

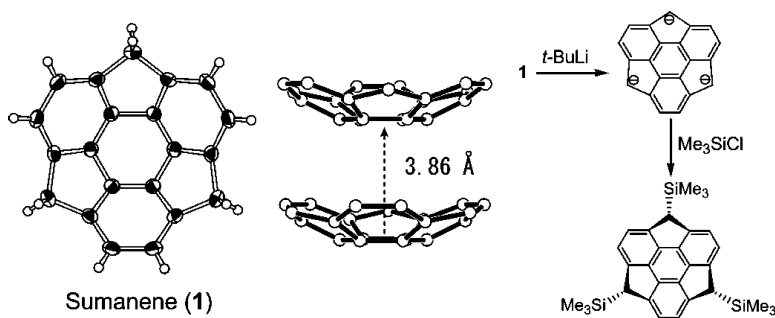
Communication

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Hidehiro Sakurai, Taro Daiko, Hiroyuki Sakane, Toru Amaya, and Toshikazu Hirao

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Structural Elucidation of Sumanene and Generation of Its Benzylic Anions

Hidehiro Sakurai,^{*,†} Taro Daiko, Hiroyuki Sakane, Toru Amaya, and Toshikazu Hirao^{*}

Department of Applied Chemistry, Graduate School of Engineering, Osaka University,
Yamada-oka, Suita, Osaka 565-0871, Japan

Received March 22, 2005; E-mail: hirao@chem.eng.osaka-u.ac.jp; hsakurai@ims.ac.jp

Bowl-shaped π -conjugated compounds, including partial structures of fullerenes, are of importance not only as model compounds of fullerenes but also for their own chemical and physical properties. Since synthetic routes to C_{5v} symmetric corannulene have been established,^{1,2} most of the investigation has been focused on corannulene derivatives. Sumanene (**1**),³ which is a key partial C_{3v} symmetric structure of fullerenes, has also drawn attention. In 2003, the first synthesis of **1** from norbornadiene was achieved in three or four steps under nonpyrolytic conditions.⁴ In addition, sumanene was demonstrated to exhibit much slower bowl-to-bowl inversion than corannulene in a less polar solution. In this paper, we report the structural elucidation of sumanene in a solid state. One advantage of sumanene over corannulene derivatives is the presence of three benzylic positions, which may permit further functionalization to create new bowl-shaped derivatives via the corresponding radicals, anions, carbenes, etc. The stereoselective formation of the silyl-substituted sumanene through generation of the benzylic anion of sumanene is also described.

The molecular structure of **1** by X-ray crystal structure analysis is illustrated in the ORTEP diagrams of Figure 1.⁵ Significant bond alternation is observed in the hub six-membered ring to give the bond lengths of *r*1a and *r*1b as 1.381 and 1.431 Å, respectively (Table 1). The magnitude of this bond alternation is slightly smaller than that in triphenylene (1.411 and 1.470 Å)^{6,7} or that in C_{60} (1.398 and 1.455 Å).⁸ In contrast, the bond lengths in the flank six-membered ring (*r*1a, *r*2, *r*3a) are almost identical except for a significantly elongated rim bond (*r*4). A geometrically optimized structure using the DFT method (B3LYP/6-31G**) is in good agreement with these experimental data, and similar calculation results have also been reported.⁹

As shown in the side view (Figure 1b), sumanene possesses the expected bowl-shaped structure. Haddon's π -orbital axis vector (POAV) analysis¹⁰ reveals that the hub six carbons are pyramidalized to an extent of 9.0°, which is consistent with the DFT calculation.⁹ By comparison, POAV angles of all the carbons of C_{60} and the five carbons at the hub of corannulene are 11.6 and 8.2°, respectively.¹¹ The curvature at the sumanene center corresponds to 78% of that of C_{60} , but is still closer than that of corannulene. On the other hand, the bowl depth is observed as 1.11 Å, which is slightly shallower than the estimated value (1.14 Å)⁹ and deeper than that of corannulene (0.87 Å).¹² The former may be due to the effect of packing, as shown in Figure 1.

Deep bowl-shaped π -aromatics sometimes favor a stacking structure in a concave–convex fashion.^{13,14} Such an arrangement was observed in an intermolecular packing structure of **1** (Figure 1d). The stacking distance is approximately 3.86 Å, which is relatively larger than that of ordinary π -stacking. It should be pointed out that columnar stacking of **1** occurs along a crystallographic 3-fold axis (Figure 1c). Such a stacking arrangement is

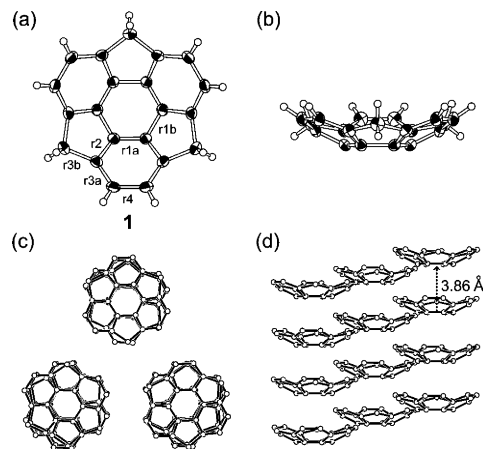


Figure 1. ORTEP drawings and packing structure of **1**: (a and c) top view and (b and d) side view.

Table 1. Observed and Calculated Bond Lengths of **1**

bond length (Å)	crystal structure	B3LYP/6-31G**
<i>r</i> 1a	1.381	1.387
<i>r</i> 1b	1.431	1.433
<i>r</i> 2	1.396	1.399
<i>r</i> 3a	1.398	1.400
<i>r</i> 3b	1.548	1.556
<i>r</i> 4	1.430	1.432
<i>r</i> 1b– <i>r</i> 1a	0.050	0.046

also observed with hemifullerene ($C_{30}H_{12}$)^{14c} and a fullerene fragment ($C_{36}H_{12}$),^{14d} being in quite sharp contrast with corannulenes.^{12,14b} Each layer of the column is stapled in a staggered fashion, which may be due to a repulsive effect of the three methylene units and/or maximization of the HOMO–LUMO overlap. It is also noteworthy that every column is present in the same direction (Figure 1d). The finding strongly suggests that **1** may be of potential utility as electrically active materials in a solid state.

The bowl-shaped structure is considered to permit stereoselective functionalization through the benzylic anions. Generation and characterization of anionic species were next investigated by the NMR tube reaction (Scheme 1). When sumanene was treated with *t*-BuLi in THF-*d*₈ below –80 °C and the temperature was immediately increased to room temperature,¹⁵ C_3 symmetric signals of sumanene (Figure 2a)¹⁶ disappeared with the appearance of new C_2 symmetric signals (Figure 2b).

Aromatic signals split into three peaks with higher-field shift, accompanied by the higher-field shift of two benzylic protons. In addition, a new singlet peak appeared at 5.87 ppm, which is assignable to the benzyl anion species. Eleven signals were observed in ¹³C NMR, which also corresponds to the C_2 symmetric structure (Supporting Information).¹⁷ Additional treatment of an equimolar

[†] Present address: Institute for Molecular Science, Myodaiji, Okazaki 444-8787, Japan.

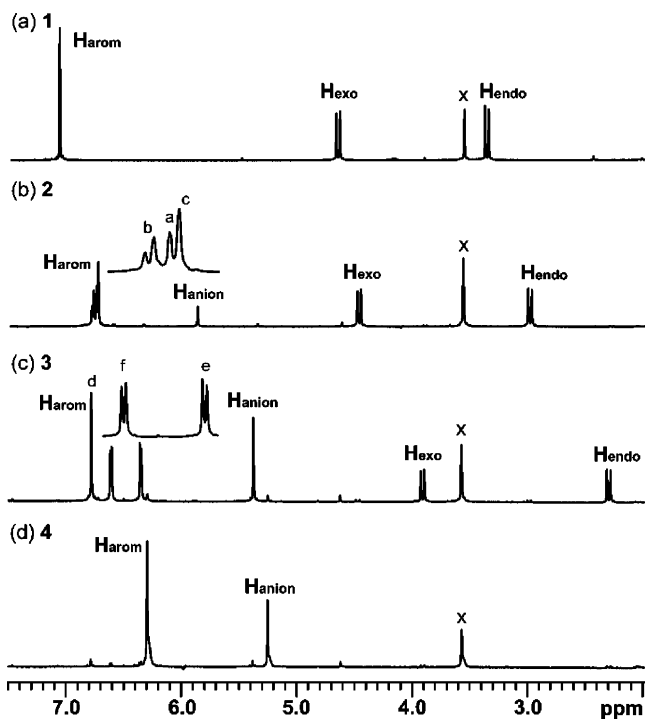
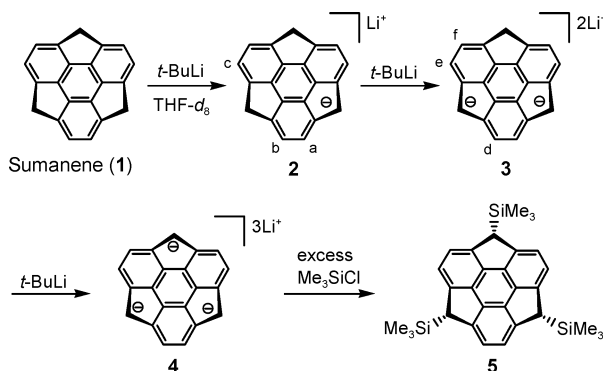


Figure 2. ^1H NMR spectra (600 MHz, $\text{THF-}d_8$) of **1** and mono/di/trianions **2–4**. x: residual THF.

Scheme 1. Generation of Mono/Di/Trianions **2–4** and Preparation of Tris(trimethylsilyl)sumanene (**5**)



amount of *t*-BuLi led to another set of C_2 symmetric signals assigned to the dianion **3** (Figure 2c).¹⁷ Benzylic, anionic benzyl, and aromatic e and f protons of **3** are higher-field shifted as compared with the corresponding protons of **2**. Furthermore, the difference in chemical shifts between exo/endo benzylic protons is bigger in **3** > **2** > **1**. These results indicate that the more diamagnetic anisotropic effect is induced in a more charged species, or geometry changes upon proton removal and/or location of the counter cations may also play a role. On the addition of a further equivalent of *t*-BuLi, only two singlets in the ^1H NMR (Figure 2d) and four signals in the ^{13}C NMR were observed (Supporting Information). Judging from the symmetry and chemical shift analysis, the trianion **4** is considered to be generated.

Finally, the reaction of **4** with an electrophile was investigated. Introduction of excess amounts of Me_3SiCl afforded the tris(trimethylsilyl) derivative **5** as the sole isomer. The appearance of the benzylic proton at 3.43 ppm indicates that the trimethylsilyl

group should be introduced at the exo-position with perfect selectivity, probably due to the steric demand.^{18,19}

As described above, sumanene shows the characteristic feature in the solid-state structure as well as the solution-state dynamics.⁴ Three benzylic positions are readily functionalized via the corresponding carbanions. Sumanene is expected to be a key compound for the construction of bowl-shaped π -aromatics.

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Supporting Information Available: Experimental details and spectral data for **1–5**. X-ray crystallographic data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) 1.7 equiv of *t*-BuLi was used to generate **2** for the consumption with the residual water.
- (16) The calculated chemical shifts (GIAO/6-31G**) of **1** were in agreement with the experimental data: See Supporting Information.
- (17) The complete assignments for ^1H and ^{13}C NMR of **2** and **3** were confirmed by 1D NOE, HMQC, and HMBC experiments; see Supporting Information.
- (18) The benzylic protons of **5** were assigned to endo-protons, judging from ring current effect and comparison with those of 9-TMSfluorene and fluorene (see Supporting Information). It is consistent with the assignment of benzylic protons of **1**, in which endo-protons at ca. 3.4 ppm are more than 1 ppm as high as exo-protons due to ring current effect. The calculation results given in ref 16 also supported the assignment of **5**.
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