

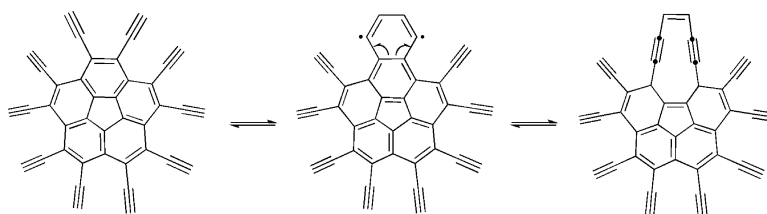
Communication

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 Eneidyne Cyclization/Interconversion of CR Isomers**

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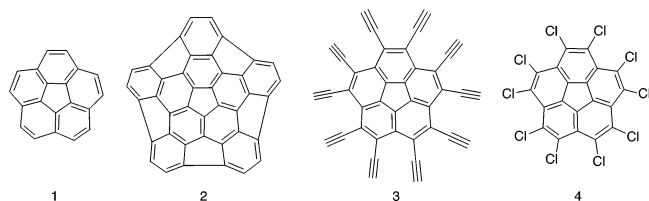
Synthesis, Structure, and Isomerization of Decapentynylcorannulene: Eneidyne Cyclization/Interconversion of C₄₀R₁₀ Isomers

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The formula C_{10n}H₁₀ includes a series of bowl-shaped carbon-rich structures wherein corannulene (**1**) represents $n = 2$, and the simplest capped nanotube, C₄₀H₁₀ (**2**), represents $n = 4$.¹ The class of $n = 4$ is also represented by another isomeric structure, decaethynylcorannulene (**3**). A simple bond-energy estimate for the energetics of **3** compared with that of **2** results in a remarkable value of 300–400 kcal/mol in favor of **2**.² The conceptual synthesis of **3** from **1** via decachlorocorannulene (**4**) and the potential of **3** as a direct precursor to **2** via Bergman cyclization³ is so attractive in its simplicity as to be irresistible. Such an approach would open a solution-phase method to the synthesis of monodispersed single-walled carbon nanotubes (SWCNT) from *per*-ethynylcorannulenes.



Per-ethynylated polynuclear aromatic hydrocarbons (PAHs) should be accessible from their perhalo cognates.⁴ Balister perhalogenation conditions produce **4** in one step from **1**,⁵ which is now available in multigram scale in five steps.⁶ Reaction of **4** and an excess of stannylpentynes in DME with Pd(OAc)₂ and IPr-HCl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)⁷ yields **5** directly, in modest yield (ca. 10%), plus the novel ring expanded product (**6**) (ca. 18%); an X-ray crystal structure for each was determined (Figures 1 and 2).⁸

The structure of **5** is flatter than **1** and has a longer rim bond but is otherwise similar (Table 1). The crystallographic core structure of **5** agrees with that calculated for **3** (B3LYP/cc-pVDZ) within 0.01 Å for bond lengths and ca. 1° for bond angles.⁹ The geometrical patterns and trends are the same. Similar computations on **2** (B3LYP/cc-pVDZ) show that the bowl depth and [5]radialene character increase monotonically for the series, **3**[**5**], **1**, **2**. The bowl depth and radialene character of the closed fullerenes, C₆₀ and C₇₀, are less than for **2**. MP2/cc-pVDZ//B3LYP/cc-pVDZ computational energy differences of **2** and **3** (388.3 [364.5 ZPE] kcal/mol) support the estimates made by using simple bond-energy arguments. Nonetheless, **5** (decapropyl-**3**) appears to be kinetically inert to the formation of decapropyl-**2** up to 100 °C.

Despite having well-formed crystals of **6**, weak diffraction required use of a synchrotron light source. Three molecular units are observed in the asymmetric unit. Stacking disorder is evident from the observed diffuse scattering. Difference Fourier maps revealed at least three orientations for two of the molecular units and two for the third; the nonpolar disc form of **6** allows it to pack in nearly random orientations. A model of these eight orientations was refined using extensive bond length and angle similarity restraints ($R = 0.12$).⁶

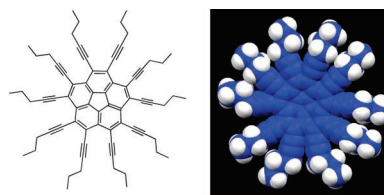


Figure 1. Line drawing and space filling models of **5**.

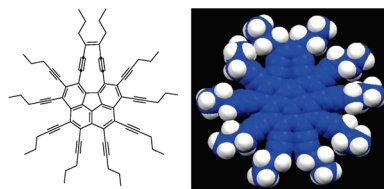


Figure 2. Line drawing and space filling models of **6**.

Table 1. Geometry of **1**, **2**, **3**, and **5**

	1 ^a	1 ^b	2 ^b	3 ^b	5 ^b
hub (Å)	1.415(2)	1.420	1.453 (1.453)	1.412	1.403(6)
spoke (Å)	1.379(2)	1.388	1.392 (1.410)	1.378	1.376(6)
flank (Å)	1.446(2)	1.449	1.444 (1.445)	1.464	1.455(6)
rim (Å)	1.383(2)	1.392	1.402 (1.416)	1.436	1.430(6)
rim/flank (deg)	121.2(1)	122.0	119.5 (119.6)	121.7	121.5(3)
flank/flank (deg)	129.9(1)	130.1	106.8 (107.0) ^d	133.6	132.9(4)
rim-sp (Å)				1.426	1.430(7)
acetylenic (Å)				1.214	1.190(7)
δ _{hub-spoke} (Å)	0.036(3)	0.032	0.061 (0.044)	0.034	0.027(8)
depth _{hub/rim} (Å)	0.87	0.87	1.53 (1.54) ^d	0.58 ^d	0.60 ^d

^a M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 5713. ^b Calcd B3LYP/cc-pVDZ(MP2/cc-pVDZ). ^c Exptl avg from this work. ^d Measured on the C₂₀ core.

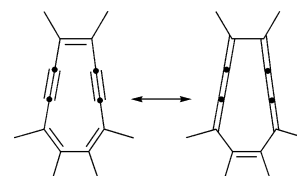
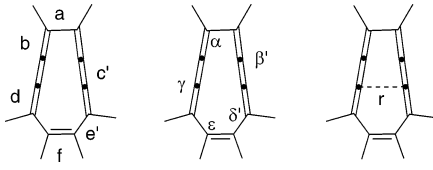


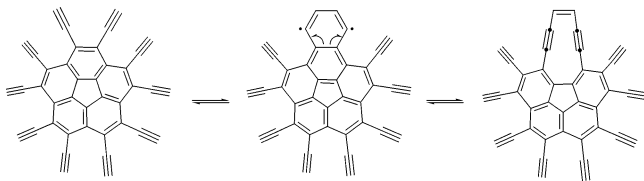
Figure 3. Two resonance forms of the [10]annulene fragment of **6**.

The structure of **6** is planar, and is a rare type of [10]annulene,¹⁰ comprising two “cumulenyl/alkynyl” linkages (Figure 3). Quantum mechanical and X-ray crystallographic geometries of **6** suggest that the alkynyl resonance form dominates (Table 2).¹¹ The alkynyl form

Table 2. Geometry of the [10]annulene Fragment of **6**


length (Å)	exptl avg	calcd ^a	angle (deg)	exptl avg	calcd ^a
a	1.387(9)	1.384 (1.401)	α/α'	116.4	118.5 (118.5)
b/b'	1.427(9)	1.398 (1.399)	β/β'	164.6	162.1 (160.7)
c/c'	1.203(9)	1.228 (1.257)	γ/γ'	176.5	177.9 (179.9)
d/d'	1.411(9)	1.404 (1.403)	δ/δ'	123.8	123.3 (122.7)
e/e'	1.401(9)	1.411 (1.423)	ϵ/ϵ'	137.5	138.2 (138.1)
f	1.475(9)	1.481 (1.469)			
r	3.113(9)	3.170 (3.139)			

^a Calcd B3LYP/cc-pVDZ(MP2/cc-pVDZ).

**Figure 4.** Conceptual enediyne cyclization of **3** to [10]annulene (**7**) via the diradical (**8**).

would retain the [5]radialene core found generally for corannulene derivatives. The cumulene/alkynyl linkages kink in such a way as to betray a substantial transannular interaction and give rise to a short “nonbonded” carbon–carbon contact “*r*” (ca. 3.1 Å).¹²

The formation of **6** can be deduced to have come from the enediyne cyclization anticipated for the formation of **2** from **3**.³ Instead of inducing a radical cyclization cascade or picking up two hydrogen atoms from the surroundings, the in situ formed naphthylidradical homolytically opens its central bond to yield **6** (Figure 4). A possible explanation for the novel reactivity of the diradical is that the flanking alkyne groups are too distant to enter the radical cascade but close enough to block interactions with solvent or hydrogen donors, thus making the ring-opening pathway viable.^{13,14} The challenge remains to find conditions which direct the diradical intermediate into the cascade and to analogues of **2**.

The [10]annulene **6** should benefit energetically from a reduction of overall ring strain and the stabilization associated with a 10-electron aromatic cycle. Full MP2/cc-pVDZ place **7** ca. 20.9 (19.2 ZPE) kcal/mol lower in energy than **3**; however, computational energies for simple 1,2-diethynylbenzene (C₁₀H₆) and its dicumuleny-[10]annulene isomer (C₁₀H₆) suggests that the parent rearrangement would be ca. 17.8 (18.7 ZPE) kcal/mol endothermic. Thus, this fragment seems to be stabilized by its incorporation into the PAH network.

Computed physical properties of derivatives of **2** (e.g., near IR absorption at 550 and 894 nm, dipole moment of 5.6 D, and thermal stability) all speak to the possibilities for this structure to be of great use in materials chemistry. Cognates **2** can be viewed as the first members in the series of 5-fold symmetric SWCNT and potential seed compounds for the preparation of monodisperse

higher order SWCNT. Given the efficient synthesis of **1** and the relatively short way from **1** via **4** to **5**, there would seem to be good reasons to be optimistic about finding efficient conditions for solution-phase syntheses of SWCNTs.

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Supporting Information Available: Synthetic procedures, computational coordinates, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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