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Reductive Benzylation of Singly Bonded 1,2,4,15-C_{60} Dimers with an Oxazoline or Imidazoline Heterocycle: Unexpected Formation of 1,2,3,16-C_{60} Adducts and Insights into the Reactivity of Singly Bonded C_{60} Dimers

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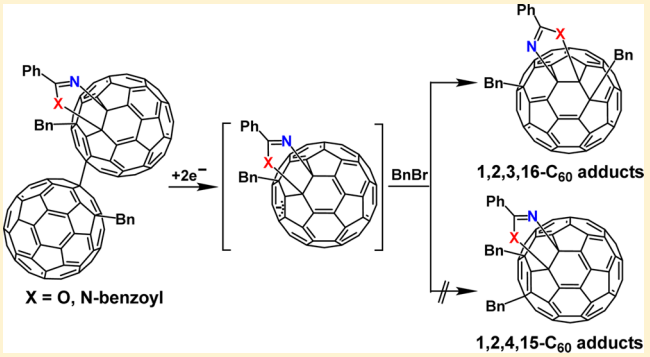
Supporting Information

ABSTRACT: Upon reduction, singly bonded 1,2,4,15-C_{60} dimers with an oxazoline or imidazoline heterocycle dissociate into monoanionic 1,2,4-C_{60} intermediates, which surprisingly leads to the formation of 1,2,3,16-C_{60} rather than 1,2,4,15-C_{60} adducts of the original configuration by further benzylation, even though the analogue of dibenzylated C_{60} oxazoline with a 1,2,4,15-configuration is stable and has been obtained. These results are corroborated by computational calculations, which rationalize the reaction and clarify the structure of the 1,2,3,16-C_{60} adducts, providing new insights into the intrinsic reactivity of singly bonded C_{60} dimers.



INTRODUCTION

Studying the chemistry of fullerenes is of importance for revealing not only the reactivity of the three-dimensional carbon cages[1,2] but also providing promising fullerene acceptors for photovoltaic applications.[3] Among various fullerene derivatives, the RC_{60}–$C_{60}R$ singly bonded fullerene dimers[4] are of special interest due to the facile cleavage of the pivot C_{60}–C_{60} bond, which would result in monomeric radical ($RC_{60}^{\bullet}$)[5] and cationic (RC_{60}^{+})[6] species as precursors for further functionalizations and may lead to the formation of fullerene derivatives that are otherwise difficult to obtain by direct functionalization of C_{60}, as shown by Matsuo and Nakamura et al. in the preparation of noncyclic 1,2-di(organo)[60]fullerene derivatives using singly bonded arylsilylmethyl C_{60} dimers.[6b] However, to the best of our knowledge, no study on functionalizing C_{60} with RC_{60}–$C_{60}R$ via the route of monomeric RC_{60}^{-} has been reported, which is intriguing as the anionic fullerene species are rather common due to the strong electron-deficiency of fullerenes.[7]

We have recently reported the synthesis of singly bonded C_{60} dimers with a 1,2,4,15-configuration that bear an oxazoline or imidazoline heterocycle on one of the carbon cages and one benzyl (Bn) group on each individual C_{60} cage (compounds **1** and **2** in Figure 1).[8] These dimeric molecules are subjected to reductive cleavage of the C_{60}–C_{60} bond,[4b,e] generating monomeric tris-organo[60]fullerene monoanions bearing a heterocycle with a 1,2,4-configuration. Surprisingly, further benzylation of the monoanionic 1,2,4-tris-organo[60]fullerene heterocyclic intermediates with benzyl bromide (BnBr) affords

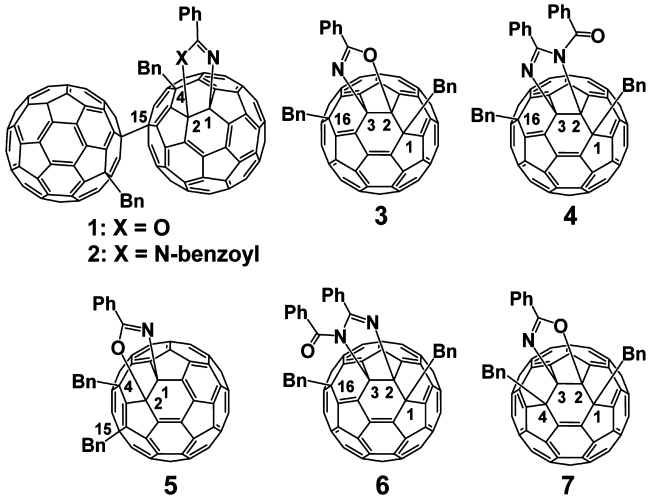


Figure 1. Structural illustrations of compounds **1**–**7** with partial labeling of the C_{60} carbon atoms reported in this and previous studies.

products with a 1,2,3,16-configuration (**3** and **4**, Figure 1) rather than products with the original 1,2,4,15-configuration of the dimers, even though the 1,2,4,15-configuration is a typical structure for C_{60} derivatives with both the 1,2- and 1,4-additions.[8,9] Further, dibenzylated C_{60} oxazoline of a 1,2,4,15-configuration (compound **5**, Figure 1) with the exact addends

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as those in **3** is stable and has been obtained.[9f] Notably, previous work has shown that the formation of 1,2,3,16-C_{60} adducts typically requires the presence of significant steric hindrance between the para-positioned addends at C3 and C16,[10] as illustrated in the example of compound **6** (Figure 1) where a significant hindrance exists between the C16-bound benzyl and the C3-bound bulky benzoyl group.[10c] However, much less steric hindrance is expected between the para-positioned benzyl and small imino nitrogen atom in compounds **3** and **4**, especially considering the fact that benzylated C_{60} oxazoline (compound **7**, Figure 1) with the identical addends as those in **3** is exclusively formed with the 1,2,3,4-configuration during benzylation of the C_{60} phenyl-oxazoline dianion,[11] suggesting unique reactivity related to the singly bonded C_{60} dimers.

RESULTS AND DISCUSSION

Reductive Benzylation of the Singly Bonded C_{60} Dimers Bearing an Oxazoline or Imidazoline Heterocycle with a 1,2,4,15-Configuration (Compounds 1 and 2): Surprising Formation of Compounds 3 and 4 with a 1,2,3,16-Configuration. Singly bonded C_{60} dimers **1** and **2** bearing an oxazoline or imidazoline heterocycle at one of the C_{60} cages, respectively, and one benzyl group at each individual C_{60} cage (Figure 1) were prepared following reported procedures.[8] Compounds **1** and **2** exhibit similar electrochemical behavior as shown in cyclic voltammograms (Figure 2). The first redox process is irreversible, suggesting that

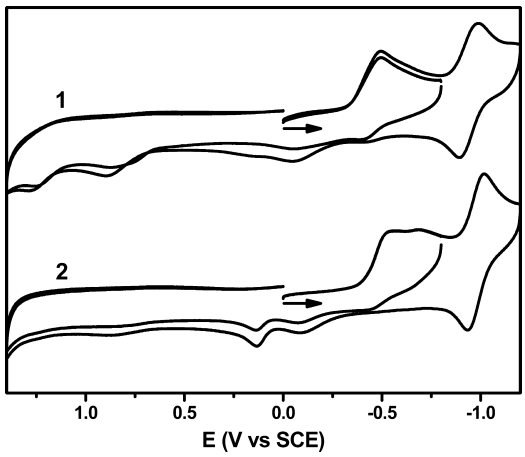

Figure 2. Cyclic voltammograms of compounds **1** (top) and **2** (bottom) in benzonitrile (PhCN) containing 0.1 M TBAP. Scan rate = 0.1 V/s. The arrow indicates the starting potential and the scan direction for the cyclic voltammetric measurements.

reductive cleavage of the dimeric molecules occurs after the first reduction, which is in fact a two-electron transfer process due to the presence of two C_{60} cages in the molecule.[4b,e] Further reduction of the two compounds results in a quasi-reversible redox process with $E_{1/2}$ of approximately −0.96 V relative to a saturated calomel electrode (SCE), which is due to the $BnC_{60}^{-}/BnC_{60}^{2-}$ redox coupling,[4e] confirming the reductive cleavage of dimeric molecules after the first reduction. Controlled potential electrolysis (CPE) was therefore performed on compounds **1** and **2** in benzonitrile under argon with the potential set at −0.80 V relative to SCE, which is appropriate for reductive cleavage of the dimeric molecules. The potentiostat was switched off after the transfer of two electrons per molecule was completed, and 20-fold BnBr was added to the solution. The reactions afforded the 1,2,3,16-adducts of **3** and **4**, respectively, along with 1,4-Bn_2C_{60} arising from benzylation of BnC_{60}^{-}. The crude products obtained were purified by HPLC with a Buckyprep column (Figures S1 and S7 in Supporting Information (SI)). Under typical conditions, compound **3** and 1,4-Bn_2C_{60} were obtained with yields of 80 and 83%, respectively, whereas compound **4** and 1,4-Bn_2C_{60} were obtained with yields of 83 and 83%, respectively.

The ESI HRMS spectra show the protonated molecular ion ($[M + H]^+$) peak at 1022.15644 for **3** and 1125.19831 for **4**, respectively (Figures S2 and S8 in SI), in agreement with the assigned structures of **3** ($[M + H]^+$: $C_{81}H_{20}NO^+$, calcd 1022.15394) and **4** ($[M + H]^+$: $C_{88}H_{25}N_2O^+$, calcd 1125.19614). The UV−vis spectra of **3** and **4** (Figures S3 and S9 in SI, respectively) show absorptions at approximately 410, 450, 523, and 706 nm for both compounds, which are essentially identical to those of previously reported 1,2,3,16-C_{60} imidazoline adducts,[10] indicating that compounds **3** and **4** are 1,2,3,16-adducts because the UV−vis absorptions are characteristic of the configuration of organofullerenes rather than the types of addends.[12]

The ^{1}H NMR spectra (Figures S4 and S10 in SI) show two AB quartets (**3**: 4.21, 3.71 ppm, J = 13.2 Hz and 3.96, 3.82 ppm, J = 12.6 Hz; **4**: 4.92, 3.84 ppm, J = 12.0 Hz and 4.01, 3.86 ppm, J = 12.6 Hz) for each compound, which arise from the two sets of diastereotopic methylene protons of the benzyls along with aromatic protons of the benzyls. The ^{13}C NMR spectra (Figures S5 and S11 in SI) show two signals at 47.20 and 45.97 ppm for **3** and two resonances at 46.94 and 45.18 ppm for **4** due to the two methylene carbon atoms of the benzyls in each compound. The spectra also show two signals at 61.27 and 59.27 ppm for **3** and two resonances at 61.90 and 58.86 ppm for **4** corresponding to the two sp^3 C_{60} carbons bound to the benzyls. In addition, resonances due to the sp^3 C_{60} carbons bound to the oxygen and nitrogen atoms appear at 97.90 and 84.00 ppm, respectively, for **3**, and resonance arising from the imino carbon is shown at 164.43 ppm, which is consistent with the formation of dibenzylated C_{60} oxazoline.[8,11,13] As for **4**, resonances due to sp^3 C_{60} carbons bound to nitrogen atoms of the imidazoline ring appear at 86.75 and 83.25 ppm, and resonances corresponding to the carbonyl and imino carbon atoms appear at 168.96 and 161.15 ppm, respectively, in agreement with the formation of dibenzylated C_{60} imidazoline.[8,10c,13d,14] A total of 53 and 52 peaks are shown for the sp^2 carbons of the C_{60} skeleton of **3** and **4**, respectively, along with peaks due to the phenyl carbons, in agreement with the C_1 symmetry of the two compounds.

The structures of **3** and **4** are further clarified by HMBC NMR characterization and computational calculations as discussed below. The expanded HMBC NMR spectra of **3** and **4** (Figure 3) show that, first, each set of the AB quartet arising from the methylene protons is correlated to only one sp^3 C_{60} carbon atom bound to a benzyl group, indicating that the two benzyls are unlikely to be positioned next to each other in both compounds, as the methylene protons would have correlations with the other benzyl-bound sp^3 C_{60} carbon atom via $^3J_{CH}$ coupling if the benzyls were positioned adjacently. Second, one set of the methylene protons have correlation with one heteroatom-bound sp^3 C_{60} carbon atom in both compounds, whereas the other set of methylene protons have no correlation with either of the heteroatom-bound sp^3 C_{60} carbon atoms, indicating that one benzyl group is positioned at

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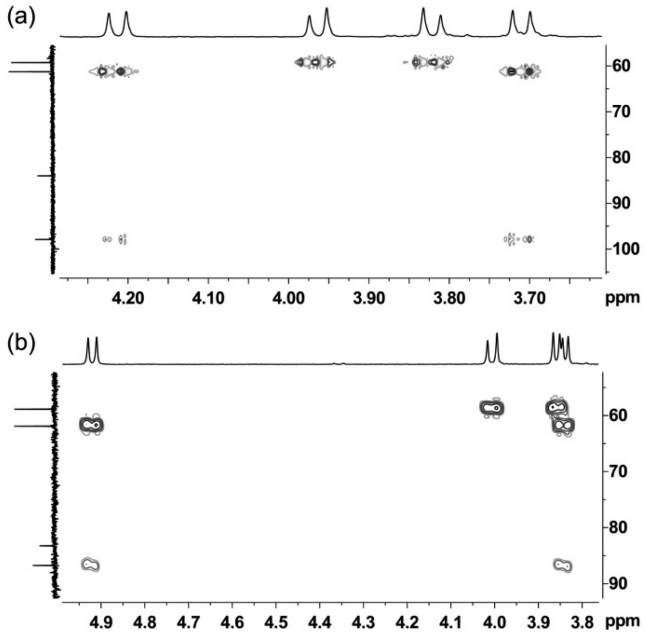

Figure 3. Expanded HMBC NMR spectra (600 MHz) of (a) **3** and (b) **4** in CS_2 with DMSO-d_6 as the external lock.

the site next to a heteroatom in both **3** and **4**, whereas the other benzyl is positioned at a site that is not adjacent to any heteroatom.

The preliminary spectral characterizations show that reductive benzylation of the singly bonded 1,2,4,15-C_{60} dimers results in products with an unexpected 1,2,3,16-configuration rather than the original 1,2,4,15-configuration. However, the exact structural assignment of the 1,2,3,16-adduct needs further clarification, which is resolved by theoretical calculations described below.

Theoretical Calculations and Mechanistic Consideration for the Formation of 3 and 4 by Reductive Benzylation of 1 and 2. Previous work has shown that the singly bonded RC_{60}–$C_{60}R$ dimers undergo reductive decomposition facilely to afford an anioinic monomeric species (RC_{60}^-) due to repulsion between the two negatively charged cages.[4b,e] Consequently, BnC_{60}^- and a monomeric monoanion of the tris-organo[60]fullerene intermediate **A** (Figure 4a) with one benzyl and an oxazoline or imidazoline heterocycle in a 1,2,4-configuration are produced when dimers **1** and **2** are reduced under the experimental conditions. Theoretical calculations with Gaussian09 were carried out to obtain a better understanding of the reactions. The natural bond orbital (NBO) charge analysis at the B3LYP/6-311G(d) level predicts that the two largest negative charges are located at C15 and C3 in intermediate **A** (Figure 4a), suggesting that the incoming benzyl group would most likely be added at either C15 or C3. The addition of a benzyl at C15 would result in a 1,2,4,15-adduct (compound **5** in Figure 1) with the original configuration of the starting dimer molecules, and the product would be exactly the same as the compound that was obtained from the oxazolination reaction of 1,4-Bn_2C_{60},[9f] indicating that the addition of a benzyl at C15 to intermediate **A** is thermodynamically feasible; the addition of a benzyl at C3 would result in a 1,2,3,4-adduct (compound **7** in Figure 1),

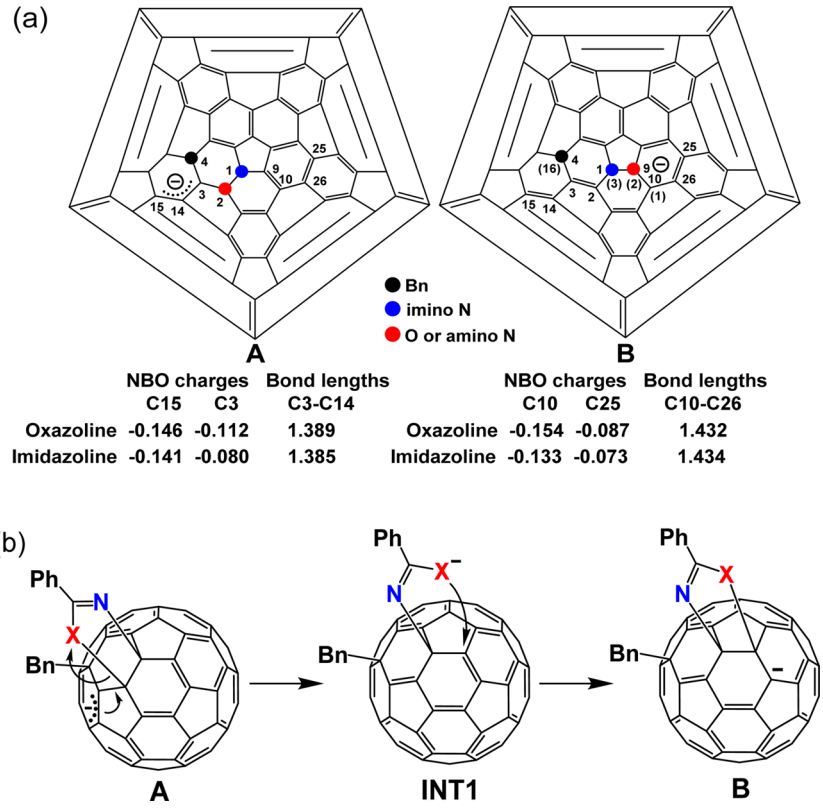

Figure 4. (a) Schlegel diagrams of monoanionic intermediates **A** and **B** with partial labeling of C_{60} carbon atoms, NBO charge distributions, and bond lengths (Å). The numbers in parentheses in **B** represent the labeling of C_{60} carbon atoms according to the numbering in compounds **3** and **4**. (b) Illustration of the rearrangement of the X–C_{60} (X = O or amino N) bond accompanied by charge relocation.

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which is expected to be stable for the oxazoline product, as the 1,2,3,4-configuration is a stable structure for C_{60} derivatives when no steric hindrance is involved.[15] No steric hindrance is envisioned between the adjacently positioned benzyl and small oxygen atom of the oxazoline ring (Figure 4a), as evidenced by the exclusive formation of the 1,2,3,4-adduct during the benzylation of C_{60} oxazoline dianion with the same heterocycle.[11] However, the HMBC NMR spectra of **3** and **4** indicate explicitly that the incoming benzyl is not added at either C15 or C3 in **A**, as addition at these two sites would not comply with the structure in which one benzyl is positioned next to the X−C_{60} (X = O or N) bond while maintaining that the two benzyls are not positioned next to each other.

The results indicate that intermediate **A** is unlikely to be stable and undergoes a fast rearrangement before being subjected to the final benzyl addition. Previous work on C_{60} oxazoline and imidazoline has shown that the O−C_{60} and amino N−C_{60} bonds can be readily cleaved when the molecule receives two electrons and migrate from a [6,6]-bond to a [5,6]-bond upon benzylation.[11b,14b] Our recent work on 1,4-(MeO)BnC$_{60}$ (Me = methyl) has shown that such reductive bond cleavage can be facilitated by the presence of a neighboring [5,6]-double bond in which cleavage of the O−C_{60} bond may happen even if the intermediate carries only one negative charge, driven by the force to remove the electronically unfavored [5,6]-double bond.[16] Indeed, calculations on intermediate **A** predict a significant [5,6]-double bond nature for the C3−C14 bond (1.389 and 1.385 Å for the oxazoline and imidazoline, respectively) and localization of a large negative charge at C3. This may in turn promote charge-induced cleavage of the neighboring X−C_{60} (X = O or amino N) bond and migration of the oxygen or amino nitrogen atom from C2 to C9 accompanied by charge relocation (Figure 4b) and the formation of intermediate **B** (Figure 4a). In contrast, in intermediate **B**, the bond length for the [5,6]-bond of C10−C26, which is adjacent to the X−C_{60} (X = O or amino N) bond, is predicted to be 1.432 and 1.434 Å for oxazoline and imidazoline, respectively, which is very close to the typical bond length of a [5,6]-single bond in C_{60} (1.450 Å).[17]

Further NBO calculations predict that the largest negative charge is located at C10 (−0.154 and −0.133 for oxazoline and imidazoline, respectively) in intermediate **B**, suggesting that the incoming benzyl would be preferentially added at C10 with the formation of a 1,2,3,16-adduct (see the labeling in parentheses in **B**, Figure 4a), whose structure is consistent with the UV−vis and HMBC NMR spectral characterizations in that one benzyl is positioned next to the X−C_{60} (X = O or amino N) bond, and the two benzyls are not positioned next to each other. Notably, previous work on direct benzylation of C_{60} oxazoline with the same heterocycle as that in **1** and **3** would result in a 1,2,3,4-C_{60} adduct,[11] whereas direct benzylation of C_{60} imidazoline with the same heterocycle as that in **2** and **4** would result in compound **6** (Figure 1), which is another 1,2,3,16-C_{60} regioisomer with the amino N−C_{60} bond and the benzyl positioned para at C3 and C16, respectively, as the predominant product, and compound **4** as only a minor product due to the considerable steric hindrance caused by the bulky benzoyl group on the amino nitrogen atom. This indicates that the reactions of singly bonded fullerene dimers undergo via a regiocontrol mechanism that differs from those of directly functionalized monomeric C_{60} derivatives.

To the best of our knowledge, this is the first time that the stability of 1,2,4- and 1,4,9-tris-organo[60]fullerene monoanionic intermediates has been studied. The results show that the 1,2,4-tris-organo[60]fullerene monoanionic intermediate is rather unstable and may convert to the 1,4,9-tris-organo[60]-fullerene monoanionic intermediate via a charge-induced pathway. The instability of the 1,2,4-tris-organo[60]fullerene monoanionic intermediate indicates that the 1,2,4,15-C_{60} adducts are unlikely to be obtained starting from 1,2-C_{60} adducts, which is consistent with previous result that the 1,2,4,15-C_{60} adducts can be obtained by direct functionalization of the 1,4-C_{60} adducts but not the 1,2-C_{60} adducts.[9c−e]

A more thorough calculation was performed for the conversion of **A** to **B** with the Gaussian09 package to provide further insight into the reaction. Geometry optimization, transition state identification, and vibrational frequency analyses were carried out at the B3LYP/6-31G level, whereas the energy was calculated at the B3LYP/6-311G(d) level. Figure 5 shows

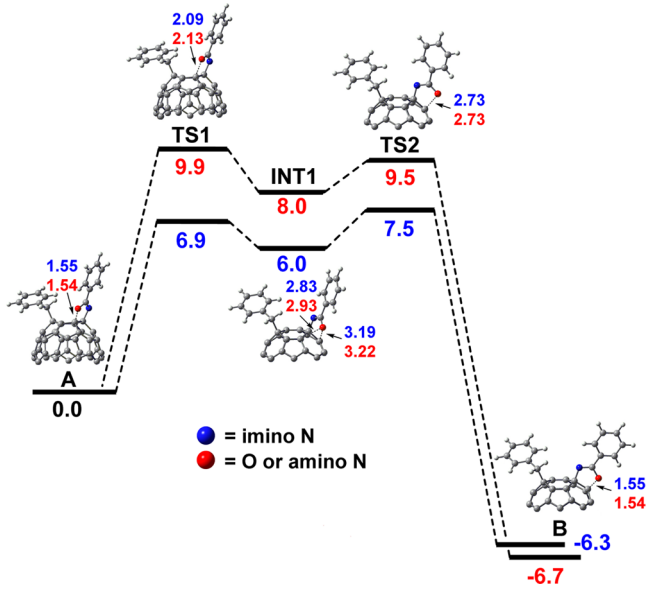

Figure 5. Computed energy profiles for the conversion of **A** to **B**. Energies are given in kcal/mol, and bond lengths are given in angstroms (Å). The blue and red numbers represent the results of C_{60} oxazoline and C_{60} imidazoline, respectively.

the energy profiles for the conversion of **A** to **B**, along with the calculated bond lengths of the O−C_{60} and amino N−C_{60} in each species. In addition to **A** and **B**, the calculations have located two transition states **TS1** and **TS2** and an intermediate state **INT1**. Small activation barriers of 7.5 and 9.9 kcal/mol are predicted for the migration of the O−C_{60} and amino N−C_{60} bonds from the [6,6]-bond to the [5,6]-bond, respectively. The calculations also predict **B** is more energetically favorable over **A** by 6.3 and 6.7 kcal/mol for oxazoline and imidazoline, respectively, consistent with the experimentally observed conversion of **A** to **B**. The variations of the O−C_{60} and amino N−C_{60} bond lengths in **A**, **TS1**, **INT1**, **TS2**, and **B** are in good agreement with cleavage and formation of the X−C_{60} bond during the relocation of the heteroatom, where the X−C2 bond is broken in **TS1**, and the X−C9 bond is formed in **TS2** by migrating the O or amino N atom from C2 to C9 via **INT1**.

On the basis of the discussion above, a reaction mechanism for the formation of **3** and **4** via the reductive benzylation of **1** and **2** is proposed and illustrated in Scheme 1. The reductive dissociation of the dimeric molecules into monomeric anionic

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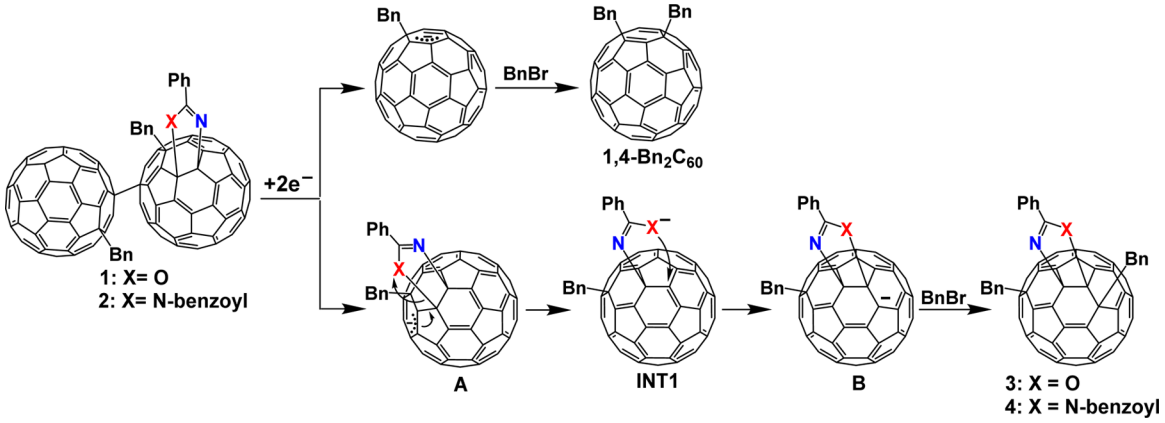
Scheme 1. Proposed Mechanism for the Formation of 3 and 4 via the Reductive Benzylation of 1 and 2



species and rearrangement of the 1,2,4-tris-organo[60]fullerene monoanionic intermediate (**A**) to the more stable 1,4,9-tris-organo[60]fullerene monoanionic intermediate (**B**) are the key steps in achieving the unique regiocontrol of the reactions.

CONCLUSION

In summary, reductive benzylation of singly bonded 1,2,4,15-C_{60} dimers with an oxazoline or imidazoline heterocycle has been studied, which unexpectedly affords products with a 1,2,3,16-configuration rather than the original 1,2,4,15-configuration. The unique reactivity of the singly bonded fullerene dimers is rationalized by the computational calculations, which reveal that the 1,2,4-tris-organo[60]fullerene monoanionic intermediate is unstable and would rearrange to the more stable 1,4,9-tris-organo[60]fullerene monoanionic intermediate via a charge-induced process. In addition, it is noteworthy that the structures of the resulting 1,2,3,16-adducts (**3** and **4**) obtained from the reactions of the singly bonded C_{60} dimers (**1** and **2**) are different than those obtained by direct reductive benzylation of C_{60} oxazoline or imidazoline with the same heterocycle (compounds **7** and **6**), indicating that singly bonded fullerene dimers have promising potential for preparing novel fullerene derivatives.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an Ar atmosphere. All reagents were obtained commercially and used without further purification, unless otherwise noted. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried under vacuum at 313 K prior to use.

Controlled-potential bulk electrolysis was carried out on a potentiostat/galvanostat using an "H" type cell. Two platinum gauze electrodes (working and counter electrodes) were separated by a sintered glass frit. For cyclic voltammetry (CV) experiment, a three-electrode cell was used, and glassy carbon and platinum wire were used as the working and counter electrodes, respectively. In both controlled potential electrolysis and CV measurements, a saturated calomel electrode (SCE) was used as a reference electrode. A fritted-glass bridge of low porosity that contained the solvent/supporting electrolyte mixture was used to separate the SCE from the bulk of the solution.

Preparation of Compound ***3***. Typically, 30 mg (17 μmol) of compound **1** in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP was electrolyzed at −0.8 V relative to SCE under an argon atmosphere. The potentiostat was switched off after the transfer of two electrons per molecule was completed, and 20-fold BnBr (40 μL, 340 μmol) was added to the solution. The benzylation reaction was allowed to proceed for 1 h under argon at room temperature. The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAP. The crude product was dissolved in toluene and was purified by eluting toluene over a semipreparative HPLC Buckyprep column (10 mm × 250 mm) with a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compounds **3** and 1,4-Bn_2C_{60} were obtained with isolated yields of 80% (13.9 mg) and 83% (12.8 mg), respectively.

Spectral Characterization of ***3***. Positive ESI FT-ICR MS, *m*/*z* calcd for $C_{81}H_{20}NO^+$ $[M + H]^+$ 1022.15394, found 1022.15644; ^{1}H NMR (600 MHz, in CS_2 with DMSO-d_6 as the external lock solvent) δ 8.09 (*d*, 2H), from 7.42 to 7.30 (*m*, 4H), 7.15 (*d*, 2H), from 7.04 to 6.97 (*m*, 3H), from 6.90 to 6.87 (*m*, 2H), from 6.85 to 6.83 (*m*, 2H), 4.21 and 3.71 (AB_q, J_{AB} = 13.2 Hz, 2H), 3.96 and 3.82 (AB_q, J_{AB} = 12.6 Hz, 2H); ^{13}C NMR (126 MHz, in CS_2 with DMSO-d_6 as the external lock solvent) δ 164.43 (C═N), 156.62, 155.92, 151.74, 150.39, 149.81, 148.50, 148.14, 148.13, 147.93, 147.86, 147.64, 147.27, 147.05, 147.00, 146.96, 146.82, 146.58, 146.55, 146.30, 146.19, 145.99, 145.72, 145.65, 145.53, 145.50, 145.47, 144.95, 144.78, 144.44, 144.39, 144.30, 144.23 (2C), 144.17, 143.81, 143.50, 143.08, 143.03, 142.71, 142.14, 141.88, 141.47, 141.40, 141.35, 140.99, 140.92, 140.58, 139.23, 139.18, 138.73, 138.25, 137.83, 135.70 (2C), 135.59 (2C), 133.80 (Ph), 132.27 (Ph), 132.09 (Ph), 131.39 (2C, Ph), 130.49 (2C, Ph), 128.89 (2C, Ph), 128.59 (2C, Ph), 128.20 (2C, Ph), 127.87 (2C, Ph), 127.14 (Ph), 127.09 (Ph), 126.97 (Ph), 97.90 (sp^3, C_{60}−O), 84.00 (sp^3, C_{60}−N═), 61.27 (sp^3, C_{60}−benzyl), 59.27 (sp^3, C_{60}−benzyl), 47.20 (CH_2), 45.97 (CH_2); UV−vis (toluene, λ_{max}/nm) 410, 450, 520, 704.

Preparation of Compound ***4***. Typically, 30 mg (16 μmol) of compound **2** in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP was electrolyzed at −0.8 V relative to SCE under an argon atmosphere. The potentiostat was switched off after the transfer of two electrons per molecule was completed, and then 20-fold BnBr (38 μL, 320 μmol) was added to the solution. The benzylation reaction was allowed to proceed for 1 h under argon at room temperature. The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAP. The crude product was dissolved in toluene and was purified by eluting toluene over a semipreparative HPLC Buckyprep column (10 mm × 250 mm) with a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm. Compounds **4** and 1,4−Bn_2C_{60} were obtained with isolated yields of 83% (15.0 mg) and 83% (12.0 mg), respectively.

Spectral Characterization of ***4***. Positive ESI FT-ICR MS, *m*/*z* calcd for $C_{88}H_{25}N_2O^+$ $[M + H]^+$ 1125.19614, found 1125.19831; ^{1}H NMR (600 MHz, in CS_2 with DMSO-d_6 as the external lock solvent) δ 7.55 (*d*, 2H), 7.23 (*d*, 2H), 7.18 (*d*, 2H), from 7.06 to 6.93 (*m*, 9H), from 6.90 to 6.82 (*m*, 5H), 4.92 and 3.84 (AB_q, J_{AB} = 12.0 Hz, 2H), 4.01 and 3.86 (AB_q, J_{AB} = 12.6 Hz, 2H); ^{13}C NMR (150 MHz, in CS_2 with DMSO-d_6 as the external lock solvent) all signals represent 1C except noted, δ 168.96 (1C, C═O), 161.15 (1C, C═N), 157.69, 154.82, 150.63, 150.58, 149.20 (2C), 148.18, 147.69, 147.67, 147.50, 147.34, 147.31, 146.66, 146.32 (2C), 146.12, 146.04, 145.80, 145.73,

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145.50, 145.38, 145.34, 145.25, 145.05, 144.89, 144.56, 144.46, 144.32, 144.15, 144.03, 143.83, 143.80, 143.70, 143.67, 143.19, 143.12, 142.58, 142.44 (2C), 142.27, 142.19, 141.71, 141.46, 141.08 (2C), 140.64, 140.41, 140.39, 140.30, 140.05, 138.40, 138.03, 137.81, 137.56, 135.78, 135.53, 135.43 (Ph), 135.32 (Ph), 132.00 (Ph), 131.34 (2C, Ph), 131.07 (Ph), 131.03 (Ph), 130.22 (Ph), 129.99 (2C, Ph), 128.20 (4C, Ph), 127.71 (2C, Ph), 127.67 (2C, Ph), 127.45 (2C, Ph), 127.40 (2C, Ph), 126.64 (Ph), 126.44 (Ph), 86.75 (sp^3, C_{60}–N–), 83.25 (sp^3, C_{60}–N=), 61.90 (sp^3, C_{60}–benzyl), 58.86 (sp^3, C_{60}–benzyl), 46.94 (CH_2), 45.18 (CH_2); UV–vis (toluene, λ_{max}/nm) 411, 450, 523, 706.

Computational Methods. All calculations were performed with the Gaussian09 program package. Geometry optimization, transition state identification, and harmonic vibrational frequency calculations were performed using the DFT/B3LYP method with the 6-31G basis set. The NBO charge distribution and enegy calculations were carried out at the B3LYP/6-311G(d) level.

■ ASSOCIATED CONTENT

Supporting Information

HPLC traces, spectra of compounds **3** and **4**, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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