

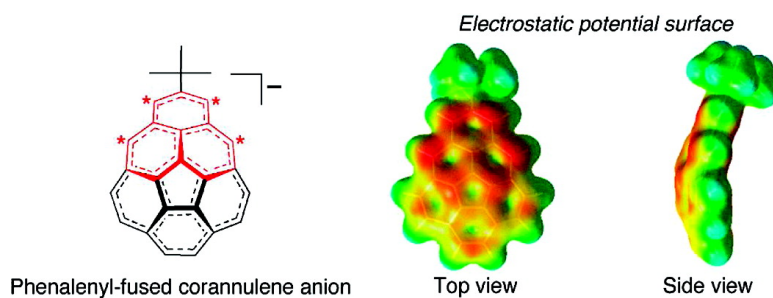
Communication

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## Curve-Structured Phenalenyl Chemistry: Synthesis, Electronic Structure, and Bowl-Inversion Barrier of a Phenalenyl-Fused Corannulene Anion

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Kanako Ogasawara,<sup>†</sup> Kazunobu Sato,<sup>‡</sup> Takeji Takui,<sup>\*,‡</sup> and Kazuhiro Nakasuji<sup>†</sup>

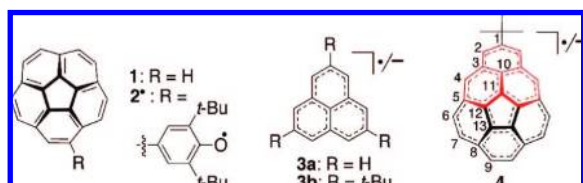
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Exotic  $\pi$ -conjugated networks of *nonplanar* polycyclic aromatic hydrocarbons, that is, bowl-shaped,<sup>1</sup> belt-shaped,<sup>2</sup> or Möbius molecules<sup>3</sup> have drawn much attention in not only organic chemistry but also materials science,<sup>4</sup> anticipating their novel molecular functionalities. We have designed and synthesized novel bowl-shaped stable neutral radicals based on corannulene **1**.<sup>5</sup> Phenoxy radical-substituted derivative **2'** allowed us to determine the crystal structure as the first example of a neutral radical with a curved  $\pi$ -system, which importantly contributed to elucidation of the unique electronic spin-delocalized nature on the corannulene moiety.<sup>5c</sup>

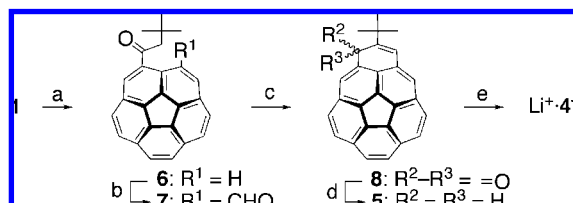
Phenalenyl radical **3a** is a *planar* polycyclic  $\pi$ -radical possessing an extensively spin-delocalized nature and a high redox ability,<sup>6</sup> but it has a low stability in air. We synthesized and isolated novel air-stable phenalenyl-based neutral radicals by introducing two oxygen<sup>7</sup> or two nitrogen atoms<sup>8</sup> together with *tert*-butyl groups. The introduction modulates in part their electronic structure, influencing the functionality of bulk materials properties. Recently, we have reported that some of these radicals show thermochromism in the solution<sup>7a</sup>/solid states,<sup>8</sup> and we have succeeded in the application to cathode-active materials of a new type of secondary batteries.<sup>9</sup>

These studies on the phenalenyl-based *planar*  $\pi$ -systems have aroused interest in the electronic structure of a *curved* phenalenyl. This has encouraged us to design a phenalenyl-fused corannulene **4**, the first six-membered *peri*-annulated corannulene featuring full-conjugation and a substructure of C<sub>70</sub>.<sup>10</sup> In this study, the anion **4<sup>-</sup>** has been generated in a degassed solution and the electronic structure has been elucidated in terms of the NMR spectra and DFT calculations, showing for the first time that salient features of the phenalenyl anion are on a curved-surface  $\pi$ -system.<sup>11</sup>



A phenalene derivative **5**, precursor of **4<sup>-</sup>**, was synthesized from **1** in four steps (Scheme 1). Friedel–Crafts acylation of **1** gave a ketone **6** in 99% yield. Formylation of **6** with dichloromethyl methyl ether in the presence of TiCl<sub>4</sub> yielded **7** as a main product by neighboring participation effect. Treatment of **7** with NaOEt gave a phenalenone derivative **8**.<sup>12</sup> Reduction of the carbonyl group with LiAlH<sub>4</sub> and AlCl<sub>3</sub> gave **5**, which possesses a low stability in air at

Scheme 1<sup>a</sup>



<sup>a</sup> Reaction conditions: (a) *t*-BuCH<sub>2</sub>COCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78 to ca. 0 °C, 99%; (b) CH<sub>3</sub>OCHCl<sub>2</sub>, TiCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp; (c) NaOEt, EtOH–THF, -30 °C to room temp, 34% in two steps; (d) LiAlH<sub>4</sub>, AlCl<sub>3</sub>, Et<sub>2</sub>O, room temp, 18%; (e) *n*-BuLi, THF-*d*<sub>8</sub>, -80 °C in a sealed tube.

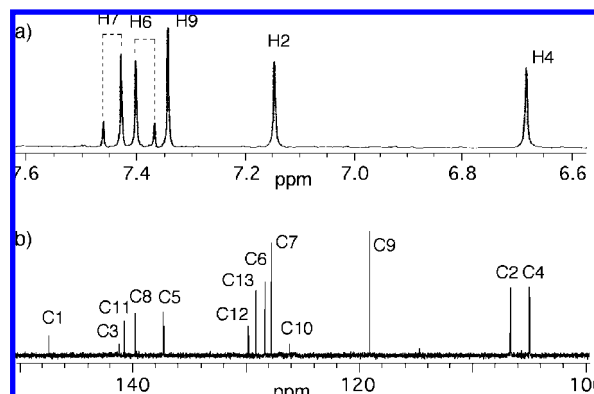


Figure 1. Aromatic regions of 600 MHz <sup>1</sup>H (a) and <sup>13</sup>C NMR (b) spectra of Li<sup>+</sup>·**4<sup>-</sup>** measured in THF-*d*<sub>8</sub> solution at room temperature.

ambient temperature and easily changes to **8** by aerobic oxidation. Finally, treatment of **5** with an equimolar amount of *n*-BuLi in a degassed THF-*d*<sub>8</sub> gave Li<sup>+</sup>·**4<sup>-</sup>** as a red purple solution. The anion Li<sup>+</sup>·**4<sup>-</sup>** is highly stable in the degassed solution.<sup>13</sup>

Figure 1 shows <sup>1</sup>H and <sup>13</sup>C NMR spectra of Li<sup>+</sup>·**4<sup>-</sup>** measured in THF-*d*<sub>8</sub> at room temperature. Five kinds of protons and 13 kinds of carbons were observed, indicating a highly symmetrical structure of **4<sup>-</sup>**. These chemical shifts were completely assigned in terms of HMQC, HMBC, and NOESY NMR spectra (Supporting Information), and summarized together with the chemical shifts calculated by the density functional theory (DFT) method (Table 1).<sup>14</sup> The calculated values were in good agreement with the observed ones. Importantly, high-field shifts of the protons and the carbons at 2,4-positions compared to the other ones indicate the occurrence of large negative charge densities at these positions.

To reveal the negative charge density distribution, we have calculated HOMO pictures and electrostatic potential surfaces of both

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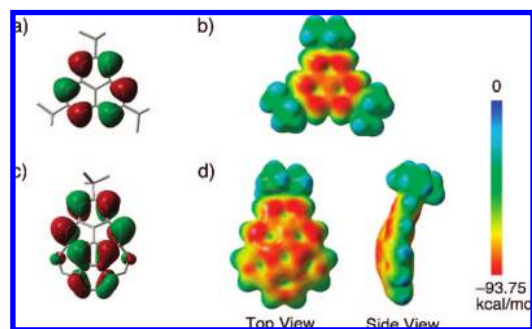
<sup>‡</sup> Osaka City University.

<sup>§</sup> PRESTO-JST.

**Table 1.** Observed and Calculated  $^1\text{H}$  and  $^{13}\text{C}$  Chemical Shifts of  $\text{Li}^+ \cdot 4^-$ 

positions	observed	calcd <sup>a</sup>	positions	observed	calcd <sup>a</sup>
H2	7.14	7.23	C5	137.4	143.0
H4	6.68	6.96	C6	128.4	133.6
H6	7.38	7.63	C7	127.9	131.8
H7	7.44	7.63	C8	139.9	134.2
H9	7.33	7.55	C9	119.1	123.2
C1	147.5	150.8	C10	126.2	129.7
C2	106.8	108.4	C11	140.8	145.5
C3	141.3	146.8	C12	130.0	134.7
C4	105.0	108.8	C13	129.2	143.4

<sup>a</sup> The GIAO-RB3LYP/6-311G\*\*//RB3LYP/6-311G\*\* level of theory.



**Figure 2.** HOMO pictures and electrostatic potential surfaces of  $3b^-$  (a and b) and  $4^-$  (c and d), respectively, calculated at the RB3LYP/6-311G\*\*//RB3LYP/6-311G\*\* level. Red regions indicate large negative charge distributions in electrostatic potential surfaces.

$3b^-$  and  $4^-$  by the DFT method, demonstrating that  $4^-$  has salient features of the phenalenyl anion-type electronic structure (Figure 2). The calculation for  $4^-$  shows that the HOMO coefficients dominate at 2, 4, and 12-positions (Figure 2c), indicating a large negative charge distribution over these positions. This result is consistent with the feature of the electrostatic potential surface of  $4^-$  (Figure 2d). Additionally, an appreciable amount of the HOMO coefficients resides on the central five-membered ring, which implies the contribution of the electronic structure of cyclopentadienyl anion as well as that of the phenalenyl anion. Theoretical consideration based on both the nucleus-independent chemical shift (NICS) method and resonance structures demonstrates that the phenalenyl anion-type structure contributes the most importantly.<sup>15</sup>

For disclosing the molecular shape of  $4^-$ , we have calculated a bowl-inversion barrier of the **4** system (nonsubstituted) on the basis of the bowl depth.<sup>16</sup> The barrier of the anion was obtained as 11.3 kcal/mol larger than that of **1** (9.2 kcal/mol), indicating increase in the bowl depth by the annelation across the *peri* positions of the corannulene skeleton.<sup>1a,16</sup> For considering any charge effects on the barrier, we have calculated on some redox species, the neutral radical (12.6 kcal/mol), the radical dianion (8.1 kcal/mol), and the trianion (5.4 kcal/mol). These calculations indicate that the curvature of the system **4** is flattened stepwise with increase in negative charge.<sup>17</sup> Thus, the bowl depth can be interpreted in terms of the setoff of the *peri*-annelation and negative charge effects.

In conclusion, we have successfully generated the first curved phenalenyl anion  $4^-$  and revealed the characteristic electronic structure both experimentally and theoretically. We also have been interested in isolation of the neutral radical and experimental elucidation of both bowl-inversion barriers<sup>16</sup> and aggregation behavior<sup>18</sup> of the anions. Thus, synthesis of new derivatives based on the system **4** by introducing bulky groups to stabilize the neutral radical state or some alkyl groups as a probe of magnetic resonance measurements at the appropriate positions is underway. Studies on

the curved phenalenyl anion provide molecular design criteria of novel polycyclic aromatic hydrocarbon anions for exploration in molecular functionalities<sup>19</sup> and importantly contribute to elucidation of electronic structures of  $\text{C}_{70}$  systems.<sup>20</sup>

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**Supporting Information Available:** Complete refs 8 and 14; experimental procedure and full characterization data for all new compounds; crystallographic data (CIF file) of **8**, CV, and NICS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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