Tailoring the curvature, bowl rigidity and stability of heterobuckybowls: Theoretical design of synthetic strategies towards heterosumanenes

U. Deva Priyakumar and G. Narahari Sastry

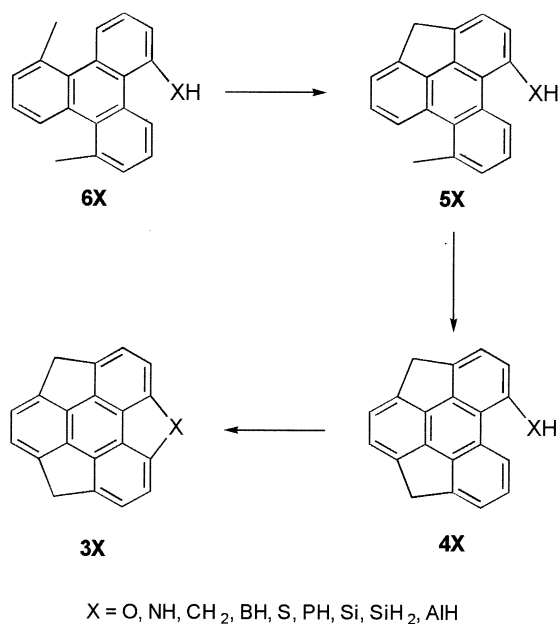*Department of Chemistry, Pondicherry University, Pondicherry India*

Quantum mechanical calculations predict that larger heteroatom substituents on the periphery increase the feasibility of the crucial third ring closure in sumanene and are responsible for the accompanying modulations in the curvature, rigidity, stability and some of the physicochemical properties of the resulting heterosumanenes. Systematic application of semiempirical, ab initio, and DFT methods reveal that the qualitative trends obtained and our principal conclusions are independent of level of theory, albeit with minor quantitative differences. © 2001 by Elsevier Science Inc.

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The unique structural feature of curvature in fullerenes and the successful application of their derivatives in wide-ranging areas, from material science to medicine, has made them one of the most important classes of compounds in the last decade.[1] Buckybowls, which are obtained by dissecting the fullerene structure and satisfying the dangling carbon valencies with hydrogens, mimic the structural properties of buckyballs and are expected to possess some of the physicochemical properties unique to the latter.[2,3] The most readily recognizable buckybowls, which form basic structural motifs of C_{60}, are corannulene (**1**) and sumanene (**2**).[2–6] Corannulene (**1**), extensively studied both theoretically and experimentally, exhibits rapid bowl-to-bowl inversion while synthetic efforts toward sumanene (**2**) have not yet met with success.[5,6] One of the strategies adopted by Mehta et al. is the sequential placement of methylene bridges starting from C_3-1,5,9 trimethyltriphenylene (**6CH$_2$**), which successfully leads to mono- (**5CH$_2$**)

1, C$_{5V}$ **2, C$_{3V}$**

Scheme 1.

6X   **5X**

3X   **4X**

X = O, NH, CH$_2$, BH, S, PH, Si, SiH$_2$, AlH
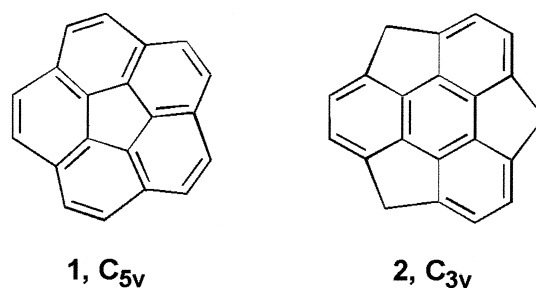
Scheme 2.

Corresponding author: Dr. G. Narahari Sastry, Department of Chemistry, Pondicherry University, Pondicherry - 605 014, India. Tel.: 0091-413-250 323; fax: 0091-413-655 211.

E-mail address: gnsastry@yahoo.com (G.N. Sastry)

Table 1. The strain energy (ΔE_{strain}) build up in the final step, pyramidalization angles[a] (Φ in degrees), bowl-to-bowl inversion barriers ($\Delta E^{\ddagger}$) and thermodynamic stabilities (ΔE) at MNDO, AM1 and PM3 levels. All the energies are given in kcal mol^{-1} (1 kcal = 4.184 kJ)

Structure	MNDO				AM1				PM3			
	ΔE_{strain}	Φ^a	$\Delta E^{\ddagger}$	ΔE	ΔE_{strain}	Φ^a	$\Delta E^{\ddagger}$	ΔE	ΔE_{strain}	Φ^a	$\Delta E^{\ddagger}$	ΔE
3O	75.9	9.6	43.2	9.2	82.5	10.2	52.1	28.8	67.3	10.1	46.5	23.2
3NH	57.1	8.7	34.3	18.1	66.5	9.6	45.4	19.6	48.0	9.3	37.2	14.8
3CH$_2$ (2)	47.2	7.5	24.4	0.0	50.5	8.6	35.0	0.0	45.0	8.5	31.4	0.0
3BH	35.3	6.6	18.7	−11.3	39.3	7.5	25.8	−12.0	b	b	b	b
3S	32.2	6.4	17.6	−0.3	36.9	7.2	23.7	3.0	29.6	6.6	17.9	1.2
3PH	21.6	5.9	13.8	−10.4	26.6	6.6	18.3	−8.9	20.0	5.3	10.3	−9.6
3Si	12.4	4.7	8.4	−24.7	6.6	5.4	11.3	−25.3	15.6	5.5	10.9	−28.0
3SiH$_2$	12.8	4.3	7.2	−24.7	13.6	5.0	10.0	−21.3	12.6	5.1	9.7	−22.2
3AlH	9.9	3.7	5.2	−26.6	13.2	4.4	7.8	−27.4	−0.2	3.9	5.2	−14.9

[a]Φ (pyramidalization angle) is the average of all the ϕs of hub atoms, $\phi = 360 - (\theta_1 + \theta_2 + \theta_3)$, where θ_1, θ_2 and θ_3 are the angles around a given hub atom.
[b]PM3 parameters for Boron are not available to us.

Table 2. The strain energy (ΔE_{strain}) build up in the final step, pyramidalization angles[a] (Φ in degrees), bowl-to-bowl inversion barriers ($\Delta E^{\ddagger}$) and thermodynamic stabilities (ΔE) at HF/3-21G and B3LYP/6-31G*[b] levels. All the energies are given in kcal mol^{-1}

Structure	HF/3-21G				B3LYP[b]		
	ΔE_{strain}	ϕ^a	$\Delta E^{\ddagger}$	ΔE	ΔE_{strain}	$\Delta E^{\ddagger}$	ΔE
3O	74.7	8.5	30.1	20.9	61.8	30.2	22.2
3NH	59.1	7.8	24.6	21.3	46.5	23.8	20.1
3CH$_2$ (2)	58.1	6.9	18.3	0.0	51.8	16.8	0.0
3BH	39.2	6.0	13.3	−17.1	36.8	12.8	−18.3
3S	39.0	4.8	8.4	−3.3	35.3	9.5	4.0
3PH	31.9	4.2	6.2	−14.3	32.2	6.8	−9.1
3Si	17.7	4.0	5.3	−26.4	21.6	5.7	−24.6
3SiH$_2$	26.4	3.4	3.8	−22.7	27.4	3.9	−19.0
3AlH	18.9	2.1	1.4	−31.0	21.5	1.2	−27.6

[a]Φ (pyramidalization angle) is the average of all the ϕs of hub atoms, $\phi = 360 - (\theta_1 + \theta_2 + \theta_3)$, where θ_1, θ_2 and θ_3 are the angles around a given hub atom.
[b]Single point energies on HF/3-21G optimized geometries.

and dibridged (**4CH$_2$**) derivatives (Scheme 1).[5,6] Attempts toward the crucial third ring closure were futile and the reasons were traced to high strain energy buildup.[4,5] Recently, we have reported that proper placement of heteroatoms on buckybowls has a significant impact on the stability, curvature, and inversion barrier in corannulenes.[7,8] Thus, interspersing heteroatoms in the buckybowl skeleton seems to be the most effective way of modulating the curvature and the consequent physicochemical properties of heterobuckybowls.[7–11] In cases where high strain energy buildup prevents the formation of desired buckybowls, optimal placement of heteroatom substituents can potentially facilitate the formation of the skeleton.

This article aims to predict achievable synthetic strategies towards heterosumanene, where one of the bridged methylene groups is replaced by a heteroatom after scrutinizing the underlying difficulties in the synthesis of sumanene (**2**). Thus, we only consider the effect of substitution at one site on the periphery of the bowl; previous results indicate that substitu-

tion at the hub is expected to give exactly opposite results.[7,8] As the crux of the problem lies in the formation of the third bridge, we explore the possibility of reducing the strain energy buildup in this step, adopting the strategy of placing a heterobridge that might facilitate the ring closure. Thus, theoretical calculations are performed to understand the variations in strain energy buildup in the final step, which effectively determines the synthetic viability of heterosumanene. Also, we investigate the utility of this methodology in tailoring the curvature and the consequent physicochemical properties of heterosumanenes (**3X**).

All calculations are done using the Gaussian 94 suite of programs.[12] Initially, all the structures considered in the study are subjected to geometry optimizations using the three popular semiempirical methods, namely MNDO,[13] AM1,[14] and PM3.[15,16] The nature of all stationary points are confirmed by frequency calculations. The geometries of dibridged structures (**4X**) and the bowls (**3X**) are fully optimized and characterized
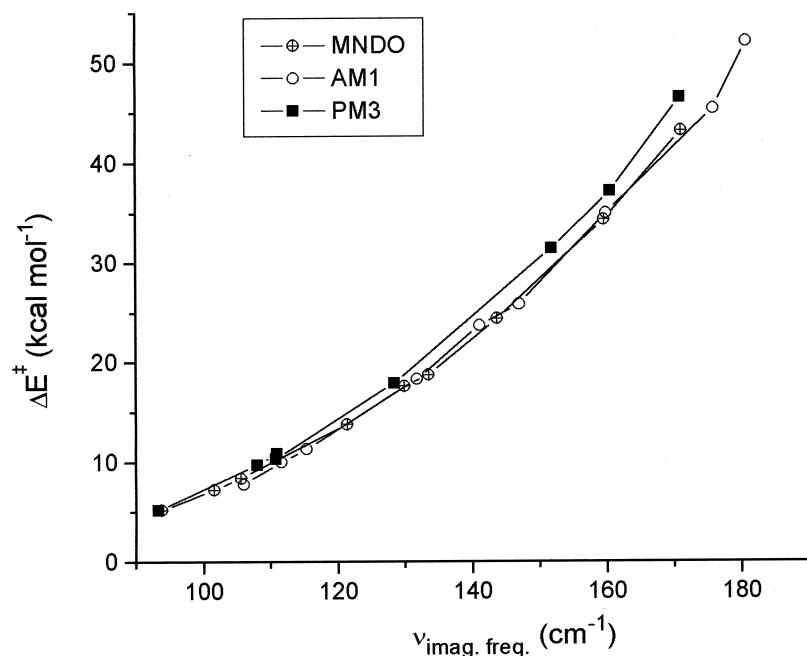
Figure 1. The plot of $\Delta E^{\ddagger}$ (bowl-to-bowl inversion barrier) versus the imaginary frequency at MNDO, AM1 and PM3 levels.

as minima. Most of the planar forms of heterosumanenes (**3X-TS**) gave rise to one imaginary frequency and the associated normal mode direction corresponds to bowl-to-bowl inversion. However, when X = NH and PH (also for AlH at the MNDO level), the idealized C_{2v}-planar geometry was characterized as the second order saddle point; while one of the imaginary modes corresponds to bowl-to-bowl inversion, the other one corresponds to out-of-plane bending of the X-H group. Correct bowl-to-bowl transition states in such cases are obtained by doing optimizations without any symmetry constraints. After unambiguously characterizing the minima and transition state structures in all cases, the geometries are further refined at HF/3-21G level. Finally, single-point energy calculations were done at B3LYP level with 6-31G* basis set.

The strain energy buildup in the third step (ΔE_{strain}), pyramidalization angle (Φ), bowl-to-bowl inversion barriers ($\Delta E^{\ddagger}$), and the thermodynamic stability (ΔE) of the resulting heterobuckybowls at the semiempirical levels are given in Table 1. The strain energy (ΔE_{strain}) is gauged by the heats of the reactions, **4X** $\rightarrow$ **3X** + H$_2$, as done by Sastry et al.[4] The computed results obtained at HF/3-21G and B3LYP/6-31G* levels are depicted in Table 2. The substituents are arranged in increasing order of atomic radii and consequently in the increasing order of the C-X bond length. First, the strain energy for the crucial third step decreases as the size of the substituent increases. Comparison of the theoretical results at various levels of sophistication (Table 1 and Table 2) indicates that the

principle conclusions drawn are independent of theoretical method employed.

Clearly, when we consider bowls with the same size bases, the bowls with longer circumference are flatter bowls than those with shorter circumference. Thus, a larger substituent, which increases the circumference, flattens the bowl and the one with a smaller size increases the curvature, which makes the bowl deeper. Consequently, larger substituents substantially reduce the strain energy buildup for the third ring closure, and the resultant heterobuckybowls are less curved. We also note that less curved buckybowls are more flexible with lower bowl-to-bowl inversion barriers. In contrast, smaller substituents at this peripheral position make the formation of the third bridge (Scheme 2) more difficult and increase the bowl depth and rigidity. The pyramidalization angle (Φ, see Table 1) was found to be a reliable quantitative measure for the curvature and bowl depth of the heterobuckybowls.[7,8] Table 1 and Table 2 clearly establish that buckybowls with larger heteroatoms substituted at the vertex position are significantly flatter (smaller Φ) than those substituted with smaller heteroatoms. The magnitude of the imaginary frequency linearly correlates with the activation barrier (Figure 1). Thus, a flexible bowl maintains a smaller pyramidalization angle and smaller magnitude of frequency compared with a rigid bowl, as shown in Table 1, Table 2, and Figure 1.

Therefore, the size of the substituent is exclusively responsible for modulating the curvature and the consequent physi-
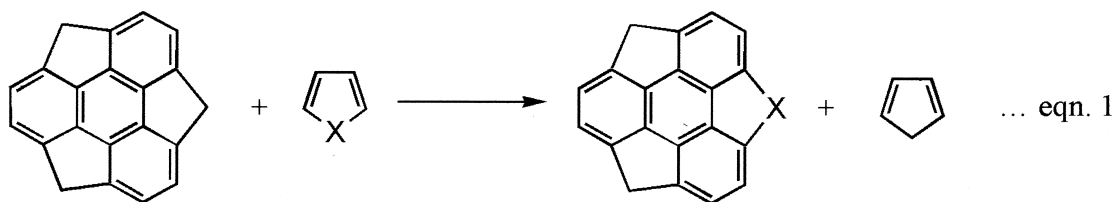
Scheme 3.

cochemical properties. The effect of heteroatom substitution on thermodynamic stability (ΔE) compared with the unsubstituted isomer is estimated using the following isodesmic equation 1 (Scheme 3). Thermodynamic stabilities of the monohetero-sumanenes are also controlled by the size of the substituent, as larger substituents diminish the strain and impart more stability. The substituted sumanenes, **3X**, may be taken as precursors for further careful ring expansion and ring closure protocols to accomplish the synthesis of elusive sumanene (**2**).

In summary, this article clearly establishes that the curvature, thermodynamic stability, and rigidity of the heterobuckybowls as well as ease of their synthesis itself, are exclusively determined by the size of heteroatom and its site of occupancy.

ACKNOWLEDGMENTS

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