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Structure−Energy Relationships in Curved Polycyclic Aromatic Hydrocarbons: Study of Benzocorannulenes

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Abstract: B3LYP/6-31G* calculations indicate that sequential annelation of benzene rings to the rim of corannulene gradually flattens the skeleton. Pentabenzocorannulene is predicted to exhibit nearly barrierless flipping motion at room temperature. A mixed quartic−quadratic potential successfully explains the inversion barrier and curvature (given by the π-orbital axis vector angle) relationship.

The significance of structure−energy correlations in a series, where the skeleton is intact and substituents are systematically varied, in elucidating the reaction mechanisms as well as in discerning the steric and electronic effects on reaction paths were highlighted by elegant crystal structure studies of Burgi et al.[1] In a recent paper, Seiders et al. using experimental results and quantum mechanical calculations have demonstrated that a double-well potential explains the structure−energy relationships in a series of substituted corannulenes.[2] We found that similar structure−energy correlations using a mixed quartic−quadratic potential successfully fits the energy and bowl depth in heterobuckybowls.[3]

Curvature and bowl-to-bowl inversions are critical features that distinguish buckybowls and polycyclic aromatic hydrocarbons.[4,5] Therefore, it will be of fundamental interest to unravel the relationship between the curvature and bowl-to-bowl inversion barrier, which helps in understanding the dynamics of curved aromatics. Designed experimental studies confirm that construction of cyclophane bridges and fusing one or more five-membered rings effectively lock the bowl conformation of corannulene at the room temperature.[5−7] The elegant experimental and computational studies by Seiders et al. have revealed that the alkyl substitution at the rim positions flattens the corannulene skeleton.[8] The site-selective heteroatom substitution seems to be an another effective strategy to modulate the curvature.[9] Understanding the structure−energy relationships will also be useful in designing feasible synthetic strategies.[10] The research groups of Scott and Mehta reported successful syntheses of benzocorannulenes, and this seems to be an attractive synthetic strategy toward the preparation of higher buckybowls.[11,12] Recently we reported semiempirical calculations in a series of benzocorannulenes; these results show a gradual flattening of the corannulene skeleton and decrease in the activation barriers with each annelation of benzene ring in a systematic fashion.[13] While most of the other buckybowls other than corannulene are rigid, i.e., locked into a single conformation at room temperature, the nature of the benzocorannulenes is less explored. Benzocorannulenes are at the intersection between PAHs and buckybowls and thus form an interesting class of compounds.

The purpose of the study is to explore the structure−inversion barrier relationship in the benzocorannulene series. Also, the present study is aimed at reporting the equilibrium geometries and activation energies, and at a qualitatively reliable level of theory, such as B3LYP/6-31G*, to present the relationship between the curvature and inversion barrier. Geometries were initially optimized within the symmetry constraints at the HF/3-21G level, and the stationary points were characterized by the frequency calculations. Later, all structures considered were refined further at the B3LYP/6-31G* level of theory. Calculations were also done at semiempirical (MNDO, AM1, and PM3) levels as well as at the B3LYP/6-31G*//HF/3-21G level, which lead to essentially the same qualitative results (see Supporting Information).[13] Prediction of inversion barriers and dynamics of buckybowls has been a challenging task computationally. Semiempirical methods and ab initio methods with inadequate basis sets have limitations in qualitatively and quantitatively reproducing reliable results. The hybrid density functional theory method, B3LYP with a double-ζ quality basis set, is found to be a good computational choice to model these compounds.[14] Therefore, only B3LYP/6-31G* geometries and energies are considered in the study, unless specified otherwise. All the calculations were done using Gaussian 94 suite of programs.[15]

For corannulene (**1**), monobenzocorannulene (**2**), and dibenzo[*a*,*g*]corannulene (**4**) the flat structures corre-

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(1) (a) Burgi, H. B.; Dubler-Steudle, K. C. *J. Am. Chem. Soc.* **1988**, *110*, 4953−4957. (b) Burgi, H. B. *Acta Crystallogr.* **1998**, *A54*, 873−885. (c) Burgi, H. B.; Dunitz, J. D. *Structure Correlation*; VCH: Weinheim, New York, 1994.

(2) Seiders, T. J.; Baldridge, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517−525.

(3) Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2001**, *66*, 6523−6530.

(4) (a) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (b) Mehta, G.; Panda, G. *PINSA-A: Proc. Indian Natl. Sci. Acad., Part A* **1998**, *64*, 587−608. (c) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

(5) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242.

(6) (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755. (b) Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2000**, *65*, 5360−5370.

(7) (a) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339−343. (b) Clayton, M. D.; Rabideau, P. W. *Tetrahedron Lett.* **1997**, *38*, 741−744.

(8) (a) Seiders, T. J.; Baldridge, K. K.; Elliot, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439−7440. (b) Seiders, T. J.; Elliot, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

(9) (a) Sastry, G. N.; Rao, H. S. P.; Bednarek, P.; Priyakumar, U. D. *Chem. Commun.* **2000**, 843−844. (b) Sastry, G. N.; Priyakumar, U. D. *J. Chem. Soc., Perkin Trans. 2* **2001**, 30−40.

(10) (a) Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. *J. Chem. Soc., Perkin Trans. 2* **2002**, 94−101. (b) Dinadayalane, T. C.; Sastry, G. N. *Tetrahedron Lett.* **2001**, *42*, 6421−6423. (c) Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2001**, *42*, 1379−1381.

(11) (a) Weitz, A.; Shabtai, E.; Rabinovitz, M.; Bratcher, M. S.; McComas, C. C.; Best, M. D.; Scott, L. T. *Chem. Eur. J.* **1998**, *4*, 234−239. (b) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430. (c) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300.

(12) Mehta, G.; Sarma, P. V. V. S. *Chem. Commun.* **2000**, 19−20.

(13) Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. *THEOCHEM* **2001**, *543*, 1−10.

(14) (a) Biedermann, P. U.; Pogodin, S.; Agranat, I. *J. Org. Chem.* **1999**, *64*, 3655−3662. (b) Priyakumar, U. D.; Sastry, G. N. *J. Phys. Chem. A* **2001**, *105*, 4488−4494. (c) Dinadayalane, T. C.; Sastry, G. N. *THEOCHEM* **2002**, *579*, 63−72.

10.1021/jo0255072 CCC: $22.00

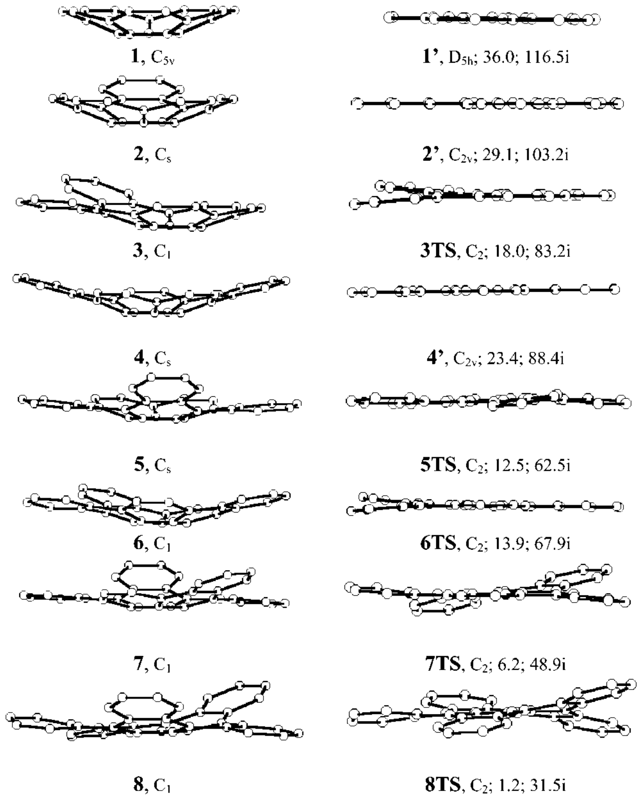

Figure 1. B3LYP/6-31G* optimized structures of minima and bowl-to-bowl inversion transition states along with the bowl-to-bowl inversion barriers (in kJ mol^{-1}). The magnitude of imaginary frequencies obtained for the transition states are given at the HF/3-21G level.

spond to the bowl-to-bowl inversion transition states (Figure 1). In contrast, for the rest of the benzocorannulenes **3** and **5**−**8** the flat structures correspond to the higher order saddle points, and in each of these cases the true transition state corresponding to the bowl-to-bowl inversion along with the minima were characterized.[16]

The three-dimensional optimized geometries of benzocorannulenes were very ruffled and they are far from a bowl structure. Therefore, unambiguous definition of bowl depth is not possible. Haddon's POAV (π-orbital axis vector) angle[17] was shown to be an effective measurement to gauge the pyramidalization at a given sp^2 center, and we have taken the average of the hub-POAV as an idealized description of curvature in benzocorannulenes.[18] Thus, we seek to explore the structure−energy relationships between the ϕ and the inversion barriers. Table 1 gives the relative energies of the minimum energy bowl structures, the flat structures, and the transition states for bowl-to-bowl inversion where the flat structure corresponds to a higher order saddle point. All POAV angles at the hub positions for the bowl structures and the values of ϕ are also given in Table 1. In all cases, where two benzene rings are annelated adjacent to each other, the corresponding flat structure was characterized as a higher order saddle point. One of these imaginary frequencies corresponds to the bowl-to-bowl inversion, and the others are originated as a result of the presence of *peri*-hydrogen repulsions. The scaled enthalpy correc-

Table 1. Relative Energies (ΔE) Obtained at HF/3-21G and B3LYP/6-31G* Levels and Enthalpy Correction (ΔH) Values at HF/3-21G Level for All Structures Considered[a]

	HF/3-21G		B3LYP/6-31G*		
structure	ΔE	ΔH^b	ΔE	POAV angles at hub	ϕ^c
1 (C_{5v})	0.0	0.0	0.0	98.1	8.1
1′ (D_{5h})	44.0	−0.5	36.0		
2 (C_s)	0.0	0.0	0.0	97.7, 97.8, 97.7	7.8
2′ (C_{2v})	36.3	−0.7	29.1		
3 (C_1)	0.0	0.0	0.0	97.0, 96.6, 96.8, 97.1, 97.0	6.9
3′ (C_{2v})	22.8 (2)	−2.9	18.8		
3TS (C_2)	22.7	−0.7	18.0		
4 (C_s)	0.0	0.0	0.0	97.3, 97.3, 97.4	7.3
4′ (C_{2v})	29.8	−0.8	23.4		
5 (C_s)	0.0	0.0	0.0	96.6, 95.8, 96.4	6.3
5′ (C_{2v})	18.6 (3)	−4.7	15.7		
5TS (C_2)	17.4	−0.6	12.5		
6 (C$_1$)	0.0	0.0	0.0	96.8, 96.3, 96.3, 96.7, 96.6	6.5
6′ (C_{2v})	18.1 (2)	−3.0	14.8		
6TS (C_2)	18.0	−0.9	13.9		
7 (C_1)	0.0	0.0	0.0	95.8, 95.2, 95.2, 95.5, 95.2	5.4
7′ (C_{2v})	20.8 (4)	−6.6	18.7		
7TS (C_2)	9.2	−0.9	6.2		
8 (C_1)	0.0	0.0	0.0	93.8, 93.9, 93.9, 93.3, 94.2	3.8
8′ (D_{5h})	43.5 (5)	−7.6	40.0		
8TS (C$_2$)	3.0	−1.2	1.2		

[a] The energies are given in kJ mol^{-1}. The number of imaginary frequencies at the HF/3-21G level for the higher order saddle points of flat structures are given in parentheses. The POAV angles (in deg) at hub positions for all of the minima obtained at the B3LYP/6-31G* level are also given. [b] Uniformly scaled by a factor of 0.8929. [c] Average of hub POAV angles − 90.0.

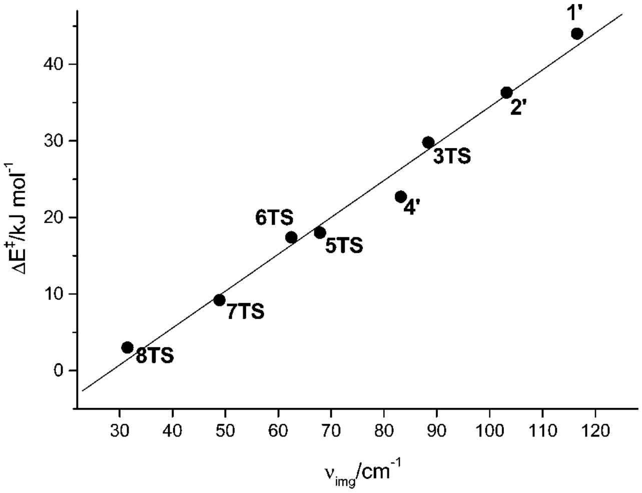

Figure 2. The magnitude of the imaginary frequency obtained for the transition state plotted against the bowl-to-bowl inversion barrier at the HF/3-21G level.

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(15) *Gaussian 94*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; 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, Inc.: Pittsburgh, PA, 1995.

(16) In the case of **5** there exists more than one minima on the potential energy surface; however, all of them are within one-fourth kJ/mol. In such case only the global minima is reported.

(17) (a) Haddon, R. C. POAV3, Release 3.0, 1993. (b) Haddon, R. C. *J. Phys. Chem.* **1987**, *91*, 3719−3720. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837−2843. (d) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389.

(18) ϕ is obtained by taking the average of POAV(hub) − 90.

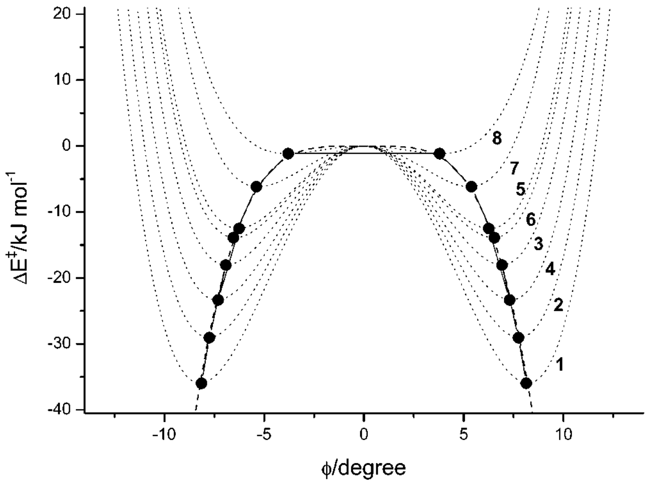

Figure 3. Plot showing the correlation of ϕ and the bowl-to-bowl inversion barrier (continuous line) at the B3LYP/6-31G* level.[18] The thick dotted line is fit with a quartic function and the dotted lines with a mixed quartic/quadratic function. The continuous line corresponds to the computed results.

tion values for all of the stationary points, using a scaling factor of 0.8929, are also given.[19] Clearly, there is a continual decrease in the inversion barrier, as the number of annelated benzene rings increases. The optimized geometries of the minima and the bowl-to-bowl inversion transition states along with the inversion barriers and the magnitudes of the imaginary frequency at the transition state are given in Figure 1. The annelated benzene rings in the pentabenzocorannulenes are like the blades of a fan, and these rings are expected to undergo facile flipping following the bowl-to-bowl inversion mode. Figure 1 indicates that the magnitude of the imaginary frequency gradually decreases as the number of annelated benzene rings increases. Also, there is a linear relationship between the magnitude of the imaginary frequency and the inversion barrier (Figure 2).

We are able to get a good fit with the double-well potential, which is a mixed quartic−quadratic function, eq 1. This reduces to a simple quartic potential when the inversion barrier is zero. Figure 3 depicts the plot of the inversion barrier ($\Delta E^{\ddagger}$) versus ϕ, which is virtually identical with the equation used in previous studies.[1]

$$\Delta E^{\ddagger} = a\phi^{4} - b\phi^{2} \qquad (1)$$

It is important to note that the quartic potential curve was very shallow, which indicates that a big change in the curvature causes little change in the energy in cases where the curvature is very low. Our results are in good agreement with those of Marcinow et al., who have shown that benzannelation significantly flattens the corannulene skeleton in cyclopentacorannulene skeleton.[20] Therefore, flattening the buckybowl skeleton upon benzannelation may be taken as a general signature.

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Supporting Information Available: Tables of the total and relative energies at B3LYP/6-31G*//HF/3-21G, HF/3-21G, and semiempirical (MNDO, AM1 and PM3) levels for all species considered; the total energies and optimized Cartesian coordinates at B3LYP/6-31G* level for all structures; figures showing the correlation of ϕ and bowl-to-bowl inversion barriers obtained at HF/3-21G, MNDO, AM1 and PM3 levels; and figures showing the optimized geometries and skeletons. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(20) Marcinow, Z.; Sygula, A.; Ellern, A.; Rabideau, P. W. *Org. Lett.* **2001**, *3*, 3527−3529.