all-Z-Tribenzo[12]-, tetrabenzo[16]- and pentabenzo[20]annulenes[†]

Yoshiyuki Kuwatani, Tadahiro Yoshida, Ayako Kusaka and Masahiko Iyoda [*]

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Abstract

A new synthetic strategy of *all-Z*-[*n*]benzo[4*n*]annulenes, which is based on the intramolecular pinacol coupling, followed by the Corey–Winter procedure, has been developed, and three annulenes have been successfully synthesized using this strategy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: annulenes; cage compounds; coupling reactions; cyclizations; cyclophanes.

Cylindrical π-conjugated molecules[1] attract continuing interest as synthetic challenges,[2] unique structures,[3] host/guest interactions,[4] and organic materials with interesting electric properties.[5] *all-Z*-[*n*]Benzo[4*n*]annulenes **1**–**3** are bowl-shaped hydrocarbons with a medium-sized concavity. Furthermore, *Z,Z,Z,Z*-pentabenzo-[20]annulene **3** can be regarded as a precursor of the cyclic belt **4** which is a central aromatic belt of C_{60} and C_{70}. Although we have previously reported the synthesis of *Z,Z,Z*-tribenzo[12]annulene **1** and its metal complexes,[6] the synthetic methodology is only limited to **1** in very low overall yield. Therefore, we developed a new strategy to synthesize *all-Z*-[*n*]benzo[4*n*]annulenes **1**–**3**.
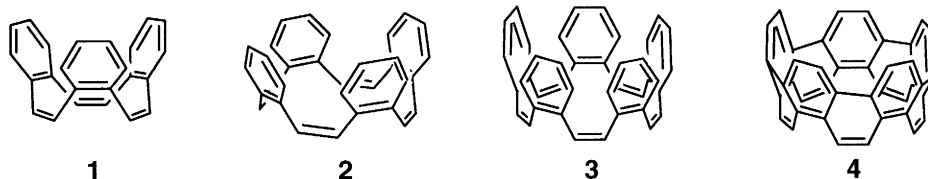
Our new synthetic strategy for **1**–**3** is based on the intramolecular pinacol coupling of the corresponding linear poly *cis*-stilbene derivative **5**, followed by formation of the final *cis*-double bond using reductive dehydroxylation as shown in Scheme 1. The second step can be expected to be achieved by the Corey–Winter procedure.[7]
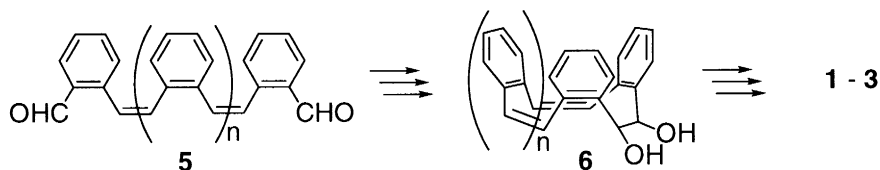
Scheme 1. Synthetic route for **1–3**

The synthesis of *Z,Z,Z*-tribenzo[12]annulene **1** was carried out using the sequence outlined in Scheme 2. Recently, we reported the synthesis and structure of *Z,Z*-tribenzo[12]annulene-1,2-dione **7**[8] which was prepared by the intramolecular cyclization of the dialdehyde **5** (*n*=1), followed by Swern oxidation. Although **7** consists of two conformational isomers (**7a** and **7b**), reduction of **7** with NaBH$_4$ in ethanol–CH$_2$Cl$_2$ afforded the *erythro*-isomer **8a** (80%) with a small amount of the *threo*-isomer **8b**. The reaction of **8a** with TCDI (thiocarbonyldiimidazole) in refluxing toluene led to the thionocarbonate **9** (78%) which was converted into **1** (84%) by the reaction with DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine) (modified Corey–Winter procedure).[9] *Z,Z,Z*-Tribenzo[12]annulene **1** was synthesized in 37% overall yield based on **5** (*n*=1).
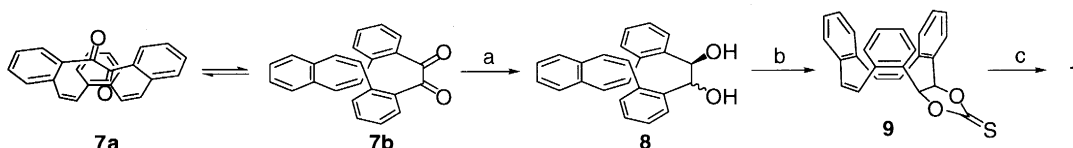
Scheme 2. Conditions: (a) NaBH$_4$, EtOH, CH$_2$Cl$_2$, 0°C (80%); (b) TCDI (thiocarbonyldiimidazole), toluene, reflux (78%); (c) DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine), benzene, reflux (84%)

In analogy with the case of **1**, the syntheses of *Z,Z,Z,Z*-tetrabenzo[16]- and *Z,Z,Z,Z,Z*-pentabenzo[20]annulenes **2** and **3** were started from the construction of the corresponding dialdehydes (Scheme 3). Thus, the Sonogashira coupling of **10** with 2-bromobenzaldehyde in the presence of Pd(PPh$_3$)$_4$ and CuI in triethylamine at rt, followed by *t*-butyldimethylsilylation, produced **12** in 92% overall yield. Reduction of **12** with NaBH$_4$ (93%), followed by partial hydrogenation in the presence of a Lindlar catalyst (99%) and Dess–Martin oxidation[10] (98%) led to the *cis*-stilbene derivative **13**. The pinacol coupling of **13** with a low-valent vanadium complex gave the *threo*-diol **14** in 92% yield. The *threo*-diol **14** was converted into the *erythro*-diol by a two-step procedure. Thus, Swern oxidation of **14** led to the diketone which was reduced with NaBH$_4$ under the chelation-controlled conditions to produce the *erythro*-diol (89% based on **14**). The *erythro*-diol was treated with thiophosgene in the presence of 4-dimethylaminopyridine to afford the thionocarbonate **15** (94%). The reaction of **15** with DMPD in refluxing benzene produced the *Z,Z,Z*-triene-bis(siloxy)ether (83%) which was treated successively with Bu^n$_4$NF in THF and the Dess–Martin reagent in CH$_2$Cl$_2$ to produce the *Z,Z,Z*-triene-dialdehyde **16** in 89% overall yield.

For the synthesis of the tetraene-dialdehyde **19**, the *cis*-stilbene derivative **13** was converted into the enyne **17** by a Wittig-type reaction with CBr$_4$ and PPh$_3$ (81%), followed by treatment with LDA in THF (89%). The Sonogashira coupling of **17** with *o*-diiodobenzene, followed by desilylation and Dess–Martin oxidation produced the diendiyne **18** in 84% overall yield. The partial hydrogenation of **18** with the Lindlar catalyst led to **19** (89%).

The syntheses of the annulenes **2** and **3** starting from the corresponding dialdehydes **16** and **19** were carried out using a combination of the intramolecular pinacol coupling[8] and modified Corey–Winter procedure (Scheme 3). The reaction of **16** with VCl$_3$(THF)$_3$ (2 equiv.)[11] and zinc (2 equiv.) in DMF–CH$_2$Cl$_2$ at rt for 1 h produced a mixture of the *threo*- and *erythro*-diols **20a** and **20b** (49 and 25%, respectively)
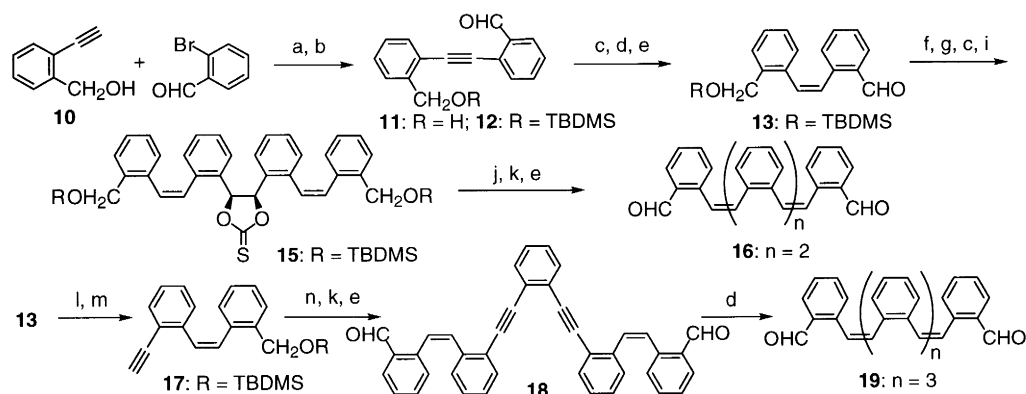
Scheme 3. Conditions: (a) Pd(PPh$_3$)$_4$ (1 mol%), CuI (2 mol%), Et$_3$N, rt; (b) Bu^{t}Me$_2$SiCl, imidazole, CH$_2$Cl$_2$; (c) NaBH$_4$ (2 equiv.), MeOH, CH$_2$Cl$_2$; (d) H$_2$, Lindar catalyst, benzene, quinoline; (e) Dess–Martin reagent, CH$_2$Cl$_2$; (f) VCl$_3$(THF)$_3$ (1.1 equiv.), Zn (1.1 equiv.), CH$_2$Cl$_2$, rt; (g) (COCl)$_2$ (4 equiv.), DMSO (5 equiv.), Et$_3$N, CH$_2$Cl$_2$, -78°C; (i) Cl$_2$C=S (1.2 equiv.), 4-dimethylaminopyridine (2.4 equiv.), CH$_2$Cl$_2$, 0°C; (j) DMPD, benzene, reflux; (k) Bu$^n_4$NF, THF; (l) CBr$_4$, PPh$_3$, CH$_2$Cl$_2$; (m) LDA, THF, -78°C; (n) o-diiodobenzene, Pd(PPh$_3$)$_4$, CuI, Et$_3$N, Δ

(Scheme 4). The *threo*-diol **20a** was converted into the *erythro*-diol **20b** by successive Swern oxidation and NaBH$_4$-reduction in 62% overall yield. The reaction of **20b** with TCDI in refluxing toluene led to the thionocarbonate **21** (80%), which was reacted with DMPD in refluxing benzene to produce the desired *all*-Z-tetrabenzo[16]annulene **2** in 62% yield.[12] In a similar manner, the intramolecular coupling of **19** with VCl$_3$(THF)$_3$ (3.5 equiv.) and zinc (3.5 equiv.) in DMF–CH$_2$Cl$_2$ at rt for 3.5 h gave a mixture of the *threo*- and *erythro*-diols **22a** and **22b** in 80% yield. In order to line up the stereochemistry of the diol part, the mixture of **22a** and **22b** was converted into the corresponding α-diketone by Swern oxidation. Reduction of the diketone with NaBH$_4$ afforded the *erythro*-diol **22b** in 72% overall yield. The reaction of **22b** with TCDI led to the thionocarbonate **23** (74%) which was treated with DMPD in refluxing benzene to produce the [20]annulene **3** (72%).[12]
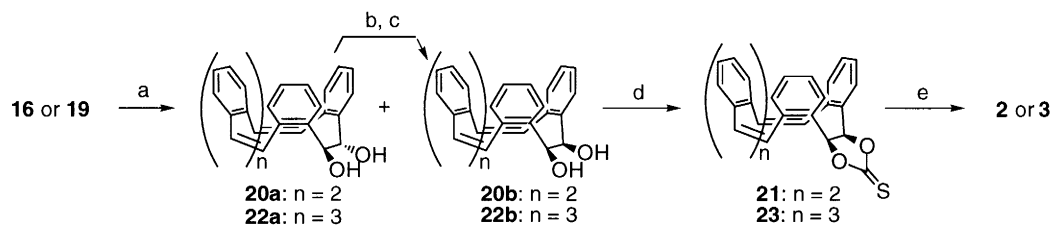
Scheme 4. Conditions: (a) VCl$_3$(THF)$_3$, Zn, DMF, CH$_2$Cl$_2$, rt; (b) (COCl)$_2$, DMSO, Et$_3$N, CH$_2$Cl$_2$; (c) NaBH$_4$, MeOH, CH$_2$Cl$_2$, 0°C; (d) TCDl, 4-toluene, reflux; (e) DMPD, benzene, reflux

Although the [12]annulene **1** has a rigid framework with C_{3v} symmetry, the ^{1}H and ^{13}C NMR spectra of the [16]annulene **2** show temperature dependence. Thus, the ^{1}H NMR spectrum of **2** in CDCl$_3$ at -50°C showed slightly complex signals consisting of one AB quartet (δ 6.74 and 6.64, J=12 Hz) and two sets of AA′BB′ multiplets (δ 7.36, 7.29, 6.52 and 6.45), which suggested that **2** adopted a C_{2v}-symmetric conformation. However, the spectrum of the same sample gradually broadened along with elevating the temperature, and the signals coalesced at about 0°C. At 50°C, the spectrum showed a simple pattern corresponding to C_{4v}-symmetry, and the activation energy for this dynamic process is calculated to be 12.7 kcal mol^{-1} using the VT ^{13}C NMR measurements. Based on the ^{1}H NMR spectra, the structure of **2** was established as a stacking form **2a** at low temperature. The π–π interaction of the benzene rings may

prefer the stacking structure **2a**, and the steric repulsion between the α-hydrogen of the benzene rings destabilizes the C_{4v} structure of **2**.
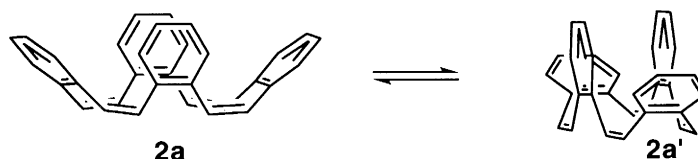
In contrast to the results obtained from **2**, the ^{1}H and ^{13}C NMR spectra of **3** showed no temperature dependence. Thus, the C_{5v}-symmetric spectra, which consisted of a set of AA′BB′ multiplets (δ 6.95 and 7.02) and a singlet (δ 6.47) in the ^{1}H NMR and 4 signals at δ 126.5, 129.1, 129.7, and 136.3 in the ^{13}C NMR, observed at rt, were almost unchanged even at −90°C except for a slight broadening of the signals. This result suggests that the molecular framework of **3** may be more flexible than that of **2**. Interestingly, the olefinic proton of **3** was observed at a higher field than the corresponding signals of **1** and **2**, reflecting the more crowded structure of the five benzene rings.

As shown in Fig. 1, the structure of **2** was determined by X-ray analysis.[13] When **2** was recrystallized from CH_2Cl_2–hexane, colorless plates and prisms of **2** were obtained. The structure of **2** confirms the expected stacking form with approximate C_2 symmetry. A pair of benzene rings is stacked face-to-face with a distance of 3.4 Å, whereas the other two are apart from each other to form a hinge-like structure. The stacked benzene rings are located parallel with a slightly deviated overlap, presumably due to release of the steric repulsion between the central olefinic hydrogens.
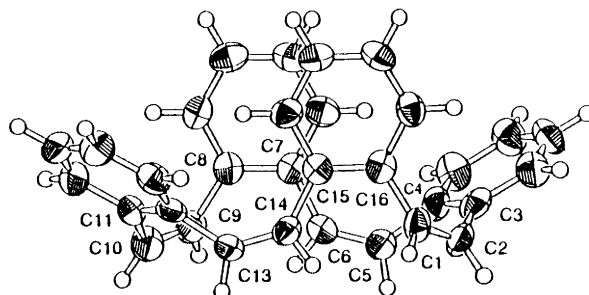

Fig. 1. ORTEP diagram of **2**. Selected bond lengths [Å] and angles [°]: C1–C2, 1.34(1); C2–C3, 1.49(1); C3–C4, 1.40(1); C4–C5, 1.49(1); C5–C6, 1.34(1); C1–C2–C3, 125.5(8); C2–C3–C4, 121.5(9); C2–C1–C16, 117.7(8)

Acknowledgements

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12. All compounds gave satisfactory analytical and spectral data. For example, **2**: colorless plates, mp 251.0–254.0°C, MS m/z 408 (M^+); ^{1}H NMR ($C_2D_2Cl_4$, 120°C) δ 6.71 (s, 8H), 6.82 (AA$'$, 8H), 6.95 (BB$'$, 8H); ^{1}H NMR ($CDCl_3$, −55°C) δ 6.44–6.49 (AA$'$, 4H), 6.51–6.53 (BB$'$, 4H), 6.45 (s, 4H), 6.76 (s, 4H), 7.28–7.30 (AA$'$, 4H), 7.36–7.38 (BB$'$, 4H); ^{13}C NMR ($CDCl_3$, 60°C) δ 126.5, 128.9, 130.5, 136.5; ^{13}C NMR ($CDCl_3$, −55°C) δ 126.3, 126.4, 127.5, 129.2, 129.7, 130.6, 134.8, 137.1; UV (cyclohexane): λ_{max} (log ε) 227sh (4.31), 274 (4.31) nm. Compound **3**: colorless prisms, mp 222.5–223.5°C, MS m/z 510 (M^+); ^{1}H NMR ($CDCl_3$, 25°C) δ 6.47 (s, 10H), 6.93–6.97 (AA$'$, 10H), 7.01–7.04 (BB$'$, 10H); ^{13}C NMR ($CDCl_3$) δ 126.5, 129.1, 129.7, 136.3; UV (cyclohexane): λ_{max} (log ε) 258 (4.63) nm.

13. Crystal data for **2**: $C_{32}H_{24}$, $Mw=408.54$, orthorhombic, space group $Pna2_1$ (# 33), $a=21.915(5)$, $b=11.983(4)$, $c=8.732(3)$ Å, $V=2293(2)$ Å^3, $Z=4$, $Dc=1.183$ g cm^{-3}, $R=0.043$, $Rw=0.040$, GOF=1.32 for 956 reflections with $I>1.50\sigma(I)$.