ChemComm

Synthesis and characterization of dehydrothieno[18]annulenes

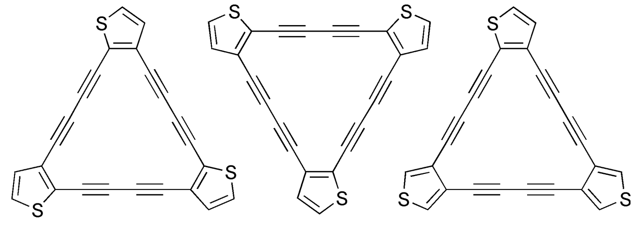
Abhijit Sarkar and Michael M. Haley*

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR 97403-1253, USA.
E-mail: haley@oregon.uoregon.edu

Received (in Corvallis, USA) 20th June 2000, Accepted 2nd August 2000
First published as an Advance Article on the web 25th August 2000

Use of a palladium/copper alkyne cross-coupling strategy provides access to three tris(thiophene-fused) dodecadehydro[18]annulenes, including examples of both highly symmetrical C_{3h} and unsymmetrical C_s structures.

We have been investigating dehydrobenzoannulenes with the aim of exploring diverse properties such as liquid crystalline behavior, solid state polymerization, and nonlinear optical activity.[1] Specifically, diacetylenic dehydrobenzoannulenes (DBAs) and related phenylacetylene macrocycles[2] have been shown to be useful precursors for a variety of carbon-rich polymeric systems, such as ladder polymers,[3] molecular tubes[4] and novel allotropes of carbon.[5] Recently, we described a simple yet versatile methodology for the preparation of site-specifically functionalized DBAs.[6] By applying a stepwise synthetic route, we were able to introduce donor and/or acceptor functional groups on the phenyl rings in a discrete manner, thereby permitting a detailed structure–property relationship study of this class of macrocycles and thus making advances toward molecular engineering.[7] In the course of further refining the design for our target annulenes, we planned to introduce thiophene rings in place of the phenyl moieties in the DBA skeleton. The choice of thiophene in our annulenes was inspired by factors such as the chemical and electrochemical polymerizability of thiophene, environmental stability of macrocycles containing thiophene, the ability to form two-dimensional π-systems useful for electronics and photonics, and interaction among the individual macrocycles due to the lone pairs present in the sulfur of thiophene rings.[8] Herein we report the preparation of three diacetylenic dehydrothieno[18]annulenes (**1**–**3**, DTAs), including the synthesis of **2** and **3** which possess unsymmetrical topologies.

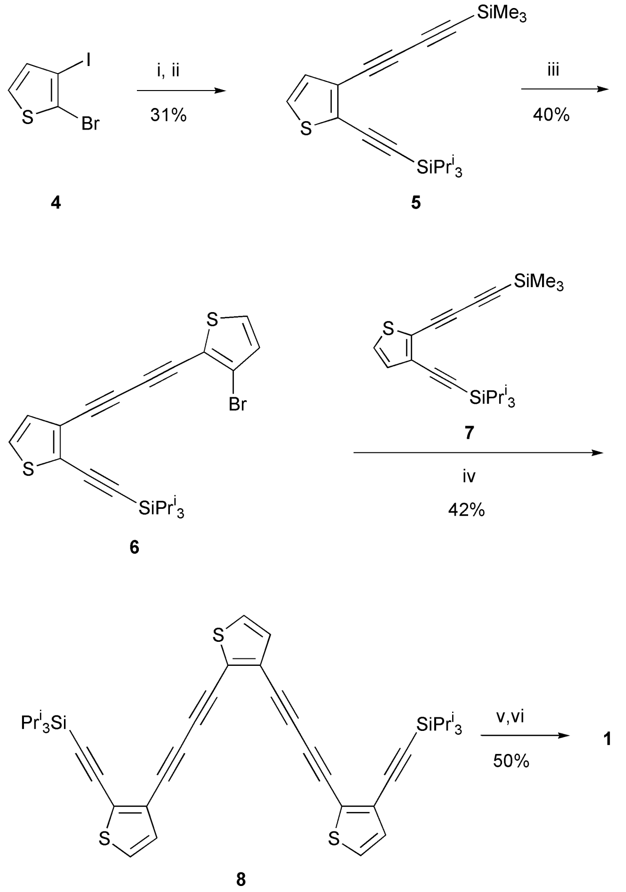


1 **2** **3**

Compounds **1**–**3** represent three of the seven possible regioisomers resulting from thiophene fusion to the [18]annulene core.[9] Other routes to thienoannulenes have relied on metal-mediated intermolecular couplings.[10] By virtue of the structure of the starting materials, only C_{nh}- and D_{nh}-symmetric macrocycles are produced. In order to probe the structure–property relationships among the various structural isomers, it is necessary to introduce the thiophene moieties in a stepwise manner to produce DTAs possessing lower symmetries (C_s), *i.e.* **2** and **3**.[11]

The synthesis of **1**, which illustrates the stepwise technique for DTA assembly, was accomplished as shown in Scheme 1. Sequential Sonogashira cross-coupling of 2-bromo-3-iodothiophene (**4**)[12] with 1-(trimethylsilyl)buta-1,3-diyne and (triisopropylsilyl)ethyne, respectively, gave triyne **5** in 31% yield. *In situ* protiodesilylation of **5** followed by Pd-catalyzed coupling[13] with an equimolar amount 3-bromo-2-iodothiophene[12] furnished bis-thiophene **6** as the major product in 40% yield. Attachment of triyne **7**, obtained in a reaction sequence similar to regioisomeric triyne **5** starting instead with 3-bromo-2-iodothiophene, provided the α,ω-bis-protected polyyne **8**. Removal of the TIPS groups with Bu_4NF in THF–EtOH and subsequent cyclization using CuCl–$Cu(OAc)_2$ in pyridine afforded **1**[†] in 50% yield. In an analogous manner, **2**[†] was prepared from **4** and two equivalents of triyne **5**, **3**[†] from **4** and two equivalents of the 3,4-regioisomeric triyne.[11]

In **1** and **2**, the thiophene moieties are fused at the 2,3-positions to the [18]annulene core, the sole difference between the macrocycles being the reversal of one thiophene ring. Therefore, the overall π-conjugation of **2** is expected to be similar to that of **1**. In **3**, two of the thiophene rings are fused to the macrocycle through the 3,4-positions. The C3–C4 bond in a thiophene ring is known to have less double bond character than the C2–C3 bond.[14] As a consequence, the overall conjugation of annulene **3** is expected to be lower than that in **1** or **2**. These arguments are supported by the electronic absorption spectra for



Scheme 1 *Reagents and conditions*: i, 1-(trimethylsilyl)buta-1,3-diyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt; ii, (triisopropylsilyl)ethyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 120 °C; iii, 3-bromo-2-iodothiophene, aq. KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 60 °C; iv, **7**, aq. KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 60 °C; v, Bu_4NF, EtOH, rt; vi, CuCl, $Cu(OAc)_2$, pyridine, O_2, 60 °C.

DOI: 10.1039/b004962j

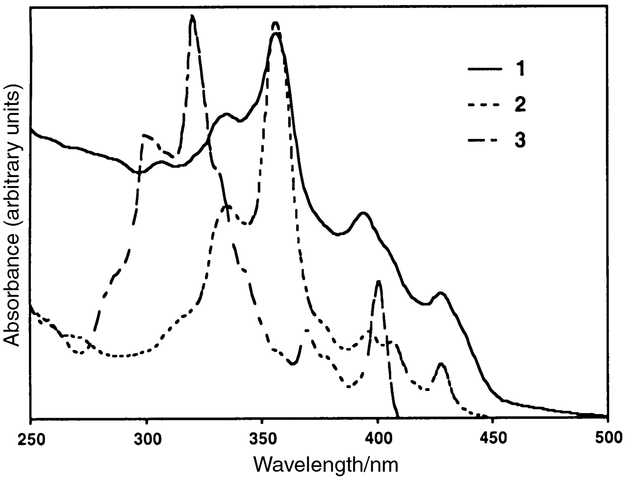


Fig. 1 Electronic absorption spectra for **1**–**3**.

1–**3** (Fig. 1). Quite expectedly, the spectra for **1** and **2** are essentially identical. Both molecules have λ_{max} at 428 nm; however, λ_{max} for **3** (401 nm) is significantly blue-shifted compared to **1** and **2**, thus indicating a lesser overall conjugation in **3**, as discussed above.

The thermal properties of **1**–**3** were studied using DSC and TGA scans. The macrocycles do not melt upon heating; instead, when heated above 150 °C, they are transformed into shiny black solids that are completely insoluble in common organic solvents. For example, DSC analysis of **1** showed a sharp exotherm at 168 °C. The TGA scan for **1** showed almost no weight loss ($< 5\%$) at the temperature range corresponding to the DSC exotherm. Therefore, the exotherm is most likely attributable to a polymerization reaction occurring in the solid state. Investigations to probe the polymerization reaction and the resultant products are in progress.

In summary, we have developed a versatile route for the synthesis of dehydrothieno[18]annulenes, including both symmetrically and unsymmetrically fused systems. A detailed structure–property relationship study of this class of macrocycles is currently underway.

We thank the National Science Foundation and the Camille and Henry Dreyfus Foundation for support of this work.

Notes and references

† *Selected spectral data*. **1**: $\delta_H(CDCl_3$, 299.96 MHz) 7.08 (d, *J* 6, 3H), 6.97 (d, *J* 6, 3H); ν_{max}(KBr)/cm^{-1} 3109, 2198, 2139, 1640, 722; *m/z* (MALDI-TOF): calcd. 390.50, found 390.47. **2**: $\delta_H(CDCl_3$, 299.96 MHz) 7.44–7.40 (m, 3H), 7.36–7.34 (m, 3H); ν_{max}(KBr)/cm^{-1} 3109, 2198, 2139, 1640, 728; *m/z* (MALDI-TOF): calcd. 390.50, found 390.68. **3**: $\delta_H(CDCl_3)$ 7.61–7.57 (m, 4H), 7.24 (d, *J* 6, 1H), 7.08 (d, *J* 6, 1H); ν_{max}(KBr)/cm^{-1} 3110, 2198, 2146, 1654, 725; *m/z* (MALDI-TOF): calcd. 390.50, found 390.53.

1 M. M. Haley, *Synlett*, 1998, 557.

2 M. M. Haley, J. J. Pak and S. C. Brand, *Topics in Current Chemistry (Carbon-Rich Compounds II)*, ed. A. de Meijere, Springer-Verlag, Berlin, 1999, vol. 201, p. 81.

3 Q. Zhou, P. J. Carroll and T. M. Swager, *J. Org. Chem.*, 1994, **59**, 1294.

4 K. P. Baldwin, A. J. Matzger, D. A. Scheiman, C. A. Tessier, K. P. C. Vollhardt and W. J. Youngs, *Synlett*, 1995, 1215.

5 R. Boese, A. J. Matzger and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1997, **119**, 2052; Y. Tobe, N. Nakagawa, K. Naemura, T. Wakabayashi, T. Shida and Y. Achiba, *J. Am. Chem. Soc.*, 1998, **120**, 4544.

6 J. J. Pak, T. J. R. Weakley and M. M. Haley, *J. Am. Chem. Soc.*, 1999, **121**, 8182.

7 H. S. Nalwa, T. Watanabe and S. Miyata, *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC Press, New York, 1997, p. 99, and references cited therein.

8 J. Roncali, *Chem. Rev.*, 1992, **92**, 711; A. K. Jen, V. P. Rao, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 90; R. Zamboni, R. Danieli, G. Ruini and C. Taliani, *Opt. Lett.*, 1989, **14**, 1321.

9 Seven possible regioisomers: C_{3h} (1 possible, *e.g.* **1**), D_{3h} (1 possible), C_{2v} (2 possible), C_s (3 possible, *e.g.* **2** and **3**).

10 D. Solooki, J. D. Bradshaw, C. A. Tessier and W. J. Youngs, *Organometallics*, 1994, **13**, 451; D. Zhang, C. A. Tessier and W. J. Youngs, *Chem. Mater.*, 1999, **11**, 3050; M. J. Marsella, I. T. Kim and F. Tham, *J. Am. Chem. Soc.*, 2000, **122**, 974.

11 The synthesis of the remaining four isomers as well as a detailed comparison of the physical properties of all seven will be detailed in a full report; A. Sarkar and M. M. Haley, work in progress.

12 S. Gronowitz and B. Holm, *Acta Chem. Scand., Ser. B*, 1976, **30**, 423.

13 M. M. Haley, M. L. Bell, J. J. English, C. A. Johnson and T. J. R. Weakley, *J. Am. Chem. Soc.*, 1997, **119**, 2956.

14 F. Fringuelli, G. Marino and A. Taticchi, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1215.