ChemComm

Effect of substitution on the curvature and bowl-to-bowl inversion barrier of bucky-bowls. Study of mono-substituted corannulenes ($C_{19}XH_{10}$, X = B^-, N^+, P^+ and Si)

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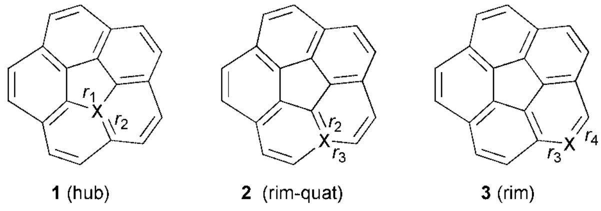
Received (in Cambridge, UK) 1st February 2000, Accepted 5th April 2000
Published on the Web 28th April 2000

***Ab initio* MO and DFT calculations predict that replacement of a single carbon by an isoelectronic species on the corannulene skeleton can effectively arrest the bowl shape or flatten it and the bowl rigidity, curvature and relative stabilties of the positional isomers are solely controlled by the size of the substituent and site of substitution.**

Corannulene, $C_{20}H_{10}$, which forms the 'polar cap' of the buckminister-fullerene is the simplest bucky-bowl, where the warping of sp^2-carbon surface enforces the molecule to adopt a bowl-like geometry. The curvature in bucky-bowls results in two distinct surfaces, convex and concave, and alters the properties such as dipole moment, ionization potential, metal binding *etc.*[1] Despite the substantial curvature present in corannulene, it is highly fluxional and the bowl-to-bowl inversion is rapid,[2,3] the resulting non-rigidity of its bowl structure is in contrast to that of fullerenes. Our interest lies in finding out simpler modifications that are required to effectively 'lock' the bowl geometry of corannulene. Previous studies indicate that locking the bowl structure requires the addition of one more fused five-membered ring.[4] Construction of a cyclophane bridge seems to be another strategy to lock the bowl structure.[5] Substitution on corannulene is not expected to have any significant effect on the rigidity or inversion barrier.[1b] It occurred to us that the simplest of the strategies might be to look at the replacement of skeletal carbon atoms on the corannulene by an electronically equivalent heteroatom substituent, such as X = B^-, N^+, P^+ or Si. Accordingly, as a first step mono-substitutions have been placed at three unique positions of corannulene namely at hub (**1**), rim-quat (**2**) and rim (**3**).

The geometries of all the structures of substituted corannulenes depicted in Scheme 1 are optimized at *ab initio* Hartree–Fock level using 3-21G basis set using the GAUSSIAN 94 program package.[6] Frequency calculations confirm that all the bowl structures are minima and planar structures are transition states corresponding to bowl-to-bowl inversion.† The effects of inclusion of electron correlation and improving the basis set quality on energetics are estimated by performing single point calculations using the B3LYP procedure with the 6-31G* basis set.



	a	b	c	d
X	B^-	N^+	P^+	Si

Scheme 1

The relative energies of the positional isomers in their minimum energy conformation as well as the TS for bowl-to-bowl inversions are given in Table 1. The reference structure is taken as the hub (**1**) substituted minimum energy isomer, which in general has a non-planar bowl-like geometry. A strong preference is shown to occupy the rim position (**3**) followed by rim-quat (**2**) and hub (**1**) positions for substituents, where X = B^-, P^+, or Si. In contrast, a complete reversal of the relative stabilities of positional isomers is seen for X = N^+, which results in the following increasing order of stability, **3b** < **2b** < **1b**. The thermodynamics of the positional isomers seems to be solely controlled by the size of the substituent. In this context, the C–X bond length is taken to gauge the size of X, as C–B, C–P and C–Si bonds are longer and C–N is shorter than the C–C bond, B^-, P^+ and Si are classified as larger substituents and N^+ as a smaller substituent. Accordingly, larger heteroatom substituents when compared to C prefer to occupy the rim position and smaller ones prefer the hub position, and this preference seem to be independent of the charge present on the system, as well as the electronegativity of the substituent. The relative stabilities of these positional isomers may be directly traced to the angular strain caused by the substituent, *i.e.* a larger atom at hub position will bring in more strain in the corannulene skeleton where as it relieves the strain at the terminal position. Accordingly, larger atoms prefer to be substituted at the rim (**3**) position, while the smaller at the hub (**1**) position. The curvature of the minimum energy bowl structures and the alteration of C–X bond lengths when going from the bowl structure to the transition state, which are key geometric changes, are depicted

Table 1 Relative energies (kcal mol^{-1}) of the various structures. Total energies are given in E_h and the frequencies in cm^{-1}

	HF/3-31G			B3LYP/6-31G*[a]	
	Bowl	Planar-TS	Imaginary frequency	Bowl	Planar-TS
1a	0.0 (−745.80417)	22.80	140.0i	0.0 (−754.91705)	22.03
2a	−20.15	−11.86	107.2i	−18.26	−11.42
3a	−17.34	−12.03	95.1i	−20.36	−16.08
1b	0.0 (−775.21444)	3.30	83.2i	0.0 (−784.58523)	4.36
2b	15.43	25.89	116.1i	16.12	26.20
3b	13.81	26.79	124.0i	13.17	24.82
1c	0.0 (−1059.97337)	88.32	184.2i	0.0 (−1071.10510)	67.57
2c	−14.83	−6.00	102.6i	−14.44	−4.66
3c[b]	−21.04	−12.66	127.9i, 69.1i	−19.18	−14.70
1d	0.0 (−1008.55907)	90.22	188.9i	0.0 (−1019.43484)	74.33
2d	−45.14	−39.56	93.4i	−39.33	−33.55
3d	−54.04	−53.20	57.3i	−52.12	−51.41

[a] Single point calculations at HF optimized geometries. [b] **3c** shows two imaginary frequencies of which the first represents the bowl-to-bowl inversion.

Table 2 The pyramidalization angle ϕ (°) and the changes in C–X bond lengths (r_n/Å) going from the bowl structure to the transition state at the HF/ 3-21G level

	$\phi^{a,b}$			$\mathbf{1}^c$		$\mathbf{2}^c$		$\mathbf{3}^c$	
	1	**2**	**3**	r_1	r_2	r_2	r_3	r_3	r_4
a	13.5	9.3	4.0	$1.513 \rightarrow 1.468$	$1.457 \rightarrow 1.420$	$1.469 \rightarrow 1.446$	$1.579 \rightarrow 1.604$	$1.581 \rightarrow 1.604$	$1.513 \rightarrow 1.527$
b	2.5	3.5	7.2	$1.376 \rightarrow 1.363$	$1.331 \rightarrow 1.323$	$1.313 \rightarrow 1.296$	$1.418 \rightarrow 1.433$	$1.396 \rightarrow 1.408$	$1.343 \rightarrow 1.361$
c	78.0	2.7	3.0	$1.815 \rightarrow 1.641$	$1.812 \rightarrow 1.606$	$1.707 \rightarrow 1.658$	$1.821 \rightarrow 1.824$	$1.859 \rightarrow 1.799$	$1.860 \rightarrow 1.742$
d	78.1	6.6	1.5	$1.852 \rightarrow 1.692$	$1.816 \rightarrow 1.645$	$1.716 \rightarrow 1.734$	$1.882 \rightarrow 1.858$	$1.860 \rightarrow 1.868$	$1.778 \rightarrow 1.784$

[a] The angle ϕ which is a measure of pyramidalization is defined as $\phi = 360 - (\theta_1 + \theta_2 + \theta_3)$ where θ_1, θ_2 and θ_3 are the bond angles around the unique hub atom, which is X in **1** and C closest to X in **2** and **3**. [b] $\phi = 6.4$ for corannulene. [c] Unsubstituted corannulene shows: $r_1 = 1.415 \rightarrow 1.393$, $r_2 = 1.359 \rightarrow 1343$, $r_3 = 1.449 \rightarrow 1.467$, $r_4 = 1.368 \rightarrow 1.383$.

in Table 2. The curvature especially of hub substituted isomers, depends on the pyramidalization tendency of the substituent. Thus, second row substituents (P^+ and Si) gives deeper and more rigid bowls compared to their first row analogs (B^- and N^+). This reflects the fact that the structures with higher barriers show greater changes in C–X bond lengths and *vice versa*. The values of ϕ ranging from 1.5 to 78.1° indicate a broad spectrum of variations in the curvatures of the bowl isomers considered in the present study.

The most interesting finding is the effect of substitution on bowl-to-bowl inversion barriers. A clear qualitative difference between the substituents with larger atomic size than carbon and those with smaller atomic size is noted. Thus, when $X = B^-$, P^+ or Si, the inversion barrier is very high for **1** and decreases while going to rim-quat (**2**) and rim (**3**) substituted ones. In sharp contrast N^+ substituted at hub (**1**) position, **1b**, substantially reduces the bowl-to-bowl inversion barrier while the rim (**3**) substituted isomer, **3b**, doubles the inversion barrier compared to that of the pristine corannulene molecule. Thus, mono-substitution with larger substituents at hub (**1**) positions rigidifies the bowl, while at rim (**3**) position makes it more fluxional and flatter compared to the parent corannulene. The substitution by smaller substituents has exactly the opposite effect with regards to bowl-to-bowl inversion. The inversion barrier for all the rim-quat substituted (**2**) positional isomers, seems to be less sensitive to the nature of substituent and in all cases the barrier is of similar magnitude to that of corannulene.

Interestingly, the isomer with largest inversion barrier is found to be the least stable and possesses the highest ϕ indicating the maximum curvature. This highlights the interconnectivity of the curvature, stability and inversion barriers in this series of isomers. Therefore, effectively the size and site of substitution decides the curvature, stability and bowl-to-bowl inversion barriers. Thus, Si, the largest substituent considered, when substituted at hub (**1**) position gives the most rigid bowl and leads to an increase in the inversion barrier by almost sevenfold compared to that of unsubstituted corannulene! In contrast, **3d**, the rim (**3**) substituted Si isomer yields the least curved surface with an insignificant inversion barrier. The magnitude of the imaginary frequency seems to give a good measure of the inversion barrier, thus the highest value of 188.9i cm^{-1} and lowest of 53.2i cm^{-1} correspond to the structures with highest (**1d**) and lowest (**3d**) bowl-to-bowl inversion barriers, respectively.

The stabilities of the mono-substituted corannulenes are estimated using the isodesmic equation eqn. (1), in which the most stable isomer is considered in each case (**2a**, **1b**, **3c** and **3d**). C_5XH_6 and C_6H_6 represent the mono- and un-substituted benzene ring respectively in eqn. (1). The results indicate that, except for **1c** (P^+) and **1d** (Si), in all other isomers the replacement of a C by the isoelectronic X is more feasible (thermodynamically) in corannulene than in benzene.‡

$$C_{20}H_{10} + C_5XH_6 \longrightarrow C_{19}XH_{10} + C_6H_6 \qquad (1)$$

X	a(2)	b(1)	c(3)	d(3)
ΔE/kcal mol^{-1}	−31.6	−19.8	−30.1	−21.6

The present study indicates that in mono-substituted corannulenes, the relative stabilities of positional isomers, curvature and bowl-to-bowl inversion barriers are interconnected and all of which seem to be mainly controlled by the size of the substituent. Rational synthetic design of fullerenes in a stepwise manner is severely hampered owing to the enormous strain energy build-up in the skeleton which is chiefly attributed to high incremental jumps in the strain as the curvature increases.[7] A rigid bowl with a substantial built-in strain might be a better precursor for further building-up of the cage structure, compared to a flat or flexible bowl. In this regard, P^+ or Si substituted corannulenes at **1** position promise to be good rigid frameworks for further fusing of five/six-membered rings *en route* to hetero-fullerene cages.

We thank UGC, New Delhi and AICTE for financial assistance.

Notes and references

† The planar isomer **3c** gives two imaginary frequencies in the force calculation. That with higher magnitude corresponds to bowl-to-bowl inversion, while the other much lower frequencies (69.1i cm^{-1}) can be ignored and the planar structure can be considered as a TS for all practical purposes.

‡ The energetics given are at HF/3-21G level.

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