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LETTERS TO THE EDITOR

Synthesis and Structure of *N*-Methyl-1-phenylfullereno-C_{60}[1,9]pyrrolidines Based on Aminoaldehydes

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In recent years the functionalization of the fullerene moiety based on Prato reaction [1, 2] is a widely used approach to the synthesis of fullerene derivatives for obtaining new materials and bioactive compounds. Availability of aldehydes allows to synthesize a number of dyad and triad donor-acceptor dyes and to investigate their biochemical and photophysical properties [3, 4].

In this work we synthesized two new 4-amino-substituted aromatic aldehydes and performed their condensation with fullerene C_{60}.

4-Amino-substituted aromatic aldehydes **I** and **II** were obtained by reacting morpholine and piperidine with fluorobenzaldehyde under microwave irradiation in the presence of a specially prepared catalyst supported on Silpearl silica activated with potassium carbonate as described in [5] (Scheme 1).

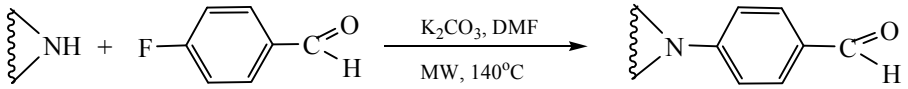
Reaction of C_{60} with *N*-methylglycine (sarcosine) and 4-*N*-aminobenzaldehydes **I** and **II** in refluxing toluene under an argon atmosphere for 4 h resulted in the formation of *N*-methyl-1-(4-aminophenyl)fullero-C_{60}[1,9]pyrrolidines **III** and **IV** in the yield of 88 and 62%, respectively (Scheme 2).

The target compounds **III** and **IV** were isolated by column chromatography on SiO_2, eluting sucsessively with toluene and pyridine. The structure of **III** and **IV** was confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

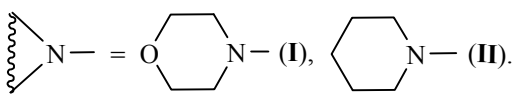
The obtained new fulleropyrrolidines are of interest as potential bioactive compounds.

***N*-Methyl-1-(4-morpholinophenyl)fullero-C_{60}-[1,9]pyrrolidine (III).** To a solution of 40 mg (0.0555 mmol) of fullerene C_{60} in 40 mL of toluene was added 5.3 mg (0.0277 mmol) of 4-morpholyl-

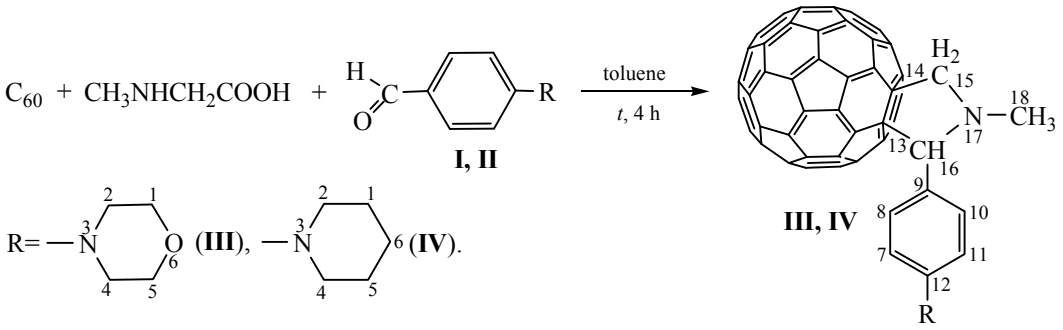
Scheme 1.



I, II



Scheme 2.



benzaldehyde **I** and 9.8 mg (0.278 mmol) of *N*-methylglycine. The mixture was refluxed for 4 h. After the reaction was completed, the reaction mixture was chromatographed on silica gel. Yield 23 mg (88%). ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$), δ, ppm, (*J*, Hz): 2.82 s (3H, H^{18}), 3.19 t (2H, H^2, $J_{1,2}$ 4.8), 3.37 t (2H, H^4, $J_{4,5}$ 4.8), 3.86 m (4H, H^1, H^5), 4.27 d (1H, H^{15b}, $J_{15a,15b}$ 9.2), 4.89 s (1H, H^{16}), 4.99 d (1H, H^{15a}, $J_{15a,15b}$ 9.2), 6.92 m (2H, H^7, H^{11}), 7.68 d (1H, H^{10}, $J_{10,11}$ 6.4), 7.76 d (1H, H^8, $J_{7,8}$ 8.8). ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$), δ_C, ppm; 135.53–156.09 (58C, C^{19}–C^{76}), 154.71 (C^{12}), 131.43 (C^{10}), 129.96 (C^8), 127.77 (C^9), 115.18 (C^{11}), 113.34 (C^7), 83.03 (C^{16}), 69.77 (C^{15}), 68.66 (C^{14}), 66.22 (C^5), 66.29 (C^4), 48.79 (C^2), 47.32 (C^4), 39.79 (C^{18}), 29.83 (C^{13}).

***N*-Methyl-1-(4-piperidylphenyl)fullero-C_{60}[1.9]-pyrrolidine (IV)** was obtained similarly from 40 mg (0.0555 mmol) of C_{60}, 5.2 mg (0.0275 mmol) of 4-piperidylbenzaldehyde **II,** and 9.8 mg (0.278 mmol) of *N*-methylglycine in 40 mL of toluene. Yield 16 mg (62%). ^{1}H NMR spectrum (400.13 MHz, $CDCl_3$), δ, ppm, (*J*, Hz): 1.75 br.s (6H, H^1, H^5, H^6), 2.81 s (3H, H^{18}), 3.21 m (2H, H^2, H^4), 4.26 d (1H, H^{15b}, $J_{15a,15b}$ 9.2), 4.88 s (1H, H^{16}), 4.99 d (1H, H^{15a}, $J_{15a,15b}$ 9.2), 6.98 br.s (2H, H^7, H^{11}), 7.65 br.s (1H, H^8, H^{10}). ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$), δ_C, ppm; 135.48–156.18 (58C, C^{19}–C^{76}), 153.89 (C^{12}), 129.90 (C^{10}), 129.60 (C^8), 116.00 (C^{11}), 115.70 (C^7), 83.11 (C^{16}), 69.78 (C^{15}), 68.71 (C^{14}), 50.10 (C^4), 49.90 (C^2), 40.80 (C^{13}), 39.78 (C^{18}), 39.60 (C^5), 24.19 (C^6). Mass spectrum, *m*/*z* 935.150 $[M - H]^+$. *M* 936.96.

Commercial fullerene C_{60} of 99.5% purity was used.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer in a $CDCl_3$–CS_2 solution (1 : 5), internal reference TMS. Mass spectra were registered on a MALDI TOF/TOF Autoflex-III Bruker spectrometer.

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