A Versatile Route to Substituted 1,4-Diazine-Fused [60]Fullerenes[†]

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An alternative route to [5,6]fullereno-C_{60}-I_h-[1,9-d]-2′-hydroxycyclohexanone (**4a**) is presented based on the [4 + 2] cycloaddition of 2,3-bis(trimethylsiloxy)butadiene (**3**) and [60]fullerene. The oxidation of the primary monoadduct with bromine yield the new [5,6]fullereno-C_{60}-I_h-[1,9-d]-1′,2′-cyclohexanedione (**5**) which can be isolated as the dimethoxime derivative (**9**). The diketone **5** constitutes a versatile reactant for the synthesis of different substituted [5,6]fullereno-C_{60}-I_h-[1,9-b]-1′,2′,3′,4′-tetrahydrophenazines (**6a**–**d**). The isolation, characterization, controlled-temperature ^{1}H NMR measurements as well as UV–vis and fluorescence studies of these new heterocycles are presented.

Introduction

Since fullerenes are accessible in preparative amounts,[1] the exohedral functionalization of this new allotropic form of carbon has attracted much attention due to its interesting chemical and physical properties. The low LUMO energy of C_{60} makes the [m + 2]cycloadditions a useful reaction to produce new fullerene derivatives.[2,3] In particular, the [4 + 2] cycloaddition is one of the most effective methods to introduce different functionalities to the fullerene framework.[3l–n] The reversibility of this process allows the use of dienes for the template activation of C_{60}[4] or the introduction of cleanly removable solubilizing groups.[5]

We recently reported on the Diels–Alder reactions with *cis*-fixed 2,3-dioxy-substituted butadienes (**1**, **2**) as a

procedure to obtain [5,6]fullereno-C_{60}-I_h-[1,9-d]-2-hydroxycyclohexanone (**4**).[6] Despite the ease of reaction of [60]fullerene as a dienophile with electron rich open chain butadienes,[3m] only few examples of [4 + 2] cycloaddition between C_{60} and 2,3-diheterosubstituted butadienes are known. The energetic HOMO levels of these dienes guarantee high efficiencies in the cycloaddition, yielding monoadducts with high symmetry and synthetically versatile functional groups. The compound **4** has a great deal of potential as a starting point to various interesting functionalities. In particular, the diketone (**5**) may be a direct precursor of different 1,4-diazine-fused [60]fullerenes (**6**) in a convergent strategy. An alternative synthetic pathway based on the [4 + 2] cycloaddition of heteroaromatic *o*-quinodimethanes and [60]fullerene requires the preparation of each particular diene.[7] (Scheme 1).

However, the synthesis of **4** suffers from two disadvantages. Firstly, the Diels–Alder adduct of [60]-fullerene and 2,3-bismethylene-1,4-dioxane (**1**) cannot be easily hydrolyzed to **4**, and secondly, the alternative cycloaddition with the less reactive 1,3-dioxolane derivative **2** requires high-pressure conditions. In the present work, we explore an alternative route to **4** by Diels–Alder reaction of 2,3-bis(trimethylsiloxy)butadiene (**3**) and the oxidative derivatization of **4** to achieve different 1,4-diazines fused to [60]fullerene (**6**) which may possess interesting properties.

Results and Discussion

Synthesis of 4. The synthesis of [5,6]fullereno-C_{60}-I_h-[1,9-d]-2-hydroxycyclohexanone (**4a**) was easily carried out by electrocyclic ring opening of 1,2-bis(trimethylsiloxy)cyclobutene (**7**) in 1,2-dichlorobenzene at 180 °C, generating the corresponding butadiene,[8] followed by [4 + 2] cycloaddition[9] to [60]fullerene (0.6 equiv), which led to the monoadduct **8** in >50% yield (Scheme 2). Direct hydrolysis using HCl/MeOH gave the acyloin derivative **4a**, which was isolated in 50% yield (89% based on recovered C_{60}).

The ^{1}H and ^{13}C NMR spectra of this compound are identical to the ones previously reported.[6] The MALDI-

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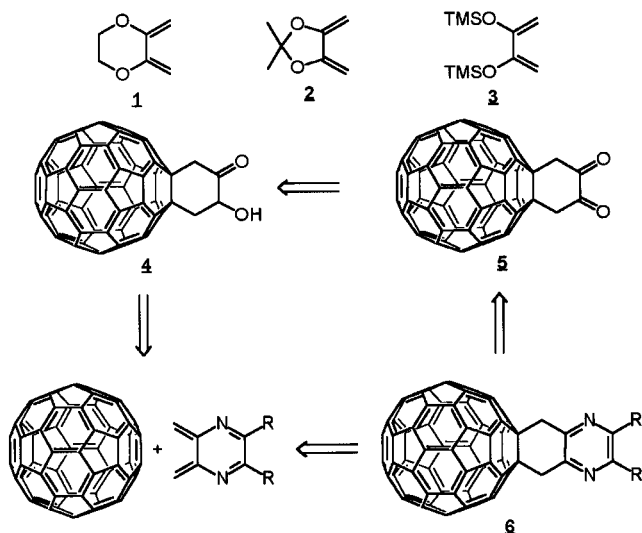
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Scheme 1

TOF mass spectrum of **4a** shows two different peaks at 807 and 1614 amu, suggesting a dimerization of the acyloin moiety under these conditions. However, the vicinal coupling constant for C*H*O*H* in its ¹H NMR spectrum ($J = 3.29$ Hz) and the presence of the carbonyl group in the IR spectrum (1729 cm⁻¹) indicate the presence of the monomer. In order to simplify the analysis, the alcohol group of **4a** was protected by means of acetic anhydride leading to **4b**. This alternative procedure provides a better yield and does not require high-pressure techniques,[6] and therefore this method it is a good choice for the synthesis of 2-hydroxycyclohexanone-fused [60]fullerene (**4a**) on a preparative scale.

Synthesis of Dimethoxime Derivative 9. We expected an easy transformation of **4a** to the diketone **5** by one of the mild oxidation procedures available from the literature. However, all attempts to perform this oxidation under various conditions were unsuccessful.[10] Evidently the intermolecular hydrogen bonding of **4a** and its low solubility in polar solvents cause this unexpected behavior. Therefore we followed a different approach based on the oxidative cleavage of the bis(trimethylsilyl) ether of **8** in nonprotic medium with bromine.[11] Although this procedure has been described previously to give only poor yields in the case of enolizable α-diketones,[12b] the low-temperature bromination of **8** followed by direct derivatization of the diketone **5** with *O*-methoxyhydroxylamine under basic conditions allowed us to isolate the corresponding dimethoxime **9** in good yield (Scheme 3).[12] The ¹H NMR spectrum presents a singlet for the methoxy group and a broadened signal for the methylene group (4.18 ppm) due to a fast ring inversion at 25 °C. The ¹³C NMR spectrum shows 16 signals at δ 134–150 for the sp² carbons of [60]fullerene besides the quaternary carbon of the C=N group (154.78 ppm), indicating C_{2v} symmetry with a 6,6-junction on the fullerene core. Further

evidence is obtained from FT-IR, UV–vis, and DEI mass spectra (see Experimental Section).

Synthesis of 1,4-Diazine-Fused [60]Fullerenes (6a–d). Analogous to the one-pot synthesis of **9** from **8**, the 1,4-diazines **6a–d** were obtained by using the *o*-diaminoarenes **10a–d**. Acidic conditions are required in order to avoid nucleophilic addition to the double bonds of the fullerene framework.[13] The overall yields are acceptable in view of the fact that the synthesis involves three consecutive steps. The particularly low yield of **6d** must be attributed to the low solubility of the 9,10-diaminophenanthrene (**10d**).

The MALDI-TOF mass spectra of **6a–d** clearly show the parent ions as base peaks. All 1,4-diazine derivatives exhibit similar ¹H NMR spectra in the upper field. At 20 °C the methylene groups show two broadened signals (one in the case of **6d**) due to the exchange between the two boat conformers of the exohedral functionality. These signals are resolved into two doublets by cooling to −10 °C. The aromatic regions of the ¹H NMR spectra resemble those of the *o*-diaminoarenes (**10a–d**). However, an increase in the chemical shifts due to a higher electron delocalization in the heterocyclic system and the proximity to the fullerene core is observed. Consequently the symmetry plane of these diamines remains in the derivatives **6a,b** and **6d**.

The ¹³C NMR spectrum of compound **6a** displays 14 signals in the fullerene region caused by an accidental overlapping, along with the carbons of the quinoxaline moiety. Some of the signals of the sp² carbons of the [60]-fullerene core appear slightly broadened due to slow exchange in the boat conformers. The aliphatic region shows only two signals assigned to the methylene groups and to the fullerene bridgehead quaternary sp³ carbons by means of the gated decoupled ¹³C NMR spectrum (48.45 and 65.92 ppm, respectively). These data indicate a closed 6,6 ring junction on the [60]fullerene cage and C_{2v} symmetry, which is related to a fast flipping motion of the cyclohexane ring (17 fullerene signals are expected). Compounds **6c** and **6d** display an analogous behavior. Surprisingly, the unsymmetrical compound **6b** presents four different carbons in the aliphatic area. However the influence of the pendant group over the fullerene core is small, and only some of the 16 signals appear split or slightly broadened (155.40, 147.52, 140.14, and 135.30 ppm). This effect has been previously reported for some C_{60}–*o*-quinodimethane adducts.[8,13]

Temperature-controlled ¹H NMR measurements of **6a–c** provide the coalescence temperature and the free energy of inversion (Table 1).[14] The values for these activation energies are similar to those previously reported for some adducts of C_{60} with *o*-quinodimethanes which are structurally similar to our compounds.[15]
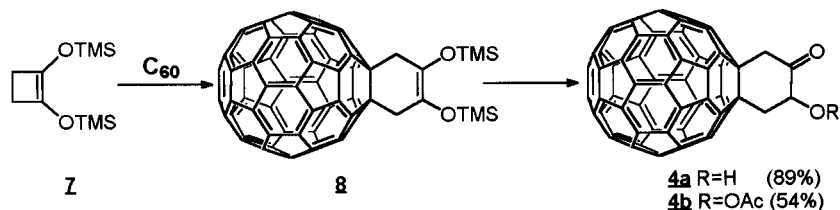
The activation free energies are surprisingly high assuming a planar transition state. However, AM1 calculations did not reproduce the experimentally obtained values.[16] It is noteworthy that the $\Delta G_c^\ddagger$ for the cycloadduct **6c** is larger than that of **6a**. Such a differ-

(10) This oxidation was attempted with various reagents: Cu(AcO)₂/AcOH/TCE; Bi₂O₃/AcOH/TCE; PDC(2–20 equiv)/CH₂Cl₂; PCC(2–20 equiv)/CH₂Cl₂; Swern oxidation and DMSO activated with Ac₂O or TFAA.

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(12) The attempts to characterize the diketone **5**, due to the low solubility, were unsuccessful. The MALDI-TOF MS shows a *m*/*z* = 805 amu, the FTIR presents different carbonyl groups, probably due to the presence of two tautomeric forms of **5**.

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Scheme 2

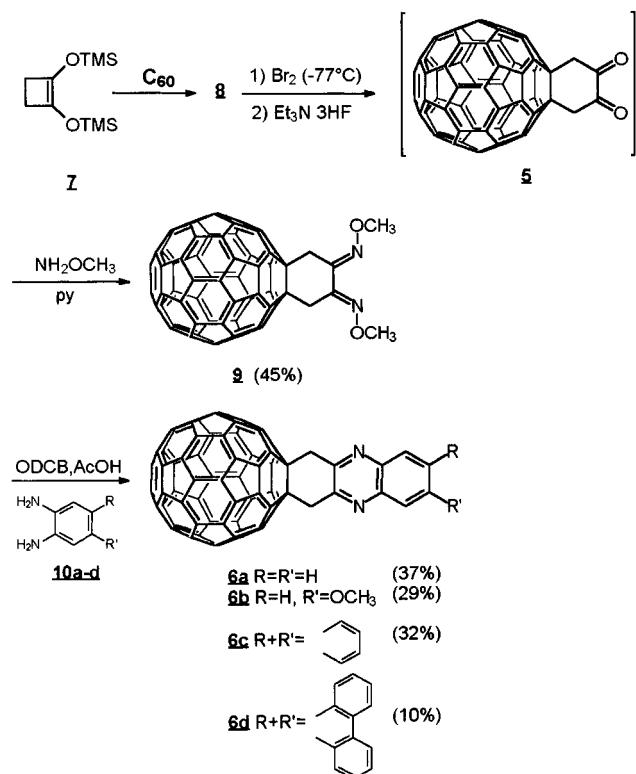**4a** R=H   (89%)
4b R=OAc (54%)

Scheme 3

5

9 (45%)

6a R=R'=H   (37%)
6b R=H, R'=OCH₃   (29%)
6c R+R'=   (32%)
6d R+R'=   (10%)

Table 1. Coalescence Temperature and Activation Free Energy of 6a–c

compd	T_c (°C)	$\Delta G_c^{\ddagger}$ (kJ mol^{-1})
6a	34	61.7
6b	35	61.8
6c	45	67.4

ence has been observed previously by Nishimura *et al.*[15] for some carbocyclic analogues and was partly assigned to electronic π-interactions between the C$_{60}$ framework and the overlying aromatic ring. These effects also explain the similarity in the peak potentials for reductions of C$_{60}$ and **6a** and **6c**.[17] However, the electron rich 1,4-diazine **6b** does not show an increase in its activation free energy for ring inversion in comparison to **6a**. This may indicate that the electronic stabilization effects are weak and nonbonded repulsion or through bond interactions also play a role in the ring-flipping process.

(16) The AM1 calculations for the compound **6a**, performed using the SADDLE method in MOPAC 6.0, indicate a planar transition state and an energy difference between the boat and planar conformations of 38.86 kJ mol^{-1}. The value for cyclohexene is 19.05 kJ mol^{-1} (see ref 12a).

(17) The reduction potentials of **6a**, −0.60, −1.00, −1.56, −1.94 V; and of **6c**, −0.65, −1.04, −1.56 and −1.73 V (all potentials *vs* SCE, toluene:acetonitrile (5:1); Bu$_4$NClO$_4$; scan rate 200 mV s^{-1}. These values are highly similar to the ones obtained with C$_{60}$, −0.6, −1.00, −1.52 and −2.04 V, but do not follow the normal behavior for other cycloadducts which usually present slightly negative-shifted reduction potentials compared to C$_{60}$. Personal communication from Prof. N. Martin (Madrid).
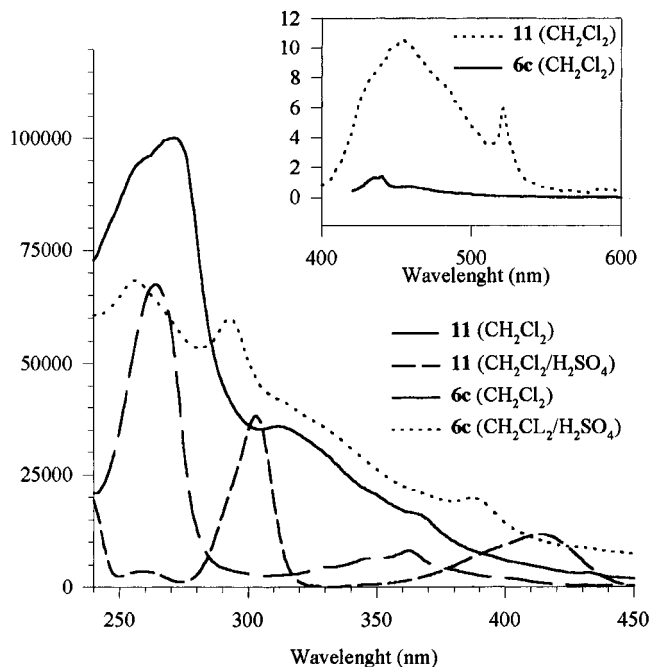

Figure 1. UV–vis under normal and acidic conditions of compounds **11** and **6c** in CH₂Cl₂. Inset shows the fluorescence emission spectra with an excitation wavelength of 259 nm.

UV–vis spectroscopy confirms that there is no strong interaction between the exohedral functionalities and the fullerene framework. The spectra of these compounds exhibit the characteristic absorption of all dihydrofullerene derivatives at *ca.* 430 and 700 nm.[18] The absorption at shorter wavelengths reveals the presence of both the 1,4-diazine and the dihydrofullerene chromophores. Further evidence was obtained from UV–vis measurements in the presence of acid. The absorption spectrum of **6c** in CH₂Cl₂ shows two peaks at 271 and 312 nm besides two shoulders at 259 and 364 nm (Figure 1). When the solution is acidified, the spectrum clearly changes. As a model compound we used 2,3-dimethyl benzo[*g*]quinoxaline (**11**), whose spectrum shows a similar response to acid, suggesting that the spectrum is the sum of both chromophores. This behavior is observed for the other 1,4-diazines (**6a**, **6b**, and **6d**) as well.

On the other hand the emission studies indicate a strong interaction between the fullerene core and the pendant group in the excited state. Whereas quinoxaline shows strong fluorescence and substitution in the aromatic ring by electron-donating groups increases this emission,[19] the fluorescence spectra of **6c** and **6a** in CH₂Cl₂ exhibit only weak fluorescence compared to the model compounds 2,3-dimethyl benzo[*g*]quinoxaline (**11**) (Figure

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1, inset) and 2,3-dimethylquinoxaline (**12**). This indicates that the dihydrofullerene component acts as an internal quencher because of its low singlet energy compared to that of the 1,4-diazines.[20]

Conclusions

[60]Fullerene undergoes a fast [4 + 2] cycloaddition with 2,3-bis(trimethylsiloxy)butadiene (**3**) to yield the acyloin-fused C_{60} **4a** in good yield. The controlled bromination of the primary cycloadduct allows isolation of the diketone **5** as its dimethoxime derivative. The condensation of **5** with various *o*-diaminoarenes yields 1,4-diazine-fused [60]fullerenes **6a−d** in a one-pot reaction. UV−vis spectra as well as temperature-controlled ^{1}H NMR measurements indicate that these electron poor heterocycles do not show any strong π-interaction in the ground state with the electronic deficient dihydrofullerene. However, fluorescence studies indicate energy transfer in the excited state from the heterocyclic ring to the dihydrofullerene. In summary, we have developed a new method for the synthesis of 1,4-diazine-fused fullerenes which may be applicable to a great number of diamines. In addition, these heterocycles are direct precursors of 1,4-dihydrodiazines which present a remarkably high electron donor capability.[21]

Experimental Section

General Procedures. Reaction progress was monitored with analytical HPLC using a Lichrosorb RP-18 column with UV detection at 310 nm and a flow rate of 1.25 mL/min (toluene:acetonitrile (1:1)). Column chromatography was conducted with silica gel 60 (Merck, 63−200 μm) or neutral alumina (ICN Alumina N, Akt. I). Matrix-assisted laser desorption ionization mass spectra (MALDI-TOF MS) were performed with 337 nm light using 9-nitroanthracene or 1,8,9-trihydroxyanthracene as matrix. NMR spectra were recorded at 300 or 350 MHz (^{1}H) and at 75 or 90.5 MHz (^{13}C) and are reported in ppm in values relative to CDCl₃ (δ = 7.24 for proton and 77 ppm for carbon) or tetrachloroethane (δ = 6.01 for proton and 74 ppm for carbon) as internal standard. [60]-Fullerene was obtained from Hoechst in *gold grade* quality (99.4%). Reagents were purchased reagent grade and solvents *per analysis* grade. Toluene, *n*-hexane, and tetrahydrofuran were distilled prior to use. 1,2-Bis(trimethylsiloxy)cyclobutene (**7**) was synthesized according to literature procedures and stored at −20 °C.[10]

1,2-Dihydro-1,2-(63-hydroxy-62-oxobutano)[60]fullerene (4a). A mixture of C_{60} (106 mg, 0.15 mmol) and 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (48 mg, 0.20 mmol) was dissolved in 1,2-dichlorobenzene (10 mL) and degassed with argon for 30 min. The solution was heated at 180 °C for 1 h, and cooled to room temperature, a methanolic solution of HCl (150 μL, 1 mL) was added, and stirring was continued for 1 h more. The solvent was then evaporated under reduced pressure, and the residue was chromatographed on silica gel (70 g), eluent toluene pure to toluene/THF (100:1) affording C_{60} (61 mg, 58%) and **4a** (45 mg, 38%, 89% based on recovered C_{60}). The product was dissolved in the minimum quantity of CS_2, precipitated with MeOH (100 mL), filtered, and dried (39 mg, 33%). ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ (9:1)): δ (ppm) 5.13

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(dd, 1H, J = 5.72, 10.01 Hz), 3.91 (d, 1H, J = 16.7 Hz), 3.80 (d, 1H, J = 16.7 Hz), 3.50 (brs, 1H), 3.43 (dd, 1H, J = 5.72, 13.83 Hz), 3.37 (dd, 1H, J = 10.01, 13.83 Hz). ^{1}H NMR (300 MHz, CS_2/acetone-d_6 (9:1)): δ (ppm) 5.40 (m, 1H), 4.77 (d, 1H, J = 15.7 Hz), 4.81 (d, 1H, J = 3.29 Hz), 4.36 (dd, 1H, J = 0.73, 15.71 Hz), 4.14 (dd, 1H, J = 10.60, 13.70 Hz), 3.91 (dd, 1H, J = 4.39, 13.70 Hz). ^{13}C NMR (75 MHz, $CS_2/CDCl_3$): δ (ppm) 209.61, 154.92, 154.83, 154.75, 154.62, 147.60, 147.55, 146.35, 146.32 (2C), 146.26, 146.14 (2C), 146.11 (2C), 145.56, 145.54, 145.50, 145.49, 145.41, 145.35, 145.28, 145.26 (2C), 145.24, 145.10, 144.62, 144.60, 144.55, 144.37 (2C), 144.27, 143.95, 143.06, 143.01, 142.52, 142.45, 142.44, 142.39, 142.02, 141.94, 141.88 (2C), 141.84, 141.62, 141.60, 141.55, 141.47, 141.42, 141.39, 141.38, 140.27, 140.23, 140.14, 140.04, 135.21, 134.92, 134.85, 134.19, 74.70, 62.00, 61.49, 50.43, 43.91. UV−Vis (CH_2Cl_2): λ_{max} (log ϵ) = 255 (4.95), 309 (4.48), 325 (sh, 4.44), 407 (sh, 3.62), 432 (3.52). UV−vis (toluene): λ_{max} (log ϵ) = 407 (sh, 3.74), 434 (3.62), 537 (sh, 3.09), 638 (sh, 2.78), 704 (2.58). FT-IR (KBr): ν_{max} (cm^{-1}) = 3435, 1729, 1423, 1267, 1095, 1026, 813, 526. MALDI-TOF MS (1,8,9-trihydroxy-anthracene): m/z = 721 (100), 735 (37), 807 (17); (9-nitro-anthracene): m/z = 721 (65), 736 (29), 792 (72), 807 (100), 1614 (34).

1,2-Dihydro-1,2-(63-acetoxy-62-oxobutano)[60]fullerene (4b). A mixture of C_{60} (130 mg, 0.18 mmol) and 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (60 mg, 0.26 mmol) was dissolved in 1,2-dichlorobenzene (10 mL) and degassed with argon for 30 min. The solution was heated at 180 °C for 1 h. The solution was allowed to cool to room temperature, a mixture of acetic anhydride (5 mL), acetic acid (5 mL), and sodium acetate (340 mg) was added, and stirring was continued at 60 °C for 1 h more. The fullerene mixture was precipitated with acetonitrile (200 mL), filtered over a Celite pad, redissolved in CS_2 (20 mL), and dried under vacuum. The residue was chromatographed on silica gel (70 g), eluent toluene affording C_{60} (91 mg, 70%) and **4b** (25 mg, 16%, 54% based on recovered C_{60}). ^{1}H NMR (500 MHz, $CS_2/CDCl_3$: (9:1)) δ (ppm) 6.21 (dd, 1H, J = 4.27, 11.85 Hz), 4.88 (d, 1H, J = 15.4 Hz), 4.39 (dd, 1H, J = 11.85, 13.33 Hz), 4.27 (d, 1H, J = 15.39 Hz), 3.78 (dd, 1H, J = 4.27, 13.33 Hz) 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CS_2/CDCl_3$): δ (ppm) 202.03, 169.07, 154.48, 154.26, 154.00, 147.51, 147.50, 146.35, 146.32, 146.28, 146.25, 146.14, 146.11, 146.08, 145.51, 145.49, 145.45, 145.38, 145.34, 145.32, 145.26, 145.23, 144.81, 144.57, 144.48, 144.34, 144.30, 144.28, 144.09, 143.03, 142.99, 142.83, 142.79, 142.52, 142.45, 142.42, 141.91, 141.88, 141.84, 141.59, 141.58, 141.56, 141.52, 141.48, 141.45, 140.22, 140.17, 135.38, 135.06, 134.87, 134.21, 74.57, 61.86, 61.44, 51.45, 41.73. FT-IR (KBr): ν_{max} (cm^{-1}) = 1734, 1425, 1226, 1078, 1028, 768, 526. MALDI-TOF MS (9-nitroanthracene): m/z = 721 (60), 849 (100). HRMS: calcd for $C_{66}H_8O_3$ 848.047 345, found 848.044 92.

1,2-Dihydro-1,2-(62,63-bis(methoxyimino)butano)[60]-fullerene (9). A mixture of C_{60} (122 mg, 0,169 mmol) and 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (54 mg, 0.234 mmol) was dissolved in 1,2-dichlorobenzene (10 mL) and degassed with argon for 30 min. The solution was heated at 180 °C for 1 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in deoxygenated CS_2 (20 mL) and cooled at −77 °C, Br_2 was added (0.1 mmol), and stirring was continued for 1 h. The CS_2 was eliminated under reduced pressure and the residue dissolved in a mixture of 1,2-dichlorobenzene (10 mL), pyridine (5 mL), Et₃N·3HF (38 mg, 0.235 mmol) and *O*-methylhydroxylamine hydrochloride (30.4 mg, 0.36 mmol), heating at 60 °C for 3 h. The fullerene mixture was precipitated with MeOH (200 mL) and filtered through a pad of Celite. The filtrates were placed on the top of a silica gel column (70 g) and chromatographed, eluent *n*-hexane/toluene (4:1) to pure toluene affording, in order, C_{60}, 82 mg (67%); **9**, 22 mg (15%, 45% based on recovered C_{60}). ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ (5:1)): δ (ppm) 4.68 (brs, 2H), 4.18 (s, 3H). ^{13}C NMR (300 MHz, $CS_2/CDCl_3$ (5:1)): δ (ppm) 154.78 (2C), 149.36 (4C), 147.70 (2C), 146.46 (4C), 146.25 (4C), 145.76 (2C), 145.52 (4C), 145.44 (4C), 144.93 (4C), 144.62 (4C), 143.12 (2C), 142.58 (4C), 142.06 (4C), 141.93 (4C), 141.64 (4C), 140.27 (4C), 135.31 (4C), 62.82 (2C), 62.32 (2C, sp³-C_{60}), 37.18 (2C). UV−vis (CH_2Cl_2) λ_{max} (log ϵ) = 256 (5.04), 310 (4.57), 432 (3.67),

695 (3.15). FT-IR (KBr): ν_{max} (cm^{-1}) = 2922, 1636, 1458, 1186, 1043, 883, 526. DEI-MS: m/z 862.0 (2, M$^+$), 720 (7, C$_{60}$). HRMS: calcd for C$_{66}$H$_{10}$N$_2$O$_2$ 862.074 228, found: 862.076 24.

General Procedure for the Synthesis of 6a–d. A mixture of C$_{60}$ and 1,2-bis(trimethylsiloxy)cyclobutene (**7**) was dissolved in 1,2-dichlorobenzene (10 mL) and degassed with argon for 30 min. The solution was heated at 180 °C for 1 h, the solvent was evaporated under vacuum, and the residue was dissolved in deoxygenated CS$_2$ (20 mL). This solution was cooled at −77 °C, Br$_2$ was added, and stirring was continued for 1 h. The CS$_2$ was eliminated under reduced pressure, and the residue was redissolved in a mixture of 1,2-dichlorobenzene (10 mL) and Et$_3$N·3HF (40 mg, 0.24 mmol). After an additional hour of stirring, a solution or dispersion of the corresponding o-diaminoarene in AcOH (5 mL) was added and heated at 60 °C for 3 h. The fullerene mixture was precipitated with MeOH (200 mL) and filtered through a pad of Celite. The filtrates were placed on the top of a silica gel or alumina column and chromatographed.

[5,6]Fullereno-C$_{60}$-I_h-[1,9-b]-1′,2′,3′,4′-tetrahydrophenazine (6a). The general procedure was followed with the molar ratio: C$_{60}$ (121 mg, 0.17 mmol), 1,2-bis(trimethylsiloxy)-cyclobutene (**7**) (56 mg, 0.24 mmol), Br$_2$ (16 mg, 0.1 mmol) and o-phenylenediamine (35 mg, 0.34 mmol). The mixture was chromatographed on a silica gel column (70 g) with eluent n-hexane/toluene (4:1) to pure toluene affording, in order, C$_{60}$ (73.2 mg, 60%) and **6a** (21 mg, 14%, 37% based on recovered C$_{60}$). ^{1}H NMR (300 MHz, CS$_2$/C$_2$D$_2$Cl$_2$ (5:1), −10 °C): δ (ppm) 8.28 (m, 1H), 7.91 (m, 1H), 5.24 (d, 1H, J = 14.26 Hz), 4.94 (d, 1H, J = 14.26 Hz). ^{13}C NMR (300 MHz, CS$_2$/C$_2$D$_2$Cl$_2$ (5:1)): δ (ppm) 156.87 (2C), 154.37 (4C), 148.70 (2C), 147.50 (8C), 147.30 (4C), 146.80 (2C), 146.48 (4C), 145.69 (8C), 144.13 (2C), 143.91 (4C), 143.63 (4C), 143.05 (8C), 142.76 (4C), 141.32 (2C), 136.52 (2C), 130.62 (2C), 130.56 (2C), 65.92 (2C), 48.45 (2C). UV–vis (CH$_2$Cl$_2$): λ_{max} (log ϵ) = 256 (4.95), 323 (4.45), 432 (3.34), 700 (2.38). UV–vis (CH$_2$Cl$_2$/H$_2$SO$_4$): λ_{max} (log ϵ) = 256 (4.95), 323 (4.45), 432 (3.34), 700 (2.38). FT-IR (KBr): ν_{max} (cm^{-1}) = 2919, 1514.6, 1335.7, 1128.3, 759.7, 526.5. MALDI-TOF MS: m/z = 876 (M$^+$), 720 (C$_{60}$). DEI-MS: m/z = 876 (21, M$^+$), 720 (100, C$_{60}$). HRMS: calcd for C$_{70}$H$_8$N$_2$ 876.068 74, found 876.070 83.

[5,6]Fullereno-C$_{60}$-I_h-[1,9-b]-7-methoxy-1′,2′,3′,4′-tetrahydrophenazine (6b). The general procedure was followed with the molar ratio C$_{60}$ (128 mg, 0.18 mmol), 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (70 mg, 0.30 mmol), Br$_2$ (17.5 mg, 0.11 mmol), and 4-methoxy-1,2-phenylenediamine (40 mg, 0.23 mmol). The mixture was chromatographed on a silica gel column (80 g) with eluent n-hexane/toluene (1:1) to THF (100:1) affording, in order, C$_{60}$ (53 mg, 41%) and **6b** (27 mg, 21%, 29% based on recovered C$_{60}$). ^{1}H NMR (300 MHz, CS$_2$/C$_2$D$_2$Cl$_2$ (5:1), −10 °C): δ (ppm) 8.10 (d, 1H, J = 8.96 Hz), 7.51 (d, 1H, J = 2.7 Hz), 7.47 (dd, 1H, J = 8.96 and 2.7 Hz), 5.17 (d, 1H, J = 14.26 Hz), 5.16 (d, 1H, J = 14.26 Hz), 4.85 (d, 2H, J = 14.26 Hz). Temperature-controlled measurements: −10, 0, 10, 20, 25, 30, 32, 35, 45 °C. ^{13}C NMR (300 MHz, CS$_2$/C$_2$D$_2$Cl$_2$ (5:1)): δ (ppm) 160.44, 155.40, 152.93, 150.26, 147.52, 146.32, 146.10, 145.56, 145.42, 145.30, 144.47, 144.29, 142.94, 142.89, 142.44, 141.92, 141.83, 141.56, 140.14, 138.70, 135.30, 130.30, 122.71, 107.03, 64.75 (sp^3-C$_{60}$), 64.66 (sp^3-C$_{60}$), 55.52 (OCH$_3$), 47.43 (CH$_2$), 47.17 (CH$_2$). UV–vis (CH$_2$Cl$_2$): λ_{max} (log ϵ) = 255 (5.01), 328 (4.54), 432 (3.70), 697 (3.18). FT-IR (KBr): ν_{max} (cm^{-1}) = 2919.1, 1618.1, 1496.2, 1345.8, 1223.5, 1023.2, 829.9, 756.8, 526.5. MALDI-TOF MS: m/z = 907 (100),

720 (37). DEI-MS: m/z 906 (27, M$^+$), 720.0 (79, C$_{60}$), 129 (100) HRMS: calcd for C$_{71}$H$_{10}$N$_2$O 906.079 313, found 906.082 16.

[5,6]Fullereno-C$_{60}$-I_h-[1,9-b]-10′,11′,12′,13′-tetrahydrobenzo[b]phenazine (6c). The general procedure was followed with the molar ratio C$_{60}$ (116 mg, 0.16 mmol), 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (60 mg, 0.26 mmol), Br$_2$ (16 mg, 0.1 mmol), and 2,3-diaminonaphthalene (35 mg, 0.22 mmol). The mixture was chromatographed on a silica gel column (70 g) with eluent n-hexane/toluene (1:1) to pure toluene affording, in order, C$_{60}$ (58 mg, 49%) and **6b** (24 mg, 16%, 32% based on recovered C$_{60}$). ^{1}H NMR (300 MHz, CS$_2$/C$_2$D$_2$Cl$_2$ (5:1), −10 °C): δ (ppm) 8.85 (s, 1H), 8.22 (m, 1H), 7.68 (m, 1H), 5.33 (d, 1H, J = 14.26 Hz), 4.97 (d, 1H, J = 14.26 Hz). Temperature-controlled measurements: −10, 0, 10, 20, 25, 30, 32, 35, 45 °C. ^{13}C NMR (300 MHz, C$_2$D$_2$Cl$_2$): δ (ppm) 155.18, 154.19, 147.55, 146.29, 146.10, 145.52 (br), 145.29, 144.84 (br), 144.47, 142.93, 142.41, 141.89, 141.79 (br), 141.51 (br), 140.08 (br), 139.28, 135.23 (br), 133.59, 128.31, 127.67, 126.99, 64.35 (sp^3-C$_{60}$), 47.67 (CH$_2$). UV–vis (CH$_2$Cl$_2$): λ_{max} (log ϵ) = 257 (4.6), 311 (4.19) 432 (3.55), 691 (3.30). FT-IR (KBr): ν_{max} (cm^{-1}) = 2921.0, 1654.2, 1508.1, 1458.4, 1376.8, 1179, 877.7, 723.1, 525.4. MALDI-TOF MS: m/z 927 (100). DEI-MS: m/z 926 (14, M$^+$), 720 (93, C$_{60}$) HRMS: calcd for C$_{74}$H$_{10}$N$_2$ 926.084 398, found 926.087 71.

[5,6]Fullereno-C$_{60}$-I_h-[1,9-b]-10′,11′,12′,13′-tetrahydrodibenzo[a,c]phenazine (6d). The general procedure was followed with the molar ratio C$_{60}$ (176 mg, 0.24 mmol), 1,2-bis(trimethylsiloxy)cyclobutene (**7**) (88 mg, 0.38 mmol), Br$_2$ (23.8 mg, 0.15 mmol), and 9,10-diaminophenanthrene (50 mg, 0,24 mmol). The mixture was chromatographed on an alumina column (50 g) with eluent toluene affording, in order, C$_{60}$ (72 mg, 41%) and **6b** (14 mg, 6%, 10% based on recovered C$_{60}$). ^{1}H NMR (360 MHz, CS$_2$/CHCl$_3$ (5:1)): δ (ppm) 9.41 (ddd, 1H, J = 0.9, 1.59, 7.52 Hz), 8.65 (dd, 1H, J = 1.36, 7.97 Hz), 7.79 (ddd, 1H, J = 1.59, 7.06, 7.97 Hz), 7.73 (ddd, 1H, J = 1.37, 7.52, 7.97 Hz), 5.16 (brs, 1H). ^{13}C NMR, 90 MHz, CS$_2$/CHCl$_3$ (5:1)): δ (ppm) 155.48, 151.41, 147.42, 146.25, 146.05, 145.36, 145.21, 144.87 (br), 144.57 (br), 144.39, 142.81, 142.37, 141.86, 141.80, 141.50, 140.73, 140.10, 138.52, 131.15, 129.90, 129.16, 127.41, 125.69, 122.54, 64.88, 47.34. UV–vis (CH$_2$Cl$_2$): λ_{max} (log ϵ) = 256 (4.42), 313 (3.91), 343 (s, 3.78), 359 (3.71), 432 (2.99). UV–vis (CH$_2$Cl$_2$ + H$_2$SO$_4$): λ_{max} (log ϵ) = 252 (4.33), 318 (s, 3.93), 331 (3.94), 385 (3.74), 417 (3.66). FT-IR (KBr): ν_{max} (cm^{-1}) = 2918.3, 1511.9, 1429.3, 1181.3, 758.8, 724.2, 526.3. MALDI-TOF MS: m/z 977 (100), 721 (67). DEI-MS: m/z 976 (12, M$^+$), 720 (49, C$_{60}$). HRMS: calcd for C$_{78}$H$_{12}$N$_2$ 976.100 048, found 976.102 85.

Supporting Information Available: ^{1}H and/or ^{13}C NMR of compounds **4b**, **9**, and **6a–d** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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