1]. Particularly cyclophane [2] and supramolecular chemistry [3] have gained a lot owing to the use of HD principle, in spite of the rather poor yields associated with its use. Another very useful synthetic tool, namely sulfone pyrolysis developed in late 1960's, has been of tremendous help in preparing highly strained (macro)cyclic compounds. Sulfone pyrolysis and its use as a synthesis method has been twice reviewed by Vögtle, first in 1979 [4] and then in 1991 [5]. The combination of these two methods into HD-SO$_2$-method (High-dilution cyclisation reaction of a bis-bromide and a bis-thiol to a cyclic **n** membered bis-sulphide followed by oxidation to the corresponding cyclic bis-sulfone and subsequent extrusion of 2 moles of SO$_2$ under vacuum and elevated temperatures leading to a (**n**-2) membered cyclophane), has had a major impact on the synthesis of strained cyclophanes as shown by the pioneering work of Vögtle over more than three decades [6]. Professor Vögtle's impact on the HD-SO$_2$-method has also materialised as inventions of specific equipment designed particularly for this type of synthetic work, these include high dilution apparatus [7] (Fig 1.) and ring oven apparatus for the vacuum pyrolysis of sulfones [8] (Fig. 2.).

During our ten year collaboration with Professor Vögtle the use of the HD- and HD-SO$_2$-method has successfully been employed to the synthesis of helically chiral cyclophanes, bicyclic compounds, extremely strained hydrocarbons, thia- and pyridinophanes and most recently concave hydrocarbon cyclophanes [9–26].

In our recent communication [26] we were able to show that also small concave hydrocarbon cyclophanes other than [2.2.2]*p,p,p*-cyclophane are capable of forming π-complexes with small metal cations, where benzene rings act as π-donors for the complex. This fascinating complexation behaviour is especially effective for [2.2.2]*p,p,p*-cyclophane and related structures [23, 27, 28]. Already in 1981 Pierre *et al.* reported the preparation of the Ag-triflate complex of [2.2.2]*p,p,p*-cyclophane and claimed that it was the first member of a new class of compounds. Owing to its structure and complexation properties they proposed the name π-prismand for such hydrocarbon cyclophanes [28]. Further studies revealed that in the π-prismand-Ag$^+$ complex the silver ion is bonded not to the centre of the benzene ring but to edge of the cavity owing to a specific interaction with one carbon–carbon double bond in each phenyl moiety [29]. Vögtle *et al.* have demonstrated that concave hydrocarbon cyclophanes are able to extract certain metal ions from aqueous phase into a non-polar phase thus acting as ionophores, accompanying sensor studies revealed that a PVC-[2.2.2] *p,p,p*-cyclophane membrane showed a remarkable sensitivity towards silver against alkali metal, alkaline earth metal and thallium ions [23].

During our studies in collaboration on concave hydrocarbons cyclophanes with Professor Vögtle, we noticed that isomeric forms of [2.2.2]*p,p,p*-cyclophane have not been prepared, neither structurally characterised nor their π-complexation surveyed. A very brief structural proof (MS and NMR) for the [2.2.2]*m,m,m*-cyclophane (tri-*m*-xylylene) as a side product of a Wurtz reaction was given by Jenny and Burri in 1966 [30]. In this paper we report the HD-2SO$_2$-synthesis of three hydrocarbon [2.2.2]cyclophanes, namely *m,m,m*-, *m,m,p*- and *m,p,p*-cyclophane, the latter two being previously unknown. The complexation with silver triflate was studied for the *m,m,p*- and *m,p,p*-cyclophanes.

Fig. 1 Photo of the two component high dilution principle (2-C-HD) apparatus designed by Professor Vögtle and marketed [7] by Normag Labor- und Verfahrenstechnik GmbH (Hofheim, Germany) used in this work.
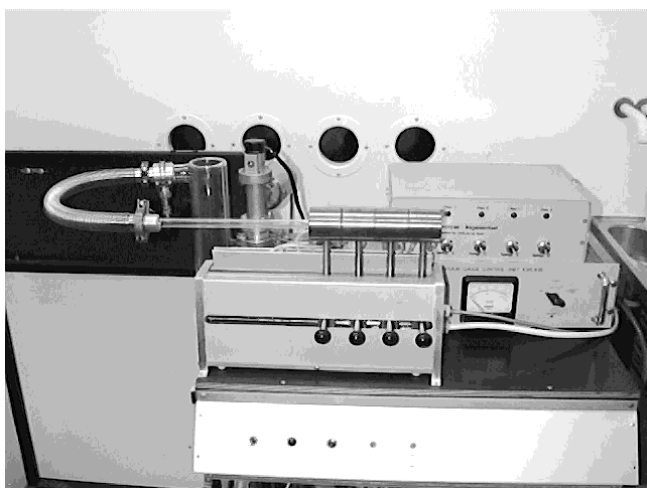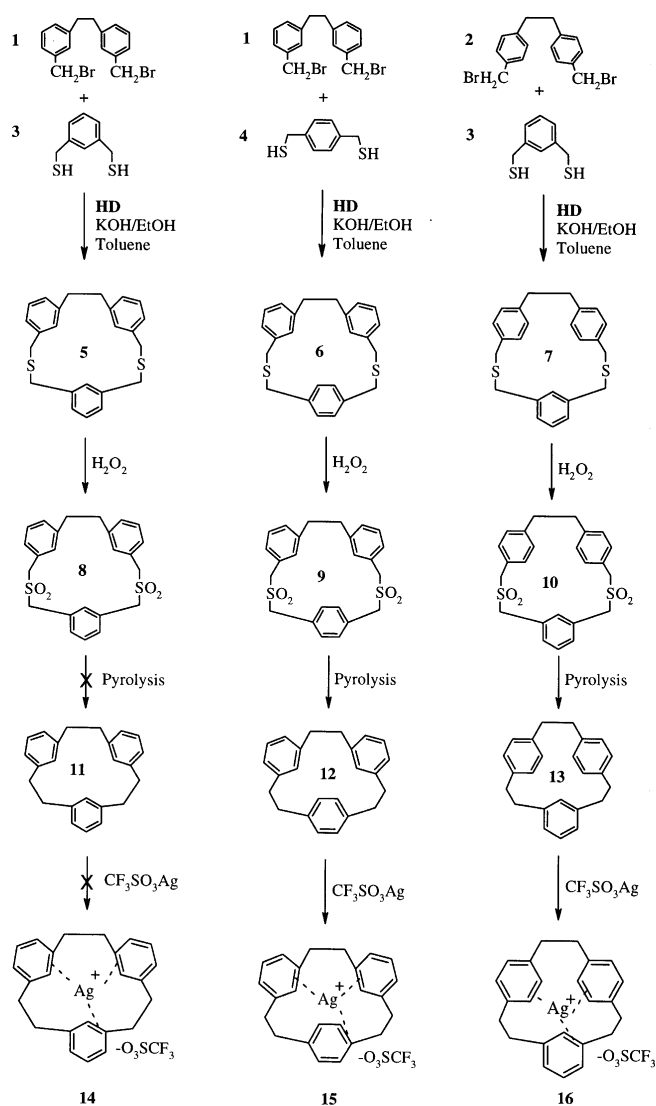

Fig. 2 Photo of the ring oven apparatus for sulfone pyrolysis in our laboratory. This equipment was build at the mechanical workshop of the Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn according to the instructions of Professor Vögtle. The oven system in connected to a vacuum system capable of producing $1-2 \times 10^{-5}$ torr vacuum.

Results and Discussion

The 9-step synthesis (Scheme 1.) of [2.2.2]*m,m,m*- **11**, [2.2.2]*m,m,p*- **12** and [2.2.2.]*m,p,p*-cyclophane **13** is based on well-known cyclophane HD-SO$_2$-methodology where sulfide cyclisation is done under high dilution condition followed by oxidation and sulfone pyrolysis [4, 5, 8, 23].

The key reactions are the high dilution cyclisations of the 1,2-bis(3-(bromomethyl)phenyl)ethane (**1**) (six step synthesis from 3-bromobenzaldehyde [31]) or 1,2-bis(4-(bromomethyl)phenyl)ethane (**2**) (*via* bromomethylation of 1,2-diphenylethane [32]) with 1,3-di(thio-methyl)benzene (**3**) or 1,4-di(thiomethyl)benzene (**4**) to form 1,10-dithia[3.3.2]*m,m,m*-cyclophane (**5**) or 1,10-dithia[3.3.2]*p,m,m*-cyclophane (**6**), 1,10-dithia[3.3.2] *m,p,p*-cyclophane (**7**) respectively, using toluene as a solvent. The cyclisation to **5** gave 57%, to **6** 80% and to **7** 44% yield. The cyclic disulfides **5**, **6** and **7** were then oxidized by H$_2$O$_2$ under reflux to 1,10-dithiatetroxide[3.3.2]*m,m,m*-cyclophane (**8**), 1,10-dithiatetroxide[3.3.2]*p,m,m*-cyclophane (**9**) and to 1,10-dithiatetroxide[3.3.2]*m,p,p*-cyclophane (**10**). The disulfones **9** and **10** were identified by IR spectroscopy which showed strong absorption at the -SO$_2$-band (1 100 – 1 330 cm^{-1}). The yields for the oxidation reactions were 33, 64 and 85% for **8**, **9** and **10**, respectively. The disulfones **9** and **10** were pyrolysed to the desired cyclophanes, namely [2.2.2]*m,m,p*-cyclophane (**12**) and [2.2.2]*m,p,p*-cyclophane (**13**) by using the ring oven pyrolysis apparatus [8, Fig 1b] at 600 °C and $1-2\times 10^{-5}$ torr. Unfortunately due to a technical fault in the vacuum system during the pyrolysis of disulfone **8** the vacuum was not high enough (2×10^{-4} torr), and the desired cyclophane **11** could not be isolated, only black tar was obtained. The yield after isolation was 56% for **12** and 69% for **13** (no -SO$_2$ absorption was detected in IR spectra). The complexation abilities of the cyclophanes **12** and **13** were surveyed by the same procedure used by Pierre *et al*. for the preparation of the silver triflate complex of [2.2.2]*p,p,p*-cyclophane [28]. The complexation was done by mixing equimolar amounts of free ligand (**12** or **13**) in dichloromethane and silver triflate in tetrahydrofuran. The mixture was stirred and allowed to evaporate very slowly to dryness in the darkness at room temperature. The complexation was proved by the changed NMR-spectra, thus giving complexes **15** and **16** (Scheme 1.).

After extensive attempts to grow crystals of all the compounds **5**–**16** (the bis-sulfones are nearly insoluble) suitable for X-ray structural analysis [33], we finally managed to obtain poor quality crystals for the bis-sulphide **7** and good quality crystals for **13**, **15** and **16**. Interestingly compound **7** is the precursor of the hydrocarbon **13**, which is the free ligand of complex **16**, thus conformational changes along the synthesis
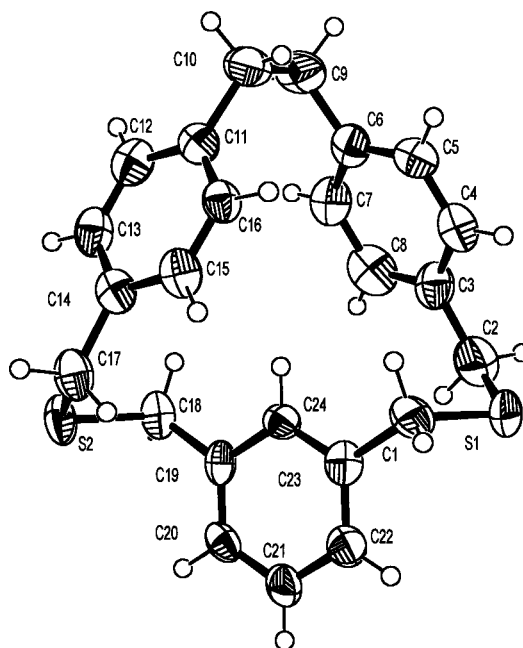
Scheme 1

Fig. 3 ORTEP [38] plot with labeling scheme for 1,10-di-thia[3.3.2] *m,p,p*-cyclophane (**7**). The thermal ellipsoids are shown at 50% probability level.
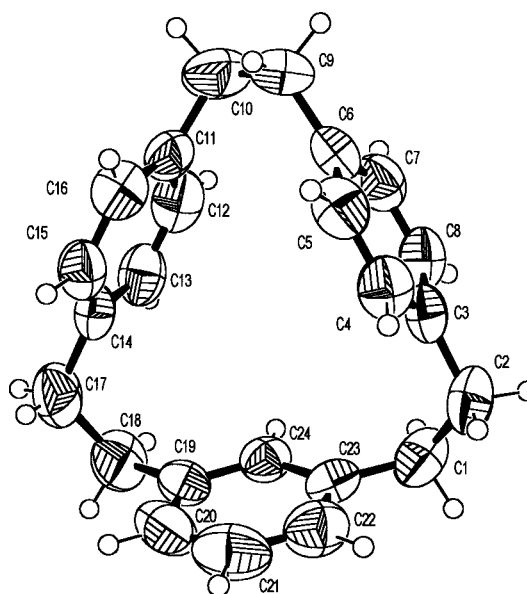
Fig. 4 ORTEP [38] plot with labeling scheme for [2.2.2] *m,p,p*-cyclophane (**13**) (molecule A). The thermal ellipsoids are shown at 50% probability level.

route could be followed. The colourless crystals of **7** were obtained by solvent diffusion of petrol ether (40–60) into diethyl ether, those of **13** by slow evaporation of *n*-hexane. The crude complex **15** was dissolved in dichloromethane-diethyl ether (1:6) and crude complex **16** in hexane-dichloromethane (1:1). Both were allowed to evaporate very slowly in the darkness, the first one in refrigerator while the other one at room temperature, to give nicely defined small well-diffracting colourless crystals.

The molecular structures with numbering schemes of **7** and **13** are shown in Fig. 3 and 4, respectively. The crystal data and the experimental details are given in Table 1 and in the experimental section.

The bis-sulfide **7** crystallised in a monoclinic space group with one molecule in the unit cell. The bond distances and angles do not show any abnormal values. The two -CH$_2$–S–CH$_2$- bridges cause the dithiaphane **7** to have a conformation in which the *meta*-substituted

benzene ring (C19–C24) is forced to enter (self-include) the cleft created by the two *para*-substituted benzene rings (C3–C8 and C11–C16, Fig. 1.). The benzene H-atom between the -CH$_2$–S–CH$_2$- bridges (H24, Fig. 1.) is located in the center of the cleft with short non-bonded contact distances to the centroids of the *para*-substituted benzene rings. The hydrogen at C24 is strongly shielded by the π-electrons of the benzene rings, and it

Table 1 Experimental crystallographic data for **7**, **13**, **15** and **16**

Compound	7	13	15	16
Formula	$C_{24}H_{24}S_2$	$C_{24}H_{24}$	$C_{24}H_{24}Ag$; CF_3SO_3	$C_{24}H_{24}Ag$; CF_3SO_3
M_r	376.55	312.43	569.37	569.37
A/Å	10.391(4)	12.411(1)	14.233(2)	8.736(1)
b/Å	10.211(3)	16.947(1)	10.134(1)	20.272(2)
c/Å	18.949(9)	17.541(1)	15.885(4)	26.112(2)
α/°	90	90	90	90
β/°	91.15(3)	90	97.29(2)	90
γ/°	90	90	90	90
V/Å^3	2010(1)	3689(1)	2272(1)	4624(1)
Z	4	8	4	8
D_{calc}/Mg m^{-3}	1.24	1.13	1.66	1.64
μ/mm^{-1}	0.27	0.47	1.03	1.01
λ/Kα	0.71073	1.54184	0.71073	0.71073
$F(000)$	800	1344	1152	2304
Space group	$P2_1/n$	$Pca2_1$	$P2_1/c$	$Pbca$
Crystal size/mm	$0.4 \times 0.2 \times 0.2$	$0.4 \times 0.4 \times 0.2$	$0.3 \times 0.15 \times 0.1$	$0.25 \times 0.25 \times 0.25$
θ-range for latt. measurement/°	8–13	10–15	8–14	8–13
θ range/°	2–27	3–75	2–25	2–25
H range	$0 \rightarrow 13$	$0 \rightarrow 15$	$0 \rightarrow 16$	$0 \rightarrow 10$
k range	$0 \rightarrow 13$	$0 \rightarrow 21$	$0 \rightarrow 12$	$0 \rightarrow 24$
λ range	$-24 \rightarrow 24$	$-1 \rightarrow 21$	$-18 \rightarrow 18$	$-1 \rightarrow 31$
Variation of std. reflections	3%	2%	6%	5%
Refl. Measured	4616	4174	4161	4258
No. of unique reflections	4376	4174	3990	4066
Refl. Used in refinement[$I > 2\sigma(I)$]	1897	1992	2581	2636
No. of parameters	235	434	298	298
Max. in final $\Delta\rho$/e Å^{-3}	0.77	0.15	0.52	0.62
R_{int}	0.159	0.000	0.036	0.013
R	0.131	0.042	0.038	0.035
R_w	0.279	0.099	0.076	0.094
Weighting scheme	A = 0.0750	A = 0.0587	A = 0.0443	A = 0.0596

$w = 1/[s^2(F_o{}^2) + (A \times P)^2]$ where
$P = (Max\ (F_o{}^2, 0\ ) + 2 \times F_c{}^2)/3.$

can be very clearly seen from the NMR-spectrum. The ^{1}H NMR chemical shift of H24 is 5.83 ppm, this up-field shift can be qualitatively explained by the X-ray structure of **7** where this particular H-atom is only 3.33 and 3.34 Å (Table 2.) from the centers of the 1,4-substi-tuted aromatic rings. The above screw-like conforma-tion of the benzene rings makes **7** helically chiral, in crystal both *P*- and *M*-forms are present [9, 20].

The uncomplexed hydrocarbon **13** crystallised in an acentric orthorhombic space group with two conforma-tionally slightly different molecules in the asymmetric unit (Table 2.). All attempts to solve the structure in a centric space group failed. The overall structure of **13** and the corresponding silver triflate complex **16** are sur-prisingly similar, indicating that **13** is so strained that it can make only small conformational adjustments dur-ing the complexation. The deviations of the distance related conformational parameters of molecule A from those of **16** are only ca. 0.1 Å, the torsion angles show deviations less than 3.2 degrees (Table 2., Fig. 4. and 6.). Due to the conformational difference between the molecules A and B the above deviations are bigger for molecule B. In the complex **16** the conformation of molecule B is not observed, so the complex formation

stabilises the conformation close to that of molecule A. An interesting feature in the ^{1}H NMR spectra of the ligands **12** and **13** and their precursors **6**, **7**, **9** and **10** is the clearly shielded resonances of the protons at posi-tion 24 in the *meta*-subsituted rings. Generally, although weaker than for dithiaphane **7** the increased shielding of the chemical shifts of the aryl protons can be similar-ly as for **7** explained by the aromatic ring current ef-fects induced by the other aryl rings of the cyclophanes. The chemical shifts for **12** and **13** are 6.18 and 6.22 ppm, respectively (5.83 ppm for **7**). Due to the silver(I) complexation these chemical shifts are changed to the values 6.31 (**15**) and 6.02 (**16**), respectively. The oppo-site signs of these changes suggest that these effects are caused not only by variations in π-electron densities but also some conformational changes joint with the com-plexation.

The molecular structures with numbering schemes of **15** and **16** are shown in Fig. 5 and 6, respectively. The X-ray structures of [2.2.2]*p*,*p*,*p*-cyclophane silver perchlorate [34] and triflate [35] showed that the 4-co-ordinate silver ion is bonded to three carbon–carbon double bonds in each phenyl moiety and the anionic oxygen (perchlorate or triflate). The bond distances from

Table 2 Selected non-bonded contact distances, torsion angles and coordination bond distances and angles for **7**, **13** , **15** and **16**

Non-Bonded Contact Distances [a]	**7**	**13** [b]	**15**	**16**
Ct1…Ct2	4.34(1)	4.20(1)/4.27(1)	5.14(1)	4.11(1)
Ct1…Ct3	5.29(1)	4.70(1)/4.55(1)	4.69(1)	4.82(1)
Ct2…Ct3	5.32(1)	4.76(1)/4.63(1)	4.61(1)	4.93(1)
H24…Ct1	3.33(1)	–	–	–
H24…Ct2	3.34(1)	–	–	–
C3…C14	–	5.47(1)/5.59(1)	–	5.31(1)
C3…C15	–	–	5.86(1)	–
C3…C22	–	–	3.07(1)	–
C3…C23	–	3.08(1)/3.02(1)	–	3.09(1)
C6…C11	–	2.91(1)/2.94(1)	–	2.86(1)
C7…C11	–	–	3.18(1)	–
C14…C19	–	3.11(1)/3.04(1)	–	3.15(1)
C15…C19	–	–	3.04(1)	–
C4…C15	–	4.90(1)/5.50(1)	–	4.67(1)
C5…C16	–	3.66(1)/3.75(1)	–	3.45(1)
Torsion angles [c]	**7**	**13**	**15**	**16**
C23–C1–S1–C2	64.0(1)	–	–	–
A–C1–C2–C3	–	– 62.2(1)/–55.0(1)	63.0(1)	– 62.3(1)
C1–S1–C2–C3	51.9(1)	–	–	–
B–C9–C10–C11	–	43.4(1)/–28.9(1)	64.4(1)	37.3(1)
C19–C18–C17–C	–	61.4(1)/58.1(1)	– 61.4(1)	64.6(1)
C19–C18–S2–C17	63.5(1)	–	–	–
C18–S2–C17–C14	52.5(1)	–	–	–
Bond distance [d]	**7**	**13**	**15**	**16**
Ag1–O1	–	–	2.350(3)	2.431(4)
Ag1–Cb1	–	–	2.518(4)	2.583(4)
Ag1–Cb2	–	–	2.532(4)	2.584(4)
Ag1–Cb3	–	–	2.474(4)	2.595(4)
Bond angle [e]	**7**	**13**	**15**	**16**
O1–Ag1–Cb1	–	–	108.3(1)	85.4(1)
O1–Ag1–Cb2	–	–	109.8(1)	117.9(1)
O1–Ag1–Cb3	–	–	100.6(1)	113.8(1)
Cb1–Ag1–Cb2	–	–	88.7(1)	124.2(1)
Cb1–Ag1–Cb3	–	–	127.0(1)	129.7(1)
Cb2–Ag1–Cb3	–	–	121.9(1)	88.7(1)

[a] in Ångströms, Ct defines the centroid of a benzene ring, Ct1= C3 – C8; Ct2 = C11– C16 and Ct3 = C19 – C24.
[b] molecule A/molecule B   [c] in degrees, A = C23 for **13** and **16**, C22 for **15**; B = C6 for **13** and **16**, C7 for **15**; C = C15 for **13** and **16**, C14 for **15**.   [d] in Ångströms, Cb defines the centroid of a bond, Cb1 = C7/C8 for **15** and C4/C4 for **16**; Cb2 = C11/C16 for **15** and C14/C15 for **16**; Cb3 = C23/C24 for **15** and C19/C24 for **16**.   [e] in degrees, Cb as above.
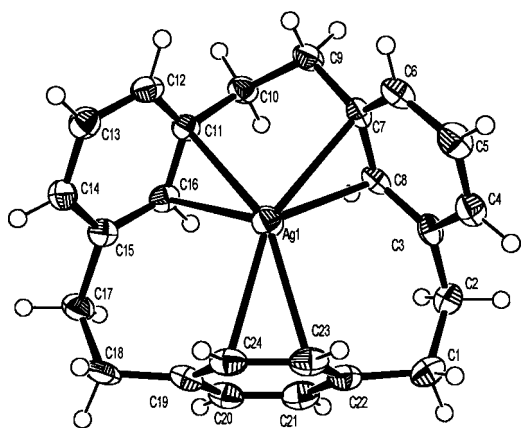

Fig. 5 ORTEP [38] plot with labeling scheme for [2.2.2] *m,p,p*-cyclophane-Ag-triflate (**15**). The thermal ellipsoids are shown at 50% probability level. The coordinated triflate anion has been omitted for clarity.

Fig. 6 ORTEP[38] plot with labeling scheme for [2.2.2] *m,p,p*-cyclophane-Ag-triflate (**16**). The thermal ellipsoids are shown at 50% propability level. The coordinated triflate anion has been omitted for clarity.
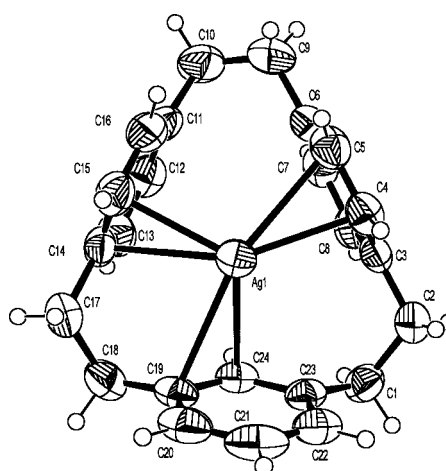
the centroids of the double bonds are, 2.497 (Cb1, see definition in Table 2.), 2.530 (Cb2) and 2.531 Å (Cb3) while the Ag–O bond is 2.315 Å. The bond angles are O1–Ag–Cb1, 96.24; O1–Ag–Cb2, 103.86; O1–Ag–Cb3, 84.73; Cb1–Ag–Cb2, 122.27; Cb1–Ag–Cb3, 122.26 and Cb2–Ag–Cb3, 114.15°. The non-bonded contact distances between the bridge head carbons are 2.902 for C3···C22, 2.934 for C6···C11 and 2.918 Å for C14···C19 [35]. The structures of the complexes **15** and **16** are remarkable similar (Table 2.) to that of [2.2.2] *p,p,p*-cyclophane silver triflate [35], keeping in mind that it has 18-membered ring while the new *m,m,p*-cyclophane has only 16-membered and *m,p,p*-cyclophane 17-membered ring. The reduction of the ring size is caused by the change of the spatial connections inside the isomeric $C_{24}H_{24}$ skeleton. Although the formal ring size is reduced from *p,p,p*- to *m,m,p*-isomer, the cavities or clefts in all the three isomers are nearly equal in size, defined by the distances between the centroids of the benzene rings and torsions angles (Table 2.). The size of the complexing cleft is defined by the non-bonded contact distances between carbon atoms, which are the closest (bonded) to the silver ion. The different spatial orientation of the phenyl rings in each isomer can readily be seen from the torsion angles of the -CH$_2$–CH$_2$--bridging bonds which are 63.0(1) (C22–C1–C2–C3), 64.4(1) (C7–C9–C10–C11) and –61.4(1)° (C15–C17–C18–C19) for **15**, –62.3(1) (C23–C1–C2–C3), 37.3(1) (C6–C9–C10–C11) and 64.6(1)° (C14–C17–C18–C19) for **16**, and 23 (C22–C1–C2–C3), 52 (C6–C9–C10–C11), 49° (C14–C17–C18–C19) for the [2.2.2]-*p,p,p*-cyclophane-Ag-triflate [35].

In all of the Ag-complexes the silver ion is located in the cleft or pocket created by the three phenyl rings. The interaction (bonding) between the silver and the cyclophane is accomplished by the π-bonding with one of the double bonds in each phenyl ring. The coordination sphere around the silver ion is supplemented by the O-atom of the triflate anion with slightly shorter bond lengths as for the carbons (Table 2.). The bonding distances are surprisingly similar, ca. 2.5 for **15**, 2.6 for **16** and 2.5 Å for the [2.2.2]*p,p,p*-cyclophane-Ag-triflate [35] in spite of the ring size reduction. These results confirm that the silver ion is indeed not bonded to the centre of the benzene rings and the ring size reduction, and conformational isomerism do not exclude the π-complex formation between the title cyclophanes and silver ions.

Due to the very small amounts of the prepared cyclophanes **11**, **12** and **13** (< 30 mg), we are currently further developing the synthesis in order to get different isomers (particularly the *m,m,m*-isomer) and more material for complexation and extraction experiments. The interesting spectroscopic properties of the π-prismates will be surveyed in a more detailed (dynamic) NMR experiments, which are currently in progress.

Experimental

Syntheses

1,10-Dithia[3.3.2]m,m,m-cyclophane (**5**)

To the refluxing solution of 125 ml of toluene were dropped a solution of 275 mg (0.75 mmol) of 1,2-bis(3-(bromomethyl)phenyl)ethane (**1**), 125 mg (0.75 mmol) 1,3-di(thiomethyl)benzene (**3**) in 100 ml toluene and of 112 mg of KOH in 100 ml abs. ethanol under an inert gas atmosphere in a period of 6 h. After that the mixture was refluxed additional 1h and cooled to room temperature. The inorganic solid material was filtered and solvent was evaporated. The residue was dissolved in a small amount of chloroform and filtered over silicagel. The solvent was evaporated to yield a white solid product. Yield 160 mg (57%). – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 3.03 (s, 4H), 3.44 (s, 4H), 3.50 (s, 4H), 5.98 (s, 1H), 6.88 (s, 2H), 6.98 (d, 2H), 7.16 (d, 2H), 7.17 (d, 2H), 7.19 (t, 2H), 7.23 (t, 1H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 34.12, 35.29, 37.04, 126.80, 127.09, 127.55, 128.62, 128.94, 129.95, 130.26, 138.30, 138.55, 141.00 – GC-MS (EI): *m/z* (%) = 376 (95).

1,10-Dithia[3.3.2]p,m,m-cyclophane (**6**)

To the refluxing solution of 125 ml of toluene were dropped solutions of 275 mg (0.75 mmol) of 1,2-bis(3-(bromomethyl)phenyl)ethane (**1**), 125 mg (0.75 mmol) 1,4-di(thiomethyl)benzene (**4**) in 100 ml toluene and of 112 mg of KOH in 100 ml abs. ethanol under an inert gas atmosphere in period of 6 h. After that the mixture was refluxed additional 1h and cooled to room temperature. The inorganic solid material was filtered and solvent was evaporated. The residue was dissolved in a small amount of chloroform and filtered over silicagel. The solvent was evaporated to yield a white solid product. Yield 226 mg (80%). – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 2.83 (s, 4H), 3.52 (s, 4H), 3.66 (s, 4H), 6.40 (s, 2H), 6.76 (t, 2H), 7.07 (d, 4H), 7.15 (s, 4H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 35.48, 36.21, 36.27, 125.91, 127.56, 127.89, 128.86, 129.90, 136.82, 137.74, 140.81 – GC-MS (EI): *m/z* (%) = 376 (81).

1,10-Dithia[3.3.2]m,p,p-cyclophane (**7**)

To the refluxing solution of 500 ml of toluene were dropped solutions of 550 mg (1.5 mmol) of 1,2-bis(4-(bromo-methyl)-phenyl)ethane (**2**), 250 mg (1.5 mmol) 1,3-di(thio-methyl)-benzene (**3**) in 125 ml toluene and of 225 mg of KOH in 125 ml abs. ethanol under an inert gas atmosphere in period of 6 h. After that the mixture was refluxed additional 1h and cooled to room temperature. The inorganic solid material was filtered and solvent was evaporated. The residue was dissolved in a small amount of chloroform and filtered over silicagel. The solvent was evaporated to yield a white solid product. The crude product was recrystallized from diethyl ether by diffusion with petrol ether yielding colourless needles. Yield 250 mg (44%). – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 3.02 (s, 4H), 3.30 (s, 4H), 3.48 (s, 4H), 5.83 (s, 1H), 6.90–7.08 (m, 8H), 7.22 (d, 2H), 7.27 (t, 1H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 33.08, 34.30, 36.70, 127.12, 128.99, 129.16, 129.18, 132.40, 134.38, 137.38, 139.29. – GC-MS (EI): *m/z* (%) = 376 (97)

1,10-Dithiatetroxide[3.3.2]m,m,m-cyclophane (**8**)

470 mg (1.25 mmol) of 1,10-dithia[3.3.2]*m,m,m*-cyclophane (**5**), 25 ml glacial acetic acid and 12.5 ml toluene were mixed and heated to reflux. After that 2.5 ml 30% H_2O_2 was added three times and refluxed 1h after each addition (total 3 h). After cooling to room temperature mixture was filtered and the white solid material (product) was washed few times with glacial acetic acid. The product was used for the following reaction without any further purification. Yield 184 mg (33%). – GC-MS (EI): *m/z* (%) = 312 (100), 440 (< 0.01).

1,10-Dithiatetraoxide[3.3.2]p,m,m-cyclophane (**9**)

163 mg (0.43 mmol) of 1,10-dithia[3.3.2]*p,m,m*-cyclophane (**6**), 9.0 ml glacial acetic acid and 4.5 ml toluene were mixed and heated to reflux. After that 0.9 ml 30% H_2O_2 was added three times and the solution refluxed 1h after each addition (total 3 h). After cooling to room temperature the mixture was filtered and the white solid material (product) was washed few times with glacial acetic acid. The product was used for the following reaction without any further purification. Yield 122 mg (64%). – IR (KBr): v/cm^{-1} = 1 100–1 330 (SO$_2$). – GC-MS (EI): *m/z* (%) = 312 (100), 440 (<1).

1,10-Dithiatetroxide[3.3.2]m,p,p-cyclophane (**10**)

90 mg (0.24 mmol) of 1,10-dithia[3.3.2]*m,p,p*-cyclophane (**7**), 5.0 ml glacial acetic acid and 2.5 ml toluene were mixed and heated to reflux. After that 0.5 ml 30% H_2O_2 was added three times and the solution refluxed 1h after each addition (total 3 h). After cooling to room temperature the mixture was filtered, and the white solid material (product) was washed few times with glacial acetic acid. The product was used for the following reaction without any further purification. Yield 90 mg (85%). – IR (KBr): v/cm^{-1} = 1 100–1 330 (SO$_2$). – ^{1}H NMR (500 MHz, DMSO): δ/ppm = 3.00 (s. 4H), 3.94 (s. 4H), 4.14 (s. 4H), 5.78 (s. 1H), 6.98–7.18 (m. 8H), 7.36–7.44 (m. 3H). – ^{13}C NMR (126 MHz, DMSO): δ/ppm = 35.59, 55.56, 57.35, 126.33, 128.09, 128.95, 129.28, 129.68, 130.64, 134.64, 140.92 – GC-MS (EI): *m/z* (%) = 312 (55), 440 (< 0.01).

[2.2.2]m,m,m-Cyclophane (**11**)

50 mg (0.11 mmol) of 1,10-dithiatetroxide[3.3.2]*m,m,m*-cyclophane (**8**) was placed at the bottom of a quartz tube (diameter 10 mm, length 500 mm). Tube was heated to 610 °C *in vacuo* (2×10^{-4} torr) using the ring oven sulfone pyrolysis apparatus (Fig. 2.). During the heating very small amount of the product condensed at the other end of the tube. After 40 minutes of pyrolysis the amount of the product did not increase (checked visually), the tube was left to cool to room temperature and the product was extracted with dichloromethane. The solvent was evaporated but no product was obtained, only black tar at the bottom of the quartz tube could be obtained (decomposed starting material). No Yield.

[2.2.2]m,m,p-Cyclophane (**12**)

50 mg (0.114 mmol) of 1,10-dithiatetroxide[3.3.2]*p,m,m*-cyclophane (**9**) was placed at the bottom of a quartz tube (diameter 10 mm, length 500 mm). The tube was heated to 600 °C in high vacuum (2×10^{-5} torr) using the ring oven sulfone

pyrolysis apparatus (Fig. 2.). During the heating the product condensed at the other end of the tube. After 40 minute pyrolysis the tube was left 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 product. Yield 19.9 mg (56%). – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 2.80–2.86 (m. 8H), 2.88 (s. 4H), 6.18 (s. 2H), 6.58 (s. 4H), 6.97 (d. 2H), 7.05 (d. 2H), 7.18 (t. 2H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 34.09, 36.90, 37.70, 125.63, 125.74, 127.91, 128.34, 129.99, 137.62, 140.08, 140.43. – HRMS *m/z* (M$^+$, C$_{24}$H$_{24}$): Calcd: 312.18780 Found: 312.18773

[2.2.2]m,p,p-Cyclophane (**13**)

60 mg (0.136 mmol) of 1,10-dithiatetroxide[3.3.2]*m,p,p*-cyclophane (**10**) was placed at the bottom of a quartz tube (diameter 10 mm, length 500 mm). The tube was heated to 600 °C in high vacuum (1.5×10^{-5} torr) using the ring oven sulfone pyrolysis apparatus (Fig. 2.). During the heating the product condensed at the other end of the tube. After 40 minute pyrolysis the tube was left 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 product. The crude product was recrystallized from *n*-hexane yielding colourless needles. – Yield 29.2 mg (69%), *m.p.* 108–109 ºC. – IR (KBr): v/cm^{-1} = 1100–1330 (SO$_2$) absorption not detected. – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 2.80–2.89 (m. 8H), 2.94 (s. 4H), 6.22 (s. 1H), 6.67 (s. 8H), 7.06 (dd. 2H), 7.24 (t. 1H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 35.00, 35.92, 36.30, 125.47, 127.80, 127.94, 128.87, 132.31, 137.12, 137.14, 140.24. – HRMS *m/z* (M$^+$, C$_{24}$H$_{24}$): Calcd: 312.18780 Found: 312.18777.

[2.2.2]m,m,p-Cyclophane-Ag-triflate (**15**)

To a solution of 15.7 mg (0.06 mmol) of silvertriflate in THF was added a solution of 19.0 mg (0.06) mmol [2.2.2]*m,m,p*-cyclophane (**12**) in dichloromethane. The mixture was stirred and 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–di ethyl ether and was allowed to evaporate very slowly in the darkness in a refrigerator to give small colourless crystals. – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 2.94 (s. 8H), 2.97 (s. 4H), 6.31 (s. 2H), 6.94 (s. 4H), 7.26 (d. 2H), 7.30 (d. 2H), 7.58 (t. 2H). – ^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 32.97, 36.68, 37.41, 123.26, 126.54, 126.81, 128.28, 132.10, 134.77, 139.66, 141.82.

[2.2.2]m,p,p-Cyclophane-Ag-triflate (**16**)

To a solution of 19.8 mg (0.08 mmol) of silvertriflate in THF was added a solution of 25.0 mg (0.08) mmol [2.2.2]*m,p,p*-cyclophane (**13**) 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 hexane–dichloromethane and was allowed to evaporate very slowly in the darkness at the room temperature to give small colourless crystals. *m.p.* 158–159 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm = 2.86 (s. 4H), 2.94 (s. 4H), 3.08 (s. 4H), 6.02 (s. 1H),

6.98 (s. 4H), 7.05 (s. 4H), 7.29 (s. 2H), 7.65 (s. 1H). –
^{13}C NMR (126 MHz, CDCl$_3$): δ/ppm = 33.97, 35.11, 35.91,
123.44, 124.76, 127.41, 128.84, 131.97, 137.62, 138.82,
139.52.

X-ray Structure Analysis

General: Enraf-Nonius CAD4 diffractometer (**7**, **15** and **16**),
Enraf-Nonius MACH3 diffractometer (**13**), *Lp* correction, psi
scan absorption correction (not used for **7**) [T_{max} 93.86%, T_{min}
61.12% for **7**; T_{max} 89.10%, T_{min} 87.98% for **13**; T_{max} 81.65%,
T_{min} 75.02% for **15** and T_{max} 74.16 %, T_{min} 71.24 % for **16**.
Data collection temperature: RT (**7**,**13** and **16**), – 100 °C for
15. Structure solution by direct methods (SHELXS [36] for **7**
and **13**, SIR92 [37] for **15** and **16**) and refinement on F^2
(SHELXL-97[1] [36]). Hydrogens calculated to their idealised
positions and refined as riding atoms with isotropic thermal
parameter (1.2 × B(C)). Extinction coefficient 0.00069(8) and
absolute structure parameter –0.5(19) for **13**.

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