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Baskets, covered baskets, and basket balls: corannulene based cyclophanes as fullerene mimics

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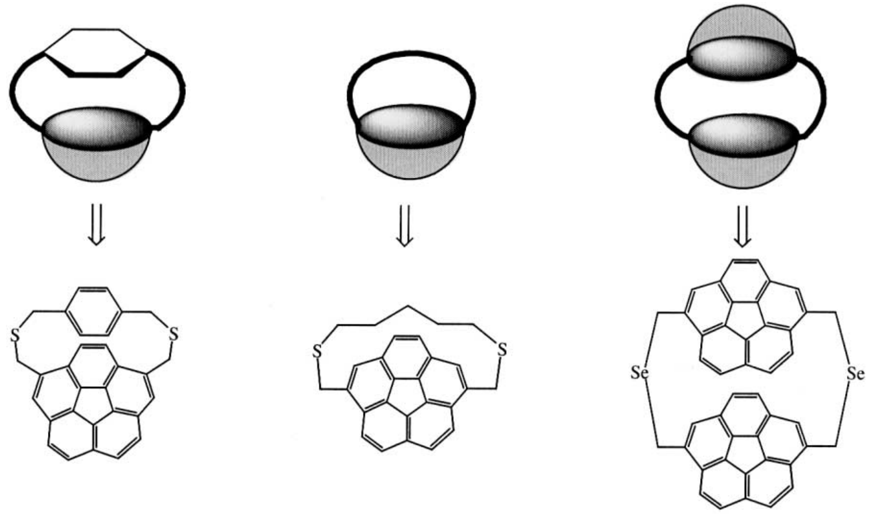
Abstract—Three cyclophanes based on corannulene have been synthesized. Aryl and alkyl groups have been strapped across the corannulene nucleus and a dimeric corannulene cyclophane has been prepared. The structure and conformational analysis of these compounds have been elucidated by NMR and ab initio quantum mechanical methods. The specific NMR effect of the corannulene system on the adjacent nuclei is discussed. These cyclophanes exhibit novel structures and are prototypical fullerene mimics. © 2001 Published by Elsevier Science Ltd.

Fullerene fragments,[1] such as corannulene, inspire the design of several cyclophane motifs:[2] covered baskets,[3] *ansa* baskets[4] and 'basket balls'[5] (Fig. 1). Corannulene based cyclophanes may serve as mimics and receptors of fullerenes as well as precursors to endohedral fullerene complexes. Receptors of fullerenes based on calixarenes,[6] cyclotriveratralenes,[7] and γ-cyclodextrins[8] have been previously reported. Specifically, Rubin has reported a cyclophane that may serve as a precursor to an endohedral fullerene complex.[9] Recently, we have developed a high yielding solution phase synthesis of corannulene and alkyl derivatives that can serve as building blocks for the construction of these fullerene cognates.[10] Using these building blocks, cyclophanes (**1**–**3**) based on corannulene have been synthesized and exhibit interesting structure and NMR properties. The diametrically opposed relationship between the 1 and 6 positions of corannulene constrains the linker to cross directly above the corannulene nucleus and offers a good way to probe the properties of the concave face of the bowl. Although



1 **2** **3**

Figure 1. Cyclophane motifs: covered-basket, ansa-basket and basket-ball.

Keywords: cyclophanes; corannulene; fullerene mimic.

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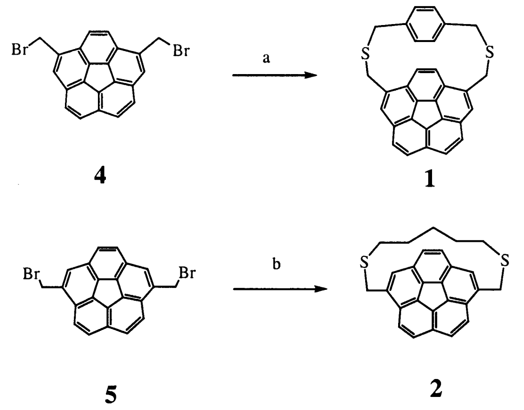


Scheme 1. (a) 1,4-Bis(mercatomethyl)benzene, KO^tBu; (b) 1,5-pentanedithiol, Cs_2CO_3.

crystals suitable for X-ray analysis remain elusive, the structures and conformational analysis of these cyclophanes have been assigned using NMR in conjunction with high level ab initio computations.

1. Syntheses

The corannulene building block for **1** is 2,5-bis(bromomethyl)corannulene in distinction from that for cyclophane **2**, which is 1,6-bis(bromomethyl)corannulene. Syntheses of cyclophanes **1** and **2** are accomplished in one ring forming reaction (Scheme 1). Generation of the benzylic bromides is accomplished by NBS bromination of 2,5-dimethylcorannulene or 1,6-dimethylcorannulene to yield the bisbromomethyl compounds (**4** and **5**) in high yield. The covered basket **1**, previously reported,[3] is synthesized by slow addition of 1,4-bis(mercaptomethyl)benzene and **4** to a solution of potassium *t*-butoxide in THF. Using a similar method, the ansa basket **2** is synthesized by slow addition of 1,5-pentanedithiol and **5** to a solution of cesium carbonate in THF.

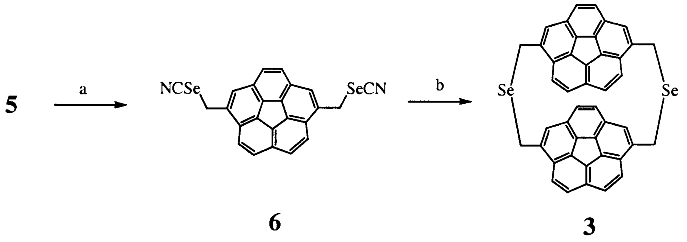
Synthesis of the basket ball **3** is not as straightforward. Attempts to prepare the dithiol from **5** were uniformly unsuccessful. Reaction of **5** with excess Na_2S, thioacetate followed by hydrolysis or thiourea followed by hydrolysis did not liberate the dithiol. Also, generation of the dithiol in situ, by reaction of **5** with KSCN followed by reaction with $NaBH_4$ in the presence of **5**, did not afford a dimeric structure. Efforts were then refocused toward the synthesis of the related seleno-bridged dimer. Following a report in the literature for the synthesis of selenocyclophanes by in situ generation of selenide anions opened an alternative route (Scheme 2).[11] Reaction of **5** with potassium selenocyanate yields the bis(selenocyanomethyl)corannulene (**6**). Generation of the selenide anions necessary for dimerization in situ was accomplished by reaction of **6** with $NaBH_4$ in the presence of **5** to yield the dimeric cyclophane **3**, a compound of poor solubility in most organic solvents.

2. Computational methods

Structural computations of all compounds were performed using hybrid density functional methods (HDFT) using GUASSIAN98.[12] The HDFT method employed Becke's 3 parameter functional[13] in combination with the Perdew and Wang 1991 gradient-corrected nonlocal correlation functional,[14] B3PW91. Dunning's correlation consistent basis set, cc-pVDZ,[15] a [3s2p1d] contraction of a (9s4p1d) primitive set, was employed. These levels of theory have been previously shown to be reliable for structural determination in these types of compounds.[16,17]

3. Structure and dynamics

Using a combination of NMR and ab initio computations, the structures of cyclophanes **2** and **3** have been unambiguously assigned. Similar to the structure of **1**, the solution structures of **2** and **3** are consistent with the linker being held



Scheme 2. (a) KSeCN; (b) **5**, $NaBH_4$.

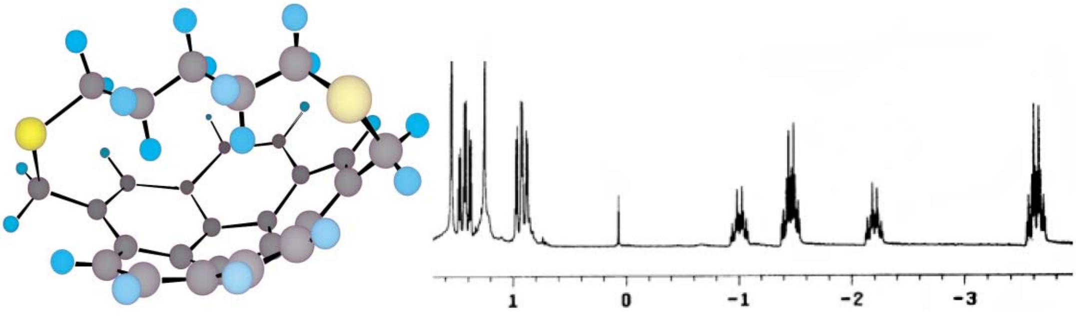
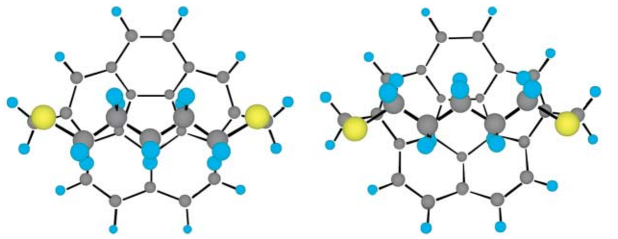


Figure 2. Ansa-basket staggered structure and ^1H NMR spectrum of the methylene region.



(0.0 kcal/mol) (1.3 kcal/mol)

2a **2b**

Figure 3. Calculated structures of cyclophanes **2a** and **2b** (relative energies in parentheses).

in a rigid conformation directly above the corannulene nucleus. This arrangement effectively locks the corannulene nucleus and stops the bowl-to-bowl inversion displayed by simple corannulene derivatives.

The solution structure of **2** indicates a very rigid conformation with the alkyl linker strapped directly across the corannulene bowl (Fig. 2). The number of signals, multiplicity and coupling constants in the ^{1}H NMR indicate a C_s symmetric structure with the alkyl strap in an extended 'all-*anti*' conformation across the corannulene nucleus. The chemical shifts of the four inner sets of protons (C, D, E and F) are all shifted upfield compared to 1,5-pentanedithiol. The furthest upfield signal (−3.6 ppm) is shifted approximately 5 ppm upfield from the same proton signal in 1,5-pentanedithiol. The geminal protons of each methylene are diastereotopic and the higher field signal of each set methylene protons is attributed to the proton pointing down into the corannulene bowl.

Ab initio calculations (B3PW91/cc-pVDZ) were carried out on two different C_s symmetric isomers of **2** (**2a** and **2b**, Fig. 3). Both structures exhibit an extended *anti* conformation along the alkyl chain and the corannulene fragments have identical bowl depths (0.96 Å). Calculations predict **2a** to be more stable than **2b** by 1.3 kcal/mol. The *endo* protons of the aromatic ring of cyclophane **1** are calculated to be 2.3 Å above the plane of the rim carbons and experience an upfield shift of 5.4 ppm. Protons D (Fig. 4) in **2a** are 2.5 Å above the plane of the rim carbons and experience a similar upfield shift (5 ppm) to cyclophane **1**.

The diastereotopicity of the methylene protons indicates that there is no 'jump rope' motion of the chain around the corannulene nucleus on the NMR timescale.[18] In addition, the large difference in chemical shifts between diastereotopic methylene protons suggests that the alkyl strap is held dominantly in one conformation above the corannulene nucleus. The magnitude of the coupling between the protons of the alkyl strap reflects a rigid all trans conformation. Each of the four upfield signals is split into an apparent quartet of triplets with coupling constants of 12.5 and 4.2 Hz. If one assumes the geminal coupling constant and the two trans vicinal coupling constants (calculated dihedrals of ~180°) are the same, 12.5 Hz, and the two gauche vicinal coupling constants (calculated dihedrals of ~60°) are the same, 4.2 Hz, an apparent quartet of triplets is produced. If rapid conformational changes in the pentane linker were occurring, the segregation of large and small coupling constants would likely not be observed.

The calculated bowl depth of the corannulene fragment in **2a** is significantly increased relative to the calculated bowl depth of free corannulene (0.96 vs. 0.88 Å). The increase in bowl depth is associated with approximately 5 kcal/mol of strain energy in the corannulene nucleus.[19] Although extrusion of the sulfur atoms of **2** to yield an all carbon linker across the corannulene nucleus (**7**) has not yet been achieved, (Scheme 3), computations predict a dramatic increase in the bowl depth (1.20 Å) upon contraction to a 7 carbon linker. The associated strain increase in the corannulene nucleus of **7** is estimated to be roughly 30 kcal/mol.[4]

As in the previous corannulene cyclophanes (**1** and **2**) the diastereotopicity of the methylene protons of cyclophane **3**, observed as a two doublets in the ^{1}H NMR (Fig. 5), indicates that rotation around the C(Ar)–C(CH_2) bond has been restricted and thus the corannulene nuclei are locked into one bowl shaped conformation. The dimeric structure can

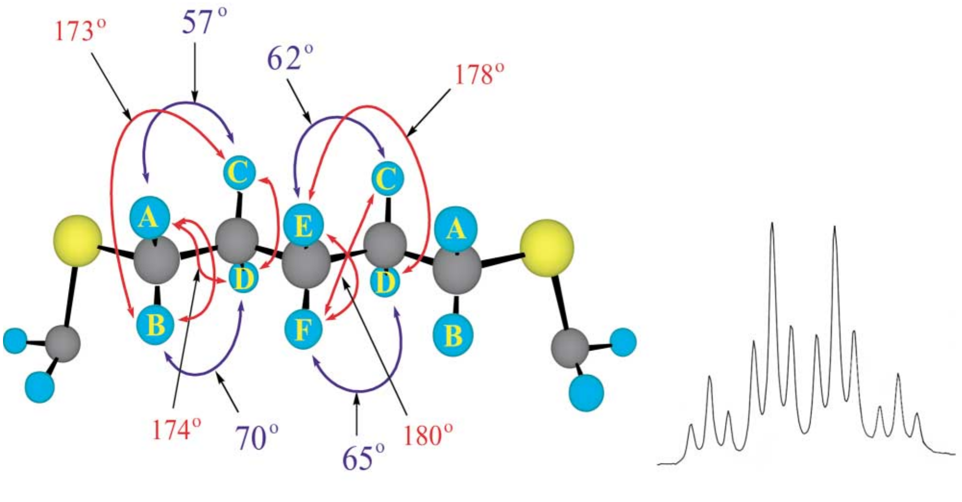
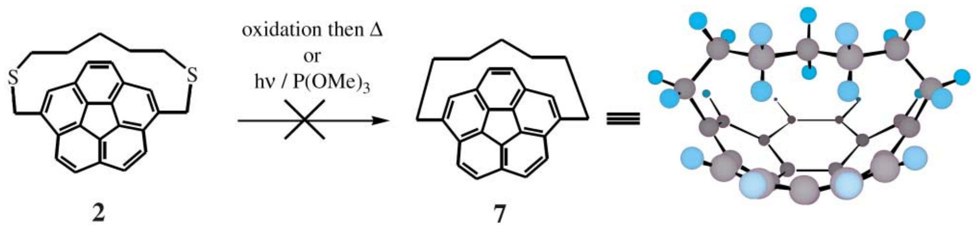


Figure 4. Calculated dihedral angles and ^{1}H NMR signal of proton D centered at −3.6 ppm.



Scheme 3.

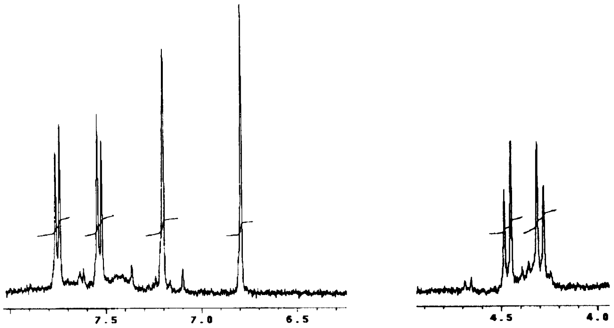


Figure 5. ^{1}H NMR of basket-ball cyclophane **3** aromatic region (left) and aliphatic region (right).

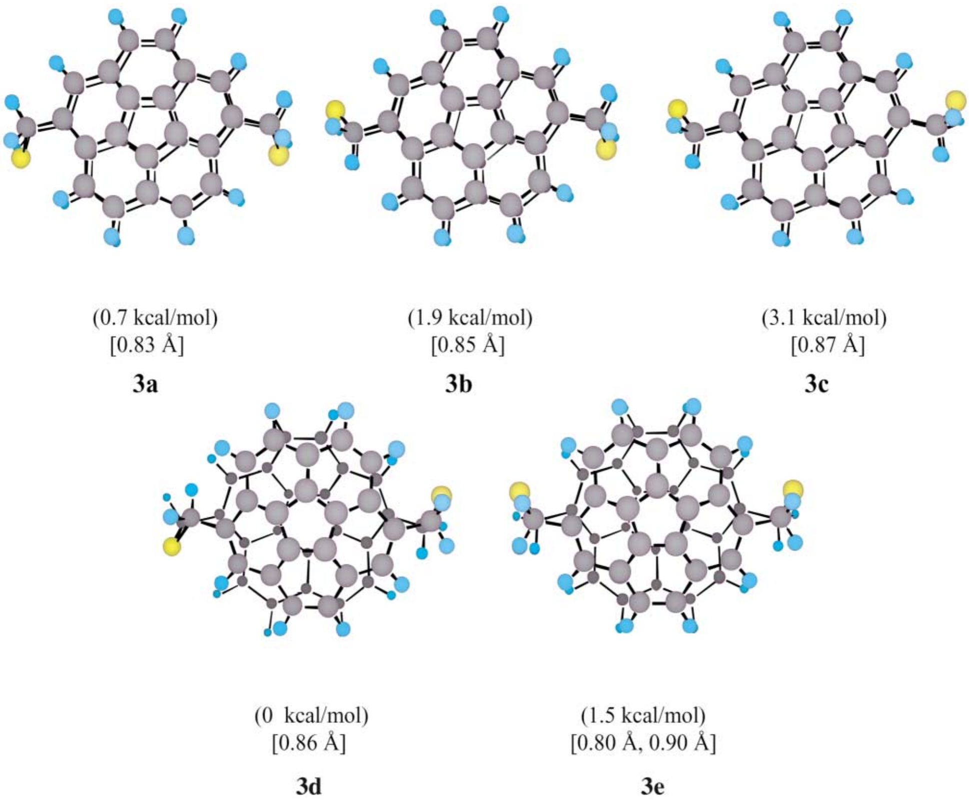


Figure 6. Calculated structures for the *syn* (**3a–c**) and *anti* (**3d**, **e**) conformers of the sulfur analog basket-ball cyclophane **3** with relative energies in parentheses and bowl depths in brackets.

form isomeric structures in which either the corannulene nuclei are parallel (C_{2v} like) or *anti* parallel (C_{2h} like) (Fig. 6). The ^{1}H NMR indicates the presence of two isomers in a ratio of approximately 10:1 and mass spectral data has confirmed the molecular weight of the compound. Ab initio (B3PW91/cc-pVDZ) computations of five sulfur analogues of **3**,[†] three *syn* isomers (**3a–c**) and two *anti* isomers (**3d** and **3e**), suggest **3d** is the lowest energy conformation.

The experimentally determined major isomer in the selenium bridged cyclophane is shown to be an anti conformer by nOe difference experiments; Irradiation of the signal at 6.8 ppm enhances the signals at 7.2 and 7.6 ppm. Alternatively, irradiation of the signal at 7.6 ppm enhances in the signals at 7.8 and 6.8 ppm. The multiplicity and nOe's to the methylene protons for the signals at 7.2 and 7.8 ppm allows for assignment of all the aromatic signals (Fig. 7). The calculated C_i symmetric structure for the sulfur analogue (**3d**) shows close contacts (3.3 Å) between the aromatic

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[†] Selenium is replaced by sulfur in the computations to minimize computational time.

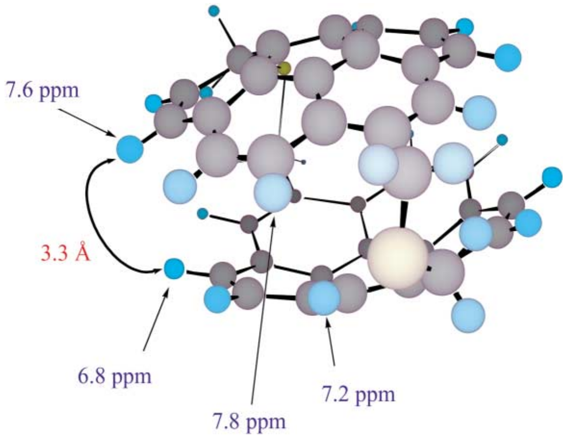

Figure 7. Calculated distance between aromatic protons.

protons of the upper corannulene nucleus to the lower corannulene nucleus. The proximity of the corannulene nuclei of **3d** may explain the inability of dimer formation in the case of sulfur as the linker. The arrangement of the corannulene fragments **3d** is the same as the arrangements of corannulene fragments in C_{60}. Looking down the five-fold axis of C_{60} or mirror plane of the C_{2h} like cyclophanes, the five-membered rings are anti with respect to each other. Bowl depths for **3a–d** (0.83, 0.85, 0.87, 0.86 Å, respectively) are calculated to be slightly shallower than the calculated bowl depth of free corannulene. The two corannulene nuclei in **3e** are symmetry independent and have bowl depths of 0.80 and 0.90 Å.

4. Conclusions

The cyclophane motifs presented in this work have been translated into novel structures. Synthesis of corannulene derivative in large quantity allows for their use as building blocks for larger structures. Development of the technology to assemble these building blocks into cyclophanes has produced the first round of derivatives with cavities. With this technology in hand, the door for host–guest chemistry using corannulene derivatives has been opened. Synthesis and possible complexation studies of cyclophanes with larger cavities are already under investigation.

5. Experimental

5.1. General data

^{1}H and ^{13}C NMR spectra were recorded on Varian (Mercury 300/400 MHz; Unity 500 MHz) or General Electric (QE 300 MHz) spectrometers with tetramethylsilane as the internal standard. Low-resolution mass spectral analyses were performed in the EI-mode on a HP GC/MS 59970-spectrometer. High resolution mass spectra were obtained from the University of California Riverside mass spectrometry facility in the FAB or DEI mode.

5.2. Techniques and materials

All experiments were carried out under argon in freshly distilled solvents under anhydrous conditions unless otherwise noted. Commercial chemicals were used as supplied. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials, unless otherwise stated. Characterization of all new compounds was done by ^{1}H and ^{13}C NMR as well as by mass spectroscopy. Preparative column chromatography was performed with silica gel (230–425 mesh) from Fisher Scientific Company. Thin layer chromatography (TLC) was performed on aluminum backed silica gel 60 F_{254} plates from Alltech. 1,6-Dimethylcorannulene, 2,5-dimethylcorannulene, 1,6-bis(bromomethyl)corannulene, and 2,5-bis(bromomethyl)corannulene were prepared by our earlier reported methods.[10,19]

5.2.1. 2,5-Dimethylcorannulene/1,4-bis(mercaptomethyl)-benzene cyclophane (1). 1,4-Bis(mercaptomethyl)benzene (41.9 mg, 0.246 mmol) was added to dry THF (50 mL) under argon. To the THF solution was added, via syringe, potassium *t*-butoxide [540 μL(1 M in THF), 0.540 mmol]. The solution was stirred at ambient temperature for 20 min while under argon. To the THF solution was added a solution of 2,5-bis(bromomethyl)corannulene (**7**) (107.2 mg, 0.246 mmol) in 10 mL dry THF over 5 min. The solution was stirred for 1 h at ambient temperature, dilute to 100 mL with benzene and extracted with water (3×50 mL). The benzene layer was dried over magnesium sulfate and evaporated in vacuo. Purification of the residue by flash chromatography on silica gel (1/1: benzene/hexane) afforded a pale yellow solid (40 mg, 40%). ^{1}H NMR ($CDCl_3$; 500 MHz): δ 1.89 (s, 2H, H_a), 2.64 (d, J=14.5 Hz, 2H, H_d), 3.31 (d, J=14.5 Hz, 2H, H_c), 4.45 (d, J=12.5 Hz, 2H, H_f), 4.68 (d, J=12 Hz, 2H, H_e), 6.75 (s, 2H, H_b), 7.62 (s, 2H, H_g), 7.73 (s, 2H, H_h), 7.91 (s, 4H, H_i and H_j). ^{13}C NMR ($CDCl_3$; 125 MHz) δ 32.39, 34.05, 122.42, 125.47, 126.48, 127.32, 128.99, 129.04, 130.12, 130.40, 130.96, 134.21, 135.09, 135.22, 135.65, 137.96. HRMS-FAB *m/z* MCs+= 577.0085; expected= 577.0061.

5.2.2. 1,5-Pentanedithiol/1,6-bis(bromomethyl)corannulene cyclophane (2). To a dry THF (10 mL) suspension of Cs_2CO_3 (0.2125 g, 1.101 mmol), a solution of 1,5-pentanedithiol (0.0150 g, 0.1101 mmol) and 1,6-bis(bromomethyl)-corannulene (0.0480 g, 0.1101 mmol) in dry THF (15 mL) was added under argon over 18 h. The mixture was then diluted with benzene (10 mL), extracted three times with a saturated solution of $NaHCO_3$ (25 mL), then water (25 mL), dried ($MgSO_4$) and evaporated to a yellow residue. The residue was purified by flash chromatography on silica gel (1/1:cyclohexane/benzene) to yield a pale yellow solid (0.035 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ −3.64 (qt, J=12.5, 4.2 Hz, 2H), −2.20 (qt, J=12.5, 4.2 Hz, 1H), −1.46 (qt, J=12.5, 4.2 Hz, 2H), −1.01 (qt, J=12.5, 4.2 Hz, 1H), 0.93 (td, J=12.5, 4.2 Hz, 2H), 1.42 (td, J=12.5, 4.2 Hz, 2H), 4.15 (d, J=12.5 Hz, 2H), 4.62 (d, J=12.5 Hz, 2H), 7.60 (s, 2H), 7.82 (s, 2H), 7.89 (d, J=9.0 Hz, 2H), 8.19 (d, J=9.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.9, 28.0, 31.6, 33.9, 126.9, 127.0, 127.2, 129.4, 131.1, 131.7, 132.1, 135.5, 136.4, 136.6, 137.6. HRMS 410.1160 actual 410.1163 calcd.

5.2.3. 1,6-Bis(selenocyanomethyl)corannulene (6). To a degassed solution of ethanol (100 mL) and dioxane (50 mL) was added potassium selenocyante (0.13 g, 0.92 mmol) and 1,6-bisbromomethylcorannulene (0.10 g, 0.23 mmol). The solution was refluxed for 30 min then allowed to cool to ambient temperature. The yellow solution was diluted with chloroform (35 mL) and THF (35 mL) and extracted three times with water (125 mL), dried ($MgSO_4$) and evaporated to a yellow powder (0.11 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.92 (s, 4H), 7.81 (s, 2H), 7.84 (s, 2H), 7.94 (AB, J^3=8.7 Hz, 2H), 8.00 (AB, J^3=8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 94.4, 123.6, 124.2, 127.4, 127.8, 128.5, 128.7, 130.7, 133.6, 135.6, 135.9, 136.3.

5.2.4. [3.3] Seleno/1,6-dimethylcorannulene cyclophane (3). To a degassed, stirred solution of $NaBH_4$ (0.0174 g, 0.4569 mmol) in THF (60 mL) and ethanol (60 mL), a solution of 1,6-bis(bromomethyl)corannulene (0.066 g, 0.152 mmol) and 1,6-bis(selenocyanomethyl)corannulene (0.074 g, 0.152 mmol) in THF (50 mL) is added over 15 h and stirred an additional 2 h. The reaction is diluted with THF (100 mL) and chloroform (100 mL), extracted with water (100 mL) three times and evaporated to yield a pale yellow solid. The solid is triturated with ethanol (10 mL) then methylene chloride (10 mL) to yield an off-white solid (0.021 g, 20%) which is only sparingly soluble in chloroform, methylene chloride, THF or tetrachloroethane at ambient temperature. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ @ 70°C) δ 4.30 (d, J^2=14.4 Hz, 4H), 4.47 (d, J^2=14.0 Hz, 4H), 6.80 (s, 4H), 7.21 (s, 4H), 7.53 (d, J^3=8.8 Hz, 4H), 7.75 (d, J^3=8.4 Hz, 4H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$ @ 70°C) δ 25.8, 124.2, 126.3, 126.4, 126.5, 127.8, 128.4, 128.7, 131.9, 132.5, 133.9, 135.2. MS *m/z* (relative intensity): 706.24 ($M-6^+$, 712.18 ($M-2^+$, 70), 712.24 (M^+, 100).

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