Versatile Synthetic Route to and DSC Analysis of Dehydrobenzoannulenes: Crystal Structure of a Heretofore Inaccessible [20]Annulene Derivative

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The synthesis and chemistry of dehydroannulenes and their benzannelated analogs, although extensively explored during the Sondheimer era,[1] has experienced a vigorous resurgence over the last few years.[2,3] Much of the renewed interest can be attributed to the recognition that these compounds can potentially serve as precursors for a variety of technologically important, carbon-rich molecular and polymeric systems, such as novel allotropes of carbon, molecular scaffolds, and ladder polymers.[2–4] To systematically study the reaction chemistry and possible materials properties, researchers need easy access to differing topologies of dehydrobenzoannulenes on greater than milligram scale. Traditional syntheses of the macrocycles have involved copper-mediated dimerization/cyclooligomerization reactions of suitable α,ω-diacetylenes.[5] While simple in design and execution, these reactions typically lead to complex mixtures of products that are difficult to separate and often provide low isolated yields of a given macrocycle. Additionally, the variation of product structure is severely limited by the ease of construction (or lack thereof) of the starting diyne. We report herein a simple, one-pot procedure that allows preparation of novel α,ω-polyynes, thus leading to dehydrobenzoannulenes of varying topologies previously available only in low yield (2[6] and 5[3b]) or altogether inaccessible by traditional routes (1, 3, and 4).[7]

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(1) For a comprehensive review of annulene chemistry, see: Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers;* CRC Press: Boca Raton, 1987; Vols. 1–3.

(2) Dehydroannulenes: (a) Diederich, F. *Nature (London)* **1994**, *369*, 199–207. (b) Diederich, F. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995. (c) Tobe, Y.; Fujii, T.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *J. Am. Chem. Soc.* **1996**, *118*, 2758–2759. (d) Tobe, Y.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1800–1802.

(3) Dehydrobenzoannulenes: (a) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294–1301. (b) Guo, L.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 243–244. (c) Baldwin, K. P.; Simons, R. S.; Rose, J.; Zimmerman, P.; Hercules, D. M.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1257–1258. (d) Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215–1218. (e) Kuwantani, Y.; Ueda, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1892–1894. (f) Kawase, T.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2664–2666.

(4) (a) Young, J. K.; Moore, J. S. in *Modern Acetylene Chemistry*, Stang, P. J.; Diederich, F., Eds.; VCH: Weinheim, **1995**. (b) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1073–1076. (c) Baughman, R. H.; Galvao, D. S.; Cui, C.; Wang, Y.; Tomanek, D. *Chem. Phys. Lett.* **1993**, *204*, 8–14. (d) Baughman, R. H.; Eckhardt, H.; Kertész, M. *J. Chem. Phys.* **1987**, *87*, 6687–6699. (e) Rubin, Y.; Parker, T. C.; Khan, S. I.; Holliman, C. L.; McElvany, S. W. *J. Am. Chem. Soc.* **1996**, *118*, 5308–5309.

(5) (a) Glaser, C. *Chem. Ber.* **1869**, *2*, 422–424. (b) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321. (c) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963**, *4*, 225–328. (d) Vögtle, F.; Berscheid, R. *Synthesis* **1992**, 58–62.

(6) Boese, R.; Matzger, A. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2052–2053. We thank Professor Vollhardt for sharing this information prior to publication.

(7) A detailed account of the synthesis of closely related dodecadehydrotribenzo[18]annulene and several derivatives in connection to the hypothetical, all-carbon polymeric network *graphdiyne* has been reported elsewhere: Haley, M. M.; Brand, S. C.; Pak, J. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, in press.
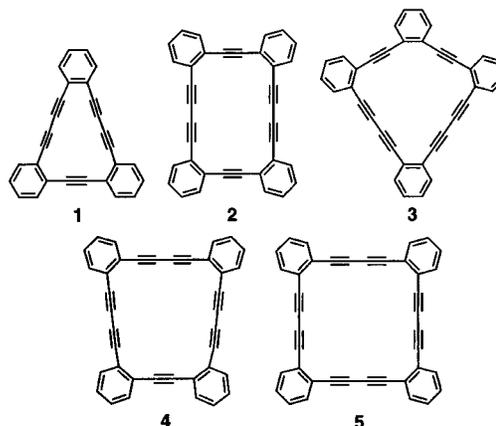
In order to ensure formation of a single product, an intramolecular dimerization of α,ω-polyynes was envisaged to prepare **1–5**. Synthesis of each polyyne would necessitate use of a suitably functionalized phenylbutadiyne. Unfortunately, the parent molecule, 1-phenyl-1,3-butadiyne, is a highly reactive compound which polymerizes rapidly when neat or in concentrated solution; even a dilute solution at −20 °C polymerizes within a few hours.[8] This extreme reactivity has limited the synthetic utility of phenylbutadiynes to date. Indeed, all of our attempts to use unprotected phenylbutadiynes in Pd-catalyzed alkynylation reactions provided intractable polymeric gums. Other approaches have been developed that formally introduce a phenylbutadiyne moiety; however, these are multistep conversions with low overall yields.[9]

To avoid the forementioned problems, we found that *in situ* generation of phenylbutadiynes gave very good to excellent yields of coupled products.[10] The route to annulene **1**, depicted in Scheme 1, illustrates the technique. 1-Bromo-2-iodobenzene[11] served as the cornerstone for construction of multigram quantities of both iodoarene **6** and butadiyne synthon **7** by repetitive alkynylation,[12] desilylation,[13] and/or iodination[14] methods. Slow addition of **7** to a vigorously stirred, degassed solution of **6** using the deprotection/alkynylation conditions (step g) furnished pentayne **8** in 84% yield. Extension of this reaction sequence to other iodoarenes provided a series of bis(triisopropylsilyl)-protected α,ω-polyynes in very good yields (Table 1). Subsequent desilylation of **8** with Bu$_4$NF and cyclization with Cu(OAc)$_2$[5] under pseudo-high dilution conditions provided pale yellow needles of **1** as the sole product in 40% overall yield. In a similar manner annulenes **2–5** were obtained, albeit in more modest overall yields (25–30%).[16] Macrocycles **1–5** are remarkably stable, showing little or no decomposition over several weeks in solution or in the crystalline state.

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(8) Brandsma, L. *Preparative Acetylenic Chemistry,* Elsevier: Amsterdam, 1971. The first edition contained the preparation of 1-phenyl-1,3-butadiyne, but stated that "...the compound proved to be very unstable, (and) can be stored at −20 °C for a very limited period." This procedure has subsequently been deleted from the second edition (1988).

(9) Bryant-Friedrich, A.; Neidlein, R. *Synthesis* **1996**, 1506–1510.

(10) Although *in situ* generation of alkynes under palladium-catalyzed coupling conditions is known, the previous examples were highly stable, monoacetylenic systems. See: (a) Rossi, R.; Carpita, A.; Lezzi, A. *Tetrahedron* **1984**, *40*, 2773–2779. (b) Carpita, A.; Lezzi, A.; Rossi, R. *Synthesis* **1984**, 571–572. (c) Huynh, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337–6344. (d) D'Auria, M. *Synth. Commun.* **1992**, *22*, 2393–2399.
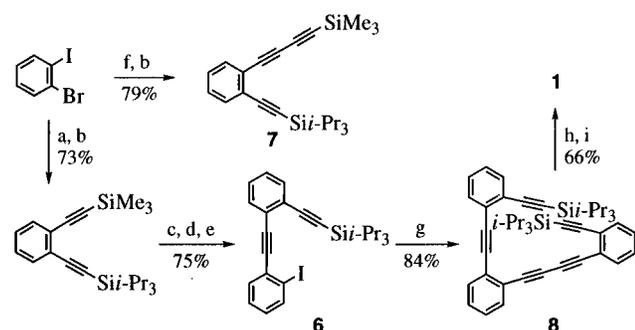
(11) Heaney, H.; Millar, I. T.; Roberts, J. D.; Montgomery, L. K. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 1120–1123. The molecule is also available from several commercial sources.

(12) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985.

(13) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

(14) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465–2466.

(15) Whitlock, B. J.; Whitlock, H. W. *J. Org. Chem.* **1972**, *37*, 3559–3561.

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Scheme 1[a]

[a] a) HC≡CSiMe₃, PdCl₂(PPh₃)₂, CuI, Et₃N; b) HC≡CSi*i*-Pr₃, PdCl₂(PPh₃)₂, CuI, Et₃N; c) K₂CO₃, MeOH; d) *N,N*-diethyl-2-iodophenyltriazene, PdCl₂(PPh₃)₂, CuI, Et₃N; e) MeI, 120 °C; f) HC≡CC≡CSiMe₃, PdCl₂(PPh₃)₂, CuI, Et₃N; g) **7**, KOH, H₂O, Pd(PPh₃)₄, PdCl₂(PPh₃)₂, CuI, Et₃N, THF; h) Bu₄NF, EtOH, THF; i) Cu(OAc)₂•H₂O, MeOH, pyridine.

Table 1. Reactants and Yields

| annulene	iodoarene	butadiyne synthon	yield of poliyne[a]	yield of annulene[b]
1	6	7	84%	66%
2	6	Me₃Si[c] Si*i*-Pr₃	77%	41%
3		7[d]	76%	43%
4		7[e]	60%	56%
5		7[f]	68%	53%

[a] Step g. [b] Combined yield of steps h and i. [c] Prepared from molecule **6** and trimethylsilylbutadiyne. [d] Prepared in two steps from **6** [e] Reference 15. [f] Reference 3b.

Examination of the solid-state structure and behavior of the macrocycles should provide some insight into the thermal stability of this class of annulenes. Accordingly, we obtained X-ray crystal structures for all of the new annulenes; the structure of compound **3** is shown in Figure 1. The molecule possesses a distorted saddle shape, with the alkyne moieties showing a deviation from linearity on the order of 1.5−8.1°. This range is slightly greater than the deformation observed in **5** (0.6−6.0°)[3b] and considerably more so than in isomeric annulene **2** (0.6−3.9°).[6] Semiempirical calculations accurately reproduce these geometrical observations.[17]

Thermal analysis of macrocycles **1**−**5** showed the molecules to be extremely reactive. All of the annulenes underwent irreversible exothermic reaction prior to melting (*ca.* 175−250 °C) as determined by differential scanning calorimetry (Table 2). Dehydrobenzo[16]annulene **1** was the notable exception, reacting around 135 °C; this was undoubtedly due to the ring strain in the constricted annulenic core. The black thermal products were completely insoluble in common solvents.
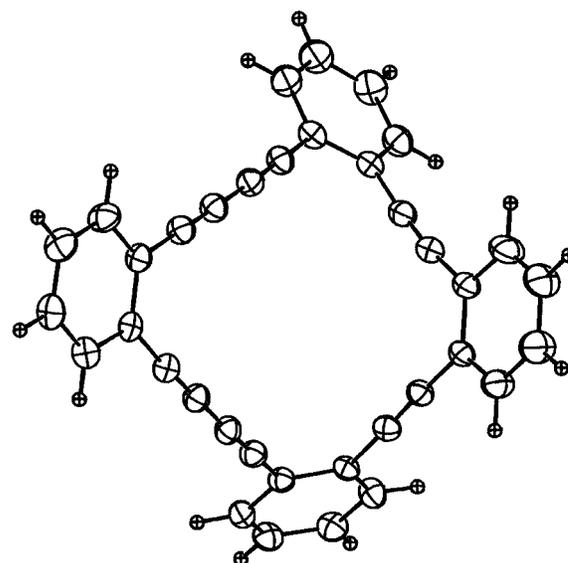
Figure 1. X-ray crystal structure of dehydrobenzoannulene **3**.

Table 2. DSC Data for Annulenes **1**−**5**[a]

annulene	T_{onset} (°C)	T_{max} (°C)	$w^{1/2}$ (°C)	ΔH_{rxn} (kJ mol⁻¹)
1	135	142	4	282
2	248	265	11	385
3	197	211	8	440
4	176	193	9	495
5	177	187	6	482

[a] Data obtained under an N₂ atmosphere.

Recent results from Vollhardt's group suggest two differing pathways for dehydrobenzoannulene decomposition. In particular, spectroscopic evidence strongly suggested that highly strained, planar, octadehydrotribenzo[14]annulene underwent topochemical polymerization at 120 °C to give a novel polydiacetylene tube structure.[3d] Alternately, nonplanar tetrabenzo molecule **2** decomposed explosively at *ca.* 250 °C to give a nearly pure carbon residue that included "bucky tubes" and "bucky onions".[6,18] In contrast, isomeric **3** reacted at 50 °C lower temperature and generated 50 kJ mol⁻¹ more energy. Although this result can be attributed partly to the greater bending in the alkyne units versus **2**, the additional exothermicity of **3** is likely due to the influence of other factors such as solid-state packing.[19] Clearly, the varying temperatures and heats of reaction in Table 2 indicate that each annulenic system behaves independently and that no generalization for accurately predicting decomposition product structure based on annulene topology can be proposed at this time. It is possible that the milder polymerization temperatures for **3**−**5** might lead to alternate pathways for dehydrobenzoannulene decomposition. It therefore appears that systematic study of the thermoproducts of each new macrocycle is warranted; this goal is being actively pursued.

Supporting Information Available: General experimental procedures, spectral data for **1**−**8**, X-ray structure of **3**, tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (14 pages). See any current masthead page for ordering information and Internet access instructions.

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(16) To date, we have limited the scale-up of the reactions to production of 500−750 mg of annulene per run, yet have observed only a minor decrease in yields.

(17) MNDO and PM3 calculations performed on a SGI workstation using Spartan molecular modeling software (version 4.1.1).

(18) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.

(19) Previous studies of the polymerization of cyclic diacetylenes with comparatively low ring strain have concluded that solid-state packing was more important than ring strain effects; see: Baughman, R. H.; Yee, K. C. *J. Polym. Sci.: Polym. Chem.* **1974**, *12*, 2467−2475. The importance of solid-state packing has been observed for highly strained systems as well.[3a]