

## Synthesis of Stable Derivatives of C<sub>62</sub>: The First Nonclassical Fullerene Incorporating a Four-Membered Ring

Wenyuan Qian, Shih-Ching Chuang, Roberto B. Amador, Thibaut Jarrosson, Michael Sander, Susan Pieniazek, Saeed I. Khan, and Yves Rubin\*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received December 11, 2002; E-mail: rubin@chem.ucla.edu

Fullerenes are unparalleled among carbon-based molecules in their combination of structural, topological, and electronic features.<sup>1</sup> With their near-spherical arrangement of sp<sup>2</sup>-hybridized carbon atoms, for which nonadjacent pentagonal rings provide curvature to an otherwise hexagonal network, these unusual compounds display a rich array of physical and chemical properties that have made them some of the most studied compounds in the last 12 years.<sup>1</sup> However, fullerenes are by no means limited to pentagonal and hexagonal ring structures. Novel frameworks such as those incorporating four-membered rings can be envisioned,<sup>2</sup> and their synthesis is likely to bring new developments to the field.

We have recently described a conceptual approach to a parent nonclassical fullerene, C<sub>2v</sub>-symmetric C<sub>62</sub> (**1**, Figure 1).<sup>2</sup> The strained four-membered ring of structure **1** is obtained by formal insertion of a C<sub>2</sub>-unit into two adjacent 5,6-ring junctions of C<sub>60</sub> (**1**). In this study, the parent fullerene C<sub>62</sub> (**1**) was generated in the gas phase from a designed precursor in a laser-induced pyrolytic extrusion of two CO moieties and two hydrogen atoms. This result constituted a clear incentive to a macroscopic preparation of C<sub>62</sub> (**1**), or stable derivatives. While the parent compound **1** has thus far eluded our efforts to isolation due to its predicted high reactivity,<sup>2</sup> the present work takes advantage of a similarly designed mechanism to generate the stable derivatives **6a–c** in a remarkable one-pot procedure involving a series of *tandem* reactions starting from tetrazines **2a–c** (Scheme 1). The formation of the four-membered ring in these products is clearly evidenced by the X-ray structure of one of the C<sub>62</sub> derivatives, compound **6a** (Figure 2).

The sequential rearrangement of cyclohexadienofullerenes to bridged bisfulleroids,<sup>3,4</sup> which proceeds via a photochemically promoted formal [4 + 4] cycloaddition and ensuing [4 + 2] ring opening, provided the intellectual background for the set of reactions shown in Scheme 1. The Diels–Alder reaction of tetrazines **2a–c** with C<sub>60</sub>, which proceeds via inverse electron demand as recently described by Komatsu et al. and Miller et al., leads to the diimine intermediates **3a–c**.<sup>5</sup> We envisioned that intermediates **3a–c** might be diverted via the [4 + 4] photocycloaddition pathway to the desired azo intermediates **4a–c**.

Surprisingly, this desired reaction sequence occurred smoothly upon irradiation with visible light, giving the four-membered ring-containing C<sub>62</sub> derivatives **6a–c** instead of the interesting nucleophilic rearrangement byproducts reported by the groups of Miller and Komatsu.<sup>5</sup> At the temperatures needed to effect this reaction (rigorously dried ODCB, reflux, 2 × 500-W halogen lamps, 2 h), final extrusion of nitrogen from the inferred azo intermediates **4a–c** likely proceeded via the “benzylic” biradicals (**5a–c**, Scheme 1) directly to **6a–c**. Interestingly, the reaction sequence is such that the two Ar–C: units of the tetrazines **2a–c** end up being transferred to two adjacent [5,6]-ring junctions (*cis*-1 addition) of C<sub>60</sub>, a feat that would be difficult to achieve otherwise for lack of carbyne precursors.

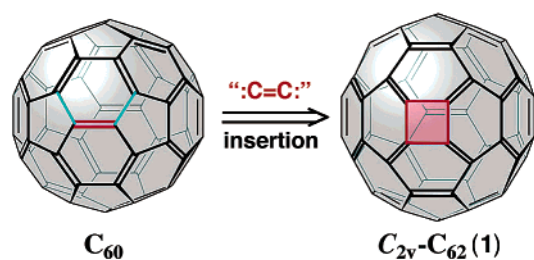
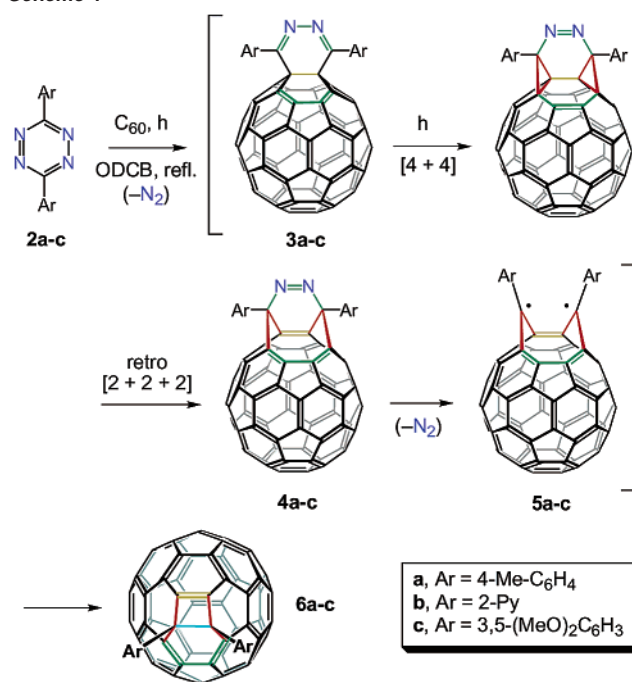


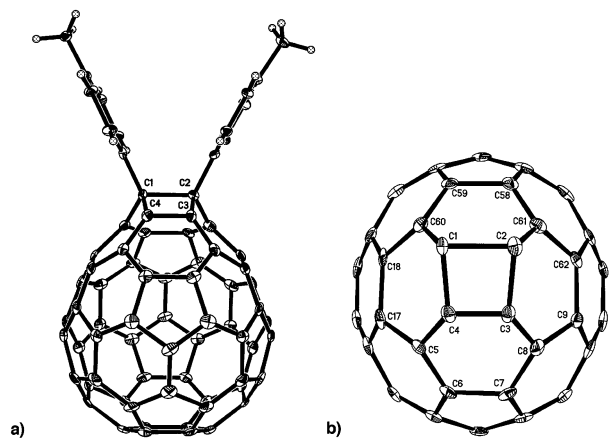
Figure 1. Conceptual insertion of a C<sub>2</sub>-unit into C<sub>60</sub> giving C<sub>62</sub> (**1**)

### Scheme 1

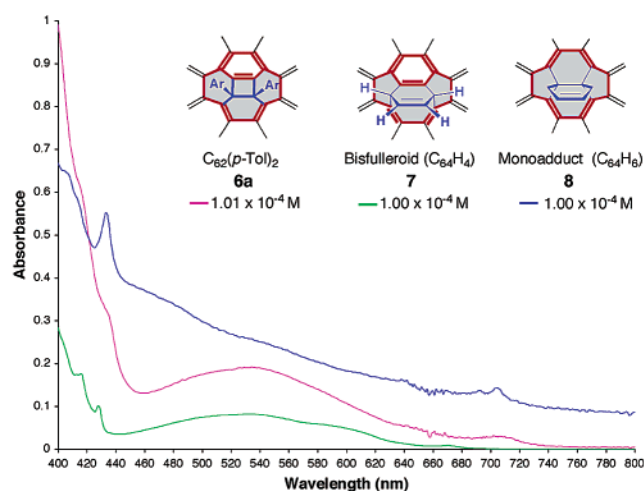


The three C<sub>62</sub>-derivatives **6a–c** are readily isolated in moderate yields (14, 20, and 22%) by column chromatography over silica gel.<sup>6</sup> The two cyclobutene sp<sup>3</sup> carbons of **6a–c** have a characteristic <sup>13</sup>C NMR absorption at 72.38, 73.57, and 72.50 ppm, respectively, in addition to the expected fullerene and aryl signals reflecting the C<sub>s</sub> symmetry of these molecules. These sp<sup>3</sup>-C chemical shifts are similar in range to those of the usual monofunctionalized C<sub>60</sub> derivatives (e.g., **8**, Figure 3).<sup>7</sup>

After numerous attempts with a range of C<sub>62</sub>-derivatives,<sup>8</sup> X-ray quality black single crystals of compound **6a** were finally obtained by slow evaporation from CS<sub>2</sub>/CDCl<sub>3</sub>. Compound **6a** crystallizes in the chiral space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>.<sup>9</sup> The crystals of **6a** incorporate carbon disulfide and chloroform in a 1:1:1 ratio. The packing structure of **6a** reflects the chiral arrangement of the molecules in the crystal, with a refined population of 0.510(7). The four-



**Figure 2.** X-ray structure of (4-Me-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>62</sub> (**6a**). (a) Side view with the *p*-tolyl substituents in the rear of the cyclobutene ring. (b) Top, partial view with the *p*-tolyl substituents omitted for clarity.



**Figure 3.** Comparison of the UV-vis spectra of **6a**, a bisfulleroid (C<sub>64</sub>H<sub>4</sub>, **7**),<sup>3</sup> and a [6,6]-monoadduct (C<sub>64</sub>H<sub>6</sub>, **8**)<sup>7</sup> with indicated concentrations in cyclohexane.

membered ring in structure **6a** is surrounded by four six-membered rings, with relevant cyclobutene bond lengths of 1.667(6) Å for C1–C2, 1.526(6) Å for C2–C3, 1.530(6) Å for C1–C4, and 1.389–(6) Å for C3–C4. The elongated bond for C1–C2 is similar to that of the Csp<sup>3</sup>–Csp<sup>3</sup> bond lengths of monofunctionalized C<sub>60</sub> derivatives.<sup>10</sup> The bond angles within the cyclobutene ring, at 84.8–(3)° (∠C3C2C1), 84.8(3)° (∠C4C1C2), 95.3(4)° (∠C4C3C2), and 95.1(4)° (∠C3C4C1), respectively, reflect the relief of strain that carbons C1–C4 have compared to those of the parent system C<sub>62</sub> (**1**).<sup>2</sup> This is highlighted in particular by the pyramidalization of both C1 and C2 atoms and flattening of the C3–C4 double bond, which has pyramidalization angles<sup>11</sup> of 19.7° and 19.2° for C1 and C2 as well as 16.4° for both C3 and C4, respectively. The corresponding pyramidalization angle for C<sub>62</sub> (**1**), at 17.9°, introduces considerable strain in the parent system, as reflected by the large frontier orbital coefficients calculated at the four-membered ring carbons.<sup>2</sup>

The nonclassical C<sub>62</sub>-derivatives, exemplified by **6a** (Figure 3), display UV-vis absorption spectra that are very similar to those of bisfulleroids (e.g., C<sub>64</sub>H<sub>4</sub>, **7**),<sup>3</sup> reflected by similar dark red-colored solutions. This can be understood from the fact that there is only a slight change in the electronic pathway for both types of compounds: the bridging units differ only in that compounds **6a–c**

have more strained cyclobutene Csp<sup>3</sup>–Csp<sup>3</sup> bridging units but similar π-conjugated perimeters (gray shaded area, Figure 3).

On the other hand, there is a more significant difference of electronic absorption features between **6a–c** and simple C<sub>60</sub>-monoadducts, exemplified by the cyclohexeno[60]fullerene derivative C<sub>64</sub>H<sub>6</sub> (**8**).<sup>7</sup> The broad band centered at 535 nm for **6a**, **7**, and **8** is overlapped in **8** by the hump spanning the range of 445–500 nm, giving this and other C<sub>60</sub>-monoadducts their characteristic dark brown colors. Altogether, one can infer combinations of additive similarities from both electronic systems (**7** and **8**), for example the red absorption centered at 705 nm in **6a**, similar to that of monoadduct **8**, but absent in bisfulleroid **7**.

The methodology described in this study allows a straightforward insertion of a C<sub>2</sub>-unit onto the framework of C<sub>60</sub>, giving stable C<sub>62</sub> derivatives in a one-pot synthesis. In principle, it could offer a way to access higher fullerenes through the sequential buildup of C<sub>2</sub>-units. The physical properties of these and related nonclassical fullerenes are currently studied and will be reported in due time.

**Acknowledgment.** We are grateful to the NSF for Grants CHE-0080942 (Y.R.), CHE-9871332 (X-ray), and CHE-9974928 (NMR) and to the Alfred P. Sloan Research Foundation for support of this work. The DAAD is gratefully acknowledged for a postdoctoral fellowship to M.S.

**Note Added after ASAP:** The version published 2/1/2003 contained errors in the caption of Figure 1. The final Web version published 2/3/2003 and the print version are correct.

**Supporting Information Available:** Experimental section, crystallographic data, and characterization data (PDF). X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) *Fullerenes and Related Structures*; Hirsch, A., Ed.; *Top. Curr. Chem.* **1999**, *199*. (b) Rubin, Y.; Diederich, F. *Stimulating Concepts in Chemistry: From Fullerenes to Novel Carbon Allotropes: Exciting Prospects for Organic Synthesis*; Wiley-VCH: New York, 2000; pp 163–186.
- (2) Qian, W.; Bartberger, M. D.; Pastor, S. J.; Houk, K. N.; Wilkins, C. L.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 8333–8334.
- (3) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775–3776.
- (4) For related methods, see: (a) Hsiao, T. Y.; Santhosh, K. C.; Liou, K. F.; Cheng, C. H. *J. Am. Chem. Soc.* **1998**, *120*, 12232–12236. (b) Iwamatsu, S.; Vijayalakshmi, P. S.; Hamajima, M.; Suresh, C. H.; Koga, N.; Suzuki, T.; Murata, S. *Org. Lett.* **2002**, *4*, 1217–1220.
- (5) (a) Komatsu, K.; Murata, Y.; Kato, N. In *Fullerenes 2000*; Martin, N., Maggini, M., Guldi, D. M., Eds.; Functionalized Fullerenes, Vol. 9; The Electrochemical Society: Pennington, NJ, 2000; p 20. (b) Miller, G. P.; Tetreau, M. C.; Olmstead, M. M.; Lord, P. A.; Balch, A. L. *Chem. Commun.* **2001**, 1758–1759. (c) Murata, Y.; Murata, M.; Komatsu, K. *J. Org. Chem.* **2001**, *66*, 8187–8191.
- (6) See Supporting Information.
- (7) An, Y.-Z.; Ellis, G. A.; Viado, A. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 6353–6361.
- (8) Other similarly prepared derivatives: C<sub>62</sub>(3-Py)<sub>2</sub>, C<sub>62</sub>(4-Py)<sub>2</sub>, C<sub>62</sub>(2-pyrimidinyl)<sub>2</sub>, C<sub>62</sub>Ph<sub>2</sub>, C<sub>62</sub>(1-naphthyl)<sub>2</sub>, C<sub>62</sub>(4-*t*-Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>, C<sub>62</sub>(CO<sub>2</sub>Me)<sub>2</sub>. These will be described in detail in a forthcoming full publication.
- (9) Compound **6a** (C<sub>76</sub>H<sub>14</sub>·CHCl<sub>3</sub>·CS<sub>2</sub>; *M*<sub>r</sub> = 1122.37) crystallized in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with cell dimensions of *a* = 10.0834 (13) Å, *b* = 17.335 (2) Å, *c* = 25.586 (3) Å, *V* = 4472.3 (10) Å<sup>3</sup>, and an occupation of *Z* = 4 in the unit cell. Data were collected at 100 K on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation, to a maximum 2θ = 56.66°, giving 10532 unique reflections; the structure was solved by direct methods and refined with full matrix least squares, yielding *R* = 0.059, *R*<sub>w</sub> = 0.136 for 6473 independent reflections with *I* > 2σ(*I*), *R*<sub>w</sub> (all data) = 0.1584.
- (10) (a) Nuber, B.; Hampel, F.; Hirsch, A. *Chem. Commun.* **1996**, 1799–1780. (b) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 391–394.
- (11) (a) For the pyramidalization concept, see: (a) Haddon, R. C. *Science* **1993**, *261*, 1545–1550. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1997**, *119*, 1797–1798. (c) Haddon, R. C.; Scuseria, G. E.; Smalley, R. E. *Chem. Phys. Lett.* **1997**, *272*, 38–42.

JA029679S