# *Z*-Tribenzo[c,g,k]-1,2,5,6-tetradehydro[12]annulene, a Concave π-Electron System

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Synthesis of *Z*-tribenzo[c,g,k]-1,2,5,6-tetradedydro[12]-annulene **1** has been carried out in a good total yield. The Bergman reaction of the closely situated acetylene bonds in the endiyne structure of **1** and the reaction of **1** with AuCl produced the corresponding cyclization products.

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Concave and bowl-shaped π-conjugated hydrocarbons attract current interest, because of host/guest interactions,[1] self-assembly,[2] formation of metal complexes,[3] and biological activities in some cases.[4] In order to reduce the molecular strain, *Z*-tribenzo[c,g,k]-1,2,5,6-tetradedydro[12]annulene **1** possesses a concave π-framework, and hence the two acetylene linkages are located so close together that their electron clouds begin to overlap. Therefore, **1** can be expected to show interesting chemical behavior. We now report the synthesis of **1** and the reactivities of its acetylenic bonds.

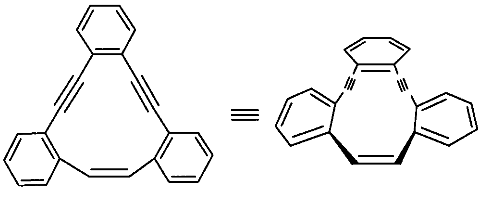
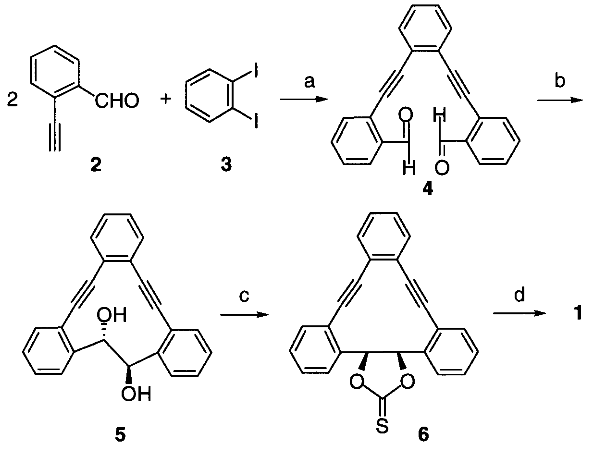


**Figure 1.** Z-tribenzo[c,g,k]tetradedydro[12]annulene **1**.

The synthesis of **1** was carried out according to the reaction sequence outlined in Scheme 1. The Sonogashira coupling of *o*-diiodobenzene **3** with **2** (2 equiv) in refluxing $Et_3N$ for 1 h gave the dialdehyde **4** (81%).[5] The intramolecular pinacol coupling of **4** with a low valent vanadium complex[6,7] generated from $VCl_3(THF)_3$ and Zn in $CH_2Cl_2$–DMF at room temperature produced selectively the *erythro*-**5** (59%) together with a small amount of the *threo*-isomer (3.4%). The reaction of **5** with TCDI (1,1'-thiocarbonyldiimidazole) in refluxing toluene for 27 h afforded the thionocarbonate **6** (80%), which, on treatment with DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine)[7] in refluxing benzene for 14 h, produced the desired [12]annulene **1** in 77% yield.



a, $Pd(PPh_3)_4$, CuI, $Et_3N$; b, $VCl_3(thf)_3$, Zn, $CH_2Cl_2$, DMF, rt; c, TCDI (thiocarbonyldiimidazole), toluene, reflux; d, DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine), benzene, reflux.

**Scheme 1.** Synthesis of **1**.

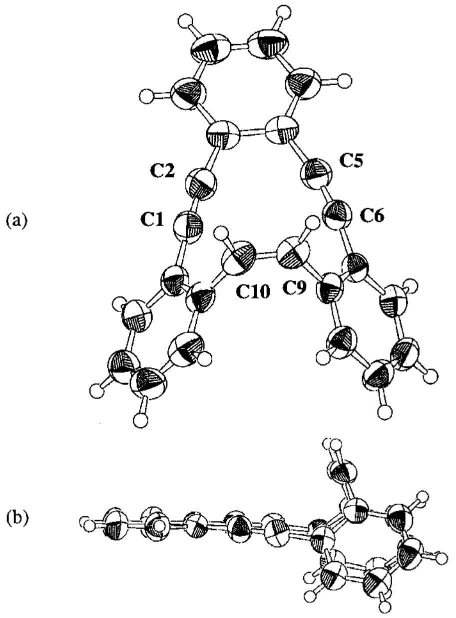


**Figure 2.** Crystal structure of **1.** a) The top view. b) The side view.

Although the [12]annulene **1** was expected to hold a fairly large strain energy, **1** proved to be a thermally stable compound. Recrystallization of **1** from $CH_2Cl_2$–isopropyl ether gave single crystals, and the crystal structure has been determined by the X-ray diffraction method.[8] The crystal lattice contains two crystallographically independent molecules, which are found to have essentially the same structure. As shown in Fig. 2, **1** has an approximate $C_s$ symmetry, and the *Z*-double bond in **1** rises up from the molecular plane to form a cage structure. Interestingly, the intramolecular $C_{sp}\cdots C_{sp}$ distances of C2···C5 (2.77 Å) and C1···C6 (3.57 Å) are definitely shorter than those (2.85 and 4.05 Å) of tribenzohexadehydro[12]annulene **7**[9] and those (2.87 and 4.11 Å) of 1,2-diethynylbenzene **8**,[9] respectively (Figure 3). It is worth noting that the averaged distance between the *Z*-olefinic and acetylenic carbons is 2.88 Å which is 15% shorter than the sum of van der Waals radii, and the C–C bond formation can be expected for the olefinic (C10 and C9) and acetylenic (C1 and C6) carbons.

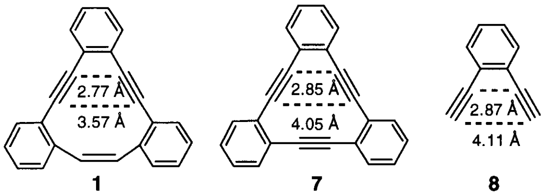
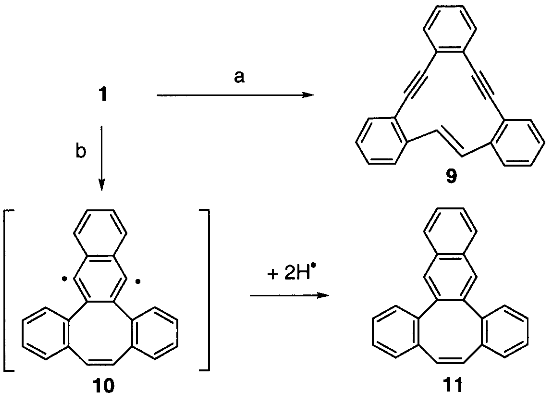


**Figure 3.**

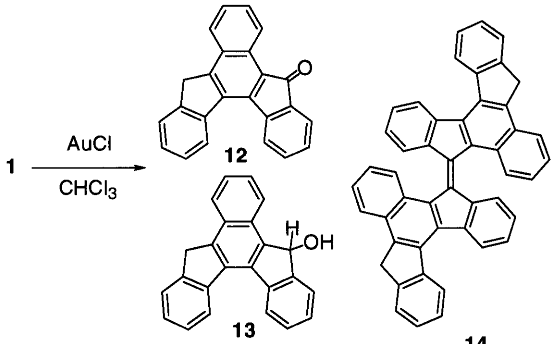
Recently, thermal and photochemical Bergman reactions have been investigated extensively.[4,10] Since **1** has closely situated acetylenic bonds in the endiyne structure, a ready Bergman cyclization can be expected. Therefore, we attempted thermal and photochemical Bergman reactions (Scheme 2). The irradiation of **1** under a high-pressure mercury lamp in benzene at room temperature produced **9** as the sole product in 93% yield, and **9** was stable under photolysis conditions.[11] In contrast, the reaction of **1** in *o*-dichlorobenzene in the presence of 1,4-cyclohexadiene (50 equiv) at 250 °C for 96 h afforded the desired product **11** in 52% yield, together with 4% of **9**, and 43% of **1** was recovered. The low reactivity of **1** for the Bergman cyclization may be due to the difficulty to form the strained diradical intermediate **10**.



a, hν (>310 nm), benzene, rt, 7.5 h ; b, 1,4-cyclohexadiene, *o*-$C_6H_4Cl_2$, 250 °C.

**Scheme 2.**

In order to examine the formation of metal complexes, we attempted the synthesis of gold(I), silver(I), and copper(I) complexes. Although no complex formation of **1** with AgOTf and CuOTf was observed in solutions, the reaction of **1** with AuCl[12] in $CHCl_3$ proceeded smoothly to form the corresponding cyclization products **12**, **13**, and **14** in 35, 25, and 14% yields, respectively (Scheme 3). The formation of **12**, **13**, and **14** indicates the reaction of the olefinic (C10 and C9) and acetylenic (C1 and C6) carbons.[13] Interestingly, a solution of **14** in $CHCl_3$ shows an intense deep blue color corresponding to the electronic absorption of $\lambda_{max}$ 570 nm.



**Scheme 3.**

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## References and Notes

1 J. Gross, G. Harder, A. Siepen, J. Harren, F. Vögtle, H. Stephan, K. Gloe, B. Ahlers, K. Cammann, and K. Rissanen, *Chem. Eur. J.*, **2**, 1585 (1996); J. Benkhoff, R. Boese, and F.-G. Klärner, *Liebigs Ann./Recueil*, **1997**, 501; C. Müller, J. A. Whiteford, and P. J. Stang, *J. Am. Chem. Soc.*, **120**, 9827 (1998).

2 K. Imamura, K. Takimiya, Y. Aso, and T. Otsubo, *Chem. Commun.*, **1999**, 1859, and references cited therein.

3 T. Nishinaga, T. Kawamura, and K. Komatsu, *Chem. Commun.*, **1998**, 2263, and references cited therein.

4 Reviews: K. C. Nicolaou and W.-M. Dai, *Angew. Chem., Int. Ed. Engl.*, **30**, 1387 (1991); M. E. Maier, *Synlett*, **1995**, 13; H. Lhermitte and D. Grierson, *Contemp. Org. Synth.*, **3**, 93 (1996); J. W. Grissom, G. U. Gunawardena, D. Klingberg, and D. Huang, *Tetrahedron*, **52**, 6453 (1996).

5 All new compounds gave satisfactory analytical and spectral data. **1**: colorless prisms, mp 159.5–163 °C (decomp.); EI-MS *m/z* 302 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ 6.90 (s, 2H), 7.13 (t, $J$ = 7.3 Hz, 2H), 7.18–7.26 (m, 4H), 7.31–7.32 (m, 2H), 7.39 (m, 2H), 7.48–7.50 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 93.3, 94.1, 122.2, 126.7, 128.0, 128.1, 129.1, 129.7, 130.5, 132.4, 140.9. **11**: colorless cryst., mp 147–149 °C, EI-MS *m/z* 304 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ 6.77 (s, 2H), 7.11 (m, 2H), 7.24–7.29 (m, 6H), 7.49 (m, 2H), 7.63 (s, 2H), 7.86 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.2, 127.0, 127.1, 127.4, 127.7, 128.6, 130.1, 132.5, 132.6, 137.3, 141.0, 141.5. **12**: orange needles, mp 233.5–236 °C; EI-MS *m/z* 318 ($M^+$); $^1$H NMR ($CDCl_3$) $\delta$ 4.25 (s, 2H), 7.31 (m, 1H), 7.40 (m, 1H), 7.45–7.68 (m, 6H), 7.91 (d, $J$ = 8.5, 1H), 8.14 (d, $J$ = 7.5, 1H), 8.33 (d, J = 7.5, 1H), 9.13 (d, $J$ = 8.5, 1H). **14**: dark blue prisms, mp 333–334.5 °C; FAB-MS *m/z* 605 $(M+1)^+$; $^1$H NMR ($CDCl_3$) $\delta$ 1.96 (d, $J$ = 22.0, 2H), 3.52 (d, $J$ = 22.0, 2H), 6.88–6.91 (m, 4H), 7.23–7.27 (m, 12H), 7.37–7.43 (m, 4H), 8.75–8.77 (m, 2H), 8.45–8.46 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 35.1, 121.6, 122.7, 124.1, 124.3, 124.4, 124.5, 124.7, 125.7, 126.1, 126.5, 128.3, 129.1, 132.4, 132.8, 140.7 (two), 141.0, 142.2, 143.6, 144.0, 144.2, 145.4, 145.7; UV–vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 370 (2.84), 570 nm (3.01).

6 J. H. Freudenberger, A. W. Konradi, and S. F. Pedersen, *J. Am. Chem. Soc.*, **111**, 8014 (1989).

7 Y. Kuwatani, T. Yoshida, A. Kusaka, and M. Iyoda, *Tetrahedron Lett.*, **41**, 359 (2000).

8 Crystal data. **1**: $C_{24}H_{14}$, $M$ = 302.37, monoclinic, space group $P2_1/n$ (#14), $a$ = 12.402(6) Å, $b$ = 11.071(9) Å, $c$ = 24.171(5) Å, $\beta$ = 97.98(2)°, $V$ = 3286(2) Å$^3$, $T$ = 296 K, $Z$ = 8, $d_{calcd}$ = 1.222 g cm$^{-3}$, $R$ = 0.0377 and $R_w$ = 0.0349 for 546 observed reflections out of 3852 unique reflections.

9 The intramolecular C···C distances in **7** and **8** are estimated based on the MOPAC AM1 calculations of **7** and **8**.

10 C.-S. Kim and K. C. Russell, *Tetrahedron Lett.*, **40**, 3835 (1999); T. Kaneko, M. Takahashi, and M. Hirama, *Angew. Chem., Int. Ed. Engl.*, **38**, 1267 (1999); *Tetrahedron Lett.*, **40**, 2015 (1999).

11 Although **1** and **9** show similar electronic spectra, the ring strain in **1** causes preferentially its photochemical isomerization to the less-strained **9**.

12 G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed., Academic Press, New York (1965), Vol. 2, p. 1055.

13 Reductive cyclization of tribenzo[c,g,k]-1,2,5,6,9,10-hexadehydro[12]annulene was reported to produce indenofluorene derivatives: W. J. Youngs, A. Djebli, and C. A. Tessier, *Organometallics*, **10**, 2089 (1991); D. Malaba, A. Djebli, L. Chen, E. A. Zarate, C. A. Tessier, and W. J. Youngs, *Organometallics*, **12**, 1266 (1993).