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"Locking" the Bowl-Shaped Geometry of Corannulene: Cyclopentacorannulene

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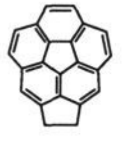
The discovery that buckminsterfullerene, C_{60}, is a stable molecule due to geodesic and electronic properties inherent in the truncated icosahedral cage structure[1] has generated a renewed interest in hydrocarbons with curved surfaces. The carbon framework of corannulene[2,3,4] (**1**), which can be considered to represent the polar cap of buckminsterfullerene, is surprisingly flexible. In spite of its substantial curvature,[5] corannulene undergoes rapid bowl-to-bowl inversion in solution,[6] and this raises the question as to how many additional fused rings on the corannulene structure will be required to "lock" the bowl conformation. Herein we provide the answer that the bowl becomes rigid, at least on the NMR time scale, with only the addition of two carbons in a fused five-membered ring.

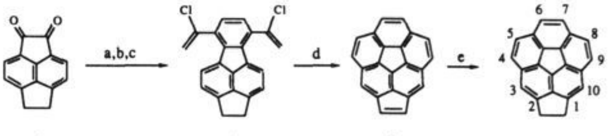
Buckminsterfullerene contains 20 hexagons and 12 pentagons, and the formal progression from **1** to C_{60} requires the formation of five cyclopentyl rings around the periphery of the corannulene structure. We now report the synthesis and NMR study of **2**, the first corannulene elaborated in this manner. The synthesis of **2** was accomplished by the Scott method[7] for the preparation of corannulene itself except that 1,2-diketopyracene (**3**)[8] served as the starting material rather than acenaphthenequinone (Scheme I). Pyrolysis of **4** was accompanied by dehydrogenation of the ethano unit, as well as by partial detachment of the ethane fragment, producing a mixture of **5** and **1** (ca. 7:3). Hydrogenation at 1 atm in the presence of P-2 nickel[9] afforded **2** quantitatively from **5**.

1



2

Scheme I[a]



3 **4** **5** **2**

[a] (a) 2,4,6-Heptanetrione, MeOH, Et_3N, overnight; 40%. (b) Norbornadiene, *n*-BuOH, reflux 2 h; 64%. (c) PCl_5, benzene, reflux 3 h; 50%. (d) Flash pyrolysis at 1000 °C, 1.5 mmHg, N_2; 10–15%. (e) P-2 nickel, H_2 (1 atm), 15 min; quantitative.

Unlike **1** and **5**, any dynamic process in **2** should be directly observable by proton NMR. The ambient-temperature 400-MHz NMR spectrum (DMSO-d_6) of **2** showed two sets of aliphatic hydrogens, centered at 2.98 and 3.75 ppm, characteristic of an AA′BB′ pattern. This is, of course, expected for **2** under conditions of slow exchange since two hydrogens are exo and two are endo. This behavior is in sharp contrast to that of the dimethyl carbinol derivative of **1**,[6] which showed only a single signal for the methyl groups at ambient temperature. Its rapid bowl-to-bowl inversion was demonstrated by the dynamic NMR behavior: the diastereotopic methyls become observable separately below −64 °C with the barrier to inversion determined as $\Delta G^{\ddagger} = 10.2$ kcal/mol.[6] Similarly, values of 8.5 and 7 kcal/mol were obtained for 1,2-dihydro- and 1,2,5,6-tetrahydrocorannulene, respectively.[4]

In contrast, **2** showed no signs of signal coalescence at the upper temperature limit of our observation (135 °C). This places a lower barrier for ring inversion at 18.8 kcal/mol. However, we also examined the dynamics of **2** by the spin polarization transfer method[10] at 127 °C. That is, a selective 180° pulse was applied to the AA′ (or BB′) half of the spectrum to reverse its polarization, followed by an nonselective 90° pulse after increasingly longer delay times (from 1 μs to 15.0 s). A delay domain between 0.0 and 8.0 s was used—at longer delay times other time-dependent processes interfere with the measurement—and data processing[10] showed only very limited spin polarization transfer. This allowed an estimation of the lower limit for inversion of ca. 26 kcal/mol at 127 °C (or $k_{\text{inv}} = 0.05\ \text{s}^{-1}$), indicating that the barrier for inversion of **2** is at least twice as large as that for corannulene **1**!

2 **2′**

The "locking" effect of the additional five-membered ring on **1** is also predicted by theory. Semiempirical AM1 calculations[11] predict the difference in energy between bowl-shaped **2** and its planar conformer to be ca. 39 kcal/mol in favor of the former. Calculations of the vibrational frequencies at the same level of theory showed the bowl conformer of **2** with C_s symmetry to be a true minimum on the potential energy surface since all vibrations are positive. On the other hand, the planar conformer showed one imaginary frequency (166*i*), and analysis of the associated eigenvector indicated the planar structure to be the transition

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(7) (a) Scott, L. T., personal communication. The new three-step corannulene synthesis after which our synthesis of **2** was patterned was reported in preliminary form by Scott, L. T.; Cheng, P.-C.; Bratcher, M. S. *Seventh International Symposium on Novel Aromatic Compounds*, Victoria Canada, July, 1992, Abstract 64. See also: Cheng, P.-C. M.S. Thesis, University of Nevada, Reno, NV, December, 1992. (b) All new compounds gave satisfactory spectral characterization.[7c] **2**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 2.98, 3.79 (4 H), 7.34 (s, 2 H), 7.70 (s, 4 H), 7.72 (s, 2 H); ^{13}C NMR (100.614 MHz, $CDCl_3$) δ 31.83, 121.74, 126.32, 126.96, 127.68 (quaternary carbons unobservable due to low concentration). MS *m/z* 276 (100), 275 (21), 274 (34), 138 (27), 137 (32), 136 (18); high-resolution mass spectrum calcd for $C_{22}H_{12}$ 276.0939, found 276.0937. **5**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 6.49 (s, 2 H), 7.31 (s, 2 H), 7.38 (s, 2 H), 7.44 (d, 2 H), 7.50 (d, 2 H); ^{13}C NMR (100.614 MHz, $CDCl_3$) δ 124.17, 126.46, 127.26, 128.28, 128.42, 129.73, 137.51, 137.89, 138.16; MS *m/z* 274 (100), 272 (18), 137 (20), 136 (18). (c) It is extremely difficult to rid these curved hydrocarbons of all solvent; most NMR spectra included traces of solvent that could be replaced by other solvents.

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state for inversion. Analogous calculations performed for **1** provide a barrier of ca. 17 kcal/mol.[4] Since the experimental estimation of the barrier for **1** is 11–12 kcal/mol,[12] it is apparent that AM1 overestimates the barrier to some extent. However, assuming a similar level of error for **2**, it is clear that the introduction of the ethane junction between C1 and C10 in corannulene drastically decreases the flexibility of the carbon network toward inversion.

AM1 predicts structural effects from the ethane bridge in **2** as well; that part of the corannulene system in proximity to the ethane bridge is more curved than the opposite side. This is demonstrated by the distances of the rim atoms from the plane defined by the five hub (central) carbon atoms. These distances are calculated to be 1.30, 1.29, 1.08, 1.01, and 0.92 Å for C2–C6, respectively, as compared to the analogous distance of 0.94 Å for corannulene. The ethane bridge carbon atoms are located 2.10 Å from the plane.

In summary, the addition of one fused, five-membered ring onto the corannulene structure is enough to effectively lock the bowl geometry. Future studies include the synthesis of suitable, optically active derivatives to test the presence of ring inversion by the decay of optical activity with time and temperature. We are also undertaking an electrochemical study of **5**.

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