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Cyclopentacorannulene: π-Facial Stereoselective Deuterogenation and Determination of the Bowl-to-Bowl Inversion Barrier for a Constrained Buckybowl

Andrzej Sygula, Atteye H. Abdourazak, and Peter W. Rabideau*

Contribution from the Department of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803

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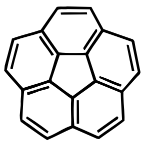
Abstract: Attachment of an ethane or ethylene unit to the rim of corannulene produced relatively rigid bowls of dihydrocyclopenta- and cyclopentacorannulene, respectively. In contrast to the parent corannulenes, their inversion barriers are too high to be determined by the NMR coalescence methods. Due to the significant curvature of cyclopentacorannulene, deuterogenation is π-facial specific; both heterogeneous and homogeneous catalysis lead exclusively to *exo*-dideuteriocyclopentacorannulene **2a**. Equilibration of the endo- and exo-isotopomers allowed the determination of $\Delta G^{\ddagger}$ at 27.61−27.67 kcal/mol over the temperature range 52.1−99.3 °C and the estimation of $\Delta H^{\ddagger}$ (27.3 ± 0.7 kcal/mol) and $\Delta S^{\ddagger}$ (−1.1 ± 0.2 eu) for the bowl-to-bowl inversion. The inversion barrier calculated at the HF/6-31G*//3-21G level (25.9 kcal/mol) compares well with the experimental result.

The discovery of buckminsterfullerene (C_{60}) and related carbon cages[1] has led to a general interest in the properties and behavior of curved carbon systems. An examination of the buckminsterfullerene surface leads to the recognition of many familiar carbon frameworks that, if removed from C_{60} and the dangling bonds occupied with hydrogen, would produce common hydrocarbons. The lower molecular weight hydrocarbons constructed in this way are planar, however, and it is not until C_{20} is reached that curvature remains as a feature of the structure. Beyond C_{20}, the bowl-shaped geometries are expected to be quite rigid, and we have referred to these fullerene-related, curved surface aromatic hydrocarbons as "buckybowls".[2]

The carbon framework of corannulene[3−6] (**1**) represents the polar cap of buckminsterfullerene. Corannulene is a fascinating molecule, initially prepared by Barth and Lawton,[3] that has now become more accessible due to some elegant synthetic work.[4,5] In spite of its substantial curvature,[6] corannulene is surprisingly flexible, undergoing rapid bowl-to-bowl inversion in solution[7] as evidenced by the dynamic NMR behavior of several derivatives. Hence, due to the bowl-shaped geometry, the attachment of suitable substituents such as dimethylcarbinol, isopropyl, and benzyl (**1**-R), leads to the observation of two sets of diastereotopic proton signals at low temperatures (−31 to −64 °C). Warming produces coalescence, and inversion barriers in the range of $\Delta G^{\ddagger} = 10-11$ kcal/mol have been determined.



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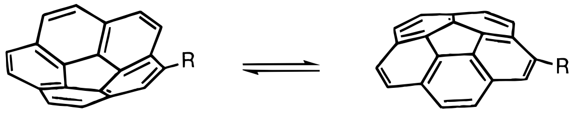

1-R **1'-R**

R = $C(CH_3)_2OH$, $\Delta G^{\ddagger}$ = 10.2 kcal/mol at -64 °C (ref. 7)
R = $CH(CH_3)_2$, $\Delta G^{\ddagger}$ = 11.3 kcal/mol at -31 °C (ref. 8)
R = CH_2Ph, $\Delta G^{\ddagger}$ = 11.2 kcal/mol at -39 °C (ref. 8)

Hence the relatively low barrier to bowl-to-bowl inversion in corannulene raises the question as to how large a section from the buckminsterfullerene surface is necessary to produce a hydrocarbon with a constrained or rigid-bowl structure. The work described herein demonstrates that rigid structures will be encountered quickly with only minor expansion of the corannulene carbon framework.

Results and Discussion

In an effort to explore the flexibility of the bowl-shaped geometry beyond corannulene, we undertook the synthesis of dihydrocyclopentacorannulene (**2**).[9] We followed the same

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1995.

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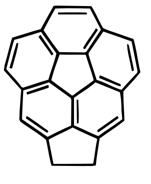

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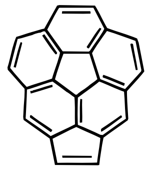
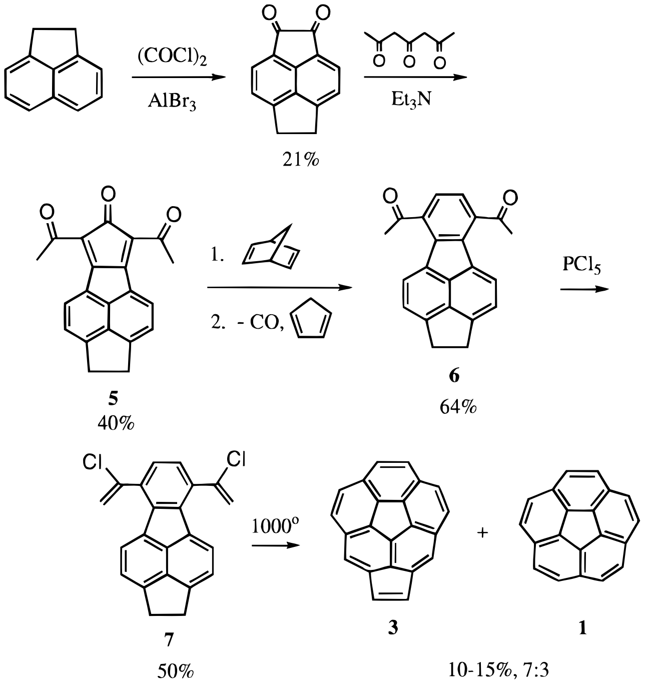


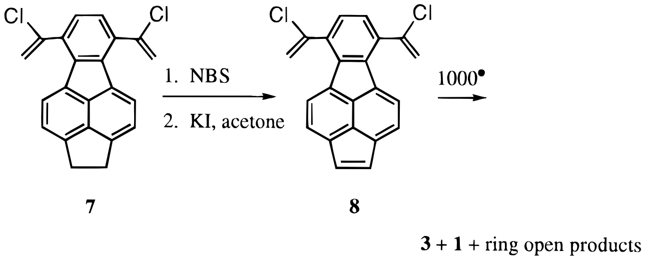
3

procedure as the Scott group,[4] but with an additional five-membered ring incorporated into the starting material (Scheme 1). This procedure was successful except that hydrogen was lost during the final pyrolysis step, producing unsaturated **3** rather than **2**, and some corannulene was also produced as a result of loss of the ethane bridge. The separation of **3** from corannulene (**1**) proved to be quite difficult, and so in an attempt to minimize the amount of **1** formed, the external five-membered ring was unsaturated in the hope that an ethene unit would be more stable to the pyrolysis conditions (Scheme 2). In fact, this afforded even poorer results since corannulene was still produced, and there was also an increase in ring open products as well as some polymerization of the unsaturated precursor in the pyrolysis apparatus before it reached the hot zone. Thus, the pathway described in Scheme 1 remains the method of choice for the synthesis of **3** at the moment. The hydrogenation of **3** to produce **2** proceeded quantatively at 1 atm in the presence of P-2 nickel.

Scheme 1



Scheme 2



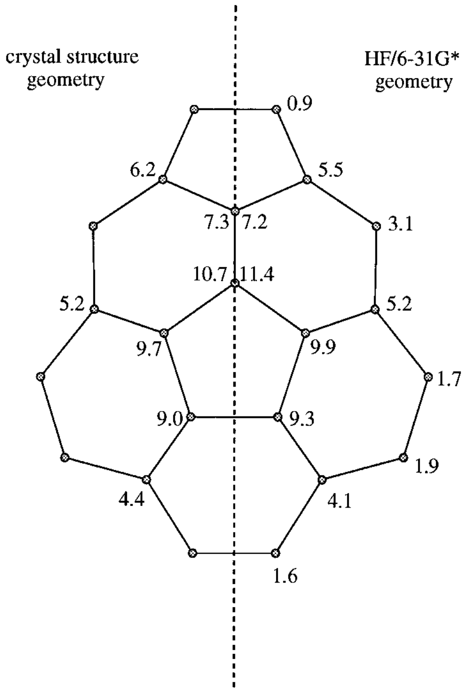


Figure 1. POAV1 pyramidalization angles for carbon atoms in **3** based on the ab initio calculated geometry (right) and crystal structure geometry (left). CH carbon angles for the latter are omitted since hydrogen atoms were placed in calculated positions in the crystal structure analysis.[10a]

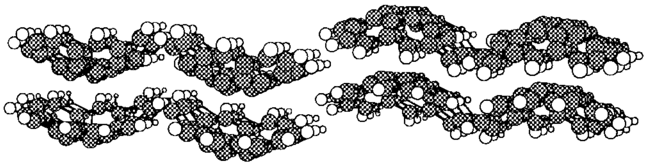


Figure 2. Crystal packing in **3** as viewed approximately along the crystallographic *a*-axis.

The incorporation of an additional five-membered ring onto the rim of corannulene produces a significant increase in curvature as demonstrated by x-ray crystal structure determination[10a] and predicted by ab initio calculations.[10b] Figure 1 shows the POAV1[11] pyramidalization angles for the carbon atoms in **3** calculated from both the crystal structure and ab initio HF/6-31G* geometries. These angles are consistently larger than those for **1**—indicating the carbon atoms to be more pyramidalized—since the POAV1 angles for corannulene are 8.4, 3.7, and 1.5° for the core, quat rim, and CH rim carbon atoms, respectively. Also, the pyramidalization of the carbon atom in **3** in the region of maximum curvature is quite comparable with the curvature of buckminsterfullerene (11.6°).[11] The very good agreement of the POAV1 angles in **3** calculated from both the experimental and theoretical geometries supports the validity of the theoretical model used.

Crystal structure determination for **3** also revealed an interesting long-range packing pattern in the solid state.[10a] The bowl-shaped molecules are stacked in a concave—convex fashion (Figure 2) in which there are 24 intermolecular C···C distances shorter than 3.8 Å for every two molecules in the crystal. While such stacking is absent in the crystal of corannulene,[6] and only a few crystal structure determinations of curved surface

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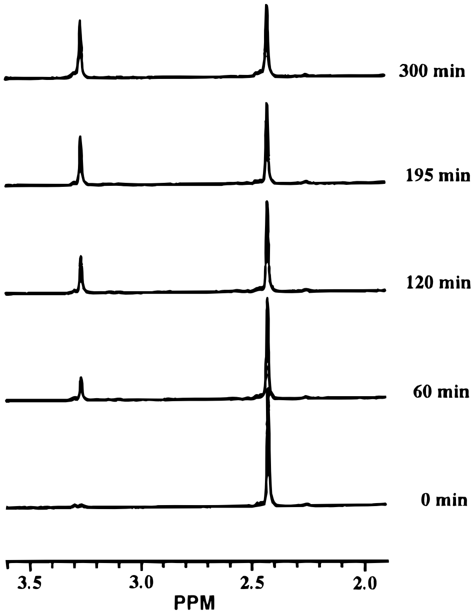


Figure 3. Equilibration of dideuteriocyclopentacorannulene isotopomers **2a** and **2b** at 78.9 °C in benzene-d_6 as monitored by ^{1}H NMR of the alicyclic region.

hydrocarbons have been done, it is not clear whether concave–convex stacking in **3** is an exception rather than common behavior for such systems. This type of stacking, however, is expected to maximize attractive van der Waals interactions.

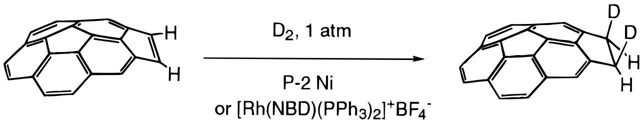
Because of its symmetry, bowl-to-bowl inversion in **3** could not be observed by NMR without appropriate substitution. In contrast, **2** has two sets of aliphatic hydrogens that would exchange with bowl-to-bowl inversion. However, the two sets of signals representing the distinguishable exo (convex) and endo (concave) hydrogens in **2** were observed up to 135 °C without change, and a lower limit for bowl-to-bowl inversion was estimated at ca. 26 kcal/mol at 127 °C by the spin polarization transfer method.[9] Thus the inversion in **2** is too slow for determination of the barrier by NMR coalescence methods.

While a suitably placed substituent would render **2** chiral, and the bowl-to-bowl barrier—a racemization process—could be determined by the thermal decay of optical activity for one of the resolved enantiomers, the relatively small amounts of **2** available made this process rather unattractive. Hence we hoped that the considerable curvature of **3** might lead to π-facial stereoselectivity in hydrogenation since, if so, deuterogenation of **3** would provide an uneven distribution of endo and exo deuterogenated products. In principle, this would allow determination of the inversion barrier by following the equilibration of the two isotopomers by ^{1}H NMR.

Heterogeneous deuterogenation of **3** with P-2 Ni as a catalyst led to the formation of a single dideuterio product as shown by the presence of a broadened singlet at 2.41 ppm (in benzene-d_6) from two benzylic protons together with a little of the partially hydrogenated product (Figure 3, bottom trace).[12] No signal was detected in the vicinity of 3.3 ppm that would indicate the presence of a second isomer. We assigned the signal at 2.41 ppm to endo (concave) protons since they have greater proximity to the center of the nearby benzene rings and are expected to be shifted upfield relative to the convex hydrogens. This assignment is also supported by NOE results.[13] Irradiation of the aromatic hydrogens proximal to the benzylic hydrogens (H_{ar} at 7.0 ppm) resulted in ca. twice the enhancement of the high-field aliphatic signal, and so the signal at 2.41 ppm remaining after deuterogenation can be assigned as concave or endo since, as calculated at the HF/3-21G level of theory, the H_{ar}–H_{endo} distance is 2.92 Å, as compared to 3.31 Å for H_{ar}–$H_{exo.}$ Thus, heterogeneous deuterogenation is π-facial specific, occurring exclusively on the convex side of **3**. Moreover, exo π-facial specificity was also observed under homogeneous conditions using the Willkinson type [Rh(norbornadiene)-$(PPh_3)_2]^+BF_4^-$ catalyst.[14] Again, only endo benzylic hydrogens at 2.41 ppm could be detected for deuterogenation of **3** with this catalyst.

Table 1. Rate Constants (k), Half-Life Times ($\tau_{1/2}$), and Free Enthalpies of Activation ($\Delta G^‡$) Determined for the Equilibration **2a**–**2b**

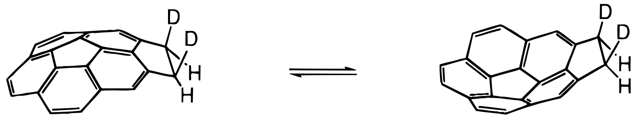
t (°C)	10^6k (s^{-1})	$\tau_{1/2}$ (min)	$\Delta G^‡$ (kcal/mol)
99.3	453 ± 6	12.8	27.67 ± 0.02
94.0	267 ± 5	21.6	27.65 ± 0.02
78.9	50.4 ± 0.8	114.6	27.65 ± 0.02
52.1	1.91 ± 0.02	3024.2	27.61 ± 0.02



3 **2a**

Clearly the significant curvature of **3**, coupled with the absence of rapid bowl-to-bowl inversion, facilitates exofacial deuterogenation. Apparently convex-face complexation of **3** with the metal surface in the heterogeneous catalysis is strongly preferred over the concave arrangement, probably due to better overlap of the π-orbitals of the external five-membered ring with the orbitals of the metal in the complex. Similarly, convex complexation of the homogeneous catalyst with the external five-membered ring in **3** is favored over concave. This was an interesting case since it allowed for the possibility of the catalyst to be complexed within the bowl. Evidently, there is not enough space inside the bowl to accommodate this bulky rhodium complex.

While *exo*-dideuteriocyclopentacorannulene (**2a**) showed no change on standing at room temperature for several days, heating the sample caused the signal at 2.41 ppm to diminish with concurrent growth of a signal at 3.26 ppm (Figure 3), indicating that bowl-to-bowl inversion does indeed take place in this system. We determined rate constants for the equilibration in the temperature range from 52.1 to 99.3 °C, and the results are presented in Table 1.



2a **2b**

The introduction of a single, additional five-membered ring to the rim of corannulene increases the barrier for inversion

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[12] The partially hydrogenated byproduct (ca. 5% by ^{1}H NMR) is most probably formed by the addition of HD, a contaminant in the D_2 gas used. ^{1}H NMR showed low-intensity multiplets centered at 2.97 and 3.78 ppm (in $CDCl_3$), and a DEPT-135 experiment (^{13}C NMR) showed two minor CH_2 carbon atoms at ca. 31.8 ppm in addition to the strong CHD triplet at 31.43 ppm.

[13] An NOE experiment was conducted on the equilibriated mixture of exo and endo dideuterio isomers.

[14] Deuterogenation was achieved according to the procedure developed by Osborn.[15] The cationic rhodium catalyst was kindly provided by Barry Misquitta and Professor George Stanley, Louisiana State University.

more than 2-fold! It is also evident from Table 1 that $\Delta G^{\ddagger}$ shows little temperature dependency since $\Delta\Delta G^{\ddagger}$ throughout the entire temperature range is 0.06 kcal/mol, only 3 times higher than the standard deviation. Apparently $\Delta S^{\ddagger}$ is small; values of $\Delta S^{\ddagger} = -1.1 \pm 0.2$ eu[16] and $\Delta H^{\ddagger} = 27.3 \pm 0.7$ kcal/mol are estimated from the data of Table 1.

At the ab initio level of theory, bowl-shaped **2** is a minimum-energy conformation with all positive vibrational frequencies and $E_{\mathrm{HF}} = -840.074\,07$ au (HF/6-31G*//3-21G). The planar conformer represents the transition state (TS) for the bowl inversion process since it exhibits one imaginary frequency (140*i*), and the eigenvector associated with this frequency distorts the planar structure toward the bowl-shaped minimum-energy conformation. At the HF/6-31G*//3-21G level, the energy of the planar TS is 25.9 kcal/mol higher than the energy of the bowl-shaped conformer. Thus, the computational results compare favorably with the experimental determination of the inversion barrier in **2**. Furthermore, a previously reported calculation for **3** at the same level of theory yielded a value of 28.8 kcal/mol,[10b] suggesting that the barrier to bowl-to-bowl inversion for **3** is even higher than **2**.

In conclusion, introduction of the additional five-membered ring to the corannulene carbon framework increased significantly both the curvature and rigidity of the system. Deuterogenation of **3** was found to be π-facial specific due to the high degree of curvature present in the hydrocarbon surface; both heterogeneous and homogeneous catalysis provided the exo-dideuterated product **2a**. Equilibration of benzene solutions of **2a** allowed the determination of $\Delta G^{\ddagger}$ for the bowl-to-bowl inversion (27.61−27.67 kcal/mol over the temperature range 52.1−99.3 °C) and an estimation of $\Delta H^{\ddagger}$ (27.3 ± 0.7 kcal/mol) and $\Delta S^{\ddagger}$ (−1.1 ± 0.2 eu).

Experimental Section

Chemicals were purchased from Aldrich Chemicals. Acenaphthene was recrystallized from ethanol, and *N*-bromosuccinimide from water. 2,4,6-Heptanetrione[17] and 1,2-diketopyracene (**4**)[18] were prepared by literature methods. Melting points are reported uncorrected. HRMS were performed at the LSU Mass Spec Facility. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, N.Y. Ab initio calculations were performed using the Gaussan92/DFT package.[19a] Geometry optimization and vibrational frequency calculations were done at the HF/3-21G level.[19b] Single-point calculations were performed with 3-21G geometries and the 6-31G* basis set[19c] (HF/6-31G*//3-21G level).

Preparation of 5,7-Diacetyl-1,2-dihydro-6*H*-dicyclopent[*a*,*fg*]acenaphthylen-6-one (5). A solution of 5.8 mL (41.7 mmol) of triethylamine in 20 mL of methanol was added dropwise to a stirred solution of 5.9 g (28.36 mmol) of 1,2-diketopyracene (**4**) and 6.8 g (47.53 mmol) 2,4,6-heptanetrione in 50 mL of methanol. The reaction mixture was stirred overnight, and filtered and the dark-silver solid washed with methanol. After drying, 3.56 g (40% yield) of crude **5** was obtained which was subsequently used without further purification. Crystallization from DMF gave a dark solid with mp 235−240 °C dec. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 8.6 (d, $J = 7.4$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 2H), 3.58 (s, 4H), 2.64 (s, 6H). HRMS: calcd 314.0942, found 314.0933.

Preparation of 1,1′-(1,2-dihydrocyclopenta[*cd*]fluoranthene-5,8-diyl)bisethanone (6). A solution of 8.6 g (28.34 mmol) of crude **5** and 5.2 mL (48.18 mmol) of bicyclo[2.2.1]hepta-2,5-diene in 150 mL of butanol was refluxed overnight. After cooling, the brown solid was separated and chromatographed on silica gel with hexane/ethyl acetate (10:1 then 5:1) or DCM to provide 5.6 g (64%) of yellowish solid. Recrystallization from ethanol−toluene (ca. 4:1) gave yellow needles, mp 249−251 °C dec. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 8.49 (d, $J =$ 7.5 Hz, 2H), 7.7 (s, 2H), 7.48 (d, $J = 7.5$ Hz, 2H), 3.53 (s, 4H), 2.8 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 29.69, 32.27, 120.91, 126.03, 128.53, 129.43, 132.04, 136.31, 137.44, 138.86, 148.17, 201.45. MS: *m/z* 312 (100, M^+), 297 (100), 269 (24), 254 (19), 226 (42). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16; O, 10.25. Found: C, 84.31; H, 5.16. HRMS: calcd 312.1150, found 312.1152.

Preparation of 5,8-Bis(1-chloroethenyl)-1,2-dihydrocyclopenta-[*cd*]fluoranthene (7). A mixture of 1.08 g (3.46 mmol) of **7** and 2.52 g (12.11 mmol) of PCl_5 was refluxed for 3 h in 40 mL of benzene. After cooling, the mixture was poured onto ice, the organic layer was washed with water and sodium carbonate solution and dried over magnesium sulfate and the solvent was evaporated. After purification by column chromatography on silica gel with cyclohexane as eluant, 0.6 g of yellow solid was obtained (50% yield). Recrystallization from methanol provided yellow needles. Mp 144−146 °C. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 8.3 (d, 2H, $J = 7$ Hz), 7.46 (d, 2H, $J = 7$ Hz), 7.37 (s, 2H), 5.92 (d, 2H, $J = 1.2$ Hz), 5.8 (d, 2H, $J = 1.2$ Hz), 3.51 (s, 4H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 32.27, 117.02, 120.88, 126.18, 127.07, 130.14, 131.32, 135.34, 136.39, 137.31, 138.30, 147.01. MS: *m/z* 350 (44), 348 (69, M^+), 313 (42), 276 (100), 263 (15), 250 (57), 138 (69). Anal. Calcd for $C_{22}H_{14}Cl_2$: C, 75.66; H, 4.04; Cl, 20.30. Found: C, 75.21; H, 4.06; Cl, 20.11. HRMS: calcd 348.0473, found 348.0458.

Pyrolysis of 7. A 985 mg sample of **7** was pyrolyzed in batches of 80 mg each at 1000 °C under a slow bleed of nitrogen at 1.5 mmHg. After each run (3 h), the pyrolysis product was washed out of the trap and the elbow with DCM and combined. The solvent was evaporated and the crude material flash chromatographed on silica gel with hexane as eluant to give a mixture of **3** and **1** (7:3, by GC/MS). Yields varied from 10 to 15%. The mixture was chromatographed again (silica gel, cyclohexane) and then recrystallized three times from ethanol and once from ether to provide pure **3** as orange platelets. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 6.49 (s, 2H), 7.31 (s, 2H), 7.38 (s, 2H), 7.44 (d, 2H, $J = 9$ Hz), 7.50 (d, 2H, $J = 9$ Hz). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 124.17, 126.46, 127.26, 128.28, 128.42, 129.73, 137.51, 137.89, 138.16. MS: *m/z* (relative intensity) 274 (100, M^+), 272 (18), 137 (20), 136 (18). Final structure proof was accomplished by X-ray crystallography.[10a]

Preparation of 8,9-dihydrodibenzo[*ghi*,*mno*]cyclopenta[*cd*]-fluoranthene (2). This procedure follows the methodology of Brown and Ahuja.[20] Nickel acetate tetrahydrate (0.07 g, 0.29 mmol) was dissolved in 3 mL of 95% ethanol and placed in a 50 mL three-neck, round-bottomed flask equipped with a magnetic stirrer. The system was purged and filled with hydrogen three times. Then 0.3 mL of a solution prepared by mixing 0.25 g of sodium borohydride, 6 mL of 95% ethanol, and 0.31 mL of 2 N aqueous sodium hydroxide was added, followed by the addition of 3 mg of **3** dissolved in 1 mL of DCM. After 15 min, the solution was filtered through a Celite pad and evaporated. The yield was quantitative by GC, and the residue was chromatographed on silica gel with hexane as eluant to afford a yellow solid. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 2.98, 3.39 (4H), 7.34 (s, 2H), 7.70 (s, 4H), 7.72 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 31.83, 121.74, 126.32, 126.96, 127.68, 130.31, 137.19, 137.53, 138.71, 139.41, 145.04, 147.51. MS: *m/z* 276 (100, M^+), 275 (21), 274 (34), 138 (27), 137 (32), 136 (18). HRMS: calcd 276.0939, found 276.0937.

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(16) $\Delta S^{\ddagger}$ for the inversion of dihydrocyclopentacorannulene **2** is expected to be ca. −2.5 eu for symmetry reasons. The bowl-shaped **2** is of C_s symmetry with symmetry number 1, while the planar TS is of C_{2v} symmetry (symmetry number 2). Thus, there is an additional $-R \ln 2$ (or −1.38 eu) symmetry contribution to $\Delta S^{\ddagger}$. In the case of **2a** and **2b**, both the minimum-energy conformers and the planar TS have the same C_s symmetry.

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Preparation of 5,8-Bis(1-chloroethenyl)cyclopenta[*cd*]fluoranthene (8). A mixture of 428 mg (1.23 mmol) of **7** and 490 mg (2.75 mmol) of NBS in 20 mL of benzene was refluxed for 6 h. The solvent was evaporated, the residue was taken in DCM and washed with water, and the organic layer was dried and evaporated. Chromatography on silica gel with DCM/hexane (10:1) gave 300 mg (57%) of the dibromide of **7**. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 8.34 (d, 2H, $J = 7.5$ Hz), 7.66 (d, 2H, $J = 7.5$ Hz), 7.36 (s, 2H), 6.03 (bs, 2H), 5.89 (bs, 2H), 5.75 (bs, 2H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 55.90, 117.77, 124.16, 127.21, 128.57, 132.21, 133.86, 136.32, 137.75, 141.03.

The above dibromide (224 mg, 0.53 mmol) was refluxed overnight with 1.1 g (7 mmol) of potassium iodide in 30 mL of acetone. After cooling, the mixture was filtered and the solid residue washed with acetone. The filtrate was evaporated and the red solid was chromatographed on silica gel with hexane affording 89 mg (49%) of a reddish solid that decomposes over 220 °C. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 5.65 (d, 2H, $J = 1.33$ Hz), 5.76 (d, 2H, $J = 1.33$ Hz), 6.52 (s, 2H), 7.11 (d, 2H, $J = 7.25$ Hz), 7.51 (d, 2H, $J = 7.25$ Hz). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 29.92, 117.29, 125.42, 125.88, 129.08, 132.21, 136.37, 137.58, 141.53. MS: *m/z* 348 (29), 346 (44, M^+), 311 (23), 276 (56), 275 (51), 274 (60), 250 (16), 155 (18), 137 (100), 124 (32). HRMS: calcd 346.0316, found 346.0305.

Heterogeneous Deuterogenation of Dibenzo[*ghi*,*mno*]cyclopenta[*cd*]fluoranthene (3). This was achieved by the method described above except that the hydrogen gas was replaced with deuterium (99.6% purity) and sodium borohydride was replaced with sodium borodeuterate: yield quantitative. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.95 (s, 2H), 7.34 (s, 2H), 7.70 (s, 4H), 7.72 (s, 2H). ^{1}H NMR (400.13 MHz, C_6D_6): δ 2.41 (s, 2 H), 7.00 (s, 2 H), 7.48 (s, 4H), 7.51 (s, 2H). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 31.43, 121.80, 126.32, 126.94, 127.68, 130.28, 137.18, 137.53, 138.69, 139.39, 145.05, 147.51. MS: m/z 278 (100), 277 (67), 276 (37), 275 (24), 139 (45), 138 (54), 137 (53), 136 (18), 125 (20).

Homogeneous deuterogenation of Dibenzo[*ghi*,*mno*]cyclopenta[*cd*]fluoranthene (3). $[Rh(NBD)(PPh_3)_2]^+BF_4^-$ (60 mg, 0.074 mmol) in 10 mL of dry THF in a 25 mL round-bottomed flask was flushed with deuterium gas three times. The orange color of the solution faded in a few seconds. The solution was stirred vigorously at room temperature and at constant pressure (1 atm) for 10 min. Next, 20 mg (0.073 mmol) of **3** in 2 mL of THF was injected into the solution, and the reaction mixture was stirred for 1 h. The solvent was removed and the black residue chromatographed on silica gel with hexane to give 15 mg of the dideuterated product which showed a ^{1}H NMR spectrum identical to that of **2a** obtained by the heterogeneous catalysis experiment.

Kinetics of the Equilibration of the Isotopomers 2a and 2b. The NMR tubes were charged with ca. 4 mg portions of **2a** dissolved in benzene-d_6, then degassed, and sealed under vacuum. The samples were kept in a thermostat for the appropriate period of time at the desired temperature (±0.1 °C), then removed, and quickly cooled in ice−water. The progress of equilibration was monitored by ^{1}H NMR at ambient temperature with a relaxation delay of 20 s. The benzylic region of each spectrum was carefully phase- and baseline-corrected before integration. The rate constants (k's) for the reversible equilibration were determined by regression analysis using the equation $2kt = \ln[a/(a - 2x)]$ where a is the initial concentration of **2a** and x is the concentration of **2b** at time t. Correlation coefficients of the linear regressions were 0.998 or higher. The standard deviations (SD's) of the slopes of the resulting regression lines were used as the estimates for the SD's of the rate constants. $\Delta G^{\ddagger}$'s were calculated from the Eyring equation, and SD's were estimated by the error propagation method.

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