

## Synthesis and crystal structure of 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)benzene

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**Abstract**—Fluorinated Dewar benzene (1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)bicyclo[2,2,0]hexa-2,5-diene) efficiently prepared from fluoro(triisopropylsilyl)acetylene was thermochemically or photochemically transformed into the corresponding highly crowded fluorinated benzene (1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)benzene) in excellent yield. The molecular structure of the crowded benzene was determined by X-ray crystallography.

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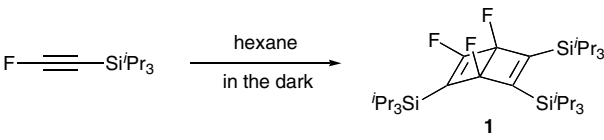
Study on highly crowded benzenes is one of the attractive themes for synthetic organic chemists as well as theoretical chemists.<sup>1</sup> These molecules must avoid their repulsive interactions between neighboring bulky substituents introduced on the benzene rings, which should force their original benzene structures to change. As a result, the corresponding bond lengths, bond angles, and torsion angles have deviated from the original ones. To the best of our knowledge, the synthesis of the following crowded benzenes has so far been reported: 1,2,3,4-tetra(*tert*-butyl)benzene,<sup>2</sup> 1,2,4,5-tetra(*tert*-butyl)benzene,<sup>3</sup> dimethyl 3,4,5,6-tetra(*tert*-butyl)phthalate,<sup>4</sup> and 1,3,5-tris(dialkylamino)-2,4,6-trinitrobenzene.<sup>5</sup> Although hexa(*tert*-butyl)benzene as the most attractive benzene has not been synthesized yet, it is noteworthy that the preparation of hexakis(trimethylsilyl)benzene as its silyl analog has already been accomplished.<sup>6</sup> Of these, 1,2,4,5-tetra(*tert*-butyl)benzene, 1,3,5-tris(dialkylamino)-2,4,6-trinitrobenzene, and hexakis(trimethylsilyl)benzene have been structurally characterized by X-ray crystallography. On the other hand, we have recently reported our finding of highly crowded Dewar benzene (1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)bicyclo[2,2,0]hexa-2,5-diene) (**1**) as a valence isomer of benzene derived from fluoro(triiso-

propylsilyl)acetylene.<sup>7</sup> As the isomerization of fluorinated Dewar benzenes to the corresponding fluorinated benzenes has already been reported in the literature,<sup>8</sup> this fluorinated Dewar benzene (**1**) carrying three bulky triisopropylsilyl groups on the ring would be a promising candidate for one of the highly crowded benzene. This letter firstly describes an improved preparation of **1**, secondly its isomerization and lastly an unambiguous characterization of 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)benzene (**2**).

Because the reaction time to prepare **1** using our previous method required about 4 months, we needed the improved reaction conditions found prior to the examination of its isomerization. The parameter of the reaction conditions was focused on the concentration, the temperature, and the influence of the light absorption. According to the literature procedure,<sup>7</sup> we initially prepared a hexane solution containing fluoro(triisopropylsilyl)acetylene at concentration of about 2.5 mol/L. After several attempts, spontaneous trimerization of the fluoroacetylene efficiently occurred to give **1** in 66% yield for only 3 days at 20 °C *under the light shielded conditions* (entry 3). It is noteworthy that a similar reaction *under the light unshielded conditions* gave no desired product (**1**) but the probably polymerized products as brown precipitates (entry 4). These results are shown in Table 1. As far as the reasonable yield (66%) is concerned, although a small amount of the starting fluoroacetylene remained in the reaction mixture, the

**Keywords:** Dewar benzene; Crowded benzene; Isomerization; X-ray structure; Fluorinated compound.

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**Table 1.** Trimerization of fluoroacetylene to Dewar benzene (**1**)


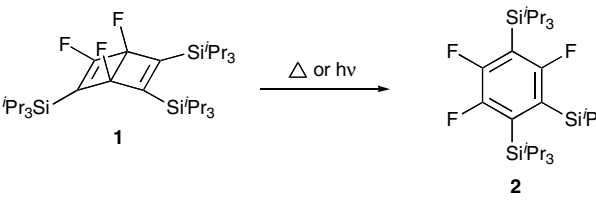
Entry	Time	Temp (°C)	Yield (%) <sup>a</sup>
1	4 month	-20	44
2	18 day	5	44
3	3 day	20	66
4 <sup>b</sup>	3 day	20	0 <sup>c</sup>

<sup>a</sup> Isolated yield.<sup>b</sup> In the light.<sup>c</sup> Polymerized product.

prolonged reaction time until the complete consumption of the fluoroacetylene caused formation of unidentified inseparable by-products.

With **1** in hand, the isomerization reaction was examined under thermal or photochemical conditions.<sup>9</sup> Initially, the flask containing **1** without solvent under an argon atmosphere was heated to 100 °C and was kept at this temperature for 30 min. The resulting oil gave no products and recovered **1** intact. However, the more forced conditions (heating at 200 °C for 30 min) gave a new product (**2**) along with **1** slightly. Ultimately, the complete consumption of **1** occurred at 220 °C for 45 min to afford **2** in 93% yield.<sup>10</sup>

On the other hand, irradiation of a degassed hexane solution of **1** in a quartz glass test tube using low-pressure Hg lamp ( $\lambda > 254$  nm) for 8 h at 40 °C produced **2** in quantitative yield.<sup>11</sup> Furthermore, the similar irradiation

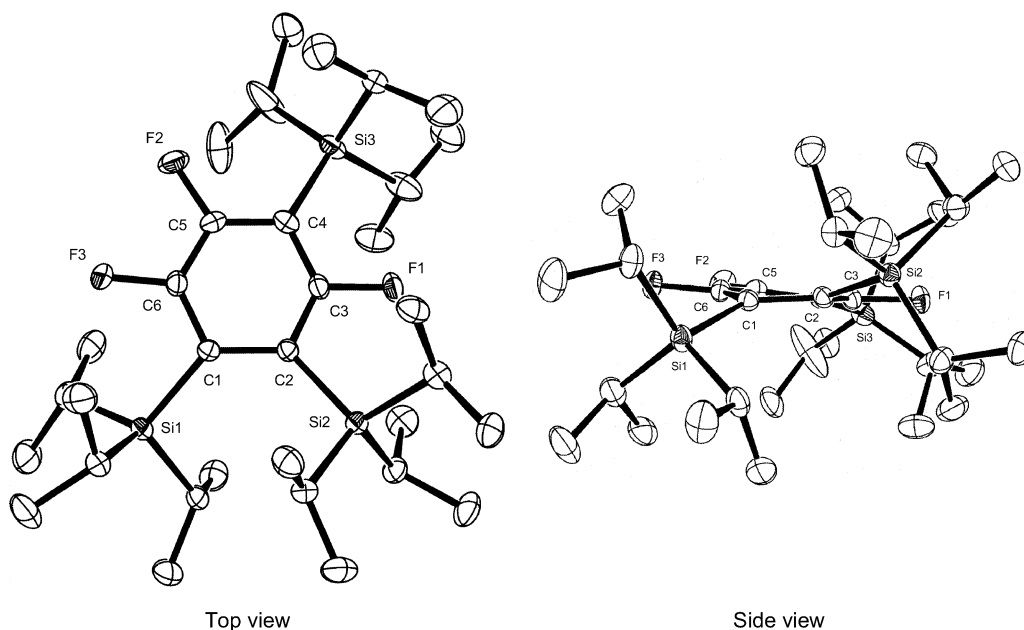
**Table 2.** Isomerization of Dewar benzene (**1**) to benzene (**2**)


Entry	<i>hν</i>	Time	Temp (°C)	Yield (%) <sup>a</sup>
1	None	45 min	220	93
2 <sup>b</sup>	>254 nm	8 h	40	Quant
3 <sup>c</sup>	>280 nm	14 h	-10	Quant

<sup>a</sup> Isolated yield.<sup>b</sup> Low-pressure Hg lamp.<sup>c</sup> High-pressure Hg lamp.

in a Pyrex glass test tube using high-pressure Hg lamp ( $\lambda > 280$  nm) for 14 h at -10 °C also afforded **2** in quantitative yield. These results are summarized in Table 2.

This product (**2**) was purified with silica gel chromatography as a white solid, which was easily soluble in hexane ( $R_f$  value = 0.95 in hexane) and melt from 111.0 to 112.8 °C.<sup>12</sup> The <sup>19</sup>F NMR spectrum displayed three signals at  $\delta = -76.12$  ppm (d,  $J = 15.3$  Hz),  $-119.76$  ppm (d,  $J = 27.6$  Hz), and  $-120.27$  ppm (dd,  $J = 27.6, 15.3$  Hz). The <sup>13</sup>C NMR showed six downfield signals at  $sp^2$  carbon regions ( $\delta = 111$ – $167$  ppm). Interestingly, as with the Dewar benzene (**1**), its GC–MS analysis gave the same peak at  $m/z$  472 with the same fragmentation pattern. This observation suggests that thermal isomerization from **1** to **2** had taken place during the GC–MS analysis. The additional TG–DTA analysis of **1** also



**Figure 1.** ORTEP drawing of structure **2** with thermal ellipsoids shown at the 50% probability level (all hydrogen atoms and the disordered methyl group have been omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–C2 1.445(3), C2–C3 1.389(3), C3–C4 1.399(3), C4–C5 1.381(3), C5–C6 1.380(3), C6–C1 1.385(3), C1–Si1 1.934(2), C2–Si2 1.937(2), C4–Si3 1.914(2), C3–F1 1.377(2), C5–F2 1.355(2), C6–F3 1.369(2), C1–C2–C3 115.14(18), C2–C3–C4 129.62(19), C3–C4–C5 111.46(19), C4–C5–C6 122.12(19), C5–C6–C1 124.85(19), C6–C1–C2 115.06(18).

supported this isomerization. The DTA curve showed the endothermic absorption at 170.6 °C, which should correspond to the isomerization starting temperature. On the basis of these data, **2** was determined as 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)benzene.

We paid great interest to the crystal structure of **2**. The molecule (**2**) was anticipated to have large out-of-plane bending deformation because of the non-bonding repulsive interactions between the adjoining triisopropylsilyl groups. Single crystals of **2** were grown by recrystallization from hexane. The X-ray diffraction data were collected at 93 K. An ORTEP drawing of **2** is shown in Figure 1.<sup>13</sup> The following features are noteworthy: (1) The bond distance between C1–C2, 1.445(3) Å, was similar or longer than that in 1,2,4,5-tetra(*tert*-butyl)benzene (1.425(5) Å) or in hexakis(trimethylsilyl)benzene (1.442(18) Å). (2) The two interior angles between C3–C4–C5, 111.46(19)° and C2–C3–C4, 129.62(19)° were deviated compared with that in 1,2,4,5-tetra(*tert*-butyl)benzene (115.0° and 129.9°). (3) As shown in Figure 1, all aromatic carbons were located nearly coplanar, while the adjoining aromatic carbon–silicon bonds bend from the connecting plane. On the basis of these data, this compound (**2**) would have one of the distorted benzene rings among the sterically crowded benzenes analyzed by X-ray crystallography so far.

In summary, we have demonstrated the facile synthesis of **1** and its isomerization for the construction of 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)benzene as one of the crowded benzene derivatives. Further studies on their synthetic utility are in progress in our laboratory.

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- Isomerization of **1** under thermal conditions: Dewar benzene **1** (60.0 mg, 0.10 mmol) is placed in a flask, which is kept for 45 min at 220 °C with a glass tube oven under argon atmosphere. After cooling to a room temperature, the resulting pale green mixture was purified by silica gel chromatography (hexane) to afford 55.2 mg (93%) of **2**.
- Isomerization of **1** under irradiation conditions: A degassed hexane solution (10 mL) containing Dewar benzene **1** (61.1 mg, 0.10 mmol) in a quartz test tube was irradiated ( $\lambda > 254$  nm) for 8 h at 40 °C. Concentration of the reaction mixture afforded 60.9 mg (quant) of **2**.
- Analytical data for **2**:  $R_f = 0.95$  (hexane); mp 111.0–112.8 °C;  $\delta_H(\text{CDCl}_3)$  1.0–2.0 (63H, m);  $\delta_F(\text{CDCl}_3)$  –76.12 (1F, d,  $J$  15.3 Hz), –119.76 (1F, d,  $J$  27.6 Hz), –120.27 (1F, dd,  $J$  27.6, 15.3 Hz);  $\delta_C(\text{CDCl}_3)$  12.2–12.3 (3C, overlapped), 14.3–14.6 (6C, overlapped), 18.7–18.8 (6C, overlapped), 19.8–20.2 (12C, overlapped), 111.6 (dd,  $J$  29.8, 49.2 Hz), 125.4 (dt,  $J$  40.8, 4.6 Hz), 136.6 (dd,  $J$  28.8, 10.4 Hz), 153.39 (dd,  $J$  229, 16.0 Hz), 155.06 (dt,  $J$  250, 19.5 Hz), 167.47 (dd,  $J$  234, 12.1 Hz); GC–MS  $m/z$  472 [12,  $M^+ - 129$ ], 115 (39), 105 (17), 87 (37), 77 (100), 73 (59), 59 (70); Anal. Calcd for  $\text{C}_{33}\text{H}_{63}\text{F}_3\text{Si}_3$ : C, 65.94; H, 10.56. Found: C, 66.13; H, 10.49.
- Crystal data for **2**: ( $\text{C}_{33}\text{H}_{63}\text{F}_3\text{Si}_3$ ):  $M = 601.10$ ,  $T = 93(2)$  K, triclinic, space group  $P1$ ,  $a = 8.576(3)$ ,  $b = 13.662(5)$ ,  $c = 17.118(7)$  Å,  $\alpha = 67.46(3)^\circ$ ,  $\beta = 79.79(3)^\circ$ ,  $\gamma = 80.06(4)^\circ$ ,  $V = 1811.0(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.102$  Mg m<sup>–3</sup>,  $\mu = 0.166$  mm<sup>–1</sup>,  $\lambda = 0.71075$  Å,  $\theta_{\text{max}} = 27.48^\circ$ , 12,447 measured reflection, 7378 independent reflections, 381 refined parameters, GOF = 1.148,  $R[F^2 > 2\sigma(F^2)] = 0.0509$ ,  $wR(F^2) = 0.1644$ . The intensity data were collected on a Rigaku RAXIS-RAPID diffractometer. The structure was solved by direct methods (SIR92<sup>14</sup>) and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures on  $F^2$  for all reductions (SHELXL97<sup>15</sup>). All hydrogen atoms were positioned geometrically and refined as riding. CCDC-279251 contains the supplementary crystallographic data for this letter. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/const/retrieving.html](http://www.ccdc.cam.ac.uk/const/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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