Formation and Characterization of Highly Strained Dibenzopentakisdehydro[14]annulene and Theoretical Study on Its Aromaticity

Ichiro Hisaki, Takeshi Eda, Motohiro Sonoda, and Yoshito Tobe*
Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University,
and CREST, Japan Science and Technology Coorporation (JST), Toyonaka, Osaka 560-8531

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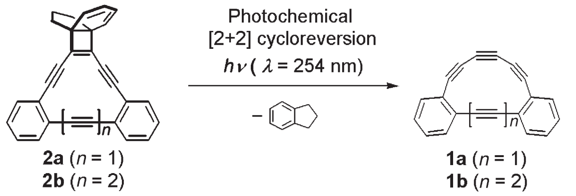
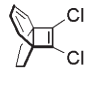
Highly reactive dibenzopentakisdehydro[14]annulene was generated and its tropicity was discussed based on the experimental and theoretical NMR spectra.

Dehydrobenzoannulenes (DBAs) have been investigated intensely in view of their possibilities as segments of 2-D carbon networks,[1] precursors of new forms of carbon clusters,[2] and materials with opto-electronic properties.[3] In addition, experimental as well as theoretical assessment of induced ring currents in dehydroannulenes remains a challenge despite the debates since the 1960's.[4] Recently, aromaticity of various DBAs are studied both experimentally[5] and theoretically[6] on the basis of nucleus-independent chemical shifts (NICS).

We became interested in highly strained dibenzodehydro[12]- and [14]annulenes (**1a** and **1b**, respectively), because they are expected to give information regarding aromaticity of highly deformed π systems. In addition, such highly reactive species would be feasible to transform into carbon clusters by explosive decomposition, regular polymers by topochemical polymerization, or highly extended, trefoil-shaped π systems by cyclotrimerization. Previously, we reported the generation of **1a** by [2 + 2] cycloreversion from its precursor **2a** by UV irradiation and its characterization by UV–vis and FT-IR spectra measured in an Ar matrix at low temperature.[7] It was not possible, however, to discuss its tropicity because **1a** was too reactive for observation by ^{1}H NMR spectroscopy in solution. On the other hand, the larger homolog **1b** should be less reactive than **1a** and would be stable enough to assess its aromaticity by NMR. Herein, we report the generation of **1b**, its spectroscopic characterization, and the discussion of its tropicity based on the experimental and theoretical NMR spectra.



Scheme 1.



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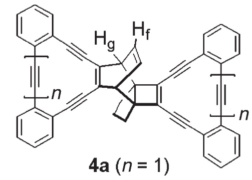
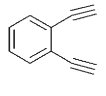


4a (*n* = 1)
4b (*n* = 2)



1c (geometry fixed as that of **1b**)
2c (geometry fixed as that of **2b**)

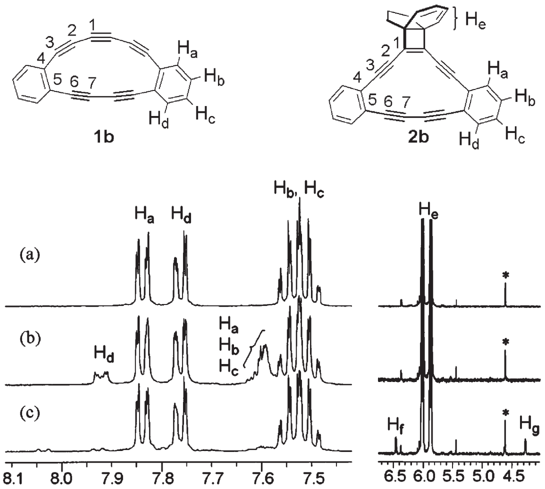


Figure 1. ^{1}H NMR spectral change of **2b** upon photolysis in THF-d_8. (a) before irradiation, (b) after irradiation for 24 h at 220 K, (c) after leaving the solution of (b) for 65 h at 303 K.

Like **1a**, we planned to generate **1b** by photochemical [2 + 2] cycloreversion of the precursor **2b** (Scheme 1). Synthesis of **2b** was accomplished by (i) cross-coupling of dichloropropellatriene **3**[8] with 2-ethynyl-1-[(triisopropylsilyl)ethynyl]benzene,[1b] (ii) desilylation, and (iii) Cu(II)-mediated intramolecular cyclization in 31% overall yield.

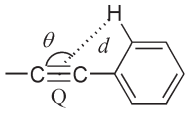
Photolysis of **2b** was undertaken by irradiation with 254 nm light in THF-d_8 at 220 K. ^{1}H NMR spectrum of **2b** and its change upon irradiation are shown in Figure 1.[9] Thus, by irradiation of **2b** for 24 h, two new multiplets appeared at 7.93–7.91 and 7.63–7.57 ppm, with a relative integration of 1:3, as shown in spectrum (b). The chemical shifts of these new signals are in good agreement with the theoretical ones for **1b** calculated by GIAO-B3LYP/6-31G*//B3LYP/6-31G* as described below (Table 1). In addition, by leaving the solution for 65 h at 303 K, these signals disappeared while two signals at 6.46 and 4.28 ppm appeared, which were ascribed to [4 + 2] adduct **4b**.[10] Compound **4b** was also detected by LCMS analysis of the solution. These results indicate that compound **1b** is formed by irradiation of **2b** and it is stable enough for characterization by ^{1}H NMR spectroscopy. As shown in Figure 1(b), the aromatic protons of **1b** show distinctly different chemical shifts from those of **2b** though both of them have 14-membered rings. These differences can be attributed to following factors; (1) change of diatropicity of **1b** because of the rehybridization of a double bond into a triple bond, (2) change of local anisotropy due to the triple bond[11] because of the geometrical change, and (3) change of anisotropy due to the 14-membered macrocycle because of the geometrical change. In order to clarify this issue,

Table 1. Theoretical ^{1}H NMR chemical shift and NICS values

	H_a	H_b	H_c	H_d	NICS
1b	7.55	7.55	7.58	8.02	−5.70
2b	8.00	7.57	7.51	7.91	−4.32
$\Delta\delta_{(1b-2b)}$	−0.45	−0.02	+0.06	+0.12	
1c	7.15	7.07	7.08	7.35	
2c	7.32	7.08	7.08	7.22	
$\Delta\delta_{(1c-2c)}$	−0.17	−0.01	+0.00	+0.13	

Table 2. Geometrical parameters

	H_a		H_d	
	d / Å	θ/ deg.	d / Å	θ/ deg.
1b	3.23	152.1	3.11	139.5
2b	3.08	137.7	3.16	144.4
$\Delta_{(1b-2b)}$	+0.15	+14.5	−0.05	−5.0



we carried out a theoretical study for **1b** and **2b**.

Theoretical chemical shifts of the aromatic protons and the NICS values at the center of the 14-membered ring were calculated using Gaussian 03 with GIAO-DFT method on the B3LYP/6-31G*-optimized geometries. The results are listed in Table 1. The theoretical chemical shifts of aromatic protons of **1b** and **2b** show good agreement with those observed experimentally. As $\Delta\delta_{(1b-2b)}$ indicates, H_a and H_d show distinct upfield shift (H_a: −0.45 ppm) and downfield shift (H_d: +0.12 ppm), respectively, upon structural change from **2b** to **1b**. On the other hand, H_b and H_c did not show notable change. The NICS values may indicate that **1b** (−5.70) is slightly more diatropic than **2b** (−4.32). However, since the distance between the center of the ring and the ring carbons of **1b** is different from that of **2b**,[12] anisotropy experienced at the center of 14-membered ring of **1b** should be different from that of **2b**. Accordingly, it is difficult to compare the tropicities of **1b** and **2b** on the basis of their NICS values.

To estimate the change of local anisotropy due to the triple bond induced by the geometrical change, we defined geometrical parameters d and θ. The parameter d denotes the distance between the aromatic proton (H_a or H_d) and the center (Q) of the adjacent triple bond ($C_2{\equiv}C_3$ or $C_6{\equiv}C_7$), and θ refers to the angle H–Q–C. Thus, Δd is the difference between d(**2b**) and d(**1b**), and $\Delta\theta$ is the difference between θ(**2b**) and θ(**1b**). The values of d, Δd, θ and $\Delta\theta$ for the optimized structures of **1b** and **2b** are shown in Table 2. The notable changes are the remarkably widen $\theta(H_a)$ by 14.5° and shorten $\theta(H_d)$ by 5.0°. Additionally, the distance $d(H_a)$ is considerably lengthened by 0.15 Å, while $d(H_d)$ is slightly shortened by 0.05 Å. To estimate the effect on the local anisotropy of the triple bond, we calculated the theoretical chemical shifts for the hypothetical acyclic molecules **1c** and **2c** whose bond lengths and angles are kept same as those of **1b** and **2b**, respectively. Theoretical chemical shifts of **1c** and **2c**, and $\Delta\delta_{(1c-2c)}$ (the difference between chemical shift of **2c** and that of **1c**) are shown in Table 1. It turned out that the geometrical change of **2c** into **1c** would make H_a shift upfield (−0.17 ppm), while it would shift H_d downfield (+0.13 ppm). Accordingly, for H_d, most of the observed downfield shift (+0.12 ppm) is attributed to the local anisotropy (+0.13 ppm). On the other hand, for H_a, more than one thirds (−0.17 ppm) of the upfield shift (−0.45 ppm) is ascribed to the change of local anisotropy. The residual upfield shift may be ascribed to the decrease of diatropicity of the 14-membered ring or the decrease of its anisotropic effect due to increasing distance, though, at this moment, it is not determined which predominates.

In conclusion, **1b** was generated by photolysis of the precursor **2b** and characterized by ^{1}H NMR spectroscopy in a THF-d_8 solution at 303 K. Upon structural change of **2b** into **1b**, chemical shifts of aromatic protons moved substantially, which is attributed to the decrease of tropicity of the 14-membered ring and/or the decrease of its anisotropic effect due to increasing distance, in addition to the change of local acetylenic anisotropy.

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9 Because of the absorption of the photoproducts, **1b** and indane, the conversion of **2b** to **1b** remained low (ca. 19%) even after prolonged irradiation.

10 We assume that the direction of the approach of **1b** to the cyclohexadiene part of **2b** is *syn* to the cyclopentane ring on the basis of the structure of the corresponding adduct **4a** determined by X-ray structure analysis (unpublished results). The same stereochemical outcome was reported for the related [4.3.2]propellanes; T. Tsuji, M. Ohkita, and S. Nishida, *J. Org. Chem.*, **56**, 997 (1991).

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12 The distance between the center of the ring and the adjacent sp carbons (C_1 and C_7) in **1b** are 2.19 and 1.82 Å, respectively, while the corresponding distance in **2b** are 2.80 and 2.07 Å, respectively.

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