J. Org. Chem. **1999,** *64,* 3655−3662

Inversion Barrier of Corannulene. A Benchmark for Bowl-to-Bowl Inversions in Fullerene Fragments

P. Ulrich Biedermann, Sergey Pogodin, and Israel Agranat*

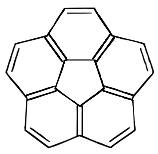
Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received January 4, 1999

In a systematic ab initio study, the Hartree−Fock, B3LYP density functional, and MP2 methods are employed to calculate the bowl-to-bowl inversion barrier of corannulene (**1**). Basis sets ranging from a minimal basis (STO-3G) to a double polarized valence triple-ζ basis (6-311G(2d,2p)) were used. In comparison with experimental data, it was found that inclusion of dynamic electron correlation (e.g., B3LYP) and a 6-311G** basis set (or other basis sets with similar complexity) are essential for quantitatively correct results. At B3LYP/6-311G**, $\Delta G^{\ddagger}_{298}$ = 44.9 kJ/mol. Thermal corrections to Gibbs energy of activation were of minor importance in the relevant range of temperatures. Inversion barriers ($\Delta E^{\ddagger}_{\mathrm{Tot}}$) of the bowl-shaped fullerene fragments $C_{26}H_{12}$ **4** and $C_{30}H_{12}$ **5** and the chiral $C_{30}H_{12}$ **6** are predicted to be 28.0, 199.4, and 277.3 kJ/mol, respectively, at B3LYP/6-311G**. Predicted enthalpies of formations and strain energies are also discussed.

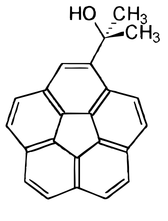
Introduction

The advent of the fullerene era has rekindled interest in corannulene (**1**), the parent bowl-shaped polycyclic aromatic hydrocarbon (PAH).[1−4] Corannulene (**1**), a $C_{20}H_{10}$ nonalternant PAH first synthesized in 1966,[5−8] represents the polar "cap" (as well as the "bottom") of both buckminsterfullerene (C_{60}) and C_{70}-fullerene and the minimum fragment of a fullerene that retains the characteristic curvature. It is composed of a central pentagonal ring or core with a periphery of five annulated benzenoid aromatic rings.[2] One of the fascinating aspects of curved fullerene fragments, including **1**, is their participation in bowl-to-bowl inversion processes.[1,2] The bowl-to-bowl inversion of corannulene (**1**) has previously been studied by DNMR spectroscopy and by theoretical methods, including relatively low-level ab initio methods (vide infra). We report here the results of a systematic computational study of the inversion barrier of **1** and three bowl-shaped fullerene fragments (buckybowls[1]), a $C_{26}H_{12}$ PAH and two $C_{30}H_{12}$ semibuckminsterfullerenes. We note that ab initio calculations using the B3LYP variant of the density functional theory (DFT), in combination with the triple-split valence basis set with polarization functions (6-311G**), is the method of choice for calculating bowl-to-bowl inversion barriers of bowl-shaped fullerene fragments.

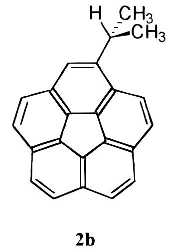


1

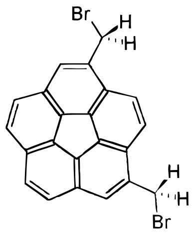
Three experimental values for the energy barrier of bowl-to-bowl inversion of corannulenes with prochiral substituents have been reported: $\Delta G_c^{\ddagger} = 42.7 \pm 0.8$ kJ/mol (209 K, acetone-d_6) in (1-hydroxy-1-methylethyl)corannulene (**2a**);[9] $\Delta G_c^{\ddagger}$ = 47.3 kJ/mol (242 K, THF-d_8) in isopropylcorannulene (**2b**);[10] and $\Delta G_c^{\ddagger} = 43.9 \pm 0.8$ kJ/mol (215 K, THF-d_8) in 1,8-bis(bromomethyl)corannulene (**2c**).[11] It has been argued that the substituent and the solvent may affect the inversion barrier.[10]



2a



2b



2c

On the basis of the AM1 calculated barriers of isopropylcorannulene (68.6 kJ/mol) and of **1** (70.7 kJ/mol) and the experimental barrier of the former (47.3 kJ/mol), Sygula and Rabideau claimed that the estimated experimental barrier of **1** is ca. 50 kJ/mol.[10] The previously reported semiempirical and low-level ab initio inversion barriers ($\Delta\Delta H_f^{\ddagger}$ and $\Delta E^{\ddagger}_{\mathrm{Tot}}$, respectively) of **1** have been derived from the difference of the semiempirical enthalpies of formation ($\Delta H_f°$) and from the difference of the ab initio total energies (E_{Tot}) of the bowl shaped C_{5v}-**1** and

---

[1] Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242.

[2] Mehta, G.; Rao, H. S. P. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1997; Vol. 6, pp 139−187.

[3] Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370.

[4] Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 3, pp 1−36.

[5] Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380−381.

[6] Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745.

[7] Shaltout, R. M.; Sygula, R.; Sygula, A.; Fronczek, F. R.; Stanley, G. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 835−836.

[8] Schulman, J. M.; Disch, R. L. *J. Comput. Chem.* **1998**, *19*, 189−194.

[9] Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921.

[10] Sygula, A.; Rabideau, P. W. *J. Mol. Struct. (THEOCHEM)* **1995**, *333*, 215−226.

[11] Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755.

10.1021/jo9900174 CCC: $18.00

Table 1. Reported Calculated Barriers for Bowl-to-Bowl Inversion of Corannulene (1)

method	barrier (kJ/mol)
semiempirical $\Delta\Delta H_f^{\ddagger}$	
MNDO	34.7[12]
AM1	70.7[10]
PM3	59.0[13,a]
Hartree−Fock $\Delta E^{\ddagger}_{\text{Tot}}$	
HF/STO-3G	37.2[14,15]
HF/3-21G	43.9[10,15,16]
HF/6-31G*	36.8[10,15,16]
MP2 (single points)[b] $\Delta E^{\ddagger}_{\text{Tot}}$	
MP2/3-21G//HF/3-21G	66.5[10,15]
MP2/6-31G//HF/6-31G	59.8[16]
density functional theory $\Delta E^{\ddagger}_{\text{Tot}}$	
LDF	47.7[17]
B3LYP/cc-pVDZ	38.2[18]

[a] 65.7 kJ/mol this work. [b] The previously reported MP2 energies are single point calculations at the Hartree−Fock optimized geometry.

the planar D_{5h}-**1**. These calculated barriers are given in Table 1. Sygula and Rabideau have argued that the MP2/3-21G correction represents a reasonable approach and that their "best theoretical estimate" of the inversion barrier of **1** is 59.4 kJ/mol (36.8 $\Delta E^{\ddagger}_{(\text{HF/6-31G*})}$ + 22.6 $\{\Delta E^{\ddagger}_{(\text{MP2/3-21G//HF/3-21G})} - \Delta E^{\ddagger}_{(\text{HF/3-21G})}\}$).[10] These authors were aware that the small basis set used for MP2 calculations may not provide enough configurational space to account for all correlation effects.[10] They argued that improvement of the basis set quality at the MP2 level increases the correlation correction to the barrier, whereas the higher order treatment up to the MP4 level decreases it slightly. Thus, the two effects cancel each other to some extent.[16] It is evident from a comparison of Table 1 values with experiment that the HF/6-31G* level underestimates the inversion barrier of **1**, whereas the low-level MP2 overestimates this barrier. The wide range of the reported theoretical barriers may be attributed to (1) the usage of only small to medium size basis sets, possibly introducing artifacts due to basis set truncation errors, and (2) the inadequate treatment of electron correlation effects by the single point MP2 approach. Relying on fortuitous cancellation of sizable errors is clearly unsatisfactory for a process as fundamental as the bowl-to-bowl inversion. Under these circumstances, it seemed worthwhile to carry out a systematic ab initio study of the bowl-shaped C_{5v}-**1** and planar D_{5h}-**1** at higher levels than have previously been reported. Ab initio calculations of the intermolecular interaction potential of a corannulene dimer in a parallel (D_{5h}) orientation using basis sets up to 6-311G(2d) at the MP2 level have recently been reported.[19,20] An ab initio study (HF, DFT, MP2) of the structural and physical properties of corannulene-based $C_{10n}H_{10}$ fullerene fragments (n = 2−5) showed a distinct point between bowl and tube-like character.[21]

Methods

The program Mopac93[22] was used for the semiempirical MNDO,[23] AM1[24] and PM3[25] calculations, and the program Gaussian94[26] was used for Hartree−Fock, density functional and MP2 ab initio calculations. Becke's three parameter hybrid density functional,[27] B3LYP, with the nonlocal correlation functional of Lee, Yang, and Parr[28−30] was used. Basis sets STO-3G, 3-21G, 6-31G*, 6-311G**, and 6-311G(2d,2p) were employed for geometry optimization. All structures were fully optimized using symmetry constraints as indicated. Frequencies were calculated to verify minima, transition states, and higher order saddle points for the Hartree−Fock and B3LYP optimized conformations of corannulene (except for the 6-311G(2d,2p) basis set) and for the HF/3-21G and B3LYP/STO-3G optimized conformations of the larger systems. Unscaled frequencies were used to calculate zero point corrections (ZPE), thermal corrections to Gibbs energy (G_{corr}) at 298.15 K, and the temperature dependence of $\Delta G^{\ddagger}$.

Results and Discussion

Corannulene (1). Table 2 gives the calculated total energies (E_{Tot}), zero point energies (ZPE), and thermal corrections to Gibbs energy at 298 K (G_{corr}) of C_{5v}-**1** and D_{5h}-**1** and their differences ($\Delta E^{\ddagger}_{\text{Tot}}$, $\Delta E^{\ddagger}_{\text{ZPE}} = \Delta E^{\ddagger}_{\text{Tot}} + \Delta ZPE^{\ddagger}$, and $\Delta G^{\ddagger}_{298} = \Delta E^{\ddagger}_{\text{Tot}} + \Delta G^{\ddagger}_{\text{Corr}}$) at the various ab initio levels. The bowl conformation, C_{5v}-**1**, is a bona fide minimum (all frequencies real), and D_{5h}-**1** is a bona fide transition state for the bowl-to-bowl inversion (one imaginary frequency, symmetry species A_2''). Figure 1 describes the calculated bowl-to-bowl inversion of corannulene at B3LYP/6-311G**. Figure 2 compares the experimental $\Delta G_c^{\ddagger}$, the semiempirical $\Delta\Delta H_f^{\ddagger}$, and ab initio $\Delta E^{\ddagger}_{\text{Tot}}$. Figure 3 gives the experimental $\Delta G_c^{\ddagger}$ (DNMR), including estimated error bars and the calculated $\Delta G^{\ddagger}$(T) as a function of temperature in the range 0−400 K.

The following picture of the inversion barrier of **1** emerges from the results given in Table 2 and Figures 2 and 3:

(1) The AM1 and PM3 semiempirical calculations considerably overestimate the inversion barrier.

(2) Basis sets with triple-split valence shell including polarization functions should be used to avoid artifacts due to an unbalanced representation of the electronic wave functions in the planar and bowl-shaped structures. Note that the series STO-3G, 3-21G, 6-31G*, 6-311G**

---

(12) Sastry, G. N.; Jemmis, E. D.; Mehta, G.; Shah, S. R. *J. Chem. Soc. Perkin Trans. 2* **1993**, 1867−1871.

(13) Hagen, S.; Christoph, H.; Zimmermann, G. *Tetrahedron* **1995**, *51*, 6961−6970.

(14) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675−5680.

(15) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1533−1536.

(16) Sygula, A.; Rabideau, P. W. *J. Chem. Soc., Chem. Commun.* **1994**, 1497−1499.

(17) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921−1923.

(18) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *262*, 97−104.

(19) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *J. Phys. Chem. A* **1998**, *102*, 740−743.

(20) No details were provided on the monomer.

(21) Baldridge, K. K.; Siegel, J. S. *Theor. Chem. Acc.* **1997**, *97*, 67−71.

(22) Stewart, J. J. P. MOPAC 93; Fujitsu Limited: Tokyo, Japan; all rights reserved.

(23) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907.

(24) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(25) Stewart, J. J. P. *J. Comput.Chem.* **1989**, *10*, 209−220.

(26) 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.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(29) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206.

(30) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

Table 2. Ab Initio Calculated Total Energies, Thermal Corrections to Gibbs Energy and Bowl-to-Bowl Inversion Barriers of Corannulene (1)

	C_{5v}-**1** bowl			D_{5h}-**1** planar			barrier		
method	E_{Tot} (hartree)	ZPE (hartree)	G_{corr} (hartree)	E_{Tot} (hartree)	ZPE (hartree)	G_{corr} (hartree)	$\Delta E^{\ddagger}_{\mathrm{Tot}}$ (kJ/mol)	$\Delta E^{\ddagger}_{\mathrm{ZPE}}$ (kJ/mol)	$\Delta G^{\ddagger}_{298}$ (kJ/mol)
HF/STO-3G	−753.903 53	0.268 73	0.234 50	−753.889 41	0.268 48	0.235 58	37.1	36.4	39.9
HF/3-21G	−758.908 18	0.249 56	0.215 05	−758.891 43	0.250 10	0.216 98	44.0	45.4	49.0
HF/6-31G*	−763.189 29	0.249 36	0.214 79	−763.175 19	0.248 94	0.215 69	37.0	35.9	39.4
HF/6-311G**	−763.331 62	0.247 34	0.212 75	−763.317 05	0.247 14	0.213 87	38.2	37.7	41.2
B3LYP/STO-3G	−758.751 90	0.244 58	0.209 57	−758.736 04	0.244 09	0.210 40	41.6	40.4	43.8
B3LYP/3-21G	−763.907 05	0.232 13	0.196 97	−763.885 71	0.232 03	0.198 18	56.0	55.8	59.2
B3LYP/6-31G*	−768.149 37	0.232 34	0.197 16	−768.135 64	0.232 13	0.198 33	36.1	35.5	39.1
B3LYP/6-311G**	−768.315 28	0.231 13	0.195 98	−768.298 97	0.230 65	0.196 79	42.8	41.6	44.9
B3LYP/6-311G(2d,2p)	−768.343 22			−768.326 96			42.7		
MP2/STO-3G	−755.095 56			−755.080 73			38.9		
MP2/3-21G	−760.655 03			−760.629 33			67.5		
MP2/6-31G*	−765.728 40			−765.709 85			48.7		
MP2/6-311G**	−766.036 71			−766.017 14			51.4		

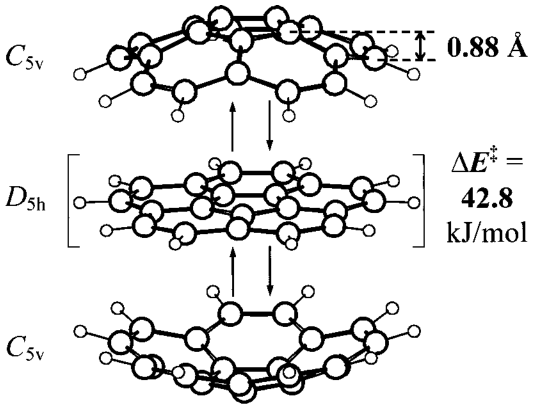


Figure 1. Bowl-to-bowl inversion of corannulene (**1**) at B3LYP/6-311G**.

shows an asymptotic behavior at HF and MP2 levels except for 3-21G, which is an outlier for all ab initio methods.

(3) The Hartree−Fock calculations, up to the HF/6-311G** level ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 38.2$ kJ/mol; $\Delta G^{\ddagger}_{298} = 41.2$ kJ/mol) underestimate the barrier.

(4) The low-level HF/3-21G calculations give a value for the bowl inversion barrier ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 43.9$ kJ/mol;[10,15,16] $\Delta G^{\ddagger}_{298} = 49.0$ kJ/mol) in very good agreement with the experiment. This fortuitous result may be due to a cancellation of errors. Note also that the $\Delta G^{\ddagger}_{298}$ barrier is 5.1 kJ/mol higher than the $\Delta E^{\ddagger}_{\mathrm{Tot}}$ value.

(5) The MP2 calculations give higher barriers as compared to the Hartree−Fock calculations. At MP2/6-311G** ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 51.4$ kJ/mol), the barrier may be somewhat overestimated. An upgrade from MP2/6-31G* to MP2/6-311G** increased the barrier by ca. 2.7 kJ/mol.

(6) The DFT (B3LYP) calculations require the use of the 6-311G** basis set ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 42.8$ kJ/mol; $\Delta G^{\ddagger}_{298} = 44.9$ kJ/mol). B3LYP/6-31G* ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 36.1$ kJ/mol; $\Delta G^{\ddagger}_{298} = 39.1$ kJ/mol) still underestimates the barrier by more than 5.8 kJ/mol. Additional polarization functions, i.e., an upgrade to B3LYP/6-311G(2d,2p) ($\Delta E^{\ddagger}_{\mathrm{Tot}} = 42.7$ kJ/mol), are not necessary.

(7) Dynamic electron correlation is essential. DFT (B3LYP) gives better results than MP2, even at 6-311G**.

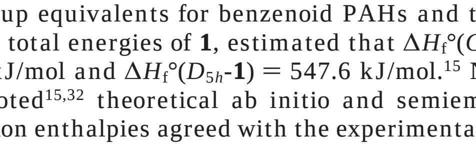
(8) Inclusion of ZPE reduces the bowl-to-bowl inversion barrier. $\Delta G^{\ddagger}$ is increasing with temperature. The thermal corrections to Gibbs energy cancel at ca. 250 K, close to the coalescence point of the DNMR experiments. However, thermal corrections may become significant at higher temperatures.

The bowl-shaped geometry of **1** may be determined quantitatively from the depth of the bowl, as measured by the distance between the plane defined by the five central (core) carbon atoms and the plane defined by the 10 peripheral (rim) carbon atoms. The X-ray crystal structure analysis of **1** confirmed the bowl-shaped conformation of the molecule, with a bowl depth of 0.87 Å.[31]

Figure 4 gives the experimental and calculated bowl depths of corannulene. The calculated bowl depth at B3LYP/6-311G** is 0.89 Å, and at HF/3-21G and B3LYP/STO-3G the bowl depth is 0.88 Å.

Enthalpy of Formation. Kiyobayashi et al. have recently determined experimentally the enthalpy of formation of corannulene (**1**), $\Delta H_f°_{(g)} = 463.7$ kJ/mol, using microbomb combustion calorimetry.[32] This value was derived from the experimental enthalpy of combustion, $\Delta H_f°_{(c)} = 342.3 \pm 5.6$ kJ/mol, and an estimated sublimation enthalpy, $\Delta H°_{(\mathrm{subl})} = 121.4$ kJ/mol. Disch and Schulman, using group equivalents for benzenoid PAHs and the HF/6-31G* total energies of **1**, estimated that $\Delta H_f°(C_{5v}\text{-}\mathbf{1}) = 510.8$ kJ/mol and $\Delta H_f°(D_{5h}\text{-}\mathbf{1}) = 547.6$ kJ/mol.[15] None of the quoted[15,32] theoretical ab initio and semiempirical formation enthalpies agreed with the experimental value. This failure may be attributed to the relatively low level of the calculations and/or to the limited training set of PAHs that included only one nonplanar PAH[33] and/or to the errors in the estimation of the sublimation enthalpy. Using four parameters for the CH group and three different types of carbon atoms in PAHs (derived for the experimental enthalpies of formation of 11 benzenoid PAHs[34]), we estimate $\Delta H_f°(C_{5v}\text{-}\mathbf{1}) = 501.5$ and 491.5 kJ/mol at the B3LYP/6-31G* and MP2/6-31G*//HF/6-31G* levels, respectively. The latter estimated enthalpy of formation of **1** overestimates the experimental value by ca. 5%.

Homodesmic Reaction. Both corannulene (**1**) and coronene (**3**) belong to the homologous series $C_{2n}H_n$. Corannulene is [5]circumannulene, and coronene is [6]-circumannulene. This relationship leads to the following homodesmic reaction:[35−38]



1 **3**

Per one molecule of corannulene → 5/6 coronene: $\Delta\Delta H_f°$(experimental) = 223.4 kJ/mol (463.7 kJ/mol[32] → 5/6 × 288.4 kJ/mol[35−37]), $\Delta\Delta E_{\mathrm{Tot}}$(B3LYP/6-311G**) = 0.095 69 au = 251.2 kJ/mol (−768.315 28 au → 5/6 × −922.093 16 au[38]),

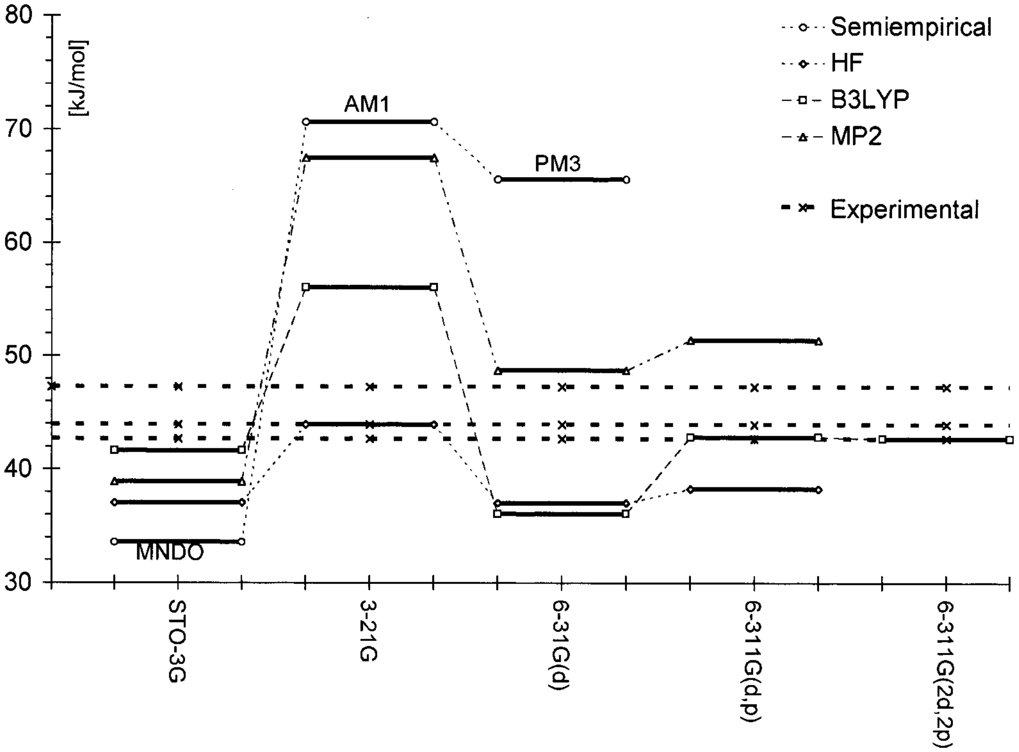


Figure 2. Experimental $\Delta G_c^{\ddagger}$, semiempirical $\Delta\Delta H_f^{\ddagger}$, and ab initio $\Delta E^{\ddagger}_{Tot}$ for the bowl-to-bowl inversion of corannulene (**1**).

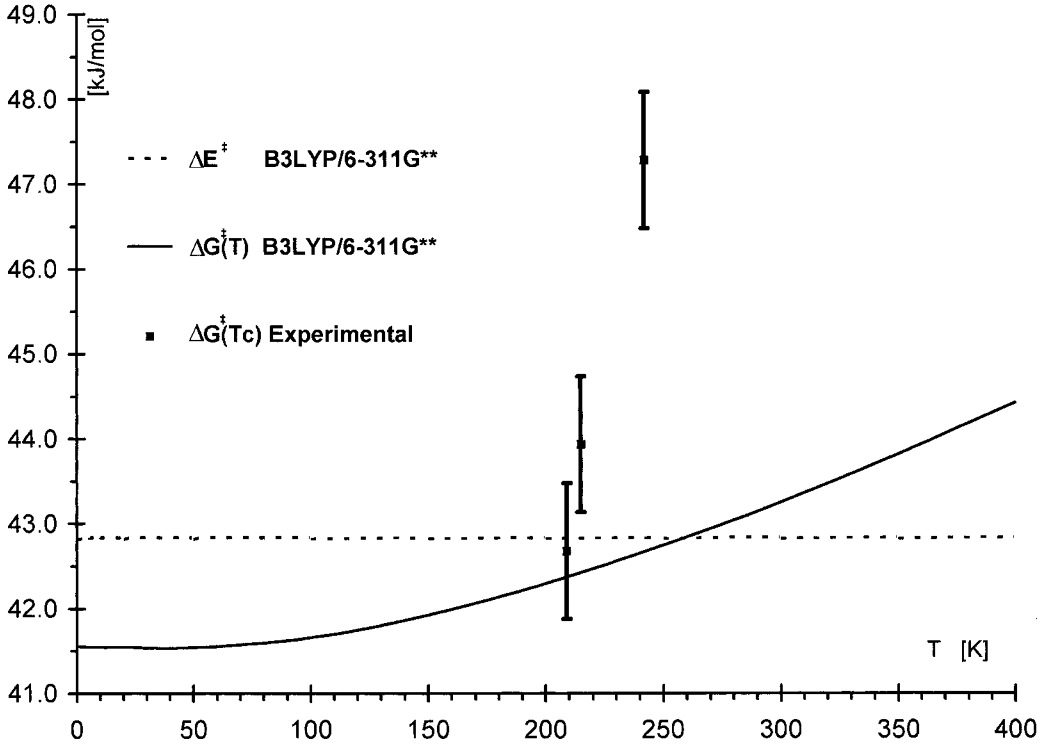


Figure 3. Bowl-to-bowl inversion barrier of corannulene (**1**) $\Delta G^{\ddagger}$ as a function of the temperature at B3LYP/6-311G** and experimental $\Delta G_c^{\ddagger}$.

and $\Delta\Delta E_{Tot}$(B3LYP/6-311G**) − $\Delta\Delta H_f°$(experimental) = 27.8 kJ/mol.

Both the experimental $\Delta\Delta H_f°$ and the calculated ΔE of $C_{20}H_{10}$ indicate the strain and reduced aromaticity inherent in corannulene (**1**) as compared with the planar benzenoid PAH coronene (**3**). The calculated B3LYP/6-311G** strain of corannulene is overestimated by 27.8 kJ/mol as compared to the experimental value. However, the reliability of the experimental gas-phase enthalpies of formation of coronene and corannulene should be born in mind.

---

(31) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1147−1153. The experimental bowl depth of **1**, 0.87 Å, is the average of values taken from the X-ray structures of **1**.

(32) Kiyobayashi, T.; Nagano, Y.; Sakiyama, M.; Yamamoto, K.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 3270−3271.

(33) Peck, R. C.; Schulman, J. M.; Disch, R. L. *J. Phys. Chem.* **1990**, *94*, 6637−6641.

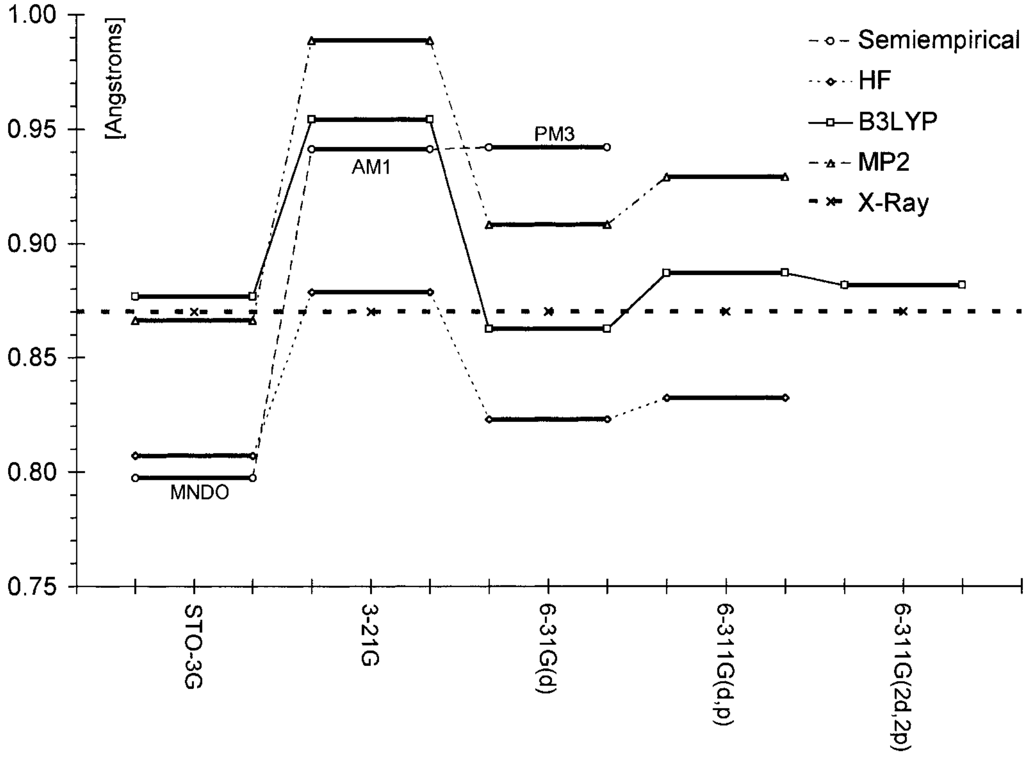
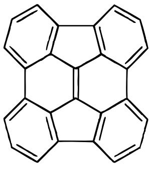


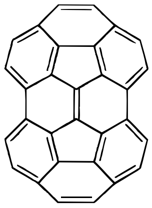
Figure 4. Experimental, semiempirical, and ab initio bowl depths of corannulene (**1**).

The good fit between the experimental and calculated B3LYP $\Delta G^{\ddagger}$ bowl-to-bowl inversion barriers of corannulene (**1**) prompted a study of the inversion barriers of higher buckybowls.

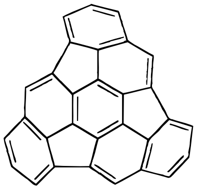
Bowl-Shaped Fullerene Fragments $C_{26}H_{12}$ and $C_{30}H_{12}$. The choice of B3LYP/6-311G** as a suitable Hamiltonian/basis set level for calculating the inversion barrier of corannulene prompted the use of this ab initio level for the calculations of larger bowl-shaped fullerene fragments, diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**4**), diacenaphtho[3,2,1,8-*cdefg*;3′,2′,1′,8′-*lmnop*]chrysene (**5**), and benz[5,6-*as*]indaceno[3,2,1,8,7-*mnopqr*]indeno-[4,3,2,1-*cdef*]chrysene (**6**). The syntheses of buckybowls **4** to **6** have recently been reviewed.[3]



4



5



6

$C_{26}H_{12}$ PAH 4. The octacyclic PAH **4**, which can be identified on the C_{60} surface, has been synthesized by flash vacuum pyrolysis (FVP) dehydrocyclization of bifluorenylidene[39] at temperatures above 700 °C[39,40] by a 2-fold thermal (>1000 °C) elimination of CO from 7,14-dioxo-7,14-dihydro-phenanthro[1,10,9,8-*opqra*]perylene[40] and by FVP of (*E*)-1,1′-dibromo-bifluorenylidene at 1050 °C.[41] Very recently, Bronstein and Scott have shown that the central double bond of **4** undergoes a nucleophilic attack, suggesting that "the reactivity of fullerenes, driven largely by strain associated with curving an aromatic network, can be extended to curved PAHs".[42] Previous PM3 calculations of **4** indicated a bowl-shaped C_{2v}-**4** minimum and a planar D_{2h}-**4** transition state with a bowl-to-bowl inversion barrier of 59.0 kJ/mol.[13,43] The ab initio calculations of the bowl-shaped C_{2v}-**4** and the planar D_{2h}-**4** were done using HF/3-21G and the B3LYP Hamiltonian with the STO-3G, 6-31G*, and 6-311G** basis sets.[44] The ab initio energies are given in Table 3, and the barriers are given in Table 4. Frequencies were calculated at the HF/3-21G and B3LYP/STO-3G levels. The C_{2v} conformation proved to be the minimum, and the D_{2h} conformation turned out to be the transition state for the bowl-to-bowl inversion in **4**. Figure 5 describes the calculated bowl-to-bowl inversion of **4** at B3LYP/6-311G**. The calculated barriers ($\Delta E^{\ddagger}_{\mathrm{Tot}} = E(C_{2v}\text{-}\mathbf{4}) - E(D_{2h}\text{-}\mathbf{4})$) for this process are 29.1 (HF/3-21G), 30.7 (B3LYP/STO-3G), 21.9 (B3LYP/6-31G*), and 28.0 (B3LYP/6-311G**) kJ/mol. These barriers are substantially smaller than the PM3 barrier (59.1 kJ/mol). It is remarkable that the calculated B3LYP barrier at the 6-311G** level is

---

[34] Herndon, W. C.; Biedermann, P. U.; Agranat, I. *J. Org. Chem.* **1998**, *63*, 7445−7448.

[35] $\Delta H_f°_{(\mathrm{coronene})} = 288.4$ kJ/mol uses $\Delta H_f°_{(\mathrm{solid})} = 152.5$ kJ/mol[36] and $\Delta H°_{(\mathrm{subl})} = 135.9$ kJ/mol,[37] cf. ref 34.

[36] Kiyobayashi, T. Doctoral Thesis. Microcalorimetry Research Center, Faculty of Science, Osaka University, Japan, 1995.

[37] Murray, J. J.; Pottie, R. F.; Pupp, C. *Can. J. Chem.* **1974**, *52*, 557−563.

[38] Schulman, J. M.; Disch, R. L. *J. Phys. Chem. A* **1997**, *101*, 9176−9179.

[39] Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Tetrahedron Lett.* **1994**, *35*, 7013−7014.

[40] Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209−217.

[41] Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300.

[42] Bronstein, H. E.; Scott, L. T. quoted in Baum, R. *Chem. Eng. News* **1997**, *75*(48), 28.

[43] Biedermann, P. U.; Luh, T.-Y.; Weng, D. T.-C.; Kuo, C.-H.; Stezowski, J. J.; Agranat, I. *Polycyclic Aromat. Compd.* **1996**, *8*, 167−175.

[44] The B3LYP/6-31G* energy of **4** has been reported: Pogodin, S.; Biedermann, P. U.; Agranat, I. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 6, pp 1110−1116.

Table 3. Semiempirical Enthalpies of Formation and Ab Initio Total Energies of the Conformations of 4, 5, and 6

		AM1 $\Delta H_f°$ (kJ/mol)	PM3 $\Delta H_f°$ (kJ/mol)	HF/3-21G E_{Tot} (hartree)	B3LYP/STO-3G E_{Tot} (hartree)	B3LYP/6-31G* E_{Tot} (hartree)	B3LYP/6-311G** E_{Tot} (hartree)
4 $C_{26}H_{12}$							
C_{2v} bowl	GM[a]	879.609	771.696	−986.005 13	−985.793 88	−997.999 37	−998.210 59
D_{2h} planar	TS	946.606	830.746	−985.994 05	−985.782 19	−997.991 01	−998.199 93
5 $C_{30}H_{12}$							
C_{2v} bowl	GM	1137.961	993.761	−1136.600 40	−1136.332 86	−1150.403 79	−1150.644 06
C_{2h}	LM	1366.756	1203.640	−1136.516 09	−1136.253 23	−1150.330 56	−1150.570 21
C_s	TS	1391.587	1223.903	−1136.513 98	−1136.251 18	−1150.329 26	−1150.568 10
D_{2h} planar	SP2	1591.084	1405.156	−1136.468 09	−1136.207 83	−1150.291 39	−1150.526 45
6 $C_{30}H_{12}$							
C_3 bowl	GM	1220.308	1065.507	−1136.573 15	−1136.308 12	−1150.381 31	−1150.622 07
C_1	TS	1633.744	1435.236				
C_{3h} planar	TS	1639.292[b]	1439.164[b]	−1136.459 60	−1136.194 91	−1150.280 29	−1150.516 46

[a] GM, global minimum; LM, local minimum; TS, transition state; SP2, second-order saddle point. [b] Second-order saddle point.

Table 4. Semiempirical and Ab Initio Calculated Barriers for Bowl-to-Bowl Inversion and Relative Energies of Local Minima or Higher Order Saddle Points of 4, 5, and 6

		AM1 $\Delta\Delta H_f°$ (kJ/mol)	PM3 $\Delta\Delta H_f°$ (kJ/mol)	HF/3-21G ΔE_{Tot} (kJ/mol)	B3LYP/STO-3G ΔE_{Tot} (kJ/mol)	B3LYP/6-31G* ΔE_{Tot} (kJ/mol)	B3LYP/6-311G** ΔE_{Tot} (kJ/mol)
4 $C_{26}H_{12}$							
D_{2h} planar	*a*	67.0	59.1	29.1	30.7	21.9	28.0
5 $C_{30}H_{12}$							
C_{2h}	*b*	228.8	209.9	221.4	209.1	192.3	193.9
C_s	*a*	253.6	230.1	226.9	214.5	195.7	199.4
D_{2h} planar	*c*	453.1	411.4	347.4	328.3	295.1	308.8
6 $C_{30}H_{12}$							
C_1	*a*	413.4	369.7				
C_{3h} planar	*a*	419.0[c]	373.7[c]	298.1	297.2	265.2	277.3

[a] Barrier. [b] Relative energy of local minimum. [c] Relative energy of second-order saddle point.

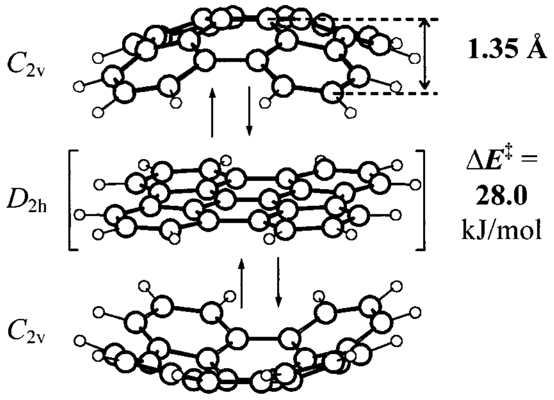


Figure 5. Bowl-to-bowl inversion of **4** at B3LYP/6-311G**.

higher by 6.1 kJ/mol, as compared with the respective barrier at the 6-31G* level. Moreover, the inversion barrier of **4** is significantly lower than the inversion barrier of **1** ($\Delta E^{‡}_{Tot}(\mathbf{4})/\Delta E^{‡}_{Tot}(\mathbf{1}) = 66\%$). It should be noted that the corannulene motif is not maintained in **4**; each of the two five-membered rings of **4** has one carbon−carbon bond which is not annulated by a benzene ring. Thus, **4** may be expected to be much more flexible than **1**.

$C_{30}H_{12}$ PAH 5. The decacyclic $C_{30}H_{12}$ semibuckminsterfullerene **5** is a buckybowl whose carbon framework is represented on the buckminsterfullerene C_{60} surface.[45] However, **5** does not correspond to a symmetrical half of buckminsterfullerene, since “removal” of its carbon framework from the C_{60} surface leaves behind a different C_{30} unit that includes two exocyclic carbons.[46] PAH **5** has been synthesized by four routes: (a) from 1,2,5,6-tetraoxopyracylene by an extension of the Scott benzannulation gas-phase FVP synthesis of **1**;[45] (b) from cyclopenta[*def*]-phenanthrene via FVP (at 1050 °C) of a 3,3′-substituted bi-4*H*-cyclopenta[*def*]phenanthren-4-ylidene;[47] (c) from a dibromodibenzopicene by FVP (at 1150 °C);[48] and (d) from 1,4,5,6,7,10,11,12-octamethylindeno[1,2,3-*cd*]fluoranthene, via a nonpyrolitic route involving a reductive coupling.[49] PAH **5** may be viewed as a double corannulene. Previous PM3 calculations of **5** indicated a bowl-shaped *syn*-C_{2v}-**5** global minimum, an *anti*-double-bowl-shaped C_{2h}-**5** as a local minimum, and an *anti*-double-bowl-shaped C_s-**5** as a transition state for the bowl-to-bowl inversion.[13,43] The planar D_{2h} conformation of **5** was found to be a second-order saddle point at the PM3 level.[13,43] Bowl-to-bowl inversion of C_{2v}-**5** proceeds in two steps via C_{2h}-**5** as an intermediate.[13,43,45] The PM3 C_{2v}-**5** → C_{2h}-**5** barrier was 230.1 kJ/mol.[43] The PM3 C_{2h}-**5** → C_{2v}-**5** barrier was 20.1 kJ/mol.[43] The corresponding AM1 barrier was 24.7 kJ/mol.[45] The PM3 relative energy $\Delta H_f°(C_{2h}\text{-}\mathbf{5}) - \Delta H_f°(C_{2v}\text{-}\mathbf{5}) = 210.0$ kJ/mol.[13,43] Previous ab initio calculations at HF/6-31G*//HF/3-21G gave $E_{Tot}(C_{2h}\text{-}\mathbf{5}) - E_{Tot}(C_{2v}\text{-}\mathbf{5}) = 213.4$ kJ/mol.[45] Adding the AM1 barrier (24.7 kJ/mol) to the above ab initio ΔE_{Tot} value of 213.4 kJ/mol led to an estimation of the barrier of 239 kJ/mol for the C_{2v}-**5** → C_{2h}-**5** inversion.[45] Previous attempts to identify the above transition state by ab initio methods have been unsuccessful.[45] The ab initio energies of the above stationary points of **5** are given in Table 3, and the barriers and relative energies of local minima and higher order saddle points are given in Table 4. The C_{2v} conformation proved to be the global minimum in the

---

(45) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H. E.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc.* **1994**, *116*, 7891−7892.

(46) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410−6411.

(47) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406−408.

(48) Mehta, G.; Panda, G. J. *Chem. Commun.* **1997**, 2081−2082.

(49) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666−12667.

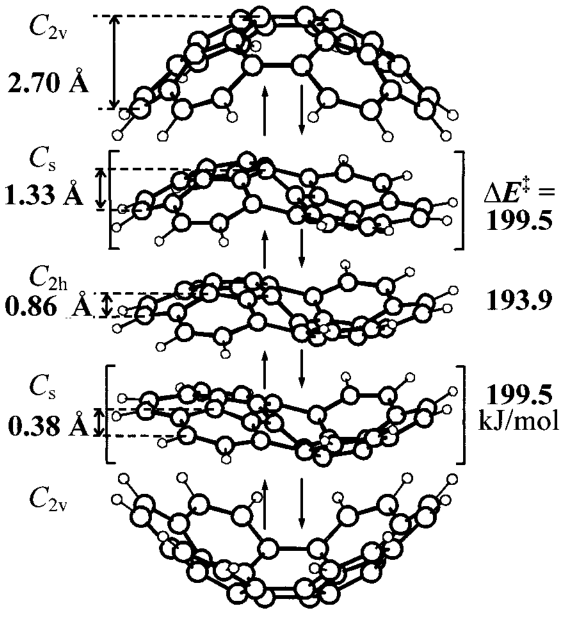


Figure 6. Bowl-to-bowl inversion of **5** at B3LYP/6-311G**.

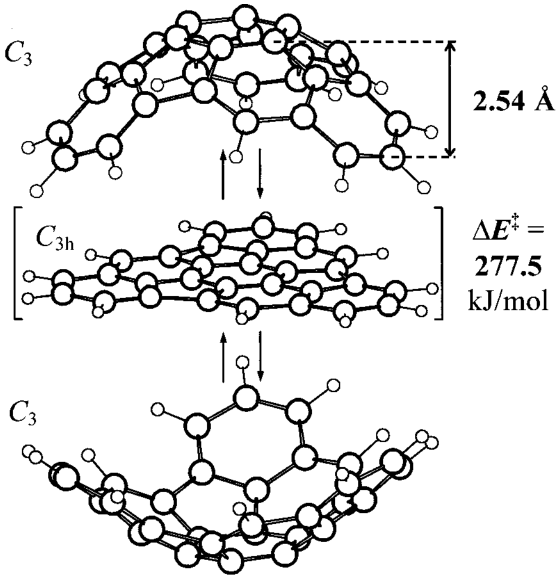


Figure 7. Bowl-to-bowl inversion of **6** at B3LYP/6-311G**.

conformational space of **5**, and the C_{2h} conformation was found to be a local minimum. $\Delta E_{\mathrm{Tot}} = E(C_{2h}\text{-}\mathbf{5}) - E(C_{2v}\text{-}\mathbf{5}) = 221.4$, 209.1, 192.3, and 193.9 kJ/mol at HF/3-21G, B3LYP/STO-3G, B3LYP/6-31G*, and B3LYP/6-311G**, respectively. The C_s-**5** conformation was identified as the transition state for the C_{2v}-**5** → C_{2h}-**5** partial bowl-to-bowl inversion.

Figure 6 describes the calculated bowl-to-bowl inversion of **5** at B3LYP/6-311G** along with the bowl depths of the relevant conformations. The corresponding ab initio barriers ($\Delta E^{\ddagger}_{\mathrm{Tot}}$) were 226.9, 214.5, 195.7, and 199.4 kJ/mol at HF/3-21G, B3LYP/STO-3G, B3LYP/6-31G*, and B3LYP/6-311G**, respectively, for the C_{2v}-**5** → [C_s-**5**] → C_{2h}-**5** partial inversion and 5.5, 5.4, 3.4, and 5.5 kJ/mol, respectively, for the C_{2h}-**5** → [C_s-**5**] → C_{2v}-**5** partial inversion. Thus, the C_{2h}-**5** intermediate is very close in energy to the C_s-**5** transition state. The ab initio barriers calculated with DFT are significantly lower than the previously calculated and estimated semiempirical and ab initio Hartree–Fock barriers.

$C_{30}H_{12}$ PAH 6. The decacyclic PAH **6** (trindenotriphenylene) represents the precise half of the C_{60} carbon framework.[46] McKee and Herndon considered the carbon frameworks of **6** and of the related benzenoid PAH benzo[*c*]naphtho[2,1-*p*]chrysene to be potential intermediates in C_{60} formation by the vaporization of graphite.[50] Semifullerene C_3-**6** has been synthesized by FVP (1000 °C) of a mixture of trichloro- and tetrachloro-5,10,15-trismethylene derivatives of 10,15-dihydro-5*H*-tribenzo[*a*,*f*,*k*]trindene[46] and by FVP (1050 °C) of 6,12,18-tribromo-benzo[*e*]naphtho[2,1-*p*]chrysene.[47] A short synthesis of **6** from 1,3,5-triformylbenzene has just been announced.[51]

Previous AM1 calculations of **6** indicated that the bowl-shaped C_3-**6** is the global minimum and that the planar C_{3h}-**6** is not a transition state of the bowl-to-bowl inversion of C_3-**6**.[16] The AM1 transition state has been located and exhibited a significant degree of nonplanarity. The MNDO barrier for inversion of **6** is 323.4 kJ/mol.[52] In contrast, previous ab initio calculations have shown that at HF/3-21G C_{3h}-**6** is indeed the transition state for the bowl-to-bowl inversion of C_3-**6**.[16] The ab initio barriers for this inversion are 298.3 and 286.2 kJ/mol at HF/3-21G and HF/6-31G*//HF/3-21G, respectively.[16] The theoretical estimate for the inversion at MP2/6-31G was 310 kJ/mol.[16] The C_3 semibuckminsterfullerene **6** was found to be less stable than its isomer **5** by 75 kJ/mol at HF/6-31G*//HF/3-21G.[46] Very recently, Schulman and Disch reported the results of an ab initio study of **6** at the HF/6-31G* and B3LYP/6-31G* levels.[8] They found that **6** adopts a bowl-shaped C_3 conformation and that the transition state for the bowl-to-bowl inversion of **6** at HF/6-31G* is the C_{3h} conformation (one imaginary frequency). The difference in energies between the two conformers were $E(C_{3h}\text{-}\mathbf{6}) - E(C_3\text{-}\mathbf{6}) = 282.0$ (HF/6-31G*), 282.8 (HF/6-31G**), and 264.8 (B3LYP/6-31G*) kJ/mol.

In our hands, the ab initio calculations of the bowl-shaped C_3-**6** and the planar C_{3h}-**6** were carried out using HF/3-21G and the B3LYP density functional with the STO-3G, 6-31G*, and 6-311G** basis sets. The ab initio energies of the above conformations of **6** are given in Table 3, and the barriers are given in Table 4. Frequencies were calculated at the HF/3-21G, B3LYP/STO-3G, and B3LYP/6-31G* levels. The C_3 conformation proved to be the global minimum, and the C_{3h} conformation was found to be a bona fide transition state (one imaginary frequency). A search for a nonplanar transition state (starting from the PM3 C_1 transition state conformation) converged toward a planar conformation at B3LYP/6-311G**. The bowl-to-bowl inversion of **6** at B3LYP/6-311G** is shown in Figure 7. Note that inversion of the chiral C_3-**6** is equivalent to an enantiomerization. The transition state, C_{3h}-**6**, is achiral. The bowl-to-bowl inversion barrier $\Delta E^{\ddagger}_{\mathrm{Tot}} = E(C_{3h}\text{-}\mathbf{6}) - E(C_3\text{-}\mathbf{6}) = 298.1$ (HF/3-21G), 297.2 (B3LYP/STO-3G), 265.2 (B3LYP/6-31G*), and 277.3 (B3LYP/6-311G**) kJ/mol. The difference in $\Delta E^{\ddagger}_{\mathrm{Tot}}$ between B3LYP/6-31G* and B3LYP/6-311G** is 12.1 kJ/mol. This significant result strengthens the conclusion drawn from the corannulene benchmark that the triple-

---

(50) McKee, M. L.; Herndon, W. C. *J. Mol. Struct.(THEOCHEM)* **1987**, *153*, 75–84.

(51) Mehta, G.; Panda, G.; Sarma, P. V. V. S. *Tetrahedron Lett.* **1998**, *39*, 5835–5836.

(52) Faust, R.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1471–1473.

split valence basis set with polarization functions on carbon and hydrogen atoms, in combination with the B3LYP variant of DFT, are superior to the B3LYP/6-31G* in calculating the bowl-to-bowl inversion barriers of the bowl-shaped fullerene fragments. Schulman and Disch claimed that the ab initio HF and B3LYP energy differences between C_3-**6** and the "putative transition state" C_{3h}-**6** were the same to within 5.0 kJ/mol, "indicating that correlation effects play a small role in determining the barrier height".[8] However, according to these authors the difference in the barriers $\Delta E^{\ddagger}_{\mathrm{Tot}} = E(C_{3h}\text{-}\mathbf{6}) - E(C_3\text{-}\mathbf{6})$ between HF/6-31G* and B3LYP/6-31G* is 17.6 kJ/mol. Thus, both the B3LYP variant of DFT and the 6-311G** basis set are important, and correlation does play an essential role in determining the barriers for the bowl-to-bowl inversions. At B3LYP/6-311G** C_3-**6** is less stable than C_{2v}-**5** by 57.7 kJ/mol. It is interesting to note that the bowl-to-bowl inversion barrier of C_3-**6** is considerably higher than that of C_{2v}-**5** (277.3 vs 199.4 kJ/mol at B3LYP/6-311G**), although the bowl depth of C_3-**6** is smaller than that of C_{2v}-**5** (2.54 vs 2.70 Å).

A comparison between the inversion barriers of the bowl-shaped fullerene fragments calculated at HF/3-21G and B3LYP/6-311G** deserves a comment. Despite the success of both methods in calculating the inversion barriers of corannulene (**1**) and the agreement of the two methods in the case of **4**, the HF/3-21G calculated barriers of **5** and **6** were substantially higher than the respective B3LYP/6-311G** barriers (by 27.5 (**5**) and 20.8 (**6**) kJ/mol). These differences may originate from the limitations inherent in HF/3-21G in calculating the highly strained transition states involved in the inversions of the more bowl-shaped **5** and **6**.

Using the four empirical parameters[34] derived for B3LYP/6-31G* we predict enthalpies of formation of 663.3, 862.8, and 924.6 kJ/mol for **4**, **5**, and **6**, respectively.

In conclusion, the inversion barrier of corannulene may serve as a benchmark for theoretical determinations of the barriers for bowl-to-bowl inversions of fullerene fragments.

JO9900174