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Photoinduced processes in fullerenopyrrolidine and fullerenopyrazoline derivatives substituted with an oligophenylenevinylene moiety

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Supplementary data
SYNTHETIC PROCEDURES AND FULL
CHARACTERIZATION
OF ALL NEW MOLECULES

Photoinduced Processes in Fulleropyrrolidine and
Fulleropyrazoline Derivatives Substituted with an
Oligophenylenevinylene Moiety

Nicola Armaroli,* Gianluca Accorsi, Jean-Paul Gisselbrecht, Maurice Gross,* Victor Krasnikov, Dimitris Tsamouras, Georges Hadzioannou,* María J. Gómez-Escalonilla, Fernando Langa,* Jean-François Eckert, Jean-François Nierengarten*

General synthetic methods. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **1**¹ and **3**² were prepared as previously reported. All reactions were performed in standard glassware under an inert Ar atmosphere. Reactions under microwaves were carried out in a focused reactor (Maxidigest MX-350 from Prolabo) equipped with an infrared temperature detector. The irradiation power and temperature were controlled with the program MPX-2 from PACAM. Evaporation and concentration were done at water aspirator pressure and drying *in vacuo* at 10⁻² Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from *E. Merck*. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 *F*₂₅₄ purchased from *E. Merck*, visualization by

UV light. Melting points were measured on an *Electrothermal Digital Melting Point* apparatus and are uncorrected. IR spectra (cm^{-1}) were measured on an *ATI Mattson Genesis Series FTIR* instrument. NMR spectra were recorded on a *Bruker AC 200* (200 MHz) or a *Bruker AM 400* (400 MHz) with solvent peaks as reference. FAB-mass spectra (m/z) were taken on a *ZA HF* instrument with 4-nitrobenzyl alcohol as matrix. MALDI-TOF mass spectra were obtained on a *Bruker ReflexIII* instrument. Elemental analysis were performed by the analytical service at the Institut Charles Sadron (Strasbourg, France).

Compound 2. A mixture of **1** (3.9 g, 4.21 mmol) and TFA (40 mL) in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ 1:1 (120 mL) was stirred at room temperature for 5 h. The organic layer was then washed with water (4 x), dried over MgSO_4 , filtered, and evaporated. Column chromatography on SiO_2 (CH_2Cl_2 /hexane 1:1) yielded **2** (3.2 g, 3.83 mmol, 91%) as yellow crystals (mp 86°C). ^1H NMR (CDCl_3): δ 10.00 (s, 1 H), 7.88 (d, $J = 8$ Hz, 2H), 7.66 (d, $J = 8$ Hz, 2H), 7.53 (s, 4H), 7.22 (AB, $J = 16.5$ Hz, 2H), 7.02 (AB, $J = 16.5$ Hz, 2H), 6.73 (s, 2H), 4.04 (t, $J = 6.5$ Hz, 4H), 4.00 (t, $J = 6.5$ Hz, 2H), 1.80 (m, 6H), 1.32 (m, 54H), 0.89 (t, $J = 6.5$ Hz, 9H). ^{13}C NMR (CDCl_3): δ 191.58, 153.31, 143.45, 138.50, 137.70, 135.62, 135.24, 132.33, 131.76, 130.25, 129.40, 127.26, 127.00, 126.85, 105.27, 73.55, 69.18, 31.93, 30.33, 29.67, 29.43, 26.12, 22.68, 14.12. IR (CH_2Cl_2): ν 1697 (C=O). UV-Vis (CH_2Cl_2) 384 (39860). Anal calcd. for $\text{C}_{59}\text{H}_{90}\text{O}_4$ (863.36): C 82.08, H 10.51; found C 82.20, H 10.60.

Compound 3PV. A 1 M LiAlH₄ solution in THF (300 µL) was added to a stirred solution of **2** (1.0 g, 1.15 mmol) in dry THF (6 mL) at 0°C under argon. After 1 h, the reaction was quenched with AcOEt, then methanol and water. The resulting mixture was filtered over celite and evaporated. The crude product was dissolved in CH₂Cl₂. The organic layer was washed with water, dried over MgSO₄, filtered and evaporated. Column chromatography on SiO₂ (CH₂Cl₂) yielded 3PV (860 mg, 86%) as a yellow solid. ¹H NMR (CDCl₃): δ 7.53 (d, *J* = 8 Hz, 2H), 7.50 (s, 4H), 7.37 (d, *J* = 8 Hz, 2H), 7.12 (s, 2H), 7.01 (AB, *J* = 16.5 Hz, 2H), 6.72 (s, 2H), 4.72 (d, *J* = 6 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 4H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.80 (m, 6H), 1.68 (t, *J* = 6 Hz, 1H), 1.32 (m, 54H), 0.89 (t, *J* = 6.5 Hz, 9H). ¹³C NMR (CDCl₃): δ 153.29, 140.26, 138.34, 136.81, 136.41, 132.50, 128.83, 128.32, 128.02, 127.38, 127.23, 126.82, 126.67, 105.19, 73.55, 69.17, 65.13, 31.93, 30.33, 29.66, 29.44, 29.38, 26.12, 22.70, 14.12. Anal calcd. for C₅₉H₉₂O₄ (865.38): C 81.89, H 10.72; found C 82.15, H 10.85.

Compound A-3PV. A mixture of **2** (370 mg, 0.42 mmol), C₆₀ (308 mg, 0.42 mmol) and *N*-phenylglycine (52 mg, 3.42 mmol) in toluene (350 mL) was refluxed under Ar for one week. After cooling, the resulting solution was evaporated and column chromatography on SiO₂ (hexane/toluene 1:1) yielded **A-3PV** (200 mg, 28%) as a brown solid (mp 215°C). ¹H NMR (CDCl₃): δ 7.79 (d, *J* = 8.5 Hz, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 7.44 (s, 4 H), 7.44 (m, 4 H), 7.08 (m, 1 H), 7.07 (s, 2 H), 7.05 (AB, *J* = 16.5 Hz, 2 H), 6.69 (s, 2 H), 6.09 (s, 1 H), 5.32 (AB, *J* = 9.9 Hz, 2 H), 4.01 (t, *J* = 6.5 Hz, 4 H), 3.96 (t, *J* = 6.5 Hz, 2 H), 1.84 (m, 4 H), 1.78 (m, 2 H), 1.32 (m, 54 H), 0.89 (t, *J* = 6.5 Hz, 9 H). ¹³C NMR (CDCl₃):

δ 155.86, 153.70, 153.40, 153.28, 153.16, 147.37, 147.28, 146.61, 146.35, 146.23, 146.16, 146.10, 145.98, 145.71, 145.58, 145.44, 145.33, 145.14, 144.69, 144.59, 144.43, 143.16, 143.03, 142.71, 142.59, 142.25, 142.13, 142.05, 141.86, 141.71, 141.55, 140.26, 140.19, 139.90, 139.46, 138.37, 137.22, 137.10, 136.84, 136.53, 136.33, 135.79, 135.69, 132.50, 129.18, 128.92, 128.60, 127.94, 127.23, 126.95, 126.84, 126.68, 122.41, 121.45, 105.21, 76.55, 73.54, 69.17, 68.50, 68.18, 31.93, 30.34, 29.67, 29.44, 29.38, 26.13, 22.70, 14.12. FAB-MS: m/z (%): 720.0 ($[C_{60}]^+$), 1672.8 ($[M + H]^+$). Anal calcd. for $C_{126}H_{97}NO_3 \cdot H_2O$ (1691.18): C 89.49, H 5.90, N 0.83; found C 89.59, H 5.89, N 0.82.

Compound A. A mixture of **3** (300 mg, 0.45 mmol), C₆₀ (328 mg, 0.45 mmol) and *N*-phenylglycine (344 mg, 2.27 mmol), in toluene (350 mL) was refluxed under Ar for 16 h. After cooling, the resulting solution was evaporated and column chromatography on SiO₂ (toluene/hexane 3:2) yielded **A** (80 mg, 10%) as a brown solid (mp 104°C). ¹H NMR (CDCl₃): δ 7.38 (m, 4H), 7.08 (m, 1H), 6.98 (s, 2H), 5.91 (s, 1H), 5.31 (AB, *J* = 9.9 Hz, 2H), 3.88 (m, 6H), 1.66 (m, 6H), 1.32 (m, 54H), 0.89 (t, *J* = 6.5 Hz, 9H). ¹³C NMR (CDCl₃): δ 155.86, 153.79, 153.66, 153.38, 153.22, 147.53, 147.39, 146.90, 146.38, 146.25, 146.10, 145.98, 145.71, 145.59, 145.43, 145.27, 144.69, 144.43, 143.19, 143.03, 142.71, 142.62, 142.20, 142.13, 142.05, 141.80, 141.69, 141.56, 140.29, 140.10, 139.61, 139.49, 138.23, 136.49, 135.95, 135.66, 132.70, 129.12, 122.29, 121.23, 107.83, 76.77, 76.61, 73.19, 69.31, 68.44, 67.98, 31.93, 30.20, 29.68, 29.43, 29.38, 29.16, 26.05, 25.99, 22.68, 14.12. Anal calcd. for C₁₀₉H₈₅NO₃ (1456.88): C 89.86, H 5.88, N 0.96; found C 90.46, H 5.73, N 0.89.

Compound 4. A solution of **2** (175 mg, 0.202 mmol), *p*-nitrophenylhydrazine (31 mg, 0.202 mmol) and acetic acid (0.1 mL) in ethanol (30 mL) was refluxed for 4.5 h. After cooling, the resulting mixture was evaporated and recrystallization from ethanol yielded **4** (187 mg, 93%) as an orange solid (mp 143-145°C). ¹H-NMR (CDCl₃): δ 8.20 (d, *J* = 9.1 Hz, 2H), 8.09 (bs, 1H), 7.80 (s, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.52 (s, 4H), 7.16 (s, 2H), 7.15 (d, *J* = 9.1 Hz, 2H), 7.01 (AB, *J* = 17 Hz, 2H), 6.73 (s, 2H), 4.07-3.95 (m, 6H), 1.87-1.76 (m, 6H), 1.27 (m, 54H), 0.89 (t, *J* = 7 Hz, 9H). ¹³C-NMR (CDCl₃): δ 153.47, 149.61, 141.17, 140.52, 138.85, 138.45, 137.27, 136.34, 133.43, 132.64, 129.42, 129.20,

127.83, 127.32, 127.16, 127.03, 126.93, 126.40, 111.91, 105.23, 73.78, 69.30, 32.12, 30.53, 29.91, 29.86, 29.62, 26.32, 22.89, 14.32; IR (KBr): ν 3284.7, 2920.7, 1596.3, 1326.1, 1310.6, 1111.3, 956.2, 837.3. MALDI-TOF: 997.6 (m/z), 998.6 ($[M + H]^+$). Anal calcd for $C_{65}H_{95}N_3O_5$ (997.73): C 78.19, H 9.59, N 4.21; found: C 77.74, H 9.69, N 4.20.

Compound B-3PV. A solution of 4 (70 mg, 0.07 mmol) and pyridine (5 μ L) in dry chloroform (10 mL) was cooled to 0°C under Ar; NCS (19 mg, 0.14 mmol) was added and the resulting mixture was stirred at this temperature for 15 min; after heating at room temperature, a solution of C_{60} (50 mg, 0.07 mmol) and Et_3N (20 μ L) in dry toluene (50 mL) was added. The mixture was irradiated in a focused microwave reactor at 210W for 40 min. Column chromatography (SiO_2 , toluene) gave 3 (69 mg, 57% or 85% based on recovered C_{60}) as a brown solid (mp > 200°C). 1H -NMR ($CDCl_3$) δ 8.35 (d, J = 9.9 Hz, 2H), 8.28 (d, J = 9.9 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.52 (s, 4H), 7.19 (AB, J = 17 Hz, 2H), 7.01 (AB, J = 17 Hz, 2H), 6.73 (s, 2H), 4.06-3.95 (m, 6H), 1.87-1.72 (m, 6H), 1.27 (m, 54H), 0.89 (t, J = 6.5 Hz, 9H). ^{13}C -NMR ($CDCl_3$): δ 153.30, 146.45, 146.11, 146.09, 145.98, 145.65, 145.40, 145.29, 145.26, 144.56, 144.37, 144.15, 143.20, 143.11, 143.00, 142.93, 142.46, 142.13, 142.10, 142.02, 141.93, 140.49, 139.41, 139.12, 137.31, 137.05, 136.20, 135.96, 132.37, 130.44, 130.05, 129.42, 129.17, 127.24, 127.08, 127.03, 126.89, 126.73, 125.36, 119.42, 105.29, 99.49, 73.52, 69.19, 31.89, 30.31, 29.71, 29.66, 29.62, 29.58, 29.42, 29.40, 29.35, 29.33, 26.10, 22.65, 14.07. IR (KBr): ν 2912.7, 1586.7, 1493.9, 1314.9, 1102.7,

963.5, 830.9, 525.9. MALDI-TOF: 1717.6 ($[M]^+$), 720 ($[C_{60}]^+$). Anal calcd for $C_{125}H_{93}N_3O_5$ (1717.13): C 87.44, H 5.46, N 2.45; found: C 87.31, H 5.47, N 2.51.

Compound 5. A solution of 3 (200 mg, 0.303 mmol), *p*-nitrophenylhydrazine (46.4 mg, 0.303 mmol), and acetic acid (0.1 mL) in ethanol (30 mL) was refluxed for 4 h. After cooling, the resulting mixture was evaporated and recrystallization from ethanol yielded 5 (204 mg, 85%) as an orange solid (mp 76-77°C); 1H -NMR ($CDCl_3$): δ 8.18 (d, $J = 9.1$ Hz, 2H), 8.04 (s, 1H), 7.69 (s, 1H), 7.11 (d, $J = 9.1$ Hz, 2H), 6.88 (s, 2H), 4.07-3.97 (m, 6H), 1.87-1.72 (m, 6H), 1.27 (m, 54H), 0.88 (t, $J = 6.5$ Hz, 9H). ^{13}C -NMR ($CDCl_3$): δ 153.66, 149.61, 141.82 (2C), 140.40, 140.05, 129.22, 126.40 (2C), 111.80 (2C), 105.42 (2C), 73.78, 69.39, 32.11, 30.51, 29.90, 29.85, 29.62, 29.56, 26.31, 22.88, 14.32. IR (KBr) ν 2945.8, 2912.7, 1593.3, 1467.4, 1314.9, 1109.3, 837.5. MALDI-TOF: 793.5 ($[M + H]^+$).

Compound B. A solution of 5 (55.6 mg, 0.07 mmol) and pyridine (5 μ L) in dry chloroform (10 mL) was cooled to 0°C under Ar; NCS (19 mg, 0.14 mmol) was added and the resulting mixture was stirred at this temperature for 15 min; after heating at room temperature, a solution of C_{60} (50.4 mg, 0.07 mmol) and Et_3N (20 μ L) in dry toluene (50 mL) was added. The mixture was irradiated in a focused microwave reactor at 210W for 40 min. Column chromatography (SiO_2 , toluene/hexane 1:1) gave B (45 mg, 43% or 63% based on recovered C_{60}) as a brown solid (mp > 200°C). 1H -NMR ($CDCl_3$): δ 8.34 (d, $J = 9.5$ Hz, 2H), 8.25 (d, $J = 9.5$ Hz), 7.46 (s, 2H), 4.08-3.96 (m, 6H), 1.81-1.75 (m, 6H), 1.26 (m, 54H), 0.88 (t, $J = 6.5$ Hz, 6H). ^{13}C -NMR ($CDCl_3$): δ 153.60, 149.98, 147.91, 147.45,

146.93, 146.71, 146.63, 146.47, 146.36, 146.21, 145.94, 145.90, 145.62, 145.56, 145.50, 144.81, 144.60, 144.42, 143.58, 143.47, 143.29, 143.21, 142.72, 142.55, 142.41, 142.35, 142.27, 142.09, 140.37, 140.17, 139.68, 137.26, 136.36, 126.34, 125.64, 119.68, 108.26, 73.85, 69.51, 32.18, 30.59, 29.98, 29.94, 29.84, 29.64, 29.51, 26.33, 22.95, 14.40. IR (KBr): ν 2924.36, 1586.92, 1497.09, 1322.42, 1112.83, 838.35, 528.94; MALDI-TOF: 1513.4 ($[M + H]^+$), 720 ($[C_{60}]^+$). Anal calcd for $C_{109}H_{81}N_3O_5$ (1512.86): C 86.54, H 5.40, N 2.78. Found: C 86.19, H 5.48, N 2.81.

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