Synthesis and Characterization of Cyclopentadienone-annelated Hexadehydrodibenzo[12]annulene

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Hexadehydrodibenzo[12]annulene annelated by a cyclopentadienone moiety was synthesized. On the basis of the theoretical calculations and experimental NMR and IR spectra, it was shown to be weakly aromatic owing to the contribution of the diatropic [15]annulenone resonance structure.

Carbon-rich organic molecules have been attracting a great deal of interest with regard to their novel structures and their potential optoelectronic applications.[1] Among them, perethynylated cyclic π-systems having a cyclobutadiene–metal complex,[2] a cyclopentadienylide–metal complex,[3] and benzene[4] as a nucleus have been synthesized as scaffolds of two-dimensional networks and three-dimensional cages as well as their substructures.[5] Even though some partially closed wheel-like structures consisting of a central π-system and peripheral aromatic dehydrobenzo[14]-[6] or [18]annulene[7] moieties have been synthesized, little has been known for those annelated by antiaromatic dehydrobenzo[12]-annulenes ([12]DBAs), because of difficulties associated with construction of the [12]DBA framework.[8] In this context, we disclosed here the first synthesis of a [12]DBA derivative **1** which is annelated by a cyclopentadienone moiety. The synthesis of **1** represents the first step toward the synthesis of the perfect wheel cyclopentadienylide **2**, which may be called corannulenyne after corannulene.[5] Additionally, **1** is an interesting molecule with regard to the contribution of the [15]annulenone resonance structure.

Indeed, the NICS[9] value calculated by the GIAO-B3LYP/6-31G* method is 3.3 at the center of the cyclopentadienone core of **1** whereas it is 7.9 for the unannelated reference compound **3**,[10] indicating that the former is less antiaromatic than the latter. The NICS value at the center of the [12]DBA ring of **1** is −1.4, indicative of its weak diatropicity. In contrast, the NICS value for the weakly antiaromatic hexadehydrotribenzo[12]annulene was estimated to be 4.4.[11] The theoretical chemical shifts of the aromatic protons H_a, H_b, and H_e of **1** locate at the downfield relative to the corrsponding protons of **3** and acetal **4** as shown later (Figure 1),[10] also indicating weak diatropicity of **1**. Consistent with the calculated magnetic property, the stretching frequencies of the carbonyl groups of **1** and **3** are expected to occur at 1772 and 1777 cm^{-1}, respectively. The calculated bond distances and angles around the twelve-membered ring of **1**, however, are not much different from those of **3** and **4**.

Our strategy for synthesis of **1** was based on the palladium-catalyzed coupling reaction for all C–C bond formation, from a commercially available 2,3,4,5-tetrachlorocyclopentadienone dimethyl acetal (**8**) (Scheme 1). Namely, regioselective Sonogashira coupling of **8** with ethynyl compounds and subsequent construction of the [12]DBA core using Sonogashira coupling of the obtained bis-ethynyl derivative with an appropriate dihalotolan followed by Suzuki–Miyaura reaction and deprotection would give the desired **1**. This strategy is secured by our previous findings that the Sonogashira ethynylation of **8** proceeds preferentially at the 3- and 4-positions compared to the 2- and 5-positions.[4c]

The reaction of **8** with 2-methyl-3-butyn-2-ol in the presence of $Pd(PPh_3)_4$, CuI, and $BuNH_2$ proceeded expectedly at the 3- and 4-positions of **8** to give 3,4-disubstituted cyclopenta-

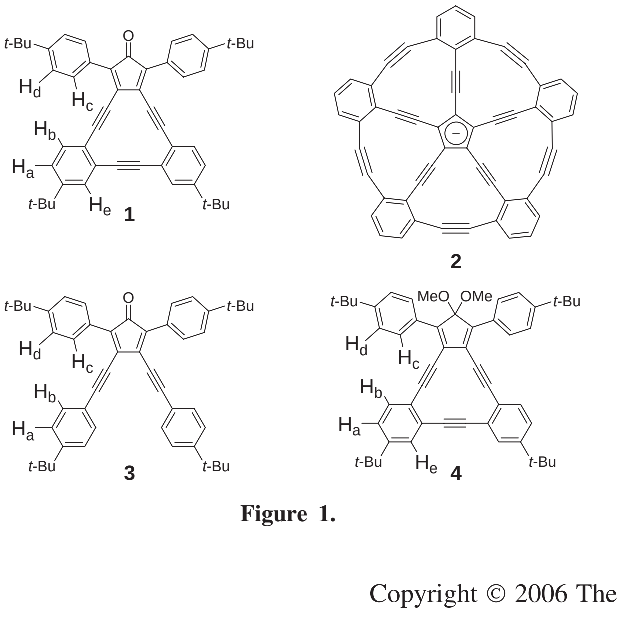
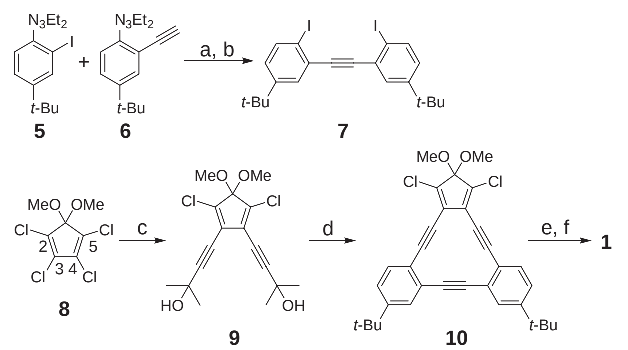


Figure 1.



Scheme 1. Reaction conditions: (a) $Pd(PPh_3)_4$, CuI, Et_3N, THF, 55 °C, 75%; (b) MeI, 125 °C, sealed tube, 90%; (c) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_4$, CuI, $BuNH_2$, THF, 55 °C, 55%; (d) **7**, $Pd(PPh_3)_4$, CuI, PPh_3, KOH, $CH_3(C_8H_{17})_3NCl$, benzene/H_2O (2:1 v/v), 85 °C, 52%; (e) 4-*tert*-butylphenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF, reflux, 92% of **4**; (f) 50% TFA aq, CH_2Cl_2, rt, 92%.

Table 1. Theoretical and experimental ^{1}H NMR chemical shifts of **1**, **3**, and **4**[a]

	H_a	H_b	H_c	H_d	H_e
1	7.53	7.71	8.17	7.54	7.86
	(7.35)	(7.73)	(8.38)	(7.34)	(7.66)
3	7.44	7.54	8.06	7.48	
	(7.28)	(7.40)	(8.16)	(7.24)	
4	7.48	7.67	8.48	7.51	7.75
	(7.08)	(7.27)	(7.85)	(7.32)	(7.37)

[a] Theoretical values are shown in parentheses.

dienone acetal **9**. The diiodotolan **7**, a coupling partner of **9**, was prepared as follows. (2-Iodophenyl)triazene (**5**) and (2-ethynylphenyl)triazene (**6**), which were prepared by the method of Haley,[12] were coupled in the presence of $Pd(PPh_3)_4$ in Et_3N at 55 °C to give 2,2′-bis(triazenyl)tolan in 75% yield, and then it was converted by iodination with MeI to **7**.[7b]

One-pot operation of deprotection of two acetone-protected termini in **9** under the basic conditions and the succeeding double Sonogashira coupling[13] with **7** afforded **10** in 52% yield. Since the 2,5-dihalo-3,4-disubstituted cyclopentadienone from deprotection of **10** is highly unstable and unisolable, the aryl groups were introduced to the 2- and 5-positions by Suzuki–Miyaura coupling with *tert*-butylphenylboronic acid, leading to **4**. Finally, deprotection of **4** with aqueous trifluoroacetic acid afforded the desired cyclopentadienone-annelated [12]DBA **1** in 92% yield.[14]

Theoretical[10] and experimental ^{1}H NMR data of **1** and the reference compounds **3**[15] and **4** are shown in Table 1. The theoretical chemical shifts are qualitatively in agreement with the observed data except for H_c of **4**.[16] The resonances of H_a, H_b, and H_e of **1** locate at the downfield compared with the corresponding protons of **3** and **4**, even though the observed chemical shift difference is less pronounced than the calculated one. These downfield shifts may be caused by deshielding effect of the diamagnetic ring current of the [15]annulenone circuit. Furthermore, in the FT-IR spectra, the C–O stretching vibration of the carbonyl group in **1** (1697 cm^{-1}) appeared at the lower frequency region than that of **3** (1703 cm^{-1}), as expected from the theoretical study. These observations coupled with the theoretical calculations strongly suggest that cyclopentadienone-annelated [12]DBA **1** is diatropic owing to the contribution of the 14π [15]annulenone resonance structure. However, attempts to protonate **1** with trifluoroacetic acid to form the corresponding hydroxy[15]annulenium ion[17] failed because of its decomposition under strongly acidic conditions.

As shown in Figure 2, the UV–vis absorption bands of **1** shift considerably to the longer wavelength than those of **3**, due to extension of conjugated π-electron system by linking with a C–C triple bond between the benzene rings.

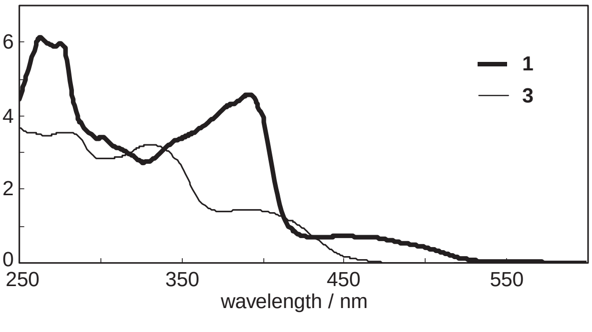


Figure 2. UV–vis spectra of **1** (bold) and **3** (plain) in THF at rt.

In conclusion, we synthesized cyclopentadienone-annelated [12]DBA **1** by efficient cross-coupling reactions. Compound **1** showed weak diatropicity owing to the contribution of the [15]annulenone resonance structure.

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10 For theoretical study, *tert*-butyl groups of **1**, **3**, and **4** were omitted for clarify.

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14 Spectroscopic data are listed in Supporting Information.

15 **3** was prepared in 61% overall yield by Sonogashira coupling of **8** with 4-*tert*-butylphenylacetylene,[4c] followed by Suzuki–Miyaura coupling with 4-*tert*-butylphenylboronic acid and deprotection of its acetal moiety with aqueous TFA.[14]

16 While the theoretical chemical shift of H_c of **1** locates at downfield relative to that of **4**, experimentally the former appears at higher field than the latter. The dihedral angles of the phenyl group relative to the five-membered ring are 27.8 and 43.2°, respectively, indicating that H_c of **1** should be more susceptible to the anisotropic deshielding effect in contrast to the observed chemical shifts. The reason for this discrepancy is not understood.

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