

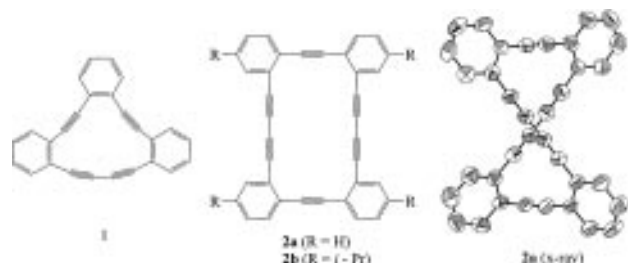
Synthesis, Crystal Structure, and Explosive Decomposition of 1,2:5,6:11,12:15,16-Tetrabenzo-3,7,9,13,17,19-hexadehydro[20]annulene: Formation of Onion- and Tube-like Closed-Shell Carbon Particles

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Dehydroannulenes and their benzofused derivatives, originally of interest mainly as molecules with which to probe cyclic π -electronic delocalization,¹ have been the subject of renewed attention, because of their potential to function as precursors to or models for new materials, in particular novel carbon allotropes and related polymers with high C/H ratios.^{2,3} We have reported that tribenzotetradehydro[14]annulene **1** undergoes topochemical polymerization that results in a novel polyanulenoene.⁴ In this connection, the “expanded” title compound **2a** suggested itself as a promising candidate on route to unprecedented annulene-crosslinked polyenyne. We report the very different physical and chemical behavior of **2a**, most importantly its explosive transformation to methane, hydrogen, and extensively ordered pure carbon.



The synthesis of **2a** was accomplished by oxidative coupling [Cu(OAc)₂·H₂O, pyridine, CH₃OH, Et₂O]⁵ of bis(2-ethynylphenyl)ethyne⁶ in 13% yield, a procedure that also gave the corresponding trimer (5%), and traces of a pentamer.⁷ In

contrast to planar and strained **1**, **2** (and the trimeric analog) adopt non-planar, essentially unstrained,^{3c,d,8} chiral configurations in the crystal.⁷ MNDO-PM3 calculations⁹ on **2a** reproduce its twisted *D*₂-symmetric conformation and predict a barrier to enantiomerization through a planar structure of 7.5 kcal mol⁻¹. To probe the occurrence of this process in solution,¹⁰ the tetrakis-(isopropyl) derivative **2b** was prepared, starting from commercial 2-bromo-4-isopropylbenzenamine in a scheme analogous to that employed for **2a** (five steps, 5.2% overall yield).⁷ Decoalescence of the diastereotopic methyl carbon resonances occurred at -87 °C (500 MHz, THF-*d*₈) indicating a $\Delta G^\ddagger = 9.3$ kcal mol⁻¹, in reasonable agreement with the calculated value.¹¹ Inasmuch as **2** can be regarded as a carbomer^{2c} of tetrabenzocyclooctatetraene, it is noteworthy that the former is considerably more mobile not only than the latter ($\Delta G^\ddagger > 45$ kcal mol⁻¹)¹² but cyclooctatetraene itself.¹³

Not surprisingly, in light of the X-ray data, and in contrast to **1**, **2a** does not undergo UV light-induced topochemical polymerization (in solution or the crystal) but is inert to irradiation. However, most dramatic is its thermal behavior:¹⁴ under vacuum at 245 °C it exploded violently with a flash of orange light, the evolution of gas, and the formation of black powder. Quantification of this reaction revealed a sharp exotherm (and no endotherm) by DSC (differential scanning calorimetry), signaling the release of 95 kcal mol⁻¹ of heat.^{15,16} TGA indicated a mass loss of 10% at this temperature, and analysis of the gases evolved (Raman spectroscopy, gas phase NMR) allowed their identification as CH₄ and H₂. Significant mass loss of hydrogen-rich molecules from **2a**, which already contains 96.4% carbon, suggested that an essentially pure carbon material is produced. An indication of what we presume to be the initial stages of this process is provided by UV (337 nm N₂ laser) LD-TOF and IR LD-FTMS¹⁷ measurements on neat thin films of **2a**.¹⁸ The former provided a clean molecular ion spectrum at low laser intensity; whereas, at higher laser power, oligomers of up to 20 units could be detected. The latter technique allowed the resolution of the oligomer signals to peak envelopes that revealed the formation of not only straight oligomers M_n^+ but also a range of molecules with ($M_n^+ - H_x$, rel intensity 100%) and [$(M_n^+ - H_x) - CH_4$, ca. 10%].¹⁹ Clearly, some stepwise “annealing” process is taking place on route to the final carbon product.

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(14) Compounds **2b** and the trimeric analog of **2a** also explode on heating and are the subject of continuing investigations.

(15) This value (47.5 kcal per diyne unit) is noticeably higher than that measured for topochemical 1,3-diyne polymerizations, typically approximately -31 to -39 kcal mol⁻¹ (Eckhardt, H.; Prusik, T.; Chance, R. R. *Macromolecules* **1983**, *16*, 732 and references therein).

(16) Two derivatives of the close analog of **2a**, 1,2:7,8-dibenzo-3,5,9,11-tetrahydro[12]annulene, polymerize with $\Delta H = -55.2$ and -39.0 kcal mol⁻¹, respectively. See: ref 3b.

(17) We thank Professor C. L. Wilkins, UC Riverside, for performing the FT experiments.

(18) For similar applications of this technique, see: ref 1 (on **1**). Hunter, J. M.; Fye, J. L.; Boivin, N. M.; Jarrold, M. F. *J. Phys. Chem.* **1994**, *98*, 7440 and references therein.

(19) For example, detected for the following: $n = 2$, $x = 1-7$; $n = 3$, $x = 1-13$; $n = 5$, $x = 1-15$.

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(2) For dehydroannulenes, see, inter alia: (a) Diederich, F. In *Modern Acetylene Chemistry*; Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, 1995; Chapter 13, p 443 and references therein. (b) Tobe, Y.; Fujii, T.; Matsumoto, H.; Naemura, K. *Pure Appl. Chem.* **1996**, *68*, 239. (c) Chauvin, R. *Tetrahedron Lett.* **1995**, *36*, 397.

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(6) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266. This procedure is greatly improved (61% in three steps) by the one-step synthesis of bis(2-bromophenyl)ethyne from commercial *o*-bromiodobenzene and gaseous ethyne (90%).⁷

(7) For experimental, spectral, and structural details, see Supporting Information.

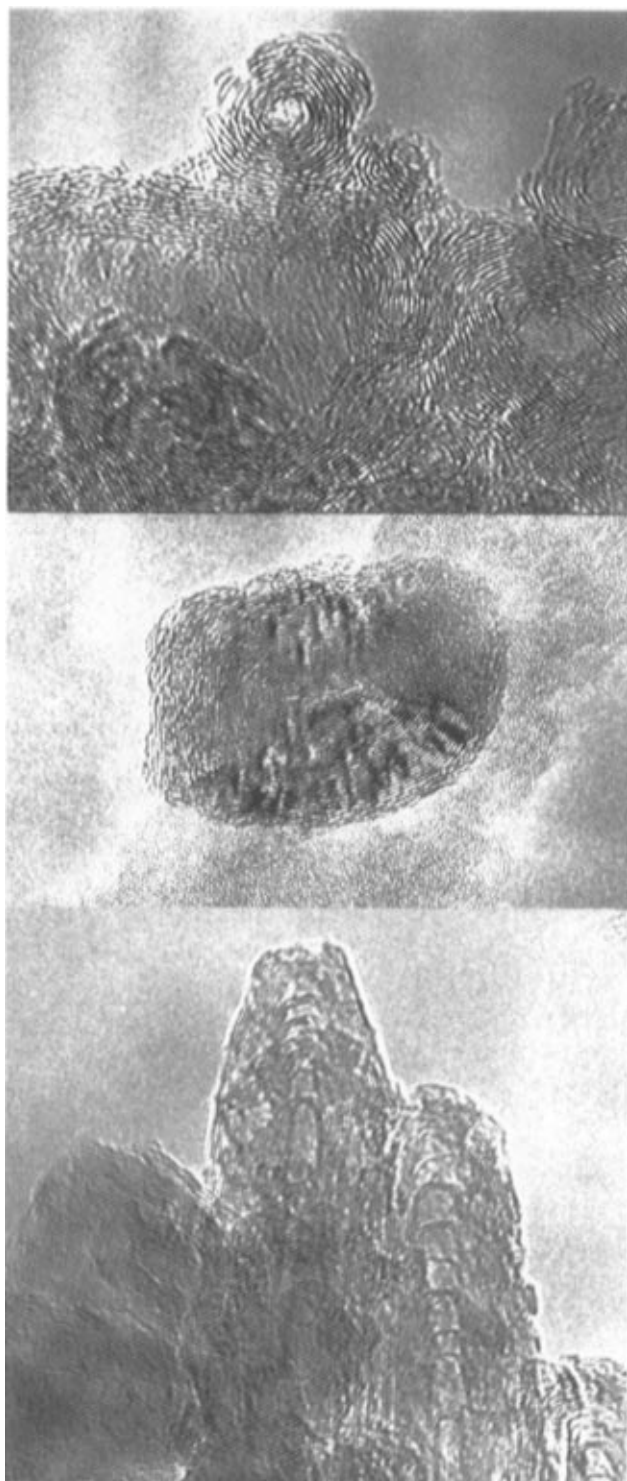


Figure 1. TEM images of various areas in samples of carbon produced from **2a**: concentric spherical nanocapsules of "hollow graphitic onions" (top); a distorted "filled graphitic onion" (center); multicapped carbon nanotubes (bottom). The distances between dark parallel lines correspond to graphitic sheet spacings.

Treatment of the black powder with various solvents (toluene, pyridine, HMPA) did not extract any soluble components (such as fullerenes). However, TEM (transmission electron microscopy) investigations²⁰ on several samples revealed the presence of not only amorphous carbon and graphite but also formation of ordered carbon layers of tube- and onion-type²¹ (Figure 1), seemingly caught at various stages of annealing from imperfect

(20) For a review of TEM studies on various forms of graphitized carbon blacks, see: *Carbon Black*; Donnet, J.-B.; Bansal, R. C.; Wang, M.-J., Eds.; Marcel Dekker: New York, 1993.

to increasingly more closed-shell carbon particles. The structures we observe are very similar to those obtained in numerous studies depicting the conversion of less- to more-highly-ordered carbon by various forms of high-energy treatment.²² As such they are not novel, but their simple method of instantaneous thermal preparation from a single, defined, high-energy organic precursor is unique^{20a,21,23} and may be general.^{14,24}

We believe that our observations open up a new area of exploration, starting with mechanistic studies²⁵ and the determination of the effect of crystal packing on the morphology of the resulting carbon allotrope, perhaps ultimately leading to designed synthesis. Moreover, the alkyne and arene functionalities in the starting material could be utilized to bind transition metals,²⁶ in order to test for the possibility of catalysis in tubular or spherical carbon formation²⁷ or on route to metal encapsulating carbon tubes or spheres.²⁸ Other structural "tailoring" can be readily envisaged in approaches to non-carbon nanotubes.²⁹ Finally, our results present a clear validation of the notion that dehydroannulenes might be potential precursors to carbon allotropes.

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Supporting Information Available: Experimental and spectral details of the routes to **2a**, **2b** and structural data for **2a** and its trimer analog (53 pages). See any current masthead page for ordering and Internet access instructions.

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