Pergamon

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Tetrahedron Letters 44 (2003) 4527–4529

TETRAHEDRON
LETTERS

Is *peri* hydrogen repulsion responsible for flattening buckybowls? The effect of ring annelation to the rim of corannulene☆

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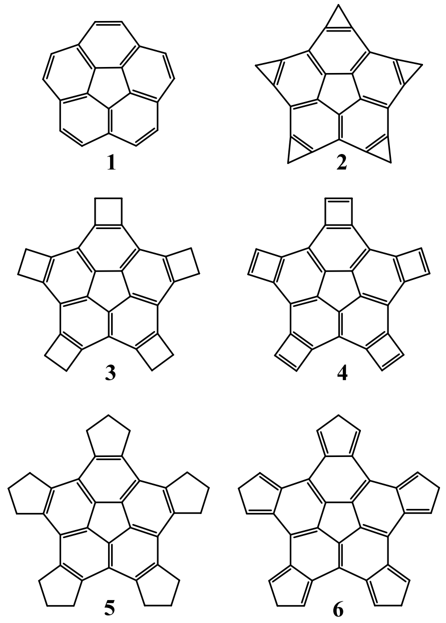
Received 12 March 2003; revised 7 April 2003; accepted 17 April 2003

Dedicated to Professor Goverdhan Mehta on the occasion of his 60th birthday

Abstract—B3LYP/6-31G* calculations indicate that annelation of three-, four-, or five-membered rings to the rim of corannulene results in lowering the bowl-to-bowl inversion barrier and flattens the bowl structure. The role of the *peri* hydrogen repulsion as a causative factor for such a behavior is disputed, the structure–energy relationships in this class of compounds were shown to fit with a mixed quartic–quadratic potential. © 2003 Elsevier Science Ltd. All rights reserved.

Fullerene derivatives have emerged as an important class of compounds and found applications in wide ranging fields, from material science to medicine. In recent years, the derivatization and extension of buckybowls, substructures of fullerenes, have also gathered momentum and the activity is centered mainly on the chemistry of corranulene.[1] The correlation between the equilibrium bowl depth and the barrier heights in buckybowls has attracted and stimulated interplay between theory and experiment.[2–7] Various strategies have been designed to modulate the curvature of corannulene **1** in a rational way. Locking the bowl conformation is achieved by (a) augmenting the skeleton with another five-membered ring,[2,4] (b) construction of a cyclophane bridge[8] or (c) a site specific heteroatom substitution.[5] On the other hand, alkyl substitution at the rim of corannulene gradually flattens the bowl and eventually the permethyl substituted corannulene was expected to yield flat structures with little barrier for inversion.[2,3] Similarly, sequential benzannelation to the corannulene core gradually flattens the bowl shape and lowers the inversion barrier.[6] Benzannelation to the rim was found to have a flattening effect even on the cyclopenta-corannulene, a rigid bowl structure.[9] While the reasons for flattening were not clearly established, *peri* repulsive interactions were put forward as a key factor.

In this letter, we report a systematic computational study on the ring annelation effect on the curvature and inversion dynamics of corannulene. The systems are designed (Scheme 1) to explore the dependence of structural variants on the structure and inversion barrier of ring annelated corannulenes and answer the following questions: How switching off the *peri* hydrogen repulsion effects the barrier? How the extra-conjugation on



Scheme 1.

Keywords: structure–energy relations; buckybowls; *peri* interactions; DFT calculations; ring annelation.

☆ IICT Communication No. 030309.

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doi:10.1016/S0040-4039(03)01011-6

the annelated ring effects the structure and inversion barrier? Is there a correlation between the structure and inversion barrier in this series of compounds?

DFT calculations employing the full geometry optimizations were done at B3LYP/6-31G level to obtain the equilibrium geometries, bowl-to-bowl inversion barrier and the extent of pyramidalization. The nature of the stationary points was characterized by frequency calculations at the same level. The geometries were further refined at B3LYP/6-31G* level. All the calculations were done using the Gaussian 98 suite of programs.[10]

Figure 1 depicts the optimized skeletons of the bowl forms of the structures considered in the study. The bowl-to-bowl inversion barriers, bowl depths, and the π-orbital axis vector angles (POAV)[11] at the hub positions are given in Table 1. The planar forms of all the structures except for **5** are the bowl-to-bowl inversion transition states. Therefore, the true transition state for the bowl-to-bowl inversion of **5** is non-planar.[12]

A comparison of geometric and energetic results indicates that all the rim annelated structures considered are flatter and have lower inversion barriers compared to that of corannulene. Both levels of theory are in excellent agreement with each other. Annelating all rim bonds with the cyclopropene rings reduced the inversion barrier by more than half. Increasing the ring size to four, structures **3** and **4**, further reduced the barrier and the cyclobutane annelation **3** seems to be more effective. Two isomeric forms are possible for the structure **4** depending on the position of the double bonds in the cyclobutadiene moieties. However, the exploratory computational studies indicated that **4** is the only viable structure.[13] The reduction in the inversion barrier values are followed by lower curvature values for the bowls quantified by the POAV angles and bowl depths. Obviously, the annelation of the three or four membered rings does not induce any repulsive *peri* hydrogen interactions. Therefore, the present computational study contradicts the argument that *peri* interaction is a causative factor in reducing the inversion barriers upon ring annelation.

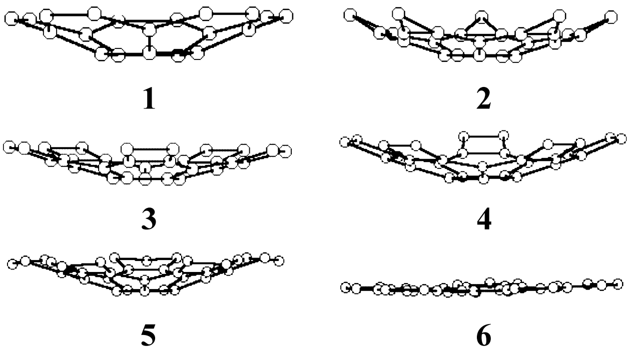
1 **2**
3 **4**
5 **6**

Figure 1. The B3LYP/6-31G* optimized geometries of the minimum energy bowl structures.

The five-membered annelated systems, **5** and **6** had decreased inversion barriers, however, the magnitudes of the reductions are contrasting. While **6** leads to a virtually flat equilibrium structure with virtually no bowl-to-bowl inversion barrier, **5** has an inversion barrier of about 24 kJ mol^{-1}. The underlying reasons for the discrepancy in the curvature and inversion barrier between **5** and **6** are not obvious. The POAV angles and bowl depth values indicate that **5** is the most curved among the ring-annelated structures. Secondly, the farthest carbons of the annelated five-membered rings are tilted towards the base of the bowl structure.

Previously, we and others have shown that, a mixed quartic–quadratic potential (Eq. (1)) nicely models the structure–energy relationship in the series where the corannulene rim is substituted, either by different groups or rings, and annelated with benzene rings.[2,6a] Similar structure–energy relations were obtained in a series of heteroatom substituted buckybowls.[7]

Table 1. The relative energies for all the structures, the bowl depth (in Å) and the POAV angles (in degrees) at the hub position for bowl structures obtained at B3LYP/6-31G and B3LYP/6-31G* levels. The zero point energy correction (ΔZPE) and the thermal correction to enthalpy (ΔH) are also given. All the energies are given in kJ mol^{-1}

Struct.	B3LYP/6-31G					B3LYP/6-31G*		
	ΔE	ΔZPE	ΔH	Bowl depth	POAV	ΔE	Bowl depth	POAV
1 (C_{5v})	0.0	0.0	0.0	0.872	98.1	0.0	0.864	98.1
1′ (D_{5h})	39.3	−1.2	−2.8	–	–	36.0	–	–
2 (C_{5v})	0.0	0.0	0.0	0.681	96.5	0.0	0.674	96.6
2′ (D_{5h})	15.6	−0.2	−2.1	–	–	14.9	–	–
3 (C_{5v})	0.0	0.0	0.0	0.597	95.5	0.0	0.572	95.3
3′ (D_{5h})	8.4	−0.1	−2.2	–	–	6.7	–	–
4 (C_{5v})	0.0	0.0	0.0	0.679	96.3	0.0	0.678	96.5
4′ (D_{5h})	14.1	−1.5	−3.4	–	–	13.0	–	–
5 (C_{5v})	0.0	0.0	0.0	0.749	97.1	0.0	0.738	97.1
5′ (D_{5h})	35.9	−3.5	−13.6	–	–	39.6	–	–
5TS (C_2)	25.4	−1.5	−5.1	–	–	24.1	–	–
6 (C_{5v})	0.0	0.0	0.0	0.222	92.1	0.0	0.093	90.0
6′ (D_{5h})	0.3	−0.1	−2.4	–	–	0.2	–	–

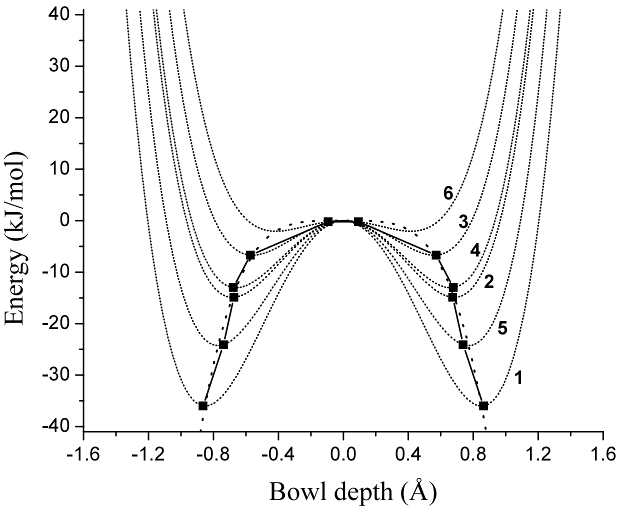

Figure 2. The correlation of bowl depth versus bowl-to-bowl inversion barrier at B3LYP/6-31G* level (continuous line). The thick dotted line is fitted with a quartic function and the thin dotted lines are fitted with a mixed quartic–quadratic function.

$$E = ax^4 - bx^2 \qquad (1)$$

Interestingly we have obtained essentially the same relationship between the structure and energy when applied to this class of compounds (Fig. 2). Figure 2 shows that the quartic potential curve was shallow which indicates that for the shallower bowls, the supply of a small amount of energy results in higher bowl-to-bowl inversion frequencies as well as amplitudes. Thus, the rim annelated corannulene structures are expected to possess a highly fluxional character near room temperature. In the post fullerene era, corannulene chemistry witnesses tremendous expansion in interesting directions and ring annelation is yet another fascinating way of extending the bowl shaped system and synthetic efforts in this direction should be rewarding.

In summary, we have shown that annelation by three-, four- and five-membered rings on the rim of corannulene results in lowering the bowl-to-bowl inversion barrier. The lowering of the inversion barrier is irrespective of whether the rings are saturated or unsaturated. A mixed quartic–quadratic potential successfully explains the inversion barrier and the bowl depth relationship.

Acknowledgements

T.C.D. thanks CSIR for a research fellowship. Dr. K. V. Raghavan, Director, and Dr. J. S. Yadav, Head, Organic Chemical Sciences, IICT are thanked for their encouragement and support.

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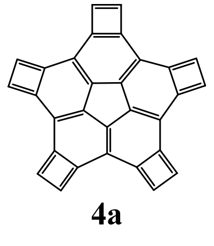
12. Several attempts to locate the true bowl-to-bowl inversion transition state were unsuccessful. The second order saddle point has two imaginary frequencies, 111i and 56i, and the structure **5TS** is considered as the transition state for all practical purposes.
13. No stable minima could be obtained for the other isomeric form and only **4a** could be characterized as a stationary point with one imaginary frequency. The normal mode corresponds to an in-plane motion. **4a** is about 57 kJ mol^{-1} higher in energy compared to **4**.



4a