

Tethered Bisadducts of C_{60} and C_{70} with Addends on a Common Hexagonal Face and a 12-Membered Hole in the Fullerene Cage

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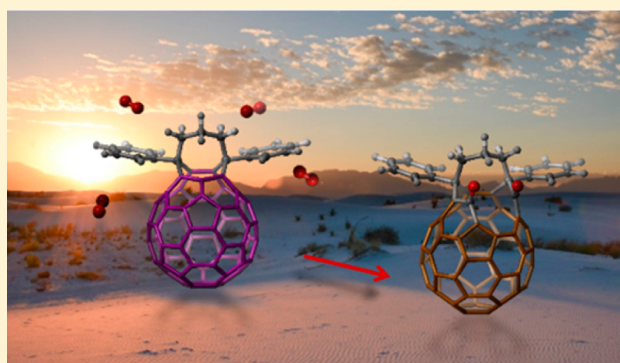
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S Supporting Information

ABSTRACT: The regioselective synthesis of easily isolable pure bismethano derivatives of C_{60} and C_{70} with high steric congestion is described using 1,3-dibenzoylpropane bis-*p*-toluenesulfonyl hydrazone as the addend precursor. When the addition occurs at two [6,6] ring junctions within the same hexagon, bisadducts with mirror symmetry are obtained for both C_{60} and C_{70} . When the addition occurs at two [5,6] ring junctions in C_{60} , a symmetrical adduct is formed, which readily undergoes photo-oxygenation and ring opening to yield a fullerene with a hole in the cage. In this work, we also propose a simple and general system to name all of the possible [6,6] bisadduct isomers on C_{70} .



INTRODUCTION

Since the discovery of fullerenes in 1985,¹ their functionalization has been extensively studied,¹ partly to increase their solubilities and to expand their applications in biomedicine, materials science, and organic photovoltaic (OPV) solar cells, among others.² The use of fullerene derivatives as electron acceptors is rapidly developing, mainly because of their low reduction potentials, their low recombination energies upon electron transfer, and their high charge transport capabilities in three dimensions.^{2,3}

Recently, bisfunctionalization of fullerenes has resulted in compounds that are very effective in OPV solar cells.^{3–6} Therefore, understanding and controlling the formation of specific regioisomers of bis- and multiple adducts of fullerenes is crucial because it has been shown that some regioisomerically pure fullerene bisadducts perform better in OPV solar cells than in the corresponding isomeric mixtures.⁷

The synthesis of fullerene bisadducts is challenging because of the many isomeric products that are typically obtained. If both addends are identical and symmetric, the number of possible isomers is 8 in the case of C_{60} ⁸ and 38 in the case of C_{70} (Figure 1), provided that additions occur exclusively on [6,6]-bonds. To increase the yield of a specific bisadduct regioisomer and to avoid high-performance liquid chromatographic separations, Diederich et al.⁸ introduced a very useful tool, the tether-directed remote multifunctionalization. This method involves the use of a variable length and rigidity tether that connects two or more reactive centers to direct the

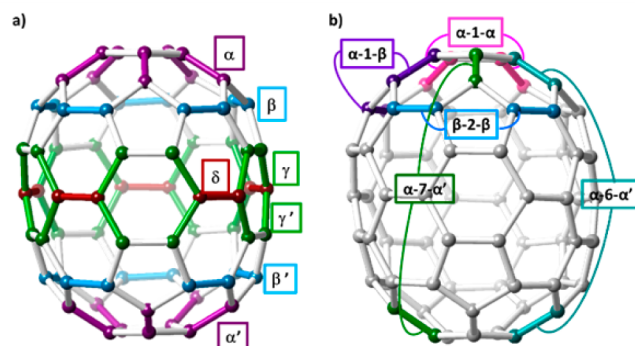


Figure 1. (a) Types of double bonds on C_{70} . The equator contains the δ -bonds; in the north pole, there are α -, β -, and γ -bonds, and in the south pole, α' -, β' -, and γ' -bonds. (b) Some examples of possible bisaddition combinations relevant to this work.

location of the multiple adducts on the fullerene surface.⁹ The most abundant nontethered bisaddition products usually observed are the *trans*-3 and equatorial isomers for C_{60} and the 12, 2, or 5 o'clock for C_{70} ,¹⁰ with very few examples of *cis*-1 or *cis*-2 on C_{60} or α -1- α and α -2- α on C_{70} because of the steric congestion; see Figure 1 for the nomenclature used.¹¹ However, for biseperoxides, $C_{60}O_2$, the isomer with both oxygen

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atoms bound to a single hexagonal surface is the most abundant isomer.¹²

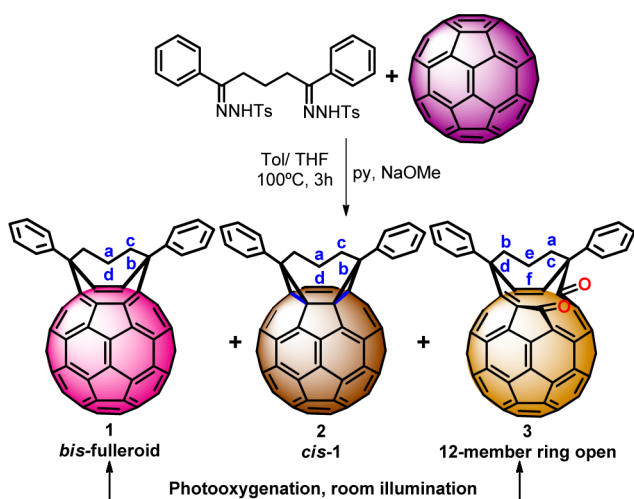
Since no systematic way is currently available to define C_{70} bisadducts, we propose a simple and straightforward method to do so (Figure 1). The method uses Greek letters to define the addition positions and numbers corresponding to the smallest number of bonds separating the addition sites. This nomenclature applies for additions to [6,6]-bonds. The same type of bonds on opposite sides across the δ -bonds are differentiated using a prime designation. Using this system, a 12 o'clock bisadduct would be designated as α -6- α' , a 2 o'clock would be α -7- α' , and a 5 o'clock would be α -9- α' .¹³

Functionalization of fullerenes via diazo cycloaddition generates two types of derivatives: the fulleroids if the addition occurs on a [5,6]-bond or the methanofullerenes if the addition occurs on a [6,6]-bond.¹⁴ Fulleroids are the kinetically-controlled products, whereas the methanofullerenes are the thermodynamic products;¹⁵ hence fulleroid derivatives are usually isomerized to the more stable methanofullerene derivatives via a π -methane transposition.¹⁶ Both fulleroid and methanofullerene derivatives of C_{60} and C_{70} have been reported before, but there are only two examples of the synthesis of bismethanofullerenes using a bisdiazo addend derived from a tether-directed remote functionalization method, which yielded seven regioisomers.¹⁷ Here, we designed a shorter, rigid, and symmetric bisdiazo addend to limit the number of possible regioisomers. To the best of our knowledge, there are no reports of the synthesis of bisfulleroids using bisdiazo cycloadditions.¹⁸

RESULTS AND DISCUSSION

Synthesis of [60]Fullerene Bisadducts 1, 2, and 3. Pure bisadducts **1** and **2** were synthesized from a bisdiazo precursor, resulting from the *in situ* base-induced decompositions of 1,3-dibenzoylpropane bis-*p*-toluenesulfonyl hydrazone (DBP), in the presence of C_{60} , as shown in Scheme 1.¹³ To prevent the formation of monoadducts, an excess of sodium methoxide (NaOMe) and pyridine (py) was added. Purification of the crude mixture using silica gel chromatography (3:2 CS_2 /hexanes) eluted unreacted pristine fullerene, followed by compounds **1** and **2**, and finally a mixture of multiple adducts.

Scheme 1. One-Step Synthesis of Bismethano Derivatives of [60]Fullerene



The yield and ratio of compounds **1** and **2** were controlled by modifying the reaction conditions; under dilute conditions in toluene/THF, the main product was compound **1** (19%) followed by compound **2** (3%); under more concentrated conditions in *ortho*-dichlorobenzene (*o*-DCB), the main product was compound **2** (13%) followed by compound **1** (4%). Characterization of compound **1** was difficult because of its unexpected high sensitivity to light, which quickly led to its conversion into a new compound **3** and a pronounced color change from pink to yellow; see details below.¹⁹

Spectroscopic Characterization of [60]Fullerene Bisadducts 1, 2, and 3. Compounds **1**, **2**, and **3** were characterized by UV-vis spectrophotometry, nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), cyclic voltammetry, and single-crystal X-ray diffraction, except where noted. Since the DBP group has a short alkane chain, after the first addition, the most accessible bonds for a second addition on C_{60} are either one or two bonds away.

Compound **1** shows a molecular mass of 940.1364 m/z by MALDI-MS. It has a UV-vis absorption spectrum that is essentially identical to that observed for pristine [60]fullerene, indicating that both additions on compound **1** have likely occurred on [5,6]-bonds. Thus, the assignment to a bisfulleroid structure is based on the fact that the cages of bisfulleroids and C_{60} are isoelectronic because there is no loss of π -conjugation of the cage upon [5,6]-additions.^{13,20} Surprisingly, the bisfulleroid derivative compound **1** in the presence of air quickly converted to a more stable derivative, compound **3**, with a molecular mass of 972.12572 m/z , corresponding to an addition of two oxygen atoms to compound **1**.

Compound **3** showed a UV-vis absorption spectrum similar to that reported for a photo-oxidized open cage fullerene.²¹ Thus, photo-oxygenation of compound **1** is favored over isomerization to a bismethanofullerene (Scheme 2).¹⁴ Compound **2**, with a molecular ion peak at 940.12571 m/z , showed an absorption spectrum similar to that reported for a *cis*-1 bisisomer.²² Thus, initial structural assignments for these compounds were made solely based on the unique UV-vis absorption patterns exhibited by each C_{60} bisadduct in the 300–700 nm region.

The 1H NMR spectrum of compound **1** showed four sets of signals with integrals of 1:2:2:1 (Figure 2), which could correspond to the presence of two protons with different chemical environments attached to the same carbon (protons **a** and **d**). Due to the proximity of the two additions, the alkane chain is not free to rotate, and this restriction generates different environments for the protons, with proton **d** probably closer to the cage, which shifts its signal to a higher field.²³ For compound **1**, it was not possible to obtain a reasonable ^{13}C NMR spectrum due to the fast photo-oxygenation of the compound. Density functional theory (DFT) calculations using the B3LYP functional and the 6-311G* basis set²⁴ suggested that the isomer with the lowest energy of the bisfulleroid has the addition pattern shown in Scheme 1, with the phenyl rings in a symmetric configuration.²⁵ Although a bisfulleroid structure with a similar addition pattern has been reported,¹⁷ to the best of our knowledge, there is no precedent for a tether-directed bisfunctionalization that gives rise directly to a sterically congested bisfulleroid. Bisfulleroids are typically obtained from cyclohexadiene-fused derivatives upon irradiation; after the [4 + 4] intramolecular photo-cycloadditions, these are followed by [2 + 2 + 2] cycloreversions.¹⁷

Scheme 2. Suggested Mechanism for the Synthesis of Bis Derivatives of [60]Fullerene

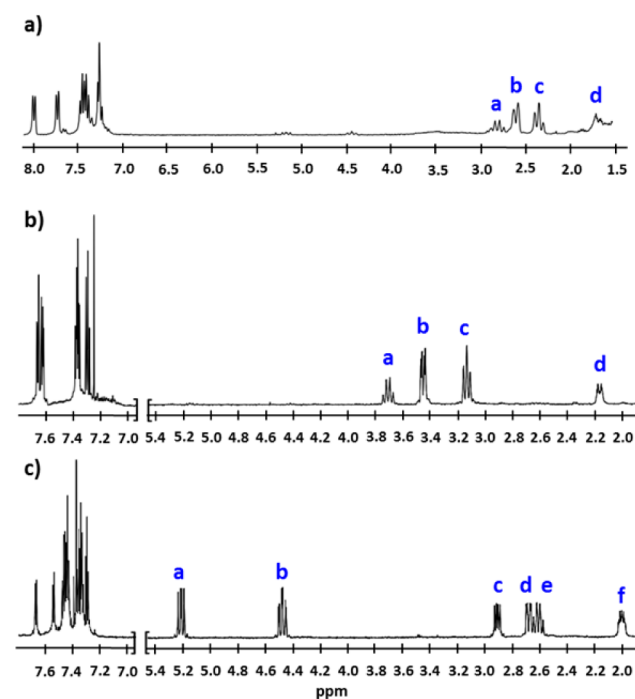
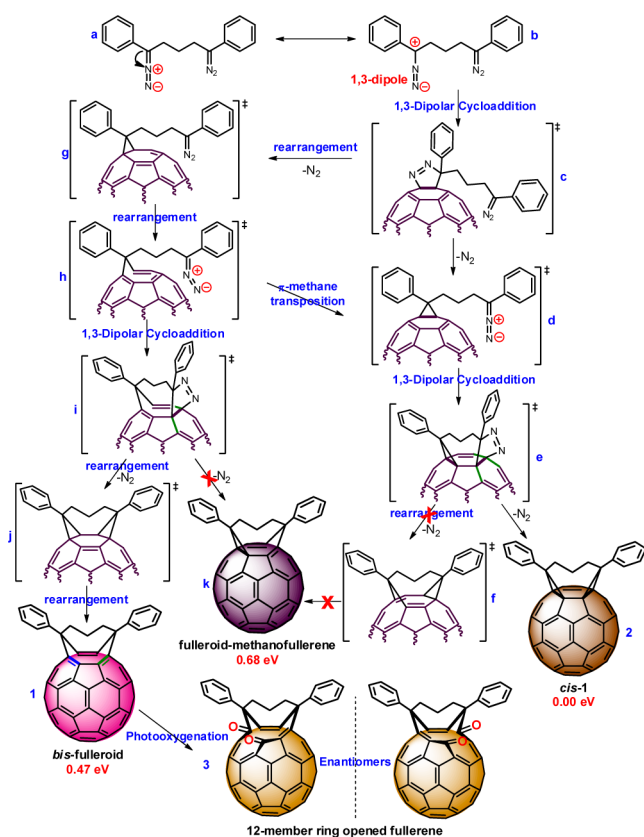


Figure 2. ^1H NMR (600 MHz, 1:1 $\text{CDCl}_3/\text{CS}_2$, 298 K) of (a) compound 1, (b) compound 2, and (c) compound 3.

Although compound 2 contains a plane of symmetry (Scheme 1), the ^1H NMR spectrum showed four sets of signals with integrals of 1:2:2:1 (Figure 2). Analogously to compound 1, the COSY (correlation spectroscopy) NMR and

the HMQC (heteronuclear multiple-quantum correlation) NMR spectra of compound 2 showed that proton d is likely closer to the cage than a, which results in an upfield shift. The ^{13}C NMR spectrum clearly established the existence of a plane of symmetry, with 28 signals observed for sp^2 carbons. The bridgehead and bridge carbons were observed at 55.86, 65.38, and 70.69 ppm, corresponding to a typical methanofullerene structure.¹⁹

The FT-IR spectrum of compound 3 showed two carbonyl absorptions at 1738 and 1689 cm^{-1} , in agreement with the observation of two extra oxygen atoms in the laser desorption/ionization with a Fourier transform ion cyclotron resonance spectrum of compound 3, resulting from the photo-oxygenation of compound 1. The ^1H NMR spectrum of compound 3 showed six sets of signals in the aliphatic region and an integral value of 10 in the aromatic region (Figure 2), consistent with an oxygen addition to an unsymmetric bond close to one of the [5,6]-additions. The COSY NMR and the HMQC NMR of compound 3 support the assignment of the signals, as well as the observation of an upfield shift for proton f. The ^{13}C NMR spectrum exhibited no plane of symmetry with 54 signals for sp^2 carbons (four double intensity signals corresponding to carbons with accidental overlap) and the bridgehead carbons at 60.14 and 64.07 ppm, corresponding to a bisfulleroid structure and the carbonyl at 162.20 and 157.52 ppm.¹⁹

Calculations were performed to determine the structure of compound 3. Analysis of the experimental data and DFT calculations suggested that the addition of one oxygen molecule to compound 1 occurred at one of the two bonds next to the fulleroid addition, in agreement with the loss of symmetry of compound 1. Fullerenes are known to self-sensitize their photo-oxygenation.²⁶ Such a photo-oxygenation of an azafulleroid was used to create the first example of a fullerene containing a hole in the cage.²⁰ Here, we report the one-step photo-oxygenation of a bisfulleroid to obtain a 12-membered open bisfulleroid (Scheme 1).

Bisdiazo compound a is stabilized by the formation of a 1,3-dipole b (see Scheme 2). 1,3-Dipolar cycloaddition of b to a [6,6]-bond of the fullerene leads to the formation of a pyrazoline intermediate (c), which can rearrange to h or undergo nitrogen elimination to yield d (see Scheme 2). The step that predominates will determine the type of addition that occurs on the fullerene: either a bisfulleroid (rearrangement) or a bismethanofullerene derivative (after nitrogen elimination).

After formation of the first pyrazoline and nitrogen elimination, the methanofullerene monoadduct d can undergo a second 1,3-dipolar cycloaddition to a [6,6]-bond in the same six-membered ring to yield e (see Supporting Information). A second nitrogen elimination would then yield compound 2, bismethanofullerene *cis*-1 (see Scheme 2). Rearrangement of the second pyrazoline could result in the formation of a fulleroid-methanofullerene bisadduct (k). Rearrangement of either of the two possible [5,6]-bonds (green bonds in e) would result in the formation of an energetically less stable fulleroid-methanofullerene bisadduct, which does not form (see Supporting Information).

On the other hand, rearrangement of pyrazoline c yields fulleroid monoadduct h, which can undergo a π -methane transposition to yield monoadduct d or a second 1,3-dipolar cycloaddition to a [6,6]-bond in the same six-membered ring i. Rearrangement of the second pyrazoline i would yield compound 1, the bisfulleroid (see Scheme 2). Nitrogen elimination could give rise to the fulleroid-methanofullerene

bisadduct **k**, which is not observed. Photo-oxygenation of compound **1** at the green or blue bonds (Scheme 2, compound **1**) gives rise to compound **3** as a pair of enantiomers.

Electrochemical Characterization of [60]Fullerene Compounds 2 and 3. The redox potentials of bis derivatives of C_{60} (compounds **2** and **3**) were measured by cyclic voltammetry (CV) and square wave voltammetry (SWV) in *o*-DCB solutions using 0.05 M *n*-Bu₄NPF₆ as supporting electrolyte. The SWV results are summarized in Table 1.

Table 1. Redox Potential^a of C_{60} Bis Derivatives 2 and 3

compound	C_{60}	compound 2	compound 3
$E^{0/-}$	-1.12	-1.33	-0.96
$E^{-1/-2}$	-1.49	-1.73	-1.37
$E^{-2/-3}$	-1.93	-2.22	-1.72
$E^{-4/-5}$	-2.40		-1.96
$E_{\text{onset,red}}$	-1.02	-1.19	-0.88
LUMO ^b	-4.08	-3.91	-4.22

^aValues obtained by square wave and cyclic voltammetry in volts vs the Fc/Fc⁺ couple. ^bValues obtained using the following formula, $E_{\text{LUMO}} = (E_{\text{onset,red vs Fc}^+/\text{Fc}} + 5.1) \text{ eV}$.²⁷

Previous studies showed that C_{60} methanofullerenes typically exhibit reversible cathodic electrochemical behavior,²⁸ analogous to those observed for C_{60} .²⁹ The CV of compound **2** showed three reduction waves with electrochemically reversible behavior, and compound **3** showed five reversible reduction waves. The reduction potentials of all bisfullerene derivatives were shifted cathodically compared to the values for C_{60} . It is well known that the additions to double bonds on C_{60} cathodically shift the reduction potentials by approximately 100–150 mV. Since compound **2** is a bisadduct, cathodic shifts around 200–250 mV were anticipated. Compound **2** exhibits a shift of 210 mV. For the case of compound **3**, the cathodic shift is less evident with redox properties very similar to those of C_{60} .

Crystallographic Analysis of Compounds 2 and 3. Single crystals of compound **2**·toluene were grown by slow evaporation of a toluene solution of the compound. The results of the X-ray structure determination are shown in Figure 3. In this drawing, the carbon atoms of the addend are colored blue. This molecule has no crystallographic symmetry, but a virtual

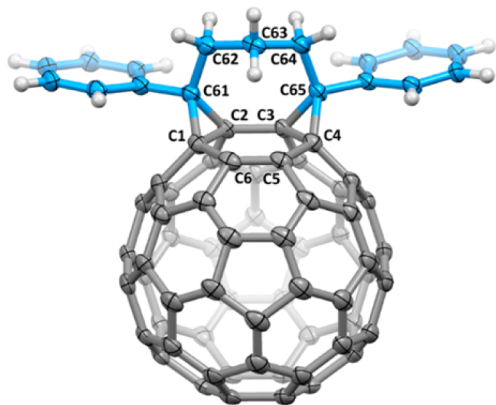


Figure 3. Molecular structure of the bismethanofullerene derivative of C_{60} , compound **2**·toluene. Thermal contours are drawn at the 50% probability level. A molecule of toluene is omitted for clarity. Selected distances (Å): C1–C2, 1.620(3) Å; C3–C4, 1.616(4) Å; C2–C3, 1.535(3) Å; C5–C6, 1.380(4) Å.

mirror plane bisects the C2–C3 and C6–C5 bonds. The bond distances for the fullerene cage fall within normal ranges. However, at the point of addition across the two 6:6 double bond, significant bond lengthening has occurred, yielding distances over 1.6 Å for the C1–C2 and C3–C4 bonds (see Figure 3).

Single crystals of compound **3**·2.5CS₂ were grown by slow diffusion of ethanol into a carbon disulfide solution of the compound. The structure, which is shown in Figure 4, reveals

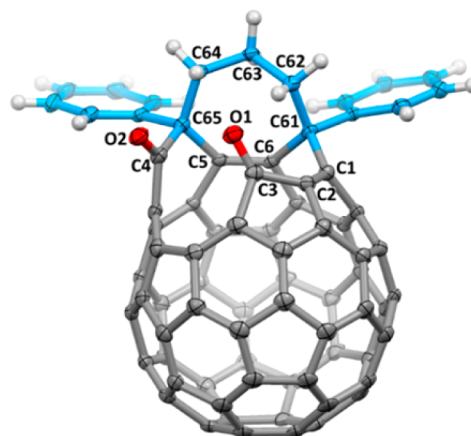


Figure 4. Molecular structure of one enantiomer of the ring-opened adduct, compound **3**, with the carbon atoms of the addend colored blue. Thermal contours are drawn at the 50% probability level. Solvated carbon disulfide molecules are omitted for clarity. Selected atom distances (Å): C1–C2, 1.384(5); C5–C6, 1.368(5); C3–O1, 1.199(4); C4–O2, 1.218(4).

the 12-membered ring-opened cage structure of the compound with the addition of two oxygen atoms. Three of the C–C bonds (C4–C5, C4–C3, and C1–C6) in the original fullerene have been broken. Thus, these nonbonded separations are C4–C5, 2.470(5) Å; C4–C3, 3.138(5) Å; and C1–C6, 2.345(5) Å, and the nonbonded O1–O2 distance is 2.705(4) Å.

Figure 5 compares the sites of adduct formation of the bisadduct compound **2** and the ring-opened adduct compound **3**. In this figure, the yellow carbon atoms belong to the original hexagonal face of the C_{60} molecule that underwent addition.

Compound **3** is a chiral molecule. The two enantiomers that are present in the centrosymmetric space group $P\bar{1}$ are depicted in Figure 6.³⁰

Based on the X-ray data, spectroscopic analysis, and DFT calculations, it was possible to assign the addition pattern (summarized in Scheme 1) for the pure bisfulleroid **1**, bismethanofullerene **2** (*cis*-1), and the 12-membered open bisfulleroid **3**.

Synthesis of [70]Fullerene Bisadducts 4 and 5. Pure bisadducts **4** and **5** were synthesized using the same method described above but using C_{70} instead of C_{60} (Scheme 3). Purification of the crude mixture using silica gel chromatography (3:2 CS₂/hexanes) eluted the unreacted pristine fullerene, followed by a mixture of compounds **4** and **5** and finally by a fraction of multiple adducts. Compounds **4** and **5** were further purified by preparative thin layer chromatography (1:1 CS₂/hexanes). The major product of the reaction was bisadduct compound **4**, which was isolated in 22% yield, followed by compound **5** in 6% yield. In contrast to the results observed with C_{60} , varying the reaction conditions did not significantly affect the yield or ratio of the final products.

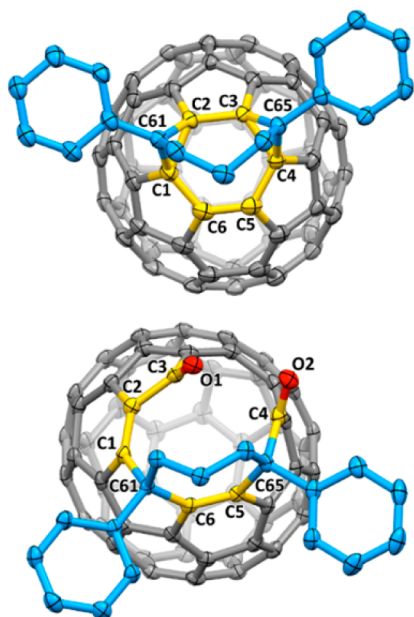


Figure 5. Comparison of compound 2 (top) and compound 3 (bottom) as viewed from the perspective of oxygen addition. Thermal contours are drawn at the 50% probability level.

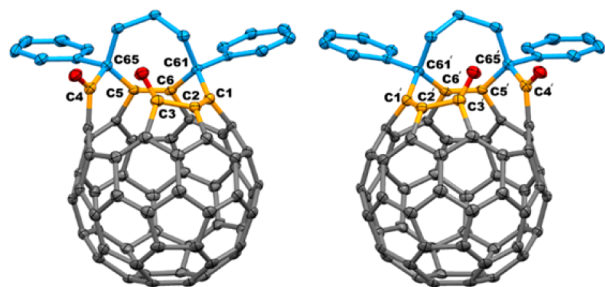


Figure 6. Enantiomers of the 12-membered ring-opened cage in compound 3. Thermal contours are drawn at the 50% probability level. Both enantiomers occur in the crystal structure due to the presence of a centrosymmetric space group.

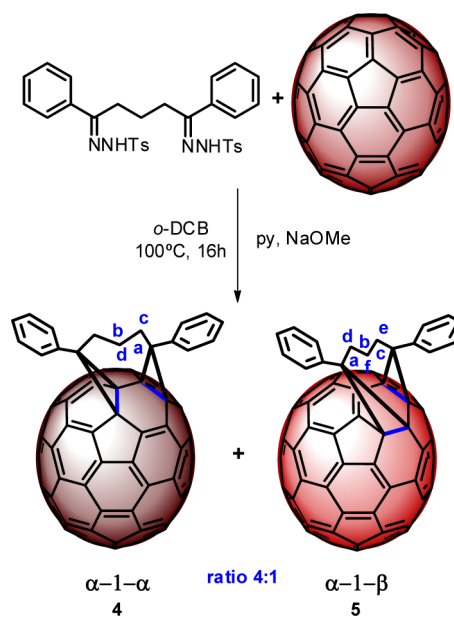
Characterization of [70]Fullerene Bisadducts 4 and 5.

Compounds 4 and 5 were characterized by UV–vis spectrophotometry, NMR spectroscopy, MALDI-TOF mass spectrometry, and cyclic voltammetry. To estimate the number of possible isomers in this reaction, we assume that the first addition occurs at an α -bond because it exhibits the highest reactivity compared to the β -, γ -, and δ -bonds on C_{70} .³¹ Due to the short alkane chain of the DBP group, after the first addition takes place, the most likely bisadducts are α -1- α , α -2- α , α -1- β , and α -3- β (Figure 1).

Assignments of the addition pattern of bisadducts on C_{70} were not based on the corresponding UV–vis absorption spectra because there are very few examples of [70]fullerene bisadducts reported in the literature.¹¹ Here we report the characterization of two new bisadducts of C_{70} for which both additions occur on the same pole of C_{70} , unlike most [70]fullerene bisadducts reported, where the additions occur on opposite poles of the molecule.

The MALDI-MS of compound 4 showed the parent molecular peak at 1060.1322 m/z , corresponding to a bisadduct. The ^1H NMR spectrum of compound 4 was very similar to that for compound 2; four sets of signals with

Scheme 3. One-Step Synthesis of Bismethano Derivatives of [70]Fullerene



integrals of 2:1:2:1 were observed (Figure 7). This result, along with the UV–vis absorption spectrum, suggests an α -1- α

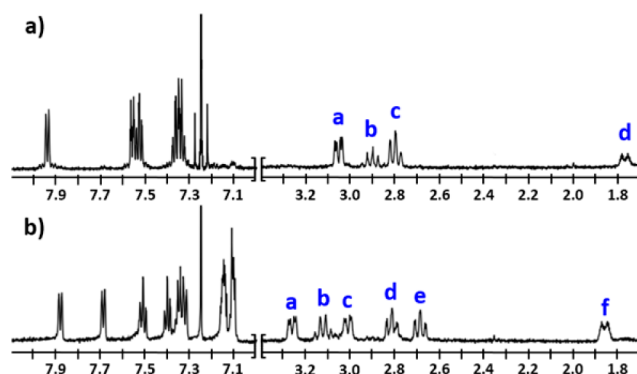


Figure 7. ^1H NMR (600 MHz, 1:1 $\text{CDCl}_3/\text{CS}_2$, 298 K) of (a) compound 4 and (b) compound 5.

addition pattern. The COSY NMR and the HMQC NMR spectra of compound 4 showed that protons **b** and **d** are bonded to the same carbon, with an upfield shift for proton **d**. The ^{13}C NMR spectrum showed the presence of a plane of symmetry with 32 signals corresponding to sp^2 carbons (one with double intensity at 147.94 ppm due to accidental overlap) and the bridgehead and bridge carbons at 41.53, 64.14, and 57.46 ppm, which correspond to a typical methanofullerene structure.¹⁹

The MALDI-MS spectrum of compound 5 showed the parent molecular peak at 1060.1383 m/z , corresponding to a bisadduct. The ^1H NMR spectrum of compound 5 exhibited diastereotopic behavior with six sets of signals in the aliphatic region (Figure 7). COSY NMR and HMQC NMR spectra of compound 5 supported the assignment of the signals, with the observation of upfield shifts for proton **f**. The ^{13}C NMR spectrum exhibited no plane of symmetry with 63 signals for the sp^2 carbons (three double intensity signals corresponding to carbons with accidental overlap). The bridgehead and bridge

carbons at 42.38, 43.84, 54.52, and 62.39 ppm correspond to methanofullerene structures.¹⁹ Calculations were performed to determine the structures of compound 5. Analysis of the experimental data and DFT calculations suggests that the addition on compound 5 is α -1- β (Scheme 3).

Electrochemical Characterization of [70]Fullerene Bisadducts 4 and 5. The redox potentials of bismethanofullerenes 4 and 5 were also measured by CV and SWV using the same conditions as used with the C₆₀ derivatives. The SWV results are summarized in Table 2.

Table 2. Redox Potentials (V)^a of C₇₀ Bis Derivatives 4 and 5

compound	C ₇₀	compound 4	compound 5
$E^{0/-}$	-0.98	-1.31	-1.27
$E^{-1/-2}$	-1.34	-1.47	-1.64
$E^{-2/-3}$	-1.75	-1.99	-1.99
$E_{\text{onset,red}}$	-0.88	-1.22	-1.14
LUMO ^b (eV)	-4.22	-3.88	-3.96

^aValues obtained by square wave voltammetry in volts vs the Fc/Fc⁺ couple. ^bValues obtained using the following formula, $E_{\text{LUMO}} = (E_{\text{onset,red vs Fc}^+/\text{Fc}} + 5.1) \text{ eV}$.²⁷

Previous studies showed that C₇₀ methanofullerene typically exhibits reversible cathodic electrochemical behavior,²⁸ analogous to that observed for C₆₀ and C₇₀.²⁹ The CV of compounds 4 and 5 showed three reduction waves with electrochemically reversible behavior. The reduction potentials of all bismethanofullerene derivatives were shifted cathodically around 300 mV compared to the corresponding values for C₇₀.³²

Crystallographic Analysis of Compound 4. Single crystals of compound 4-toluene were grown by slow evaporation of a toluene solution of the compound. As shown in Figure 8, the adduct with the carbon atoms colored blue occupies a symmetrical position near the cap of the D_{5h}-C₇₀ fullerene. As was the case for the C₆₀, addition across the

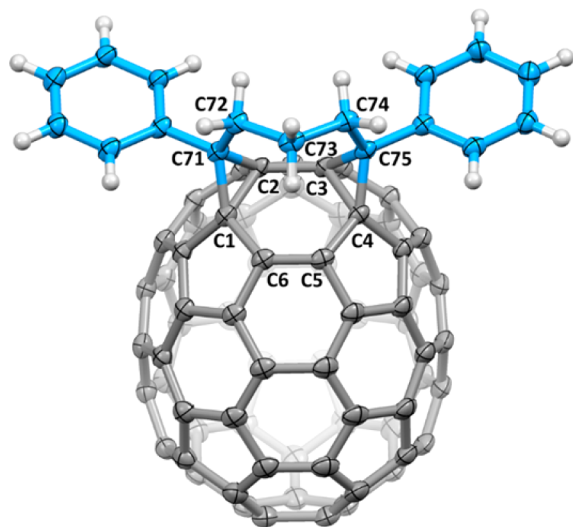


Figure 8. Molecular structure of the first highly steric congested bismethanofullerene derivative of C₇₀, compound 4 showing thermal displacement parameters at the 50% probability level and selected atom numbers. The molecule of toluene is omitted for clarity. Selected distances (Å): C1–C2, 1.633(3); C3–C4, 1.626(3); C2–C3, 1.524(3); C5–C6, 1.374(3).

double bonds of the fullerene caused bond lengthening but not bond breaking. The other fullerene C–C bonds were not greatly affected by adduct formation. Although the molecule has no crystallographically imposed symmetry, it does have effective mirror symmetry with the virtual mirror plane perpendicular to the plane of Figure 8, passing through C73 and bisecting the C2–C3 and C6–C5 bonds.

CONCLUSION

New double addition products of both C₆₀ and C₇₀ have been prepared with both additions occurring within one six-membered ring of the fullerene through the use of 1,3-dibenzoylpropane bis-*p*-toluenesulfonyl hydrazone as the addend precursor. When the addition occurs at two [6,6] ring junctions within a hexagon, bisadducts 2 and 4 with mirror symmetry have been obtained for both C₆₀ and C₇₀.

When the addition occurs at two [5,6] ring junctions of C₆₀, a symmetrical bisfulleroid is formed. This adduct readily undergoes photo-oxygenation and ring opening to yield a fullerene with a 12-membered hole in the cage.

Electrochemical measurements showed that the reduction potentials of all synthesized bisadducts were shifted cathodically between 200 and 300 mV compared to the corresponding values for the pristine fullerenes.

ASSOCIATED CONTENT

Supporting Information

Detailed synthesis and characterization of compounds 1–5, including X-ray .cif files and DFT calculations results. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03768.

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Notes

The authors declare no competing financial interest.

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