Through-Bond Interactions

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Stereoelectronic Effect of Curved Aromatic Structures: Favoring the Unexpected *endo* Conformation of Benzylic-Substituted Sumanene**

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Since the discovery of fullerene and carbon nanotubes, curved aromatic compounds, including bowl-shaped buckybowls, have elicited much attention in science and industry. One principal question regarding these curved aromatic compounds revolves around the differences between the concave face and the convex face. The curvature affects the nature of the two faces, thus resulting in differences of the through-space and through-bond effects. The latter would appear as a stereoelectronic effect between the curved aromatic structure and a connected functional group. In general, the stereoelectronic effect is reflected in the conformational stability and chemical reactivity of a molecule.[1] Therefore, it is important to understand such conformations or chemical reactivities as a consequence of stereoelectronic effects. The interpretation of the stereoelectronic effect of curved aromatic compounds would lead to understanding the differences of the two faces. However, no example of stereoelectronic effects of curved aromatic compounds have been found and studied to date. We have found the first example of the stereoelectronic effect of a curved aromatic structure, an effect which dominates the *endo*/*exo*-R conformational stability of benzylic-substituted sumanenes (**1**; Figure 1). Herein we report the experimental observations and the theoretical investigations including natural bond orbital (NBO) analysis[2] to elucidate the stereoelectronic effect.

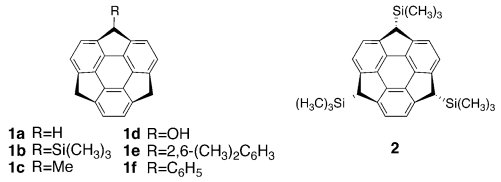

Figure 1. Benzylic-substituted sumanenes (**1**) and *cis*-tris(trimethylsilyl)sumanene (**2**).

Benzylic-substituted sumanenes (**1**) can adopt two conformers, *endo*-R-**1** and *exo*-R-**1**, which differ in the direction of the aromatic bowl shape, concave or convex, with respect to the substituent R (Figure 2A). The bowl can thermally

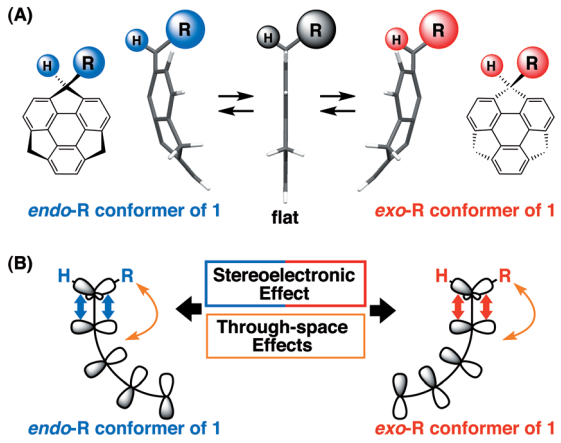

Figure 2. A) *endo*-R and *exo*-R conformers of benzylic-substituted sumanenes (**1**). B) Schematic showing the stereoelectronic effects and through-space effects between the bowl and the C-H or C-R moieties of **1**.

invert through a flat transition state and the bowl inversion energies of sumanenes are around 20 kcal mol^{-1}.[3] Therefore, the relative stability of *endo*-R-**1** versus *exo*-R-**1** is thermodynamically determined by the through-bond stereoelectronic effect or the through-space effects (such as steric repulsion, CH–π interaction), depending on the relative configuration between the bowl and the substituent R (Figure 2B).[4] The *exo*-R conformer of *cis*-tris(trimethylsilyl)-sumanene (**2**; Figure 1) was reported to be much more stable than the *endo*-R conformer because only the *exo*-R conformer was observed in the ^{1}H NMR spectrum.[5] We also confirmed that trimethysilylsumanene (**1b**) exists only in the *exo*-R conformation (Table 1). These results are reasonable, judging from the steric repulsion of the substituent by the nearby aromatic hydrogen atoms, as clearly seen in the optimized structure, shown in Figure 3A, from the DFT calculations [M06-2x/6-311++G(d,p)]. Thus, we presumed that repulsive steric hindrance governs the thermodynamic stability between *endo*-R-**1** and *exo*-R-**1** in general, and therefore resulting in *exo*-R-**1** being more stable than *endo*-R-**1** even with substituents other than R = Si(CH$_3$)$_3$. However, in

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Table 1: Experimental and calculated data for *endo*-R-**1** and *exo*-R-**1**.

Compound	R	Experimental *endo*-R/*exo*-R[a]	Conformer[b]	ΔE[c]	Calculated Conformer[d]	ΔE[e]	NBO analysis of C–H bond Conformer[f]	ΔE_{NBO}[g]
1a	H	–	–	–	–	–	–	−0.5
1b	$Si(CH_3)_2$	0:100	*exo*-R	–	*exo*-R	2.0	*exo*-R	4.4
1c	CH_3	81:19	*endo*-R	−0.9	*endo*-R	−1.4	*endo*-R	−1.1
1d	OH	90:10	*endo*-R	−1.3	*endo*-R	−2.3	*endo*-R	−0.9
1e	2,6-$(CH_3)_2C_6H_3$	82:18	*endo*-R	−0.9	*endo*-R	−4.6	*exo*-R	4.2
1f	C_6H_5	49:51	*endo*/*exo*-R	0.0	*endo*-R	−2.1	*endo*-R	−0.3

Experimental *endo*-R-**1**/*exo*-R-**1** ratio from ^{1}H NMR spectra and the energy difference, ΔE, between *endo*-R-**1** and *exo*-R-**1**. Calculated energy difference, ΔE, between *endo*-R-**1** and *exo*-R-**1** [M06-2x/6-311++G(d,p)]. The difference ΔE_{NBO} of hyperconjugation energies for the *exo* C–H bond in *endo*-R-**1** and the *endo* C–H bond in *exo*-R-**1** as determined by NBO analysis of **1** [M06-2x/6-311G(d,p)]; the favored conformers in each case are indicated.[a] ^{1}H NMR ratio in $CDCl_3$ (296 K). [b] Observed more-stable conformer. [c] $\Delta E = E$(*endo*-R) − E(*exo*-R) = −RT ln K kcal mol^{-1}, K: equilibrium constant between *endo*-R-**1** and *exo*-R-**1**. [d] More-stable conformer from calculations. [e] $\Delta E = E$(*endo*-R) − E(*exo*-R) kcal mol^{-1}. [f] More-stable conformer in NBO analysis. [g] $\Delta E_{NBO} = E_{NBO}$(*exo* C–H bond of *endo*-R-**1**)-E_{NBO}(*endo* C–H bond of *exo*-R-**1**) kcal mol^{-1}, E_{NBO}: hyperconjugation energy of *exo*/*endo* C–H bond of *endo*-R-**1** or *exo*-R-**1** by NBO analysis.

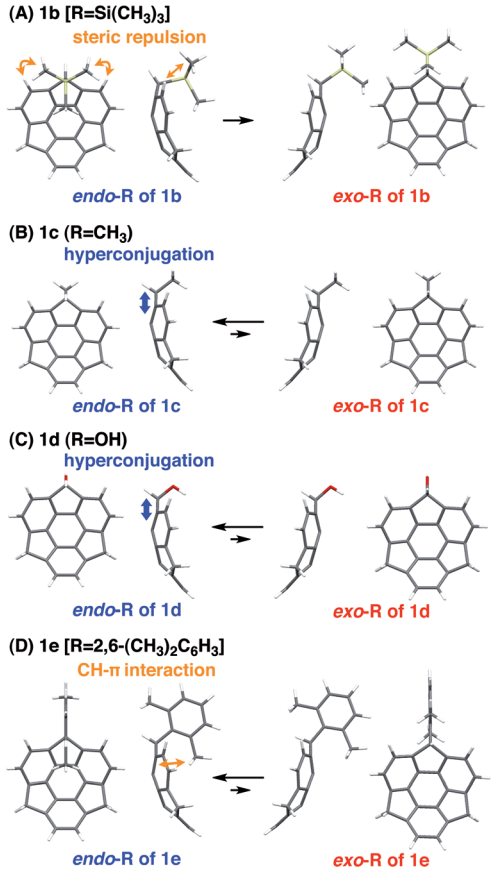

Figure 3. The *endo*-R and *exo*-R conformers of **1b**, **1c**, **1d**, and **1e** as determined by DFT calculations [M06-2x/6-311++G(d,p)].

spite our presumption, we recently discovered that methylsumanene (**1c**), hydroxysumanene (**1d**), and (2,6-dimethylphenyl)sumanene (**1e**)[6] favor the *endo*-R conformation over the *exo*-R conformation, and phenylsumanene (**1f**) shows an almost even ratio (Table 1). The *endo*-R conformer was more stable than the *exo*-R for **1c** (CH_3), **1d** (OH), and **1e** [2,6-$(CH_3)_2C_6H_3$] with $\Delta E = 0.9$, 1.3, and 0.9 kcal mol^{-1}, respectively. The optimized structures obtained from DFT calculations [M06-2x/6-311++G(d,p)] (Figures 3B–D) indicate that no steric factors favor the *endo*-R stability in **1c**, **1d**, and **1e**, however CH–π interactions between the substituent and the sumanene core could exist in **1e**, thus favoring the *endo*-R conformation.[7] M06-2x/6-311++G(d,p) calculations reproduced the relative conformational stability of **1a–e**, albeit with an overestimation of the *endo*-R stability in **1e** and **1f** (Table 1). These experimental and calculated results strongly indicate the existence of through-bond stereoelectronic effects in **1c** and **1d**, effect which favor the *endo*-R conformation.

For the elucidation of the stereoelectronic factors, we conducted NBO analysis of **1** [M06-2x/6-311G(d,p)]. After thorough analysis of the output results, we found that hyperconjugation of the benzylic methine C–H bond of **1** can be a factor controlling the conformation of **1** (Figure 2B, Table 1).[1c] The C–H bond possesses conjugation energy through hyperconjugation as a donor orbital to acceptor orbitals, mainly π* orbitals of the aromatic bowl. The strengths of the conjugation energies E_{NBO} of the *exo* and *endo* C–H bonds are different because of the difference of the acceptor π* orbitals in the concave and convex faces of the bowl. In the nonsubstituted **1a** (R = H), the conjugation energy, E_{NBO}, of the *exo* C–H bond of the methylene is 11.1 kcal mol^{-1} and that of the *endo* C–H bond is 10.6 kcal mol^{-1}. Therefore, the *exo* C–H bond has stronger hyperconjugation ($\Delta E_{NBO} = 0.5$ kcal mol^{-1}) than the *endo* C–H bond (Table 1). Similarly, the *exo* C–H bond of the *endo*-R conformer of **1c** (CH_3) and **1d** (OH) exhibits stronger hyperconjugation ($\Delta E_{NBO} = 1.1$ and 0.9 kcal mol^{-1}) than the *endo* C–H bond of the *exo*-R conformer. Therefore, this effect favors the *endo*-R conformer of **1c** and **1d**, and is consistent with the observed and calculated *endo*-R stabilities. We also considered other stereoelectronic effects from the NBO analysis, such as the conjugation of the orbitals of the OH group of **1d**. However, the conjugation energy of the lone-pair orbital or the O–H bond orbital of the OH group of **1d** as a donor orbital is almost equal in the *endo*-R and *exo*-R conformers, and does not support the *endo*-R stability. While the steric repulsion to favor the *exo*-R conformer in **1b** [R = $Si(CH_3)_3$] and the CH–π interaction to favor the *endo*-R

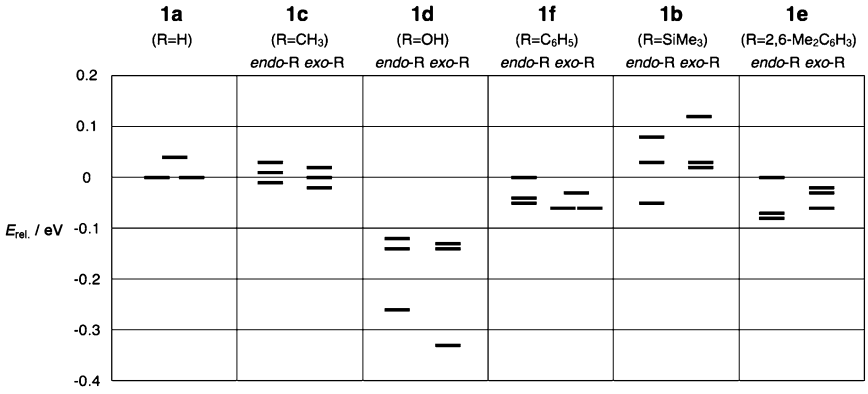

Figure 4. The energy levels of the π* orbitals (LUMO, LUMO + 1, LUMO + 2) of the *endo*-R and *exo*-R conformers of **1a–f** as determined by DFT calculations [M06-2x/6-311 + + G(d,p)]. Values in eV vs. LUMO of **1a**.

conformer in **1e** [R = 2,6-$(CH_3)_2C_6H_3$][7] are the controlling factors in determining the stable conformation, NBO analysis of **1b** and **1e** indicates that the hyperconjugation of the *endo* C–H bond is stronger than that of the *exo* C–H bond to favor the *exo*-R conformer (Table 1), and is opposite to what is indicated by NBO analysis for **1a**, **1c**, and **1d**.[8] In **1b**, NBO analysis indicates that the conjugation between the C-Si σ* orbital and π orbital also favors the *exo*-R conformer (2.2 kcal mol^{-1}).

It is also noteworthy that the difference in the stereoelectronic effects between the *endo*-R and *exo*-R conformers of **1** are reflected in the energy levels of the acceptor π* orbitals. Figure 4 shows the energy levels of LUMO, LUMO + 1, and LUMO + 2 orbitals of the *endo*-R and *exo*-R conformers of **1a–f** obtained by DFT calculations. In an overall trend, these π* orbitals of the *endo*-R conformers of **1c**, **1d**, and **1f** are higher in energy than those of the *exo*-R conformer as a result of a stronger interaction with the donor C-H orbital, whereas those of the *exo*-R conformers of **1b** and **1e** are higher than those of the *endo*-R conformers. These results are consistent with those of the NBO analysis (Table 1).

In conclusion, as the first example of the through-bond stereoelectronic effect of curved aromatic compounds, methylsumanene and hydroxysumanene were found to favor the unexpected *endo*-R conformation. Natural bond orbital (NBO) analysis indicates that the stereoelectronic effect of the aromatic bowl is different for the concave and convex faces, and is reflected in the different strengths of hyperconjugation of the benzylic *exo*/*endo* C–H bonds with the bowl in the benzylic-substituted sumanenes. The hyperconjugation is a dominant factor for determining the *endo*-R conformational stability of methylsumanene and hydroxysumanene. Our finding reveals the potential through-bond stereoelectronic effect of curved aromatic compounds, an effect that results from the differences in the concave and convex faces. This finding helps to further our understanding of the nature of curved aromatic compounds and to control properties such as conformation, chemical reactivity, and interaction.

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[7] The stronger CH–π interaction to favor the *endo*-R-**1e** was analyzed by the CH–π distance and AIM (atoms in molecules) analysis (see the Supporting Information).

[8] The reason for the reverse strength of hyperconjugation of **1b** and **1e** can be explained by the angle changes between the C–H bond and the π face (see the Supporting Information).

