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1,3,6,9,12,14,17,20-Octaethynyltetrabenz-[*a*,*b*,*f*,*j*,*k*,*o*]-4,5,10,11,15,16,21,22-octadehydro[18]annulene: A Carbon-Rich Hydrocarbon

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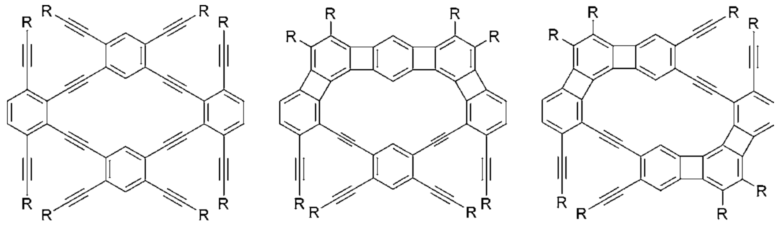
ABSTRACT



1a: R = Hex
1b: R = Pr
1c: R = DMTS
1d: R = H

2a: R = Hex
2b: R = Pr

3a: R = Hex
3b: R = Pr

Dodecaynes 1a–d have been prepared via a convergent strategy that employs Sonogashira couplings as the carbon–carbon bond-forming tool. Due to the steric bulk of the DMTS groups, 1c adopts a nonplanar conformation, the dynamics of which have been probed by VT-NMR. The cobalt-catalyzed isomerization of 1a,b produced the new conjugated phenylenes 2a,b and 3a,b, respectively.

Dehydrobenzannulenes have been subject to intense scrutiny because of their potential applications as optoelectronic, liquid crystalline, conducting, and sensing materials, as building blocks in the construction of allotropes of carbon, as scaffolds for supramolecular assemblies, and as monomers in topochemical and other polymerizations.[1] In this connection, the title compound and its derivatives **1** constitute a new topology combining the 1,2,3,4- with the 1,2,4,5-tetraethynylbenzene motifs in an elaborated octaethynylated tetrabenz[*a*,*b*,*f*,*j*,*k*,*o*]-4,5,10,11,15,16,21,22-octadehydro[18]-annulene,[2] endowed with internal hydrogens that can serve as probes for the effect of peripheral alteration on the aromaticity of the central core. Parent **1d** is also the only second hydrocarbon of composition $C_{48}H_{16}$ to be made.[3] Apart from its intrinsic interest, system **1** is an attractive substrate for an unprecedented[4] 4-fold CpCo-catalyzed isomerization to circular [8]phenylene **4** (Scheme 1). Cyclic

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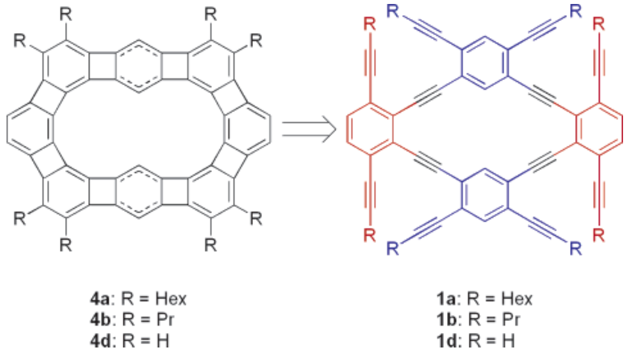
[1] For a highlight, see: (a) Höger, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 3806. For recent reviews, see: (b) Tobe, Y.; Sonoda, M. In *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004; pp 1−40. (c) Marsden, J. A.; Palmer, G. J.; Haley, M. M. *Eur. J. Org. Chem.* **2003**, 2355. (d) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153. (e) Haley, M. M. *Synlett* **1998**, 557. For very recent work, see, inter alia: (f) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464. (g) Johnson, C. A.; Haley, M. M.; Rather, E.; Han, F.; Weakley, T. J. R. *Organometallics* **2005**, *24*, 1161. (h) Baxter, P. N. W.; Dali-Youcef, R. *J. Org. Chem.* **2005**, *70*, 4935. (i) Hisaki, I.; Eda, T.; Sonoda, M.; Niino, H.; Sato, T.; Wakabayashi, T.; Tobe, Y. *J. Org. Chem.* **2005**, *70*, 1853.

[2] (a) For the parent annulene, made by alkyne metathesis, see: Miljanić, O. Š.; Vollhardt, K. P. C.; Whitener, G. D. *Synlett* **2003**, 29. (b) For a di-*tert*-butylderivative of the parent annulene, made by a stepwise protocol, see: Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227.

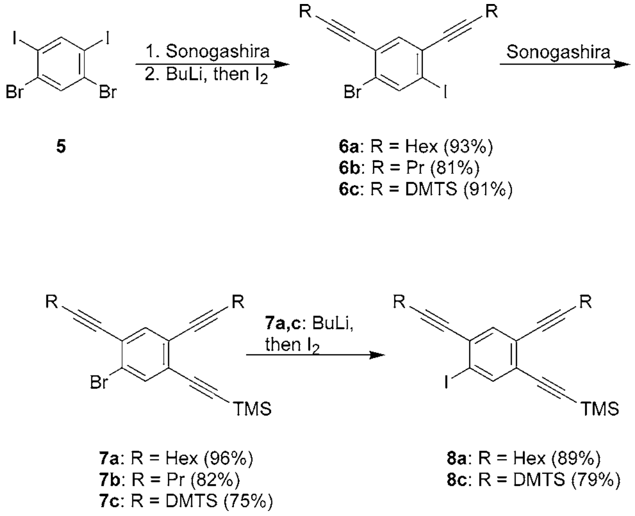
[3] For an isomeric dehydrotetrabenz[32]annulene, see: Haley, M. M.; Bell, M. L.; Brand, S. C.; Kimball, D. B.; Pak, J. J.; Wan, W. B. *Tetrahedron Lett.* **1997**, *43*, 7483.

10.1021/ol051572x CCC: $30.25

Scheme 1



Scheme 2



phenylenes of this type are important because bond alternation induced by the cyclobutadienoid rings, as pictured in the structural drawing and supported by a calculated structure (B3LYP/6-31G*) of **4d** (for this and other calculations, see Supporting Information), is expected to enable superdelocalization.[5] In **4**, such an effect would involve the Hückel-aromatic 18 and 30 electron supercircuits, respectively, of the inner and outer periphery of the polycycle.

We report on the synthesis of **1d** and its derivatives **1a**−**c** and on partly successful attempts to reach **4**.

The preparative strategy to **1**[2b] entailed the independent formation of 1,2,4,5- and 1,2,3,4-substituted arene fragments that translate into the "blue" and "red" arene units of **1** (Scheme 1), respectively. Synthesis of the "blue" building blocks **7** and **8** (Scheme 2) commenced with a Sonogashira[6] reaction (PdCl$_2$(PPh$_3$)$_2$, CuI, NEt$_3$) that targeted the more reactive iodinated positions in 1,5-dibromo-2,4-diiodobenzene **5**.[7] The ensuing bromine−iodine exchange produced **6** in high yields, which was functionalized via a second Sonogashira reaction, this time with TMSA, to give **7**. The final replacement of bromine with iodine furnished **8**, ready to be coupled with the "red" component.

The triynes **9**, reported previously,[5c,8] were chosen as the precursors for the "red" moieties of **1** (Scheme 3). Selective TMS removal from **9** generated the corresponding terminal alkynes, which were coupled with iodides **8** to give the highly functionalized diarylacetylenes **10**. Compounds **10** were the source of both pieces needed to assemble **13**. Protodetrimethylsilylation provided **11**; alternatively, another bromine−iodine exchange led to **12**. Sonogashira coupling of **11** and **12** created **13**, possessing all the carbon atoms of **1**. Finally, bromine−iodine exchange, followed by TMS deprotection and an intramolecular Sonogashira coupling, afforded **1**. A topological alternative to the above scheme is presented by the approach to **1b** and proceeded with comparable efficiency. Overall, the yields from **5** are 33% to **1a**, 7.6% to **1b**, and 16% to **1c**, a rather satisfactory outcome.

Dodecaynes **1a**−**c** are yellow-brown waxy solids that are stable to air, both neat and in solution. On the other hand, parent **1d** decomposed quickly, even in solution, thus precluding its isolation and full characterization. The electronic spectra are characterized by a lowest-energy band (λ_{max} = 369−377 nm) that is significantly shifted bathochromically relative to that of the parent dehydrobenz[18]annulene (λ_{max} = 341 nm), a reflection of the extensive alkynyl substitution. The NMR spectra feature the characteristically deshielded intracyclic hydrogen signals at $\delta \sim 7.8$ ppm[2] and the appropriate number of ^{1}H and ^{13}C peaks. An exception is **1c**, in which the DMTS spectral regions revealed not two but four sets of resonances for each of the three methyl groups, illustrated for the silylmethyls on top of Figure 1. DFT calculations predict a nonplanar configuration for **1c**, rendering these groups diastereotopic in the NMR experiment at slow exchange. Enantiomerization, tantamount to rotation around the core diarylalkyne bonds,[9] and hence coalescence, appears to be remarkably sluggish, as measured by VT-NMR at 62 and 90 °C, respectively (Figure 1, bottom). Peak-shape analysis[10] provided an activation barrier of 19.4 (±0.4) kcal mol^{-1}. In contrast, neither acyclic precursor analogues nor a related hexaethynyldehydrobenz[12]annulene[5c] were mobile conformationally at temperatures as low as −80 °C.[11]

With systems **1a**−**d** available, experiments were executed aimed at accessing circular [8]phenylene **4**. Since **1c** proved

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(4) For triple cyclizations of this type, see: Bruns, D.; Miura, H.; Vollhardt, K. P. C.; Stanger, A. *Org. Lett.* **2003**, *5*, 54 and references therein.

(5) For reviews of the phenylenes, see: (a) Miljanić, O. Š.; Vollhardt, K. P. C. In *Carbon-Rich Compounds: Molecules to Materials*; Haley, M. M., Tykwinsky, R. R., Eds.; Wiley-VCH: Weinheim, 2005; in press. (b) Vollhardt, K. P. C.; Mohler, D. L. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI: London, 1996; pp 121−160. For a related approach to circular [6]phenylene, "antikekulene", see: (c) Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103.

(6) Sonogashira, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; Wiley: New York, 2002; Vol. 1, pp 493 and references therein.

(7) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

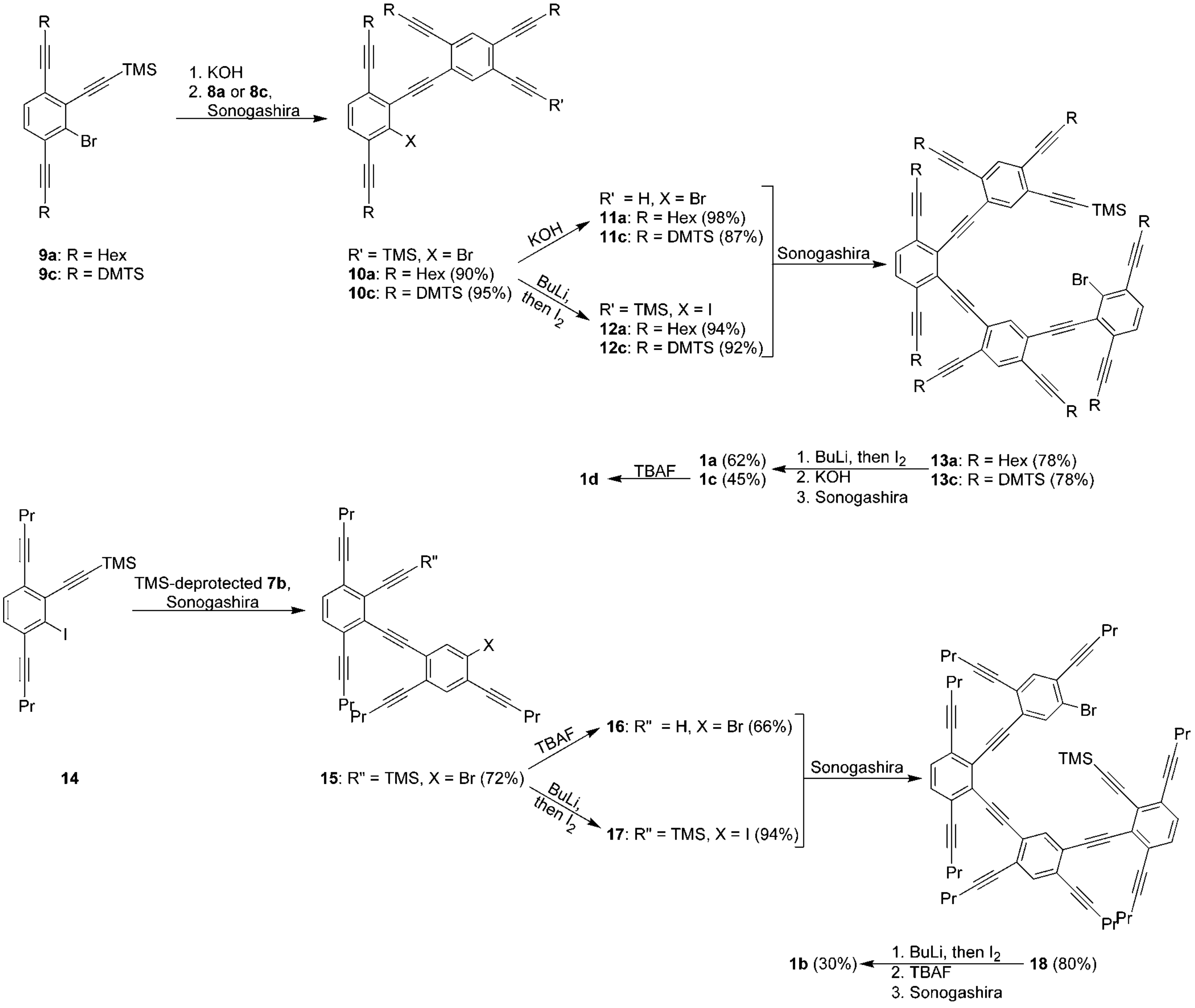
(8) While **9a** was not known prior to this work, it was readily prepared using the procedure described for **9b**,**c** (see Supporting Information).

(9) For the observation of hindered rotation in 2,2′,6,6′-tetrakis(alkynyl)-diphenylacetylenes, see: Miljanić, O. Š.; Han, S.; Holmes, D.; Schaller, G. R.; Vollhardt, K. P. C. *Chem. Commun.* **2005**, 2606.

(10) (a) Ôki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Weinheim, 1985. (b) Gasparro, F. P.; Kolodny, N. H. *J. Chem. Educ.* **1977**, *54*, 258.

(11) Hisaki, I.; Vollhardt, K. P. C. Unpublished results.

Scheme 3



to be inert and **1d** decomposed in the presence of $CpCoL_2$, even using in situ deprotection protocols,[1b,c,e] most efforts focused on the isomerizations of **1a** and **1b** (Scheme 4). Disappointingly, only double cyclizations were achieved to the deep-red doubly bent [5]- and yellow angular [3]-phenylene derivatives **2** and **3**, respectively. DFT calculations of all possible cyclization intermediates of **1d**, either in their most stable or in a constrained planar conformation, indicate that, as the quite exothermic cycloisomerization sequence progresses, the remaining triple bonds in the product of each step become increasingly separated, thus likely retarding the normally facile cobaltacyclopentadiene(alkyne) formation.[12] A similar phenomenon had frustrated an approach to circular [6]phenylene.[5c] It is noteworthy that the third possible isomeric product of biscyclization (the angular [5]phenylene version of **2**) was not observed. Attempts to induce further conversion of **2b** or **3b** in the presence of $CpCo(CO)_2$ in boiling 1,2-dichlorobenzene led to recovery of the respective starting materials, while switching the solvent to boiling 1,2,4-trichlorobenzene led to decomposition.

This failure notwithstanding, systems **2** and **3** represent only the third and fourth examples of phenylenocyclynes in which the terminal rings of a phenylene are linked by a conjugating bridge, and the changes in their properties as a result of this feature are of interest. Indeed, the molecules appear to be more air sensitive than their component phenylenes,[5a−c] and solutions ($CHCl_3$) of, e.g., **2a** in air decomposed within hours. In this case, the mass spectra of the complex product mixture revealed molecular ions consistent with the addition of one and two molecules of oxygen, and the IR spectrum exhibited a strong band at 1645 cm^{-1}, suggesting oxidation via initial single and double endoperoxidation, as observed for angular [3]- and zigzag [5]phenylene.[5a,13] The electronic spectra, e.g., of **3a** and **3b**,

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(12) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247.

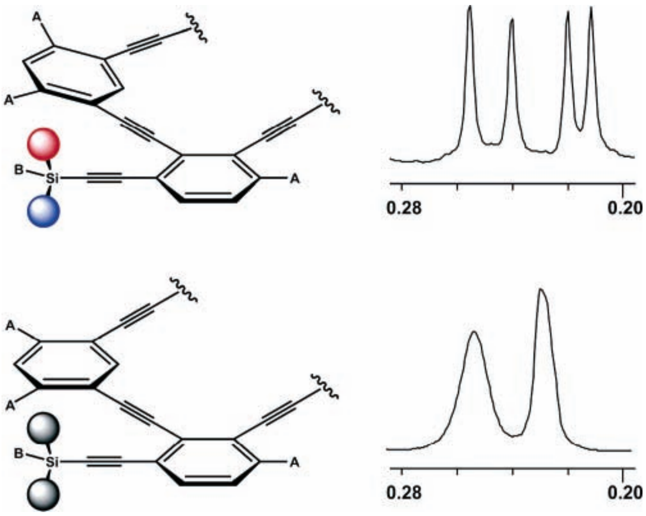

Figure 1. Silylmethyl ^{1}H NMR spectra (dioxane-d_8) of **1c** at 22 (top) and 99 °C (bottom). The colored spheres represent the (potentially) diastereotopic methyl substituents; A = DMTS−C≡C−, B = $(CH_3)_2CH(CH_3)_2C-$.

provide a quantitative measure of increased delocalization in longest wavelength maxima, which are shifted to lower energies when compared to the parent phenylene substructures, e.g., $\Delta\lambda_{max} = 35$ nm for **2b** and $\Delta\lambda_{max} \sim 84$ nm for **3b**.[5a−c,14] A similar comparison of the ^{1}H NMR spectra of **2** and **3** with those of their component phenylenes and of **1** illustrates the absence of any significant "super ring current" effects. For example, the two relatively sharp singlets at $\delta = 7.69$ (inner H) and 7.49 ppm (outer H) of the tetraalkynylbenzene ring hydrogens in **2a** compare well with the

Scheme 4[a]

$$\begin{matrix}\textbf{1a}\\ \textbf{1b}\end{matrix} \xrightarrow[\text{(4 equiv)}]{\text{CpCo(CO)}_2} \begin{matrix}\textbf{2a}\text{: R = Hex (10\%)}\\ \textbf{2b}\text{: R = Pr (7\%)}\end{matrix} + \begin{matrix}\textbf{3a}\text{: R = Hex (10\%)}^a\\ \textbf{3b}\text{: R = Pr (36\%)}\end{matrix}$$

[a] Inseparable mixture with **2a**. Isomer **2a** was the only product (11%) when 6 equiv of $CpCo(CO)_2$ was employed.

corresponding signals in **1a**: $\delta = 7.81$ and 7.43 ppm. The more coupled[15] central phenylene hydrogens at $\delta = 6.67$ (inner H) and 6.47 ppm (outer H) have counterparts in the parent [5]phenylene at $\delta = 6.73$ and 6.58 ppm. The assignments in **2a** (inner vs outer H) were corroborated by NOE experiments.

In summary, a convergent and robust synthetic route to the octaalkynylated dehydrobenz[18]annulenes **1** has been developed. These macrocycles appear to adopt a nonplanar conformation, the dynamics of which can be probed by NMR with suitable diastereotopic probes. The derivatives **1a** and **1b** were partly cyclized to the cyclically delocalized phenylenes **2** and **3**, in which the remaining alkyne units seem too distant to undergo CpCo-catalyzed cyclotrimerization to circular [8]phenylene **4**. Future work will aim to modify chemically the phenylene skeletons of **2** and **3** to circumvent this problem.

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Supporting Information Available: Experimental and calculational procedures, characterization of all new compounds, and .pdb files of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Kumaraswamy, S.; Jalisatgi, S. S.; Matzger, A. J.; Miljanić, O. Š.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 3771. (b) Eickmeier, C.; Holmes, D.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 800.

(14) Bong, D. T.-Y.; Chan, E. W. L.; Diercks, R.; Dosa, P. I.; Haley, M. M.; Matzger, A. J.; Miljanić, O. Š.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J.; Stanger, A. *Org. Lett.* **2004**, *6*, 2249.

(15) Strained ring fusion increases J_{para} in arenes. For a review, see: Frank, N. L.; Siegel, J. S. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: London, 1995; Vol. 3, pp 209−260.