Synthesis, structures, and properties of new thiophosphorylated fullerenopyrrolidines. First example of the Pishchimuka reaction in fullerene derivatives

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The reactions of fullerene C_{60} with thiophosphorylated mono- or dialdehydes and *N*-methylglycine in toluene afforded new thiophosphorylated fullerenopyrrolidines, including those containing the free aldehyde group. The purity and compositions of the reaction products were confirmed by MALDI-TOF mass spectrometry and HPLC. The structures of the reaction products were established by two-dimensional homo- and heterocorrelation NMR experiments. The properties of the products were studied by cyclic voltammetry and quantum chemical methods. The Pishchimuka rearrangement in thiophosphorylated derivatives of fullerenopyrrolidines was performed for the first time, and thiol esters of phosphonic acids of fullerenopyrrolidines were prepared.

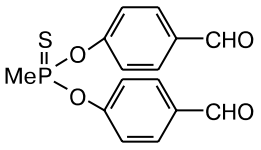
Key words: fullerene C_{60}, thiophosphorylated fullerenopyrrolidines, NMR spectroscopy, cyclic voltammetry, MALDI-TOF mass spectrometry.

Heteroorganic derivatives of fullerene have attracted attention because they can combine the properties specific for both fullerene and a heteroorganic addend. Earlier,[1—8] the properties of organophosphorus derivatives of fullerene containing the phosphoryl (P=O) group and belonging primarily to methanofullerenes have been documented. Fullerene derivatives containing the thiophosphoryl (P=S) group have remained unknown. It is known that the P=S group actively interacts with salts of different metals[9] and alkyl halides.[10] This type of compounds would be expected to be promising as biologically active compounds and new materials for nanotechnology.

In the present study, we synthesized first representatives of thiophosphorylated fullerene derivatives. The character of the addend attachment to the fullerene cage was unambiguously established with the use of modern correlation NMR techniques.

Results and Discussion

We prepared new thiophosphorylated dialdehydes **1** and **2** and aldehydes **3** and **4** by the reactions of the corresponding thiophosphonic acid chlorides and 4-hydroxybenzaldehyde in the presence of sodium hydride. The reaction products were isolated in pure form by silica gel column chromatography. The structures of these compounds were established by spectroscopic methods (^{1}H and ^{31}P NMR and IR).



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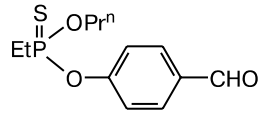

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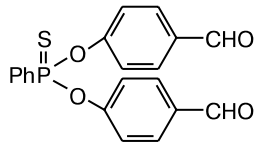

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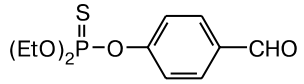

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The Prato reaction with the use of dialdehydes[11] can yield different products, *viz.*, monofullerenopyrrolidines containing the free aldehyde group, dumbbell-shaped bisfullerenes, and bis-adducts fused onto the fullerene cage.

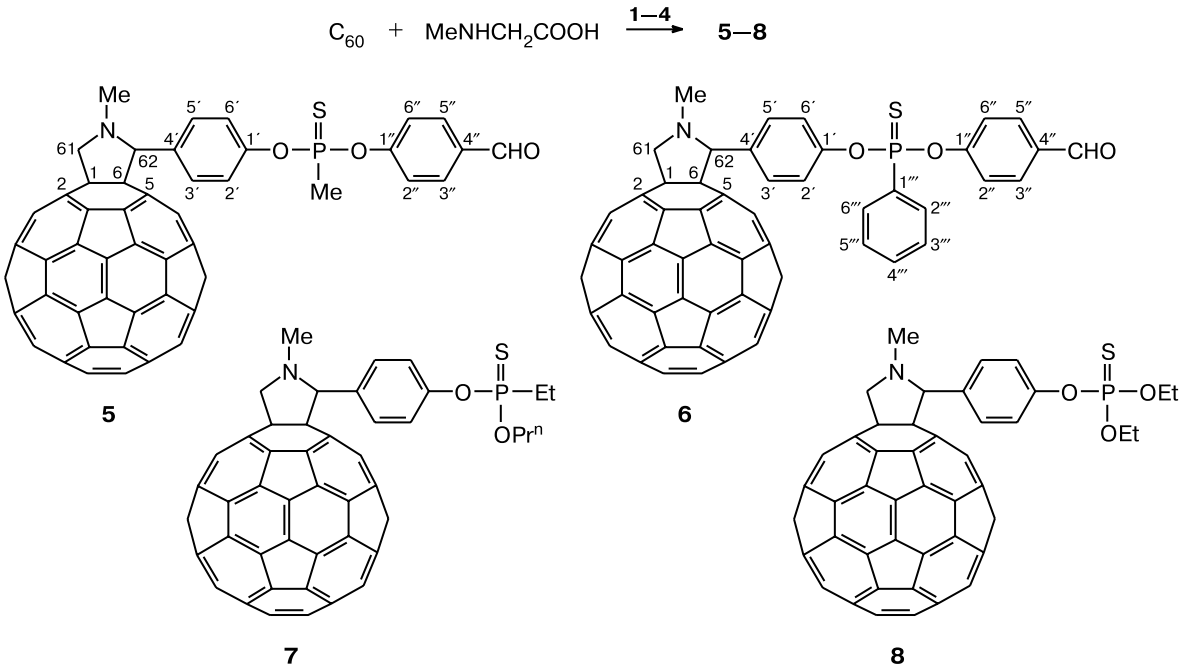
It appeared that heating of compounds **1—4** with *N*-methylglycine and fullerene C_{60} in a toluene solution (Prato reaction[11]) afforded the corresponding thiophosphorylated monofullerenopyrrolidines **5—8** (Scheme 1).

Compounds **5—8** were isolated by silica gel column chromatography. The purity of these compounds was

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 489—497, March, 2006.

1066-5285/06/5503-0507

Scheme 1



checked by HPLC. The compositions of fullerenopyrrolidines **5—8** were confirmed by MALDI-TOF mass spectrometry. The mass spectra contain molecular ion peaks at *m/z* 1067.75 (calculated 1067.99) (**5**), *m/z* 1129.98 (calculated 1130.07) (**6**), *m/z* 1019.44 (calculated 1020.03) (**7**), and *m/z* 1021.71 (calculated 1021.99) (**8**). The UV spectra of compounds **5—8** show characteristic absorption bands at 258, 268, 328, and 430 nm, respectively. The absorption band at 430 nm is indicative of the formation of [6,6]-closed monoadducts.[11—14] The IR spectra of these compounds show absorption bands at 525 and 1425 cm^{-1} belonging to vibrations of the fullerene cage and a number of other bands corresponding to stretching vibrations of the attached fragments. The spectra of all compounds contain absorption bands of P=S groups at 775—800 cm^{-1}. The spectra of fullerenopyrrolidines **5** and **6** show absorption bands of C=O groups at 1700 and 1702 cm^{-1}, respectively.

The assignment of the lines in the ^1H and ^{13}C NMR spectra of compound **5** was made based on the DEPT, 2D COSY, 2D HSQC, and 2D HMBC experiments.[15] The structures of individual fragments, starting from the characteristic group (for example, from the aldehyde group), were established by a combination of 1D and 2D experiments, which revealed homo- and heteronuclear correlations.

The ^1H NMR spectrum of compound **5** shows signals for the aldehyde proton (δ 9.94), aromatic protons, and protons of the pyrrolidine fragment and the Me groups. The signals for the aromatic protons appear as doublets at δ 7.81 (4 H, J = 8.1 Hz), 7.23 (2 H, J = 8.8 Hz), and 7.20 (2 H, J = 8.1 Hz). The doublet at δ 7.81 has a strongly broadened base due, apparently, to the overlap of two signals, one of which corresponds to the H(3′) and H(5′) protons and the other signal corresponds to the H(3″) and H(5″) protons (the atomic numbering scheme is given in Scheme 1). The doublets at δ 7.20 and 7.23 were assigned to the H(2′), H(6′) and H(2″), H(6″) protons. The signals for the geminal protons of the $C(61)H_2$ group of the pyrrolidine fragment appear as an AB system at δ 4.30 and 5.00 (both d, 1 H each, J = 9.2 Hz); the H(62) proton of this fragment resonates at δ 4.96 (s, 1 H). The signal of the Me group at the nitrogen atom is observed at δ 2.84 (s, 3 H), and the signal of the Me group at the phosphorus atom appears at δ 2.20 (dd, 3 H, J = 15.4 Hz, J = 1.8 Hz). This assignment of the signals in the ^1H NMR spectrum was unambiguously confirmed by the results of the 2D HMBC experiment (see below).

In the ^{13}C NMR spectrum of compound **5**, the signals for the carbon atoms bound to the hydrogen atoms were assigned based on the analysis of the 2D HSQC experiment (Fig. 1). The spectrum contains the corresponding cross-peaks between the signals for the protons and the C atoms bound to these protons due to the direct spin-spin coupling constant.

The 2D HMBC spectrum of compound **5** (Fig. 2) shows a correlation between the signals for the aldehyde protons and the C atoms at δ 130.84 and 122.05. Taking into account that the spin-spin coupling constant ^3J is larger than $^{2,4}J$, the higher intensity of the cross-peak is

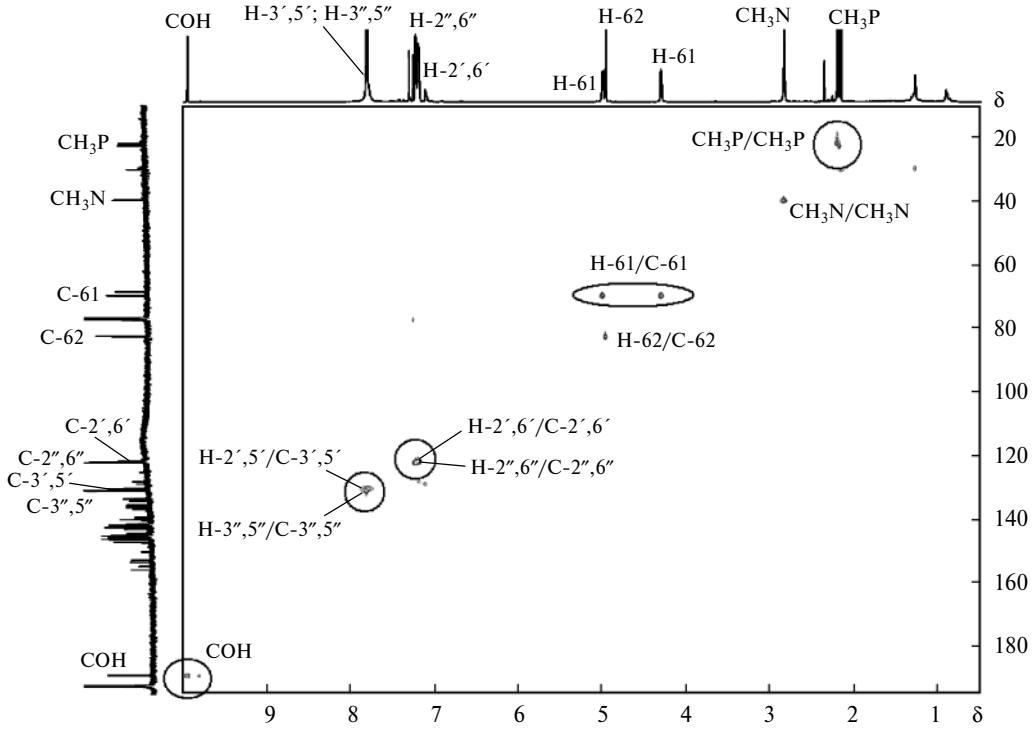


Fig. 1. 2D HSQC spectrum (^{1}H—^{13}C) of compound **5**.

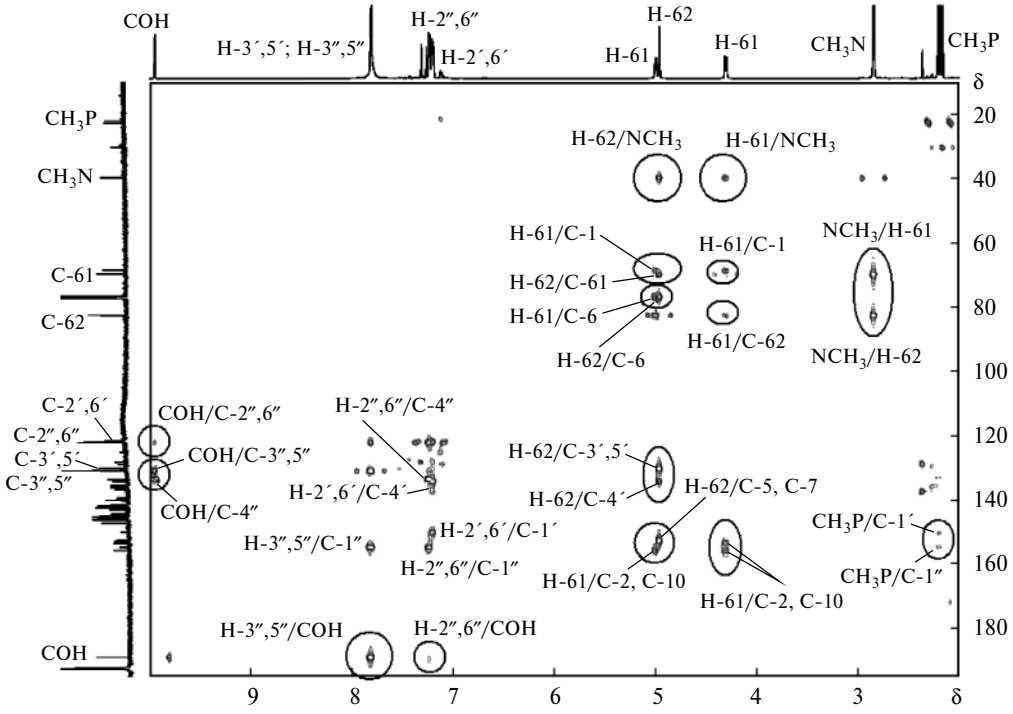


Fig. 2. 2D HMBC spectrum (^{1}H—^{13}C) of compound **5**.

evidence that this peak corresponds to the correlation of this proton with the C(3″) and C(5″) atoms (δ 130.84). The second (less intense) cross-peak corresponds to the correlation of the aldehyde proton with the C(2″) and C(6″) atoms. Therefore, the C(3″), C(5″), C(2″), and C(6″) atoms were unambiguously identified. The assignment of the corresponding protons, *viz.*, H(3″), H(5″) (δ 7.81) and H(2″), H(6″) (δ 7.23), was confirmed using

the 2D HSQC experiment. In addition, the 2D HMBC spectrum (see Fig. 2) contains cross-peaks between the H(2″), H(6″)/H(3″), and H(5″) protons and the C atom at δ 154.57 (d, C(1″), $^2J_{C,P}$ = 9.7 Hz). There is also a correlation between the protons at δ 7.23 (H(2″) and H(6″)) and the C atom at δ 133.45 (C(4″)). This made it possible to establish the structure of the fragment from the aldehyde group up to the second oxygen atom.

The resonances for the carbon atoms of the pyrrolidine ring were determined from the analysis of the 2D HSQC spectrum (see Fig. 1; δ 69.73 (C(61)) and 82.50 (C(62)). The cross-peak in the 2D HMBC spectrum between the signal for the pyrrolidine proton at δ 4.96 (H(62)) and the signal for the carbon atom of one of the benzene fragments at δ 130.16 (see Fig. 2) provides evidence that this signal corresponds to the C(3′) and C(5′) atoms. The assignment of the H(3′) and H(5′) protons (δ 7.81) was confirmed based on the results of the 2D HSQC experiment (see Fig. 1). The resonance for the H(2′) and H(6′) protons (δ 7.20) was identified from the 2D COSY spectrum. Analogously, the C(2′) and C(6′) atoms (δ 121.66) were determined from the HSQC spectrum (see Fig. 1) after the identification of the H(2′) and H(6′) protons. The 2D HMBC spectrum (see Fig. 2) shows cross-peaks between the H(2′), H(6′), and H(62) protons and the carbon atom at δ 134.09 (C(4′)) and between the H(2′) and H(6′) protons and the carbon atom at δ 150.00 (d, C(1′), $^2J_{C,P}$ = 9.7 Hz). Therefore, the structure of the second benzene fragment was confirmed, and the bond between this fragment and the pyrrolidine ring was established.

In addition, we revealed the correlation between the protons and the carbon atoms of the pyrrolidine ring. The 2D HMBC spectrum (see Fig. 2) shows the H(61)/C(62) and H(62)/C(61) correlations and has cross-peaks between the H(61) and H(62) protons and the carbon atom of the NMe group at δ 39.71. The protons at δ 2.84 (MeN) interact with the carbon atoms at δ 69.73 (C(61)) and 82.50 (C(62)).

The bonds between the fragments located on the opposite sides of the phosphorus atom were determined based on the characteristic through-two-bond spin-spin coupling constant for the quaternary C(1′) and C(1″) atoms ($^2J_{C,P}$ = 9.7 Hz).[16] Moreover, the 2D HMBC experiment independently confirmed the presence of the bond between the fragments based on the cross-peaks between the PMe protons (δ 2.20) and the C(1′) and C(1″) atoms (see Fig. 2).

The 2D HMBC experiments allowed us, first, to unambiguously reveal the bond between the pyrrolidine fragment and the fullerene cage and, second, to determine the chemical shifts of the sp^3-hybridized C atoms, to which the pyrrolidine fragment is attached, and thus establish the character of this bond. The 2D HMBC spectrum shows a correlation between the H(61) protons (δ 5.00 and 4.30) and the C(1) atom (δ 68.57) and between the H(61) (δ 5.00) and H(62) protons (δ 4.96) and the C(6) atom (δ 76.73). In addition, there are cross-peaks between the H(61) protons (δ 5.00 and 4.30) and the C(2) and C(10) atoms (δ 155.67 and 153.41, respectively) and between the H(62) proton (δ 4.96) and the C(5) and C(7) atoms (δ 152.68 and 152.48, respectively). Therefore, we identified the C atoms of the fullerene cage adjacent to the attachment site of the addend. The chemical shifts of the C(1) and C(6) atoms (their nonaromaticity) confirm the closed character of the attachment of the addend.

It should be noted that a broadening of the signals observed for the H(3′) and H(5′) protons and, to a lesser extent, for the H(2′) and H(6′) protons is, evidently, attributed to relatively slow (on the NMR time scale) rotation about the C(62)—C(4′) bond. Apparently, this is associated with the steric factors due to the closely spaced fullerene cage. Analogously, the signals for the C(2′), C(6′) and C(3′), C(5′) atoms of this fragment are also broadened compared to other resonances.

The structure of **6** differs from that of **5** by the substituent at the thiophosphoryl group (the Ph fragment instead of the Me group). The ^{1}H NMR spectrum of compound **5** is similar to that of **6**. The only difference is that the aromatic region shows additional signals belonging to the protons of the phenyl group at the phosphorus atom, whereas the signal for the protons of the PMe group disappears. The structure of compound **6** was established as described above. The chemical shifts in the ^{1}H and ^{13}C NMR spectra are given in the Experimental section.

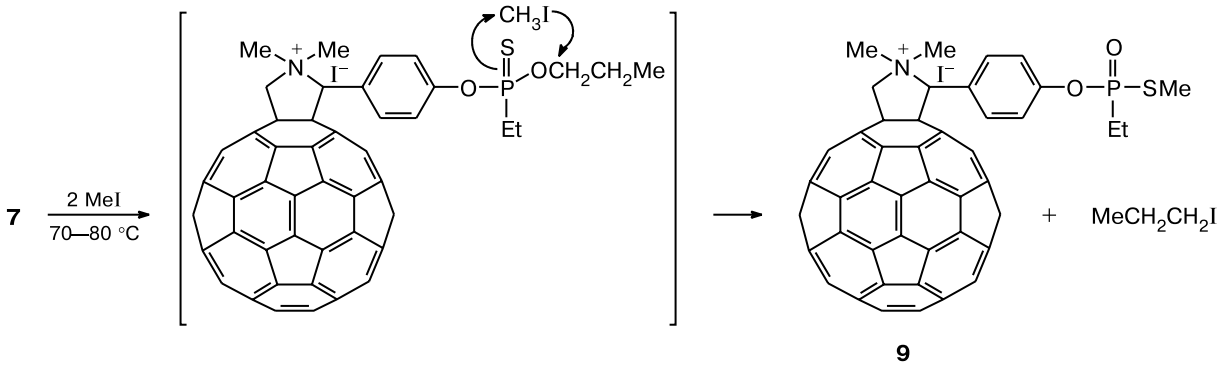
The ^{13}C NMR spectrum of compound **6** shows resonances for the corresponding carbon atoms of the phenyl fragment at the phosphorus atom. The assignment of the signals for the C atoms of this fragment bound to the H atoms was made based on the analysis of the 2D HSQC spectrum. Then all other signals were unambiguously assigned based on the 2D HMBC spectrum.

The character of the attachment of the addend to the fullerene core was also established based on the HMBC correlations. The 2D HMBC spectrum shows the corresponding cross-peaks between the H(61) protons of the pyrrolidine ring and the C(1) atom at δ 68.96 and between the H(61) and H(62) protons and the C(6) atom at δ 77.12. In addition, the 2D HMBC spectrum shows cross-peaks between the protons of the pyrrolidine fragment and the C(2)/C(10) and C(5)/C(7) atoms of fullerene. Therefore, the closed type of the attachment of the addend is observed both in compounds **6** and **5**.

The structures of compounds **7** and **8** were analogously confirmed by NMR spectroscopic data.

The chemistry of functionalized fullerene derivatives is poorly studied. However, it is known that, in the presence of alkyl halides, thionophosphates are prone to the thione-thiol rearrangement discovered by Pishchimuka.[10] Earlier,[12] it has been demonstrated that the reaction of

Scheme 2



fullerenopyrrolidines with MeI produces their cationic derivatives, which are higher soluble in polar solvents compared to the starting compounds. Based on these data, we studied the reaction of thiophosphorylated fullerenopyrrolidine **7** with iodomethane. Actually, this reaction with excess MeI leads to quaternization of the nitrogen atom of the pyrrolidine fragment with the simultaneous rearrangement of the phosphorus-containing group (Scheme 2). The yield of the final product was 76%.

Therefore, we synthesized the first onium thiolophosphoryl derivative of fullerenopyrrolidine **9** by the Pishchimuka thione-thiol rearrangement. This compound is readily soluble in polar solvents, for example, in DMSO. The structure of compound **9** was confirmed by spectroscopic methods. For example, the mass spectrum of compound **9** has the fragment peak $[M^+ - MeI]$ at m/z 900. In the IR spectrum of compound **9**, the low-intensity absorption band of the P=S-group (782 cm^{-1}) is absent, and the more intense band of the P=O group (1174 cm^{-1}) is observed. The ^{31}P NMR spectrum of compound **9** shows a signal with the chemical shift characteristic of the thiolophosphoryl fragment (δ_P 60.80; *cf.* δ_P 100.00 for the starting compound **7**).

The structure of product **9** was confirmed also by 1D and 2D NMR experiments. The signals for the protons of the pyrrolidine fragment (H(62), δ 7.27; H(61), δ 6.03 and 5.79; Me_2N^+, δ 4.23 and 3.68) are observed at lower field compared to the corresponding protons in compounds **5—8** due to the presence of the positive charge on the nitrogen atom. The structure of the pyrrolidine fragment as well as the fact and the character of its attachment to the fullerene cage were unambiguously established based on the 2D HMBC spectrum.

With the aim of examining the possibility of the use of compounds **5—8**, we studied their electrochemical properties. In particular, electrochemical reduction on a glassy-carbon electrode in an *o*-dichlorobenzene (DCB)—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 system was studied by cyclic voltammetry.

Electrochemical reduction of fullerenopyrrolidines **7** and **8** proceeds analogously to reduction of the representatives of this class of [60]fullerene derivatives studied earlier.[13,14] The cyclic voltammograms show three reduction peaks as well as three conjugated oxidation peaks on the reverse scan (Table 1, Fig. 3). The heights of the reduction peaks correspond to the one-electron level. The

Table 1. Cyclic voltammetric data (reduction peak potentials ($E_{p,red}$) and oxidation peak potentials ($E_{p,ox}$)) for electrochemical reduction of C_{60} and fullerenopyrrolidines **5—8** in an DCB—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 solution system on a glassy-carbon electrode*

Compound	$-E^1_{p,red}$	$-E^1_{p,ox}$	$-E^2_{p,red}$	$-E^2_{p,ox}$	$-E^3_{p,red}$	$-E^3_{p,ox}$	$-E^4_{p,red}$	$-E^4_{p,ox}$
	V							
C_{60}	0.96	0.90	1.40	1.33	1.90	1.84	2.39	2.32
5	1.08	1.02	1.51	1.45	2.10	2.02	2.33	2.27
6	1.06	1.00	1.49	1.43	2.09	2.00	2.32	2.26
7	1.09	1.02	1.53	1.46	2.10	2.04	—	—
8	1.09	1.02	1.53	1.46	2.10	2.03	—	—

* The potentials were measured relative to the standard potential of the Fc^+/Fc redox system with the use of Ag/0.01 *M* $AgNO_3$ solution in MeCN as the reference electrode at a potential scan rate of 20 mV s^{-1}.

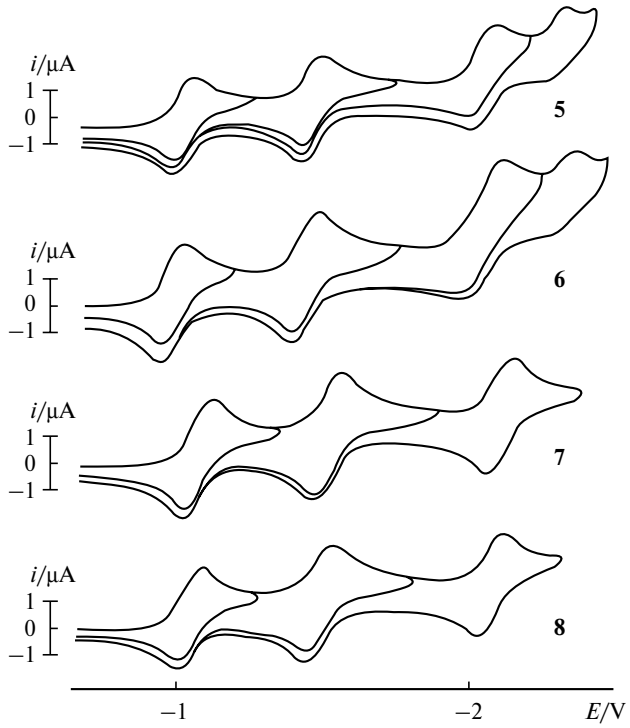


Fig. 3. Cyclic voltammograms of fullerenopyrrolidines **5—8** recorded on a glassy-carbon electrode in an DCB—DMF (3 : 1, v/v)/Bu_4NBF_4 system (C = 0.1 mol L^{-1}) at a potential scan rate of 20 mV s^{-1}, T = 295 K, and $C = 1 \cdot 10^{-3}$ mol L^{-1}.

difference between the reduction peak potentials and the corresponding oxidation peaks is equal to the theoretical value for the reversible one-electron transfer[17]

$$\Delta E_p = E_{p,ox}{}^m - E_{p,red}{}^m \approx 60 \text{ mV},$$
$$m = 1—3.$$

Consequently, fullerenopyrrolidines **7** and **8** reversibly and stepwise accept three electrons per molecule to form finally the radical trianions in the accessible potential region (Scheme 3).

Scheme 3

$$A + e \overset{E^1_{p,red}}{\rightleftharpoons} A^{\bullet -} + e \overset{E^2_{p,red}}{\rightleftharpoons} A^{2-} + e \overset{E^3_{p,red}}{\rightleftharpoons} A^{3\bullet -}$$

The cyclic voltammograms of compounds **5** and **6** have four reduction peaks. The first two reduction steps are identical to reduction of fullerenopyrrolidines **7** and **8**. The stepwise reversible two-electron transfer to the fullerene cage giving rise to stable radical anions and dianions was observed. The potential of the third step also corresponds to the third electron transfer to the fullerene cage of fullerenopyrrolidines. However, unlike fullerenopyrrolidines **7** and **8**, the radical trianions of compounds **5** and **6** are unstable. Hence, the anodic oxidation peaks of the latter compounds are lower than those of compounds **7** and **8** at the reverse potential sweep from the third reduction peak. Yet another characteristic feature of the third reduction peak is that it is higher than the one-electron level. The ratio of the height of the third peak to the height of the first peak (H) increases with decreasing potential scan rate, which is indicative of the kinetic nature of the peak current.

Compound	H at a potential scan rate/mV s^{-1}		
	20	50	100
5	1.3	1.1	1.0
6	1.7	1.2	1.1

Evidently, slow chemical reactions proceed in the radical trianions to give species electrochemically active in this potential region. The radical trianion of fullerenopyrrolidine **7**, which contains an analogous thiophosphonate group but in which the benzaldehyde group is absent, is stable. Consequently, the possibility of subsequent chemical reactions in the radical trianions of compounds **5** and **6** is associated with the simultaneous presence of the thiophosphonate and benzaldehyde fragments. The absence of the fourth peak for compounds **7** and **8** and its presence for fullerenopyrrolidines **5** and **6** is unambiguous evidence that this reduction peak is associated with the electron transfer to the benzaldehyde fragment. The thiophosphonate fragment possesses the electron-withdrawing properties, thus facilitating the electron transfer.

It is known[18] that aryl phosphates are electrochemically efficiently reduced not only at an electrode but also homogeneously by organic electron carriers. This process is accompanied by the two-electron irreversible C—O bond cleavage to form the phosphate ion and arenes. Analogously, it can be assumed that electrochemical reduction of compounds **5** and **6** is accompanied by the slow intramolecular electron transfer from the radical trianion of the fullerene cage to the thiophosphonate fragment facilitated by the presence of the electron-withdrawing benzaldehyde group. This process is responsible for an increase in the hight of the third reduction peak relative to the one-electron level and consumption of the radical trianions.

Consequently, the stepwise three-electron transfer to the fullerene cage gives rise to stable radical anions, dianions, and unstable radical trianions. The radical trianions of bis-fullerenopyrrolidines, in which the thiophosphonate group is absent, are quite stable.

Therefore, the presence of the thiophosphonate and thiophosphate groups in the molecule has no effect on electrochemical reduction of fullerenopyrrolidines **7** and **8**. The presence of the thiophosphonate and/or benzaldehyde groups in compounds **5** and **6** is responsible for the specific features of their behavior in particular reduction

steps. At the same time, the transfer of the first three electrons to the fullerene cage occurs in all cases, and the properties typical of monofullerenopyrrolidines are observed in these steps.

It is more difficult to reduce fullerenopyrrolidines **5—8** than [60]fullerene. The first peak of monoadducts **5—8** is shifted to more cathodic potentials by 100—130 mV. The differences between the potentials of the second electron transfer are approximately equal to the above values. The difference in the potentials of the third reduction peaks is more substantial. These results mean that the distortion of the overall conjugation π-system of fullerene C_{60} by introducing the pyrrolidine ring decreases the electron affinity of the compound.

We studied the structure of fullerenopyrrolidine **7** by density functional theory with the use of the nonempirical exchange-correlation potential[19] and the triple-zeta basis set DFT/PBE/TZ2P using the PRIRODA program package.[20] According to the calculations, the pyrrolidine ring adopts an *N*-envelope conformation. The methyl group deviates toward the C—H bond of the pyrrolidine ring. The plane of the benzene ring is perpendicular to that of the pyrrolidine ring. Depending on the C—O—P=S torsion angle, which characterizes internal rotation of the thiophosphoryl group relative to the plane of the benzene ring about the P—O bond, the molecule adopts two stable conformations referred to as **A** and **B** (Fig. 4). The major structure **A** is characterized by the deviation of the P=S bond toward the fullerene cage. The total (E) and relative (ΔE) energies, the dipole moments (μ), the C—O—P=S torsion angles (τ), and the P=S bond lengths ($d_{P=S}$) for the conformers **A** and **B** of compound **7** calculated by the DFT/PBE/TZ2P method are given below.

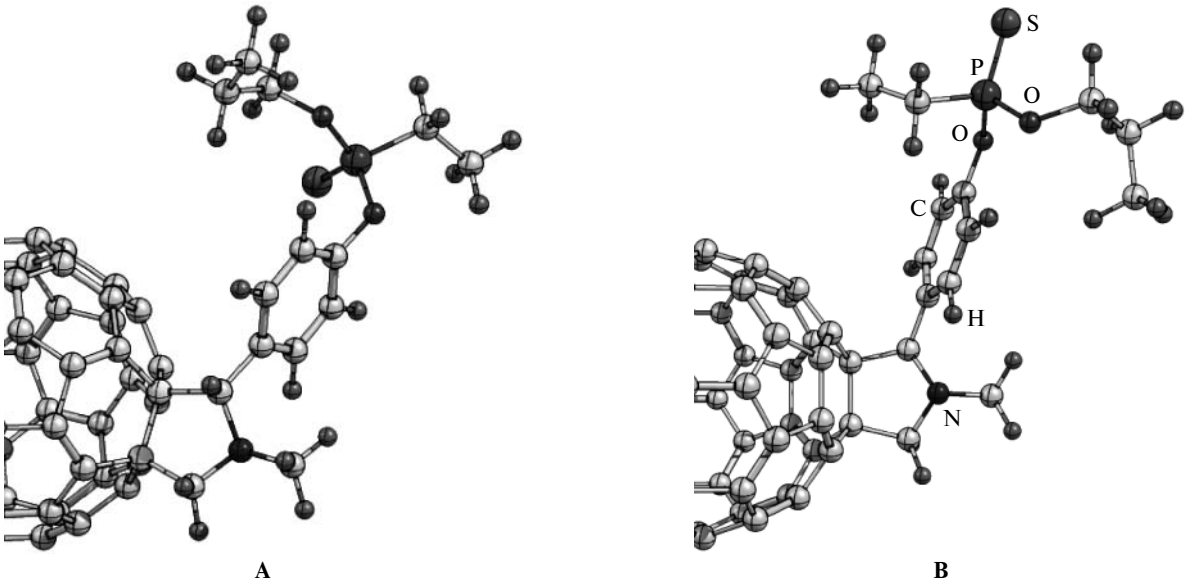
Conformer	E /au	ΔE /kcal mol^{-1}	μ/D	τ /deg	$d_{P=S}$ /Å
A	−3774.88773	0.00	5.92	−47	1.951
B	−3774.88377	2.48	3.89	165	1.944

The preferable structure **A** is more polar compared to the conformer **B**. The dipole moment calculated for the conformation **A** is equal to the experimental value (5.3 D).[21]

Experimental

Analysis by HPLC was carried out on a Gilson chromatograph equipped with an UV detector (C_{18} reversed-phase column (Partisil-5 ODS-3); toluene—MeCN, 1 : 1, v/v, as the eluent). The organic solvents were dried and distilled before use. Fullerene C_{60} of 99.9% purity (produced by the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod) was used. The starting thiophosphorylated aldehydes and dialdehydes **1—4** were prepared according to known procedures.[22,23] All chemical operations were carried out under dry argon.

The UV spectra were recorded on a Specord M-40 spectrophotometer in CH_2Cl_2. The IR spectra were measured on a Bruker Vector 22 Fourier-transform spectrometer (KBr pellets). The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker MSL-400 (400.00 MHz for ^{1}H, 162.0 MHz for ^{31}P, and 100.6 MHz for ^{13}C) and Bruker Avance-600 (600 MHz for ^{1}H) spectrometers at 30 °C. The 1D DEPT, 2D COSY, 2D HSQC, and 2D HMBC experiments were performed on a Bruker Avance-600 spectrometer. The chemical shifts were measured relative to the signals for the residual protons of the deuterated solvent or the carbon nuclei of $CDCl_3$ (^{1}H and ^{13}C, respectively) or relative to 85% H_3PO_4 (^{31}P) as the external standard. The mass spectra were obtained on a MALDI-TOF MS in-



A **B**

Fig. 4. Stereo view of the conformations **A** and **B** of compound **7** according to calculations by the DFT/PBE/TZ2P method.

strument (DynamoThermo-BioANALYSIS) using trihydroxyanthracene as the matrix.

Cyclic voltammograms were recorded on a PI-50-1 potentiostat equipped with an H307/2 X-Y recorder. A glassy-carbon disk electrode (d = 2 mm) pressed into glass served as a working electrode. A platinum wire was used as an auxiliary electrode. Before each measurement, the electrodes were subjected to mechanical polishing. The potentials were measured relative to the standard potential of the ferrocene—ferrocenium ion redox system (Fc/Fc^+) using an $Ag/AgNO_3$ silver reference electrode (0.01 mol L^{-1}) in MeCN. Dissolved oxygen was removed by bubbling nitrogen through the solution at 295 K. Quantum chemical calculations were carried out using the PRIRODA program[19,20] (DFT).

Bis-*O*,*O*-(4-formylphenyl) methylthiophosphonate (1). A solution of 4-hydroxybenzaldehyde (4 g, 0.0164 mol) in THF was added dropwise to a suspension of NaH (1.0 g, 0.042 mol) in THF at 10 °C. The reaction mixture was stirred at ~20 °C for 40 min. Then a solution of methylthiophosphonic acid dichloride (2.4 g, 0.0161 mol) in THF was added dropwise. The reaction mixture was stirred for 12 h and extracted with $CHCl_3$. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt—hexane, 1 : 3, as the eluent). Compound **1** was obtained in a yield of 3.1 g (60%) as white crystals, m.p. 89—90 °C. Found (%): C, 56.30; H, 4.10; P, 9.63; S, 10.02. $C_{15}H_{13}O_4PS$. Calculated (%): C, 56.25; H, 4.09; P, 9.65; S, 10.01. IR, ν/cm^{-1}: 622, 649, 706, 729, 799, 830, 904, 1010, 1103, 1157, 1211, 1304, 1391, 1422, 1501, 1597, 1700, 2922. ^{31}P NMR ($CDCl_3$), δ: 92.16. ^{1}H NMR ($CDCl_3$), δ: 2.25 (d, 3 H, J = 15.9 Hz); 7.27 and 7.29 (both dd, 4 H, H arom., J = 2.5 Hz, J = 8.5 Hz); 7.87 and 7.99 (both d, 4 H, H arom., J = 8.5 Hz); 9.96 (s, 2 H, C(O)H)).

Bis-*O*,*O*-(4-formylphenyl) phenylthiophosphonate (2). Compound **2** was synthesized analogously as white crystals, m.p. 93—95 °C, in a yield of 4.5 g (83%) from NaH (0.9 g, 0.01 mol), 4-hydroxybenzaldehyde (4.2 g, 0.0098 mol), and phenylthiophosphonic acid dichloride (3.0 g, 0.008 mol) followed by purification by silica gel column chromatography (AcOEt—hexane, 1 : 3, as the eluent). Found (%): C, 62.96; H, 3.81; P, 8.03; S, 8.21. $C_{20}H_{15}O_4PS$. Calculated (%): C, 62.83; H, 3.95; P, 8.10; S, 8.39. IR, ν/cm^{-1}: 606, 655, 693, 711, 730, 753, 768, 836, 850, 910, 950, 970, 1014, 1123, 1156, 1190, 1207, 1222, 1296, 1393, 1423, 1438, 1501, 1588, 1706, 2362, 2823. ^{31}P NMR ($CDCl_3$), δ: 82.60. ^{1}H NMR ($CDCl_3$), δ: 7.27 and 7.29 (both dd, 4 H, H arom., J = 1.3 Hz, J = 8.5 Hz); 7.87 and 7.99 (both d, 4 H, H arom., J = 8.5 Hz); 7.59 and 8.10 (both m, H arom.); 9.93 (s, 2 H, C(O)H).

***O*-(4-Formylphenyl) *O*-propyl ethylthiophosphonate (3).** Compound **3** was synthesized as a viscous yellow oil in a yield of 1.9 g (87%) according to the above-described procedure from NaH (0.25 g, 0.01 mol), 4-hydroxybenzaldehyde (1.2 g, 0.0098 mol), and *O*-propylethylthiophosphonic acid chloride (1.5 g, 0.008 mol) followed by purification by silica gel column chromatography. Found (%): C, 52.61; H, 6.02; P, 11.03; S, 11.52. $C_{12}H_{17}O_3PS$. Calculated (%): C, 52.93; H, 6.29; P, 11.37; S, 11.78. IR, ν/cm^{-1}: 643, 742, 822, 936, 1020, 1099, 1123, 1222, 1502, 1704, 2925. ^{31}P NMR ($CDCl_3$), δ: 100.30. ^{1}H NMR ($CDCl_3$), δ: 0.92 (t, 3 H, Pr^n); 1.22 (t, 3 H, Me); 1.31 (t, 2 H, CH_2); 2.18 (m, 2 H, CH_2); 3.98 and 4.13 (both m, 2 H, Pr^n); 7.13 and 7.29 (both dd, 2 H, H arom., J = 9.6 Hz, J = 17.9 Hz); 7.81 and 7.86 (both d, 2 H, H arom., J = 8.5 Hz); 9.91 (s, 1 H, C(O)H).

***O*,*O*-Diethyl *O*-(4-formylphenyl) thiophosphate (4).** Under the conditions described above for the synthesis of compounds **1—3**, compound **4** was synthesized as a viscous yellow oil in a yield of 2.8 g (41%) from NaH (0.5 g, 0.0208 mol), 4-hydroxybenzaldehyde (2.1 g, 0.017 mol), and *O*,*O*-diethylthionophosphonic acid chloride (3 g, 0.016 mol). Found (%): C, 47.95; H, 5.32; P, 10.06; S, 11.54. $C_{11}H_{15}O_4PS$. Calculated (%): C, 48.18; H, 5.51; P, 11.29; S, 11.68. IR, ν/cm^{-1}: 647, 740, 822, 926, 1023, 1099, 1160, 1220, 1504, 1599, 1704, 2986. ^{31}P NMR ($CDCl_3$), δ: 58. ^{1}H NMR ($CDCl_3$), δ: 1.32 (t, 6 H); 4.17 and 4.23 (both m, 4 H); 7.26 and 7.81 (both dd, 4 H, H arom.); 9.93 (s, 1 H, C(O)H).

1-{4-[*O*-(4-Formylphenyl)methylthiophosphonoxy]phenyl}-*N*-methyl[60]fullereno[1,2-*c*]pyrrolidine (5). A solution of fullerene C_{60} (0.216 g, 0.3 mmol), *N*-methylglycine (0.080 g, 0.9 mmol), and compound **1** (0.144 g, 0.45 mmol) was refluxed in toluene (200 mL) under argon for 15 h. The reaction mixture was washed with water (2×30 mL) and concentrated *in vacuo*. The product was isolated by silica gel column chromatography (hexane—toluene, 1 : 1, as the eluent). Compound **5** was obtained in a yield of 0.0733 g (34% based on consumed C_{60}). UV, λ_{max}/nm (ε): 258 (45000), 326 (13000), 431.2 (1800), 696 (280). IR, ν/cm^{-1}: 524, 573, 598, 643, 748, 796, 832, 905, 1014, 1099, 1122, 1155, 1189, 1295, 1329, 1422, 1460, 1498, 1593, 1656, 1700, 2777, 2853, 2924, 3429. ^{31}P NMR (CS_2—$CDCl_3$), δ: 89.96. ^{1}H NMR (CS_2/$CDCl_3$), δ: 2.20 (dd, 3 H, P(S)Me, J = 15.4 Hz, J = 1.8 Hz); 2.84 (s, 3 H, NMe); 4.96 (s, 1 H, CH of pyrrolidine); 4.30, 5.00 (both d, 2 H, CH_2 of pyrrolidine, J = 9.2 Hz); 7.20 and 7.23 (both d, 4 H, H arom., J = 8.8 Hz); 7.81 (d, 4 H, H arom., J = 8.1 Hz); 9.94 (s, 1 H, C(O)H). ^{13}C NMR (CS_2—$CDCl_3$), δ: 22.00 (P(S)Me); 39.71 (s, NMe); 68.57 (C(1)); 69.73 (C(61)); 76.75 (C(6)); 82.50 (C(62)); 121.66 (C(2′, C(6′)); 122.05 (C(2″), C(6″)); 130.16 (C(3′), C(5′)); 130.84 (C(3″), C(5″)); 133.45 (C(4″)); 134.09 (C(4′)); 135.41; 135.68; 136.21; 136.67; 139.19; 139.72; 139.99; 141.30; 141.43; 141.53; 141.60; 141.69; 141.78; 141.89; 141.96; 142.35; 142.77; 142.91; 144.30; 144.44; 145.05; 145.34; 145.42; 145.86; 146.04; 146.19; 147.02; 150.00 (d, C(1′), $^2J_{C,P}$ = 9.7 Hz); 152.48 (C(7)); 152.68 (C(5)); 153.41 (C(10)); 154.57 (d, C(1″), $^2J_{C,P}$ = 9.7 Hz); 188.86 (C(O)H). MALDI-TOF MS, found: m/z 1067.75 $[M]^+$. $C_{77}H_{18}NO_3PS$. Calculated: M = 1067.99.

1-{4-[*O*-(4-Formylphenyl)phenylthiophosphonoxy]phenyl}-*N*-methyl[60]fullereno[1,2-*c*]pyrrolidine (6). Under the conditions described above for the synthesis of fullerenopyrrolidine **5**, compound **6** was prepared from fullerene C_{60} (0.216 g, 0.3 mmol), compound **2** (0.1375 g, 0.36 mmol), and *N*-methylglycine (0.080 g, 0.9 mmol) in toluene (200 mL) in a yield of 0.035 g (14% based on consumed C_{60}). UV, λ_{max}/nm (ε): 255.8 (46200), 326 (11000), 429.8 (2100), 697 (310). 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 ($CDCl_3$), δ: 2.80 (s, 3 H, NMe); 4.93 (s, 1 H, CH of pyrrolidine); 4.26 and 4.98 (both d, 2 H, CH_2 of pyrrolidine, J = 9.2 Hz); 7.15 and 7.27 (both d, 4 H, H arom., J = 8.8 Hz); 7.52—8.08 (m, 5 H, Ph); 7.83 (d, 4 H, H arom.); 9.98 (s, 1 H, C(O)H). ^{13}C NMR ($CDCl_3$), δ: 39.98 (s, NMe); 68.96 (C(1)); 69.96 (C(61)); 77.12 (C(6)); 82.75 (C(62)); 122.30 (C(2′), C(6′)); 125.27 (C(2″), C(6″)); 128.19 (C(3′), C(5′)); 128.62 (C(3‴), C(5‴), $^2J_{C,P}$ = 15.8 Hz); 129.00 (C(3″), C(5″)); 131.55 (C(2‴), C(6‴), $^2J_{C,P}$ = 12.2 Hz); 132.41 (C(1‴));

133.26 (C(4‴), $^2J_{C,P}$ = 3.1 Hz); 133.50 (C(4″)); 134.46 (C(4´)); 136.20; 137.10; 138.60; 139.00; 139.20; 139.50; 140.00; 140.90; 141.10; 141.30; 141.40; 141.50; 141.60; 141.70; 141.90; 142.00; 142.30; 142.60; 143.30; 143.50; 143.60; 143.80; 144.00; 144.50; 144.60; 144.70; 144.80; 145.10; 145.22; 145.44; 145.60; 145.70; 145.80; 146.00; 146.50; 149.59; 150.36 (d, C(1´), $^2J_{C,P}$ = 9.7); 153.06 (C(7)); 153.09 (C(5)); 153.83 (C(10)); 155.22 (d, C(1″), $^2J_{C,P}$ = 9.7 Hz); 156.16 (C(2)); 190.10 (C(O)H). MALDI-TOF MS, found: *m/z* 1129.98 $[M]^+$. $C_{82}H_{20}NO_3PS$. Calculated: M = 1130.07.

***N*-Methyl-1-{4-[(*O*-propyl)ethylthiophosphonoxy]phenyl}[60]fullereno[1,2-*c*]pyrrolidine (7).** A solution of fullerene C_{60} (0.216 g, 0.3 mmol), compound **3** (0.167 g, 0.6 mmol), and *N*-methylglycine (0.080 g, 0.9 mmol) in toluene (200 mL) was refluxed under argon for 17 h. The reaction mixture was washed with water (2×30 mL) and concentrated *in vacuo*. The product was isolated by silica gel column chromatography (hexane—toluene—MeCN, 1 : 2 : 0.5, as the eluent). Compound **7** was obtained in a yield of 0.101 g (40% based on consumed C_{60}). UV, λ_{max}/nm (ε): 256 (45800), 326 (12000), 431.6 (1900), 696 (290). IR, ν/cm^{-1}: 525, 753, 782, 842, 906, 989, 1215, 1502. ^{31}P NMR (CS_2—$CDCl_3$), δ: 100.00. ^{1}H NMR (CS_2—$CDCl_3$), δ: 0.89 (dd, 3 H, *J* = 7.3 Hz, *J* = 3.0 Hz); 1.61 (t, 3 H, Et, *J* = 7.3 Hz); 2.10 and 2.16 (both q, 4 H, *J* = 7.3 Hz, *J* = 7.9 Hz); 2.83 (s, 3 H, NMe); 3.90 (s, 1 H, CH of pyrrolidine); 4.06 (d, 2 H, *J* = 10.1 Hz); 4.29 and 4.96 (both s, 1 H each, CH_2 of pyrrolidine); 7.28 (d, 2 H, H arom., *J* = 21.2 Hz); 7.77 (br.s, 2 H, H arom.). ^{13}C NMR (CS_2—$CDCl_3$), δ: 7.03; 10.16; 23.73; 28.40; 39.89 (NMe); 68.80; 68.57 (C(1)); 69.83; 76.73 (C(6)); 82.86, 121.86, 130.22, 133.26, 135.81 (C arom.); 136.57; 136.82; 139.52; 139.89; 140.14; 140.18; 141.53; 141.69; 141.81; 141.97; 142.05; 142.10; 142.15; 142.18; 142.27; 142.29; 142.57; 142.59; 142.69; 143.00; 143.10; 143.16; 144.38; 144.41; 144.60; 144.73; 145.15; 145.21; 145.25; 145.29; 145.32; 145.35; 145.46; 145.55; 145.79; 145.94; 146.01; 146.09; 146.21; 146.25; 146.29; 146.35; 146.39; 146.47; 146.65; 147.39; 153.05; 153.20. MALDI-TOF MS, found: *m/z* 1019.43 $[M]^+$. $C_{74}H_{22}NO_2PS$. Calculated: M = 1020.02.

1-[4-(*O*,*O*-Diethylthiophosphoxy)phenyl]-*N*-methyl[60]fullereno[1,2-*c*]pyrrolidine (8). Under the conditions described above for the synthesis of compound **7**, compound **8** was prepared from fullerene C_{60} (0.216 g, 0.3 mmol), *N*-methylglycine (0.080 g, 0.9 mmol), and compound **4** (0.165 g, 0.6 mmol) in a yield of 0.088 g (31% based on consumed C_{60}). UV, λ_{max}/nm (ε): 258 (43700), 327 (13500), 430 (1700), 696 (300). IR, ν/cm^{-1}: 526, 744, 794, 802, 917, 1109, 1164, 1214, 1455, 1504, 1652. ^{31}P NMR ($CDCl_3$), δ: 61.9. ^{1}H NMR ($CDCl_3$), δ: 1.31 (t, 6 H); 2.81 (s, 3 H, NMe); 4.19 and 4.21 (both m, 4 H); 4.27 and 4.97 (both d, 2 H, CH_2 of pyrrolidine); 4.93 (s, 1 H, CH of pyrrolidine); 7.25 (d, 2 H, H arom.); 7.79 (br.s, 2 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 15.93; 40.03 (s, NMe); 65.15; 68.96 (C(1)); 69.92; 72.64 (C(6)); 82.87, 121.22, 130.39, 135.72, 135.91 (C arom.); 136.59; 136.97; 139.53; 139.94; 140.23; 140.27; 141.60; 141.75; 141.87; 141.98; 142.07; 142.11; 142.16; 142.22; 142.29; 142.61; 142.64; 142.76; 143.07; 143.21; 144.43; 144.47; 144.66; 144.78; 145.24; 145.29; 145.31; 145.35; 145.40; 145.42; 145.46; 145.58; 145.63; 145.81; 146.01; 146.09; 146.19; 146.21; 146.25; 146.28; 146.34; 146.38; 146.47; 146.65; 147.39; 153.04; 153.21; 153.95; 156.16. MALDI-TOF MS, found: *m/z* 1021.71 $[M]^+$. $C_{73}H_{20}NO_3PS$. Calculated: M = 1021.99.

1-[4-(*P*-Ethyl-*P*-methylthiophosphonoxy)phenyl]-*N*,*N*-dimethyl[60]fullereno[1,2-*c*]pyrrolidinium iodide (9). A mixture of fullerenopyrrolidine **7** (0.030 g, 0.00003 mol) and MeI (0.3 mL, 0.005 mol) was heated in a sealed tube to 70—80 °C for 28 h. Then the precipitate was filtered off and washed with toluene. Compound **9** was obtained in a yield of 0.025 g (76%). IR, ν/cm^{-1}: 526, 747, 849, 909, 972, 1174 (P=O), 1216, 1427, 1459, 1507, 2924, 3444. ^{31}P NMR (DMSO-d_6), δ: 60.85. ^{1}H NMR (DMSO-d_6), δ: 1.22 (3 H, CH_3 (Et)); 2.27 (2 H, CH_2 (Et)); 2.29 (3 H, PSMe); 3.83 and 4.22 (6 H, NMe_2); 7.27 (s, 1 H, CH of pyrrolidine); 5.78 and 6.04 (both s, 2 H, CH_2 of pyrrolidine); 7.52 (d, 2 H, H arom.); 8.11 (br.s, 2 H, H arom.). ^{13}C NMR (DMSO-d_6), δ: 5.80; 11.27; 18.20; 46.42, 52.35 (NMe_2); 67.11 (C(1)); 72.64 (C(6)); 73.26, 83.33, 121.38, 122.33, 134.94, 146.25 (C arom.); 137.05; 139.15; 139.57; 140.55; 140.68; 140.95; 141.05; 141.36; 141.53; 141.97; 142.06; 142.17; 142.39; 143.65; 143.91; 144.42; 144.47; 144.64; 144.77; 144.88; 144.95; 145.04; 145.35; 145.49; 145.65; 146.02; 148.85; 150.46; 150.96; 152.98. MALDI-TOF MS, found: *m/z* 720.00 (C_{60}), 990.73 ($[M]^+$ – MeI). $C_{73}H_{21}INO_2PS$. Calculated: M = 1132.74.

We thank N. P. Evlampieva for measuring the dipole moment of compound **7**.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32900, 03-03-96248rTatarstan, 04-03-32287, and 05-03-32633) and the Academy of Sciences of the Republic of Tatarstan.

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Received February 4, 2005;
in revised form February 17, 2006