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Nanochannel Array within a Multilayered Network of a Planarized Dehydro[24]annulene

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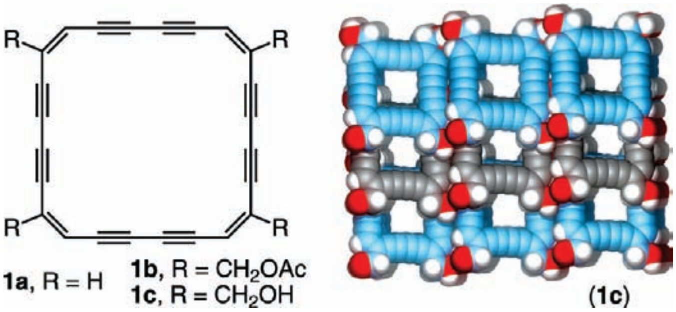
ABSTRACT



Dehydro[24]annulene 1c adopts an unusual planarized conformation in the crystal. A multilayered stack of hydrogen-bonded grids delineates tightly packed nanotubular channels. The related macrocycles 1a and 1b, on the other hand, have the expected puckered conformations in the crystal.

Acetylenic macrocycles offer a significant advantage in a synthetic approach to nanosized carbon allotropes and carbon-rich materials.[1] Each alkyne carbon stores a large amount of energy and is prone to expand its coordination. Vollhardt[2] and Bunz[3] have shown that the explosive solid-state decomposition of dehydroannulenes can afford carbon nanostructures. However, a downside of this high energy content is that the transformations usually give a chaotic array of nanostructures.

An attractive strategy for converting carbon-rich macrocycles into well-defined nanostructures lies in a stepwise nonexplosive topochemical polymerization approach (Figure 1), followed by graphitization. Indeed, this strategy has been invoked in work on various acetylenic systems.[4] So far, this approach has been challenging, with the required solid-state molecular organization necessary for topochemical polymerization being achieved mostly by chance. There is strong potential in using noncovalent self-assembly to drive the organization of macrocyclic diacetylenes into topochemically polymerizable arrays. Remarkable single-crystal-to-single-crystal topochemical polymerization of self-assembled di-

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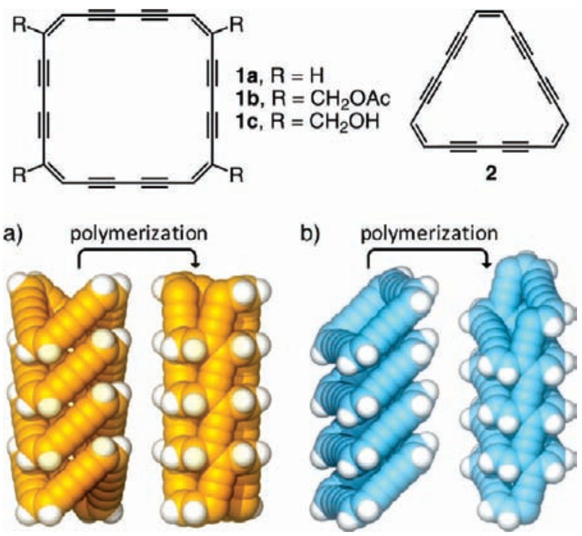

Figure 1. (top) Dehydroannulenes discussed in this work. (bottom) Examples of potential topochemical polymerization pathways for dehydro[24]annulene **1a**: (a) stack of puckered rings undergoing 4-fold polymerization of diacetylene units; (b) a planar conformation undergoing 2-fold polymerization.

acetylenes has enabled unambiguous characterization of the products, providing a clear understanding of the reaction pathway.[5]

With this in mind, we targeted the topochemical polymerization of macrocycles incorporating multiple butadiyne units. Among a number of possible structures,[6] nonbenzoannulated dehydroannulenes seemed best suited for this goal. Benzoannulation can have a stabilizing effect on a dehydroannulene, and the steric encumbrance by aromatic rings near reaction sites may impede polymerization.[4b,c,7] Conversely, many simple dehydroannulenes are notoriously unstable, restricting availability of data on their crystal packing.[6]

To explore noncovalent interactions in the solid state, the crystal structures of parent dehydro[24]annulene **1a**, as well as its tetrasubstituted derivatives **1b** and **1c**, were obtained (Figures 1, 2, and 3). We were curious about the crystal structure of parent compound **1a** (Figure 2). Although Sondheimer et al. prepared this compound in 1970,[8] the crystal structure was never reported, presumably because of its extreme heat and shock sensitivity (see below). We synthesized compound **1a** through oxidative coupling of *cis*-3-hexen-1,5-diyne under high-dilution conditions ($\sim 10^{-2}$ M), which provided tetramer **1a** and trimer **2** in 5% and 20% yields, respectively.[9] It is worth noting that macrocycle **1a** has not previously been isolated through this route. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a $CDCl_3$ solution of **1a** at −14 °C. After several attempts at mounting crystals, which exploded easily upon touching, an amber plate provided the structure shown in Figure 2.[10,11] The 24-membered macrocyclic framework has the expected tub-shaped conformation. With pucker angles[12] of 62.5(2)° and 66.6(3)°, it is slightly flatter than the DFT calculated structure[9] (83.0°), which is presumably due to distortion by crystal packing forces. Additionally, the C≡C−C angles in **1a** (Figure 2a) are generally smaller in the crystal than calculated,[9] whereas the C═C−C angles are essentially identical between theory and experiment. Thus, most of the angle strain caused by the planarization is localized at the most flexible sp-hybridized carbons. A similar

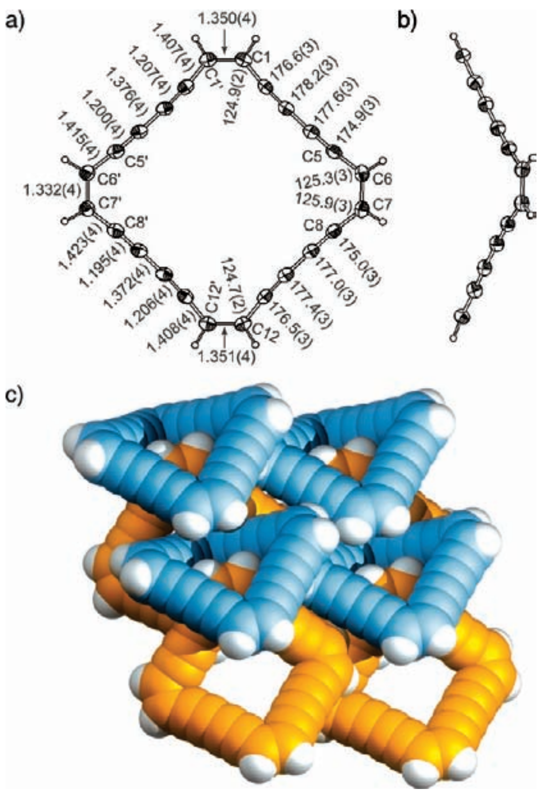

Figure 2. Crystal structure of dehydro[24]annulene **1a**: (a,b) ORTEP plots drawn with 50% probability ellipsoids. (c) Packing diagram with space-filling view.

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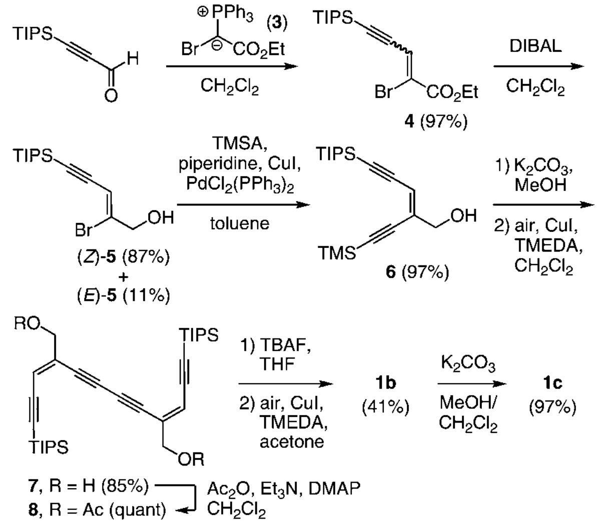
(10) X-ray data: **1a**, yellow plate ($CDCl_3$), space group $Ccm2_1$; a = 8.276(8) Å; b = 20.80(2) Å; c = 9.536(9) Å; V = 1641(3) Å^3; Z = 4; T = 156(2) K; N_{ref} = 1300; R_1 = 0.0434; wR_2 = 0.0883; **1b**, yellow prism (CH_2Cl_2/Et_2O) space group $Ccca$; a = 12.4522(9) Å; b = 12.4742(2) Å; c = 19.6932(15) Å; V = 3059.0(4) Å^3; Z = 4; T = 100(2) K; N_{ref} = 2068; R_1 = 0.0352; wR_2 = 0.0892; **1c**, red prism (THF/MeOH) space group $P\bar{1}^1$; a = 7.1356(9) Å; b = 7.5011(9) Å; c = 11.3348(14) Å; V = 591.17(13) Å^3; Z = 1; T = 100(2) K; N_{ref} = 3147; R_1 = 0.0442; wR_2 = 0.1134.

(11) For the crystal structure of dehydro[18]annulene **2**, see Supporting Information.

(12) The pucker angle is defined between a set of two mean planes passing through each edge of opposing ≡C-C═C-C≡ units, e.g., C6′−C5′−C5−C6 and C7′−C8′−C8−C7, Figure 2a.

Scheme 1. Synthesis of Tetrasubstituted Derivatives **1b** and **1c**



degree of planarization has been observed for a dehydro[16]-annulene derivative.[13]

Compound **1a** crystallizes without solvent inclusion and has a number of short C···C contacts.[9] As a result, the crystals are highly unstable and decompose in minutes at 25 °C, turning black upon standing or detonating violently upon mechanical shock.[8] This extreme instability needed to be addressed for a controlled polymerization strategy. A simple way to attenuate solid-state reactivity is through the introduction of substituents that effectively separate molecules from each other. However, too much steric bulk would not be conducive to achieving the molecular arrangement necessary for efficient polymerization. Thus, the derivatives **1b** and **1c** possessing four relatively small substituents were prepared (Scheme 1).

The butadiyne linkages in **1b** and **1c** were formed in two oxidative dimerization steps to avoid the formation of unsymmetrical isomers as well as [18]annulenes.[4f,8] Wittig reaction of 3-(triisopropylsilyl)propynal[14] and ylide **3**[15] gave bromoenyne ester **4**, which afforded alcohol **5** by reduction with DIBAL (1:9 *E*/*Z* mixture). The two diastereomers were separated by flash chromatography on silica gel (hexanes/AcOEt, 20:3). Sonogashira coupling of bromoenyne (*Z*)-**5** with trimethylsilylacetylene (TMSA) afforded enediyne **6** in 97% yield. After removal of the TMS group from **6** followed by Hay coupling, the resulting dimer **7** was converted to bisacetate **8** (quant). Desilylation of **8** and subsequent oxidative coupling under high dilution conditions ($\sim 10^{-3}$ M) afforded macrocycle **1b** in 41% yield as a bright yellow crystalline solid. The tetraol **1c** was obtained by saponification of **1b** in 97% yield.

The X-ray structure for **1b** is shown in Figure 3a−d. Whereas corresponding carbon−carbon bonds within mac-

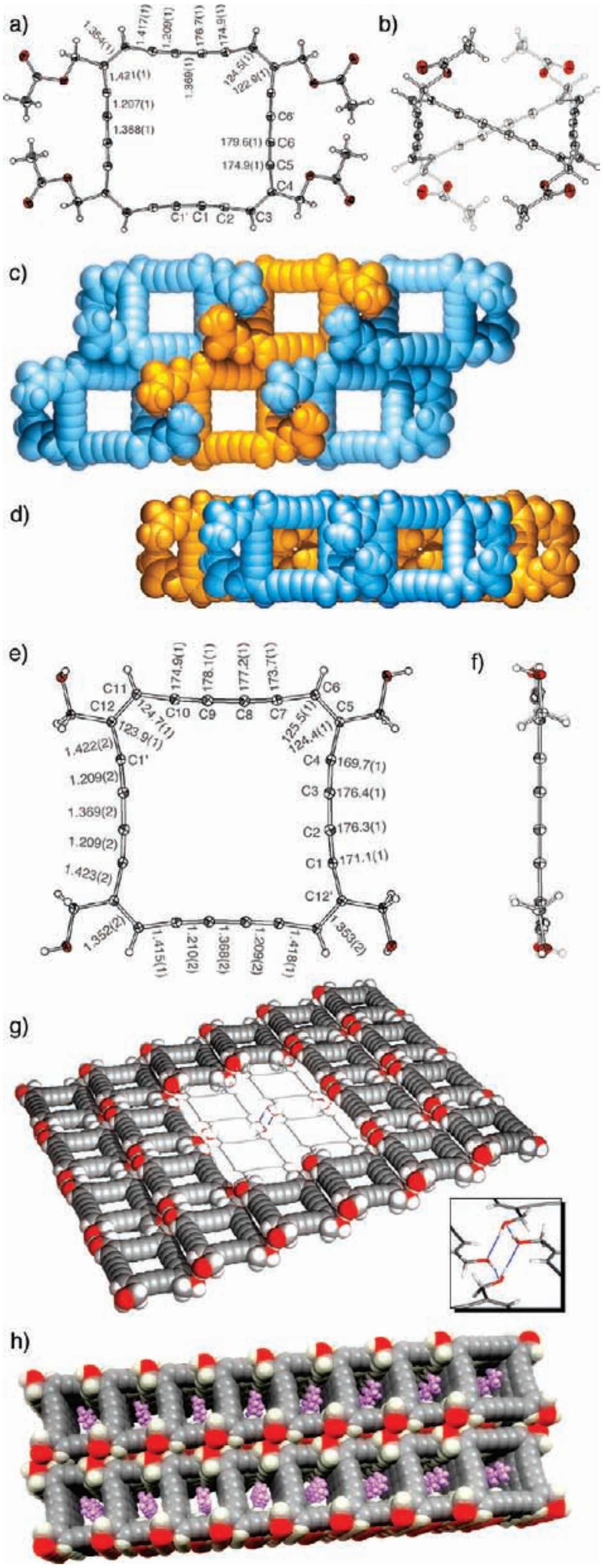


Figure 3. Representations of the crystal structures of **1b** and **1c**: (a,b) ORTEP plots of **1b** with 50% probability ellipsoids. Packing diagram for **1b** showing (c) rings interlocked by acetate substituents, and (d) superposition of two layers. (e,f) ORTEP plots of **1c** with 50% probability ellipsoids. (g) Packing diagram of **1c**; inset: detail of hydrogen-bonding motif. (h) Packing diagram of **1c** viewed down the nanochannels. Disordered solvent shown in purple.

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rocycles **1a** and **1b** have very similar lengths (Figures 2a and 3a), the pucker angle is larger for **1b** (74.5(0)°) than for **1a**.[9] Compound **1b** has a smaller inner angle at the vinyl carbons (C2−C3−C4; 122.9(1)°) compared to the corresponding angles at C1, C6, C7, and C12 for **1a** (124.7(2)−125.9(3)°), which is the cause of the larger pucker angle. The crystal packing diagram of **1b** (Figure 3c) shows that the macrocycles are intertwined through their acetate substituent "arms", forming a linear chain of repeating units. The chains stack in a staggered fashion (Figure 3d), and each diacetylene unit is well separated from others even though the molecules are tightly packed without any incorporated solvent. This explains the much higher solid-state stability of **1b** compared to that of **1a**: crystals of **1b** have been stored over 2 months without any decomposition, in striking contrast to **1a**. In addition, crystals of **1b** did not explode either by rubbing or heating up to 150 °C in air, although they gradually darkened between 120−130 °C. Thus, the introduction of relatively small substituents effectively improves the solid-state stability of otherwise highly unstable dehydroannulenes.

We expected that tetraol **1c** would adopt a very different molecular packing mode from that of **1a** or **1b**, owing to its ability to form hydrogen bonds. Interestingly, **1c** forms deep red crystals, whereas it is bright yellow in solution. This is in contrast to compounds **1a** and **1b**, which are yellow both in solution and in the crystalline state. A similar deep red color is characteristic of cyclobutene-fused dehydro[24]-annulenes that are forced to adopt a planar conformation through small-ring annulation.[16] Additionally, the solid-state UV−vis spectrum of **1c** shows an absorption edge around 560 nm (Figure 4, inset) that is in good agreement with the reported data for planar cyclobutene-fused dehydro[24]-annulenes.[16a] This was a strong indication that macrocycle **1c** has a planar conformation in the crystalline state.

The planarity of **1c** was confirmed by its single crystal X-ray structure (Figure 3e−h). The average deviation from the mean plane defined by the 24 carbons on the macrocycle perimeter is only 0.034(1) Å, with the maximum deviation being 0.068(1) Å. This near-perfect planarity is unusual considering that no annulation[16,17] or intra-annular bridging constraints are present in the molecule.[18] In addition, tetraol **1c** forms a network of hydrogen bonds in the crystal: a square motif of O···H contacts leads to a corrugated sheet built from the planar macrocycles (Figure 3g). The sheets stack into an array of nanochannels walled by the highly polarizable π-electrons of the butadiyne units (Figure 3h). Each nanochannel is filled with disordered solvent molecules.

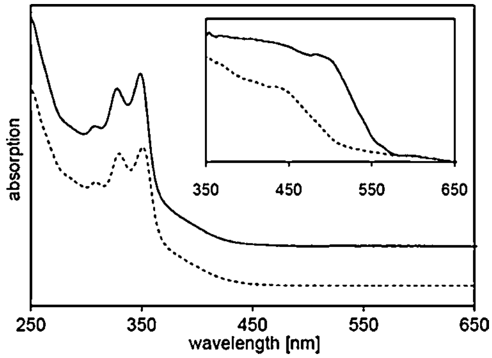

Figure 4. UV−vis spectra of **1b** (- - -, 1.7 × 10^{-5} M, MeCN) and **1c** (—, 1.9 × 10^{-5} M, MeOH). Inset: solid-state UV−vis spectra.

The energetic effect of the planarization was calculated by density functional theory (BHandHLYP/6-31G*).[9] The nonplanar and planar conformers of **1c** were optimized with C_2 and C_i symmetry constraints, respectively.[9] The energy difference between the two conformers is only 1.92 kcal/mol after zero-point energy correction. This value is much smaller than the calculated energy barriers for the ring flip process of cyclooctatetraenes (≥10 kcal/mol)[19] and is so small that ring planarization can be easily compensated by van der Waals interactions and the formation of multiple hydrogen bonds per molecule.[20] Experimentally, crystalline samples of **1c** are as thermally stable as tetraacetate **1b**: no significant change in appearance is observed up to 110 °C in air, at which point crystals start to slowly turn brown.

In summary, the use of noncovalent interactions has provided a step toward achieving the desired ordering of dehydroannulenes in the solid state and their controlled topochemical polymerization. Simple, small substituents effectively stabilize the dehydro[24]annulene system and significantly affect macrocycle conformation as shown between tetraacetate **1b** and tetraol **1c**. The planarization of an otherwise tub-shaped π-conjugated macrocycle results in an intriguing exaltation of its paratropic nature. We are exploring a variety of derivatives of tetraol **1c** to obtain an optimal molecular arrangement favoring the targeted multifold topochemical polymerization.

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Supporting Information Available: Experimental procedures and spectroscopic data for compounds **1a**−**c**, calculation details, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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