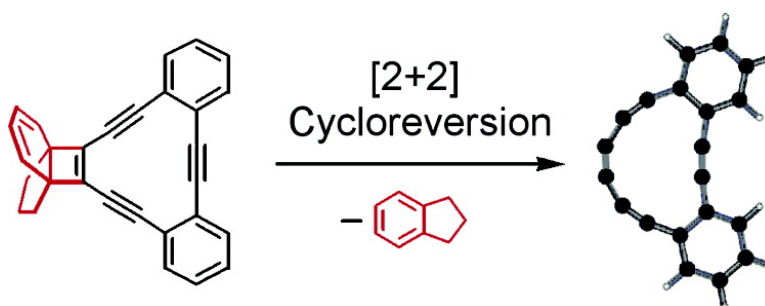


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## Generation and Characterization of Highly Strained Dibenzotetrakisdehydro[12]annulene

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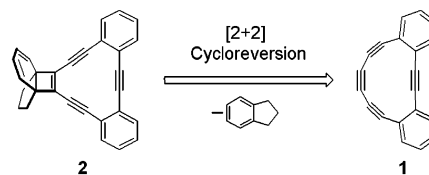
Dehydroannulenes are compounds that have been studied both experimentally and theoretically since the 1960s in connection with the aromaticity–antiaromaticity of cyclic  $\pi$  electron systems.<sup>1</sup> Recently, considerable interest has been focused on these compounds because of their new aspects such as materials with optoelectronic properties<sup>2</sup> (e.g., second-order or third-order nonlinear optical properties), segments of two-dimensional carbon networks<sup>3</sup> (e.g., graphyne), precursors of onion- and tube-like closed shell carbon clusters<sup>4</sup> formed by their explosive decomposition, and precursors of cyclo[*n*]carbons<sup>5</sup> (themselves members of dehydroannulenes). We became interested in the title compound, dibenzotetrakisdehydro[12]annulene (**1**), because of the following reasons: (1) It would provide information about the reactivity of the smallest identified cyclocarbon, C<sub>12</sub>, because it possesses a remarkably deformed triyne unit incorporated in a ring structure. (2) Aromaticity under highly deformed circumstance is a subject of considerable interest.<sup>6</sup> (3) Decomposition or polymerization of **1** would form novel forms of carbon cluster. (4) Cyclotrimerization<sup>7</sup> of the central triple bond of the triyne unit would give a partial structure of graphyne.

In this Communication, we report the generation of **1** and its characterization by the UV–vis and FTIR spectra in an argon matrix at low temperature. In the geometry of **1** optimized by the density functional theory (DFT) at the B3LYP/6-31G\* level, the triple bonds in the triyne component are highly deformed from linearity; the bond angle of the most strained triple bond is as small as 150°.<sup>8</sup> To surmount this large strain, we planned to generate **1** by photochemical [2+2] cycloreversion of propellane-annulated dehydroannulene **2** extruding indan (Scheme 1), because we have already reported that a number of highly reactive polyynes were generated successfully from the corresponding precursors possessing the [4.3.2]propellatriene unit under laser desorption as well as photochemical conditions.<sup>5c,9</sup>

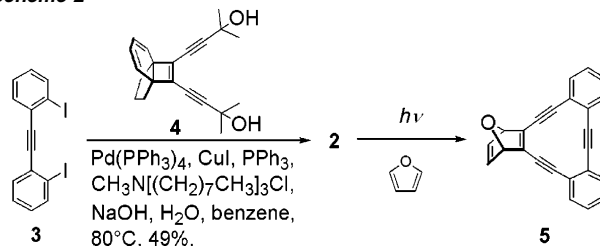
The precursor **2** was prepared in 49% yield by in situ deprotection and the cross-coupling reaction of bis(2-iodophenyl)acetylene **3**<sup>10</sup> and diethynyl[4.3.2]propellatriene derivative **4**<sup>5c</sup> under the phase-transfer conditions (Scheme 2).

First, we investigated [2+2] fragmentation of **2** under the laser-desorption time-of-flight (LD-TOF) mass spectrometric condition. In the negative mode spectrum, an intense peak due to **1**<sup>−</sup> formed by the loss of an indan fragment from **2** was observed (see the Supporting Information). Moreover, a peak due to an adduct formed by the [4+2] ion molecule reaction of **1** and **2** was also detected. As a preliminary study of the photochemical [2+2] cycloreversion,

### Scheme 1



### Scheme 2



a solution of **2** in THF-*d*<sub>8</sub> was irradiated at room temperature with a low-pressure mercury lamp, and the reaction was monitored by <sup>1</sup>H NMR spectra. Upon irradiation, the signals of **2** decreased, and, instead, the signals ascribed to indan appeared, indicating that [2+2] cycloreversion of **2** took place. However, any signals ascribable to **1** were not observed, but those assigned to a [4+2] adduct of **1** and **2** were observed in a low intensity (see the Supporting Information), which was also characterized by LC-MS of the photolyzate. To trap the reactive intermediate generated by the photolysis of **2**, irradiation was then carried out using furan as a solvent. As a result, [4+2] adduct **5** was obtained in 20% yield (Scheme 2).<sup>11</sup> X-ray crystallographic analysis<sup>12</sup> of **5** revealed that the indan unit of **2** was replaced by the furan moiety, indicating that the addition took place at the central, most strained triple bond of **1**. These results indicate that the photolysis of **2** leads to the generation of **1**, which is too reactive to survive for characterization in solution.

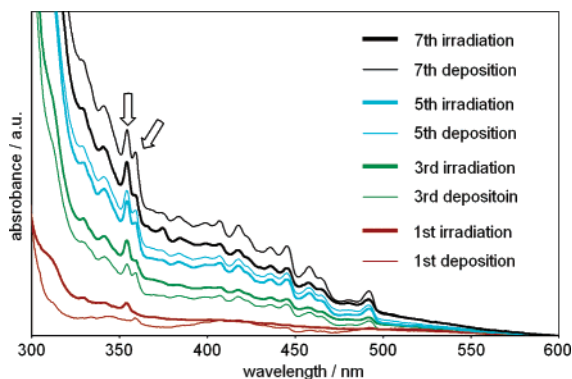
For spectroscopic characterization of **1**, precursor **2** was dispersed in an argon matrix film under 20 K, and its photolysis was monitored by UV–vis and FTIR spectroscopic methods. When the matrix was thick, photolysis of **2** took place only on the surface of the matrix presumably because of the filter effect of the products, resulting in low conversion of **2**. Accordingly, the thickness of the film per deposition was reduced, and the deposition–irradiation cycle was repeated to achieve enough intensity of the IR spectra.

The UV–vis spectral change upon irradiation is shown in Figure 1. After the first irradiation, the absorption band of **2** at 359 nm disappeared, and a new absorption band appeared at 355 nm. After each deposition, the absorption band at 359 nm was newly added, and, upon subsequent irradiation, this band decreased, while the

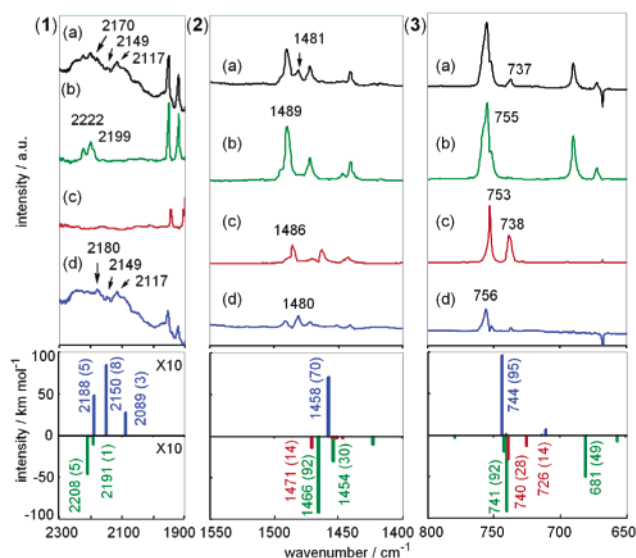
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<sup>§</sup> Kyoto University.



**Figure 1.** UV-vis absorption spectra of precursor **2** upon irradiation with fourth harmonic generation (FHG) pulses of Nd:YAG laser ( $\lambda = 266$  nm) after deposition (thin line), after irradiation (bold line).



**Figure 2.** Selected FTIR spectra of C–C stretching of acetylenes (column 1), in-plane C–H bending vibration (column 2), and out-of-plane C–H bending vibration (column 3). (Top) Observed spectra: (a) after irradiation, (b) precursor **2**, (c) indan, and (d) differential spectra subtracting (b) and (c) from (a). (Bottom) Theoretical IR spectra calculated at the B3LYP/6-31\* level: precursor **2** (green), **1** (blue), and indan (red).

band at 355 nm increased. The deposition–irradiation cycle was repeated seven times, accumulating enough quantity of **1** for IR measurement. Irradiation of **2** in a glass matrix of 2-methyltetrahydrofuran (MTHF) at 77 K resulted in the growth of a similar new band at 361 nm which was lost when the matrix was thawed by warming to room temperature and then refrozen at 77 K (see the Supporting Information).

The FTIR spectra in argon matrix observed after irradiation are shown in Figure 2a together with those of unphotolyzed precursor **2** and indan (Figure 2b and c). In spectra 2a and 3a, two IR bands at 1481 and 737  $\text{cm}^{-1}$  are appearing, which are ascribed to C–H in-plane and out-of-plane bending modes of the photoproducts, respectively. In the high-frequency region (spectra 1a), three weak IR bands at 2117, 2149, and 2170  $\text{cm}^{-1}$  appeared and are attributed to the stretching modes of C(sp)–C(sp) bonds. These frequencies are slightly lower than those observed for the precursor **2** (2199 and 2222  $\text{cm}^{-1}$ ).

It has been established that theoretical IR spectra by the DFT calculation can well reproduce the experimental spectra and can be used to identify the unusual molecules isolated in low-temperature matrixes.<sup>13</sup> Theoretical spectra at the B3LYP/6-31G\*

level predict two IR-active C≡C stretching bands at 2191 and 2208  $\text{cm}^{-1}$  for **2** and three bands at 2089, 2150, and 2188  $\text{cm}^{-1}$  for **1**. Therefore, it should be highly possible that the observed three weak bands are ascribed to **1**. For C–H in-plane and out-of-plane bending modes, DFT calculations predict IR modes at 1458 and 744  $\text{cm}^{-1}$  for **1**. Because these bands should overlap with those of **2** and indan in the observed IR spectra (2a and 3a) after irradiation, we subtract (b) and (c) from (a) with appropriate scaling factors to eliminate the contribution from the latter two, yielding the spectra in 2d and 3d of Figure 2. As shown in spectra 2d and 3d of Figure 2, the conspicuous bands at 1480 and 756  $\text{cm}^{-1}$  are in good agreement with the predicted C–H bending modes of **1**. Thus, the observed IR bands in (d) are, in total, in good agreement with the theoretical IR spectrum of **1**. This should be direct spectroscopic proof of the generation of **1** in the argon matrix.

In conclusion, photolysis of propellane-annulated dehydro[12]-annulene **2** led to the generation of dibenzotetrakisdehydro[12]-annulene **1**, a highly reactive, unsaturated annulene. Compound **1** was isolated in an argon matrix at 20 K or in a glass matrix of MTHF at 77 K, and, under those conditions, it was characterized by FTIR and UV-vis spectra.

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**Supporting Information Available:** Detailed procedures of the synthesis of **2** and its photolysis in THF-*d*<sub>8</sub>, furan, MTHF, and argon matrix, LD-TOF mass spectra, <sup>1</sup>H NMR spectra upon irradiation in THF-*d*<sub>8</sub>, UV-vis spectra in MTHF matrix, whole scale FTIR spectra in argon matrix, and computational data (PDF); crystallographic information of furan adduct **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) The starting material **2** was recovered in 50% yield.
- (12) Crystal data for furan adduct **5**: C<sub>24</sub>H<sub>12</sub>O, *M* = 316.36, monoclinic, space group *P2<sub>1</sub>/n*, *a* = 5.9175(1) Å, *b* = 17.8060(1) Å, *c* = 15.1418(1) Å,  $\beta$  = 93.1104(6), *V* = 1593.11(2) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.319 g/cm<sup>3</sup>, final *R* indices (*I* > 2 $\sigma$ (*I*)) *R* = 0.067, *R<sub>w</sub>* = 0.100, GOF = 0.76. Detailed data are shown in the Supporting Information.
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