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Synthesis and Properties of Trefoil-Shaped Tris(hexadehydrotribenzo[12]annulene) and Tris(tetradehydrotribenzo[12]annulene)

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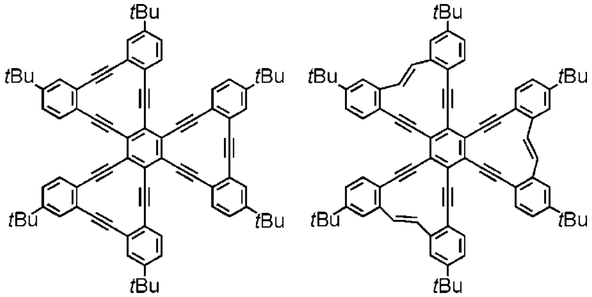
ABSTRACT



Trefoil-shaped tris(hexadehydrotribenzo[12]annulene) possessing a substructure of the ultimate two-dimensional C(sp)–C(sp^2) network, graphyne, and the related tris(tetradehydrotribenzo[12]annulene) were synthesized, and their ground- and excited-state properties were investigated.

Carbon-rich organic molecules have been attracting much interest regarding their novel structures and potential applications.[1] Dehydrobenzoannulenes (DBAs), which were investigated extensively during the late 1950s through the mid-1970s with regard to their aromaticity/antiaromaticity,[2] constitute one of the central classes of carbon-rich molecules.[3] Thus, multiple fused DBAs have been synthesized as scaffolds of two-dimensional carbon networks such as graphyne[4a] and graphdiyne[4] as well as one-dimensional oligomers.[5] These one- and two-dimensional systems are predicted to exhibit semiconductive and/or nonlinear optical

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[†] Osaka University.

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properties. A number of such molecules consisting of aromatic [18]DBA[6] or [14]DBA[7] subunits have been reported. On the other hand, there are few examples of such systems constructed from hexadehydrotribenzo[12]annulene, [12]DBA (**1a**).[8] This is presumably because of the difficulty associated with the construction of the [12]DBA framework. The weakly antiaromatic [12]DBA exhibits interesting properties such as complexation with transition metals[9] and forbidden electronic transitions between S_0 and S_1 states.[10] Only diamond-shaped[11] and bow-tie-shaped[11a,12] bis[12]DBA derivatives have been prepared. We therefore undertook the synthesis of the trefoil-shaped tris[12]DBA **2b** to investigate the effect of the mode of fusion of the [12]DBA rings on the ground- and excited-state properties of multiply fused [12]DBAs and to establish a synthetic route to the “full wheel-shaped” hexakis[12]DBA, a substructure motif of graphyne. In addition, the structure and magnetic properties of the parent compound **2a** were investigated by DFT calculations. We also planned to prepare tris[12]DBA **3**, having peripheral double bonds with internal hydrogens that should allow better assessment of the effect of the multiple fusion on the tropicity on the [12]DBA ring.

DFT calculations (B3LYP/6-31G* level) of **2a** predict that it possesses a D_3 symmetric structure in which the three 12-membered rings are twisted slightly (with a dihedral angle of 7.5° between the peripheral triple bond and the bond shared by the 12-membered ring and the central benzene ring) because of the steric repulsion between the hydrogen atoms of the peripheral benzene rings. The central benzene ring adopts a very shallow chair conformation with a dihedral angle of 0.8° (C(1)−C(2)−C(3)−C(4) = 0.838°, C(2)−C(3)−C(4)−C(5) = −0.840°); see Figure 1 for numbering. In general, fusion of the antiaromatic [12]annulene ring to a benzene ring causes bond length alternation in the latter, in such a way that the endocyclic bond shared by the [12]-annulene ring becomes longer than that of the exocyclic bond.[13] It is expected that the fusion of three [12]annulene rings to the central benzene ring of **2a** in an alternate fashion would emphasize the bond length alternation. However, this is not the case because the calculated bond lengths of the internal benzene ring of **2a** (C(2)−C(3), C(4)−C(5), C(1)−C(6)) are slightly longer than those of **1a** and the peripheral ring of **2a** presumably for the above-mentioned steric repulsion.[14] The other calculated bond lengths of **2a**, however, are similar to those of **1a**. The chemical shift of the aromatic protons and nucleus-independent chemical shifts (NICS)[15] of **1a** and **2a** were calculated using the GIAO-HF/6-31G*//B3LYP/6-31G* methods.[16] The NICS values of the 12-membered ring (4.41) and benzene rings (−6.79) of **1a** using the GIAO-B3LYP/6-31G*//B3LYP/6-31G* methods were reported by Vollhardt et al.[17] Our results are summarized in Table 1 together with the experimental data for the *tert*-butyl derivatives **1b** and **2b** described later. Despite the smaller bond length alternation of the central benzene ring of **2a**, the less negative NICS value (−7.83) indicates that this ring is substantially less aromatic than those of **1a** (−10.35) and the peripheral benzene rings of **2a** (−10.25). Because of the slight twisting of the [12]annulene rings of **2a**, they are slightly less paratropic than that of **1a**, and the chemical shifts of peripheral benzene protons are predicted to resonate at a lower field than those of **1a**.

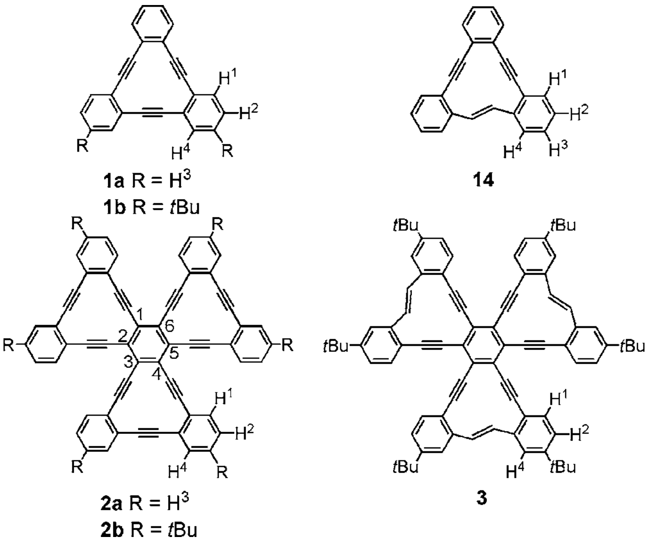

Figure 1. Structures and numbering of the internal benzene ring of **2a**,**b** and the aromatic protons of tris[12]DBAs and their corresponding reference compounds.

As we wished to extend our synthetic strategy to the synthesis of the full wheel-shaped hexakis[12]DBA, we avoided using cross-coupling reactions, which are extensively employed to construct [12]DBA structures, to form the peripheral triple bonds. To introduce the peripheral triple

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(14) Calculated bond lengths of **1a** and **2a** are listed in Table S1 in the Supporting Information.

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(16) The NICS value of the 12-membered ring of **2a** using GIAO-B3LYP/6-31G*// B3LYP/6-31G* methods (3.57) was also smaller than that of **1a** (4.41).

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Table 1. Calculated and Experimental ^{1}H NMR Chemical Shifts and NICS Values for **1a**,**b** and **2a**,**b**[a]

	1a	**2a**
^{1}H NMR Chemical Shift [b]		
H^1	7.56 (7.26)	7.62 (7.38)
H^2	7.36 (7.20)	7.45 (7.29)
H^3		7.45
H^4	(7.39)	7.90 (7.41)
NICS[c]		
peripheral benzene ring	−10.35	−10.25
central benzene ring		−7.83
[12]annulene ring	2.92	2.72

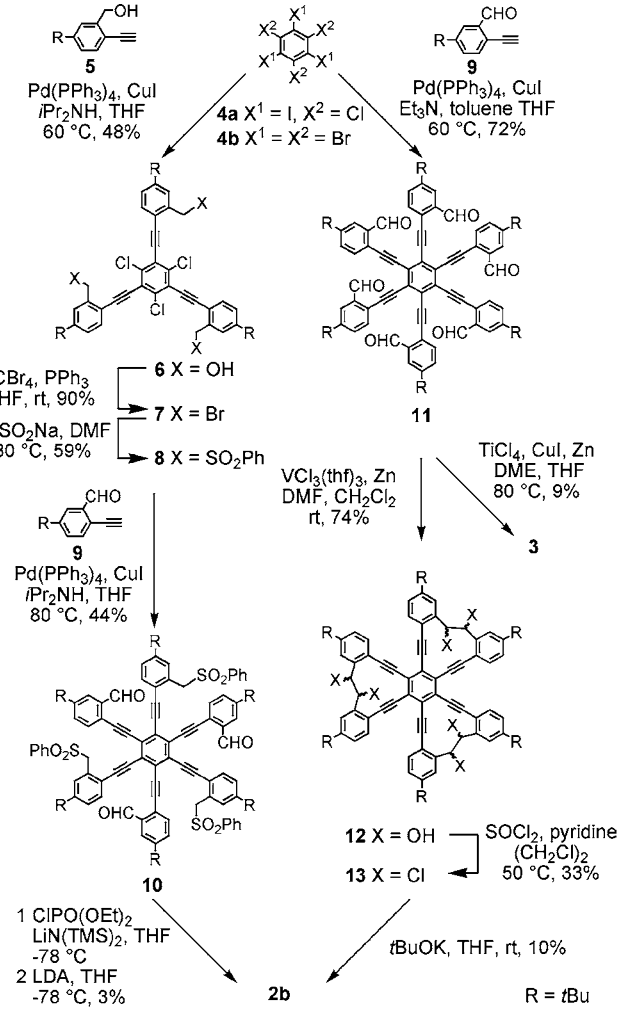
[a] Calculated values were obtained using the GIAO-HF/6-31G*//B3LYP/6-31G* method. [b] Experimental values observed for the *tert*-butyl derivatives **1b** and **2b** are listed in parentheses. [c] At the center of each ring.

bonds while avoiding severe steric crowding, we employed double elimination from an intermediate with peripheral single bonds and appropriate leaving groups. We viewed the coupling of a sulfone with an aldehyde[18] and the pinacol coupling as reasonable routes to such an intermediate.

The syntheses of compounds **2b** and **3** are shown in Scheme 1. Triol **6** was prepared in 48% yield by the regioselective Sonogashira coupling of **4a** with hydroxyalkyne **5**.[19] After conversion of **6** to sulfone **8**, the Sonogashira coupling with formylalkyne **9** gave **10** in 44% yield.[20] Treatment of **10** with lithium hexamethyldisilazide and diethyl chlorophosphonate followed by an excess amount of lithium diisopropylamide furnished trefoil-shaped tris[12]-DBA **2b** in 3% yield as a yellow solid. The low yield of **2b** is ascribed to intermolecular reactions because the nucleophilic C−C bond formation could take place randomly, leaving unreacted functional groups which are susceptible to further reactions.

Next, for the pinacol coupling approach, hexaaldehyde **11** was prepared in 72% yield by the Sonogashira coupling of hexabromobenzene (**4b**) with an excess of **9**. Pinacol coupling of **11** using a low-valent vanadium reagent gave hexaol **12** as a mixture of isomers in 74% yield. The ^{1}H NMR spectrum of **12** indicates that the hydroxy groups are anti in each 12-membered ring. Chlorination of **12** using thionyl chloride gave hexachloride **13**, in which the stereocenters possessed both syn and anti stereochemistry. Finally, double elimination using potassium *tert*-butoxide gave **2b** in 10% yield. Compound **3** was prepared by the McMurry coupling of **11**. Treatment of **11** with TiCl$_4$, Zn, and CuI in a mixture of DME and THF (1:2) gave **3** in 9% yield as a sparingly soluble orange solid. The low yield of **3** is again ascribed to the site-random coupling reaction as in the case of the cyclization of **10**.

Scheme 1



To assess the effect of the mode of fusion on the tropicity of the [12]DBA rings of **2b** and **3**, we compared their ^{1}H NMR chemical shifts with those of reference compounds **1b** and **14**.[21] The chemical shifts of H^1, H^2, and H^4 of **2b** (7.38, 7.29, and 7.41 ppm, respectively) appeared at a slightly lower field than those of **1b** (7.26, 7.20, and 7.39 ppm, respectively), indicating a small decrease of paratropicity in **2b** compared to **1b**. It seems likely that H^1 of **2b** suffers from the anisotropic effect of the neighboring benzene rings to show more pronounced downfield shifts than H^2 and H^4. The observed chemical shifts agree qualitatively with the theoretical values obtained for the DFT optimized geometry of **2a** (Table 1). It is, therefore, concluded that the observed downfield shifts are attributed to the slight twisting of the [12]annulene ring. Similarly, in the case of **3**, the chemical shifts of its aromatic protons (7.42, 7.19, and 7.31 ppm) shifted slightly downfield compared to the corresponding reference compound **14** (7.40, 7.13, and 7.29 ppm). Moreover, the vinyl protons of **3** and **14** serve as good probes for the assessment of their tropicity, which appear as sharp singlets owing to the fast rotation of the vinyl group. The

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(20) Compound **10** was synthesized only by this sequence of coupling reactions. Namely, the first coupling of **4a** with **9** followed by the second coupling with **5** or the phenyl sulfone derived from **5** did not give the desired hexaethynylbenzene derivatives.

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remarkably low field resonance of **14** (8.54 ppm) was ascribed to both the local anisotropic effect of the triple bonds to the inner hydrogen and the paratropicity of the 12-membered ring, either upfield or downfield shifting depending on the position (inner or outer) of the hydrogen.[21] The observed upfield shift of the vinyl proton of **3** (8.42 ppm) relative to that of **14** indicates that the paratropicity of the former is smaller than that of the latter.

To investigate the excited-state properties of **2b** and **3**, UV−vis and fluorescence spectra were measured, as shown in Figures 2a and 2b, respectively, together with those of **1a**, **14**, and hexakis(phenylethynyl)benzene (**15**).[22] It has been reported by Wirz that compound **1a** exhibits characteristic absorption/emission spectra owing to its unique electronic structure due to the D_{3h} symmetry of the molecule.[10] There is a strongly allowed absorption band at around 290 nm, a weakly allowed band at ca. 350 nm, and a strongly forbidden band at 400 nm. Even though **14** is not of D_{3h} symmetry, it also exhibits a similar absorption spectrum. On the other hand, the spectra of **2b** and **3** are different from those of **1a** and **14**, as shown in Figure 2a. Not only do **2b** and **3** exhibit bathochromic shifts compared to **1a** and **14** but also the intensities of the bands relative to those of **1a** and **14** are completely different. The difference between the absorption spectra can be ascribed to the loss of D_{3h} symmetry in **2b** and **3**. However, the profiles of the spectra of **2b** and **3** are different from that of a hexaethynylbenzene derivative **15**; the former exhibit absorptions at a longer wavelength owing to their extended conjugation.

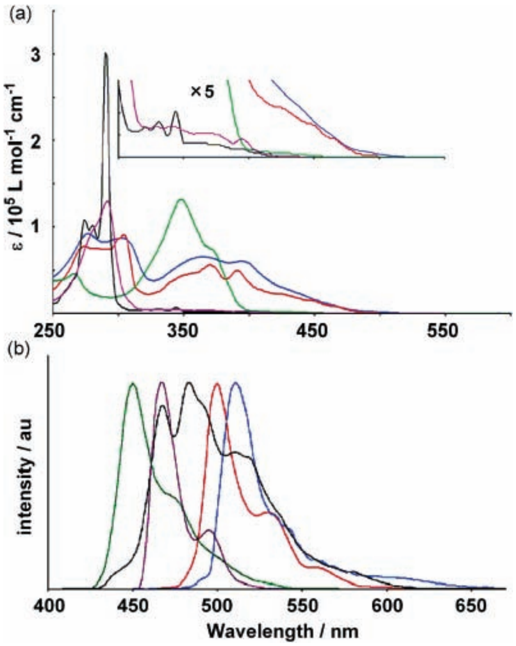

Figure 2. (a) Electronic absorption spectra of **1a** (black), **2b** (red), **3** (blue), **14** (violet), and **15** (green) in $CHCl_3$ at 25 °C. (b) Normalized fluorescence spectra of **1a** (black), **2b** (red), **3** (blue), **14** (violet), and **15** (green) in $CHCl_3$ at 25 °C.

The characteristic fluorescence spectrum of **1a** exhibits apparent vibrational splitting.[10] The profile of the fluorescence spectrum of **2b** is different from that of **1a**, with the 0−0 transition band as the strongest band, a typical profile for phenylacetylene derivatives such as **15** (Figure 2b). The profiles of **3** and **14** are similar, though the fluorescence band of **3** exhibits a considerable red shift relative to that of **14**.[23]

In conclusion, trefoil-shaped tris[12]DBA **2b** and **3** have been synthesized by constructing the 12-membered rings through peripheral single-bond formation using intramolecular coupling followed by double elimination. Their [12]-annulene rings show slightly smaller paratropicities than that of the corresponding mono[12]DBAs **1a** and **14** presumably because of the decrease of planarity due to steric repulsion. Similarly, their excited-state properties are considerably different from those of **1a** and **14**.

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Supporting Information Available: Experimental procedures and spectral data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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