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Synthesis of novel nitroso-fulleropyrrolidines

Giuseppe Vasapollo,[a,*] Giuseppe Mele,[a] Luigia Longo,[a] Roberto Ianne,[a] Brian G. Gowenlock[b] and Keith G. Orrell[b]

[a]*Dipartimento di Ingegneria dell'Innovazione, Università di Lecce, via Arnesano 73100 Lecce, Italy*
[b]*School of Chemistry, University of Exeter, Exeter EX4 4QD, UK*

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Abstract—Novel fulleropyrrolidines containing differently head groups (-NO_2, -NH_2 -NO) spaced by a long chain from the fulleropyrrolidine moiety have been synthesised and characterised.

The increasingly better availability of [C_{60}] fullerene has led to an extensive range of studies on this molecular allotrope of carbon. Many fundamental properties of fullerene derivatives have been discovered and reported[1] and their metal complexes evidence attractive characteristics, such as superconductivity[2–4] or charge-transfer behaviour.[5–7] It is well known also that the ball-like structure of C_{60} molecules is very rigid, hydrophobic and exhibits peculiar properties totally different from those of rod-like self-assembling amphiphilic molecules.

Further, the use of highly organised fullerene derivatives in the form of supramolecular arrays (thin films, nanotubes, etc.) could represent new technological potentialities and one of the most common approaches to control the architecture of organised thin films containing the fullerene moiety[8,9] is the functionalisation of C_{60}.

On the other hand, there are many interesting studies concerning the structure of a variety of C-nitroso compounds both in the solid and in solution,[10–13] but there are no reports on C_{60}-nitroso derivatives. The introduction of a nitroso group, as a suitable ligand for a large variety of metals, into C_{60}-containing structures offers the possibility to prepare new molecules with potential features.

We have therefore pursued the strategy of preparing new molecules that contain both the fullerene moiety and the nitroso group in order to prepare nitroso fullerene compounds with potential utility as a source for new materials or biologically active compounds.

We therefore report in this paper the preparation of nitroso fullerene compounds together with a simple procedure that involves the reaction sequence $RNO_2 \rightarrow RNH_2 \rightarrow RNO$.

In particular, we report the synthesis and characterisation of the fulleropyrrolidines derivatives **1**–**4**, **8**, **9** and of the nitroso fulleropyrrolidines **5**, **6** and **10**.

The compounds **1** and **2** (**1**: R = CH_3; **2**: R = C_6H_5) have been prepared according to the literature (Scheme 1) by the condensation of α-amino acids (*N*-methylglycine or *N*-phenylglycine), with aldehydes and C_{60} through a typical 1,3-dipolar addition of azomethine ylides[14] generated in situ. In a typical procedure, a solution of 4-nitrobenzaldehyde (34 mg), C_{60} (144 mg) and *N*-methylglycine (10 mg) in toluene (500 ml) was refluxed for 24 h. After cooling the resulting solution was evaporated to dryness. Purification by column chromatography (SiO_2, toluene) yielded **1** (60% yield). Compound **2** (55% yield) was obtained under similar condition but using *N*-phenylglycine.

N-Methyl-2-(4-aminophenyl)-fulleropyrrolidine **3** (R = CH_3) and *N*-phenyl-2-(4-aminophenyl)-fulleropyrrolidine **4** (R = C_6H_5) were synthesised respectively by simple reduction of *N*-methyl-2-(4-nitrophenyl)-fulleropyrrolidine **1** and *N*-phenyl-2-(4-nitrophenyl)-fulleropyrrolidine **2**, in chloroform, with powdered Sn and H_2O/HCl as reported in Scheme 1.

The compounds **5** and **6** were prepared by selective oxidation of primary aromatic amines **3** and **4** using H_2O_2 in the presence of [$Mo(O)(O_2)_2(H_2O)$(hmpa)] (hmpa = hexamethyl-phosphoramide) as catalyst through a procedure analogous to that reported by

* Corresponding author. Tel.: +00-39-832-320252; fax: +00-39-832-320279; e-mail: giuseppe.vasapollo@unile.it

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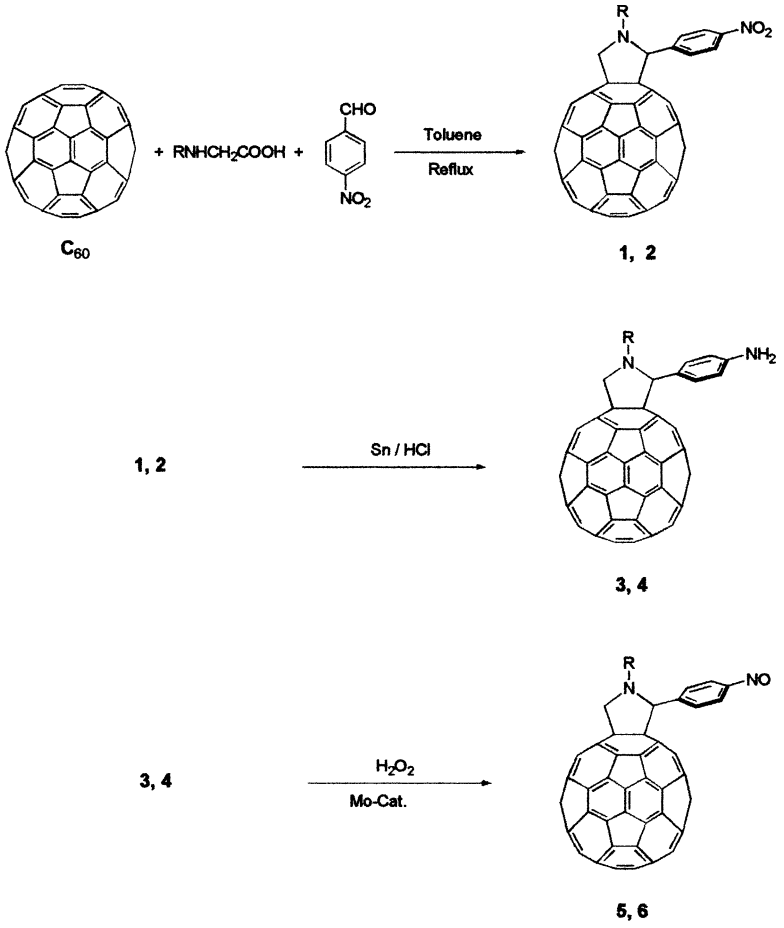


Scheme 1.

Porta and co-workers.[15] In a typical experiment 50 mg of the amine **4**, for example, were dissolved in chloroform, H_2O_2 (30% ww solution in water) added together with [Mo $(O)(O_2)_2(H_2O)$(hmpa)] in catalytic amount. The mixture was stirred for 5 h at room temperature and then filtered on a silica gel column using toluene/petroleum ether (2/1) as eluant (>95% yield). Analytical data for compounds **5** and **6** are consistent for the formulation of these compounds.

A nitroso group spaced by a long alkyl chain from the fulleropyrrolidine was also prepared, as shown in Scheme 2.

The spacer precursor **7** was reacted in the presence of sarcosine and C_{60} to give **8** in 50% isolated yield which was reduced quantitatively to amino derivative **9** which was then selectively oxidised to give **10** through a sequence of reactions analogous to that for the synthesis of nitroso the fulleropyrrolidines **5** and **6**.

The presence of a long alkyl chain groups significantly improves its solubility in organic solvents. The incorporation of a long alkyl chain having at its end a polar group certainly also influences the interfacial properties of the fullerene derivatives on the water surface especially when the formation of thin films is required.

The ^{1}H NMR spectra of compound **10** in $CDCl_3$ solution show typical signals of the pyrrolidino (C_{60}) fullerene system, as a singlet for H-2 at 4.87 ppm and the A–B system for CH_2-5, as two doublets centred at 4.97 and 4.24 ppm, respectively, with a geminal coupling $J_{AB}=9.5$ Hz.

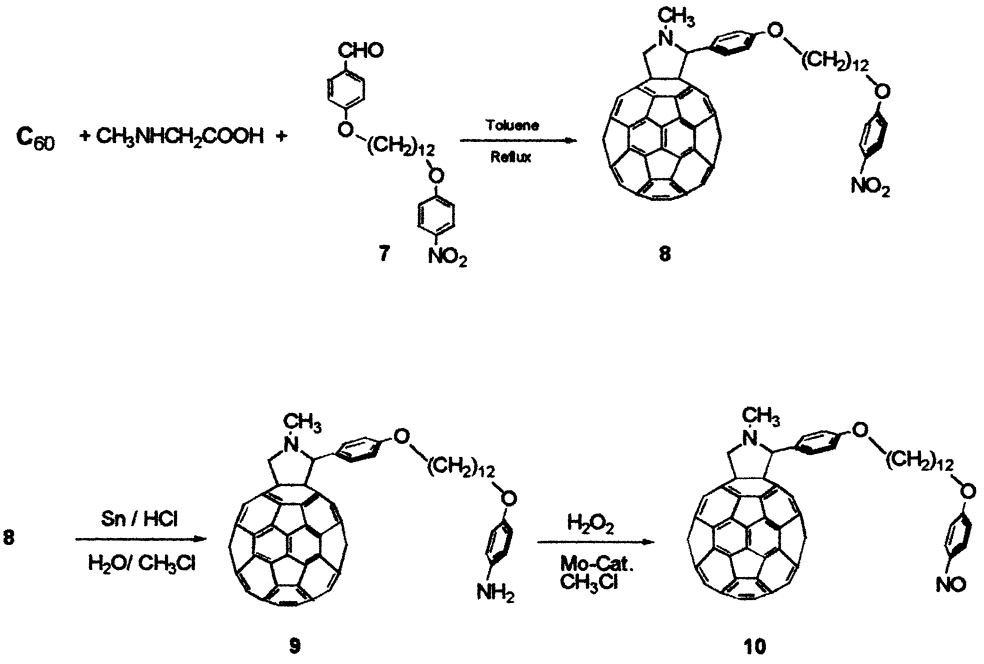
Representative data for compounds 5, 6, 7, 8, 9 and 10[16]

*N-Methyl-2-(4-nitrosophenyl)-fulleropyrrolidine (**5**)*

FT-IR 2924, 2852, 2780, 1734, 1617, 1503, 1461, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.13 (broad signal, 2H); 8.00 (d, $J=8.8$ Hz, 2H); 5.03 (d, $J=9.2$ Hz, 1H); 4.80 (s, 1H); 3.75 (d, $J=9.2$ Hz, 1H); 2.83 (s, 3H) ppm. LC–MS (APCI) calcd M 882 obsd 883 ($M-H^+$) uma.

*N-Phenyl-2-(4-nitrosophenyl)-fulleropyrrolidine (**6**)*

FT-IR 2918, 2849, 1732, 1463, 1380, 1261, 1073, 1037, 824, 802, 720, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.10 (d, $J=8.3$ Hz, 2H); 7.89 (d, $J=8.3$ Hz, 2H); 7.73–7.35 (m, 5H); 6.17 (s, 1H); 5.68 (d, $J=5$ Hz, 1H); 5.02 (d, $J=5$ Hz, 1H) ppm. LC–MS (APCI), calcd M 944, obsd 945 ($M-H^+$) uma.



Scheme 2.

Compound ***7***

FT-IR: 2923.56, 2852.20, 2729.74, 1681.62, 1592.21, 1575.56, 1508.06, 1469.49, 1331.61, 1258.32, 1214.93, 1158.04, 1108.87, 996.05, 858.17, 835.03, 751.14, 653.75 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 8.12 (d, $J=9.1$, 2H), 7.77 (d, $J=8.6$, 2H), 6.96–6.86 (m, 4H), 3.99 (t, $J=6.4$, 4H), 1.83–1.70 (m, 4H), 1.41–1.22 (m, 16H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$) δ: 190.48, 164.06, 131.73, 129.55, 125.63, 114.54, 114.20, 68.70, 68.22, 29.33, 29.14, 28.85, 28.77, 25.76, 25.71 ppm. LC–MS (APCI), calcd 427 M, obsd 428 ($M-H^+$) uma.

Compound ***8***

FT-IR: 2922.59, 2851.24, 2788.92, 1607.38, 1591.95, 1509.99, 1462.74, 1333.53, 1260.25, 1171.54, 1109.83, 842.74, 752.10 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 8.21–8.16 (m, 2H), 7.71–7,67 (m, 2H), 6.95–6.90 (m, 4H), 4.96 (d, $J=9.4$, 1H), 4.87 (s, 1H), 4.23 (d, $J=9.4$, 1H), 4.03 (t, $J=6.4$, 2H), 3.94 (t, $J=6.4$, 2H), 2.78 (s, 3H), 1.84–1.62 (m, 4H), 1.43–1.25 (m, 16H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$) δ: 164.22, 159.18, 156.40, 154.14, 153.69, 147.28, 146.81, 146.52, 146.40, 146.29, 146.25, 146.19, 146.14, 146.11, 146.08, 145.92, 145.77, 145.54, 145.49, 145.44, 145.33, 145.29, 145.27, 145.22, 145.20, 145.13, 144.70, 144.59, 144.37, 143.12, 142.98, 142.66, 142.57, 142.53, 142.27, 142.25, 142.15, 142.12, 142.09, 142.02, 141.97, 141.80, 141.67, 141.51, 141.33, 140.15, 140.11, 139.87, 139.53, 136.77, 136.55, 135.79, 135.76, 130.44, 129.02, 128.73, 128.21, 125.89, 125.28, 114.54, 114.39, 83.20, 77.39, 69.99, 68.98, 68.88, 67.97, 39.97, 29.69, 29.53, 29.40, 29.31, 29.29, 28.96, 26.07, 25.90, 22.67, 14.10 ppm. LC–MS (APCI), calcd M 1174, obsd 1175 ($M-H^+$) uma.

Compound ***9***

FT-IR: 3446.17, 3364.21, 2921.63, 2851.24, 2779.89, 1509.99, 1461.78, 1240.97, 1174.44, 823.46 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.71–7.67 (m, 2H), 6.96–6.92 (m, 2H), 6.76–6.61 (m, 4H), 4.97 (d, $J=9.4$, 1H), 4.87 (s, 1H), 4.23 (d, $J=9.4$, 1H), 3.95 (t, $J=6.2$, 2H), 3.87 (t, $J=6.5$, 2H), 2.78 (s, 1H), 1.85–1.59 (m, 4H), 1.42–1.26 (m, 16H).

^{13}C NMR (200 MHz, $CDCl_3$) δ: 167.66, 159.19, 156.39, 154.12, 153.69, 152.33, 147.27, 146.81, 146.51, 146.38, 146.28, 146.24, 146.18, 146.10, 146.07, 145.91, 145.76, 145.52, 145.48, 145.43, 145.31, 145.28, 145.25, 145.20, 145.11, 144.68, 144.60, 144.37, 143.11, 142.96, 142.64, 142.55, 142.52, 142.27, 142.24, 142.10, 142.07, 142.01, 141.95, 141.80, 141.65, 141.51, 140.13, 140.09, 139.87, 139.77, 139.55, 136.74, 136.55, 135.76, 132.32, 130.86, 130.42, 128.81, 128.66, 116.39, 115.66, 114.53, 114.37, 83.19, 77.37, 69.98, 68.96, 68.87, 67.97, 39.96, 29.68, 29.54, 29.40, 29.34, 29.26, 28.55, 26.05, 23.03, 22.67, 14.10 ppm. LC–MS (APCI), calcd M 1144, obsd 1145 ($M-H^+$) uma.

Compound ***10***

FT-IR: 2921, 2851, 2779, 1504, 1461, 1258, 1111, 838, 736, 619 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.92–7.88 (m, 2H), 7.71–7.67 (m, 2H), 7.02–6.91 (m, 4H), 4.97 (d, $J=9.5$ Hz, 1H), 4.87 (s, 1H), 4.24 (d, $J=9.5$, 1H), 4.09 (t, $J=6.4$, 2H), 3.95 (t, $J=6.4$, 2H), 2.79 (s, 3H), 1.86–1.59 (m, 4H), 1.43–1.25 (m, 16H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$) δ: 164.24, 159.22, 154.16, 153.71, 146.17, 143.15, 142.99, 130.89, 129.03, 128.75, 128.22, 125.90, 125.30, 114.40, 114.27, 83.24, 77.41, 77.21, 68.93, 67.99, 31.93, 30.04, 29.70, 29.66, 29.53,

29.40, 29.36, 28.99, 26.07, 25.92, 22.69, 14.10, 13.7 ppm. LC–MS (APCI), calcd M 1158, obsd 1159 ($M-H^+$) uma.

Acknowledgements

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16. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 at room temperature and chemical shifts are reported relative to tetramethylsilane. IR spectra were performed on a Jasco FT-IR-430 instrument. Mass spectrometry analyses were performed using an LC mass spectrometer 1100 Series (Agilent) equipped with an Atmospheric Pressure Chemical Ionisation (APCI) interface.