Synthesis and Characterization of Annulene-Fused Pseudorotaxanes

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Abstract: A 24-crown-8 ether-fused dehydrobenzo[18]annulene has been prepared via a stepwise Pd/Cu-mediated strategy. This annulene-crown ether hybrid forms a pseudorotaxane complex in CD₂Cl₂ with dibenzylammonium hexafluorophosphate when they are combined in a 1:1 ratio, as indicated by ¹H NMR spectroscopy and mass spectrometry.

Key words: annulenes, crown compounds, macrocycles, pseudorotaxanes, supramolecular chemistry

Phenylacetylene macrocycles² and networks³ are potential building blocks for the assembly of tubular and/or porous molecular crystals.⁴ Key to such a transformation is preorganization of the precursor molecules so that they may undergo controlled oligomerization/polymerization to form ordered arrays. Unfortunately, such preorganization in the solid state⁵ is often rare and impossible to predict a priori. For example, tribenzo[14]annulene (1, Figure 1)⁶ packs in the solid state according to the parameters outlined by Enkelmann⁷ for a topochemical diacetylene polymerization. Indeed, 1 readily undergoes 1,4-polymerization when heated or exposed to UV light.⁶ Subsequent studies of a number of other dehydrobenzoannulenes (DBAs) show the reactivity displayed by 1 to be unique.⁸ More often than not the packing of the macrocycles in the crystal lattice precludes any type of ordered polymerization, which is reflected in the broader (w¹⁰² = 5–10 °C) than normal (w¹/² ≈<1 °C) DSC exotherms of the annulenes.

A possible solution to the preorganization problem involves supramolecular chemistry.⁹ Over the last decade a tremendous number of ordered arrays and assemblies have been prepared utilizing various noncovalent bonding interactions (hydrogen bonding, π-stacking, dipole-dipole interactions, etc.).¹⁰ One of the more interesting and relevant examples was the recent use of supramolecular organization for the first 1,6-polymerization of a triacetylene.¹¹ Similar preorganization has been successfully used for the polymerization of a number of other diacetylenes.¹² Encouraged by these reports, we decided to target a new class of pseudorotaxanes using crown ether-dehydrobenzoannulene hybrids (e.g, 2) in order to organize the DBA molecules. These systems can utilize external forces such as the interpenetrating guest-host interaction between secondary dialkylammonium ion centers in guests containing one or more binding sites for crown ether hosts.¹³ The resultant supramolecular complexes might thermally generate dimer fragments, which could provide insight into diacetylene polymerization for DBA systems. We describe herein our initial work to-

Figure 1 The structure of tribenzo[14]annulene (1)

Figure 2 The structures of crown ether-dehydrobenzoannulene hybrid 2 and mono- and dicationic hexafluorophosphate salts 3 and 4
Towards the assembly of novel supramolecular architectures containing hybrid 2 and the mono- and dicationic hexafluorophosphate salts 3 and 4, respectively (Figure 2).

Hybrid 2 was assembled using the same strategy as that reported previously for the construction of site-specifically functionalized DBAs (Scheme 1).8b,3g Cyclization of ditosylates 5 with 4,5-diodocatehol15 using high dilution conditions gave diiododibenzo-24-crown-8 (6) in moderate yield. Cross-coupling 6 with two equivalents of 1-(4-trimethylsilylbuta-1,3-diynyl)-2-(triisopropylsilyl-ethynyl)benzene8g using in situ desilylation/coupling conditions furnished the 1,2,3-polyyne 7 in 81% yield. Desilylation of 7 with Bu4NF and subsequent Cu-mediated intramolecular oxidative cyclization under pseudohigh dilution conditions generated the benzo-24-crown-8-fused annulene 2 as a light yellow solid in 55% yield.

Slow evaporation of a THF solution of 2 afforded yellow blocks suitable for X-ray diffraction. The crystal structure of macrocycle 2 is shown in Figure 3.16 The annulenic core is essentially planar with a mean deviation less than 0.07 Å. The bond lengths and bond angles are typical for those found in other dehydrobenzoannulenes.6,8 Interestingly, the crown ether curves around the end of a second annulene. Although there are no π-stacking interactions in the crystal lattice, there are short CH...O hydrogen bonds that help dictate the crystal packing. With such a curved arrangement, it might be possible to thread both the crown ether and annulene, a motif we are actively pursuing.

Mixing equimolar amounts of hybrid 2 and salt 3 in CD2Cl2 at room temperature resulted in a significant difference in the 1H NMR spectra (Figure 4), thus indicating formation of the pseudorotaxane host-guest complex. The top spectrum, which represents free 2, is relatively uncomplicated, reflecting the C2v symmetry of the crown.

Scheme 1 (a) 4,5-diodocatehole, CsCO3, MeCN; (b) 1-(4-trimethylsilylbuta-1,3-diynyl)-2-(triisopropylsilyl-ethynyl)benzene, aq KOH, PdCl2(PPh3)2, CuI, Et3N, THF; (c) Bu4NF, MeOH, THF; (d) Cu(OAc)2, CuCl, pyridine

Figure 3 Molecular structure of 2 (left); ellipsoids drawn at the 30% level. Side view of two molecules (right). THF solvate molecules omitted for clarity.
ether moiety. The bottom spectrum shows a number of
changes upon addition of an equimolar amount of 3, all of
which support strong complexation. The most noticeable
differences are in the crown ether region, where the cen-
tral ethylene protons (H^e) change from a singlet in free 2
to two multiplets in pseudorotaxane 2•3 (Figure 5) with an
upfield shift of ca. 0.25 ppm. Crown ether protons H^e and
H^f show increased separations between the two sets of
multiplets as well as slight upfield shifts. The resonances
in the aromatic region also exhibit notable changes. The
broad singlet attributable to the four H^b protons in 2 splits
into the expected AA'B'B' multiplet with an upfield shift
of ca. 0.1 ppm once the complex is formed. The singlet for
H^e shifts upfield by 0.15 ppm. Resonances of the ammo-
nium ion were observed at δ = 7.57 (broad singlet), 7.32–
7.13 (multiplets), and 4.74 (broad triplet) representing H^3,
H^1, and H^2, respectively. Based on the large number of
previous pseudorotaxane studies,^{13} the observed chemical
shift changes, as well as there being no indication of free
2, are consistent with strong complexation between the
host and guest molecules.

The supramolecular complex 2•3 was also analyzed by
FAB mass spectrometry. Although the spectrum did not
show the parent peak of m/z 1085, peaks corresponding to
M^+–PF_6 and hybrid 2 were observed at 940 and 742 mass

\[ \text{Figure 4} \quad \text{^1H NMR (300 MHz, CD}_2\text{Cl}_2) \text{ spectra of the free hybrid 2 (top) and of the 1:1 pseudorotaxane 2•3 (bottom)} \]

\[ \text{Figure 5} \quad \text{The structures of 1:1 pseudorotaxane 2•3 and 2:1 pseudorotaxane 2•4} \]
units, respectively. Attempts to obtain single crystals suitable for X-ray diffraction have been unsuccessful to date. The complexation between DBA and the bis-ammonium salt was also performed in CD2Cl2 by mixing a 2:1 ratio of host and thread molecules (Figure 5). The results of this experiment are considerably more complicated. 1H NMR spectra indicated the presence of a mixture of pseudorotaxane complexes and their free components in solution. The FAB mass spectrum showed very small peaks of the 2:1 complex corresponding to M+−PF6 and M+−2PF6, and crown ether containing a sodium ion. Further efforts to decipher these results are in progress.

In conclusion, we have demonstrated an efficient synthesis of crown ether containing dehydrobenzoannulene and its ability to complex secondary dialkylammonium ions. The formation of a pseudorotaxane from a 1:1 mixture of 2 and 3 is facile in CD2Cl2, according to 1H NMR spectroscopic data. The formation of the corresponding [3]pseudorotaxane from a 2:1 mixture of 2 and 4 was incomplete under analogous conditions. Synthetic efforts towards making bis- and tris-crown ether-fused annulenes are underway and experiments to probe the formation of more complicated supermolecules will be reported in due course.

Reagents and instrumentation used have been described previously.

4,5-Diodidobenzo-24-crown-8 (6)

A suspension of Cs2CO3 (18.4 g, 56.5 mmol) in anhyd MeCN (250 mL) was placed under N2 and brought to reflux. To this was added diiodide (7.72 g, 11.3 mmol) and 4,5-diodocatechol (4.09 g, 11.3 mmol) dissolved in anhyd MeCN (250 mL) over a 24 h period. The mixture was refluxed for an additional 48 h and then cooled. The suspension was filtered and concentrated in vacuo. The residue was dissolved in CH2Cl2 (150 mL) and washed withaq sat. NaHCO3 solution (300 mL). The aqueous layer was extracted with CH2Cl2 (2 × 100 mL) and the combined organics were dried (MgSO4), filtered, and concentrated. Chromatography on silica gel (hexanes–EtOAc, 1:1) gave 6 (3.09 g, 39%) as a white solid; mp 91.7–93.6 °C.

IR (CDCl3): 3062, 2922, 2870, 1592, 1249, 1127 cm−1.

1H NMR (CDCl3): δ = 7.24 (s, 2 H), 6.92–6.84 (m, 4 H), 4.16–4.12 (m, 4 H), 4.10–4.06 (m, 4 H), 3.93–3.86 (m, 8 H), 3.84–3.77 (m, 8 H).

13C NMR (CDCl3): δ = 149.44, 148.85, 123.89, 113.97, 96.47, 71.35, 71.23, 69.91, 69.64, 69.56, 69.32.

MS (APCI): m/z (%) = 718 (100, M+ + H2O), 701 (5, M+ + H).


Crown Ether/Annulene Hybrid 2

Polyne 7 (850 mg, 0.78 mmol) was dissolved in THF–MeOH (3:1, 20 mL) and treated with Bu4NF (2 mL, 1 M THF solution, 2.0 mmol) at r.t. The reaction was monitored by TLC and was complete within 30 min. The mixture was diluted with Et2O (30 mL), washed with H2O (3 × 20 mL) and brine (2 × 20 mL), and then dried (MgSO4). The organic layer was concentrated in vacuo. The residual oil was redissolved in pyridine (10 mL). The pyridine solution was added over 12 h via syringe pump to a flask charged with Cs2CO3 (3.54 g, 19.5 mmol), CuCl2 (2.10 g, 15.6 mmol), and pyridine (200 mL) at 60 °C. The addition was done under house air and stirred further for 8 h. Upon completion, the mixture was concentrated in vacuo and redissolved in CH2Cl2. The mixture was filtered through a thin cake of silica gel using CH2Cl2 and concentrated. Chromatography on silica gel (hexanes–THF, 3:1) afforded 2 (320 mg, 55%) as a light yellow solid; mp 230 °C (dec.).

IR (KBr): 2926, 2866, 2211, 2192, 2140 cm−1.

1H NMR (CDCl3): δ = 7.74–7.66 (m, 6 H, 7.49–7.42 (m, 4 H), 7.13 (s, 2 H), 6.89 (br s, 4 H), 4.19–4.15 (m, 4 H), 4.12–4.08 (m, 4 H), 3.92–3.82 (m, 8 H), 3.77 (br s, 8 H).

13C NMR (CDCl3): δ = 150.47, 129.54, 133.35, 133.15, 129.61, 129.40, 125.63, 125.29, 121.89, 118.97, 116.84, 114.69, 81.76, 81.32, 80.96, 78.49, 78.16, 77.00, 71.83, 71.63, 70.41, 70.00, 69.97, 69.76.

MS (FAB): m/z = 742.2 (100, M+).

Anal. Calcd for C66H60O4Si2 (814.93): C, 76.64; H, 5.69. Found: C 76.54, H 5.65.

Pseudorotaxane 2-3

CD3Cl (0.7 mL) was added to hybrid 2 (11 mg, 0.015 mmol) and dibenzylammonium hexafluorophosphat (4.8 mg, 0.014 mmol). The reaction mixture was sonicated for 3 min and then filtered through a plug of glass wool into an NMR tube.

1H NMR (CDCl3): δ = 7.74–7.69 (m, 4 H), 7.58 (br s, 2 H), 7.50–7.44 (m, 4 H), 7.36–7.27 (m, 4 H), 7.25–7.17 (m, 6 H), 6.88 (BB’, 2 H), 6.72 (AA’, 2 H), 4.68–4.62 (m, 2 H), 4.16–4.13 (m, 2 H), 4.05–4.02 (m, 2 H), 3.89–3.86 (m, 2 H), 3.74–3.71 (m, 2 H), 3.60–3.55 (m, 2 H), 3.53–3.49 (m, 2 H).

MS (FAB): m/z = 940.3 (82, M+ + PF6), 742.2 (13, M+ + Bz2NH2PF6).

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