

## Stacking of Molecules Possessing a Fullerene Apex and a Cup-Shaped Cavity Connected by a Silicon Connection

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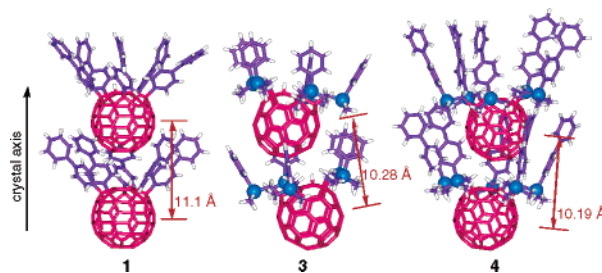
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Research on the synthesis of large, structurally defined molecules<sup>1</sup> and on the method to connect them with tunable connective joints<sup>2</sup> is a growing area of chemical research in nanoscience. We previously synthesized molecules possessing the shape of a badminton shuttlecock, C<sub>60</sub>R<sub>5</sub>H [**1**, R = C<sub>6</sub>H<sub>4</sub>-Ph-4 and **2**, R = C<sub>6</sub>H<sub>4</sub>-{OCO-C<sub>6</sub>H<sub>3</sub>-(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,4}-4], conical molecules with a fullerene apex, which stack head-to-tail to form a polar column.<sup>3</sup> In this first generation design, the cone is shaped by the five aryl groups (R), protruding directly from the fullerene core and ensuring tight fitting of another fullerene molecule in the cone to form a rigid column in crystals and liquid crystals (LCs). The tightness of this connection restricts the structural mobility of the column. In light of the interest in this new class of mesogenic structure<sup>4</sup> as well as in molecular cavities in general,<sup>5</sup> we considered it important to make a larger cavity that possesses larger loading capacity and allows a more structurally flexible connection between the molecules in the column. To this end, we have chosen an (aryl)-(dimethyl)silylmethyl group as the R group (cf. **3**–**7**; Chart 1) so that one can expand the cavity by outward parallel translation of the aryl groups in **1** and **2** with the aid of a silicon connection. The result is a cavity in the shape of a cup created on top of a fullerene group (Figure 1). Although the new side chain may look too flexible, we considered, as verified later by experiments, that the torsional strain around the CH<sub>2</sub>-Si(Me)<sub>2</sub> bond is large enough to let the aryl group point away from the fullerene core.

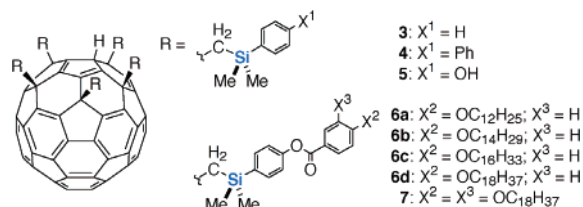
Among various possibilities to achieve the synthetic goal, we have chosen the well-established chemistry of triorganosilylmethyl organometallics, which are easy to prepare and thermally stable. Thus, we took SiCl(CH<sub>2</sub>Cl)Me<sub>2</sub> as the linker to connect the fullerene group<sup>6</sup> (to replace Cl on CH<sub>2</sub>Cl) and the aryl group that forms the cavity wall (to replace Cl on Si). SiAr(CH<sub>2</sub>Cl)Me<sub>2</sub><sup>7</sup> was synthesized first and then converted to Mg(Cl)CH<sub>2</sub>SiMe<sub>2</sub>Ar under the standard Grignard conditions. We expected that the cavity size can be expanded this way by several angstroms because of the rather long Si-C bond (1.89 Å).

The crystalline prototype, C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>5</sub>H (**3**), was synthesized by the reaction of [60]fullerene with Mg(Cl)CH<sub>2</sub>SiMe<sub>2</sub>Ph in the presence of CuBr·SMe<sub>2</sub>.<sup>8</sup> Similarly, C<sub>60</sub>{CH<sub>2</sub>SiMe<sub>2</sub>(biphenyl)}<sub>5</sub>H (**4**) was obtained by the reaction of the corresponding organocopper reagent. The LC molecules bearing hydrocarbon side chains were obtained through a penta-phenol C<sub>60</sub>{CH<sub>2</sub>SiMe<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-OH-4)}<sub>5</sub>H (**5**), which was obtained by the penta-addition of 4-(THPO)C<sub>6</sub>H<sub>4</sub>-SiMe<sub>2</sub>CH<sub>2</sub>MgCl/CuBr·SMe<sub>2</sub> reagent (THP = tetrahydropyranyl protective group) followed by deprotection. Acylation of **5** with an appropriate benzoic chloride derivative possessing an alkyl chain afforded C<sub>60</sub>[CH<sub>2</sub>SiMe<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>-(OCO-C<sub>6</sub>H<sub>4</sub>-OR-4)-4}]<sub>5</sub>H (**6a**, R



**Figure 1.** Two stacked molecules of **1**, **3**, and **4** in a unit cell shown along crystal *B* (for **1** and **3**) and *C* (for **4**) axes. Side chain carbon atoms are colored blue, fullerene cores are red, and silicon atoms are light blue. Intermolecular spacing is represented by the distance between the centroids of the C<sub>60</sub> moiety in the neighboring molecules.

### Chart 1



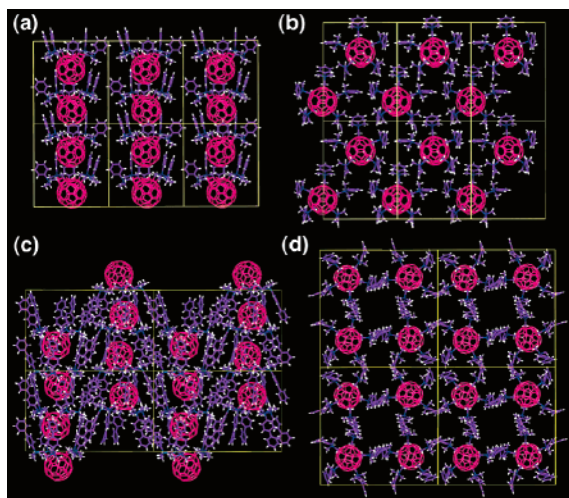
= C<sub>12</sub>H<sub>25</sub>; **6b**, R = C<sub>14</sub>H<sub>29</sub>; **6c**, R = C<sub>16</sub>H<sub>33</sub>; **6d**, R = C<sub>18</sub>H<sub>37</sub>). All derivatives were characterized by the <sup>1</sup>H and <sup>13</sup>C NMR and APCI-MS analyses.

Red-colored rectangular crystals of **3** and **4** suitable for X-ray crystallographic study were obtained by slow diffusion of methanol into a chloroform (for **3**) or toluene (for **4**) solution. Figure 1 shows two stacked molecules of **1**, **3**, and **4** found in a unit cell. Because of the restricted conformational possibility, anticipated a priori, all aryl groups in **3** and **4** point upward to form a cavity. The diameter of the cone as measured at the bottom ipso position of the biphenyl group is 12.6 Å, ca. 5 Å larger than that of **1** (7.4 Å), and the axis of the biphenyl side chain in **4** forms a ca. 25° angle against the pseudo-C<sub>5</sub> axis of the molecule as opposed to ca. 45° in **1**.<sup>3</sup> As the result of the larger cavity size, the fullerene moiety is loosely fitted into the cavity, causing the molecular symmetry axis in **3** and **4** to be off by 11.5° and 6.5° from the column axis (crystal axis) unlike that in **1** where it is almost exactly parallel to the column axis.

The second consequence of the larger cavity is the shorter intracolumnar spacing in the crystals of **3** and **4** than in those of **1**. The distance between the two neighboring molecules is 10.28 and 10.19 Å for **3** and **4**, respectively, and 11.1 Å for **1**. In the crystals of **3** and **4**, the fullerene moiety is supported by the cyclopentadienyl hydrogen atom in the bottom of the cavity and also by the *m*-hydrogen atoms of the bottom phenyl group in the biphenyl group, as opposed to the fact that the fullerene moiety in the crystal

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**Figure 2.** Crystal packing of **3** and **4**. (a) View from *C* axis of the packing of **3**. (b) View from *B* axis of the packing of **3**. (c) View from *A* axis of the packing of **4**. (d) View from *C* axis of the packing of **4**. For clarity, solvent molecules are omitted and only a single layer of the molecules is shown.

of **1** is supported only by the edge of the cavity (Figure 1) and does not touch the bottom of the cavity. This suggested to us that LCs of the second generation design will have a more flexible intracolumnar interaction than the first generation.

The packing of the stacked columns was found to depend on the molecular structure. Thus, the columns of the phenylsilyl molecule **3** are packed in a hexagonal manner characterized by two rectangular arrays for each column direction (Figure 2a,b), while those of the biphenylsilyl molecule **4** are packed in a tetragonal columnar manner (Figure 2c,d). The latter is because of the biphenyl/biphenyl interaction among the adjacent columns. The intercolumnar voids in the crystals are filled by solvent molecules (toluene).

With the crystal structure of **3** and **4** in hand, we next examined the molecules bearing long methylene side chains (**6a–d**). In addition to the cavity/fullerene interaction, microphase segregation<sup>9,10</sup> between the fullerene/aromatic array and the saturated hydrocarbon side chain will help form a stable columnar mesophase. Differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffraction analysis were used to identify the mesophase. Optical textures (see Supporting Information) of **6a–d** are characteristic of columnar LCs.

The DSC analysis and microscope observation of **6a–d** is summarized in Table 1. As expected, the glass transition temperature of **6a–d** rises progressively from 2.2 to 35.4 °C as the side chain becomes longer from C-12 to C-18. On the other hand, the isotropization temperatures fall within a rather limited range between 176 and 187 °C. These temperatures are much higher than those of the first generation LCs (ca. 140 °C).<sup>3</sup> Equally notable is the large transition enthalpies (Table 1) and unusual supercoolability in the LC–Iso transition (ca. 17.4 °C, see Supporting Information). The data support our initial conjecture that the columnar structure of the new LC material is constitutionally more stable but conformationally more flexible.

The X-ray diffraction pattern for **6a** at 60 °C showed reflections with *d*-spacing values of 32.9 Å (100), 19.2 Å (110), 16.5 Å (200), 12.9 Å (001), and 12.3 Å (210), and a broad halo being typical for

**Table 1.** Phase Transition Behavior of the LC Molecules **6a–d** and **7** on the Second Heating<sup>a</sup>

compd		phase transition temperature (°C) <sup>b</sup>			
<b>6a</b>	G	2.2	Col <sub>h</sub>	186.6 (27.4)	Iso
<b>6b</b>	G	10.1	Col <sub>h</sub>	175.9 (28.2)	Iso
<b>6c</b>	G	18.2	Col <sub>h</sub>	181.6 (31.3)	Iso
<b>6d</b>	G	35.4	Col <sub>h</sub>	185.7 (34.5)	Iso
<b>7</b>	Cryst	53.4 (178.8)	Iso		

<sup>a</sup> Abbreviations: Iso, isotropic; Col<sub>h</sub>, hexagonal columnar; G, glassy; Cryst, crystalline. Transition temperatures were determined by DSC at the rate of 10 °C min<sup>-1</sup> and were taken at the maximum of each transition peak. <sup>b</sup> Transition enthalpies (kJ mol<sup>-1</sup>) are in parentheses.

molten aliphatic moieties at 4.6 Å. The reciprocal *d*-spacings of the first three peaks are in a ratio of 1:√3:2, which are characteristic of a hexagonal columnar structure. It should be noted the intracolumnar spacing of 12.9 Å is smaller than the 14.3 Å spacing of **2**, while the intercolumnar spacing (38.4 Å) is much larger (35.3 Å). This shortening of the intracolumnar spacing coincides with the shortening in the crystals (vide supra). In contrast to **6** that has five long side chains, compound **7** bearing 10 side chains did not show the LC property.

The second generation molecules have several useful properties unavailable for the first generation molecules. First, they have a larger cup-shaped cavity that can comfortably accommodate the second fullerene molecule. Second, the cavity wall is less tapered than before: As the result, the connection between the two neighboring molecules (Figure 1) may look more like a “ball-joint” rather than stacked shuttlecocks. Third, the intracolumnar spacing has been much shortened. This would enhance the fullerene/fullerene interaction especially when the cyclopentadienyl hydrogen atom is removed.

**Supporting Information Available:** Procedures for the synthesis of the new compounds, crystallographic data of **3** and **4** (CIF), optical texture and DSC data of **6a**, and X-ray data of **6a–d** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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