Trimethylsilyl-substituted Dibenzodehydro[12]annulene Having High Thermal and Chemical Stability

Wataru Setaka,* Shoko Kanai, Chizuko Kabuto, and Mitsuo Kira*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

(Received September 6, 2006; CL-061029; E-mail: setaka@mail.tains.tohoku.ac.jp, mkira@mail.tains.tohoku.ac.jp)

1,4,9,12-Tetrakis(trimethylsilyl)dibenzodehydro[12]annulene (**3**) was synthesized by the Eglinton coupling reaction in a good yield. In contrast to parent dibenzodehydro[12]annulene, **3** has extremely high thermal and chemical stability, probably due to the steric protection of the annulene ring by bulky trimethylsilyl substituents on benzene.

Much attention has been focused on the electronic structure and properties of macrocyclic conjugated π-electron systems (annulenes).[1] Among annulenes, dibenzodehydro[12]annulene (**1**) is unique because it has distorted acetylenic bonds and shows remarkably red-shifted fluorescence at $\lambda_{\max}$ 532 nm.[2] Incorporation of the π system of **1** having unique photophysical properties into functional materials is an interesting research target. However, parent dibenzodehydroannulene **1** is unstable both thermally and chemically; **1** polymerizes upon heating and irradiation and reacts with various reagents. While a number of studies have shown that not only **1** but also its derivatives are too unstable to be applied to functional materials,[2,3] introduction of four butyl groups into the benzene rings of **1** giving **2** stabilizes remarkably the cyclic π system due to avoided intermolecular interaction between the diyne units.[3,4] We wish to report herein the synthesis and remarkable thermal and chemical stability of trimethylsilyl-substituted dibenzodehydro[12]annulene **3** (Chart 1).

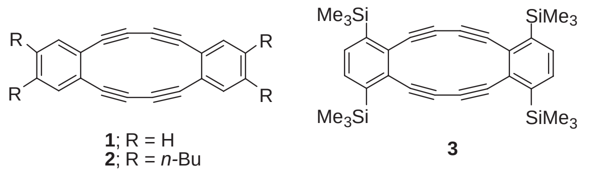
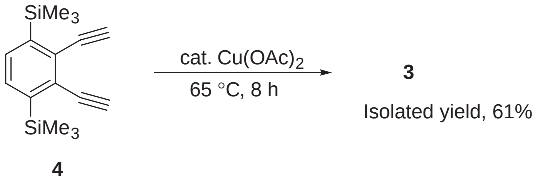


Chart 1.

The Eglinton coupling was applied for the synthesis of **3** (eq 1). To a mixture of pyridine (150 mL), methanol (150 mL), diethyl ether (26 mL), and cuprous acetate mono hydrate (5.1 g, 26 mmol) was added 2,3-diethynyl-1,4-bis(trimethylsilyl)benzene[5] (**4**, 250 mg, 0.92 mmol) in a mixture of pyridine (50 mL) and methanol (50 mL) over 2 h, and then the mixture was stirred at 65 °C for 8 h. The reaction mixture was hydrolyzed, extracted with ether, and then dried over sodium sulfate. Removal of volatile materials in vacuo gave yellow solids of **3**[6] almost quantitatively. Recrystallization from a methanol/tetrahydrofuran mixture gave yellow crystals of **3** (600 mg, 1.1 mmol) in 61% isolated yield. No higher cyclic oligomers of **4** were detected in the reaction mixture by NMR spectroscopy, whereas a similar Eglinton-type coupling of 1,2-diethynylbenzene has been shown to afford parent dibenzodehydro[12]annulene **1** in 58% together with trimeric and tetrameric cyclic annulenes in 20% yied (eq 2).[2f]



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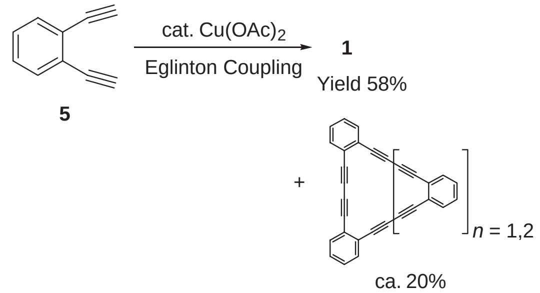
(1)



(2)

Figure 1 shows molecular structure of **3** determined by X-ray crystallography.[7] Structural parameters of **3** are similar to those of **1** reported by Bunz and Enkelmann.[2e] The distances of C13–C17 and C16–C20 of **3** are smaller than the corresponding distances for **1** probably due to the buttressing effect of trimethylsilyl substituents in **3**; the distances (C13–C17/C16–C20) for **3** and **1** are 2.703 Å/2.682 Å and 2.734 Å/2.735 Å, respectively. Highly selective formation of **3** may be ascribed to the buttressing effect making the formation of higher cyclic oligomers of **3** unfavorable. Four trimethylsilyl groups of **3** effectively protect dehydroannulene ring from intermolecular π contact between two annulene planes rings; the shortest distance between two annulene π planes in the crystal is

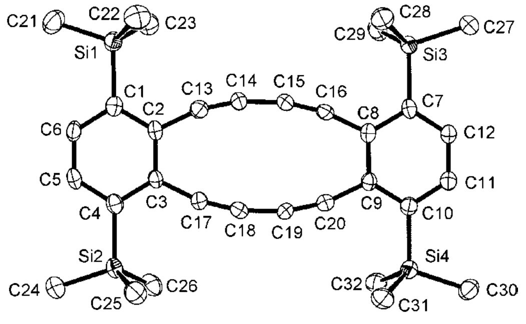
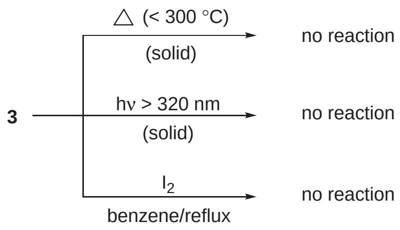


Figure 1. Molecular structure of **3** determined by X-ray crystallography. Two structurally independent molecules exist in a unit cell. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1–C1 1.894(5), C2–C13 1.435(7), C13–C14 1.198(7), C14–C15 1.383(7), C15–C16 1.211(7), C16–C8 1.418(7), C3–C17 1.437(7), C17–C18 1.210(7), C18–C19 1.370(7), C19–C20 1.210(7), C20–C9 1.436(7), C1–C2–C13 123.3(5), C2–C13–C14 165.5(5), C13–C14–C15 167.1(5), C14–C15–C16 167.4(5), C15–C16–C8 167.8(5).



Scheme 1.

6.5 Å, which is about two times as large as that of parent annulene **1** (3.5 Å). In accordance with the relationship between the distortion of polyynes and their ^{13}C NMR chemical shifts,[8] the corresponding shifts for **3** (δ 86.6 and 92.7) as well as for **1** (δ 84.4 and 92.0)[9a] are found at significantly lower fields than those for unstrained 1,4-diphenyl-1,3-butadiyne (δ 74.2 and 81.9).[9b]

Dibenzodehydro[12]annulene derivatives such as **1** and **2** are known to be unstable in the solid state both thermally and photochemically.[2c] Annulenes **1** and **2** decompose at 80 and 120 °C, respectively, to give polymeric products.[3] Annulene **1** in the solid state decomposes under visible-light irradiation. On the other hand, tetrasilyl-substituted annulene **3** is quite stable in the solid state; no decomposition occurs even at 300 °C or no reaction of **3** takes place under the irradiation (Scheme 1). The thermal stability of **3** in the solid state would be ascribed to the larger distance between two neighboring annulene π systems prohibiting solid-state polymerization (vide supra).[10]

Although annulene **1** reacts with iodine to give intramolecular cross-linked compound in a moderate yield,[3d] annulene **3** does not react with iodine at all in benzene (Scheme 1). The thermal and chemical stability of **3** in solution is ascribed to the effective steric protection by bulky trimethylsilyl groups.

Annulene **3** in cyclohexane at room temperature shows three absorption bands in the UV–vis region; $\lambda_{\max}$/nm (ε) of these bands are 320 (1.0×10^5), 378 (2.7×10^3), and 447 (8.2×10^2), which are assigned to the HOMO → LUMO+1, HOMO −1 → LUMO, and HOMO → LUMO transitions, respectively, on the basis of the TD-B3LYP/6-31G* calculations.[11] All these bands are accompanied by the vibrational structures; the vibrational separation of 2100 cm^{-1} for the 320-nm band corresponds to the C≡C stretch, while other two bands show more complicated vibrational structure. All these three bands of **3** are red-shifted from the corresponding bands of parent dibenzodehydro[12]annulene **1**, which shows the following $\lambda_{\max}$/nm (ε) in cyclohexane: 303 (9.9×10^4), 361 (4.8×10^3), and 432 (9.0×10^2).[10] The red-shift of 1750–1000 cm^{-1} of the band maxima of **3** from those of **1** may be ascribed to the electronic effects of trimethylsilyl-substituents, which are weakly electron-donating to the bonding π orbitals, while electron-accepting to the anti-bonding π orbitals.[12] Fluorescence spectra of **1** and **3** in cyclohexane show the band maxima at 532 and 555 nm, respectively, with the vibrational structures.[11]

In summary, we have revealed that introduction of trimethylsilyl groups to dibenzodehydro[12]annulene increases thermal and chemical stability of the π system. The electronic perturbation to the annulene due to the trimethylsilyl substituent is not large but significant.

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5 See the Supporting Information for the details of the synthesis of compound **4**. Supporting Information is also available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.

6 **3**: Yellow crystals; mp 316–318 °C (Decomp.); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.28 (s, 36H), 7.13 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −1.2, 86.6, 92.7, 133.1, 136.1, 141.9; ^{29}Si NMR (59 MHz, CDCl$_3$) δ −2.5; HRMS (ESI) m/z calcd for $C_{32}H_{40}Si_4 + Na$, 559.2105 ($M + Na^+$); found, 559.2093; Anal. Calcd for $C_{32}H_{40}Si_4$: C, 71.57; H, 7.51%. Found: C, 71.74; H, 7.51%.

7 Crystal data for **3**: $C_{32}H_{40}Si_4$, $M_r = 537.00$, yellow prism, $0.2 \times 0.2 \times 0.1$ mm^3, monoclinic, space group Pn, $a = 13.519(2)$ Å, $b = 12.3148(8)$ Å, $c = 20.865(2)$ Å, $\beta = 99.806(2)°$, $V = 3423.1(6)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.042$ g cm^{-3}, Mo Kα ($\lambda = 0.7107$ Å), $T = 173(2)$ K; 7140 unique reflections were collected. The structure was solved by direct methods (SIR92). It was refined by full-matrix least squares (SHELXL-97) on F^2 with anisotropic temperature factors for non-hydrogen atoms. Final *Goof = 1.112*, $R1 = 0.054$ for 6028 [$I > 2\sigma(I)$] observed reflections, 649 parameters. Crystallographic data reported in this paper has been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-619692.

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