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C_{62}, a Non-Classical Fullerene Incorporating a Four-Membered Ring

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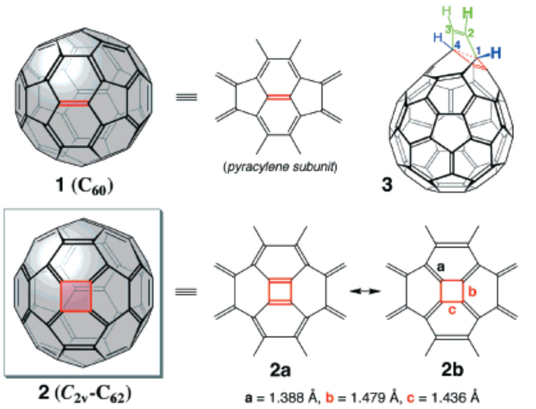
Fullerenes are characterized by their unique arrangement of pyramidalized sp^2-carbons into spherical structures.[1] The two most abundant fullerenes formed by evaporation of graphite are C_{60} (**1**) and C_{70}, both of which are formed as sole geometric isomers.[1,2] With increasing size however, the number of isomers rapidly multiplies,[3,4] and as a consequence of steric strain and the high temperature conditions of their formation, only “classical” fullerene isomers with five- and six-membered rings have been isolated. In fact, all of them are part of a subset having non-adjacent pentagons, a fact known as the isolated-pentagon rule (IPR).[4,5] According to this *empirical* rule, C_{70} is the first higher fullerene that is “stable” after C_{60} because the intermediate fullerenes $C_{62}-C_{68}$ include at least two energetically unfavorable fusions of two five-membered rings within their structures. For C_{62}, three non-IPR isomers with minimally strained geometries have been proposed, and a non-classical structure with fused heptagon−pentagon units having an even lower energy has been predicted.[4,6] Along this line, the energetic penalty for introducing four-membered rings into fullerene structures has been examined.[7] Energy differences for the best single-square structures favor the classical forms of these fullerenes (C_{40}, $C_{62}-C_{68}$) by about 35−120 kcal·mol^{-1} (QCFF/PI method).[7a] Thus, their strain energy makes them unlikely to be isolable from the fullerene soot produced at high temperatures.[8] Here, we report a rational synthetic approach to a four-membered ring isomer of C_{62} (**2**, Figure 1). Evidence for the generation of this structure in mass spectroscopic experiments is presented.



1 (C_{60})

(pyracylene subunit)

3

2 (C_{2v}-C_{62})

2a

2b

a = 1.388 Å, b = 1.479 Å, c = 1.436 Å

Figure 1. Structures of C_{60} (**1**) and $C_{2v}-C_{62}$ (**2**). B3LYP/6-31G* bond lengths shown for **a**, **b**, and **c**.

The structure of classical fullerenes such as C_{60} (**1**) can be considered as a juxtaposition of pyracylene subunits (Figure 1). In the present structure of C_{62}, the central C═C bond of one of these subunits is extruded into a strained four-membered ring surrounded by four six-membered rings, all rigidly held by the surrounding framework.[7a] This structural change can be expected to give rise to unusual physical and chemical properties, as the potential “antiaromatic” nature of the four-membered ring could affect the overall electronic properties of this compound.[7c,9]

Full geometry optimizations were performed at a hybrid density functional theory level (B3LYP) on the singlet and triplet states of **1** and **2**, to obtain meaningful structural and energetic properties.[7a,9,10] Whether the square subunit of **2** should behave more like an antiaromatic cyclobutadiene or a [4]radialene is important for its stability and isolation.[11,12] Since the [4]radialene form forces two double bonds into unfavorable adjacent five-membered rings,[13] the energetic compromise may be in favor of either form. We find that the optimized structure (B3LYP/6-31G*) favors the [4]radialene form **2b** rather than the cyclobutadiene resonance form **2a**, as reflected by the bond lengths **a**, **b**, **c** within and adjacent to the square ring (Figure 1).

The energies of the optimized singlet and triplet states of **2** may be used as an index of chemical stability.[10,11] Interestingly, the triplet energy of **2** is only 12.9 kcal·mol^{-1} (0.56 eV) higher than its singlet state, indicating that the triplet state would be reached very easily. This can be compared to the calculated S−T gap of 36.2 kcal·mol^{-1} for C_{60} (**1**), in good agreement with the experimental value of 36.0 kcal/mol, and easily reached in ambient light.[14] Moreover, the frontier orbitals of **2**, particularly the HOMO, are localized mainly around the four-membered ring (Figure 2). Compound **2** could be therefore quite reactive under normal isolation conditions, a possibility further supported by the fact that the HOMO and LUMO levels are raised and decreased, respectively, compared to those of C_{60}, resulting in a considerably reduced HOMO−LUMO gap (1.84 eV for **2** vs 2.76 eV for **1**).[11,15]

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(11) Local strain as measured by the pyramidalization angle (PA) is also an important factor determining the reactivity of fullerenes. The PA for carbons within the four-membered ring of **2** is 17.9°, much larger than for fullerenes and organic molecules that can be isolated in the condensed phase (PA ≤ 13°, the PA for a tetrahedral carbon is 19.5°!), see: Haddon, R. C.; Scuseria, G. E.; Smalley, R. E. *Chem. Phys. Lett.* **1997**, *272*, 38−42.

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(15) RHF/6-31G* single-point energies also yield a significant decrease (1.3 eV) in HOMO−LUMO gap of **2** relative to **1**. Also, RHF/6-31G* single-point calculations yield very similar FMO distributions in **1** and **2**, compared to the B3LYP/6-31G* results.

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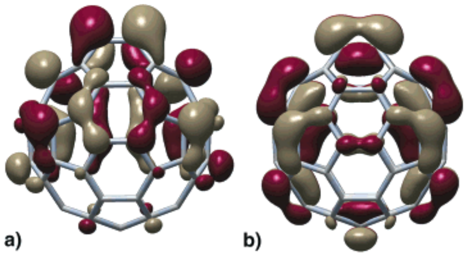
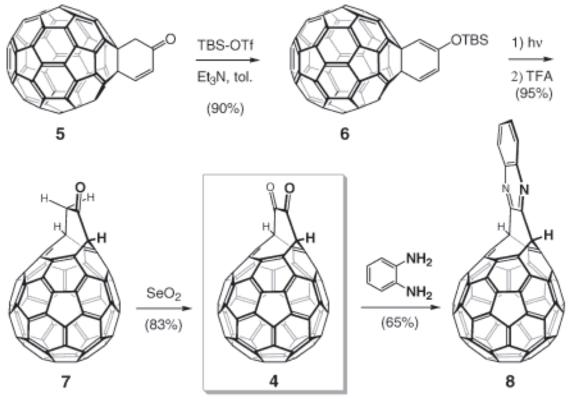
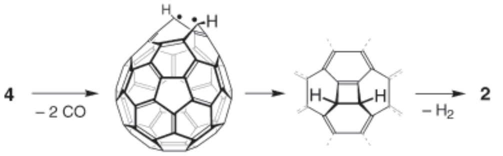


Figure 2. (a) HOMO and (b) LUMO orbitals of C_{62} (**2**, B3LYP/6-31G*), viewed perpendicular to the main C_2 axis (four-membered ring at top).

Scheme 1. Synthesis of C_{62} Precursor **4**



Scheme 2. Proposed Mechanism of C_{62} (**2**) Formation from Precursor **4** ($C_{62}H_2(CO)_2$)



A designed synthesis of C_{62} (**2**) from C_{60} (**1**) requires the appropriate insertion of two carbon atoms into one of the pyracylene subunits as already pointed out by Fowler et al.[7a] This challenging molecular "surgery" became possible with our discovery of an efficient photochemically promoted *tandem* [4 + 4]/[2 + 2 + 2] rearrangement giving ethylene-bridged bisfulleroids (e.g., **3**, Figure 1).[16,17] This rearrangement introduces two bridgehead methines—the fulleroid carbons C1/C4—linked directly to the rest of the C_{60} framework. Both methines are bridged by the ethylene unit C2−C3. Hence, removal of this unit and connection of C1 and C4 gives the desired C_{62} framework. On the basis of this analysis, the dicarbonyl bridged bisfulleroid **4** was deemed suitable as the key precursor to C_{62} (Schemes 1 and 2). Examples of photolytic α-fragmentation of 1,2-dicarbonyl compounds with loss of two CO units have been described,[18] behavior that was also observed in mass spectrometric fragmentations.[19] In the case of **2**, removal of both carbonyl groups under photochemical or thermal excitation should result in two adjacent radicals recombining to the desired four-membered ring. Subsequently, facile dehydrogenation that is characteristic of hydrofullerenes,[20] would give C_{62} (**2**).

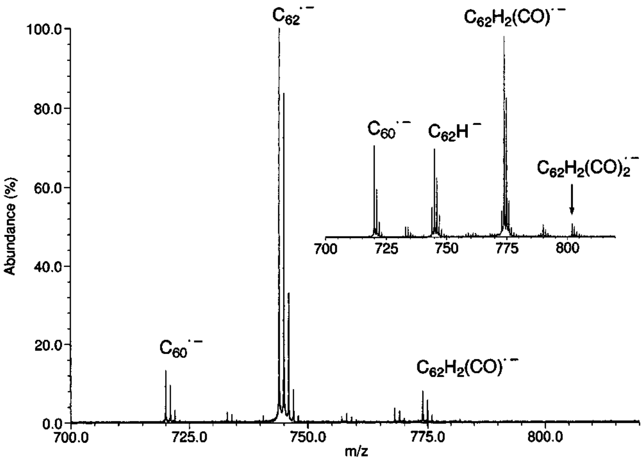


Figure 3. Negative ion LD-FTMS mass spectrum of **4** at medium and low laser power (inset).

Compound **4** was prepared by a stepwise strategy, as direct approaches from **3** proved unworkable (Scheme 1).[10] Compound **5**[21] was converted to the silyl enol ether **6** (Et_3N, TBS−OTf, $PhCH_3$, refl). Visible light irradiation initiated its sequential [4 + 4]/[2 + 2 + 2] rearrangement[16] to the corresponding bisfulleroid (quant), which was deprotected with TFA to the α-methylene ketone **7**. Oxidation of **7** with SeO_2 cleanly afforded diketone **4**. Compound **4** has only one singlet at 7.03 ppm in its ^1H NMR spectrum ($C_2D_2Cl_4$). Due its poor solubility, ^{13}C NMR characterization was precluded. However, reaction of **4** with 1,2-phenylenediamine gave the soluble, fully characterized quinoxaline **8**.[10]

Laser-desorption Fourier transform mass spectrometry (LD-FTMS, CO_2-laser; 10.6 μm, negative ion mode) on **4** produced abundant ions clearly arising from the sequential loss of its two carbonyls (Figure 3). The C_{62} radical anion ($m/z = 744$) forms very readily as the base fragment, while the usually prominent C_{60} peak is comparatively weak. Considering that the internal strain in C_{62} is higher than that of C_{60}, the remarkable intensity of the C_{62} radical anion under the LDMS conditions can be attributed to substantial gas-phase kinetic stability of this species. At lower laser powers, the predominant species is the parent ion with one loss of carbonyl ($C_{62}H_2CO$), while the following loss of CO is accompanied by partial hydrogen-loss ($C_{62}H^-$ principal peak). We take this as a strong indication that the fragmentation occurs according to the proposed mechanism (Scheme 2).[22]

Experiments were carried out to prepare C_{62} from **4** in solution. It was found that diketone **4** is thermally very stable: After heating **4** (e.g., 5 h reflux in ODCB), no appreciable decomposition was observed. Photolysis experiments (e.g., Hanovia lamp, Pyrex, −78 °C) gave only baseline products together with recovered starting material. We are currently working on the preparation of $C_{62}H_2$ to generate **2**.[22]

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Supporting Information Available: Experimental procedures and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] To address one reviewer's suggestion, although an eight-membered ring biscarbene form of **2** cannot be entirely discounted, we have recently prepared the derivative $C_{62}Py_2$ (Py = 2-pyridyl) in solution using a very similar mechanism and shown by X-ray crystallography that it has a cyclobutene ring. Qian, W.; Amador, R.; Comito, A.; Jarrosson, T.; Sander, M.; Verheul, S.; Khan, S. I.; Rubin, Y., unpublished.