4:6 allowed two-dimensional COSY and ROESY ^{1}H NMR spectroscopy to be carried out at 260 K (uncorrected temperature) and the spectra obtained were fully consistent with the expected structure and symmetry of the complex. Most importantly, the ROESY spectra (see Figure 3b) showed clear NOE cross peaks between the ligand and the host. In particular, the bridging protons (q in Figure 3a) showed NOE peaks to the central portion of the ligand (CH$_2$ nos. 4–6, Figure 3b). Moreover, the calculated interproton distances (see Supporting Information) obtained from integration of the cross peaks in the ROESY spectra are only consistent with the structure **4:6**.

In conclusion, a combination of UV/Vis and ^{1}H NMR binding studies using a simple bidenate ligand as a molecular ruler have unambiguously demonstrated the structural difference between the hosts **4** and **5**: only one (*syn* isomer **4**) could form strong intramolecular complexes with **6**. In other words, molecular recognition studies were used for the structural determination of **4** and **5**, something that could not be achieved with conventional spectroscopic techniques on the compounds themselves. In other work,[14] we have shown that the molecular ruler concept can be used also for determination of the cavity size in ditopic chiral porphyrin-appended Tröger's bases.[15]

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# A Four-Step Alternating Reductive Dimerization/Bond Cleavage of Indenocorannulene**

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The reduction of polycyclic aromatic hydrocarbons (PAHs) with alkali metals yields negatively charged π-conjugated molecules,[1] which may undergo structural changes, from structural distortions[2] and aggregation,[3] to the formation of new chemical bonds.[4] An anionic dimer is produced when a new σ bond forms between two identical units.[5] Such a reductive dimerization process, that is, radical anion coupling, was observed in the reduction of azulene[6] and in the reductions of certain benzofulvene derivatives.[7] In the former case, further reduction dissociates the newly formed σ bond to afford the azulene dianion and, to our knowledge, this sequence was the first reductive dimerization/bond-cleavage process ever observed.[6] The formation of aggregates upon reduction of PAHs has been observed with the lithium salt of the corannulene tetraanion,[3a] which is the smallest curved subunit of a fullerene. However, aggregation was not observed in the reductions of corannulene derivatives with extended π frameworks, towards fullerenes.[8] Here we report that a curved polycycle, indenocorannulene (**1**), undergoes an unprecedented, alternating, four-step dimerization/bond-cleavage process upon reduction with potassium.

Reduction of **1** with potassium, by successive one-electron transfers, produces four diamagnetic reduction states. Each reduction stage was visually apparent from the change in color and this was monitored by NMR spectroscopy. The first and third stages of reduction give ions **2** (dianion, dark brown) and **4** (hexaanion, green), respectively (Scheme 1), which exhibit doubling of all the NMR resonance signals (Figure 1). The second and fourth stages of reduction give ions **3** (dianion, purple) and **5** (tetraanion, violet), respectively, which have the same simple resonance pattern as the neutral **1** (Figure 1), and their ^{13}C NMR spectra (Table 1) indicate the presence of only sp^2-hybridized carbon atoms. The ^{1}H NMR spectra of **2** and **4** did not show the presence of any dynamic processes over a wide range of temperatures; their ^{13}C NMR spectra (Table 1) each show an extremely upfield signal at $\delta = 56.5$ and 47.6 ppm, respectively (assigned to C3′, see Scheme 1). The

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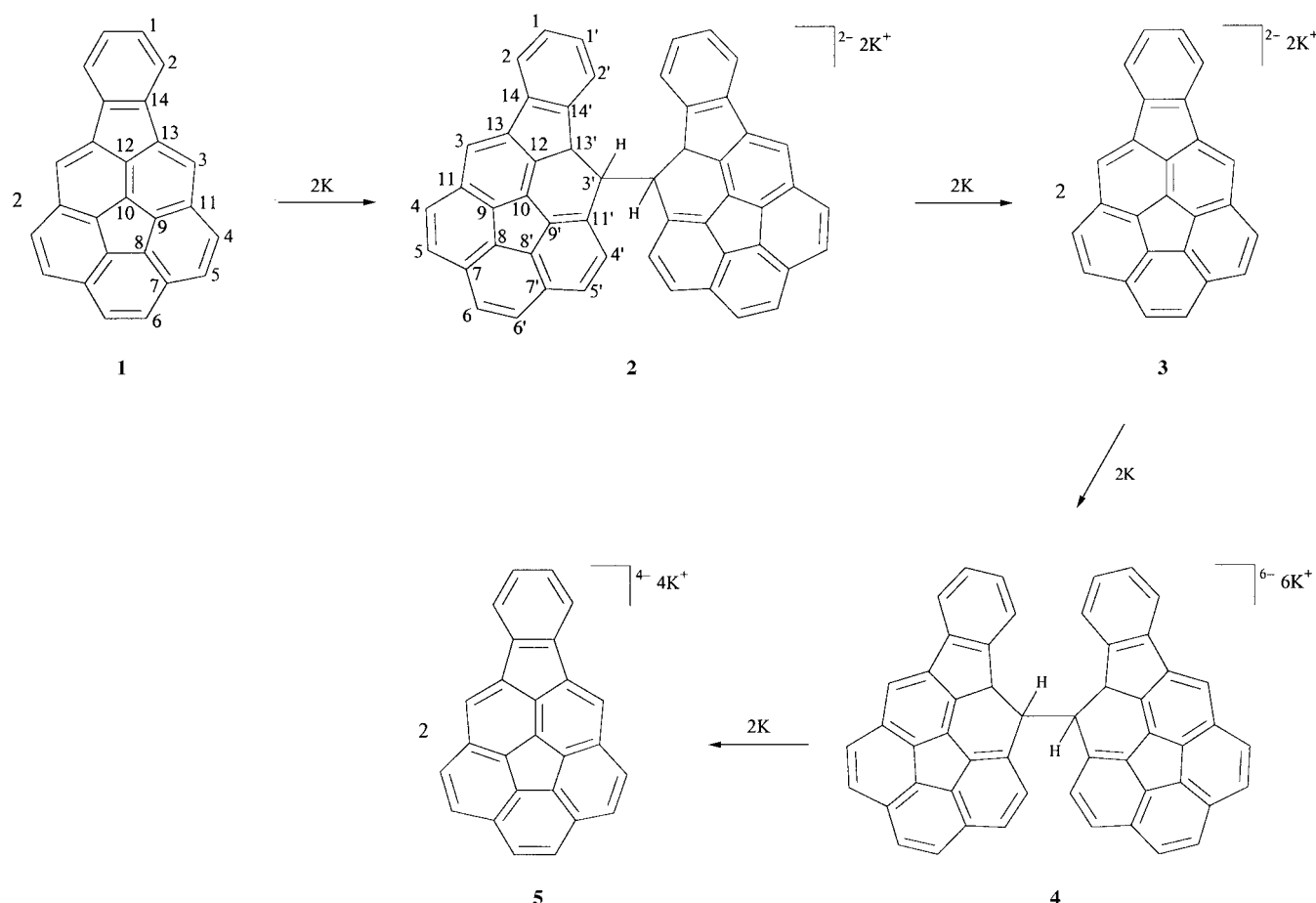
Scheme 1. The stepwise reduction process of **1** with potassium.

long-range $^{13}C - {^1}H$ correlation experiments (HMBC) conducted on species **2** and **4** exhibited an unexpected $^{13}C - {^1}H$ correlation, in addition to the three-bond interactions that helped in the full assignment of the carbon spectra. The unexpected interaction was a long-range correlation between C3′ and H3′, which is attached to carbon atom C3′. In addition to the expected one-bond couplings ($^1J_{C3',H3'} = 131.7$ and 124.6 Hz, respectively, for **2** and **4**), long-range couplings between H3′ and its symmetrical equivalent were observed from the ^{13}C NMR satellite signals ($^3J_{H3',*H3'} = 10.0$ and 10.5 Hz, respectively, for **2** and **4**) in the short-range $^{13}C - {^1}H$ correlation experiments (HSQC).

Oxygen-quench experiments conducted on all the reduced species afforded the neutral species **1**, which indicates that the reduction process might be reversible and that the carbon framework does not degrade.

The process depicted in Scheme 1 is based on the results attained from the ^1H NMR, ^{13}C NMR, and 2D NMR spectroscopic measurements. The alternate doubling of signals in the NMR spectra, both in the ^{13}C NMR and in the ^1H NMR spectra, indicates that the reduction with potassium affords species of different molecular structures, depending on the degree of reduction. The upfield resonance signal of carbon atom C3′ in species **2** and **4**, and the magnitude of its $^1J_{C,H}$ coupling constant, are compatible with an sp³-hybridized carbon atom. The extra interaction observed in the HMBC experiments on species **2** and **4** indicates that a reaction has taken place between two identical C3 carbon atoms, which thus forms the sp³-hybridized carbon atoms. All these observations suggest that the alternating duplication of both ^1H NMR and ^{13}C NMR spectra is a result of a σ-bond formation between the C3 carbon atoms of two units of **1**, which lowers the symmetry of each component in the system.

Further evidence for the dimerization process can be gained from calculations of the atomic-orbital coefficients of both the LUMO and the LUMO + 1 of **1**. DFT calculations (B3LYP/6-311G**),[9–11] predict a high spin density for the odd electron in the monoanion radical and the trianion radical of **1** at C3, which supports the hypothesis of a radical coupling at this carbon atom. The upfield chemical shift of the NMR resonance signals of all the C3 carbon atoms also lends strength to our conclusions. The presence of a dibenzofulvene moiety in **1**, and its dimerization when reduced to an anion radical (Scheme 2), is reminiscent of the behavior of the parent dibenzofulvene.[5, 7]

The bowl shape of **1**, which does not undergo a dynamic process on the NMR spectroscopy timescale, imparts chirality to each half of the dimer. This property leads to the interesting possibility of multiple diastereomeric reduced species, depending on the position of the connection. Even if one assumes that the new σ bond forms on the less hindered *exo* faces of both indenocorannulenes in each dimer, two possible isomers still remain (Figure 2). The NMR spectra of dimers **2** and **4**, however, contain only one major set of signals,
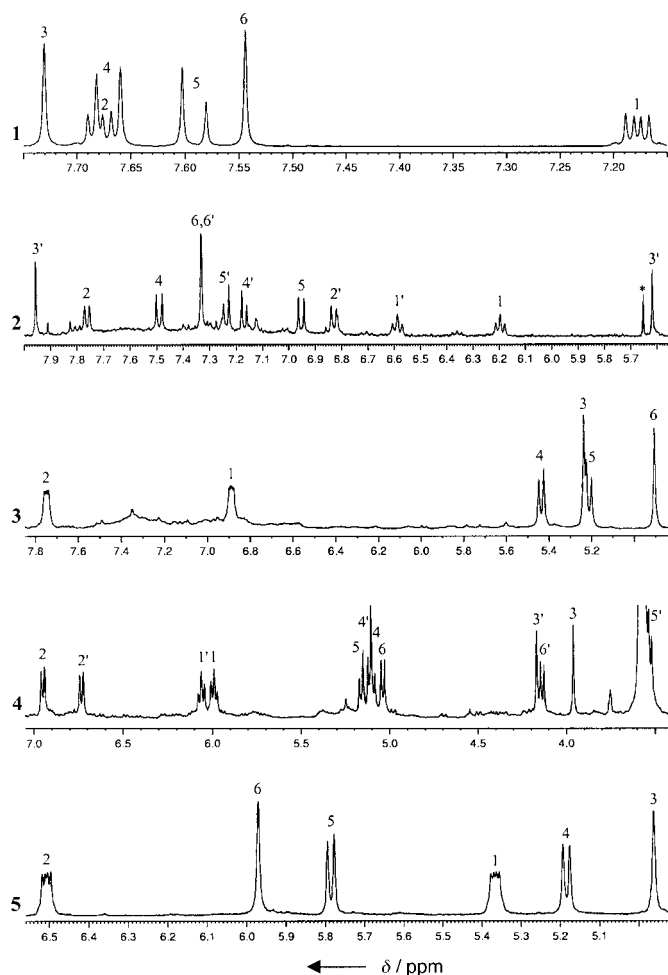
Figure 1. The ^{1}H NMR (400 MHz) spectra of **1–5** in [D$_8$]THF. The signal assigned to hydrogen atoms 6 and 6′ in spectrum **2** appears to be a singlet because their chemical shifts are coincident. The * in **2** denotes the signal of an impurity.

Table 1. The ^{13}C NMR (100 MHz) chemical shifts (δ) of **1–5** in [D$_8$]THF.

Compound	δ [ppm]
1	145.54 (C12), 142.35 (C13), 140.74 (C14), 140.43 (C10), 139.27 (C9), 138.87 (C11), 138.60 (C8), 131.26 (C7), 129.25 (C1), 129.19 (C4), 127.95 (C6), 127.73 (C5), 123.01 (C3), 122.52 (C2)
2	148.41(C14′), 145.99 (C9′), 143.15 (C12), 142.29 (C9), 138.88 (C8), 136.22 (C8′), 133.08 (C13), 132.94 (C14), 132.50 (C11′), 131.85 (C4′ + C7′), 130.37 (C10), 129.75 (C4), 129.69 (C7), 128.81 (C11), 126.27 (C6), 125.30 (C6′), 124.36 (C3), 123.42 (C1′), 121.91 (C5′), 121.57 (C2), 118.04 (C5), 113.56 (C2′), 108.69 (C1), 95.88 (C13′), 56.56 (C3′, $^1J_{C,H} = 131.7$ Hz, $^3J_{H,*H} = 10.0$ Hz)
3	163.22 (C10), 156.73 (C8), 140.48 (C9), 138.43 (C12), 133.14 (C14), 132.28 (C11), 132.02 (C7), 131.77 (C4), 126.81 (C5), 118.98 (C2), 113.79 (C6), 113.58 (C13), 110.44 (C1), 107.72 (C3)
4	146.14 (C8′), 145.79 (C9), 145.48 (C7′), 142.31 (C8), 141.65 (C11), 141.04 (C9′), 139.39 (C12′), 131.92 (C10, C11′), 125.96 (C14′), 125.38 (C6), 123.79 (C5), 119.35 (C4′), 118.71 (C7), 118.27 (C14), 118.18 (C4), 114.44 (C2), 112.97 (C2′), 109.93 (C1′), 107.94 (C1), 106.28 (C13′), 104.48 (C13), 103.87 (C6′), 92.87 (C5′), 87.52 (C3), 47.59 (C3′, $^1J_{C,H} = 124.6$ Hz, $^3J_{H,*H} = 10.5$ Hz)
5	143.12 (C11), 124.74 (C8), 123.69 (C9), 123.21 (C12), 122.51 (C13), 119.92(C7), 117.58 (C10), 115.22 (C2), 114.12 (C14), 113.46 (C6), 111.03 (C5), 109.82 (C1), 96.96 (C4), 82.62 (C3)
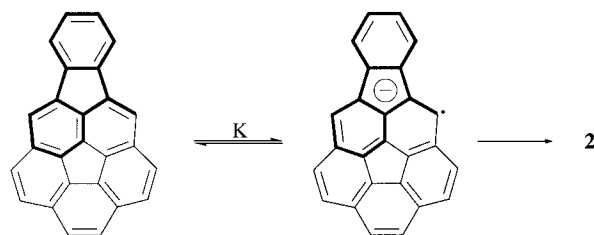
Scheme 2. The dibenzofulvene-like behavior of the radical anion of **1**.

so one species clearly dominates in each case.[12] Presumably the various stereoisomeric dimers interconvert on the time-scale of the experiment, either by dissociation–recombination, or by slow bowl-to-bowl inversion, or both, and the equilibration is driven by thermodynamic considerations. From the data available, unfortunately, it is not possible to assign fully the stereochemistry of dimers **2** and **4**, although it is apparent from the $^3J_{H,*H}$ coupling constant mentioned above that they adopt an *anti* conformation.
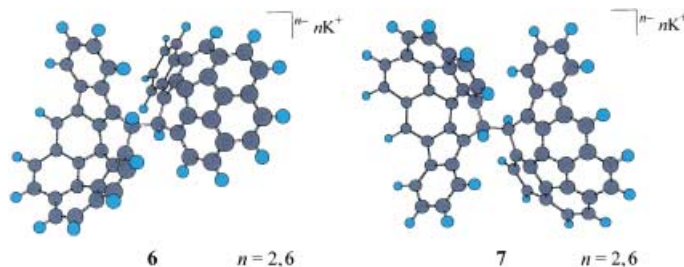

Figure 2. Proposed structures for the observed dimer. Structure **6** depicts the chiral diastereomeric dimer (racemic) and structure **7** depicts the *meso* dimer.

This is the first time that a large nonplanar PAH has demonstrated such a fascinating repetitive dimerization/bond-cleavage process upon reduction. It is also the first time that such a process has been extended beyond a single dimerization/bond-cleavage stage. The ability of **1** to exhibit a second round of this behavior is presumably a consequence of its relatively large size, which allows it to accommodate a high degree of charge, in addition to its electronic structure, which makes the radical coupling possible.[13]

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[12] A duplication pattern of a minor component is observed in the ^{1}H NMR spectrum of **3**, which is in a ratio of 1:5 to the major component.

[13] The ability to accommodate a high degree of charge is not the only factor required for the repetition of the process. Azulenes with extended π-conjugation afforded only a single coupling/bond-cleavage process upon reduction, whereas their trianion radicals did not dimerize. For example: a) M. Baier, J. Daub, A. Hasenhündl, A. Merz, K. M. Rapp, *Angew. Chem.* **1981**, *93*, 196–197; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 198–199; b) J. Daub, J. Salbeck, *Chem. Ber.* **1989**, *122*, 727–735; c) J. Salbeck, J. Daub, *Chem. Ber.* **1989**, *122*, 1681–1690.

Per(6-amino-2-O-carboxymethyl-6-deoxy-3-O-methyl)-α-cyclodextrin: Helical Self-Assembly of a Polyionic Amino Acid into Nanotubes**

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Designed macrocyclic oligopeptides[1] and oligosaccharides[2] serve as versatile building units (tectons) for supramolecular self-assembly of nanotubes.[3] In this respect, cyclodextrin derivatives possessing a hollow, chiral, truncated-cone

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interior with a variable diameter deserve particular interest. The two rims of cyclodextrin, respectively bearing primary and secondary hydroxy groups, can be selectively modified to create complementary binding sites. Cyclodextrins monofacially persubstituted at the primary rim with carboxy groups were already shown[4] to self-assemble in nonpolar solvents into dimeric head-to-head hydrogen-bonded aggregates. Analogous amino-persubstituted cyclodextrins associate, on treatment with the corresponding monofacially carboxymethyl-persubstituted derivatives, by means of ionic hydrogen bonds into head-to-head heterodimers, which persist even in aqueous solutions.[5, 6] This strongly suggests that hermaphroditic cyclodextrins bearing complementary donor and acceptor groups on the opposite rims might self-assemble into infinite head-to-tail chiral nanotubes. We designed hexakis(6-amino-2-O-carboxymethyl-6-deoxy-3-O-methyl)-α-cyclodextrin (**6**) as a model for such investigation. Here we report on its synthesis and its unique architecture in the solid state.

The persubstituted amino acid **6** is an elusive target because of the array of incompletely substituted derivatives that can arise and persist in the course of synthesis.[7] To obtain a chemically uniform persubstituted product, which is indispensable for X-ray diffraction analysis, we employed a novel procedure[8] for the facial percarboxymethylation of cyclodextrins. Starting from the easily accessible[9] hexakis(6-azido-6-deoxy)-α-cyclodextrin (**1**; Scheme 1), all secondary hydroxy
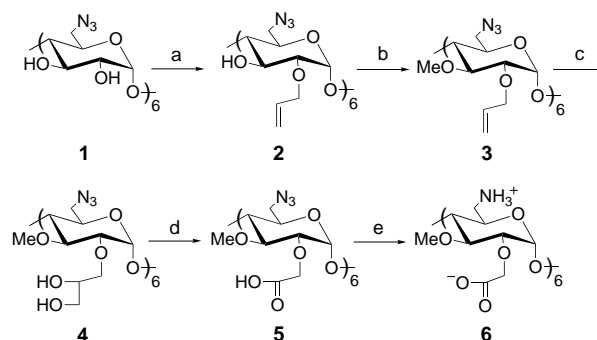
Scheme 1. a) Allyl bromide, Ba(OH)$_2$·H$_2$O, BaO, DMF, 25°C, 24 h, 52%; b) MeI, NaH, DMF, 25°C, 3.5 h, 99%; c) OsO$_4$, 4-methylmorpholine N-oxide, acetone/water, 25°C, 24 h, 71%; d) 1. NaIO$_4$, H$_2$O, 25°C, 2.5 h; 2. TEMPO, NaBr, NaClO, 25°C, 2.5 h, 91%; e) H$_2$S, pyridine/water, 25°C, 72 h, 90%. TEMPO = 2,2,6,6-tetramethyl-1-piperidineoxyl.

groups at C2 were selectively allylated, and the pure hexaallyl derivative **2** was isolated in 52% yield by chromatography. Subsequent methylation of the free hydroxy groups at C3 furnished the peralkylated compound **3** in a quantitative yield. The allylic groups of **3** were catalytically dihydroxylated with osmium tetroxide and 4-methylmorpholine N-oxide as auxiliary oxidant, and the resulting mixture of diastereoisomers **4** was isolated by reversed-phase chromatography in 71% yield. The diol groups were cleaved with sodium periodate and, in the same pot, the intermediate polyaldehyde was oxidized to the carboxymethyl derivative **5** with TEMPO/NaClO/KBr in an overall yield of 91%. Customary reduction of per-6-azidocyclodextrins with triphenylphosphane surprisingly failed. However, an excellent alternative for the reduction