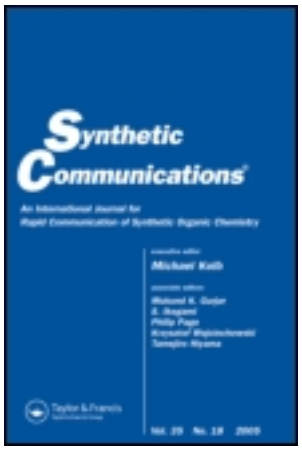

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Direct Formation of Cycloadducts Between Fullerenes and Amino Acids Through Electron-Transfer Processes

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DIRECT FORMATION OF CYCLOADDUCTS BETWEEN FULLERENES AND AMINO ACIDS THROUGH ELECTRON-TRANSFER PROCESSES

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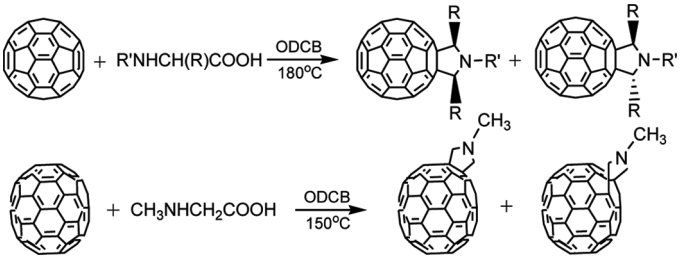
GRAPHICAL ABSTRACT



Abstract *The reactions of [60]fullerene and amino acids in the absence of aldehyde in* o*-dichlorobenzene (ODCB) at 150°C have been investigated. Fulleropyrrolidines* **1** *[$C_{60}(CH_2N(CH_3)CHC_6H_2(NO_2)_3)$],* **2** *[$C_{60}(CH_2N(CH_3)CH_2)$],* **3** *[$C_{60}(CH_2NHCH_2)$], and* **5a–b** *[$C_{60}(RCHNHCHR)$, R=$CH_3$ (***5a***), R=CH_2Ph (***5b***)] were obtained in moderate yields from the reactions of C_{60} and corresponding amino acids. The reaction of C_{70} and* N*-methylglycine in the absence of aldehyde was also studied and was found to give the positional isomers of* N*-methyl[70]fulleropyrrolidines* **6** *(1,9-isomer) and* **7***(7,8-isomer). All products were fully characterized by ultraviolet–visible, Fourier transform–infrared (FT-IR), NMR, and mass spectrometry. The reactions were also carried out in the dark to exclude the possible interference of the photoinduced reactions, and almost the same yields of products were obtained.*

Keywords Amino acids; cycloaddition reaction; [60]fullerene; [70]fullerene; fulleropyrrolidine

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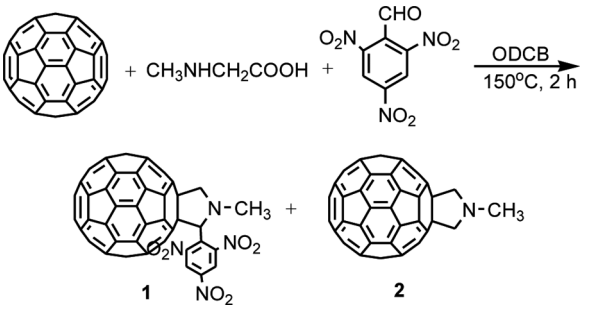
INTRODUCTION

Because of its unusual spherical structure and unique physical and chemical properties, fullerene has attracted much attention for applications in materials science and life science.[1–10] Functionalization of fullerene is one of major strategies in exploring the practical use for fullerene. Since its first discovery and isolation, chemical modifications of fullerene have been extensively explored, and an impressive number of fullerene derivatives have been synthesized by various functionalization methods.[11–16] Among them, the reaction of fullerene with amino acids or amino acid esters to prepare biologically and pharmacologically active fullerene derivatives is of great appeal to chemists.[17–23] It is well known that amino acids can react with C_{60} and aldehydes/ketones to afford fulleropyrrolidines through the 1,3-dipolar cycloadditions of C_{60} and corresponding azomethine ylides.[17] Fullerene can react with *N*-substituted glycines in the absence of aldehyde under high-speed vibration milling (HSVM) conditions to give fulleropyrrolidines.[24] Amino acid esters can also directly react with C_{60} to afford the corresponding fulleropyrrolidines under the photoirradiation and ultrasonification conditions.[18–20] Wang's group has explored thermal reactions of C_{60} with amino acid ester hydrochlorides and triethylamine in refluxing o-dichlorobenzene (ODCB) to afford fulleropyrrolidine derivatives.[22]

Recently, we have reported novel reactions of C_{60} with amino acids and quaternary ammonium salts in toluene, which afford fulleropyrrolidine derivatives containing a RCH moiety that originated from quaternary ammonium salts through C–N bond cleavages.[23] In continuation of our interest in fullerene chemistry, we have investigated the reactions of C_{60} with amino acids in the absence of aldehydes/ketones in ODCB at 180 °C and unexpectedly discovered the direct reactions of C_{60} and amino acids to give fulleropyrrolidines. The reaction of C_{70} with *N*-methylglycine without aldehyde in ODCB at 150 °C was also studied and was found to give the positional isomers of [70]fulleropyrrolidines. On the basis of further experimental results, a possible reaction mechanism involving a thermoinduced electron-transfer process has been proposed.

RESULTS AND DISCUSSION

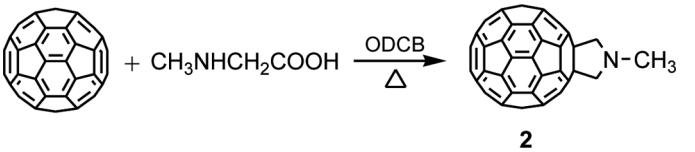
The 1,3-dipolar cycloaddition of C_{60} with amino acid and aldehyde is one of the easiest methods to prepare functional fulleropyrrolidines.[17] Our previous work was to synthesize some nitro fulleropyrrolidines using this method. Typically, a mixture of C_{60} (36.0 mg), *N*-methylglycine (26.7 mg), and 2,4,6-trinitrobenzaldehyde (24.1 mg) was stirred at 150 °C for 2 h in 20 mL ODCB. The target product *N*-methyl-2-(2,4,6-trinitrophenyl)fulleropyrrolidine **1** was obtained in moderate yields as shown in Scheme 1. The structure of **1** was confirmed by ultraviolet–visible (UV-vis), Fourier transform-infrared (FT-IR), ^{1}H NMR, ^{13}C NMR, and mass spectrometry (MS). A noteworthy fact is that we unexpectedly isolated *N*-methylfulleropyrrolidine **2** as a minor product besides the corresponding fulleropyrrolidine **1** in the reaction of C_{60} with *N*-methylglycine and 2,4,6-trinitrobenzaldehyde. The identity of product **2** was confirmed by comparison of their spectral data with those reported in literature.[17] Actually, compound **2** was also obtained as an unexpected product by Yin and Izquierdo via 1,3-dipolar cycloaddition reactions of fullerene,



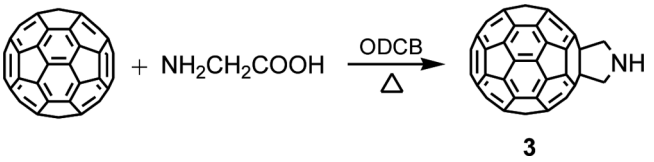
Scheme 1. Synthesis of adducts **1** and **2** by the reactions of C_{60}, *N*-methylglycine, and 2,4,6-trinitrobenzaldehyde in ODCB.

N-methylglycine, and other aldehydes, but the mechanism of this unusual transformation has not been reported.[25,26] We thought product **2** might be prepared by the direct reaction of fullerene and *N*-methylglycine, so we tried making direct reaction of fullerene and *N*-methylglycine without using 2,4,6-trinitrobenzaldehyde. To our pleasure, when a binary mixture of C_{60} (36.0 mg) and *N*-methylglycine (53.4 mg) was stirred at 170 °C for 24 h in ODCB, product **2** was obtained in 31% yield (71% based on consumed C_{60}) (Scheme 2).

To probe the generality of this type of reaction for other amino acids, treatment of C_{60} with other amino acids in place of *N*-methylglycine was examined in the absence of aldehyde. As desired, when C_{60} (36.0 mg) with glycine (45.4 mg) were added into 20 mL ODCB and heated to 180 °C for 48 h, the corresponding adduct **3** was prepared in 11% yield (59% based on consumed C_{60}) (Scheme 3). During the work on the reactions of C_{60} with amino acids **4a–b**, it was found that the corresponding *cis*- and *trans*-1,3-disubstituted fulleropyrrolidines were obtained. A mixture of C_{60} (36.0 mg) and alanine **4a** (66.8 mg) was dissolved in 30 mL of ODCB and heated to 180 °C with stirring for 48 h, and then isolation by flash column chromatography on silica gel using a mixture of *n*-hexane and toluene as the eluent afforded *cis*-**5a** and *tran*-**5a** in 29% and 16% yields respectively (50% and 25% respectively based on consumed C_{60}) (Scheme 4). When C_{60} (36.0 mg) and phenylalanine (139.4 mg) were added into 30 mL of ODCB and heated to 180 °C for 36 h, products *cis*-**5b** and *tran*-**5b** were obtained in 22% and 14% yields respectively (36% and 23% respectively based on consumed C_{60}) (Scheme 4). The structures of products **3**,[17] *cis*/*trans*-**5a**,[27] and *cis*/*trans*-**5b**[27] were unambiguously confirmed by their MS, ^{1}H NMR, FT-IR, and UV-vis spectral data, and all these spectral data are fully consistent with those reported previously.

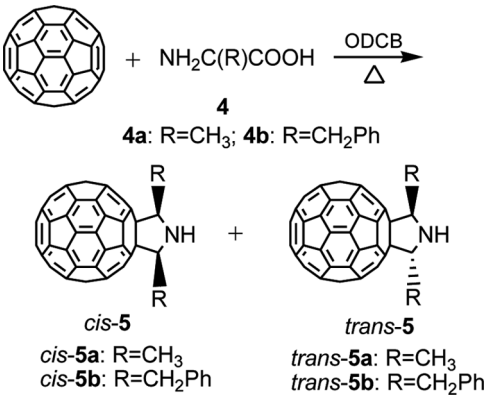


Scheme 2. Synthesis of adduct **2** by the direct reaction of C_{60} and *N*-methylglycine in ODCB.



Scheme 3. Synthesis of adduct **3** by the direct reaction of C_{60} and glycine in ODCB.

It was reported that C_{70} can react with paraformaldehyde and *N*-methylglycine to produce three positional isomers of *N*-methyl[70]fulleropyrrolidines (1,9-isomer, 7,8-isomer, and 22,23-isomer).[28,29] To find out if a similar reaction of C_{60} with amino acids occurs for C_{70}, treatment of *N*-methylglycine with C_{70} in place of C_{60} was examined in the absence of aldehyde. When a mixture of C_{70} (44.8 mg) and *N*-methylglycine (38.1 mg) was stirred at 150 °C for 10 h in 20 mL of ODCB, a mixture of *N*-methyl[70]fulleropyrrolidines monoadducts was isolated by column chromatography in a total yield of 70%. High-performance liquid chromatography–mass spectrometry (HPLC-MS) was used to rapidly identify the constituents of the *N*-methyl[70]fulleropyrrolidine monoadducts mixture (Fig. 1). As depicted in Fig. 1, the HPLC analysis result showed that the mixture contains **A**, **B**, **7**, and **6** in a 1:1:50:40 ratio, and the MS analysis results showed that both **6** (m/z: 898) and **7** (m/z: 898) were the *N*-methyl[70]fulleropyrrolidine monoadduct isomer. The structures of **6** and **7** were also confirmed by their ^{1}H NMR. Product **6** exhibited three singlets at δ 2.76, 3.60, and 3.94 in a 3:2:2 ratio and product **7** exhibited one singlet at δ 2.63 and two doublets at δ 3.46 and 3.71 in a 3:2:2 ratio, which indicated that product **6** and product **7** were the 1,9-isomer and 7,8-isomer respectively (Scheme 5).[28] The 22,23-isomer *N*-methyl[70]fulleropyrrolidine was not obtained, and it was consistent with the failure of formation of 22,23-isomer from the reaction of C_{70} with *N*-methylglycine in the absence of paraformaldehyde under high-speed vibration milling (HSVM) conditions.[24]



Scheme 4. Synthesis of adducts *cis*/*trans*- **5a–b** by the direct reactions of C_{60} and amino acids **4a–b** in ODCB.

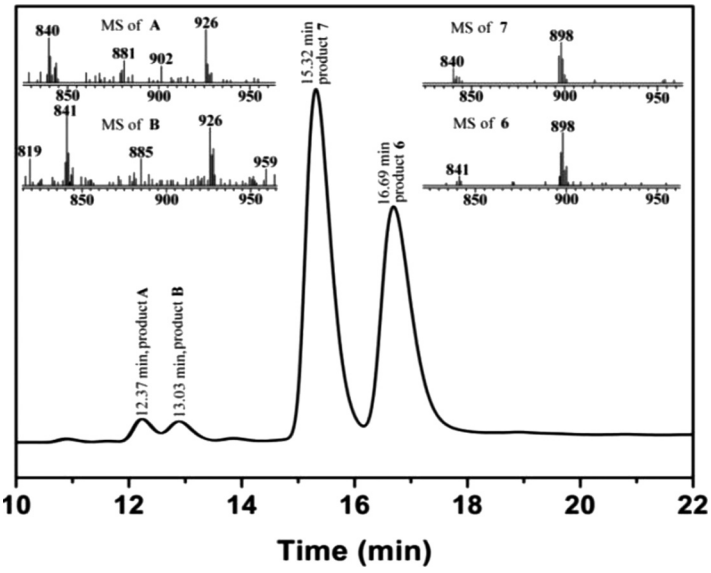
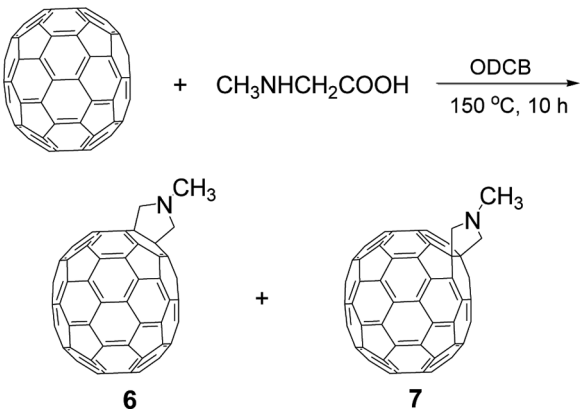


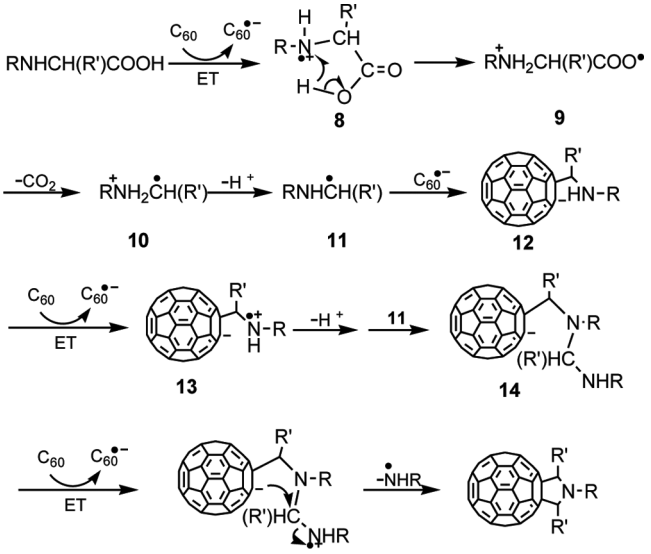
Figure 1. HPLC chromatogram and mass spectra of the mixture of isomeric monoadducts **6** and **7**. HPLC conditions: 250- × 10-mm Buckyprep column, toluene mobile phase (3 mL/min), UV-vis detection at 330 nm. MS conditions: APCI ion source.

The reactions were conducted in the dark to exclude the possible interference of photoinduced reactions, because there have already been some examples of photoinduced radical reactions of C_{60} with amino acid esters.[18,19] When a mixture of C_{60} (36.0 mg) and *N*-methylglycine (53.4 mg) was added into 20 mL of ODCB and heated to 170 °C in the dark and high-purity Ar atmosphere (99.99%) conditions for 24 h, product **2** was also obtained in 31% yield (70% based on consumed C_{60}).

Amines can react with C_{60} to form amine cation radicals and $C_{60}^{-\bullet}$ anion radical.[18,19,22,30,31] In most cases, the electron transfer between an amine and C_{60} has been initiated by photochemically,[18,19] but there is evidence that amines can transfer



Scheme 5. Synthesis of adducts **6** and **7** by the direct reaction of C_{70} and sarcosine in ODCB.



Scheme 6. Proposed reaction mechanism for the formation of fulleropyrrolidine derivatives.

single electrons to C_{60} without photoirradiation.[22,30,31] Thus, under our high-temperature conditions, a primary or secondary amine may transfer an electron to C_{60} even in the dark (Scheme 6).[22,30,31] As shown in Scheme 6, the reaction starts with the electron transfer from the amido of amino acids to C_{60} to afford C_{60} radical anion and **8**. Intramolecular hydrogen transfer of **8** through a five-membered cyclic transition state gives the radical cation **9**. Radical cation **9** loses CO_2 and a proton to afford radical **11**, which couples with C_{60} radical anion to form anion **12**. The anion **12** transfers electron to C_{60} to afford intermediate **13**, which loses a proton and couples with radical **11** to give the anion **14**. Anion **14** with C_{60} undergoes intermediate electron transfer and then cyclizes with the loss of the alkyl amine radical to afford fulleropyrrolidines.

CONCLUSION

In summary, the reaction of C_{60} with *N*-methylglycine and 2,4,6-trinitrobenzaldehyde in ODCB under 150 °C was investigated. Both the expected product *N*-methyl-2-(2,4,6-trinitrophenyl)fulleropyrrolidine **1** and the product *N*-methylfulleropyrrolidine **2** were obtained from the reaction. Through further experimental studies, a novel thermal reaction of C_{60} with amino acid without aldehyde was found. Fulleropyrrolidines **1–3** and **5a–b** were obtained in moderate yields from the reactions of C_{60} and corresponding amino acids. The reaction of C_{70} and *N*-methylglycine in the absence of aldehyde was also studied and was found to give the positional isomers of *N*-methyl[70]fulleropyrrolidines **6** (1,9-isomer) and **7** (7,8-isomer). Plausible reaction mechanisms for the product formation involving the thermoinduced electron-transfer from amines to C_{60} was proposed on the basis of further experimental results.

EXPERIMENTAL

C_{60} and C_{70} were prepared by arc discharge method.[32] 2,4,6-Trinitrobenzaldehyde was prepared from 2,4,6-trinitrotoluene by a published method.[33] All other commercially available reagents are of analytical grade. NMR spectra were recorded on a Bruker AC 300/600 spectrometer with $CS_2/CDCl_3$ as the solvent. Mass spectra were taken on a Varian 1200LC/MS mass spectrometer and a Bruker BiFlexIII mass spectrometer using 4-hydroxy-α-cyanocinnamic acid as the matrix. The IR spectra were measured on a Nicolet 380 FT-IR spectrometer (KBr pellet) with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}. UVvis spectra were recorded on Unicon UV-2102 PCS spectrometer with $CHCl_3$ as the solvent. Chromatographic purifications were carried out with 300- to 400-mesh silica gel. HPLC was carried out by using a 250- × 10-mm Buckyprep column.

General Procedure for Synthesis of Fulleropyrrolidines 1 and 2 by the Reaction of C_{60} with 2,4,6-Trinitrobenzaldehyde and *N*-Methylglycine

A mixture of C_{60} (36.0 mg, 0.05 mmol), N-methylglycine (22.6 mg, 0.3 mmol), and 2,4,6-trinitrobenzaldehyde (24.1 mg, 0.1 mmol) was heated to 150 °C for the 2 h in 20 mL ODCB. The solution was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to give final products **1** and **2**.

General Procedure for Synthesis of Fulleropyrrolidines 2–5 by the Reactions of C_{60} and Amino Acids

A mixture of C_{60} and amino acids was heated to 180 °C for the time indicated in ODCB. The solution was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel.

General Procedure for Synthesis of Fulleropyrrolidines 6 and 7 by the Reaction of C_{70} and *N*-Methylglycine

A mixture of C_{70} (42.0 mg, 0.05 mmol) and N-methylglycine (35.6 mg, 0.4 mmol) was heated to 150 °C for 12 h in 20 mL ODCB. The solution was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the mixture of monoadducts. The monoadducts were separated using a Buckyprep column to give **6** and **7** in a 4:5 ratio.

Selected Data

***N*-Methyl-2-(2,4,6-trinitrophenyl)fulleropyrrolidine (1).** UV-vis ($CHCl_3$) λ_{max}: 260 (s), 309 (m), 431 (w) nm; ^{1}H NMR ($CS_2/CDCl_3$, 600 MHz) δ: 7.79 (s, 2H), 5.00 (d, $J = 9.2$ Hz, 1H), 4.95 (s, 1H), 4.28 (d, $J = 9.2$ Hz, 1H), 2.84 (s, 3H) ppm; ^{13}C NMR ($CS_2/CDCl_3$, 150 MHz) δ: 156.22, 153.99, 153.42, 153.30, 147.35, 146.80, 146.50, 146.38, 146.33, 146.28, 146.22 (2C), 146.20, 146.16, 146.00 (2C),

145.83, 145.68, 145.61, 145.58, 145.46 (2C), 145.36, 145.30 (2C), 145.29, 145.22, 144.78, 144.71, 144.45, 143.23, 143.09, 142.76, 142.69, 142.66 (2C), 142.35, 142.32, 142.23, 142.17, 142.15, 142.13, 142.08, 142.00, 141.90, 141.77, 141.62, 140.31, 140.26, 140.00, 139.59, 136.97, 136.92, 136.67, 135.92, 135.82, 129.41, 128.87, 128.63, 83.70 (CH), 70.17, 69.03 (CH_2), 63.00, 40.10 (CH_3) ppm; IR (KBr) υ: 2944, 2831, 2779, 1602, 1539, 1463, 1453, 1428, 1333, 1179, 1107, 940, 905, 767, 574, 527, 479 cm^{-1}; MS (MAIDI-TOF) m/z: 987.4 $[M-1]^+$.

***N*-Methylfulleropyrrolidine (2)[17].** UV-vis($CHCl_3$) λ_{max}: 257 (s), 306 (m), 431 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 300 MHz) δ: 4.42 (s, 4H), 3.02 (s, 3H) ppm; ^{13}C NMR ($CS_2/CDCl_3$, 75 MHz) δ: 154.54 (2C), 147.04, 146.01 (2C), 145.82 (2C), 145.75 (2C), 145.43, 145.23 (2C), 145.04 (2C), 144.31 (2C), 142.87, 142.41 (2C), 141.98 (2C), 141.85 (2C), 141.66 (2C), 139.97 (2C), 136.04 (2C), 70.91(2C, sp^3-*C* of C_{60}), 69.80 (2C, *C*H_2), 41.28 (N*C*H_3) ppm; IR (KBr) υ: 2967, 2938, 2836, 2774, 1629, 1425, 1340, 1185, 1162, 1114, 1091, 1034, 571, 526 cm^{-1}; MS (MAIDI-TOF) m/z: 777 $[M]^+$, 720 $[C_{60}]^+$.

Fulleropyrrolidine (3)[17]. UV-vis($CHCl_3$) λ_{max}: 258 (s), 310 (m), 430 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 4.84 (s, 4H) ppm; IR (KBr) υ: 3430, 2929, 2836, 1428, 1340, 1180, 1162, 1114, 1091, 1034, 770, 577, 555, 526 cm^{-1}; MS (APCI) m/z: 764 $[M+H]^+$, 720 $[C_{60}]^+$.

***Cis*-2,5-Dimethylfulleropyrrolidine (*cis*-5a)[27].** UV-vis($CHCl_3$) λ_{max}: 259 (s), 306 (m), 430 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 4.85 (q, $J=6.8$ Hz, 2H), 2.07 (d, $J=6.8$ Hz, 6H) ppm; IR (KBr) υ: 3274, 2958, 2921, 1426, 1376, 1184, 1086, 1032, 806, 778, 574, 554, 527 cm^{-1}; MS (APCI) m/z: 792 $[M+H]^+$, 720 $[C_{60}]^+$.

***Trans*-2,5-Dimethylfulleropyrrolidine (*trans*-5a)[27].** UV-vis($CHCl_3$) λ_{max}: 257 (s), 308 (m), 430 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 5.12 (q, $J=6.8$ Hz, 2H), 2.11 (d, $J=6.8$ Hz, 6H) ppm; IR (KBr) υ: 3292, 2962, 2923, 1512, 1428, 1381, 1185, 1150, 1096, 1051, 794, 779, 575, 555, 529 cm^{-1}; MS (APCI) m/z: 792 $[M+H]^+$, 720 $[C_{60}]^+$.

***Cis*-2,5-Dibenzylfulleropyrrolidine (*cis*-5b)[27].** UV-vis($CHCl_3$) λ_{max}: 257 (s), 308 (m), 431 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 7.43 (d, $J=7.2$ Hz, 4H), 7.34 (t, $J=7.2$ Hz,4H), 7.24 (t, $J=7.2$ Hz, 2H) 4.78 (dd, $J=10.8$, 3.2 Hz, 2H), 3.91 (dd, $J=13.2$, 3.2 Hz, 2H) 3.40 (dd, $J=13.2$, 10.8 Hz, 2H), 2.56 (br s, 1H) ppm; IR (KBr) υ: 3330, 3027, 2918, 2836, 1512, 1494, 1453, 1427, 1387, 1348, 1181, 1077, 891, 743, 700, 618, 574, 562, 527 cm^{-1}; MS (APCI) m/z: 944 $[M+H]^+$, 720 $[C_{60}]^+$.

***Trans*-2,5-Dibenzylfulleropyrrolidine (*trans*-5b)[27].** UV-vis($CHCl_3$) λ_{max}: 257 (s), 309 (m), 432 (w) nm; ^1H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 7.48–7.00 (m, 10H), 5.15 (dd, $J=11.2$, 3.6 Hz, 2H), 3.72 (dd, $J=13.2$, 3.2 Hz, 2H), 3.54 (dd, J = 13.2, 11.2 Hz, 2H), 2.70 (br s, 1H) ppm; IR (KBr) υ: 3334, 3024, 2919, 1494, 1452, 1428, 1392, 1183, 1075, 1029, 743, 721, 699, 575, 563, 552, 527 cm^{-1}; MS (APCI) m/z: 944 $[M+H]^+$, 720 $[C_{60}]^+$.

***N*-Methyl[70]fulleropyrrolidine (1,9-Isomer) (6).** ^{1}H NMR ($CS_2/CDCl_3$, 400 MHz) δ: 3.94 (s, 2H), 3.60 (s, 2H), 2.76 (s, 3H) ppm; MS (APCI) m/z: 898 $[M+H]^+$, 841 $[C_{70}+H]^+$.

***N*-Methyl[70]fulleropyrrolidine (7,8-isomer) (7).** ^{1}H NMR ($CS_2/CDCl_3$, 300 MHz) δ: 3.70 (d, $J=9.3$ Hz, 2H), 3.46 (d, $J=9.3$ Hz, 2H), 2.64 (s, 3H) ppm; MS (APCI) m/z: 898 $[M+H]^+$, 840 $[C_{70}]^+$.

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