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Synthesis and Properties of Butyl-Capped Dehydrothieno[14]annulenes and Their Conversion into Terthiophenes

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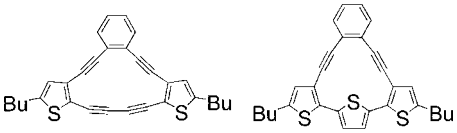
ABSTRACT



A series of butyl end-capped dehydrothieno[14]annulenes (DTAs) has been prepared. These compounds were further transformed into electron-rich terthiophenes (3TPs) by reaction with sodium sulfide. The DTA and 3TP macrocycles were compared qualitatively using UV−vis spectroscopy, and the latter were found to have lower energy absorptions. The conformations of these molecules were also examined by DFT-YFLP computations.

Electron-rich unsaturated compounds have been of considerable focus in recent years.[1] Conjugated acetylenic systems, in particular,[2] have garnered the bulk of this interest, which can be attributed to the ease of preparation[3] and interesting materials properties such as nonlinear optical (NLO) activity,[4] liquid crystalline behavior,[5] and molecular switching.[6] Our group has had a long-standing interest in the preparation of these highly unsaturated systems, particularly arene/acetylene motifs such as dehydrobenzoannulenes (DBAs).[7−9]

Concurrently, conjugated thiophene systems have also attracted much interest due to their highly conductive properties, optical properties, and relative environmental stabilities over many of their benzene-based analogues.[10,11] Incorporating thiophenes into arene/acetylene motifs was originally explored by the groups of Youngs (e.g., **1**, Figure 1)[12] and Marsella (e.g., **2**),[13] which produced macrocycles of higher order symmetries through intermolecular cyclization reactions of simple synthons.[12,13] Our desire for improved syntheses via intramolecular ring closure led to our initial communication that focused on the [18]annulene skeleton (e.g., **3**);[14] however, stability problems with the intermediate thienyldiynes forced us to examine 14-membered dehydrobenzothienoannulene (DBTA, e.g., **4**, **5**)

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(1) Inter alia: (a) *Topics in Current Chemistry (Carbon Rich Compounds I)*; de Meijere, A., Ed.; Springer-Verlag: Berlin, 1998; Vol. 196. (b) *Topics in Current Chemistry (Carbon Rich Compounds II)*; de Meijere, A., Ed.; Springer-Verlag: Berlin, 1999; Vol. 201. (c) *Carbon-Rich Compounds: From Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006. (d) *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007.

(2) Inter alia: (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644. (b) Nielsen, M. B.; Diederich, F. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002; pp 196−216. (c) *Acetylene Chemistry: Chemistry, Biology, and Material Science*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2005.

(3) (a) *Metal Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004. (b) *Transition Metal Catalyzed Reactions − IUPAC Monographs Chemistry for 21st Century*; Davies, S. G., Murahashi, S., Eds.; Blackwell Science: Oxford, 1998.

(4) (a) Sarkar, A.; Pak, J. J.; Rayfield, G. W.; Haley, M. M. *J. Mater. Chem.* **2001**, *11*, 2943–2945. (b) Slepkov, A.; Hegmann, F. A.; Tykwinski, R. R.; Kamada, K.; Ohta, K.; Marsden, J. A.; Spitler, E. L.; Miller, J. J.; Haley, M. M. *Opt. Lett.* **2006**, *31*, 3315–3317. (c) Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 13972–13973.

(5) (a) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655–2656. (b) Pesak, D. J.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1636–1639. (c) Seo, S. H.; Jones, T. V.; Seyler, H.; Peters, J. O.; Kim, T. H.; Chang, J. Y.; Tew, G. N. *J. Am. Chem. Soc.* **2006**, *128*, 9264–9265.

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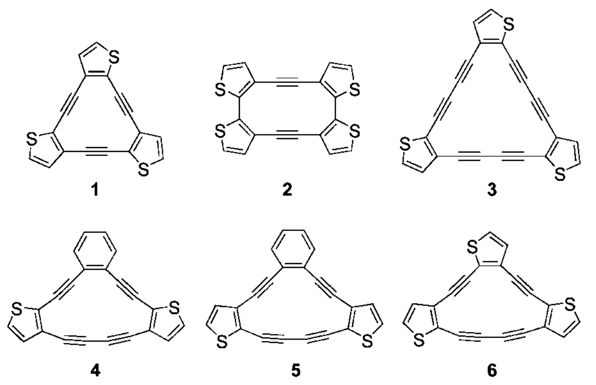

Figure 1. Previously prepared DBTAs and DTAs.

and dehydrothienoannulene (DTA, e.g., **6**) topologies, with greater success.[15]

To further our understanding and scalability of thiophene-containing macrocycles, we elected to incorporate α-butylated thiophenes as part of the macrocycle (e.g., **7**−**12**) to improve solubility and, more importantly, to protect the compounds from unwanted oxidation.[11,16] The added stability conferred by the alkyl chain should also permit us to investigate the conversion of the diacetylene linker into a thiophene ring by reaction with Na$_2$S.[17] The resultant terthiophenes (3TPs, e.g., **13**−**18**) contain more π-electron density from the thiophene sulfur atom and better electron delocalization than the diyne linker. Furthermore, the bridging 1,2-diethynylarene unit limits the rotation of the 3TPs, ideally coplanarizing the 3TP moiety and thus enhancing π-orbital overlap further. We report herein the synthesis and optical properties of DBTAs/DTAs **7**−**12** and their conversion into 3TPs **13**−**18** (Figure 2).

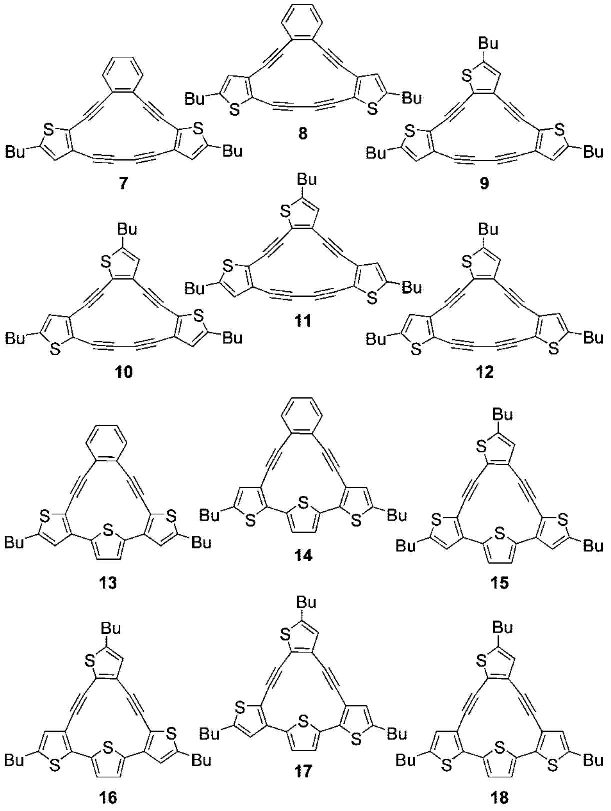

Figure 2. Target thieno-fused dehydro[14]annulenes **7**−**12** and 3TPs **13**−**18**.

As in previous work, the macrocycles were assembled from basic building blocks, namely core dihaloarenes **19** and **20** and differentially silylated diynes **24** and **26**, through a convergent design. Bromoiodothiophenes **19** and **20** were prepared according to Scheme 1. Iodination of commercially available 2-butylthiophene furnished **21**. Use of the lithium−halogen "dance" reaction[18] afforded **22** in 42% yield for the two steps. NBS bromination of **22** provided multigram quantities of **19** in 36% overall yield. Regioisomer **20** was easily prepared in an analogous manner: bromination of 2-butylthiophene and subsequent lithium-halogen dance reaction on **23**[19] followed by iodine quench generated arene

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(6) (a) Gobbi, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 674–678. (b) Gobbi, L.; Seiler, P.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **2000**, *83*, 1711–1723.

(7) (a) Marsden, J. A.; Palmer, G. J.; Haley, M. M. *Eur. J. Org. Chem.* **2003**, *235*, 5–2369. (b) Spitler, E. L.; Johnson, C. A.; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344–5386.

(8) (a) Jones, C. S.; O'Connor, M. J.; Haley, M. M. In ref 2c, pp 303−385. (b) Zhao, D.; Moore, J. S. *Chem. Commun.* **2003**, *n/a*, 807–818. (c) Zhang, W.; Moore, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4416–4439.

(9) Recent contributions, inter alia: (a) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476. (b) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213–10226. (c) Johnson, C. A., II; Lu, Y.; Haley, M. M. *Org. Lett.* **2007**, *9*, 3725–3728. (d) Tahara, K.; Johnson, C. A., II; Fujita, T.; Sonoda, M.; De Schryver, F.; De Feyter, S.; Haley, M. M.; Tobe, Y. *Langmuir* **2007**, *23*, 10190–10197. (e) Spitler, E. L.; Monson, J. M.; Haley, M. M. *J. Org. Chem.* **2008**, *73*, 2211–2223.

(10) (a) Varnavski, O.; Bäuerle, P.; Goodson, T., III. *Opt. Lett.* **2007**, *32*, 3083–3085. (b) Bhaskar, A.; Ramakrishna, G.; Hagedorn, K.; Varnavski, O.; Mena-Osteritz, E.; Bäuerle, P.; Goodson, T., III. *J. Phys Chem. B.* **2007**, *111*, 946–954.

(11) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinham, 1999. (b) Bäuerle, P. Sulfur-Containing Oligomers In *Electronic Materials: The Oligomer Approach*; Müllen K., Wegner, G., Eds.; Wiley-VCH: Weinheim,; pp 105−231.

(12) (a) Solooki, D.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1994**, *13*, 451–455. (b) Zhang, D.; Tessier, C. A.; Youngs, W. J. *Chem. Mater.* **1999**, *11*, 3050–3057. (c) See also: (ca) Iyoda, M.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M.; *Tetrahedron Lett.* **1998**, *39*, 4701−4704.

(13) (a) Marsella, M. J.; Kim, I. T.; Tham, F. *J. Am. Chem. Soc.* **2000**, *122*, 974–975. (b) Marsella, M. J.; Wang, Z.-Q.; Reid, R. J.; Yoon, K. *Org. Lett.* **2001**, *3*, 885–887. (c) Marsella, M. J.; Piao, G.; Tham, F. S. *Synthesis* **2002**, 1133–1135. (d) Marsella, M. J.; Reid, R. J.; Estassi, S.; Wang, L.-S. *J. Am. Chem. Soc.* **2002**, *124*, 12507–12510.

(14) Sarkar, A.; Haley, M. M. *Chem. Commun.* **2000**, 1733–1734.

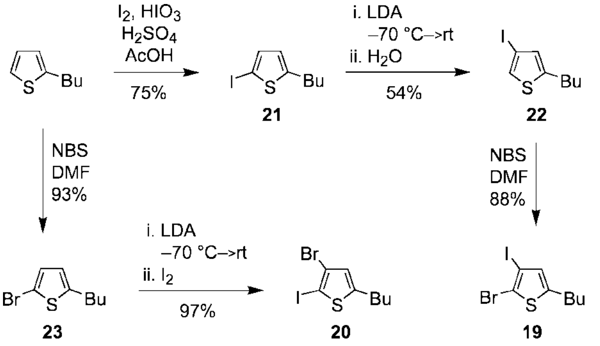
(15) (a) O'Connor, M. J.; Yelle, R. B.; Zakharov, L. N.; Haley, M. M. *J. Org. Chem.* **2008**, *73*, 4424–4432. (b) O'Connor, M. J., *Ph.D. Thesis*, University of Oregon, 2008.

(16) (a) Hotta, S.; Waragi, K. *J. Mater. Chem.* **1991**, *1*, 835–842. (b) Mohanakrishnan, A. K.; Amaladass, P.; Clement, J. A. *Tetrahedron Lett.* **2007**, *48*, 779–784. (c) Wakamiya, A.; Daisuke, Y.; Nishinaga, T.; Kitagawa, T.; Komatsu, K. *J. Org. Chem.* **2003**, *68*, 8305–8314. (d) Turbiez, M.; Frére, P.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 5357–5360.

(17) Krömer, J.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debärdemäker, T.; Mena-Osteritz, E.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3481–3486.

(18) Schnürch, M. L.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046–1057.

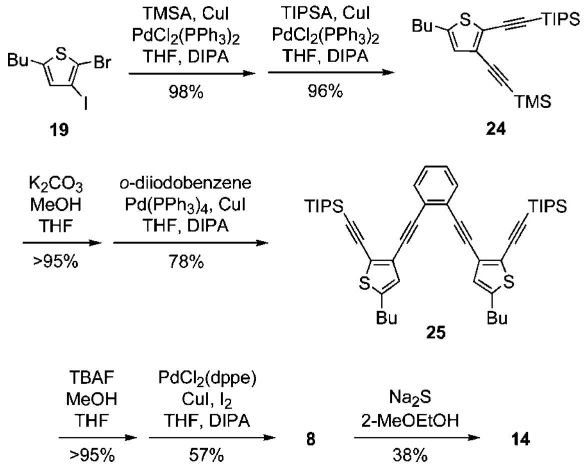
Scheme 1



20 in 90% overall yield. Halides **19** and **20** were subsequently converted into protected diynes **24** and **26** by sequential Sonogashira cross-coupling with (trimethylsilyl)acetylene (TMSA) and (triisopropylsilyl)acetylene (TIPSA) in excellent yields (vide infra).

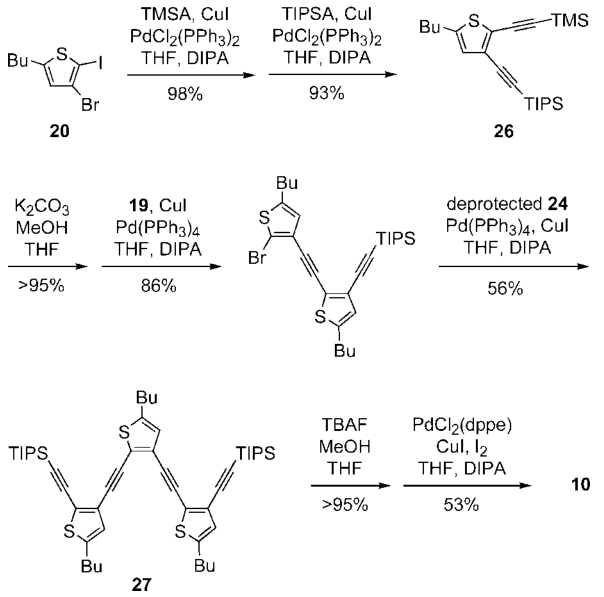
[14]DBTAs **7** and **8** and [14]DTAs **9** and **12** possess two fused thiophenes in a "symmetrical" orientation on the lower portion of the annulene and thus were assembled via 2-fold cross-coupling of the respective diyne to a central dihaloarene core. Scheme 2 illustrates a representative synthesis starting from **19**. Sequential Sonogashira reactions with TMSA and TIPSA afforded diyne **24** in 94% yield for the two steps. Selective removal of the TMS group with K_2CO_3 in MeOH followed by cross-coupling to 1,2-diiodobenzene furnished tetrayne **25** in 78% yield. Protiodesilylation with TBAF and subsequent acetylenic homocoupling utilizing $PdCl_2$(dppe) catalyst, CuI cocatalyst, and iodine as an oxidant[9a,20] gave **8** in 57% yield.

Scheme 2



[14]DTAs **10** and **11** possess two fused thiophenes in unsymmetrical orientations on the lower portion of the annulene and are thus formed by sequential cross-couplings to the dihaloarene "crown". Scheme 3 shows a representative synthesis of "unsymmetrical" DTA **10**. Dihalothiophene **20** was sequentially cross-coupled with TMSA and TIPSA under Sonogashira conditions to afford **26** in 91% yield. Selective desilylation of **26** with K_2CO_3, cross-coupling to 1 equiv of arene **19**, and then cross-coupling of the resultant bromodiyne to monodesilylated **24** furnished **27** in 48% combined yield. Macrocyclization was performed as before utilizing the Pd(II)/Cu(I) catalyst system under oxidizing conditions, affording **10** in 53% yield.

Scheme 3



Formation of the 3TPs was accomplished easily by treating the corresponding [14]annulenes with Na_2S in 2-methoxyethanol (Scheme 2). A summary of the syntheses of all six annulenes and the 3TPs is given in Table 1. Attempting 3TP formation on the previously reported nonalkylated macrocycles[15a] afforded promising results; however, the products were found to be extremely unstable to air and light, decomposing rapidly after a few hours to give uncharacter-

Table 1. Synthesis and Yields of DBTAs and DTAs **3**−**14**

arene	monodesilylated diyne (equiv) 24	26	precursor, yield (%)	annulene, yield (%)	3TP, yield (%)
19	2		pre**7**, 80	**7**, 64	**13**,46
19		2	pre**8** (**25**), 78	**8**, 57	**14**,38
19	2		pre**9**, 52	**9**, 52	**15**,43
20	1 (second)	1 (first)	pre**10** (**27**), 48	**10**,53	**16**,58
20	1 (first)	1 (second)	pre**11**, 56	**11**,66	**17**,16
19		2	pre**12**, 69	**12**,32	**18**,42

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(19) Mohanakrishnan, A. K.; Amaladass, P.; Arul Clement, J. *Tetrahedron Lett.* **2007**, *48*, 779–784.

izable mixtures.[15b] In contrast, all of the butylated products were much more stable to air, light, and silica gel, though overall yields were somewhat lower than their nonbutylated counterparts.[15a]

The UV−vis spectra for DBTAs **7** and **8** and the corresponding 3TPs **13** and **14** are shown in Figure 3a. Compared to **4** and **5**, electronic donation of the two butyl groups in **7** and **8** red shifts the respective peaks by 6−12 nm. The previously noted trends with thiophene orientation are also maintained: an increased extinction coefficient and red shift are observed for both **5** (408 nm) and **8** (422 nm) with "down" oriented thiophenes (sulfur atom adjacent to the butadiyne linkage) compared to **4** (374 nm) and **7** (381 nm) with "up" thiophenes, whereas the highest intensity peak is slightly blue-shifted for **5** (325 nm) and **8** (331 nm) over **4** (329 nm) and **7** (337 nm). Upon terthiophene formation, the lowest energy bands in **13** and **14** are significantly red-shifted from **7** and **8** (381 → 415 and 422 → 442 nm, respectively), thus reflecting enhanced electron delocalization within the 3TP macrocycles over the diacetylenic DBTAs. Additionally, thiophene connectivity via α-α linkages as in **14** affords a smaller HOMO−LUMO gap than the α-β thiophene links in **13**, which is a well-established phenomenon.[11,21]

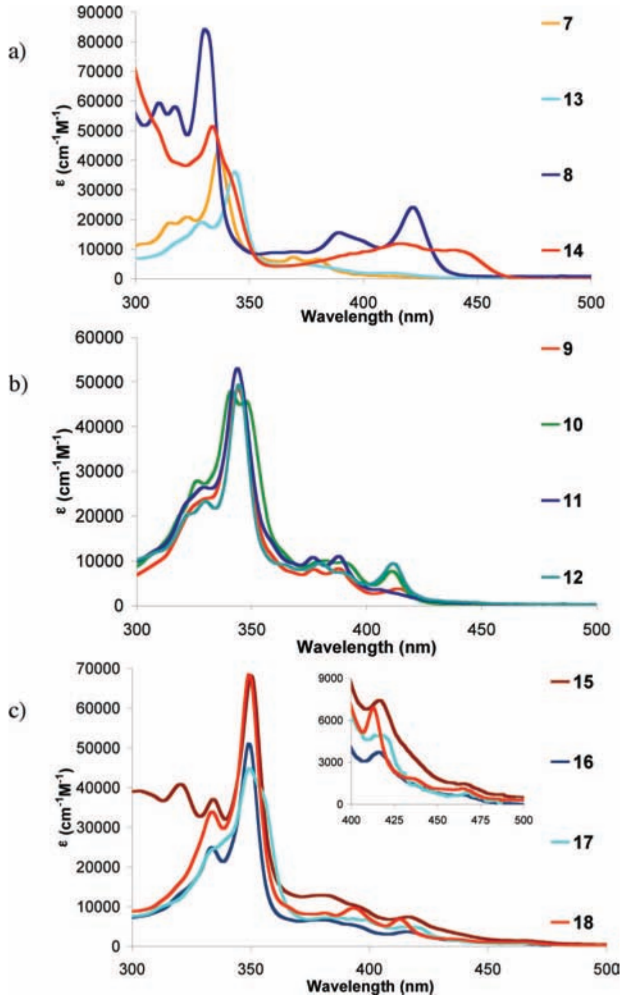

Figure 3. UV−vis absorption spectra of (a) **7**−**8**, **13**−**14**, (b) **9**−**12**, and (d) **15**−**18**. All spectra were recorded in CH_2Cl_2 at analyte concentrations of 15−25 μM.

The UV−vis spectra for DTAs **9**−**12** are depicted in Figure 3b. The most intense peak is approximately the same for **9**−**12** (ca. 345 nm), with slight variations in vibronic structure, and is red-shifted compared to **5** (335 nm), again due to the electron donation of the butyl groups. In the low energy region, the most red-shifted peak belongs to **9** (415 nm) followed by DTAs **11** and **12**, with a common peak at 412 nm, and then **10** (409 nm). Analogous to what was observed with the nonalkylated [14]DTAs,[15a] there are no discernible trends of the low energy absorptions with respect to thiophene orientation.

Sulfide-induced cyclization to generate 3TPs **15**−**18** results in further red shifting (ca. 5 nm) of the main band to 350 nm, as well as a small bathochromic shift and broadening of the low energy transitions (Figure 3c). In addition, there is a new, very weak, low energy transition centered around 465−470 nm, a feature unique to the all-thiophene 3TPs (Figure 3c inset).

DFT-YFLP calculations suppport the observed optical behavior (see the Supporting Information). The optimized structure for **14** shows a coplanar conformation across the terthiophene having the lowest energy, whereas the structure of **13** has an out of plane tilt of the central thiophene by ca. 20° due to H-atom interactions arising from the α-β thiophene links. The coplanarity of **14** results in the lowest energy/highest intensity absorption band, and the lack thereof in **13** explains the reduced intensity and absence of fine structure.

In conclusion, six α-butylated, thieno-fused dehydro[14]-annulenes were prepared that exhibit enhanced stability and synthetic scalability over their unsubstituted counterparts, which allows for subsequent conversion to a class of linked terthiophenes with enhanced planarity. Future reports will discuss the electrochemical and emissive properties of the butylated DTAs and 3TPs.

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Supporting Information Available: Experimental details and spectroscopic data for all new compounds; DFT optimized structures for **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Marsden, J. A.; Miller, J. J.; Haley, M. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1694–1697.

(21) Bredas, J. L.; Street, G. B.; Themans, B.; Andre, J.-M. *J. Chem. Phys.* **1985**, *83*, 1323–1329.