A Simple Hybrid Cyclyne Consisting of 1,3-Diethynylbenzene and Ether Units: Synthesis and Novel Ag$^+$-Induced Cyclization Leading to the Perylene Skeleton Formation

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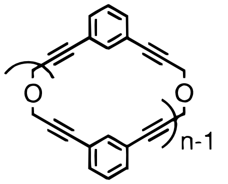
Structurally well-defined macrocycles[1] continue to attract strong interest from many research groups, because of the emerging unique properties (such as specific recognition, selective binding, and complexation) and the resulting molecular functions. As such a macrocycle, we have been interested in a novel family of hybrid cyclynes (**1**) consisting of 1,3-diethynylbenzene units and ether units, which have three kinds of donor groups.



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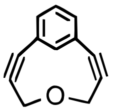

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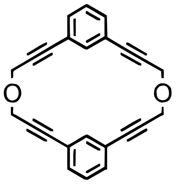


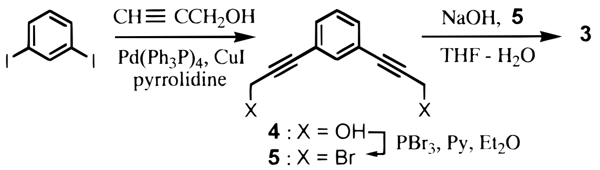
3

The hybrid cyclynes (nanomolecules) having a larger cavity ($n > 3$) are expected to form functional supramolecular complexes with various substrates. On the other hand, the simple members, **2** ($n = 1$) and **3** ($n = 2$), of this family arouse special interest in structure and reaction behavior owing to bond angle strain,[2] besides the expected complex formation with transition metals. We report here synthesis and novel Ag$^+$-induced highly selective cyclization of **3** as well as an attempted synthesis of **2**.

On the basis of the MM2 structure for **2** and **3**, we chose the Pd-mediated coupling reaction of *m*-diiodobenzene with acetylenes in the presence of CuI and pyrrolidine.[3] The single step synthetic strategy from *m*-diiodobenzene and propargyl ether did not give **2** and/or **3** but oligomer. As shown in Scheme 1, Williamson's synthesis of ether from diol **4** and the corresponding dibromide **5** provided **3** as colorless nonfluorescent crystals in around 20% yield.[4]

The structure of **3** was confirmed by spectral data (^{1}H NMR, ^{13}C NMR, and IR)[5] and the MS spectrum[6] of the saturated derivative of **3** prepared by the catalytic hydrogenation, and finally determined by single-crystal X-ray analysis (Figure 1).[7]

Scheme 1



As shown in Figure 1, **3** is not coplanar, and has the small bond angle strain[2] at C−C≡C−C(178.8° and 177.2°) and C−O−C (113.6 °). The size and shape of the cavity of **3** is different from those of folded "tublike" cyclotetrayne.[8] However, **3** seems to allow π complexes to form with the certain metal ions, because formation of the inner or outer π complex with transition metals at their triple bond is reported for cyclynes.[1i,8,9] Of transition metals, we are particularly interested in the reaction of silver(I) ion, since Komatsu' group[8] reported the inner Ag(I) π complex with cyclotetrayne, and Youngs' group[1i] reported the sandwich-type Ag(I) π complex with cyclotriyne. On the basis of the various trials, we carried out the reaction of **3** with AgOTf (7.5 equiv) in benzene at 25−80 °C (see Supporting Information). TLC monitoring of the reaction demonstrated the reaction mixtures to be essentially composed of starting compound and product. Workup and subsequent silica gel column chromatography afforded blue fluorescent product **6** (yield: almost quantitative). The ^{1}H NMR spectrum[10] of **6** in CDCl$_3$ showed two new signals at 5.29 ppm (d, $J = 0.3$ Hz) and 5.56 ppm corresponding to the $-CH_2-O-$ which were not observed in **3**. The IR and ^{13}C NMR spectra[10] of **6** demonstrated no presence of triple bonds. The EI-MS spectrum[10] of **6** clearly showed the molecular ion peak at *m*/*z* 336. The molecular structure of **6** was determined to be 1,2:7,8-bis[tetrahydrofuro]perylene by single-crystal X-ray analysis[11] (Figure 2). Therefore **6** is a strucrural isomer of **3**, and not the silver(I) π complex (**6**·AgOTf).

From this figure, the molecule of **6** is shown to have coplanar structure with normal bond angles and bond lengths. It is to be noted that reaction of **3** (a kind of tetracyclyne) with AgOTf does not provide the Ag(I) π complex, but tetrahydrofuran ring-fused perylene having intense blue fluorescence (Φ_f 0.5 in CHCl$_3$). This Ag(I) ion-induced cyclization leading to the highly selective formation of the perylene skeleton is unprecedented and quite interesting from the synthetic viewpoint, because the five-membered heterocyclic ring-fused perylenes seem to be valuable for creation of functional materials.

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(1) For example: (a) Newkome, G. R.; Lee, H.-W. *J. Am. Chem. Soc.* **1983**, *105*, 5956. (b) Ransohoff, J. E. B.; Staab, H. A. *Tetrahedron Lett.* **1985**, *26*, 6179. (c) Dobler, M.; Dumic, M.; Egli, M.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 792. (d) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (e) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009. (f) Bell, T. W.; Guzzo, F.; Drew, M. G. B. *J. Am. Chem. Soc.* **1991**, *113*, 3115. (g) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227. (h) Pak, J. J.; Timothy, J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 8182. (i) Youngs, W. J.; Tessier, C. A.; Bradshow, J. D. *Chem. Rev.* **1999**, *99*, 3153.

(2) Strain energy was estimated as 83.5 kcal/mol for **2** and 18.1 kcal/mol for **3** from ΔH_f (AM1) for given and reference compounds. The MM2 structure of **3** was almost the same as its X-ray structure.

(3) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.

(4) We are currently trying to synthesize **2** by the quite different strategy. The results will be reported in due course.

(5) Spectral data for **3**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.54 (s, 8H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 4H), 7.70 (s, 2H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 59.2, 86.0, 86.3, 123.0, 128.3, 131.6, 135.5; IR (KBr, cm^{-1}) 2918, 2906, 2862, 2231, 1477, 1434, 1373, 1253, 1074, 1033, 887, 792, 680, 557.

(6) Spectral data for the saturated derivative of **3**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.89 (tt, $J = 6.6$, 6.9 Hz, 8H), 2.68 (t, $J = 6.9$ Hz, 8H), 3.32 (t, $J = 6.6$ Hz, 8H), 6.98 (s, 2H), 7.00 (d, $J = 8.4$ Hz, 4H), 7.19 (t, $J = 8.4$ Hz, 2H); MS (EI, 70 eV) *m*/*z* 352, 203, 190, 176, 158, 143, 132, 117, 105, 91, 79, 41; HRMS (EI, 70 eV) calcd 352.2402, found 352.2407.

(7) Crystal data for **3**: $C_{24}H_{16}O_2$, $M = 336.39$, monoclinic, $P2_1/n$, $a = 11.113(1)$ Å, $b = 4.1207(6)$ Å, $c = 19.5511(8)$ Å, $\beta = 101.064(1)°$, $V = 878.7(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.271$ g/cm^3, $R = 0.051$, $R_w = 0.155$, Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer, 2101 measured reflections, Mo Kα, 1844 unique ($R_{int} = 0.015$), 151 variables [$I > 2\sigma(I)$].

(8) Nishinaga, T.; Kawamura, T.; Komatsu, K. *J. Chem. Soc., Chem. Commun.* **1998**, 2263.

(9) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

(10) Spectral data for **6**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.56 (s, 4H), 5.29 (d, $J = 0.3$ Hz, 4H), 7.79 (s, 2H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.59 (dd, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (75.4 MHz, CDCl$_3$), δ 72.3, 75.3, 119.1, 124.4, 126.2, 127.8, 131.6, 134.1, 134.7, 139.8; IR (KBr, cm^{-1}) 2960, 2923, 2854, 1261, 1097, 1056, 1024, 806, 669, 518; MS (EI, 70 eV) *m*/*z* 336, 307, 280, 138, 40; HRMS (EI, 70 eV) calcd 336.1150, found 336.1158.

(11) Crystal data for **6**: $C_{24}H_{16}O_2$, $M = 336.39$, monoclinic, $P2_1/c$, $a = 9.344(2)$ Å, $b = 6.3811(9)$ Å, $c = 13.484(1)$ Å, $\beta = 102.601(8)°$, $V = 784.7(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.424$ g/cm^3, $R = 0.089$, $R_w = 0.146$, Rigaku AFC7R diffractometer, 2089 measured reflections, Mo Kα, 1810 unique ($R_{int} = 0.040$), 143 variables [$I > -10.00\sigma(I)$].

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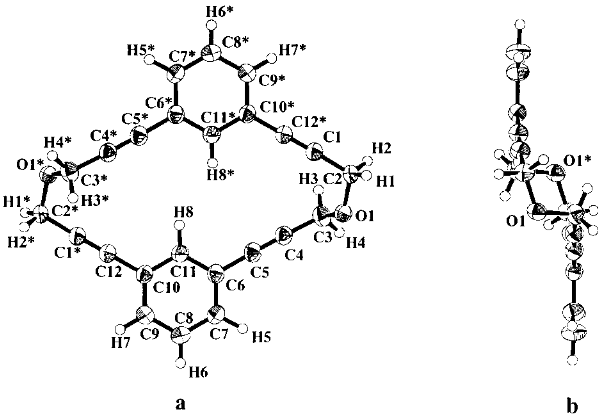


Figure 1. ORTEP drawing of **3** (a, front view; b, side view). Ellipsoids are drawn at 50% probability.

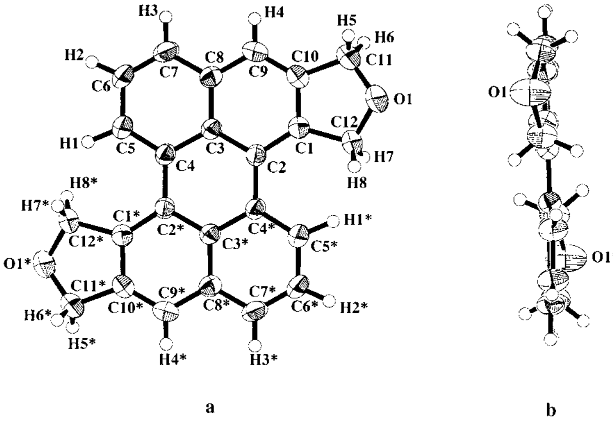
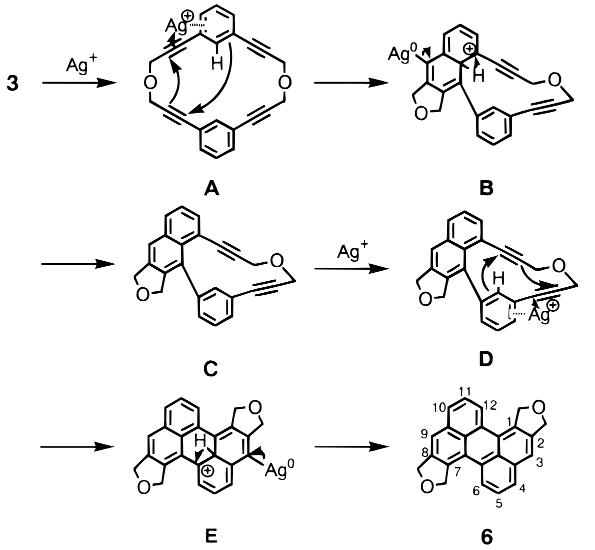


Figure 2. ORTEP drawing of **6** (a, front view; b, side view). Ellipsoids are drawn at 50% probability.

Scheme 2



We examined this reaction by changing the reaction conditions. Consequently we confirmed that (i) metal ions other than Ag(I) ion did not afford **6**, (ii) HCl as well as CF_3SO_3H were not effective for the formation of **6**, and (iii) any reaction key intermediate was not detected by TLC. From (1) our experimental data described here, (2) our AM1 calculation on HOMO coefficents in **3** and **C** (Scheme 2) and heat of formation (ΔH_f) for **3**, **6,** and **C**, and (3) reported evidence for Ag(I)-catalyzed intramolecular cyclization of *o*-hydroxyphenyl phenylethynyl ketone to aurone[12] and X-ray structure of Ag(I) π complexes with condensed aromatic hydrocarbons,[13] the silver(I) ion-induced cyclization leading to highly selective formation of the perylene skeleton is considered to proceed by the double zipper (concerted) reaction involving aromatization and successive proto-dematalation (**B** → **C**, **E** → **6**) shown in Scheme 2.

ΔH_f is considered to be a measure of the stability of **3**, **C**, and **6**, because they are structural isomers. The ΔH_f values (kcal/mol) calculated by AM1 are 171.3 for **3**, 118.1 for **C**, and 20.3 for **6**, indicating that product **6** is most stable, and the stability decreased in the following order: **6** > **C** > **3**. If we assume that the reaction rate for both zipper reactions is correlated with $\Delta\Delta H_f$, the reason we could not detect the key intermediate **C** during the reaction is explained by the fact that the second zipper reaction ($\Delta\Delta H_f$ = 97.8 kcal/mol) is much faster than the first one ($\Delta\Delta H_f$ = 53.2 kcal/mol). Our electrophilic cyclization leading to the perylene skeleton is similar to Swagers' electrophilic cyclization leading to the phenanthrene skeleton,[14] but differs from Youngs' nucleophilic cyclization leading to the chrysene skeleton[15] in the reaction mode.

The product **6** is a coplanar heterocyclic ring system and a strong electron donor. To examine a possibile solid-state application of **6**, we have investigated its stacking mode (see Supporting Information).

Consequently it is shown that molecules of **6** make columns composed of a nice $\pi-\pi$ stacking of **6** having interplane distances of 3.47−3.63 Å, and the intercolumn distance is about 2.60 Å. Both pentacyclic aromatic electron donors, perylene (ionization potential (IP) 6.90 eV) and pentacene (IP 6.64 eV), have a similar ionization potential and almost the same π electron area. Since preparation of efficient photovoltaic diodes by doping of pentacene crystals with iodine is very recently reported,[16] product **6** and related systems where oxygen replaced by a heteroatom such as S, PR_2, SiR_2, and GeR_2 are expected to be valuable for creation of such functional materials. Our reaction could be extended to prepare such various heterocyclic ring-fused perylenes.[17]

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Supporting Information Available: Synthetic procedures, crystallographic data for **3** and **6**, stacking structure of **6**, and HOMO coefficients in **3** and **C** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Synthesis and properties of S and Si analogues of **6** will be reported in due course.