Bowl-to-bowl Inversion in Polynuclear Aromatic Hydrocarbons with Curved Surfaces: An *Ab initio* Study

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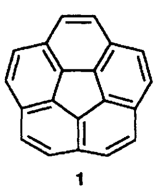
Ab initio calculations predict planar transition states for bowl-to-bowl inversions in corannulene, ethenocorannulene and semibuckminsterfullerene with barriers of 14.4, 34.4 and *ca.* 74 kcal mol^{-1}, (1 cal = 4.184 J), respectively, but a non-planar transition state for 1,2-dihydrocorannulene with a barrier of 10.9 kcal mol^{-1}.

The recent discovery of buckminsterfullerene, C_{60}, and related carbon cage structures,[1] has generated a renewed interest in aromatic compounds that possess curved surfaces. Indeed bowl-shaped aromatic hydrocarbons may serve well as models for the investigation of both the chemical and physical properties of the fullerenes including their formation from the vapourization of graphite. Unlike the fullerenes, however, these convex hydrocarbons have the potential to undergo bowl-to-bowl inversion, and the dynamics of this process are of special importance in understanding their overall behaviour. The *ab initio* results[2] herein for corannulene **1**, 1,2-dihydrocorannulene **2**, ethenocorannulene **3**, and semibuckminsterfullerene **4**, suggest a failure of the previously reported semiempirical calculations in properly identifying the transition states for bowl-to-bowl inversion in two of these cases (**2** and **4**).

Three of these systems (**1–3**) are known and characterized while **4**, which represents one-half of the C_{60} surface in its carbon framework, remains elusive. Due to the topology of the carbon skeletons, all these molecules prefer bowl-shaped minimum energy conformations.

Corannulene. Based on the behaviour of its derivatives, **1** is presumed to undergo a fast bowl-to-bowl inversion with a likely barrier of 11–12 kcal mol^{-1};[3,4] its planar D_{5h} conformer is believed to represent the transition state (TS) for this process. Theory is in good agreement with the experimental results and vibrational frequency calculations for the TS as both the semiempirical and *ab initio* levels reveal one imaginary frequency (117*i* at the HF/3-21G level; Table 1). This eigenvalue is associated with the mode of A_2'' symmetry, leading to a distortion of D_{5h} symmetry to C_{5v} that describes the pathway for bowl-to-bowl inversion.

1,2-Dihydrocorannulene. By analogy with **1**, a planar TS was also suggested for the inversion of **2**, and support was provided by semiempirical AM1 calculations which produced only one imaginary eigenvalue for its planar C_{2v} conformation.[4] However, our calculations at the HF/3-21G level show that this conformer is not a TS, but rather it is a higher-order stationary point on the potential energy surface of **2** since it exhibits two imaginary frequencies: 103.4*i* of A_2 symmetry and 102.7*i* (B_1). Distortion of planar **2** along the former frequency lowers the symmetry from C_{2v} to C_2, whereas the latter mode lowers the symmetry to C_s. Both structures have been optimized, giving two distinct TSs with one imaginary frequency each (Table 1, Fig. 1). The C_2 conformer, which represents the TS for bowl-to-bowl inversion, consists of an essentially planar skeleton of the 16 sp^2 carbon atoms but includes significant non-planarity of the partially reduced ring. The calculated torsion angles C(2a)–C(10c)–C(10a) and C(10a)–C(1)–C(2)–C(2a) are 5.7 and 27.0°, respectively, close to the analogous angles in the minimum energy conformer of C_1 symmetry (6.0 and 30.9°, respectively).



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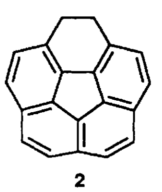

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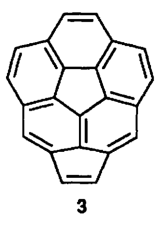

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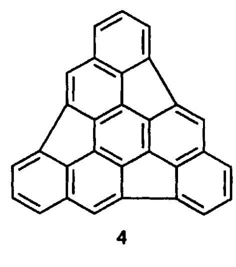

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The conformer of C_s symmetry, with an eclipsed conformation along the C(1)–C(2) bond, represents the TS for inversion of the partially saturated six-membered ring, a process analogous to ring inversion in cyclohexa-1,3-dienes. The

Table 1 The results of *ab initio* calculations for **1–4**. Total energies in hartrees, relative energies in kcal mol^{-1}

		3-21G	6-31G*	MP2/6-31G	ZPE[a]
1	C_{5v}	−758.908 18	−763.188 91	−764.641 09	156.6 (0)
	D_{5h}	10.5	8.8	14.3	156.9 (1)
2	C_1	−760.070 85	−764.351 43	−765.808 08	171.9 (0)
	C_{2v}	7.4	6.5	12.2	172.0 (2)
	C_s	0.7	0.7	1.4	171.8 (1)
	C_2	7.0	5.9	10.8	172.1 (1)
3	C_s	−834.173 25	−838.881 92	−840.483 59	164.3 (0)
	C_{2v}	31.8	28.8	34.3	164.4 (1)
4	C_3	−1136.573 15	−1143.008 61		
	C_{3h}	71.3	68.4		212.4 (1)

[a] Zero-point vibrational energy at 3-21G level, unscaled, kcal mol^{-1}. The number of imaginary frequencies in parentheses.

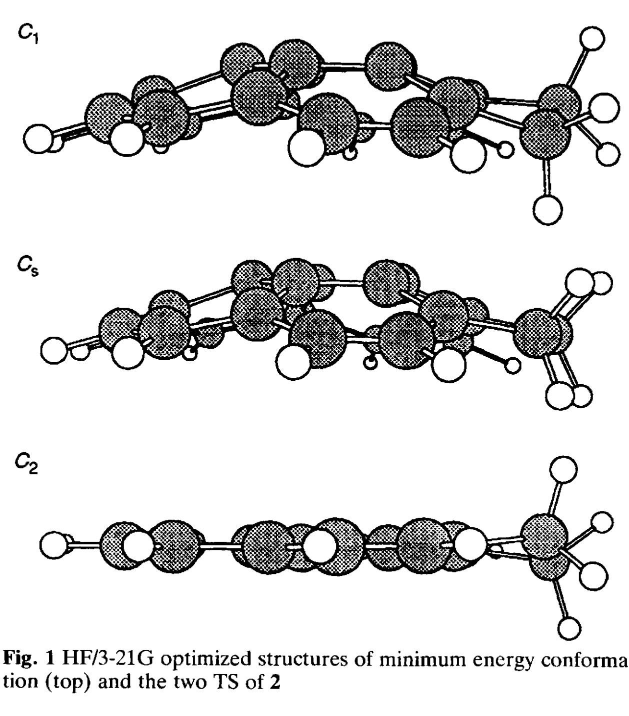

Fig. 1 HF/3-21G optimized structures of minimum energy conformation (top) and the two TS of **2**

calculated barrier for this process is only 1.4 kcal mol^{-1} (Table 1), significantly lower than the barrier calculated at the same level of theory for cyclohexa-1,3-diene (3.7 kcal mol^{-1}).[5] The difference may be rationalized by the observation that the partially reduced ring in the minimum energy conformation of **2** is forced to be flatter than cyclohexa-1,3-diene itself.†

The failure of AM1 to predict the correct structure for the TS in **2** is a consequence of its inadequate description of the minimum energy structure of 1,2-dihydrocorannulene. The AM1 optimized **2** exhibits an essentially eclipsed conformation around the C(1)–C(2) bond similar to C_s **2** (Fig. 1). In contrast, both our *ab initio* and MM2 calculations suggest a significant degree of twisting around this particular bond. *Ab initio* Local Density Theory (LDF) calculations also predict some twisting around this bond, but to a lesser extent.[4] However, we believe our HF/3-21G results to be more reliable since the same level of approximation gives an excellent description of the minimum-energy conformers of cyclohexa-1,3-diene, and related compounds,[5] as well as for corannulene.[3b,6] Moreover, our recent X-ray crystal structure and NMR studies of some 1-alkyl derivatives of **2** show a significant degree of twisting around the C(1)–C(2) bond.[7] Consequently, we conclude that the conformation of C_2 symmetry better describes the TS for the bowl-to-bowl inversion of **2** than the planar C_{2v} structure.

Ethenocorannulene. **3** is especially interesting since the introduction of an additional two-carbon bridge onto corannulene halts the bowl-to-bowl inversion, at least on the NMR timescale.[8] However, the calculated mechanism for inversion seems to be analogous to **1** since the planar C_{2v} conformer of **3** exhibits one imaginary frequency (143*i*) associated with the B_1 symmetry mode which distorts the planar structure toward the bowl conformation with C_s symmetry. In this case, the planar C_{2v} **3** TS predicted by *ab initio* calculations is in agreement with AM1 results for both **3** and its dihydro derivative.[8]

Semibuckminsterfullerene. Very recent MNDO studies suggest that the planar C_{3h} conformer of **4** is not a TS for the inversion since it exhibits three imaginary frequencies,[9] and our own AM1 studies lead to the same conclusion. We have also located the TS at the AM1 level, and while it exhibits a significant degree of non-planarity (Fig. 2), it represents only a modest decrease in energy when compared to the planar structure (1 kcal mol^{-1}). In contrast, HF/3-21G frequency calculations for planar C_{3h} **4** reveal one imaginary frequency only (124*i*) associated with the eigenvector of A″ symmetry. Due to the size of the molecule we were not able to perform Intrinsic Reaction Coordinate calculations to unequivocally prove that the C_{3h} structure is the only TS for the bowl-to-bowl inversion. However, since a slight distortion of planar **4** along the eigenvector associated with the imaginary frequency lowers the symmetry of the molecule to C_3, and subsequent geometry optimization leads to the minimum energy bowl-shaped **4**, it seems safe to assume that the planar C_{3h} structure is the TS for the inversion of **4** at this level of theory.

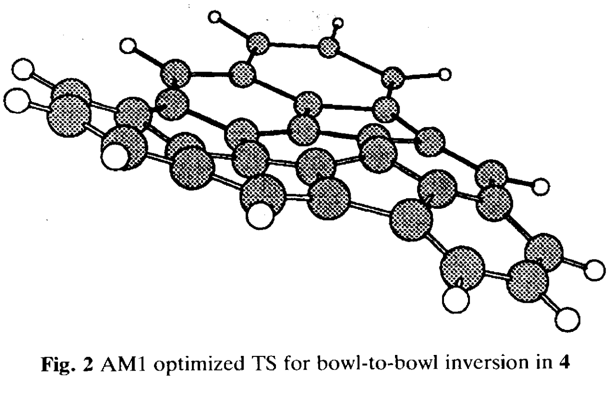

Fig. 2 AM1 optimized TS for bowl-to-bowl inversion in **4**

The *ab initio* results for the minimum energy bowl structure of **4** also differ from the semiempirical results. The HF/3-21G C–C bond lengths are shorter than those from MNDO[9] by 0.020–0.038 Å with the exception of the C(4)–C(5) and C(10)–C(11) distances (0.005 Å shorter and 0.027 Å longer, respectively). The *ab initio* picture of the frontier orbitals of **4** is also different from MNDO[9] and AM1. The latter methods predict degeneration of both HOMO and LUMO orbitals, whereas *ab initio* results predict only degeneration of the HOMO (−7.41 eV at the 6/31G*//3-21G level). The LUMO is predicted to be of A symmetry with an energy of 1.59 eV while the LUMO + 1 orbital is also shown to be degenerate (1.70 eV). The very small gap between LUMO and LUMO + 1 suggests the possibility of the addition of up to six extra electrons resulting in the formation of a hexaanion.

Inversion Barriers. The barriers for bowl-to-bowl inversion calculated at the HF/3-21G level are 10.5, 7.0, 31.8 and 71.3 kcal mol^{-1} for **1**–**4**, respectively. Improvement of the basis set quality slightly lowers the barriers. Most of the effect at the 6-31G* level must be attributed to the improvement of the Slater orbital quality (from 3-21G to 6-31G), while the inclusion of polarization functions does not significantly impact the barriers.‡

The electron correlation effects calculated at the MP2/6-31G level§ increase the barriers considerably by 5.6–6.0 kcal mol^{-1} in **1**–**3**. If this also holds for **4**, the best theoretical estimates for the barriers are 14.4, 10.9, 34.4 and 74 kcal mol^{-1} for **1**–**4**, respectively. The numbers are in reasonable agreement with the available experimental data, *i.e.* 11–12 and 8.5 kcal mol^{-1} for **1**[3] and **2**,[4] respectively. The estimated lower limit for the dihydro-derivative of **3** (26 kcal mol^{-1})[8] provides a first approximation for the barrier in **3**.¶ Thus, the calculations provide a theoretical support for the experimental finding that a flexible corannulene unit as in **1** and **2** becomes much more rigid upon the addition of only two carbon atoms in a fused five-membered ring as in **3**. Indeed, the calculated inversion barrier for **3** is more than twice that in **1**. The expected barrier for **4** is again at least twice as large as for **3**, due to a significantly higher degree of curvature of the former in its minimum energy conformation.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, of the US Department of Energy, and by SNCC (Louisiana State University) for allocation of computer time.

Received, 27th January 1994; Com. 4/00524D

Footnotes

† HF/3-21G torsion angles of 15.2 and 44.5° [C(1)–C(2)–C(3)–C(4) and C(1)–C(6)–C(5)–C(4), respectively] were calculated for the minimum energy structure of cyclohexa-1,3-diene.[5]

‡ The barriers calculated with 6-31G basis set (8.7, 5.8, 28.7 and 68.5 kcal mol^{-1} for **1**–**4**, respectively) are basically identical with the 6-31G* results (Table 1).

§ We are aware that the small basis set used for MP2 calculations may not provide enough configurational space to account for all correlation effects. The size of the molecules studied here prevented us from the calculations at MP2/6-31G* level. However, we have recently shown that such a limited post-HF treatment give an reasonable estimation of the correlation effects, if the barriers for ring inversion are considered. Improvement of the basis set quality at the MP2 level increases the correlation correction to the barriers, whereas the higher order treatment up to MP4 level decreases it slightly. Thus, the two effects cancel each other to some extent.[5]

¶ The barrier in **3** is expected to be slightly higher than in its dihydro derivative, as demonstrated by AM1 calculations, which predict the barrier of 39 kcal mol^{-1} for the dihydro-**3**, as compared to 44 kcal mol^{-1} for the parent **3**.

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