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# Synthesis of fulleropyrrolidines through the reaction of [60]fullerene with quaternary ammonium salts and amino acids

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ABSTRACT

The reactions of [60]fullerene with amino acids and quaternary ammonium salts in toluene afforded two fulleropyrrolidine derivatives. One fulleropyrrolidine derivative contained a RCH moiety originating from quaternary ammonium salts through C–N bond cleavages and other fulleropyrrolidine derivatives contained a PhCH moiety originating from toluene through C–H bond cleavage. By using chlorobenzene instead of toluene as solvent, only one fulleropyrrolidine derivative containing a RCH moiety was obtained in the reactions.

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Since their first discovery and isolation, chemical modifications of fullerene have been intensively explored and an impressive number of fullerene derivatives have been synthesized by various functionalization methods because of their potential applications in many fields such as materials science and life science.[1] Fulleropyrrolidines are one of fullerene derivatives frequently employed in these fields.[2] The reaction between azomethine ylides and fullerene is one of the first reported fullerene reactions and has been widely studied in order to synthesize fulleropyrrolidine derivatives.[3] A very simple and powerful way to afford azomethine ylides is the decarboxylation of iminium salts derived from the condensation of amino acids and aldehydes/ketones.[4] Azomethine ylides can also be successfully generated by thermal ring opening of aziridines[3,5] or the acid-catalyzed/thermal desilylation of trimethylsilyl amino derivatives.[6] Photochemical treatment of tertiary amine with $C_{60}$ also leads to fulleropyrrolidines.[7] Gan's group has explored direct reactions between amino acid esters and $C_{60}$ induced by photo irradiation and ultrasonification to afford the fulleropyrrolidines.[8] Recently, Wang's group has reported novel thermal reactions of $C_{60}$ with amino acid ester hydrochlorides and triethylamine in o-dichlorobenzene at reflux afforded fulleropyrrolidine derivatives.[9]

We have recently investigated the reactions of $C_{60}$ with amino acids and tetra-*n*-butylammonium chloride (TBAC) in toluene at 105 °C, and unexpectedly discovered the incorporation into two fulleropyrrolidine derivatives. One contained a $CH_3CH_2CH_2CH$ moiety originating from TBAC through C–N bond cleavage and the other contained a PhCH moiety originating from toluene through C–H bond cleavage. Furthermore, detailed investigation of these reactions resulted in a discovery of the reactions of $C_{60}$ with amino acids and other quaternary ammonium salts. Here, we report these novel reactions.

The reaction of $C_{60}$ with amino acids and aldehydes is one of the easiest methods to prepare some functional fullerene compounds.[3] Our previous work was to synthesize some nitro fullerene derivatives with this method. Initially, a mixture of $C_{60}$, glycine and 2,4-dinitrobenzaldehyde was stirred at refluxing temperature for several days in toluene to synthesize 2-(2,4-dinitrophenyl)fulleropyrrolidine, and the reaction was followed by TLC. However, TLC results revealed that the reaction did not occur. Considering the poor solubility of glycine in toluene, the phase transfer catalysis (PTC) of tetra-*n*-butylammonium chloride (TBAC) was added into the toluene solution to improve the reaction. Unexpectedly, it was found that $C_{60}$ reacted with TBAC and glycine (1:10:8) in toluene at 105 °C for 40 h to afford adducts **3a** and **4a** in 23% and 32% yields, respectively (based on consumed $C_{60}$) (Scheme 1). Adduct **3a** possessed an $n$-$C_3H_7CH$ moiety, which might conceivably have originated from TBAC. To substantiate the assumption, other quaternary ammonium salts and amino acids were used in the reaction to see if products in which the $n$-$C_3H_7CH$ group had been replaced by the RCH moiety could be obtained. When $C_{60}$ with quaternary ammonium salts **1a–c** and amino acids **2a–b** were added

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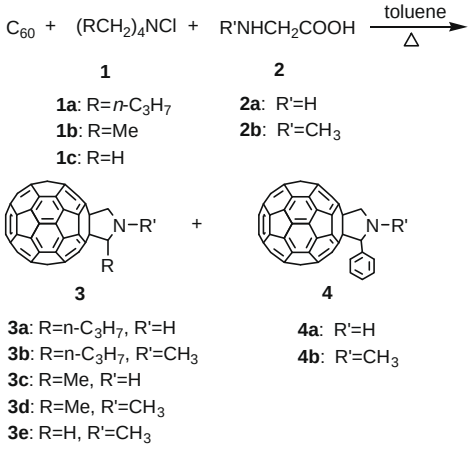
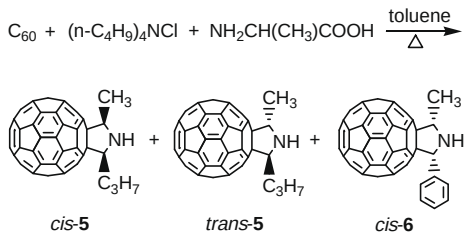



**Scheme 1.** Synthesis of adducts **3a**–**e** and **4a**–**b** by the reactions of $C_{60}$ with quaternary ammonium salts **1a**–**c** and amino acids **2a**–**b** in toluene.

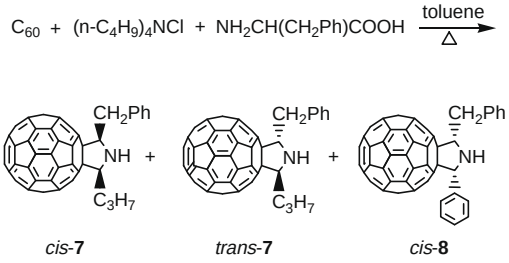
into toluene and heated to 105 °C for a given time, the corresponding adducts **3b**–**e** and **4a**–**b** were prepared (Scheme 1).

During the work of the reaction of $C_{60}$ with TBAC and alanine/phenylalanine, it was found that the *cis*- and *trans*-2,5-disubstituted fulleropyrrolidines were obtained. A mixture of $C_{60}$ (36.0 mg), TBAC (97.0 mg) and alanine (26.7 mg) was dissolved in 60 mL of toluene and heated to 105 °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 eluents afforded *tran*-**5**, *cis*-**5** and *cis*-**6** in 49%, 25% and 13% yields, respectively, based on consumed $C_{60}$ (Scheme 2). When $C_{60}$ (36.0 mg), TBAC (97.0 mg) and phenylalanine (41.3 mg) were added into toluene and heated to 105 °C for 48 h, the *trans*-**7**, *cis*-**7** and *cis*-**8** were obtained in 35%, 32% and 21% yields, respectively (Scheme 3, based on consumed $C_{60}$).

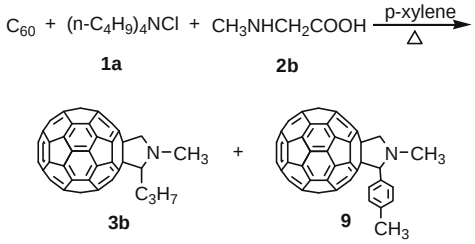
All above-mentioned results revealed that adducts **3a–e**, *cis*/*trans*-**5** and *cis*/*trans*-**7** each possessed a RCH moiety, which was changed with the different quaternary ammonium salts. So there was no question that the RCH moiety originated from quaternary ammonium salts through C–N bond cleavages. However, it was very interesting that adducts **4a–b**, *cis*-**6** and *cis*-**8** each possessed a common PhCH moiety. Obviously, PhCH moiety did not originate from the corresponding quaternary ammonium salts and amino acids. The solvent toluene might have involved in the reactions and the PhCH moiety originated from toluene. In order to confirm the assumption, *p*-xylene and chlorobenzene were used in the reaction as the solvent to substitute toluene. As desired, when a mixture of $C_{60}$ (36.0 mg), TBAC (242.0 mg) and sarcosine (30.5 mg) was added in 20 mL *p*-xylene and heated to 105 °C for 3 h, the products **3b** and **9** were obtained in 9% and 50% yields, respectively (Scheme 4, based on consumed $C_{60}$). When $C_{60}$ with quaternary ammonium salts **1a**–**c** and amino acids **2a**–**b** were




**Scheme 2.** Synthesis of adducts *cis*/*trans*-**5** and *cis*-**6** by the reactions of $C_{60}$ with TBAC and alanine in toluene.



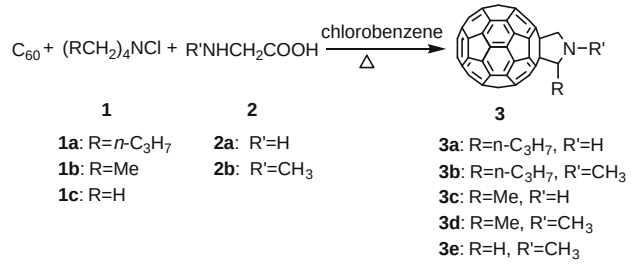

**Scheme 3.** Synthesis of adducts *cis*/*trans*-**7** and *cis*-**8** by the reactions of $C_{60}$ with TBAC and phenylalanine in toluene.




**Scheme 4.** Synthesis of adducts **3b** and **9** by the reactions of $C_{60}$ with **1a** and **2b** in *p*-xylene.

added into chlorobenzene and heated to 105 °C for a period of time, only adducts **3a**–**e** were synthesized in 23%, 59%, 36%, 54% and 45% yields, respectively, as shown in Scheme 5.

The structures of products **3a–e**[10], **4a–b**, *cis*/*trans*-**5**,[11] *cis*-**6**,[12] *cis*/*trans*-**7**,[13] *cis*-**8**[14] and **9**[10] were unambiguously confirmed by their MS, $^1$H NMR, $^{13}$C NMR, FT-IR and UV–vis spectral data. The spectral data of adducts **3d**–**e** and **4a**–**b** are fully consistent with those reported previously.[3,9,15] The $^1$H NMR spectra of compounds **3a**–**c** and **9** each shows two doublets at $\delta$ = 4.18–4.96 ppm for the two nonequivalent methylene protons in the pyrrolidine ring. Product **3b** exhibits a singlet at $\delta$ = 3.00 ppm in their $^1$H NMR spectra for N-substituted methyl group ($NCH_3$) in the pyrrolidine ring. Products **3a**–**b** each exhibits three multiplet and a triplet at $\delta$ = 1.13–2.68 in their $^1$H NMR spectra for 2-substituted *n*-$C_3H_7$ group in the pyrrolidine ring. Product **9** exhibits two singlets at $\delta$ = 2.75 and 2.31 ppm in their $^1$H NMR spectra for *N*-$CH_3$ and Ph-$CH_3$ in the pyrrolidine ring. The $^1$H NMR spectra of *cis*/*trans*-**5** and *cis*/*trans*-**7** show a similar pattern, respectively, and the signals of the pyrrolidine methine protons for the *cis*-isomers appear further upfield than the corresponding signals for the *trans*-isomers,[16] which is different with Wilson's report that *the signals for the cis-isomers always appear further downfield than the corresponding signals for the trans-isomers*.[17] The *trans*-**5** shows a methine quartet at $\delta$ = 4.98 ppm and a methine doublet of doublets at $\delta$ = 4.88 ppm, while the corresponding methines from *cis*-**5** appears as a quartet at 4.76 ppm and a doublet of doublets at 4.66 ppm, respectively.




**Scheme 5.** Synthesis of adducts **3a**–**e** by the reactions of $C_{60}$ with quaternary ammonium salts **1a**–**c** and amino acids **2a**–**b** in chlorobenzene.

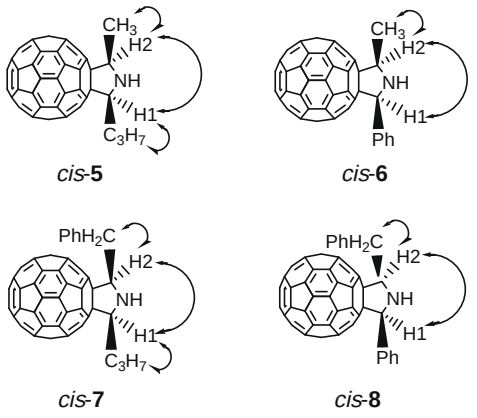



**Figure 1.** Partial NOEs involving the hydrogens in compounds *cis*-**5**, *cis*-**6**, *cis*-**7** and *cis*-**8**.

Similarly the pyrrolidine methine signals for *trans*-**7** appear as a doublet of doublets at 5.16 ppm and a doublet of doublets at 5.00 ppm. The spectrum of *cis*-**7** shows a methine doublet of doublets at 4.89 ppm and a methine doublet of doublets at 4.60 ppm. The $^1$H NMR spectra of *cis*-**6** and *cis*-**8** exhibit 6 signals and 9 signals, respectively. Two methine signals of *cis*-**6** appear as a singlet at 5.79 ppm and a quartet at 4.95 ppm, and two methine signals of *cis*-**8** appear as a singlet at 5.70 ppm and a doublet of doublets at 5.03 ppm.

The stereochemistry of the products *cis*/*trans*-**5**, *cis*-**6**, *cis*/*trans*-**7** and *cis*-**8** were also revealed by the $^1$H NOESY spectra. The NOEs involving the hydrogens are indicated by the curved arrows in Figure 1. The NOESY spectrum of *cis*-**5** shows no correlation between H1 and methyl H, and *cis*-**7** shows no correlation between H1 and benzyl H. Both *cis*-**5** and *cis*-**7** show correlation between H1 and H2 in their NOESY spectra. These results indicated that *cis*-**5** and *cis*-**7** are *cis*-isomer. The NOESY spectrum of *cis*-**6** (Fig. 2) shows correlation between H1 and H2 but no correlation between H1 and methyl H, and *cis*-**8** shows correlation between H1 and H2 but no correlation between H1 and methylene H. Obviously, the NOESY spectra indicate that *cis*-**6** and *cis*-**8** are *cis*-isomer, and the previous Wilson's report that *cis*-**6** and *cis*-**8** are *trans*-isomer was incorrect.[16,17]

In summary, a new protocol to prepare fulleropyrrolidines from amino acids and quaternary ammonium salts has been developed. Fulleropyrrolidines have wide application involving molecular electronics, photochemistry, biology and materials sciences.[2] The most common method to synthesize fulleropyrrolidines involves amino acids and aldehydes, in which some desired aldehydes usually are expensive or not commercially available. This Letter provides an alternative method to make fulleropyrrolidines from ammonium salts. Further studies aimed at the reaction mechanism are in progress.

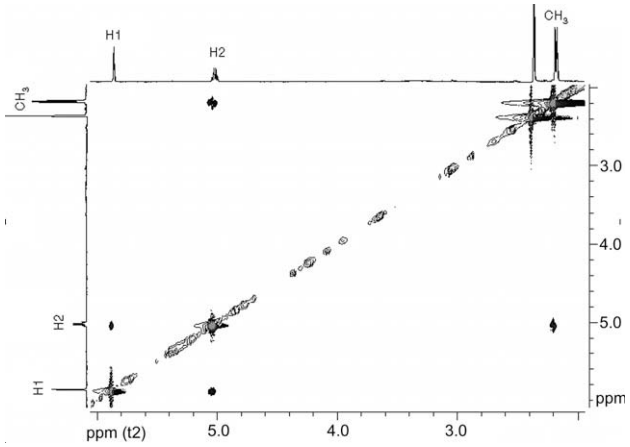



**Figure 2.** The NOESY spectrum of *cis*-**6**.

## Acknowledgements

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## Supplementary data

Supplementary data (MS and NMR spectra of fulleropyrrolidines **3a**–**e**, **4a**–**b**, *cis*/*trans*-**5**, *cis*-**6**, *cis*/*trans*-**7** and *cis*-**8** and experimental procedure for the preparation of all fulleropyrrolidines) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.097.

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10. *2-Propylfulleropyrrolidine* (**3a**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 310 (m), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 4.95 (d, $J$ = 11.7 Hz, 1H), 4.71 (d, $J$ = 11.9 Hz, 1H), 4.68 (dd, $J$ = 10.4, 3.0 Hz, 1H), 2.62–2.68 (m, 1H), 2.05–2.18 (m, 2H), 1.89–1.96 (m, 1H), 1.21 (t, $J$ = 7.4 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 150 MHz) $\delta$: 156.04, 154.43, 154.40, 153.02, 147.10 (2C), 146.60, 146.50, 146.38, 146.34, 146.31, 146.24 (2C), 146.10, 146.06, 146.01 (2C), 145.73, 145.39 (4C), 145.35 (2C), 145.30, 145.23, 144.63, 144.50, 144.38 (2C), 143.30, 143.22, 143.13, 142.75 (3C), 142.41, 142.31, 142.28, 142.25, 142.12 (2C), 141.97, 141.87, 141.81, 140.39, 140.27, 140.22, 139.93, 136.48, 135.83, 135.78, 135.56, 78.63 ($sp^3$-*C* of $C_{60}$), 75.70 ($sp^3$-*C* of $C_{60}$), 74.72 (*C*H), 63.14 (*C*H), 36.17 ($CH_2CH_2CH_3$), 22.06 ($CH_2CH_2CH_3$), 14.70 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 2957, 2923, 2864, 1628, 1533, 1457, 1401, 1184, 1098, 569, 526 $cm^{-1}$; MS (MAIDI-TOF) $m/z$: 805 $[M]^+$, 720 $[C_{60}]^+$. *N-Methyl-2-propylfulleropyrrolidine* (**3b**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 309 (m), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 300 MHz) $\delta$:

4.80 (d, $J$ = 9.6 Hz, 1H), 4.18 (d, $J$ = 9.7 Hz, 1H), 3.92 (t, $J$ = 4.8 Hz, 1H), 3.00 (s, 3H), 2.46–2.57 (m, 1H), 2.29–2.42 (m, 1H), 1.90–2.04 (m, 2H), 1.13 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 75 MHz) $\delta$: 156.25, 154.21, 154.14, 153.21, 147.01, 146.97, 146.56, 146.32, 146.14, 146.09, 146.09, 145.95 (2C), 145.88, 145.83, 145.76, 145.74, 145.60, 145.34, 145.24 (3C), 145.14, 145.06 (3C), 144.98, 144.55, 144.39, 144.20, 144.15, 142.99, 142.86, 142.49, 142.46 (2C), 142.43, 141.97 (3C), 141.90, 141.86, 141.64, 141.53, 141.48, 140.10, 140.03, 139.62, 139.45, 137.04, 136.10, 135.66, 135.33, 77.87 (*C*H), 76.06 ($sp^3$-*C* of $C_{60}$), 70.24 (*C*H), 69.89 ($sp^3$-*C* of $C_{60}$), 39.71 ($NCH_3$), 33.32 ($CH_2CH_2CH_3$), 21.07 ($CH_2CH_2CH_3$), 14.92 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 2951, 2864, 2776, 1630, 1536, 1458, 1425, 1342, 1184, 1158, 1114, 1026, 571, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 819 $[M]^+$, 720 $[C_{60}]^+$. *2-Methylfulleropyrrolidine* (**3c**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 311 (s), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 4.96 (d, $J$ = 12.0 Hz, 1H), 4.81 (q, $J$ = 6.6 Hz, 1H), 4.75 (d, $J$ = 12.0 Hz, 1H), 2.11 (d, $J$ = 6.6 Hz, 3H) ppm; IR (KBr) $\nu$: 3415, 2966, 2918, 2848, 1637.6, 1617.7, 1400, 1261, 1185, 1090, 1028, 805, 768, 619, 570, 561, 552, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 777 $[M]^+$, 720 $[C_{60}]^+$. *N-Methyl-2-(4-methylphenyl)fulleropyrrolidine* (**9**): UV–vis ($CHCl_3$) $\lambda_{max}$: 259 (s), 310 (s), 430 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 7.60 (d, $J$ = 7.8 Hz, 2H), 7.15 (d, $J$ = 7.8 Hz, 2H), 4.92 (d, $J$ = 9.6 Hz, 1H), 4.84 (s, 1H), 4.20 (d, $J$ = 9.0 Hz, 1H), 2.75 (s, 3H), 2.31 (s, 3H) ppm; MS (MAIDI-TOF) $m/z$: 867 $[M]^+$, 720 $[C_{60}]^+$.

11. *trans*-2-Methyl-5-propylfulleropyrrolidine (*trans*-**5**): UV–vis ($CHCl_3$) $\lambda_{max}$: 260 (s), 310 (m), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 4.98 (q, $J$ = 6.6 Hz, 1H), 4.88 (dd, $J$ = 11.4, 3.6 Hz, 1H), 3.11 (s, 1H), 2.35–2.40 (m, 1H), 2.28–2.33 (m, 1H), 2.01 (d, $J$ = 6.6 Hz, 3H), 1.99–2.06 (m, 1H), 1.76–1.83 (m, 1H), 1.61 (t, $J$ = 7.8 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 100 MHz) $\delta$: 156.37, 155.80, 153.17, 153.00, 146.93, 146.34 (3C), 146.13 (2C), 146.09, 145.86 (3C), 145.67, 145.38, 145.19 (2C), 145.09, 145.00 (2C), 144.40, 144.37, 144.25 (3C), 144.07, 143.08, 142.55 (3C), 142.48, 142.42 (2C), 142.08, 142.02 (2C), 141.77, 141.72 (2C), 141.66, 140.14, 140.08, 139.86, 139.76, 139.50, 136.34, 134.89, 79.14 ($sp^3$-*C* of $C_{60}$), 79.08 ($sp^3$-*C* of $C_{60}$), 71.67 (*C*H), 66.65 (*C*H), 37.10 ($CH_2CH_2CH_3$), 21.64 ($CH_2CH_2CH_3$), 19.91 ($CHCH_3$), 14.36 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 2955, 2922, 2862, 1630, 1452, 1491, 1184, 1152, 1092, 1031, 774, 565, 527 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 819 $[M]^+$, 720 $[C_{60}]^+$. *cis*-2-Methyl-5-propylfulleropyrrolidine (*cis*-**5**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 309 (m), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 4.76 (q, $J$ = 6.6 Hz, 1H), 4.66 (dd, $J$ = 10.8, 2.4 Hz, 1H), 2.56–2.62 (m, 1H), 1.98–2.08 (m, 2H), 2.02 (d, $J$ = 6.6 Hz, 3H), 1.82–1.88 (m, 1H), 1.16 (t, $J$ = 7.2 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 150 MHz) $\delta$: 154.50, 154.32, 153.63, 153.27, 147.06 (2C), 146.64, 146.48, 146.40, 146.37, 146.34, 146.21 (2C), 146.06, 145.97, 145.69, 145.39 (3C), 145.36, 145.22, 145.21, 144.59 (2C), 144.35, 144.34, 143.32, 143.12, 142.80, 142.78 (2C), 142.73, 142.72, 142.30, 142.29, 142.24, 142.12, 142.02, 142.00, 141.82, 141.79, 140.34, 140.20, 140.01, 139.88, 136.59, 136.34, 135.77, 135.69, 79.79 ($sp^3$-*C* of $C_{60}$), 79.62 ($sp^3$-*C* of $C_{60}$), 73.58 (*C*H), 68.78 (*C*H), 35.93 ($CH_2CH_2CH_3$), 22.38 ($CH_2CH_2CH_3$), 18.03 ($CHCH_3$), 14.91 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 2956, 2866, 1628, 1425, 1184, 1147, 1090, 1029, 572, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 819 $[M]^+$, 720 $[C_{60}]^+$.
12. *cis*-2-Methyl-5-phenylfulleropyrrolidine (*cis*-**6**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 310 (m), 430 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 600 MHz) $\delta$: 7.75 (d, $J$ = 7.2 Hz, 2H), 7.35 (t, $J$ = 7.2 Hz, 2H), 7.27 (t, $J$ = 7.2 Hz, 1H), 5.79 (s, 1H), 4.95 (q, $J$ = 6.6 Hz, 1H), 2.12 (d, $J$ = 6.6 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 150 MHz) $\delta$: 153.90, 153.64, 147.18, 146.85, 146.63, 146.39, 146.35, 146.26, 146.14, 146.10, 145.93, 145.71, 145.55, 145.48, 145.35, 145.32, 145.21, 144.64, 144.38, 143.23, 143.07, 142.76, 142.72, 142.65, 142.55, 142.38, 142.28, 142.22, 142.13, 142.11, 142.08, 142.04, 141.94, 141.75, 141.60, 140.32, 140.01, 139.85, 139.59, 137.49, 137.31, 136.64, 135.97, 135.89, 128.84 (2C, aryl *C*), 128.56 (aryl *C*), 128.34 (2C, aryl *C*), 78.37 ($sp^3$-*C* of $C_{60}$), 76.48 ($sp^3$-*C* of $C_{60}$), 76.02 (*C*H), 67.11 (*C*H), 18.39 ($CH_3$) ppm; IR (KBr) $\nu$: 2961, 2923, 2867, 2808, 1493, 1453, 1183, 1153, 1095, 1030, 763, 698, 571, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 853 $[M]^+$, 720 $[C_{60}]^+$.
13. *cis*-2-Benzyl-5-propylfulleropyrrolidine (*cis*-**7**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 308 (m), 431 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 300 MHz) $\delta$: 7.53 (d, $J$ = 7.3 Hz, 2H), 7.38–7.47 (m, 2H), 7.29–7.37 (m, 1H), 4.89 (dd, $J$ = 10.7, 2.7 Hz 1H), 4.60 (dd, $J$ = 10.3, 2.8 Hz, 1H), 4.00 (dd, $J$ = 13.8, 2.7 Hz, 1H), 3.38 (dd, $J$ = 13.2, 10.7 Hz, 1H), 2.53–2.64 (m, 1H), 2.17–2.09 (m, 1H), 1.88–1.95 (m, 1H), 1.73–1.82 (m, 1H), 1.16 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 75 MHz) $\delta$: 154.07, 153.79, 153.28, 152.85, 146.86 (2C), 146.40, 146.35, 146.21, 146.17, 146.10, 146.07, 145.94, 145.81 (2C), 145.69, 145.49, 145.20 (2C), 145.16, 145.10, 145.07, 144.96, 144.93, 144.40, 144.33, 144.07 (2C), 143.01, 142.81, 142.48 (2C), 142.45 (2C), 142.30, 142.24, 142.00, 141.93, 141.91, 141.86, 141.73, 141.70, 141.49 (2C), 139.92, 139.89, 139.60, 139.54, 138.79 (2C), 138.60, 136.81, 136.42, 135.70, 135.52, 129.05 (2C), 128.93, 128.68 (2C), 126.70, 77.65 ($sp^3$-*C* of $C_{60}$), 77.30 ($sp^3$-*C* of $C_{60}$), 73.05 (*C*H), 71.99 (*C*H), 39.65 ($CHCH_2Ph$), 35.69 ($CH_2CH_2CH_3$), 21.87 ($CH_2CH_2CH_3$), 14.60 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 2956, 2917, 2849, 1637, 1493, 1472, 1463, 1400, 1262, 1179, 1126, 949, 889, 807, 777, 765, 728, 719, 693, 615, 574, 561, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 896 $[M+1]^+$, 720 $[C_{60}]^+$. *trans*-2-benzyl-5-propylfulleropyrrolidine (*trans*-**7**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 307 (m), 432 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 300 MHz) $\delta$: 7.52 (d, $J$ = 7.4 Hz, 2H), 7.40 (t, $J$ = 7.6 Hz, 2H), 7.27 (t, $J$ = 7.2 Hz, 1H), 5.16 (dd, $J$ = 10.9, 3.9 Hz, 1H), 5.00 (dd, $J$ = 10.8, 3.3 Hz, 1H), 3.77 (dd, $J$ = 14.0, 4.0 Hz, 1H), 3.64 (dd, $J$ = 13.8, 10.9 Hz, 1H), 2.44–2.55 (m, 1H), 2.20–2.28 (m, 1H), 1.87–1.98 (m, 1H), 1.74–1.86 (m, 1H), 1.18 (t, $J$ = 7.3 Hz, 3H) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 75 MHz) $\delta$: 155.92, 155.65, 153.14, 152.87, 146.94, 146.31 (2C), 146.07 (3C), 145.96, 145.84 (2C), 145.60, 145.42 (2C), 145.18 (3C), 145.06 (2C), 144.38 (2C), 144.20, 143.05, 142.55 (2C), 142.51 (2C), 142.35, 142.26, 141.99 (3C), 141.75, 141.69, 141.65, 140.08, 139.73, 139.04, 136.61, 136.38, 135.34, 135.15, 129.27, 128.59, 126.67, 78.09 ($sp^3$-*C* of $C_{60}$), 77.88 ($sp^3$-*C* of $C_{60}$), 71.89 (*C*H), 70.32 (*C*H), 40.73 ($CHCH_2Ph$), 36.62 ($CH_2CH_2CH_3$), 21.65 ($CH_2CH_2CH_3$), 14.42 ($CH_2CH_2CH_3$) ppm; IR (KBr) $\nu$: 3025, 2953, 2922, 2863, 1633, 1509, 1455, 1424, 1219, 1184, 1149, 1032, 729, 697, 568, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 895 $[M]^+$, 720 $[C_{60}]^+$.
14. *cis*-2-Benzyl-5-phenylfulleropyrrolidine (*cis*-**8**): UV–vis ($CHCl_3$) $\lambda_{max}$: 257 (s), 312 (m), 430 (w) nm; $^1$H NMR ($CS_2$/$CDCl_3$, 300 MHz) $\delta$: 7.83 (d, $J$ = 7.2 Hz, 2H), 7.58 (d, $J$ = 7.3 Hz, 2H), 7.44 (t, $J$ = 7.3 Hz, 2H), 7.26–7.40 (m, 4H), 5.70 (s, 1H), 5.03 (dd, $J$ = 11.1, 2.5 Hz 1H), 4.04 (dd, $J$ = 13.1, 2.4 Hz, 1H), 3.52 (dd, $J$ = 13.1, 11.2 Hz, 1H), 2.88 (s, N*H*) ppm; $^{13}$C NMR ($CS_2$/$CDCl_3$, 75 MHz) $\delta$: 153.33, 153.16, 153.08, 152.93, 146.93, 146.89, 146.46 (2C), 146.08, 145.98, 145.95 (2C), 145.89 (2C), 145.81, 145.79, 145.63, 145.60, 145.42, 145.33, 145.18 (2C), 145.00, 144.98, 144.89 (2C), 144.39, 144.33, 144.08, 144.03, 142.83, 142.73, 142.42, 142.37 (2C), 142.31, 142.01, 141.91 (2C), 141.88 (2C), 141.78 (2C), 141.75, 141.67, 141.60, 141.40, 141.27, 139.94, 139.69, 139.47, 139.30, 138.86 (2C), 137.39 (2C), 137.30, 136.54, 135.96, 135.55, 128.97 (2C), 128.89 (2C), 128.35, 128.23 (2C), 128.19 (2C), 126.83, 77.20 ($sp^3$-*C* of $C_{60}$), 74.83 (*C*H), 74.37 ($sp^3$-*C* of $C_{60}$), 72.05 (*C*H), 39.80 ($CHCH_2Ph$) ppm; IR (KBr) $\nu$: 3026, 2849, 2820, 1633, 1602, 1494, 1462, 1452, 1400, 1260, 1183, 1097, 1027, 770, 745, 717, 697, 613, 600, 573, 563, 544, 526 cm$^{-1}$; MS (MAIDI-TOF) $m/z$: 929 $[M]^+$, 720 $[C_{60}]^+$.
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