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Synthesis of Oxo- and Methylene-Bridged C_{60} Dimers, the First Well-Characterized Species Containing Fullerene−Fullerene Bonds

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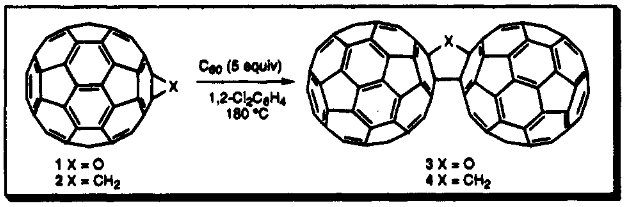
The preparation and characterization of dimers and polymers, wherein two or more cages are directly linked, represents an important frontier in the chemistry of fullerene derivatives.[1] Eklund reported the generation of a C_{60} polymer via [2 + 2] photocycloaddition in a C_{60} film,[2] complementing studies involving laser desorption of C_{60},[3] plasma polymerization of C_{60} films,[4] and crystalline products of metal-doped C_{60}.[5] Reversible dimerization of C_{60}-derived radicals has been observed by ESR, with an unusually low dissociation energy for the putative $C_{60}-C_{60}$ bond.[6] In addition, a C_{119} cluster has been detected by mass spectrometry in both the photolysis of C_{60} and benzil[7] and the thermal decomposition of $C_{60}O$.[8] Despite this array of pioneering work, however, no discrete compound containing a fullerene−fullerene bond has heretofore been isolated and characterized.[9]

Our interest in this problem was stimulated by Taylor's proposed mechanism for the generation of C_{119}, via thermal decarbonylation of $C_{60}O$ and addition of the resultant C_{59} carbene to C_{60}.[10] This hypothesis suggested that $C_{60}O$ could serve as an important precursor of novel fullerene derivatives. In 1992 we described the first synthesis of $C_{60}O$ and assigned the [6,6] epoxide structure **1**;[11] soon thereafter we prepared and characterized the prototypical [6,6] fullerene cyclopropane **2** ($C_{61}H_2$).[12] Herein we report that thermolyses of **1** and **2** in the presence of C_{60} afford the oxygen- and methylene-bridged C_{60} dimers **3** and **4**, embodying the first well-characterized carbon−carbon bonds linking fullerene cages.

For the synthesis of **3**, a mixture of $C_{60}O$ and 5 equiv of C_{60} in 1,2-dichlorobenzene (4 mM in $C_{60}O$) was heated at reflux (ca. 180 °C) for 3 days (Scheme 1).[13] The sole significant nonpolymeric product (**3**) was isolated in 26% yield via reverse-phase flash chromatography followed by precipitation from toluene solution with methanol.[14] To our surprise, the anticipated C_{119} species was not found under these reaction conditions. Analysis of **3** by mass spectrometry, crucial as the only indicator of the molecular weight, proved decidedly nontrivial as standard procedures (e.g., laser desorption) furnished only C_{60} and $C_{60}O$ fragment ions. Negative-ion atmospheric pressure chemical ionization with N_2 as reagent gas, a relatively soft technique, yielded a parent ion for **3** with *m/z* 1457.4 ($C_{120}O$), as well as fragment ions with *m/z* 720.3 (C_{60}) and 736.0 ($C_{60}O$) (Figure 1). Ultimately, we employed negative-ion electrospray ionization with *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine as the electron transfer reagent;[15] this exceptionally gentle method yielded dominant singly and doubly charged parent ions for **3**.

Scheme 1



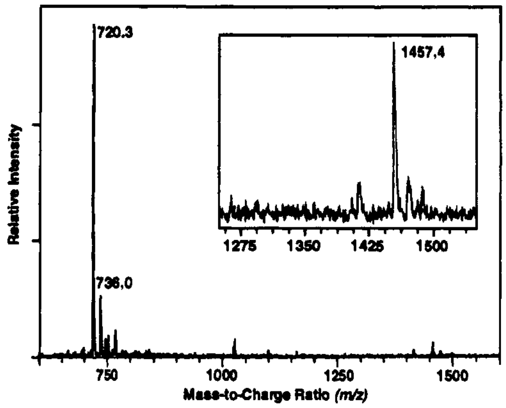


Figure 1. Negative-ion chemical ionization mass spectrum of **3** at atmospheric pressure (N_2 reagent gas) (inset: molecular ion region).

To facilitate ^{13}C NMR analysis we prepared isotopically enriched **3** by thermolysis of enriched C_{60} and $C_{60}O$ (12−13% ^{13}C).[16] The resultant ^{13}C NMR spectrum (125 MHz, 1,2-dichlorobenzene-d_4) contained 32 lines (Figure 2), indicative of a highly symmetric structure. Thirty fullerene skeletal carbons resonated between 136.2 and 153.7 ppm; upfield signals at 78.9 and 99.0 ppm were assigned to the sp^3 carbons linking

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[13] The reaction was monitored by reverse-phase HPLC with a Dynamax 60-Å C-18 column (21.4 mm × 25 cm), 45% MeOH/toluene eluant, 10 mL/min flow rate, UV detection at 325 nm; retention time for **3** = 44.3 min.

[14] For reverse-phase flash chromatography we employed octyl-functionalized silica gel (Aldrich). Following elution of unreacted C_{60} with 50% MeOH/toluene, a 10:1 mixture of **3** and C_{60} was isolated via gradient elution (50% MeOH/toluene → toluene).

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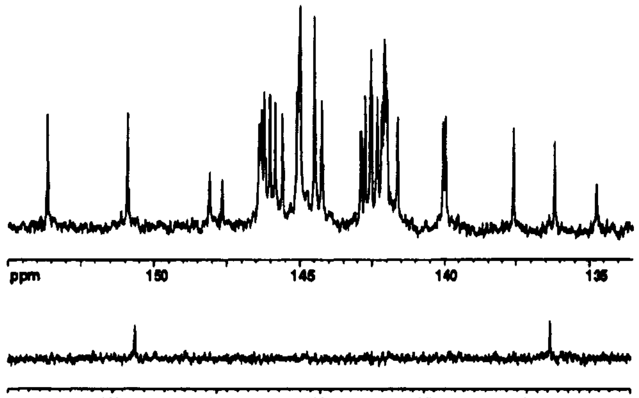


Figure 2. ^{13}C NMR spectrum of **3** (125 MHz, 1,2-dichlorobenzene-d_4).

the fullerene cages and those bound to the oxygen atom, respectively. We next executed two complementary thermolyses, combining enriched and unenriched $C_{60}O$ with unlabeled and labeled C_{60}, respectively; in each case only one cage of the $C_{120}O$ skeleton could be labeled with ^{13}C. As anticipated, the ^{13}C NMR spectra of all three samples were identical, consistent only with a structure of C_{2v} symmetry. On this basis we formulated the oxido-bridged C_{60} dimer as **3**.

The striking results obtained with epoxide **1** led us to examine the thermolysis of the methylene analog, cyclopropane **2**, in the presence of C_{60} (1,2-dichlorobenzene-d_4, reflux). Monitoring by ^1H NMR revealed a product singlet at 6.15 ppm; the methylene singlet of **2** resonated at 3.80 ppm.[12] After 1 week the conversion reached ca. 50%; reverse-phase flash chromatography followed by preparative HPLC then furnished pure **4** in 15% yield as the only isolable product, apart from insoluble polymeric materials. Negative-ion atmospheric pressure chemical ionization mass spectrometry as described above for **3** generated a parent ion for **4** with *m/z* 1455.5 ($C_{121}H_2$) and fragment ions with *m/z* 720.3 (C_{60}) and 734.0 ($C_{61}H_2$). The FT-IR spectrum showed C−H stretching and CH_2 bending bands at 2850 and 1460 cm^{-1}, respectively.

For NMR analysis a sample of **4** was synthesized with ^{13}C-labeled C_{60} and **2**, the latter prepared from enriched C_{60} and diazomethane containing 99% ^{13}C. The ^1H NMR spectrum (500 MHz) consisted of a doublet at 6.15 ppm with $J_{CH} = 137$ Hz. In the proton-coupled ^{13}C NMR spectrum (125 MHz, 1,2-dichlorobenzene-d_4) the methylene resonance at 59.9 ppm is a triplet with $J_{CH} = 137$ Hz. The proton-decoupled spectrum revealed a 34-Hz satellite carbon coupling between the methylene carbon at 59.9 ppm and the adjacent quaternary carbons at 68.4 ppm; the second pair of quaternary carbons appeared at 82.4 ppm. Both ^{13}C NMR spectra contained 32 peaks, consistent with the C_{2v} symmetry of the methylene-bridged dimeric structure **4**.

The UV absorptions at 208, 256, and 327 nm for **3** (Figure 3) and 211, 258, and 328 nm for **4** suggest electronic structures generally similar to those of C_{60} and its monoadducts **1** and **2**.[12] However, the visible regions of the spectra of **3** (Figure 3 inset) and **4** are essentially featureless, in contrast with the corresponding curves for C_{60}, **1**, and **2**.

The formation of **3** and **4** may involve homolysis or heterolysis of **1** and **2**,[17] or it may proceed via SET mechanisms[18] (Scheme 2). In the latter processes, several pathways can be envisioned for conversion of the radical pairs to the observed products. Known reactions involving cleavage of fullerene−substituent bonds include thermal reversions of numerous C_{60} adducts to C_{60},[1] [6,5] fulleroid (annulene) to [6,6] methanofullerene (cyclopropane) rearrangements,[19] acid-promoted cleavage of fused cyclobutane derivatives,[20] rearrangements of aziridine analogs of **1** and **2**,[21] and the aforementioned generation of radicals via the apparent dissociation of fullerene dimers.[6]

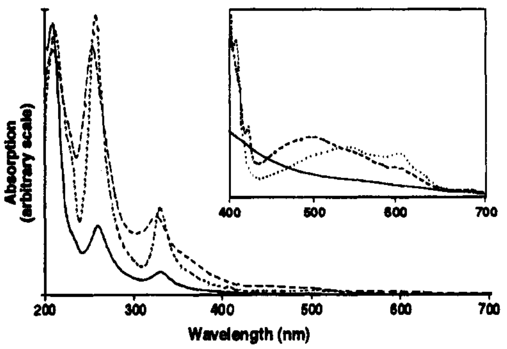
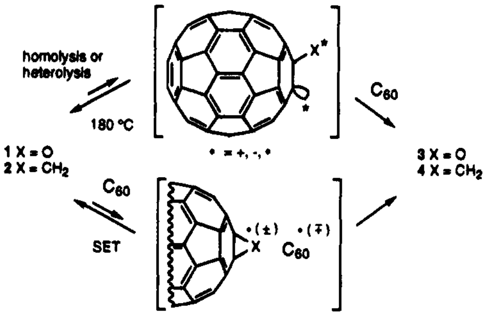


Figure 3. UV−vis spectra of C_{60} (•••), $C_{60}O$ (- - -), and **3** (—) in hexane (inset: visible region in toluene).

Scheme 2



In summary, we have prepared novel oxo- and methylene-bridged C_{60} dimers, the first well-characterized compounds containing fullerene−fullerene bonds. We are currently exploring the scope of the thermolytic transformations of oxo- and methanofullerenes and studying the chemical and physical properties of the novel adducts **3** and **4**. Additions of **1** and **2** to simple alkenes would provide invaluable mechanistic insights as well as synthetic access to new families of fullerene derivatives.

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Supporting Information Available: Preparative procedures and spectroscopic data for **3** and **4** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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