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Isolated pentagon rule in buckybowls: a computational study on thermodynamic stabilities and bowl-to-bowl inversion barriers☆

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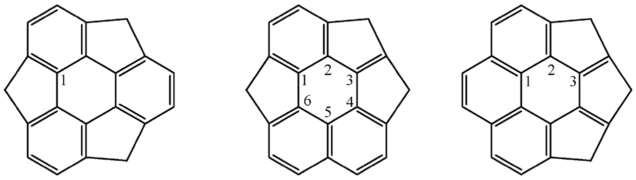
Dedicated to Dr K. V. Raghavan, Director, IICT, on the ocassion of his 60th birthday

Abstract—Computations on a series of sumanene and pinakene isomers reveal that the isolated pentagon species are found to be more stable than non-isolated pentagon structures. However, the present study indicates that there is no correlation between the bowl-to-bowl inversion barrier and the relative stability. Unexpectedly, the least stable isomer has the lowest bowl-to-bowl inversion barrier in pinakene isomers. Thus, curvature cannot be taken as a measure to evaluate the stability of buckybowls. The relative energy ordering and HOMO–LUMO gap correlate well in the series of pinakene isomers considered.

1. Introduction

Polycyclic aromatic hydrocarbons with contiguous six-membered aromatic rings are strain free and planar. Replacing one or more six-membered rings with five-membered rings results in warping of the surface due to angular strain.[1] These curved polycyclic systems are called buckybowls, especially when their skeletons map on to the surface of fullerenes.[1–5] Unsaturated organic compounds with adjacent five-membered rings are unstable and violate the isolated pentagon rule (IPR).[6–8] The closed geodesic domes consisting of five and six-membered rings should have 12 five-membered and remaining six-membered rings.[9] The pentagons embodied in the cage structures are responsible for the curvature and according to the IPR, the maximum possible separation of the five-membered rings results in the lowest energy isomers.[6–8] Importantly, in fullerenes, the isolated pentagon rule was remarkably successful in explaining the special stability of C_{60} and related fullerenes.[6–8] Our group is engaged in theoretical studies aimed at understanding the inversion dynamics of buckybowls and how to effectively modulate the curvature and to design the effective theoretical strategies for the synthesis of bowls.[10–15] We are also interested in exploring the structure–energy relationships in buckybowls.[14,15] In recent years, several fullerene structures which violate IPR have been synthesized, which lead to meaningful interplay between experimentalists and theoreticians.[16–21] While the isolated pentagon rule is firmly established in fullerenes,[6–8, 20,21] to our knowledge, the quantitative assessment of the same concept in buckybowls is scarce, which prompted us to undertake the current study.

The purpose of the present study is to quantitatively assess how the disposition of five and six-membered rings in buckybowl moieties affects their stabilities, curvature, and bowl-to-bowl inversion barrier by taking **1** and **4** as models (Schemes 1 and 2). To our knowledge, this is the first study on the isomers of the buckybowl structures in assessing the isolated pentagon rule and the relationship between the stability and the bowl-to-bowl inversion barrier. The three possible isomers of sumanene (**1–3**) are shown in Scheme 1 and six possible isomers of pinakene (**4–9**) are shown in Scheme 2. In all these isomers, the hybridization is not disturbed. B3LYP/6-31G* calculations were performed on the bowl and planar structures of the isomers considered, and all of them were characterized by frequency calculations.



1 **2** **3**

Scheme 1.

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Keywords: bowl-to-bowl inversion barrier; relative stability; density functional theory; isolated pentagon rule; buckybowls.

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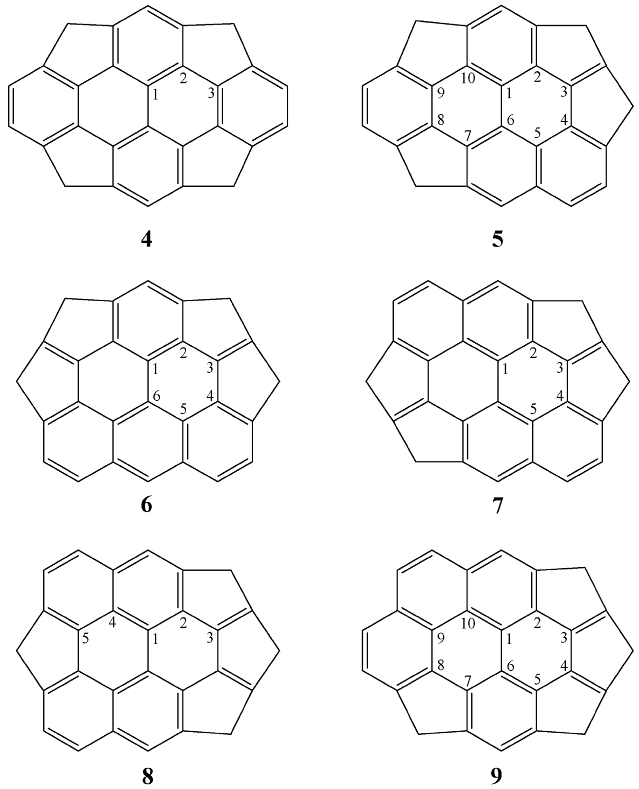


Scheme 2.

2. Computational details

The hybrid density functional theory B3LYP calculations were done using 6-31G* basis set for the planar and the bowl structures of all the sumanene and pinakene isomers considered. The frequency calculations done at the same level indicate that all the bowl structures are minima and flat structures as transition states. The normal mode of the imaginary frequency corresponds to bowl-to-bowl inversion in all the cases. All the calculations were done using the Gaussian 98 program package.[22]

3. Results and discussion

The present study examines the isolated pentagon rule in buckybowls by taking the isomers of sumanene and pinakene. The isomers are constructed by systematically altering the positions of the five and six-membered rings in each of the model systems without disrupting the hybridization of skeletal carbon atoms. The pristine model compounds sumanene **1** and pinakene **4** possess isolated pentagons. The isomers of sumanene **2** and **3** contain two and three fused pentagons, respectively. Coming to the isomers of pinakene, structure **5** has two adjacent pentagons while the isomers **6** and **7** possess two pairs of fused pentagons. As it is impossible to construct a structural model with all fused five-membered rings in pinakene, **8** and **9** represent the isomers with maximum number of adjacent pentagons as both of them have three contiguous pentagon rings.

The present study identified all the minimum energy bowl structures and characterized all of them as stable minima on the potential energy surface. Thus, according to the theoretical calculations, all the structural isomers may exist as stable species if synthesized. After obtaining bowl minima, the corresponding bowl-to-bowl inversion transition states were explored. Figures 1 and 2 depict the bowl structures and bowl-to-bowl inversion transition states for sumanene and pinakene isomers. In all cases, the flat structures were characterized as the bowl-to-bowl inversion transition states, possessing one imaginary frequency whose direction clearly corresponds to bowl-inversion.

Curvature is the most captivating feature of buckybowls, and in cases such as the present one, unambiguous definition of curvature is not possible. A perusal of bowl structures **8** and **9** indicates that the region with contiguous pentagon rings is more warped compared to the rest (Fig. 2). In the present study, we employ the Haddon's π-orbital axis vector (POAV) angle,[23,24] which proved to be one of the effective and reliable ways to measure the curvature in buckybowls.[14,15] The POAV angles were measured for all the bowl structures and the values are listed in Tables 1 and 2 correspondingly for sumanene and pinakene isomers. The numbering for atoms is given in Schemes 1 and 2. The extent of pyramidalization is higher at carbon 3 in structures **2** and **3**, the POAV angles are 100.9 and 101.9°, respectively. Table 2 shows that the POAV angles at carbon 3 are higher for structures **5**–**7**, the values are between 99.8 and 100.4°, indicating that pyramidalization is higher at these carbons compared to other carbons. Similarly, carbon 3 in structure **8** and carbons 3 and 4 in structure **9**, the degree of pyramidalization at these positions is higher than other carbons. The present study indicates that the carbon atoms sharing the five-membered rings are more pyramidal, and also the degree of pyramidalization increases marginally (by about 1–2°) with addition of a five-membered ring.

Table 3 gives the bowl-to-bowl inversion barriers, the relative energies of the minimum energy bowl structures, the frontier molecular orbital energies and HOMO–LUMO energy gap for all the bowl structures. The relative energies of the bowl structures were calculated relative to sumanene **1** for **1**–**3** and relative to pinakene **4** for **4**–**9**. Figure 3 depicts the variation of the bowl-to-bowl inversion barriers

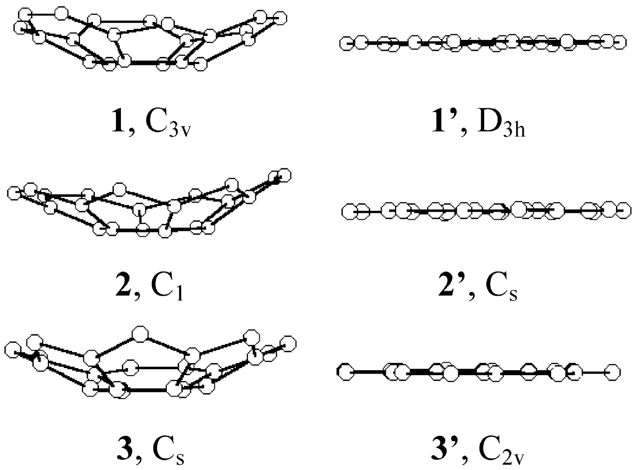
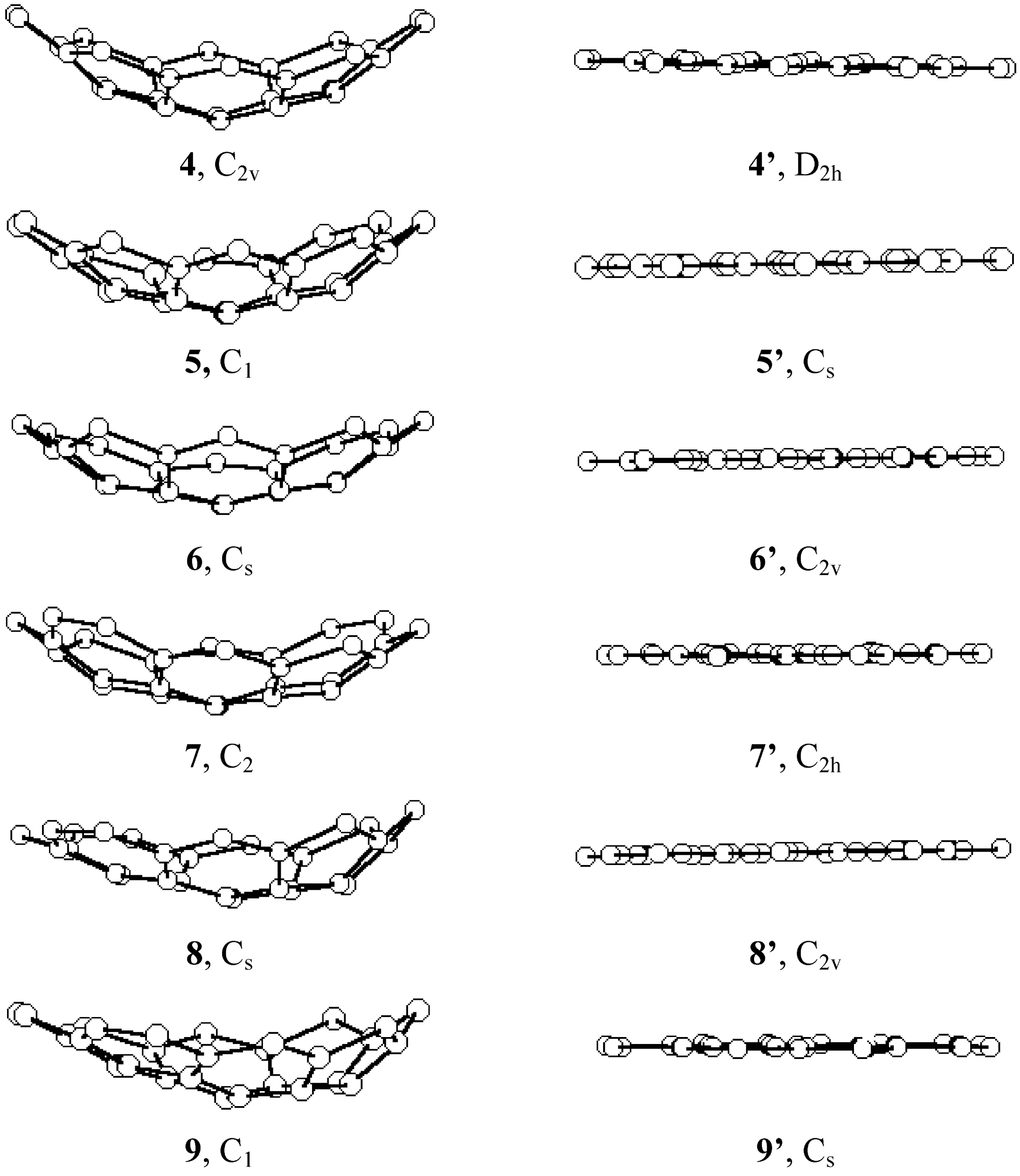


Figure 1. The B3LYP/6-31G* optimized bowl and transition state structures of the sumanene isomers.



4, C_{2v} **4'**, D_{2h}

5, C_1 **5'**, C_s

6, C_s **6'**, C_{2v}

7, C_2 **7'**, C_{2h}

8, C_s **8'**, C_{2v}

9, C_1 **9'**, C_s

Figure 2. The B3LYP/6-31G* optimized bowl and transition state structures of the pinakene isomers.

Table 1. The POAV angles (in °) for the inner carbons for the bowl structures of the sumanene isomers (see Scheme 1 for numbering of atoms)

Structure	1	2	3	4	5	6
1	98.7	–	–	–	–	–
2	98.5	99.6	100.9	98.4	96.8	98.0
3	96.3	98.2	101.9	–	–	–

and the relative stabilities for both sumanene and pinakene isomers. In the case of sumanene isomers, the bowl-to-bowl inversion barrier increases as the number of adjacent pentagons increases, albeit the difference in bowl-to-bowl inversion barriers between **1** and **2** is only 0.4 kcal/mol. On the other hand, no correlation is seen between the bowl-to-bowl inversion barrier and the relative stability for pinakene

Table 2. The POAV angles (in ° for the inner carbons for the bowl structures of the pinakene isomers (see Scheme 2 for numbering of atoms)

Structure	1	2	3	4	5	6	7	8	9	10
4	98.5	97.9	98.2	–	–	–	–	–	–	–
5	98.7	98.7	100.4	98.1	96.6	97.8	97.2	97.9	97.8	97.5
6	98.5	98.3	99.8	97.6	95.5	96.9	–	–	–	–
7	97.8	98.3	100.2	97.5	95.7	–	–	–	–	–
8	97.4	99.0	102.1	94.6	95.7	–	–	–	–	–
9	97.5	98.9	102.2	102.3	99.5	98.6	96.0	95.5	94.5	94.2

Table 3. The bowl-to-bowl inversion barriers ($\Delta E^{\ddagger}$, in kcal/mol), relative energies of the bowl structures (ΔE, in kcal/mol), HOMO and LUMO energies (E_{HOMO} and E_{LUMO}, in eV), and HOMO–LUMO energy gap ($E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}}$, in eV) for the bowl structures of the sumanene (**1**–**3**) and pinakene (**4**–**9**) isomers obtained at B3LYP/6-31G* level

Structure	$\Delta E^{\ddagger}$	ΔE	E_{HOMO}	E_{LUMO}	$E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}}$
1	16.8	0.0	−5.48	−0.72	4.76
2	17.2	19.9	−4.79	−1.42	3.37
3	19.3	39.3	−4.90	−1.43	3.47
4	40.5	0.0	−5.04	−0.98	4.06
5	35.9	19.8	−4.76	−1.47	3.29
6	31.4	48.3	−4.44	−1.89	2.55
7	32.0	39.5	−4.50	−1.68	2.82
8	36.0	42.8	−4.43	−1.83	2.60
9	41.9	39.3	−4.78	−1.55	3.23

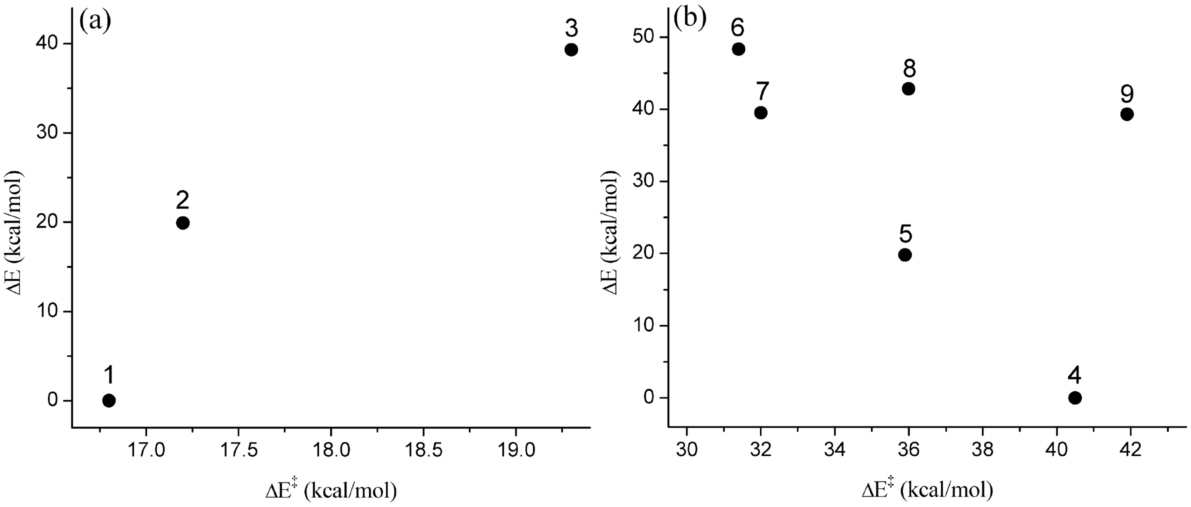


Figure 3. The variation of bowl-to-bowl inversion barriers ($\Delta E^{\ddagger}$) and the relative energies of bowl structures (ΔE) for (a) sumanene isomers (**1**–**3**) and (b) pinakene isomers (**4**–**9**).

isomers (Fig. 3). Sumanene **1** and pinakene **4** are the most stable isomers in their respective classes, indicating that pentagon isolation increases the stability. **1** is more stable by about 20 and 40 kcal/mol than isomers **2** and **3**, respectively. A perusal of the relative stability orderings of **6**, **8** and **9** reveals that the structures with three contiguous pentagons are more stable compared to those with two pairs of fused pentagons. Isomers **9** and **6** have the highest and the lowest bowl-to-bowl inversion barrier in pinakene isomers. Isomer **6** is the least stable in pinakene isomers.

The HOMO–LUMO energy gap is a good indicator of kinetic stability for fullerene isomers.[25] The isomers **6**, **7** and **8** are having lower HOMO–LUMO gap, may be kinetically less stable compared to **4**, **5** and **9**. Thus, according to this measure, sumanene **1** and pinakene **4** have the highest HOMO–LUMO energy gap, indicating that they are kinetically the most stable isomers in their respective classes.

4. Conclusions

B3LYP/6-31G* calculations on sumanene and pinakene isomers reveal that parent isomers **1** and **4** are the most stable isomers. However, no correlation exists between bowl-to-bowl inversion barrier and the relative stability particularly in pinakene isomers. The least stable isomer **6** has the lowest bowl-to-bowl inversion barrier among pinakene isomers. The HOMO–LUMO energy gap, which gauges the kinetic stability of the isomers essentially follows the same trend as the thermodynamic stabilities. The compounds, which do not obey IPR are expected to be less stable, more reactive but however their bowl rigidity is comparable with other isomers. These novel bowl structures can be potential synthetic targets. As all the bowl structures are characterized as minima, experimental attempts in this direction should be rewarding.

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