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Oxygen-Bridged 1,2-1′,4′-$RC_{60}-O-RC_{60}$ Unsymmetrical Dimer

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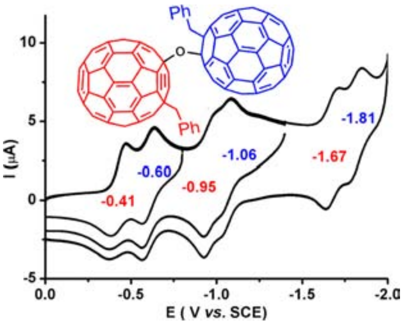
ABSTRACT



A novel oxygen-bridged unsymmetrical dimer composed of C_{60} cages with 1,2- and 1,4-configurations is obtained. The dimer is interesting due to the existence of only one regioisomer, unique regioselectivity, presence of organo functionalities, and exhibition of stepwise reductions via the alternative sequential electron transfer to the 1,4- and 1,2-C_{60} cages.

Fullerene dimers[1] are attractive not only because they are subunits for fullerene polymers,[2] but also because they have exhibited enhanced performance as organic electronic materials for light harvesting,[3] optical switches,[4] charge separation,[5] and photovoltaic devices[6] due to the presence of two fullerene cages in one molecule. Among various fullerene dimers, the singly bonded $RC_{60}-C_{60}R$ dimers are of particular interest due to the rich structural variation brought by the organic functionalities and also the facility for preparation.[7] However, two major problems are associated with the singly bonded dimers: one is the formation of both the meso and racemic regioisomers,[7] which are inseparable in most cases, with the exception of only one case so far of the dimer with phosphonate esters.[7e] The other one is the electrochemical instability upon reduction, which results in decomposition of the dimers into $RC_{60}^{-\bullet}$ due to the repulsion of the negative charges between two closely positioned C_{60} cages.[7c,f] In contrast, the oxygen-bridged dimer $C_{120}O$,[8] where the two fullerene cages are connected by a tetrahydrofuran ring, is quite special since it has only one regioisomer and, more importantly, is stable upon receiving multiple electrons.[9] However, the $C_{120}O$ dimer

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lacks structural variations compared with the singly bonded $RC_{60}-C_{60}R$ dimers due to absence of organic functionalities. A combination of the merits of both the singly bonded dimers and the oxygen-bridged $C_{120}O$ dimer is therefore quite desirable.

We have recently reported the nucleophilic reaction of OH^- with C_{60} and PhCN,[10] where a strong nucleophilic intermediate of $C_{60}^{-}-O^{-}$ is proposed to form and react with the nitriles resulting in fullerene oxazolines.[10,11] However, it is intriguing that no reaction of this nucleophilic intermediate with the electron-deficient C_{60} has occurred. Herein, we report OH^--initiated dimerization of C_{60} followed by an electrophilic reaction with benzyl bromide, which results in an oxygen-bridged unsymmetrical 1,2-1′,4′-$PhCH_2C_{60}-O-C_{60}CH_2Ph$ dimer (**1**). Notably, a radical coupling mechanism is typically involved for the formation of dimers;[2,7] this work presents an unusual approach for preparing a fullerene dimer via a nucleophilic addition mechanism.[12]

The use of ODCB (*o*-dichlorobenzene) instead of benzonitrile as the reaction medium is crucial for the formation of dimer **1** due to the inertness of ODCB toward the anionic nucleophilic intermediates. In addition, raising the reaction temperature (~100 °C) is also pivotal, since only a small amount of **1** was obtained if the reaction was carried out at rt. $PhCH_2Br$ was added after C_{60} reacted with OH^- for 30 min (see Supporting Information for details). Under typical conditions, **1** is obtained with an isolated yield of 41.8%, along with a small amount of 1,4-$(PhCH_2)_2C_{60}$[13] and unreacted C_{60}.

The purity of the obtained compound **1** is confirmed by HPLC analysis (Figures S2 and S3). The HRMS of **1** (Figure S4) shows the $[M + H]^+$ ion at 1639.11159, in agreement with the theoretical value ($C_{134}H_{15}O^+$, 1639.11174). The UV−vis spectrum of **1** (Figure S5) exhibits an absorption peak at 432 nm, suggesting the existence of 1,2-addition in the molecule.[10,14] The ^1H NMR spectrum of **1** (Figure S6) exhibits two sets of AB quartets centered at 5.09 and 4.07 ppm, corresponding to the two sets of diastereotopic methylene protons bonded to the C_{60} cages. The significant chemical shift difference suggests that the two benzyls are likely bonded to the C_{60} cages with the 1,2- and 1,4-configuration respectively in dimer **1**, since such a difference has been shown between the 1,2- and 1,4-adducts (1,2- and 1,4-$(PhCH_2)_2C_{60}$: 5.03 vs 3.71 ppm;[15] 1,2- and 1,4-$(PhCH_2)(CH_3O)C_{60}$: 4.63 vs 4.09 ppm;[10] 1,2-$H(PhCH_2)C_{60}$: 4.77 ppm[16]). Notably, the two AB quartets of the methylene protons exhibit equal intensity, which is unlike the case for the singly bonded $PhCH_2C_{60}-C_{60}CH_2Ph$,[7f] indicating that there is only one regioisomer for dimer **1**.

The ^{13}C NMR spectrum of **1** of natural abundance is in general consistent with the structural assignment; however, the sp^3 C_{60} carbon atoms bonded to the oxygen atom are missing, probably due to the poor solubility of **1** (~1 mg/mL in ODCB) similar to other fullerene dimers,[2,7,17] and also the low sensitivity of these resonances.[18] Compound **1** enriched with 20−25% ^{13}C was therefore prepared to overcome this problem. The ^{13}C NMR spectrum of the ^{13}C enriched **1** (Figure S8) clearly shows two sp^3 C_{60} carbon atoms resonating at 103.85 and 94.25 ppm, which are within the typical range for C_{60} carbons bonded to an oxygen atom.[10,18,19] The ^{13}C NMR spectrum also shows two resonances at 47.97 and 47.88 ppm for the two methylene carbon atoms, and two resonances at 64.54 and 59.38 ppm for the sp^3 C_{60} carbon atoms bonded to the benzyls. Notably, the chemical shifts of the sp^3 C_{60} carbon atoms are also characteristic of the addition patterns. The benzyl-bonded sp^3 C_{60} carbon atoms are less shielded for 1,2-adducts compared to the 1,4-adducts (67.5 vs 60.2 ppm for 1,2- and 1,4-$(PhCH_2)_2C_{60}$,[15] 67.2 vs 59.3 ppm for 1,2- and 1,4-$(PhCH_2)(OCH_3)C_{60}$,[10] 66.0 ppm for 1,2-$H(PhCH_2)C_{60}$,[16] and 61.9 ppm for the meso and racemic 1,4-1′,4′-$PhCH_2C_{60}-C_{60}CH_2Ph$[7f]). The exhibited resonances at 64.54 and 59.38 ppm therefore strongly suggest that the two benzyls are bonded to the two C_{60} cages with a 1,2- and 1,4-configuration respectively with respect to the $C_{60}-O-C_{60}$ bond. In addition, the large difference between the resonances for the two sp^3 C_{60} carbon atoms bonded to the oxygen atom (103.85 vs 94.25 ppm) also suggests the existence of both 1,2- and 1,4-additions in the molecule, in agreement with the significant difference (93.4 vs 80.5 ppm) between the respective carbon atoms of 1,2- and 1,4-$(PhCH_2)(OCH_3)C_{60}$.[10] The considerable downfield shifts for the oxygen-bonded C_{60} sp^3 carbons of **1** compared with 1,2- and 1,4-$(PhCH_2)(OCH_3)C_{60}$ are due to the strong electron-withdrawing effect of the two C_{60} cages. A total of more than 70 resonances for the sp^2 C_{60} carbon atoms are shown in the spectrum, along with resonances due to the phenyl carbons, consistent with the formation of an oxygen-bridged unsymmetrical C_{60} dimer bearing two benzyls with 1,2- and 1,4-configurations.

Figure 1 displays the expanded HMBC NMR spectrum of **1** enriched with 20−25% ^{13}C (see Figure S9 for the full spectrum).[20] Importantly, the AB quartet I (5.60 ppm, $\Delta\nu = 303$ Hz, $J_{AB} = 13.2$ Hz) is correlated with the O-bonded sp^3 C_{60} carbon resonating at 103.85 ppm, demonstrating unambiguously that this benzyl is positioned next to

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[13] 1,4-$(PhCH_2)_2C_{60}$ is likely formed via the reaction of $PhCH_2Br$ with $C_{60}^{-\bullet}$, which was produced via a charge transfer from $C_{60}^{-}-OH$ and/or $C_{60}^{-}-O-C_{60}^{-}$ to C_{60}. Refer to ref 2b. The mechanism for the reaction of $PhCH_2Br$ with $C_{60}^{-\bullet}$ is currently under investigation in our laboratory.

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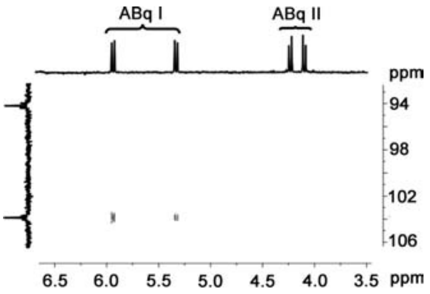


Figure 1. Expanded HMBC NMR spectrum of **1**.

the C_{60}–O bond with a 1,2-configuration; as for AB quartet II (4.13 ppm, $\Delta\nu$ = 68 Hz, J_{AB} = 13.2 Hz), however, it has no correlation with the other oxygen-bonded C_{60} carbon atom resonating at 94.2 ppm, indicating that this benzyl is not placed adjacent to the C_{60}–O bond, but should be positioned with the 1,4-configuration with respect to the C_{60}–O bond, which is conventional for the singly bonded fullerene dimers,[7] and is preferred when steric hindrance is involved.[21] Only one regioisomer is possible for a molecule with such a configuration, consistent with the ^1H and ^{13}C NMR results. The spectroscopic characterizations therefore explicitly show that **1** is 1,2-1′,4′-$PhCH_2C_{60}$–O–$C_{60}CH_2Ph$.

Deuterium isotope experiments were performed to probe further into the reaction. No secondary kinetic isotope effect (SKIE) was observed between the $PhCH_2Br$ and $PhCD_2Br$ according to the ^1H NMR spectrum (Figure S10) of product **1A**, which was obtained by quenching the reaction mixture of C_{60} and OH^- with a mixture of equal amounts of $PhCH_2Br$ and $PhCD_2Br$ (molar ratio, $PhCH_2Br$:$PhCD_2Br$:C_{60} = 10:10:1). The experiment with stepwise addition of $PhCD_2Br$ followed by $PhCH_2Br$ (molar ratio, $PhCH_2Br$:$PhCD_2Br$:C_{60} = 10:10:1) with a time interval of 3 min was performed, which led to the formation of **1B**, to differentiate the benzyls added to C_{60} during different steps.[22] Since a clean control of the stepwise addition of $PhCD_2Br$ and $PhCH_2Br$ to C_{60} is unlikely, the benzyls added during each step should consist of an isotopic mixture.

Figure 2 shows the expanded ^1H NMR spectrum of **1B** for the methylene protons. Impressively, the intensities of the AB quartet I are much lower than those of AB quartet II. The result indicates explicitly that the AB quartet I is due to the benzyl added during the first step, while the AB quartet II arises from the second added benzyl, in considering that there is no significant SKIE between $PhCH_2Br$ and $PhCD_2Br$. Since the AB quartet I originates from the benzyl with the 1,2-configuration as indicated by the HMBC NMR, while the AB quartet II corresponds to the benzyl with the 1,4-configuration, it shows unequivocally that the benzyl added during the first step adopts a 1,2-pattern, while the benzyl added during the second step takes the 1,4-configuration.

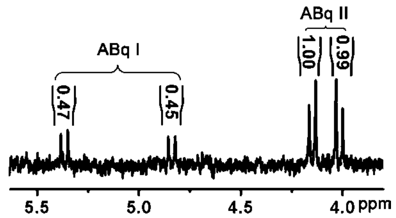
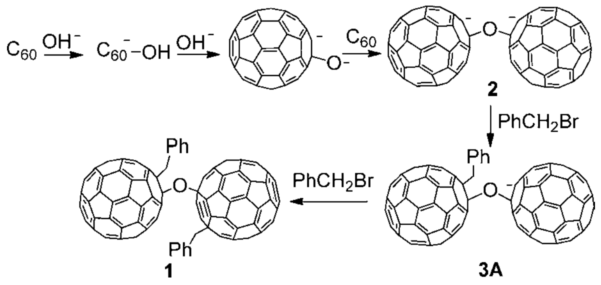


Figure 2. Expanded ^1H NMR spectrum of **1B** recorded in CS_2 ($DMSO\text{-}d_6$ as the external lock) on a 400 MHz instrument.

Scheme 1. Proposed Formation Mechanism for Dimer **1**



Previous work on the nucleophilic addition of OH^- to C_{60} has shown that the reaction results in a very reactive C_{60}^-–O^- intermediate, which may further react with nitriles and form C_{60} oxazolines.[10] Under the current experimental conditions with ODCB as the solvent, the reactive C_{60}^-–O^- intermediate would still be likely produced via the nucleophilic attack of OH^- to C_{60} followed by deprotonation of C_{60}^-–OH by excessive OH^-. However, a subsequent attack of the electron-deficient C_{60} would likely occur to form the C_{60}^-–O–C_{60}^- intermediate (**2**) due to the inertness of ODCB toward nucleophiles and the absence of other electrophiles. A plausible reaction mechanism is proposed for the formation of dimer **1** as shown in Scheme 1.

DFT calculations were performed with Guassian09 to rationalize the regioselectivity of benzyl additions. The structures were optimized at the HF/3-21G level, while the energies and charge distributions were calculated at the B3LYP/6-311G(d) level. The calculations predict a small energy difference between 1,2- and 1,4-$PhCH_2C_{60}$–O–C_{60}^- intermediates (**3A** and **3B**, Figure S12), with **3A** being more stable by 0.40 kcal/mol, implying that both intermediates could be formed. Meanwhile, calculations for the NBO charge distribution of C_{60}^-–O–C_{60}^- predict that the most negative charges are located on the *ortho*- and *para*-carbon atoms with respect to the C_{60}–O bond, with the *ortho*- one having −0.098 and the *para*- one bearing −0.084 (Figure S13), suggesting that the addition site for the first benzyl is likely directed by the charge distribution on the C_{60} cages of C_{60}^-–O–C_{60}^-.

As for 1,2-$PhCH_2C_{60}$–O–C_{60}^- (**3A**), calculations predict that the 2′-carbon of the unarylated C_{60} cage with

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(20) The difference in chemical shift for the AB quartets between Figures 1 and S6 is due to the use of different solvents.

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respect to the $C_{60}-O$ bond bears the greatest negative charge (−0.120), while the 4′-carbon possesses the second most negative charge (−0.088) (Figure S14). However, a greater energy difference of 2.2 kcal/mol is predicted between 1,2-1′,2′-$PhCH_2C_{60}-O-C_{60}CH_2Ph$ (**1′**, Figure S12) and 1,2-1′,4′-$PhCH_2C_{60}-O-C_{60}CH_2Ph$ (**1**), with the 1,2-1′,4′-isomer being more stable. Compared with the calculated 0.40 kcal/mol difference between **3A** and **3B**, it suggests that the steric hindrance is likely the key factor controlling the addition site of the second benzyl.[21]

The optimized structures of **3A** and **1′** (Figure S12) clearly show that the steric hindrance for the benzyl addition arises mainly from the interactions between the two benzyls, rather than the interactions with the C_{60} cage. Therefore, it is rational that the addition of the first benzyl prefers a 1,2-addition, while the addition of the second benzyl favors a 1,4-addition. The formation of intermediate **2** is also supported by MS analysis of the reaction mixture of C_{60} with OH^- quenched with I_2, where a peak at 1458.2 corresponding to $[C_{120}O + H]^+$ is observed (Figure S15).

Figure 3 shows the cyclic voltammograms of **1**. The compound exhibits six quasi-reversible one-electron transfer redox processes, with $E_{1/2}$ at −0.41, −0.60, −0.95, −1.06, −1.67, −1.81 V vs SCE. The six redox waves can be sorted into three divisions, with the first and second, third and fourth, and fifth and sixth in each distinctive group. A smaller peak separation is exhibited between the two subdivided redox waves, suggesting that dimer **1** is likely reduced via a stepwise process with the electron being added alternatively to each individual C_{60} cage. Previous work on the electrochemical study of the 1,2- and 1,4-R_2C_{60} has shown that the 1,4-adducts are more electron-deficient than the 1,2-adducts,[15,23] and the observed reduction processes should therefore correspond to the sequential electron additions to the 1′,4′-C_{60} cage and the 1,2-C_{60} cage alternatively. Notably, the first reduction potential is more anodically shifted compared with that of 1,4-$(PhCH_2)_2C_{60}$ (−0.52 V vs SCE),[15] demonstrating the strong electron-withdrawing effect of the $-OC_{60}$.

The HOMO of the anions has been shown to be well correlated with the redox behaviors of fullerene derivatives.[24] Calculations with Guassian09 at the HF/3-21G level on the HOMOs of the anionic species of **1** were performed to obtain a better understanding of the reduction processes. The calculated HOMO for anionic **1** (Figure 4) shows that the major electron density is located alternatively on the 1,4- and 1,2-C_{60} cage as it goes from $\mathbf{1}^-$, $\mathbf{1}^{2-}$, $\mathbf{1}^{3-}$, and $\mathbf{1}^{4-}$, consistent with the electrochemical behavior of **1** and also the results showing that the 1,4-adducts are more electron-deficient than the 1,2-counterparts.[15,23] Notably, previous work on $C_{120}O$ also reported similar sequential reductive behavior, but was accounted for by the electronic communication between the two closely positioned C_{60} cages.[9]

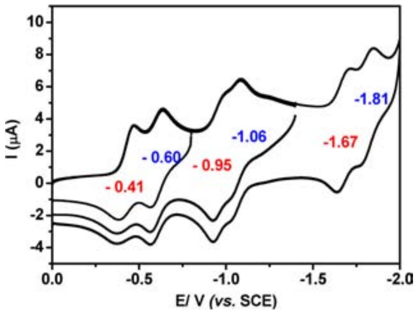

Figure 3. Cyclic voltammogram of dimer **1** recorded in PhCN containing 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) with a scan rate of 0.1 V/s.

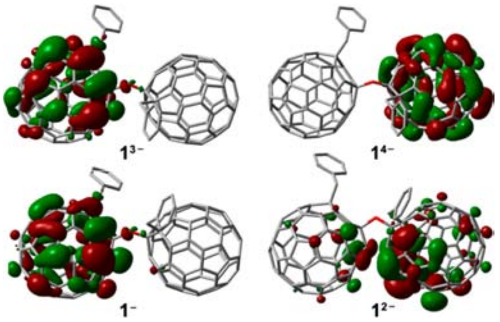

Figure 4. HOMO (0.02 isosurface) for the anions of dimer **1**.

In summary, a novel oxygen-bridged unsymmetrical C_{60} dimer, which incorporates two C_{60} cages with 1,2- and 1,4-configurations, is obtained for the first time via a nucleophilic reaction followed by electrophilic addition. Due to the wide substrate scope for the reaction of anionic fullerenes,[25] the reaction is expected to be of potential use in preparing a variety of dimers with different functionalities. Such a type of dimer is attractive due to the existence of only one regioisomer, possible structural variations by the introduction of organo functionalities, and also the exhibition of distinctive stepwise reductions via the alternative electron transfer to the 1,4- and 1,2-C_{60} cages, which implies the fascinating perspective of selecting one of the two C_{60} cages for manipulation for future study.

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Supporting Information Available. Experimental and calculation details and spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.