Novel fluorene-containing fullerenes C_{60}: synthesis and structures*

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Reactions of fullerene C_{60} with fluorene-2-carbaldehyde or 2,7-diacetylfluorene in toluene gave novel spiromethanofullerenes containing a reactive free formyl group. A novel fluorene-containing fullerenopyrrolidine was obtained by the Prato reaction. The purity and compositions of the compounds obtained were confirmed by MALDI TOF mass spectrometry and HPLC. Their structures were confirmed by 2D homo- and heterocorrelation NMR techniques.

Key words: fullerene C_{60}, fluorene-2-carbaldehyde, 2,7-diacetylfluorene, spiromethanofullerenes, fullerenopyrrolidine, homo- and heterocorrelation NMR spectroscopy, MALDI TOF mass spectrometry.

The chemistry of fullerenes has much advanced in the study of the Bingel—Hirsch[1,2] and Prato reactions[3] yielding methanofullerenes and fullerenopyrrolidines. These compounds are stable and their properties strongly depend on the nearest environment in the attached addend. For this reason, more and more attention is being given to their derivatives containing fragments of polycyclic hydrocarbons or heterocycles. The presence of such fragments can impart unusual photophysical properties to the resulting compounds.

Here we describe a method for the synthesis of novel fluorene-containing spiromethanofullerenes and fullerenopyrrolidine. The distinctive feature of spiromethanofullerenes is the spatial orientation of the addend rigidly bound to the methano fragment. These compounds can exhibit specific properties of addends. Fluorene-containing fullerenes C_{60} are promising as precursors of donor—acceptor polymeric products, as well as for creation of film and layered electron- and photoconductive and light-emitting materials.[4]

Up to date, fluorene-containing methanofullerenes have been obtained according to Wudl´s method[5,6] through intermediate diazo compounds. The electrochemical properties of the resulting compounds have been also studied.[5,6] Here we synthesized novel fluorene-containing fullerene derivatives by the Bingel—Hirsch and Prato reactions.[1—3]

* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

Results and Discussion

The acidity of the methylene H atoms in fluorene and its derivatives is sufficient for *in situ* preparation of bromo derivatives in base-catalyzed reactions with CBr_4. Carbanions generated in reactions of bromofluorene with a base add to the double bond of fullerene to give methanofullerene. The room-temperature Bingel—Hirsch reactions[1,2] of fullerene C_{60} with fluorene-2-carbaldehyde and 2,7-diacetylfluorene in the presence of CBr_4 and DBU gave the corresponding fluorene-containing spiromethanofullerenes **1** and **2**. Compounds **1** and **2** were isolated by column chromatography on SiO_2 in 12.3 and 17.3% yields, respectively.

The presence of two fullerene-reactive groups in the starting fluorene-2-carbaldehyde allows one to obtain two types of fullerene derivatives: spiromethanofullerene **1** and fullerenopyrrolidine **3**. For the synthesis of the latter, a mixture of fullerene C_{60}, *N*-methylglycine, and fluorene-2-carbaldehyde was refluxed in toluene under dry argon for 8 h. The composition of the reaction mixture was monitored by HPLC. Fullerenopyrrolidine **3** was isolated by column chromatography on SiO_2 in 16.1% yield (with respect to the consumed fullerene). The reactivities of fullerenes **1**—**3** toward a second fullerene C_{60} molecule will be discussed elsewhere.

The structures of the compounds obtained were proved by spectroscopic data; their compositions were determined by MALDI TOF mass spectrometry.

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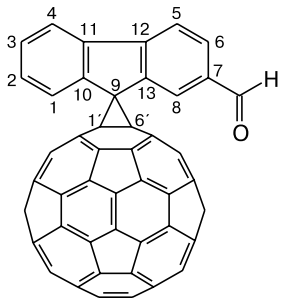
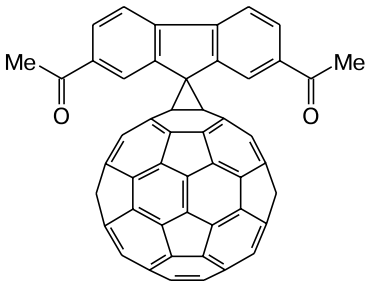


1



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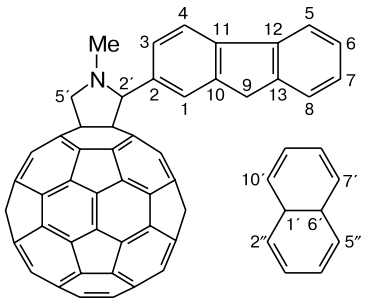

Fragment of the fullerene sphere

3

The UV spectra of spiromethanofullerenes **1** and **2** show absorption bands of the fullerene cage atoms at 258, 326, 431, 492, and 696 nm. The band at 431 nm is characteristic of the methano fragment attached to the 6,6-closed bond of the fullerene sphere. In contrast to the UV spectra of compounds **1** and **2**, the UV spectrum of fullerenopyrrolidine **3** does not contain the wide absorption band at 492 nm, which is more pronounced for methanofullerenes.

The IR spectra of all the compounds show an absorption band at 527 cm^{-1} characteristic of the vibrations of the fullerene cage bonds and bands at 1702 and 1696 cm^{-1} due to the vibrations of the formyl group in compound **1** and the acetyl groups in compound **2**, respectively.

The compositions of compounds **1**—**3** were confirmed by their MALDI TOF mass spectra containing molecular ion peaks with m/z 913.10, 968.77, and 943.10, respectively.

To determine the structures of the compounds obtained and the character of cycloaddition of the fluorene addends to the fullerene sphere, we employed ^1H and ^{13}C 1D NMR spectroscopy in combination with 2D homo- and heterocorrelation NMR techniques (COSY, HSQC, and HMBC).[7] These 2D techniques were used to avoid incorrect signal assignment from ^1H and ^{13}C 1D NMR data alone.[8—12]

The numbering of the carbon atoms in the fluorene fragment and in the nearest environment of the fullerene cage for compounds **1**—**3**, which was used in the interpretation of the spectra, is given above (see the formulas of the compounds).

The ^1H NMR spectrum of compound **1** shows a signal at δ 10.17 for the formyl proton and signals for the aromatic protons. The fluorene protons are manifested as a singlet at δ 9.32, two doublets at δ 8.86 (1 H, J = 7.7 Hz) and 8.13 (1 H, J = 7.7 Hz), two doublets of doublets at δ 7.67 (2 H, J = 7.7 Hz) and 7.61 (1 H, J = 7.7 Hz), and a multiplet at δ 8.19 and 8.14 (AB system, J = 7.7 Hz). The signal for the proton of the AB system is superimposed by the doublet at δ 8.13.

The cross-peaks in the 2D COSY spectrum suggest a correlation between the protons at δ 8.86 and 7.67 and at δ 8.13 and 7.61, as well as between the protons of the AB system.

In the ^{13}C NMR spectrum, signals for the carbon atoms bound to the protons were assigned from the 2D HSQC spectrum showing the corresponding cross-peaks for directly coupled protons and carbon atoms. For instance, the spectrum contains a cross-peak between a signal at δ 10.17 for the formyl proton and a signal for the corresponding formyl C atom (δ 191.0).

The 2D HMBC spectrum (Fig. 1) tuned to long-range $^1H—^{13}C$ coupling constants reveals a correlation between the signal for a formyl proton and the signals for the carbon atoms at δ 136.01, 130.79, and 126.40. The signal for the carbon atom at δ 136.01 was assigned to the C(7) atom of the fluorene fragment because it is directly coupled with no protons. Other cross-peaks reveal correlations between the formyl proton and the C(6) and C(8) atoms. The H(6) (δ 8.14) and H(8) protons (δ 9.32) can be assigned from 2D HSQC data. In addition, the 2D HMBC spectrum shows cross-peaks between the signal for the proton at δ 9.32 (H(8)) and the signals for the carbon atoms at δ 45.94 (C(9)), 130.79 (C(6)), and 146.81 (C(12)), as well as between the signal for the proton at δ 8.14 (H(6)) and the signals for the carbon atoms at δ 126.40 (C(8)) and 146.81 (C(12)). The signal for the proton at δ 8.19 has a cross-peak with the signals for the carbon atoms at δ 136.01 (C(7)), 142.99 (C(13)), and 139.65 (C(11)). Thus, we succeeded to determine the structure of the molecular fragment from the formyl group to the methano C(9) atom.

Now let us turn to the six-membered fluorene ring. The signal for a proton at δ 8.86 was assigned to the H(1) atom because of its cross-peak in the 2D HMBC spectrum (see Fig. 1) with the signal for the C(9) atom at δ 45.94, as well as with the signals for the C(11) (δ 139.65) and C(3) atoms (δ 128.97). Then we confirmed the assignment of the H(5) proton (δ 8.19) by 2D HSQC data. The signals for the H(2) (δ 7.61), H(3) (δ 7.67), and H(4) protons (δ 8.13) were identified from the 2D COSY spectrum. In a similar way, the C(1) (δ 125.38), C(2) (δ 129.36), C(3) (δ 128.97), and C(4) atoms (δ 121.33) were located from the HSQC spectrum for the known

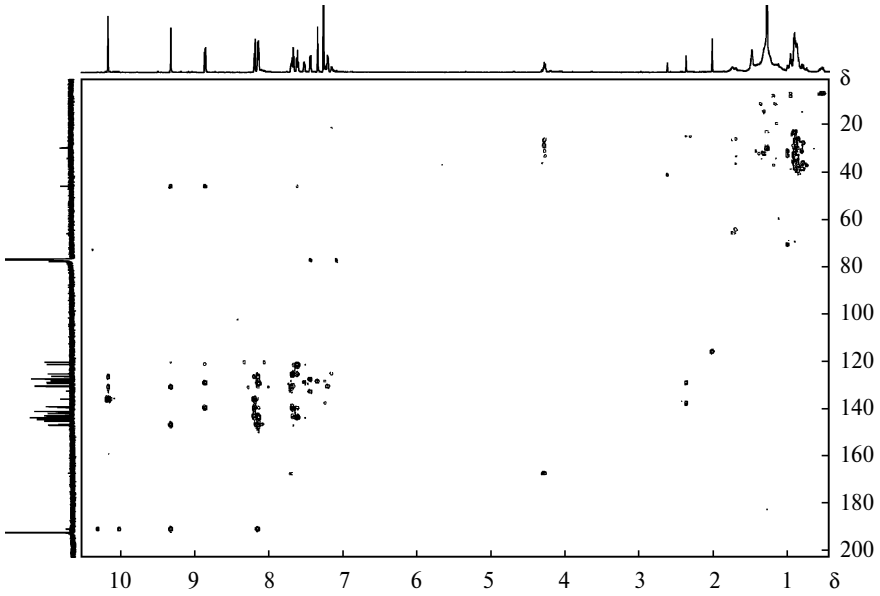

Fig. 1. 2D HMBC spectrum of compound **1**.

signals for the H(1)—H(4) protons. The 2D HMBC spectrum (see Fig. 1) also shows cross-peaks between the signal for the H(2) proton and the signals for the C(10) (δ 143.4) and C(4′) atoms (δ 134.09), between the signal for the H(3) proton and the signal for the C atom at δ 139.65 (C(11)), and between the signal for the H(4) proton and the signal for the C(10) atom at δ 143.4. Thus, we confirmed the structure of the fluorene fragment in methanofullerene **1**.

The ^{13}C NMR spectrum of adduct **1** contains 29 signals for the sp^2 range of the fullerene fragment with an intensity of 1 C (4 signals), 2 C (21), and 4 C (3), including a signal for the C(sp^3) atom with an intensity of 2 C. The intensity 4 C seems to result from superposition of two 2 C signals for the C(sp^2) atoms with close chemical shifts.

Compounds **1** and **2** have different substituents in the fluorene fragments. In adduct **2**, the acetyl groups are in symmetrical positions 2 and 7. The aromatic range of its ^1H NMR spectrum is substantially simplified, consisting of a singlet at δ 9.87 and two doublets at δ 8.17 (J = 7.7 Hz) and 8.75 (J = 7.7 Hz). In addition, an additional signal due to the methyl protons of the acetyl groups appears at δ 2.5. The ^{13}C NMR spectrum contains 17 signals with different intensities for the sp^2 range of the fullerene fragment. The structure of compound **2** was determined as described above; the ^1H and ^{13}C chemical shifts are given in Experimental.

The ^1H NMR spectrum of fullerenopyrrolidine **3** consists of signals for the aromatic, pyrrolidine, and methyl protons. The fluorene protons are manifested at room temperature as three doublets at δ 7.81 (H(4), J = 7.7 Hz), 7.72 (H(5), J = 7.7 Hz), and 7.50 (H(8), J = 7.7 Hz) and two doublets of doublets at δ 7.33 (H(6), J = 7.7 Hz) and 7.27 (H(7), J = 7.7 Hz). The doublet at δ 7.81 is broadened; its integral intensity corresponds to one proton. The spectrum also contains two strongly broadened signals at δ 7.95 for the H(1) proton and at δ 7.85 for the H(3) proton. The signals for the geminal CH_2 protons of the pyrrolidine ring form an AB system with a doublet at δ 5.02 (1 H, J = 9.2 Hz) and 4.32 (1 H, J = 9.2 Hz); the H(2′) proton of this fragment resonates at δ 5.03 (s, 1 H). The signal for the methyl group at the N atom appears at δ 2.87 (s, 3 H); the H(9) protons of the fluorene fragment resonate at δ 3.92 (s, 2 H). The above assignment of the signals in the ^1H NMR spectrum was unambiguously confirmed by 2D HSQC and 2D HMBC data.

In the ^{13}C NMR spectrum, the signals for the carbon atoms bound to the protons were assigned from the 2D HSQC spectrum showing the corresponding cross-peaks for directly coupled protons and carbon atoms. For instance, the spectrum contains cross-peaks between the signals for the pyrrolidine protons, the methylene protons of the fluorene fragment, and the protons of the methyl group at the N atom and the corresponding signals for the C(2′) (δ 83.73), C(5′) (δ 69.94), C(9) (δ 36.98), and $\underline{C}H_3$ atoms (δ 39.92).

The presence of a cross-peak in the 2D HMBC spectrum (Fig. 2) between the signal at δ 5.03 for the H(2′) proton of the pyrrolidine ring and the signals at δ 135.3, 127.5, and 126.5 for the carbon atoms allows these signals to be assigned to the C(2), C(3), and C(1) atoms, respectively, of the fluorene fragment. This assignment was confirmed by 2D HSQC data. Thus, we proved the structure of the fluorene fragment covalently bound to the pyrrolidine fragment.

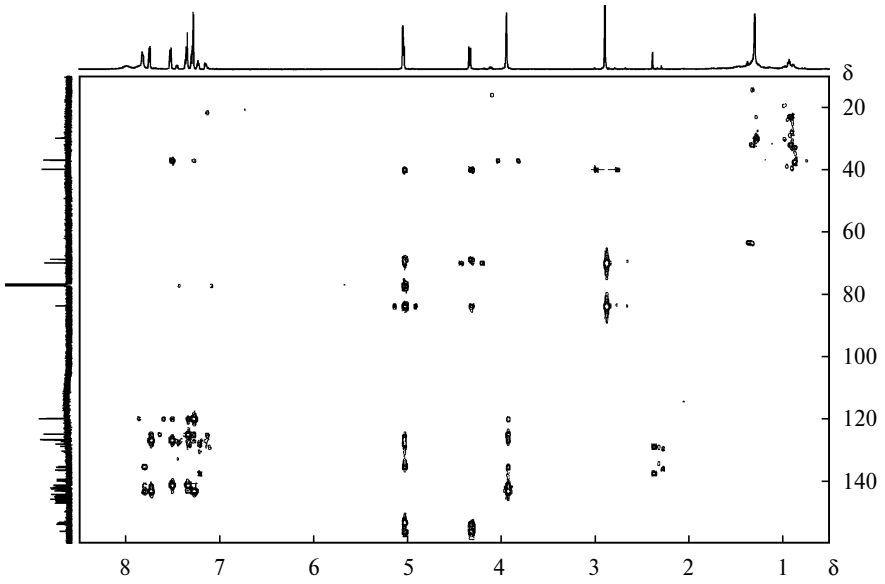

Fig. 2. 2D HMBC spectrum of compound **3**.

In addition, we found correlations between the protons and the carbon atoms in the pyrrolidine ring. The 2D HMBC spectrum (see Fig. 2) shows correlations between the H(5′) proton and the C(2′) atom, the H(2′) proton and the C(5′) atom, and the H(2′) and H(5′) protons and the C atom of the NMe group at δ 39.92. In turn, the spectrum reveals cross-peaks between the signal for the NMe protons at δ 2.87 and the signals for the C(5′) (δ 69.94) and C(2′) atoms (δ 83.73).

A 2D HMBC experiment allows, first, unambiguous detection of a bond between the pyrrolidine fragment and the fullerene sphere and, second, determination of the chemical shifts of the carbon atoms of C_{60} at which cycloaddition occurs and the character of this addition. The 2D HMBC spectrum reveals a correlation between the H(5′) protons (δ 5.02 and 4.32) and the C(1′) atom (δ 68.81) and between the H(5′) protons and the C(6′) atom (δ 77.2). In addition, the spectrum contains cross-peaks between the signals for the H(5′) protons and signals for the C(2″) and C(10′) atoms at δ 156.03 and 153.80, respectively, and between the signal for the H(2′) proton at δ 5.03 and the signals for the C(5″) and C(7′) atoms at δ 153.16 and 153.31, respectively. Thus, we identified the carbon atoms of the fullerene shell that are closest to the site the addend is attached to. The chemical shifts of the C(1′) and C(6′) atoms (δ 68.80 and 77.21, respectively) (*i.e.*, their nonaromaticity) confirmed the closed character of the addend attachment.

The signal broadening observed at room temperature for the fluorene H(1), H(3), and, to a lesser degree, H(4) protons is attributable to relatively slow rotation (on the time scale of the NMR experiment) about the C(2′)—C(2) bond, probably because of steric factors arising from the vicinity of the fullerene sphere. The signals for the C(1) and C(3) atoms of the fluorene fragment are also substantially broader than other signals.

It is known that in room-temperature NMR spectra of phenylfullerenopyrrolidines, the signals for the protons of the phenyl group bound to the pyrrolidine ring are usually broadened because of hindered rotation.[13] A similar pattern has been noted by other researchers.[14] Ajamaa *et al.*[15] have obtained a series of (phenylpyrrolidino)fullerenes and analyzed in detail their conformations with temperature-variable ^{1}H NMR experiments and computer-assisted simulation; they have observed dynamic phenomena due to hindered rotation about the phenyl—pyrrolidine bond, which gives rise to two possible atropoisomers.

A decrease in the recording temperature resulted in narrowing of all the lines in the ^{1}H NMR spectrum of compound **3**; however, the spectrum itself became more complicated (Fig. 3). Apparently, fullerenopyrrolidine **3** can exist as two atropoisomers, depending on the orientation of the fluorene fragment relative to the pyrrolidine

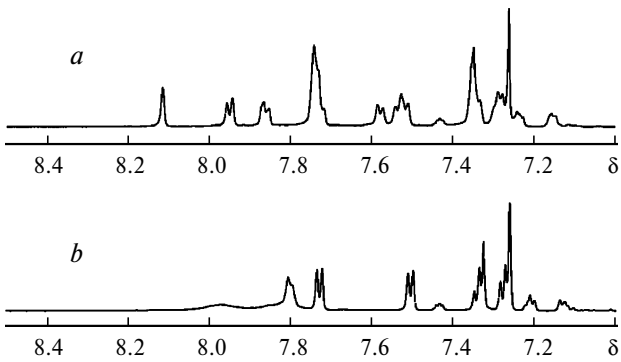

Fig. 3. ^{1}H NMR spectra of compound **3** at −60 (*a*) and ~20 °C (*b*).

ring. At –60 °C, an NMR experiment detects both conformers because of slow dynamic exchange between them (see Fig. 3, *b*). A detailed analysis of the spectra showed that neither conformer is dominant: the ratio of the conformers was 10 : 11. The signals for the conformers were assigned from 2D COSY data and are based on the downfield shift of the signals for the protons close to the fullerene sphere.

In conclusion, we synthesized novel fluorene-containing fullerenes C_{60} and confirmed their structures by 1D and 2D NMR techniques. The electrochemical properties of compounds **1**—**3** have been described earlier.[16]

Experimental

An HPLC analysis was carried out on a Gilson chromatograph (UV detector, reversed-phase column with C18 (Partisil-5 ODS-3), toluene—MeCN (1 : 1, v/v) as an eluent). Organic solvents were dried and distilled. Fullerene C_{60} (99.9% purity) was manufactured at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhny Novgorod); the starting fluorene derivatives were commercial chemicals (Lancaster). All chemical manipulations were carried out under dry argon.

UV spectra were recorded on a Specord M-40 spectrophotometer in CH_2Cl_2. IR spectra were recorded on a Bruker-Vector 22 FTIR spectrometer (KBr pellets).

Products were examined at the NMR Division of the Federal Collective Spectroanalytical Center for physicochemical investigations of the structures, properties, and compositions of compounds and materials and the Federal Collective Center for physicochemical investigations of compounds and materials (State Contracts of the Ministry of Education and Science of the Russian Federation 02.451.11.7036 and 02.451.11.7019). ^{1}H and ^{13}C NMR spectra were recorded on an Avance-600 spectrometer (Bruker) (600 and 150.926 MHz, respectively) at 30 °C with a residual signal of $CDCl_3$ as the internal standard (δ_H 7.26, δ_C 77.0). The structures of the products were determined by correlation 1D and 2D NMR experiments (DEPT, ^{1}H—^{1}H COSY, ^{1}H—^{13}C HSQC, and ^{1}H—^{13}C HMBC). Experimental data were optimized for the coupling constant $J_{C,H}$ = 8 Hz.

Mass spectra were recorded on a MALDI TOF MS instrument (DynamoThermo-BioANALYSIS, Germany) with a trihydroxyanthracene matrix.

2-Formylspiro[fluorene-9,61´-methano[C_{60}]fullerene] (1). Fluorene-2-carbaldehyde (0.058 g, 0.3 mmol), CBr_4 (0.119 g, 0.36 mmol), and DBU (0.055 g, 0.36 mmol) were added to a solution of fullerene C_{60} (0.216 g, 0.3 mmol) in toluene (200 mL). The reaction mixture was stirred at ~20 °C for 8 h. The course of the reaction was monitored by HPLC. The mixture was acidified with three drops of 2 *N* H_2SO_4, washed with water (2×15 mL), and concentrated in water aspirator vacuum. Column chromatography on SiO_2 with toluene—hexane (3 : 1) as an eluent gave compound **1** (0.025 g). The yield was 12.3% with respect to the consumed C_{60}. UV, λ_{max}/nm (ε): 326 (14712), 430.8 (2100), 491 (1986), 697 (210). IR, ν/cm^{-1}: 525.5, 725, 906, 1121, 1156, 1186, 1216, 1282, 1502, 1597, 1702. ^{31}P NMR ($CDCl_3$), δ: 83.44. ^{1}H NMR (CS_2—$CDCl_3$), δ: 7.61 (dd, 1 H, *J* = 7.7 Hz); 7.67 (dd, 2 H, *J* = 7.7 Hz); 8.13 (d, 1 H, *J* = 7.7 Hz); 8.14, 8.19 (both m); 8.86 (d, 1 H, *J* = 7.7 Hz); 9.32 (s); 10.17 (s, 1 H, C(O)H). ^{13}C NMR (CS_2—$CDCl_3$), δ: 45.94, 77.83 (C(sp^3)), 120.37, 121.33, 125.38, 126.40, 128.96, 129.36, 130.79, 135.35, 136.01, 138.55, 138.67, 138.96, 139.64, 140.58, 140.70, 140.78, 141.54, 141.61, 142.01, 142.09, 142.31, 142.38, 142.48, 142.77, 142.96, 143.24, 143.40, 143.87, 143.96, 144.13, 144.21, 144.55, 144.66, 146.13, 146.30, 146.47, 146.81, 191.10 (C(O)H). MALDI TOF MS, found: *m/z* 913.10 [M]$^+$. $C_{74}H_8O$. Calculated: M = 912.87.

2,7-Diacetylspiro[fluorene-9,61´-methano[C_{60}]fullerene] (2). 2,7-Diacetylfluorene (0.1125 g, 0.45 mmol), CBr_4 (0.1494 g, 0.45 mmol), and DBU (0.0685 g, 0.45 mmol) in toluene were successively added to a solution of fullerene C_{60} (0.216 g, 0.3 mmol) in toluene. The reaction mixture was stirred under argon at ~20 °C for 5 h. The completion of the reaction was checked by HPLC. The precipitate that formed was filtered off, washed with toluene, and dried in air to give a solid (0.0794 mg). The filtrate was acidified with three drops of 2 *N* H_2SO_4, washed with water (2×15 mL), and concentrated in water aspirator vacuum. The nonconsumed fullerene C_{60} (0.0336 mg) was recovered with toluene—hexane (1 : 1). A mixture of bisadducts (52.3 mg) was also obtained. Product **2** was isolated by column chromatography on SiO_2 with toluene—MeCN (15 : 0.1) as an eluent. The yield was 0.0425 g (17.3% with respect to the consumed C_{60}). UV, λ_{max}/nm (ε): 258 (45000), 326 (13000), 431.2 (1800), 492 (2018), 696 (280). IR, ν/cm^{-1}: 525, 554, 575, 591, 711, 729, 822, 1034, 1120, 1190, 1247, 1426, 1467, 1605, 1696, 2922. ^{1}H NMR (C_6D_6), δ: 2.45 (s, 3 H); 8.17, 8.75 (both d, $J_{H,H}$ = 7.7 Hz); 9.87 (s). ^{13}C NMR (C_6D_6), δ: 26.9, 45.07, 67.06 (C(sp^3)), 121.50 (C(4), C(5)), 126.5 (C(1), C(8)), 129.81 (C(3), C(6)), 135.04, 135.20, 136.81, 138.04, 138.45 (C(2), C(7)), 140.15, 142.18, 142.57, 143.08 (C(10), C(13)), 143.21 (C(11), C(12)), 143.86, 144.04, 144.29, 144.53, 144.74, 145.59, 146.11, 146.18, 146.24, 147.94, 196.26 (C=O). MALDI TOF MS, found: *m/z* 968.77 [M]$^+$. $C_{77}H_{12}O_2$. Calculated: M = 968.94.

2-(Fluoren-2-yl)-1-methyl[60]fullereno[1,2-*c*]pyrrolidine (3). A solution of fullerene C_{60} (0.216 g, 0.3 mmol), fluorene-2-carbaldehyde (0.087 g, 0.45 mmol), and *N*-methylglycine (0.080 g, 0.9 mmol) in toluene (200 mL) was refluxed under argon for 8 h. The completion of the reaction was checked by HPLC. The reaction mixture was washed with water (2×30 mL) and concentrated in water aspirator vacuum. Compound **3** was isolated by column chromatography on SiO_2 with hexane—toluene—MeCN (1 : 3 : 1) as an eluent. The yield was 0.035 g (16.1% with respect to the consumed C_{60}). UV, λ_{max}/nm (ε): 326 (12000), 430.6 (1980), 696 (290). IR, ν/cm^{-1}: 527, 553, 575, 598, 766, 781, 845, 904, 1034, 1122, 1179, 1215, 1332, 1401, 1428, 1465, 2778, 2850, 2920. ^{1}H NMR (CS_2—$CDCl_3$), δ: 2.87 (s, 3 H); 3.92 (s, 2 H, CH_2 fluorene); 4.32, 5.02 (both d, 1 H each, *J* = 9.2 Hz); 5.03 (s, 1 H); 7.27, 7.33 (both dd, 1 H each, *J* = 7.7 Hz); 7.50, 7.72 (both d, 1 H each, *J* = 7.7 Hz); 7.81 (br.d, 1 H, *J* = 7.7 Hz); 7.85, 7.95 (both br.s, 1 H each). ^{13}C NMR (CS_2—$CDCl_3$), δ: 36.97, 39.92, 68.80, 69.93, 83.73, 119.89, 124.91, 126.50, 126.74, 126.85, 127.40, 135.31, 135.64, 136.42, 139.64, 139.98, 141.13, 141.33, 141.49, 141.63, 141.71, 141.80, 141.84, 141.89, 141.96, 142.06, 142.10, 142.81, 142.90, 142.95, 143.10, 144.19, 144.43, 144.50, 144.94, 144.99, 145.02, 145.03, 145.09, 145.18, 145.23, 145.31, 145.33, 145.40, 145.55, 145.72, 145.88, 145.92, 145.96, 145.98, 146.01, 146.03, 146.12, 146.25, 146.55, 147.06, 147.08, 153.15, 153.30, 153.79, 156.03.

MALDI TOF MS, found: m/z 943.10 $[M]^+$. $C_{74}H_8O$. Calculated: M = 941.96.

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References

1. C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
2. X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1595.
3. M. Maggini, G. Scorrano, and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.
4. F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.
5. M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 8479.
6. M. Eiermann, R. C. Haddon, B. Knight, Li Q. Chan, M. Maggini, N. Martin, T. Ohno, M. Prato, T. Suzuki, and F. Wudl, *Angew. Chem.*, 1995, **107**, 1733.
7. (a) W. R. Croasmun and R. M. K. Carlson, *Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, 1987; (b) A. E. Derome, *Modern NMR Techniques for Chemistry Research*, Pergamon, 1988; (c) Atta-ur-Rahman, *One and Two Dimensional NMR Spectroscopy*, Elsevier, Amsterdam, 1989, 579.
8. C. A. Burley, P. A. Keller, S. G. Pyne, and G. E. Ball, *Chem. Commun.*, 1998, 2539.
9. C. A. Burley, P. A. Keller, S. G. Pyne, and G. E. Ball, *Chem. Commun.*, 2000, 1717.
10. C. A. Burley, P. A. Keller, S. G. Pyne, and G. E. Ball, *Chem. Commun.*, 2001, 563.
11. C. A. Burley, P. A. Keller, S. G. Pyne, and G. E. Ball, *J. Org. Chem.*, 2002, **67**, 8316.
12. G. E. Ball, C. A. Burley, L. Chaker, B. C. Hawkins, J. R. Williams, P. A. Keller, and S. G. Pyne, *J. Org. Chem.*, 2005, **70**, 8572.
13. J. F. Nierengarten, *New J. Chem.*, 2004, **28**, 1177.
14. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Maeks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, *Nature*, 1999, **397**, 14, 121.
15. F. Ajamaa, T. M. Figueira Duarte, C. Bourgogne, M. Holler, P. W. Fowler, and J. F. Nierengarten, *Eur. J. Org. Chem.*, 2005, 3766.
16. V. V. Yanilkin, N. V. Nastapova, V. I. Morozov, V. P. Gubskaya, F. G. Sibgatullina, L. Sh. Berezhnaya, and I. A. Nuretdinov, *Elektrokhimiya*, 2007, **43**, 195 [*Russ. J. Electrochem.*, 2007, **43**, 184 (Engl. Transl.)].

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