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Novel Twin Corannulene: Synthesis and Crystal Structure Determination of a Dicorannulenobarrelene Dicarboxylate

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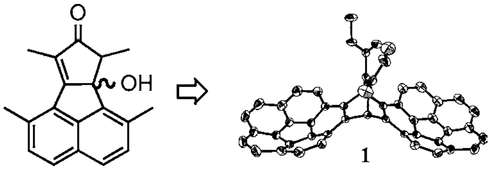
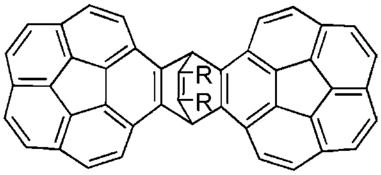
ABSTRACT



The dicorannulenobarrelene 1 was synthesized with the final step achieved by a nickel-mediated fourfold intramolecular coupling of dibromomethyl with bromomethyl groups. Low-temperature ^{1}H NMR spectra of 1 show a presence of three conformers with approximate populations of 0.82:0.13:0.05, in good agreement with theoretical predictions. In the crystal, 1 incorporates two CCl_4 molecules and adopts the *bis-exo* conformation.

Curved surface polycyclic aromatic hydrocarbons whose carbon frameworks can be identified on the surface of buckminsterfullerene C_{60} have been the subject of considerable research over the past decade.[1] Synthetic methodologies involving flash vacuum pyrolysis developed in the early 1990s[2] are being supplanted, where possible, with more practical condensed phase synthetic methods based on transition metal-mediated intramolecular coupling leading to the formation of strained "buckybowl" systems.[3] Recently, we showed that the critical ring formation step can be conveniently achieved by simple and inexpensive procedures if sufficient strain is introduced into the precursors.[4] For example, the coupling of sterically congested dibromomethyl and bromomethyl groups leads to the formation of strained six-membered rings in good yield upon heating the precursors with aqueous sodium hydroxide[4a−c] or with commercial nickel powder.[4c,d] In the present communication, we report the synthesis of a large, twin corannulene (**1**) with the final step involving the formation of four new rings by nickel powder-mediated coupling of a dodecabrominated precursor. Furthermore, the two corannulene substructures in **1** are in a topological arrangement that has the potential for the accommodation of guest molecules within the cavity between the rings.



1: R = COOMe

Our synthesis (Scheme 1) starts with alcohol **2**, which was introduced by Siegel as a precursor to formation of the corannulene framework.[3a] Alcohol **2** was dehydrated to cyclopentadienone **3** and then reacted with benzoquinone at room temperature to form a Diels−Alder monoadduct (only). The application of harsher conditions (high temperature and/

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[1] For recent reviews see: (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291. (c) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325. (d) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Anselms, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209.

[2] (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920. (c) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963.

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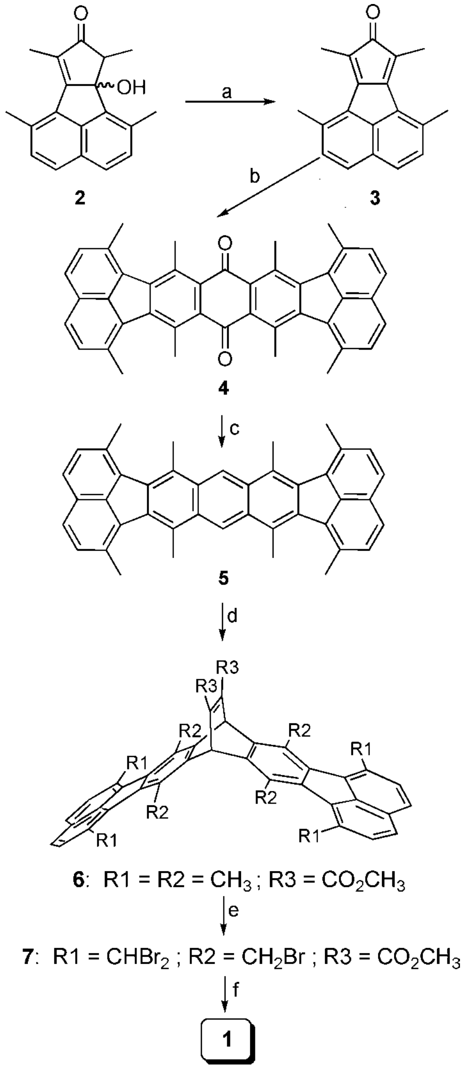
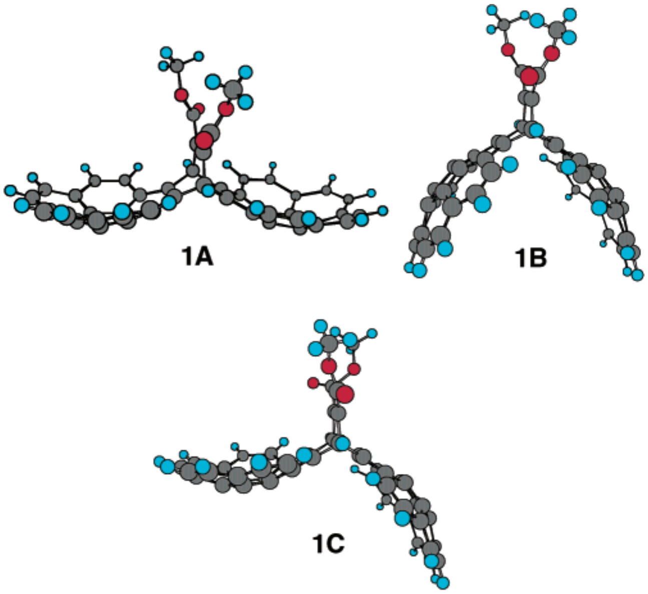
Scheme 1[a]



[a] Reaction conditions: (a) Ac_2O, 1 drop of H_2SO_4, rt, 30 min, 80%. (b) 1,4-Benzoquinone, DMF, Et_3N, then DBU, rt, 24 h, 70%. (c) $Al(OC_6H_{11})_3$, cyclohexane, reflux, 4 days, 76%. (d) MeOOC-COOMe, tetrachloroethane, reflux, 2 h, 72%. (e) NBS, dibenzoyl peroxide, CCl_4, $h\nu$, reflux, 3 h, quantitative. (f) DMF, Ni powder, 80−90°, 16 h, 40%.

or strong bases) did not promote the formation of desired **4** but rather produced complicated mixtures. After several trials, we discovered a single-pot procedure with target anthraquinone **4** formed from **3** in ca. 70% yield by treatment with benzoquinone and triethylamine in DMF followed by the addition of DBU. The anthraquinone was then reduced to anthracene **5** by aluminum cyclohexoxide in cyclohexanol. However, several attempts at bromination of the methyl groups in **5** all led to mixtures of unidentifiable products. The reactive central anthracene ring in **5** may be responsible for the failure since the distinctive ^{1}H NMR resonances of the $C_{9,10}$ aromatic hydrogens at ca. 8.9 ppm disappear at early stages of the reaction, perhaps due to ring bromination and/or photodimerization. Thus, to protect the reactive sites, we prepared Diels−Alder adduct **6** by reaction of **5** with dimethyl acetylenedicarboxylate. In contrast to **5**, **6** was smoothly dodecabrominated to symmetrical derivative **7** in essentially quantitative yield. By analogy with similar polybrominated systems reported previously, we assumed that the “outer” four methyl groups (R1) were doubly brominated to $CHBr_2$, while the “inner” methyls (R2) were only monobrominated due to steric congestion. Finally, dodecabromide **7** was converted to **1** with a respectable yield of 40% by nickel powder-mediated intramolecular coupling of the bromomethyl and dibromomethyl groups.[4d]

Since**1** possesses two corannulene subunits that, like the parent compound, are bowl-shaped with a low barrier for bowl inversion,[1] three distinct conformations (**1A**−**C**) are expected. Calculations[5] at both the semiempirical AM1 and density functional Becke3/6-311G**//Becke3/3-21G levels suggest **1A** to be the most stable and **1B** the least stable conformations with relatively small energy differences.



At the highest level of theory employed, conformers **1B** and **1C** are predicted to have higher energies than **1A** by only 1.1 and 0.5 kcal/mol, respectively. Considering the flexibility of the corannulene bowl, equilibration of these conformers would be achieved quickly in both the gas-phase and in solution. Indeed, the room-temperature ^{1}H NMR spectrum of **1** is very simple, exhibiting only five different proton signals. However, upon cooling, the spectrum broadens and subsequently sharpens again resulting in a more complicated pattern. The presence of three different species is clearly

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(3) (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754. (b) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666. (c) Seiders, T. J.; Baldridge, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439. (d) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800. (e) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804. (f) Reish, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427. (g) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517.

(4) (a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323. (b) Sygula, A.; Marcinow, Z.; Fronczek, F. R.; Guzei, I.; Rabideau, P. W. *Chem. Commun.* **2000**, 2439. (c) Sygula, A.; Xu, G.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron* **2001**, *57*, 3637. (d) Sygula, A.; Karlen, S. D.; Sygula, R.; Rabideau, P. W. *Org. Lett.* **2002**, *4*, 3135.

evident by the splitting of the carbmethoxy methyl protons (a singlet at 3.80 ppm at rt in THF-d_8) into three signals at 4.01, 3.71, and 3.40 ppm (−71°) with approximate populations of 0.82, 0.13, and 0.05, respectively. X-ray analysis[6] of a crystal grown from CCl_4/toluene solution revealed that two molecules of CCl_4 were incorporated into the crystal lattice of **1**, which adopted the *bis-exo* conformation **1A** (Figure 1). The curvatures of the corannulene portions of the molecule are very similar to corannulene itself with average POAV pyramidalization angles[7] of 8.2 and 3.9° for the hub and quaternary rim carbon atoms, respectively.

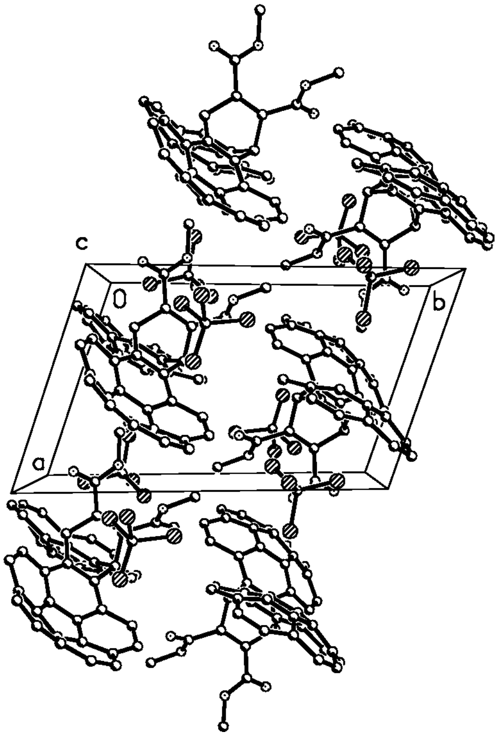

Figure 1. Crystal packing view of **1**. Hydrogen atoms have been omitted for clarity.

We are pursuing further X-ray studies of **1**, trying to grow crystals from different solvents in the hope of observing other conformers. The *bis-endo* **1B** is of special interest since it exhibits a significant cavity formed by the concave sides of the corannulene units with the potential for host−guest complexation. Intriguingly, the size of the cleft in **1B** is comparable with the size of buckminsterfullerene C_{60}. At the MM2 level of theory,[8] the complex of **1B** with C_{60} is over 4 kcal/mol more stable than the lowest energy complexes of both **1A** and **1C**. Apparently, stabilization of the **1B**/C_{60} complex by attractive van der Waals forces between the concave surfaces of the corannulene moieties and C_{60} is the decisive factor for the above stability pattern.[9,10] So far, we have failed to observe formation of a strong complex of **1** with C_{60} by NMR spectroscopy,[11] but we continue to study its interactions with C_{60}, including attempts to grow mixed crystals.

In conclusion, our recently developed methodology for the practical synthesis of buckybowls has allowed the preparation of the title barrelene **1** with two flexible corannulene substructures.

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Supporting Information Available: Synthetic procedures and spectroscopic characterization for **1** and **3**−**7**, optimized geometries for **1A**−**C** along with their B3LYP/6-311G** single-point energies, crystal structure data for **1** (CIF), and variable-temperature ^1H NMR spectra for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(6) Crystal data: $C_{50}H_{24}Cl_8O_4$, FW = 972.29; triclinic, *P*-1; $a = 9.347(2)$, $b = 15.163(4)$, $c = 16.451(4)$ Å; $\alpha = 103.057(4)$, $\beta = 98.130(4)$, $\gamma = 106.156(4)°$; $V = 2128.9(8)$ Å^3; $Z = 2$; $D_{calcd} = 1.517$ g/cm^{-3}; $F(000) = 984$; $T = 173$ K; $R = 0.0778$; $R_w = 0.2023$ for 9559 observed data. Intensity data were collected on a Bruker CCD-1000 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Hydrogen atoms were placed at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The significant residual of electron density on a final Fourier difference map (in solvent molecules) and the comparatively high value of *R*-factors are the result of common disorder of Cl atoms in both CCl_4 solvent molecules.

(7) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem*. **1986**, *58*, 137. Haddon, R. C. *Acc. Chem. Res*. **1988**, *21*, 243. Haddon, R. C. *J. Am. Chem. Soc*. **1990**, *112*, 3385. Haddon, R. C. *Science* **1993**, *261*, 1543.

(8) MM2 calculations were performed using the CS Chem3D Pro (v. 5.0) program package from CambridgeSoft Corp., Cambridge, MA 02140-2317.

(9) Same stabilizing interaction was previously proposed for the observed formation of the stable radical cation of corannulene/C_{60} complex in the gas phase[10a] as well as for the solution complexation studies of C_{60} with sym-pentakis-substituted corannulenes.[10b]

(10) (a) Becker, H.; Javahery, G.; Petrie, S.; Cheng, P.-C.; Schwartz, H.; Scott, L. T.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 11636. (b) Mizyed, S.; Georghiou, P. E.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770.

(11) Failure may be partially blamed on the very limited solubility of buckminsterfullerene in common NMR solvents. In solvents “good” for C_{60} (toluene-d_8, benzene-d_6, tetrachloroethane-d_2, or carbon disulfide), the changes of chemical shifts of the protons in **1** upon saturation with C_{60} are only in the range of 0.01−0.02 ppm (i.e., too subtle to estimate the association constant K_a precisely).