

Synthesis of New Fullerene Dimers and Open-Cage Fullerenes by Solid-State and Liquid-Phase Reactions of C₆₀ with N-Containing Aromatics and with Organosilicon Compounds

Koichi Komatsu, Yasujiro Murata, Koichi Fujiwara,
Mitsuharu Suzuki, and Michihisa Murata

Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611-0011, Japan

We recently developed a new method to functionalize C₆₀ in the solid state, by the use of a mechanochemical technique of high-speed vibration milling. This method has been successfully applied to the first [2+2] dimerization of C₆₀,¹ cross-dimerization of C₆₀ and C₇₀,² trimerization³ and [4+2] cycloadditions of C₆₀,⁴ in addition to the complexation with water-soluble host molecules⁵ and a nucleophilic addition to C₆₀.⁶

Particularly when the reaction was conducted with a nitrogen-containing (diaz) aromatic compound such as phthalazine, the [4+2] reaction took place, which was followed by extrusion of nitrogen and further addition or rearrangements to give novel C₆₀ derivatives, a dimer connected by a bicyclic framework **1** (by a solid-state reaction) and a bonzo-derivative of an open-cage fullerene **2** with an eight-membered ring orifice (by a thermal liquid-phase reaction).⁷

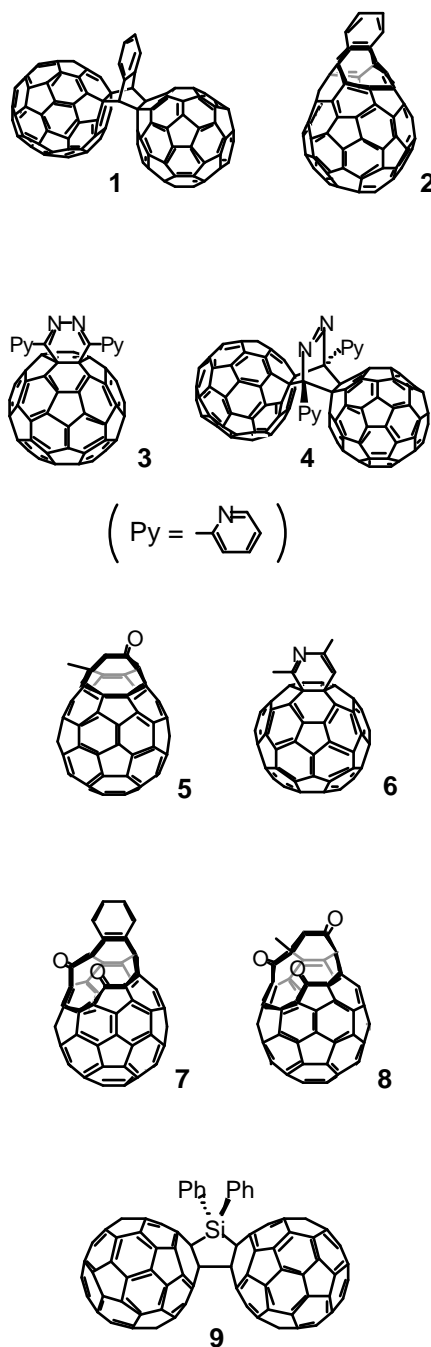
Similarly, when a solid-state reaction of C₆₀ was conducted with 3,6-di-2-pyridyl-1,2,4,5-tetrazine under high-speed vibration milling, the [4+2] addition/nitrogen-extrusion product **3** was formed quantitatively. This can further react with C₆₀ in solid state to give the dimer **4**. Both dimers **1** and **4** undergo the photochemical intramolecular [2+2] reaction between the two C₆₀ cages.

On the other hand, a thermal liquid-phase reaction of C₆₀ with 4,6-dimethyl-1,2,3-triazine at 180 °C afforded, after silica-gel chromatography, an open-cage fullerene derivative **5** with an eight-membered ring orifice in addition to an azacyclohexadiene fused C₆₀ **6**. A photochemical reaction of the open-cage fullerenes **2** and **5** with singlet oxygen was found to give the fullerene derivatives with 12-membered ring orifice **7** and **8** respectively.

Furthermore, the solid-state reaction of C₆₀ with dichlorodiphenylsilane and lithium metal afforded a new C₆₀ dimer with the two C₆₀ cages connected by a silicon atom and a single bond, **9**.

For the new fullerene dimers **1**, **4**, and **9**, the two C₆₀ cages were found to be able to communicate with each other upon electrochemical reduction, and were reduced stepwise but not at the same time for each of the three-wave redox steps as observed by cyclic voltammetry.

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