Syntheses and Photophysical Properties of Boomerang-shaped Bis(dehydrobenzo[12]annulene) and Trapezoid-shaped Tris(dehydrobenzo[12]annulene)

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A boomerang-shaped bis(dehydrobenzo[12]annulene) and a trapezoid-shaped tris(dehydrobenzo[12]annulene) were synthesized, and their ground- and excited-state properties were investigated.

Synthesis of the multiply fused dehydrobenzoannulenes becomes current interests because of their unique electronic and optical properties, local aromaticity as well as potential utilities in supramolecular chemistry.[1] Though the parent dehydrobenzo[12]annulene (**1**, DBA, Chart 1) has been extensively investigated since 50 years ago,[2] its multiply fused homologues have still been unknown expect for rhombic-shaped and bow-tie-shaped bisDBA derivatives[3] and a trefoil-shaped trisDBA derivative.[4] It is therefore of interest to know how the number and mode of fusion of DBAs would affect their local aromaticity and electronic properties.[5] In this respect, we report herein the syntheses and photophysical properties of novel multiply fused DBAs; boomerang-shaped bisDBA derivative **2b** and trapezoid-shaped trisDBA derivative **3b**, the latter being one of the remaining fragments of the full-wheel-shaped hexakisDBA.

We recently reported on the theoretical studies based on the DFT calculations for the parent compounds **2a** and **3a** at the B3LYP/6-31G* level of theory; **2a** adopts a nonplanar conformation while **3a** is planar, the nucleolus independent chemical shift (NICS) calculations indicate that aromaticity of the central benzene ring reduces as the number of fused DBA ring increases (NICS = −9.13 for **2a** and NICS = −8.49 for **3a** calculated by GIAO method at the HF/6-31G*//B3LYP/6-31G* level of theory), and there is little difference between their HOMO–LUMO gaps (2.99 eV for **2a** and 3.02 eV for **3a**).[5]

Our approach to the synthesis of the multiply fused DBAs **2b** and **3b** relies on a double elimination strategy which was employed for the synthesis of trefoil-shaped trisDBA to construct the peripheral triple bonds.[4] First, the peripheral benzene rings are connected by single bonds with appropriate leaving groups. Then, elimination of the leaving groups leads to the formation of triple bonds at the periphery.

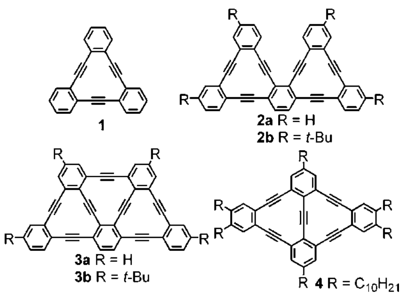
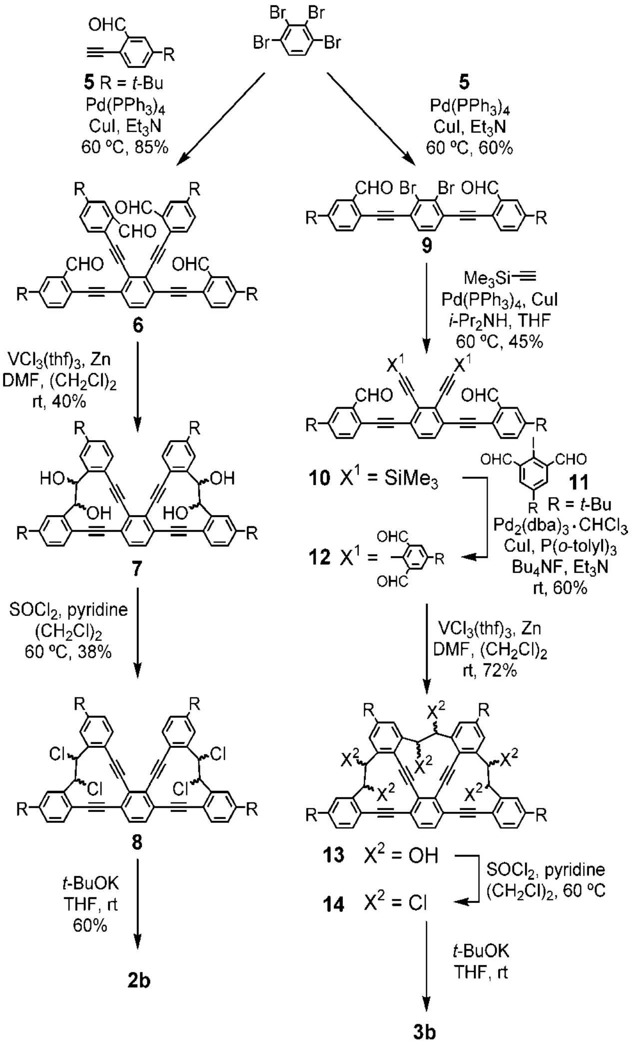


Chart 1.



Scheme 1. Syntheses of bisDBA **2b** and trisDBA **3b**.

The synthetic routes for **2b** and **3b** are shown in Scheme 1.[6] Reaction of 1,2,3,4-tetrabromobenzene and an excess amount of formylalkyne **5** under the Sonogashira coupling conditions afforded tetraaldehyde **6**. Intramolecular pinacol coupling of **6** using a low-valent vanadium reagent gave tetraol **7** as a mixture of isomers, which was transformed to tetrachloride **8** by treatment with thionyl chloride. Finally, a double elimination reaction of **8** using potassium *tert*-butoxide furnished boomerang-shaped bisDBA **2b** in 60% yield.

Similarly, the synthesis of trapezoid-shaped trisDBA **3b** began with 1,2,3,4-tetrabromobenzene. Regio-selective Sonogashira reaction at the 1,4-positions of tetrabromobenzene

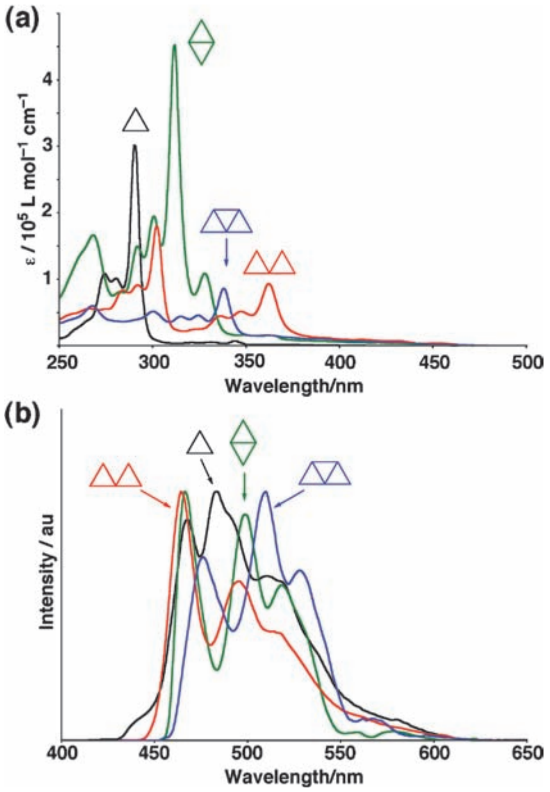


Figure 1. Electronic absorption spectra (a) and normalized fluorescence emission spectra (b) of **1** (black line), **2b** (red line), **3b** (blue line), and **4** (green line) in CHCl$_3$ at 30 °C. The symbols indicated the respective π-conjugated core of the [12]DBAs.

with two equivalents of formylalkyne **5** gave dialdehyde **9**.[7] Then, two-fold cross-coupling reaction of **9** with trimethylsilylacetylene afforded tetraethynyl derivative **10**. Introduction of the latter two alkylne units required a high catalyst loading (25 mol %) because of the low reactivity of **9** probably owing to steric hindrance around the reaction center. In situ deprotection of the silyl groups of **10** and the cross-coupling reaction with iodoformylarene **11** gave hexaaldehyde **12**. Pinacol coupling reaction of **12**, forming hexaol **13**, and subsequent chlorination gave hexachloride **14**. Elimination of HCl from **14** produced a trace amount of the desired trapezoid-shaped trisDBA **3b** ($<1\%$). The yield of **3b** was much lower than those of **2b** and trefoil-shaped tris[12]DBA[4] owing to the formation of side products possessing double bond(s) at the periphery which were not easily separated from **3b**.

Comparison of the ^{1}H NMR spectra of **2b** and **3b** reveals the decrease of the diamagnetic ring current at the central benzene ring of **3b** compared with that of **2b**. Indeed, protons attached to the central benzene ring of **2b** and **3b** resonate at 7.10 ppm for **2b** and 6.91 ppm for **3b**. These results qualitatively agree with the theoretical predictions by GIAO calculations for model compounds **2a** (7.34 ppm) and **3a** (7.15 ppm).[8] In addition, NICS values of **2a** and **3a** also indicate decrease of diamagnetic ring current at the central benzene ring (vide supra).[5] Another possibility to induce the upfield shift of the benzene protons is the effect of paratropic 12-membered ring.

The absorption spectra of **2b** and **3b** exhibit distinctly different profiles from those **1** and **4**, except for the lowest energy transitions at 400–450 nm as shown in Figure 1a. While **2b** and **3b** show absorption maxima at 362 and 338 nm, respectively, attributable to the *p*-bis(phenylethynyl)benzene chromophore,[9] they do not show intense absorptions at shorter wavelength region which are observed in **1** and **4**, indicating that absorptions of **2b** and **3b** in the UV region are dominated by the linearly conjugated chromophore.

DBAs **2b** and **3b** emit bright blue fluorescence ($\lambda_{\max} = 462$ nm for **2b** and $\lambda_{\max} = 510$ nm for **3b**) in chloroform (Figure 1b). Whereas the 0–0 vibrational transition band of **2b** is the most intense like the alternately fused DBA reported previously,[4] the fluorescence profile of **3b** with strong 0–1 band is similar to those of **1** and **4**. The reason for the difference in the vibrational profile between the twisted and planar [12]DBAs is not certain.

In summary, we synthesized two novel multiply fused DBAs, boomerang-shaped bisDBA **2b** and trapezoid-shaped trisDBA **3b** by the double elimination strategy. As theoretically predicted, aromaticity of the central benzene ring reduces with increasing number of DBA ring. On the other hand, **3b** maintains better the characteristic of the [12]DBA chromophore than **2b** judging from the absorption and fluorescence spectra. These insights are useful for the design and synthesis of novel fused DBAs and their application in organic materials.[10]

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