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# Lowering Inversion Barriers of Buckybowls by Benzannelation of the Rim: Synthesis and Crystal and Molecular Structure of 1,2-Dihydrocyclopenta[*b*,*c*]dibenzo[*g*,*m*]corannulene

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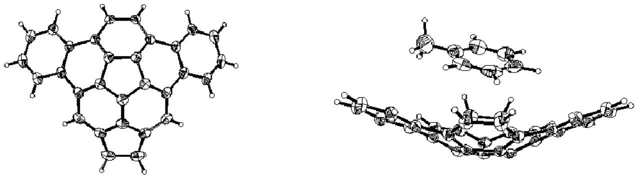
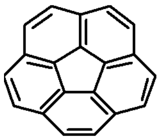
## ABSTRACT

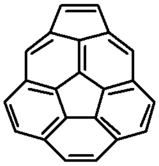


**The title compound (3) has been synthesized by a non-pyrolytic route providing a 36% isolated yield in the final step. X-ray crystal structure determination shows that 3 crystallizes with one solvating molecule of toluene and exhibits slightly lower curvature than the parent cyclopentacorannulene. DFT calculations predict a substantially lower bowl-to-bowl inversion barrier for 3 than for dihydro-cyclopentacorannulene, and this is confirmed by dynamic $^1$H NMR experiments.**

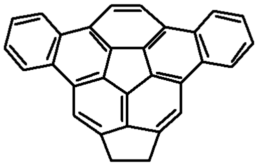
“Buckybowls”, or fullerene fragments, represent a novel class of curved-surface polynuclear aromatic hydrocarbons with carbon networks represented on the surfaces of fullerenes.[1] The synthesis of these novel aromatics presents a serious challenge, however, as a result of the considerable strain involved. Since the early 1990s, flash vacuum pyrolysis, employed originally by the Scott group, has been the major methodology and has led to the successful synthesis of several buckybowls, albeit in moderate to low yields.[1] Only recently have more practical, condensed phase protocols been developed.[2] Although “wet” syntheses of corannulene (**1**, the smallest member of the family) and its derivatives have been reported with yields in excess of 80%, similar protocols applied to the synthesis of more strained buckybowls exhibited a dramatic drop in yields.[2] For example, solution phase syntheses of cyclopentacorannulene (**2**), with only one



**1**



**2**



**3**

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(1) For recent reviews, see: (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (c) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (d) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Anselms, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

(2) (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755. (b) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666−12667. (c) Seiders, T. J.; Baldrige, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439−7440. (d) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800−7803. (e) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813. (f) Reish, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430. (g) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323−6324. (h) Sygula, A.; Marcinow, Z.; Fronczek, F. R.; Guzei, I.; Rabideau, P. W. *Chem. Commun.* **2000**, 2439−2440. (i) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517−525.

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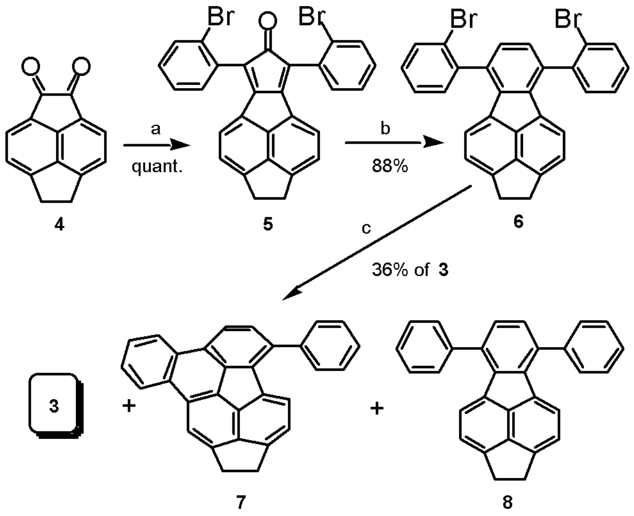
**Scheme 3**[a]



[a] (a) 1,3-Bis(2-bromophenyl)-2-propanone, methanol, NaOH; rt, 12 h. (b) Norbornadiene, $Ac_2O$; 160 °C, 24 h. (c) $Pd(PCy_3)_2Cl_2$, DBU, *N*,*N*-dimethylacetamide; 145 °C, 2 days.

more five-membered ring at the rim of **1**, have been much less successful with reported yields of ca. 20%.[2d,e,i] In the present communication we report a non-pyrolytic synthesis of 1,2-dihydrocyclopenta[*b*,*c*]dibenzo[*g*,*m*]corannulene (**3**) with a modest 36% isolated yield, as well as the results of crystal and molecular structure studies showing that the annulation of two benzene rings on the rim of the parent cyclopentacorannulene causes a reduction in curvature and, consequently, a lowering of the inversion barrier.

As outlined in Scheme 1, this route follows the recently published protocol of Reisch, Bratcher, and Scott for dibenzo[*a*,*g*]corannulene.[2f] It starts with known diketopyracylene **4**,[3] which is condensed under Knoevenagel conditions with 1,3-bis(2-bromophenyl)-2-propanone to give the cyclopentadienone **5** in nearly quantitative yield. Diels–Alder reaction of **5** with norbornadiene produces fluoranthene **6** in 88% isolated yield. Cyclodehydrohalogenation of **6** with $Pd(PCy_3)_2Cl_2$ as a catalyst in the presence of DBU produces a mixture of **3** along with debrominated, single ring closure byproduct **7** and diphenyl benzopyracylene **8** (59:38:3 by $^1$H NMR). The crude material affords 36% of **3** after flash column chromatography (silica gel, cyclohexane/DCM, 10:1).[4]

Several solvent systems were used for growing a crystal of **3** suitable for X-ray diffraction; all but one produced very tiny needles, too small for study. However, high quality crystals could be grown from toluene, and crystal structure determination[5] shows that **3** crystallizes with one molecule of solvent (Figure 1).

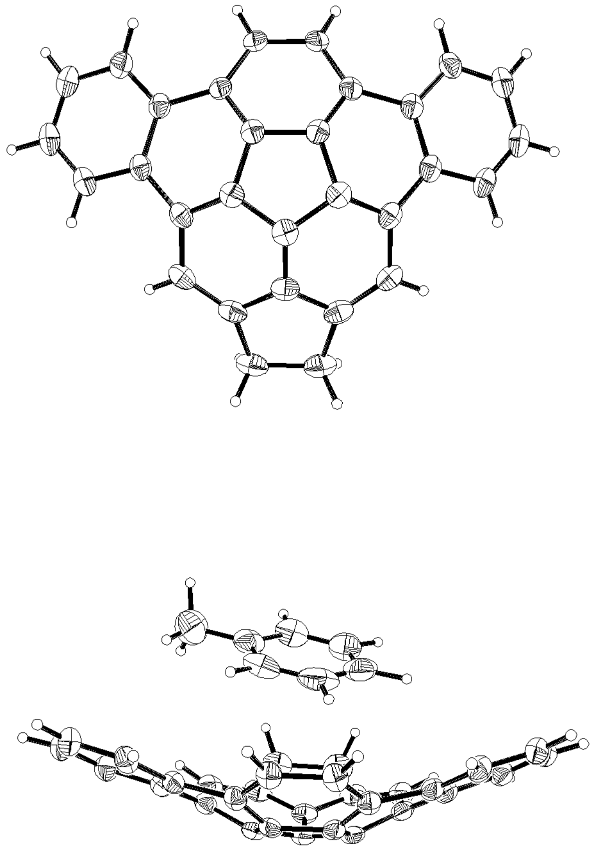


**Figure 1.** ORTEP view of **3** (top) and **3** with the solvating molecule of toluene at 50% probability level (bottom).

The presence of the solvent molecule prevents concave-convex stacking of **3** in the crystal. This latter interesting crystal packing arrangement of buckybowls was observed in **2**[6] as well as in the largest buckybowl to date, $C_{36}H_{10}$.[7] However, it is absent in the crystals of both **1**[8] and tetramethylsemibuckminsterfullerene $C_{34}H_{20}$.[2h]

As expected, **3** exhibits significant curvature. The $\pi$-orbital axis vector (POAV)[9] pyramidalization angles calculated for the carbon atoms in the central five-membered ring are 100.7°, 100.0°, 99.6°, 98.7°, and 98.4°. These numbers are very close to those found earlier for the crystal of cyclopentacorannulene (**2**).[6] Also, the bowl depth of **3**, defined as the average distance of the rim carbon atoms of the

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[3] Trost, B. M. *J. Am. Chem. Soc.* **1969**, *91*, 918–923.

[4] Pale yellow solid, mp 256–258 °C. $^1$H NMR (300 MHz, $CDCl_3$): 8.67–8.58 (m, 4H), 8.23 (s, 2H), 7.76 (s, 2H), 7.74–7.70 (m, 4H), 3.84, 3.09 (m, 4H). $^{13}$C NMR (75.4 MHz, $CDCl_3$): 149.61, 144.15, 138.96, 135.92, 135.26, 134.33, 133.73, 128.18, 127.56, 127.51, 125.17, 125.15, 124.63, 120.35, 32.42. MS (EI, 70 eV) *m*/*z* (rel intensity) 376 (100). HRMS (EI, 70 eV): calcd for $C_{30}H_{16}$ 376.1252, found 376.1258.

[5] Crystal data: $C_{37}H_{24}$, FW = 468.56; orthorhombic, *P*2(1)2(1)2(1); $a = 9.0353(17)$, $b = 9.8916(18)$, $c = 26.543(5)$ Å; $V = 2372.2(8)$ Å$^3$; $Z = 4$; $D_{calc} = 1.312$ g cm$^{-3}$; F(000) = 984; $T = 173$ K; $R = 0.0385$, $Rw = 0.0868$ for 5538 observed data. Intensity data were collected on a Bruker CCD-1000 diffractometer with Mo–K$\alpha$ radiation ($\lambda = 0.71073$ Å). Hydrogen atoms were refined in isotropic approximation. See Supporting Information for crystallographic data in CIF format.

[6] Sygula, A.; Folsom, H. E.; Sygula, R.; Abdourazak, A. H.; Marcinow, Z.; Fronczek, F. R.; Rabideau, P. W. *Chem. Commun.* **1994**, 2571–2572.

[7] Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766–5767.

[8] Hanson, J. C.; Nordman, C. E. *Acta Crystallogr.* **1976**, *B32*, 1147–1153.

[9] 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.

corannulene portion of the molecule from the best plane of the central five-membered ring (1.033 Å) is similar to the one found for **2** (1.05 Å).[6] Unfortunately, the crystal structure of the more closely related 8,9-dihydrocyclopentacoranulene (**9**) (i.e., **2** with an external ethane bridge rather than ethylene) has not yet been determined so we turned to theoretical DFT studies to assess the effect of double benzannelation on corannulene bowl depth and inversion barrier.[10]

The curvature of **3** is well described at the Becke3LYP/3-21G level of theory. The average POAV angle calculated for all sp$^2$ hybridized carbon atoms is 93.4° for the DFT optimized structure as compared to 93.5° for **3** in the crystal. The pyramidalization angles for the carbon atoms in the central five-membered ring (101.0°, 100.1°, 100.1°, 98.8°, and 98.8°) are close to the ones found in the crystal (see above). At the same level of theory, the parent **9** is predicted to exhibit slightly but consistently higher pyramidalization of the analogous carbon atoms (101.4°, 100.3°, 100.3°, 99.4°, and 99.4°), indicating that the corannulene unit is flattened as a result of dibenzannelation. The calculated bowl depth of **9** (1.114 Å) is also slightly larger than that predicted for **3** (1.057 Å). Recently Siegel and co-workers correlated inversion barriers with the bowl depths for several corannulenes and showed that even a small change in the latter may cause a significant change of the barrier.[2i] Our calculations for **3** and **9** predict inversion barriers of 19.3 and 24.1 kcal/mol, respectively, at the Becke3LYP/6-31G**//Becke3LYP/3-21G level with zero point energy correction. Thus, **3** is predicted to have a barrier to inversion that is lower than **9** by almost 5 kcal/mol! Since the experimentally determined inversion barrier for 8,9-dideuteriocyclopentacorannulene is 27.7 kcal/mol,[11] the expected barrier for **3** is ca. 23 kcal/mol.

In contrast to **9**,[12] variable temperature $^1$H NMR spectra of **3** show temperature-dependent changes in the AA′BB′ spectral system over the temperature range 160−184° (Figure 2). While the coalescence temperature could not be reached because of spectrometer limitations, dynamic spectrum simulation[13] allowed an experimental estimation of the inversion barrier, $\Delta G^* = 23.5-23.6$ kcal/mol, in the temperature range 165−184°.

These results are in very close agreement with the theoretical prediction, and they demonstrate that the benzannelation of the corannulene core indeed flattens the bowl and consequently lowers its barrier for inversion.[14]

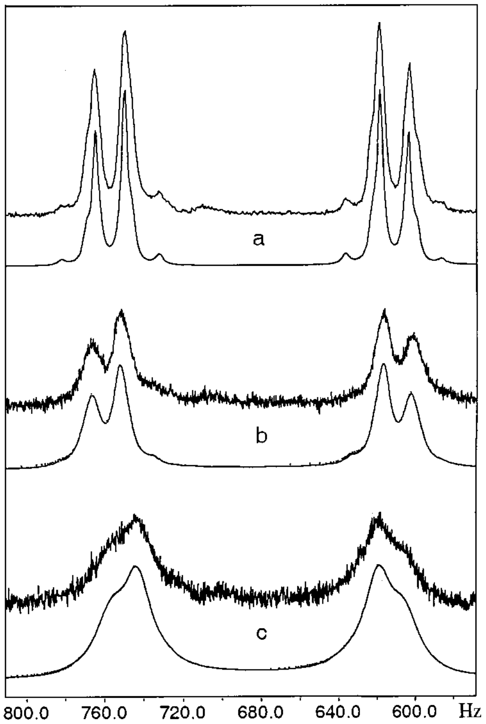

**Figure 2.** AA′BB′ portion of the $^1$H NMR spectrum of **3** in nitrobenzene-$d_5$ at 200 MHz (top traces) with the simulated spectra (lower traces) at (a) room temperature ($k_{inv} = 0$ s$^{-1}$), at (b) 165° ($k_{inv} = 17$ s$^{-1}$), and at (c) 184° ($k_{inv} = 48$ s$^{-1}$).

Although a number of inversion barriers in the range of 9−17 kcal/mol have been determined for flexible corannulene derivatives,[2f] there is a scarcity of such data for more strained corannulene systems. The present determination of the barrier for **3** represents only the second example (after **9**)[11] of a corannulene system with $\Delta G^*$ for the inversion above 20 kcal/mol. As such it contributes to the understanding of the structure/energy relationships of the fascinating class of curved surface polycyclic aromatic hydrocarbons.

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**Supporting Information Available:** Experimental procedures and characterization for compounds **3** and **6**; CIF file for **3**; Gaussian94 archive files for **3** and **9** (minimum energy bowls and planar transition states for inversion). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc*. **1996**, *118*, 339−343.

[12] Abdourazak, A. H.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc*. **1993**, *115*, 3010−3011.

[13] Dynamic NMR simulations were done with the MEXICO method (Bain, A. D.; Duns, G. J. *Can. J. Chem*. **1996**, *74*, 819−824.) implemented into SpinWorks program package (*SpinWorks*, v.1.2; Kirk Marat and the University of Manitoba: Winnipeg, MB, Canada, copyright 2001; available from pauli.chem.umanitoba.ca.)

[14] According to a personal communication from L. T. Scott, the bowl-to-bowl inversion barrier for a dimethylcarbinol derivative of benzocorannulene is ca. 9.0 kcal/mol at −90 °C (McComas, C. C., B.S. Thesis, Boston College, 1996), and the barrier for a dimethylcarbinol derivative of dibenzo-[*a,g*]corannulene is <7.5 kcal/mol at −114 °C (Bratcher, M. S., Ph.D. Dissertation, Boston College, 1996). Both numbers are lower than the inversion barrier of dimethylcarbinol derivative of corannulene (10.2 kcal/mol at −64 °C. Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc*. **1992**, *114*, 1920−1921).