Modification of fullerene C₆₀ by phosphorylated diazo compounds

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New representatives of phosphorylated methanofullerenes were prepared by the reactions of [60]fullerene with O,O-diethyl α -diazoethyl- and O,O-diethyl α -diazobenzylphosphonates. Electrochemical reduction of the above-mentioned products proceeded stepwise and reversibly.

Key words: [60]fullerene, O,O-diethyl α -diazoethyl- and O,O-diethyl α -diazobenzylphosphonates, phosphorylated methanofullerenes, electrochemistry, quantum-chemical calculations.

The modification of fullerenes by diazo compounds is one of procedures most widely used for fixing various organic fragments at the carbon skeleton of fullerenes.¹ It is assumed that a combination of hydrophilic phosphorus-containing groups and hydrophobic fullerene fragments in one molecule can lead to the construction of new phospholipid substances.² It should be noted that all known phosphorylated derivatives of fullerene C_{60} , are 6,6-closed adducts regardless of the procedure for their preparation.²⁻¹² In the reaction of C_{60} with O,O-dimethyl diazomethylphosphonate,⁸ an adduct was detected, which is, most probably, a 5,6-open adduct (or homofullerene). However, this adduct was not isolated in individual form. We studied the reaction of C_{60} with O,O-diethyl α -diazoethyl- (1) and O,O-diethyl α -diazobenzylphosphonates (2). It was of interest to reveal the influence of the substituent at the α -carbon atom of phosphonate on the structures of the resulting adducts.

Several HPLC peaks (C18 reversed-phase column) were observed in the mixture prepared by the reaction of C_{60} with α -diazoethylphosphonate **1** in toluene (110 °C, 4-5 h). Based on the retention times, the main peak in the chromatogram (5.2 min) can be assigned to the monoadduct and the remaining low-intensity peaks are attributable to unconsumed [60]fullerene (6.3 min) and polyadducts (3.8, 4.2, 5.8, and 6.7 min). The unconsumed fullerene was separated by column chromatography to give a fraction containing three products, as demonstrated by HPLC (normal-phase column) and NMR spectroscopy. The ${}^{31}P - {}^{1}H$ NMR spectra (CDCl₂) have three signals (δ 26.00, 20.62, and 20.04) in the region characteristic of phosphonates. The ¹H and ¹³C NMR spectra of this fraction also show three sets of signals for the hydrogen atoms of the methyl groups and ethoxy substituents at the phosphorus atom. The ${}^{13}C-{}^{1}H$ NMR spectrum has three broadened singlets at δ 15.93, 16.14, and 16.96,

three doublets at δ 17.02 (${}^{3}J_{P,C} = 5.1 \text{ Hz}$), 16.88 (${}^{3}J_{P,C} = 3.3 \text{ Hz}$), and 17.27 (${}^{3}J_{P,C} = 2.0 \text{ Hz}$) and also at δ 63.63 (${}^{2}J_{P,C} = 6.0 \text{ Hz}$), 63.46 (${}^{2}J_{P,C} = 4.6 \text{ Hz}$), and 63.97 (${}^{2}J_{P,C} = 5.0 \text{ Hz}$) and 63.97 7.9 Hz). In addition, the spectra have signals at δ 138–148 corresponding to the carbon atoms of the fullerene sphere, which indicates that the fraction under study consists of a mixture of three fullerene-containing adducts. Since we failed to separate these adducts by column chromatography, their mixture was heated in o-dichlorobenzene (o-DCB) at 140 °C until only one signal at δ 19.65 persisted in the ³¹P NMR spectrum (o-DCB) and only one peak was observed in the HPLC chromatogram (normalphase column). o-Dichlorobenzene was removed in vacuo and the resulting dark-brown powdered compound was identified by physicochemical methods. The laser-desorption mass spectrum of this compound has peaks at m/z 884, 907, and 923. The first peak corresponds to the monoadduct of fullerene with diazo compound 1 with a loss of the dinitrogen molecule and the remaining two peaks correspond to the sodium and potassium salts of this monoadduct, respectively. The elemental analysis data are also indicative of this monoadduct. The ³¹P NMR spectrum of this compound (in CDCl₂) has a signal at δ 20.00, whose chemical shift is identical with that of the most intense signal in the initially isolated mixture of adducts (§ 20.04). The IR spectrum shows a high-intensity band at 526 cm⁻¹ characteristic of [60]fullerene monoadducts. The UV spectrum has a band at 424 nm indicative of the formation of the 6,6-closed monoadduct. All the above data provide evidence that the compound synthesized is an individual monoadduct 3 with the methano[1,2][60]fullerene structure. The NMR spectroscopic studies completely confirmed this conclusion.

Theoretically,¹³ based on the C_s symmetry of the molecule (the symmetry plane is perpendicular to the bond between two sp³-hybridized carbon atoms), the fullerene

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sphere in adduct **3** should be characterized by $31 \, {}^{13}$ C NMR signals (4 signals with an intensity of 1C each and 27 signals with an intensity of 2C each) for the sp²-hybridized carbon atoms and one 13 C NMR signal (with an intensity of 2C) for the sp³-hybridized carbon atoms of the cyclopropane fragment. The latter signal is generally observed at δ 60–80 and the signals for the sp²-hybridized carbon atoms are observed at δ 134–148.^{10,11}

In reality, the fullerene sphere of adduct 3 is characterized (Table 1) by 27 13 C NMR signals at δ 138–148 (25 signals with an intensity of 2C each and 2 signals with an intensity of 4 C each), which is attributed to the random superposition of the signals, and also by a doublet at δ 74.41 with $J_{P,C} = 2.1$ Hz. The presence of the phosphorus atom made it possible to identify signals for some carbon atoms of the fullerene sphere. Thus, the signals at δ 147.21 and 147.66 have $J_{P,C} = 5.3$ and $J_{P,C} = 4.2$ Hz, respectively, and these signals, most likely, belong to the sp²-hybridized carbon atoms directly bound to the sp³-hybridized carbon atoms of the sphere. The signal for the exohedral carbon atom of the cyclopropane fragment (C(61)) is observed at δ 35.90 ($J_{P,C} = 180$ Hz). In the proton-decoupled ¹³C NMR spectrum, two equivalent ethoxy fragments at the phosphorus atom are characterized by two doublets at δ 63.41 ($J_{P,C} = 7$ Hz) and 16.80 $(J_{P,C} = 5.3 \text{ Hz})$. Since the ¹³C NMR spectrum of the starting diazophosphonate 1 (see Table 1) has a signal of the methyl group at the α -carbon atom as a doublet with $J_{P,C} = 8.3$ Hz, the signal of the methyl group at C(61) in the spectrum of adduct **3** should also be characterized by a doublet. However, the ¹³C-{¹H} NMR spectrum has a singlet at δ 15.68 rather than a doublet due, apparently, to a small constant of spin-spin coupling between the carbon atom of the methyl group and the phosphorus atom.

The ¹H NMR spectrum of adduct **3** (Table 2) confirms the equivalence of two ethoxy groups at the phosphorus atom and the presence of the methyl substituent at the C(61) atom.

Therefore, the results of physicochemical studies indicate that O,O-diethyl α -methyl(methano[1,2][60]fullerenyl)phosphonate (**3**) is the most thermally stable product of the reaction of C₆₀ with diazophosphonate **1**. The reaction proceeds through the formation of two intermediates, which are transformed into adduct **3** upon heating.

According to the data from HPLC and ³¹P NMR spectroscopy, the reaction of C_{60} with diazophosphonate **1** in *o*-DCB at 140 °C for 3 h afforded the same mixture of adducts as that prepared by the reaction in toluene at 110 °C. An increase in the temperature of heating to 180 °C (3 h) also led to the formation of adduct **3**.

According to the scheme of dipolar cycloaddition of diazo compounds to C_{60} ,¹⁴ the reaction under consideration can proceed through the intermediate formation of fullerenopyrazoline **4** or homofullerenes **5** and **6** (Scheme 1). Taking into account the reaction temperature (higher than 60 °C), homofullerenes **5** and **6**, which

3 C atom 1 2 7 $\underline{C}H_3 - C - P$ 9.06 15.68 (q, ${}^{1}J_{C,H} = 132.5$, d, ${}^{2}J_{P,C} = 8.3$) $(q, {}^{1}J_{C,H} = 130.5,$ d, ${}^{2}J_{\rm P,C} = 0.0$) CH₃CH₂O 16.30 16.33 16.80 16.83 $(q, {}^{1}J_{C,H} = 126.9,$ $(q, {}^{1}J_{C,H} = 125.5,$ $(q, {}^{1}J_{C,H} = 127.2,$ $(q, {}^{1}J_{C,H} = 127.2,$ d, ${}^{3}J_{\rm P,C} = 5.8$, d, ${}^{3}J_{\rm P,C} = 6.2$, d, ${}^{3}J_{\rm P.C} = 6.9$) d, ${}^{3}J_{\rm P.C} = 5.3$) t, ${}^{2}J_{C,H} = 2.8)$ t, ${}^{2}J_{C,H} = 2.9$) CH3CH2O 62.45 63.10 63.41 64.12 $(t, {}^{1}J_{C,H} = 147.5,$ $(t, {}^{1}J_{C,H} = 149.0,$ $(t, {}^{1}J_{C,H} = 147.4,$ $(t, {}^{1}J_{C,H} = 148.2,$ d, ${}^{2}J_{\rm P,C} = 5.5$, d, ${}^{2}J_{P,C} = 5.6$) d, ${}^{2}J_{P,C} = 6.3$) d, ${}^{2}J_{\rm P,C} = 6.5$, q, ${}^{2}J_{C,H} = 4.2$) q, ${}^{2}J_{C,H} = 4.4$) C_{α} or C(61) 21.42 50.77 35.89 49.02 (d, ${}^{1}J_{P,C} = 226.1$) $(d, {}^{1}J_{P,C} = 136.0)$ $(d, {}^{1}J_{P,C} = 180.0)$ $(d, {}^{1}J_{P,C} = 179.5)$ 2C: 73.65 (d, ${}^{2}J_{P,C} = 2.18$), 2C: 74.41 (d, ${}^{2}J_{P,C} = 2.11$), C₆₀ 138.63, 140.96, 141.10, 141.46, 138.53, 140.97, 141.01, 141.89, 142.43, 142.51, 143.05, 143.26, 142.02, 142.11, 142.44, 142.51, 143.29, 143.37, 143.69, 143.98, 142.97, 143.23, 143.25, 143.41, 144.30, 144.48, 144.86, 144.93, 143.50, 144.08, 144.41, 144.67, 144.98, 145.04, 145.29, 145.38, 144.80, 144.96, 145.04, 145.12, 145.45, 145.59, 145.67, 145.13, 145.39, 145.48, 145.53, 147.21 (d, ${}^{3}J_{P,C} = 5.2$), 145.57, 146.03, 147.66 (d, ${}^{3}J_{P,C} = 4.2$) 146.87 (d, ${}^{3}J_{P,C} = 5.8$), 148.30 (d, ${}^{3}J_{P,C} = 3.6$), 4C: 142.06, 145.51 1C: 144.76, 145.26

Table 1. ¹³C NMR spectra (CDCl₃, δ , J/Hz) of compounds 1–3 and 7

Com- pound		δ, <i>J</i> /Hz		
	CH ₃ (3 H)	Ph (5 H)	$OCH_2C\underline{H}_3$ (6 H)	$OC\underline{H}_2CH_3$ (4 H)
1	1.77 (d, ${}^{3}J_{\rm P,H} = 9.8$)	_	1.26 (t, ${}^{3}J_{\rm H,H} = 7.0$)	4.03 (dq, ${}^{3}J_{PO,CH} = 7.0, {}^{3}J_{H,H} = 7.0$)
2		6.97 (t, H_p , ${}^{3}J_{H,H} = 7.3$); 7.18 (t, H_m , ${}^{3}J_{H,H} = 7.7$); 7.30 (d, H_o , ${}^{3}J_{H,H} = 8.1$)	1.03 (t, ${}^{3}J_{\rm H,H} = 7.3$)	3.86, 4.00 (both dq, ${}^{3}J_{PO,CH} = 10.2$, ${}^{3}J_{H,H} = 7.3$)
3	2.44 (d, ${}^{3}J_{P,H} = 12.4$)		1.55 (t, ${}^{3}J_{\rm H,H} = 7.3$)	4.47 (dq, ${}^{3}J_{PO,CH} = 7.7, {}^{3}J_{H,H} = 7.3$)
7	_	7.49–7.55 (m); 7.96 (ddd, H_o , ${}^{3}J_{H,H} = 7.8$, ${}^{4}J_{H,H} = 2.0$, ${}^{4}J_{P,H} = 1.6$)	1.45 (t, ${}^{3}J_{\rm H,H} = 7.0$)	4.29 (dq, ${}^{3}J_{\text{PO,CH}} = 7.0, {}^{3}J_{\text{H,H}} = 7.0$)

Table 2.	¹ H NMR spectra ((CDCl ₃) of com	pounds 1-3 and 7
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Scheme 1



Reagents and conditions: i. toluene, 110 °C, 4–5 h or o-DCB, 140 °C, 3 h; ii. o-DCB, 180 °C, 4 h.

differ in the arrangement of the phosphonate fragment above the five- or six-membered rings, are the most probable intermediates.

With the aim of preparing thermally less stable adducts 4, 5, and 6, we changed the conditions of the reaction of C_{60} with diazophosphonate 1. Taking into account that the dipolar cycloaddition to olefins proceeds more efficiently in polar solvents, we used *o*-DCB instead of toluene and the reaction temperature was decreased to 25 °C. However, according to the HPLC data, the target adducts were not produced even after stirring of the reagents for four weeks. An increase in the reaction temperature to 50–60 °C also did not afford adducts.

The reaction of C_{60} with *O*,*O*-diethyl α -diazobenzylphosphonate (2) was carried out in a toluene solution both at room temperature (one month) and at the boiling point of the solvent (110 °C, 2–3 h) (Scheme 2). The reaction mixture prepared at 110 °C was chromatographed on a column of silica gel to give unconsumed fullerene, polyadducts, and a fraction, which, unlike the fraction





i. toluene, 110 °C, 2–3 h or 25 °C, 1 month.

formed in the reaction of C_{60} with phosphonate 1, contained (according to the data from HPLC and ³¹P NMR spectroscopy) only product 7. This product was also prepared by the reaction of C_{60} with phosphonate 2 at room temperature. It should be noted that no polyadducts were detected by HPLC in the reaction mixture obtained at room temperature. Dry adduct 7 was prepared as a darkbrown powder. Its structure was established by ³¹P, ¹³C, and ¹H NMR, IR, and UV spectroscopy and mass spectrometry.

According to the mass-spectrometric data, compound 7 is the fullerene monoadduct with diazo compound 2 whose formation was accompanied by liberation of the dinitrogen molecule. The ³¹P NMR spectrum of 7 has one signal at δ 15 characteristic of phosphonates. The IR spectrum of 7 contains a band at 1198 cm⁻¹ characteristic of the P=O group of the phosphonate fragment and a band at 526 cm^{-1} assigned to the fullerene sphere of the monoadduct. The UV spectrum of adduct 7, like that of adduct 3, has a band with $\lambda_{max} = 426 \text{ cm}^{-1}$ characteristic of 6,6-closed adducts. The ¹³C NMR spectrum of adduct 7 (see Table 1) has two doublets at δ 73.68 ($^2J_{CP}$ = 2.2 Hz) and 49.02 (${}^{1}J_{C,P} = 178$ Hz) belonging to the sp³-hybridized carbon atoms of the fullerene sphere and the exocyclic C(61) atom of the cyclopropane fragment, respectively. These data as well as the results of UV spectroscopy are indicative of the methanofullerene structure of adduct 7. In addition, the ¹³C NMR spectrum of adduct 7 has a set of signals at δ from 138 to 148 (28 signals with an intensity of 2C each and 2 signals with an intensity of 1C each) for the sp²-hybridized carbon atoms of the fullerene sphere. According to the C_s symmetry of the molecule, the fullerene sphere of adduct 7 should be characterized by 31 ¹³C signals for the sp²-hybridized carbon atoms (27 signals with an intensity of 2C each and 4 signals with an intensity of 1C each). Apparently, the chemical shifts of two signals with an intensity of 1C each, like those in the spectrum of adduct 3, have close values to an extent that these signals overlap. To refine this question, we carried out quantum-chemical calculations of the chemical shifts of the ¹³C NMR signals for the carbon atoms of the fullerene sphere in adduct 7. The results of these calculations are given in Table 3. The calculations demonstrated that the signals for the individual sp²-hybridized carbon atoms should be observed at δ 144–145 and ~142. The experimental chemical shifts of the signals for the C(27) and C(18) atoms are in good agreement with the calculated data. It should be noted that the real spectrum of adduct 7 has only signals with an intensity of 2C each at δ 141–142, which confirms the assumption that the signals for the C(45) and C(36) atoms overlap. Two signals in the real spectrum of adduct 7 at δ 148.03 and 146.59 have $J_{C,P}$ of 3.6 and 5.8 Hz, respectively, and, hence, they can be assigned to the C(3), C(6) and C(9), C(12) atoms, which are directly bound to the sp³-hybridized carbon atoms of the fullerene sphere. However, it should be noted that the calculated chemical shifts of the signals for these carbon atoms differ substantially from

Table 3. Theoretical (δ_{calc}) and experimental (δ_{exp}) chemical shifts of the signals for the carbon atoms in the ¹³C NMR spectrum of methanofullerene 7



C atom	$\boldsymbol{\delta}_{calc}$	δ_{exp}	C atom	$\boldsymbol{\delta}_{calc}$	δ_{exp}		
1C				1C			
45	142.72	140.07	27	144.36	144.76		
36	142.98	142.97	18	145.22	145.26		
	2	С		2C			
21, 15	138.32	138.53	57, 58	144.34	144.67		
24, 30	138.37	140.97	53, 52	144.44	144.80		
10, 11	139.26	141.01	20, 16	144.49	144.96		
26, 28	140.86	141.89	25, 29	144.68	145.04		
42, 48	140.95	142.02	55, 60	145.22	145.12		
23, 31	141.05	142.11	8,13	145.24	145.13		
39, 33	141.12	142.44	54, 51	145.40	145.39		
19, 17	141.16	142.51	7,14	145.56	145.48		
22, 32	141.91	143.23	56, 59	145.62	145.53		
41, 49	142.24	143.25	44, 46	145.70	145.57		
40, 50	142.29	143.41	37, 35	145.75	146.03		
43, 47	143.36	143.50	3, 6	152.08	146.87 ^a		
38, 34	143.98	144.08	9, 12	153.33	148.30 ^b		
5,4	144.28	144.41					

^{*a*} d, ${}^{3}J_{P,C} = 5.8$ Hz. ^{*b*} d, ${}^{3}J_{P,C} = 3.6$ Hz.

the experimental values. In all other cases, there is a satisfactory agreement between the calculated and experimental data, which made it possible to identify the signals in the experimental ¹³C NMR spectrum of adduct 7.

The ¹³C and ¹H NMR spectra of adduct 7 (see Tables 1 and 2) also confirm the presence of the phenyl fragment and two equivalent ethoxy groups at the phosphorus atom.

Therefore, the reaction of C₆₀ with diazophosphonate 2, like the reaction with diazophosphonate 1, afforded the 6,6-closed adduct, viz., O,O-diethyl α -phenyl(methano[1,2][60]fullerenyl)benzylphosphonate (7). However, it should be emphasized that other homofullerenes were not detected in this reaction at all. In addition, it should be noted that compounds 3 and 7 are thermally very stable. Thus, after refluxing of these compounds in o-DCB for 20 h, even traces of C₆₀ were not detected by HPLC and TLC.



Fig. 1. Cyclic voltammogram of adduct 7.

To reveal the influence of the phosphonate fragment on the electronic structure of the fullerene sphere in methanofullerenes 3 and 7, we studied electrochemical reduction of these compounds by cyclic voltammetry.

Four one-electron reversible reduction peaks were observed in the cyclic voltammograms of methanofullerenes **3** and **7** (Fig. 1, an example for adduct 7). Each peak corresponds to the transfer of one electron to the fullerene sphere giving rise finally to the tetraanion. Compared to the positions of the peaks of unmodified C_{60} , all reduction peaks of adducts **3** and **7** were observed in the higher cathodic region (Table 4). The electron affinities (*EA*) of adducts **3** and **7** calculated from the experimental potentials of the first reduction peaks are in good agreement with the corresponding values calculated by the PM3 and DFT methods. The potentials of the reduction peaks of adducts **3** and **7** are consistent with the results of electrochemical reduction of tetraethyl and tetraisopropyl (methano[1,2][60]fullerenyl)diphosphonates reported ear-

Table 4. Potentials (E_p^{red}) and peak currents (I_p^{red}) in cyclic voltammograms,^{*a*} the experimental electron affinities (EA_{exp}) for C₆₀ and compounds **3** and **7**, and the corresponding electron affinities calculated (EA_{calc}) by the PM3 and DFT methods

Com-	$E_{\rm p}^{\rm red}/{\rm V}$				EA/eV		
pound		$(I_{\rm p}^{\rm red}/\mu {\rm A})$			EA _{exp} ^b	EAcalc	
						PM3	DFT
C ₆₀	-0.83	-1.24	-1.70	-2.16	2.65	2.65	2.65
	(4.2)	(3.8)	(3.9)	(4.6)			
3	-0.91	-1.30	-1.81	-2.25	2.57	2.54	2.53
	(9.2)	(8.3)	(9.0)	(10.7)			
7	-0.93	-1.32	-1.84	-2.30	2.55	2.51	2.51
	(9.2)	(7.3)	(8.3)	(11.7)			

^{*a*} In a 3 : 1 *o*-dichlorobenzene—acetonitrile mixture at 25 °C. ^{*b*} Calculated from $E_p^{1,\text{red}}$. lier.¹⁵ However, unlike the latter compounds, which undergo the retro-Bingel reaction in the second step of reduction, reduction of methanofullerenes **3** and **7** was unexpectedly completely reversible. Generally, methanofullerenes undergo opening of the cyclopropane ring, which takes place in different steps of their electrochemical reduction depending on the nature of substituents.^{16,17}

One possible explanation of the electrochemical and thermal stabilities of methanofullerenes 3 and 7 is the presence of intramolecular interactions between the organic fragments at the bridging C(61) atom and the fullerene sphere in the molecules of these compounds. Interactions of this type should, most likely, influence the spectroscopic characteristics of the adducts. In this connection, we compared the chemical shifts of the signals for the carbon and hydrogen atoms in the ¹H and ¹³C NMR spectra of methanofullerenes 3 and 7, phosphonates 1 and 2, and O,O-diethyl benzylphosphonate 8.

The signals for the hydrogen atoms of the ethoxy groups at the phosphorus atom and the signals of the Me or Ph groups in the ¹H NMR spectra of methanofullerenes **3** and 7 are observed at lower field compared to the signals for the corresponding hydrogen atoms in the spectra of phosphonates 1 and 2 (see Table 2). However, the ${}^{13}C$ NMR signals for the carbon atoms of the EtO groups in methanofullerenes 3 and 7 (see Table 1) differ only slightly from the signals of these groups in the spectra of phosphonates 1 and 2. At the same time, the signal for the carbon atom of the Me group in the spectrum of phosphonate 3 is substantially shifted downfield relative to the signal of this group in the spectrum of phosphonate 1. The signals for the carbon atoms of the phenyl ring in the spectrum of methanofullerene 7 are shifted to a different extent compared to the positions of the corresponding signals in the spectrum of phosphonate 2 (Table 5). The largest shift is observed for the signal of the C_o atom, the signal being shifted compared to the corresponding signals in the ¹³C NMR spectra of both phosphonate 2 and phosphonate 8. Noteworthy are the large constants of spin-spin coupling of this carbon atom with the ortho- and para-protons.

However, taking into account the difference in the environment about the groups of atoms under consideration in methanofullerenes **3** and **7** and phosphonates **1** and **2**, we additionally carried out quantum-chemical calculations of the chemical shifts of the ¹³C NMR signals for the carbon atoms of the phenyl ring in methanofullerene **7** (see Table 5). To estimate the contribution of the fullerene core to the shielding of the carbon atoms, we examined the cyclopropane derivative $C_3H_4(Ph)P(O)(OMe)_2$ (**9**). A comparison of the chemical shifts of the signals for the carbon atoms of the phenyl ring in methanofullerene **7** and compound **9** demonstrated that the fullerene sphere substantially shields the C_{ipso} atom and deshields the *ortho*- C_o atom. The mutual effect

Atom	δ, ${}^{n}J_{(^{3}1P-^{1}3C)}, {}^{n}J_{(^{1}3C-^{1}H)}/Hz$						
	2	7		8	9		
	(experiment)	Experiment	Calculation*	(experiment)	(calculation)		
C _o	122.8 (d, ${}^{1}J_{C,H} = 160.9$, d, ${}^{3}J_{P,C} = 4.2$,	134.4 (d, ${}^{1}J_{C,H} = 162.0$, d, ${}^{4}J_{P,C} = 3.4$,	134.88	128.7 (d, ${}^{1}J_{C,H} = 158.8$, d, ${}^{3}J_{P,C} = 6.7$, d, ${}^{3}J_{C,H} = 5.7$,	132.75		
C _m	d, ${}^{3}J_{C,H} = 5.5$) 129.4 (d, ${}^{1}J_{C,H} = 160.9$, d ${}^{4}L = 2.8$ dd ${}^{2}L = 3.5$	t, ${}^{3}J_{C,H} = 7.6$) 127.8 (d, ${}^{1}J_{C,H} = 160.9$, d ${}^{3}I_{L} = 2.2$	127.71	t, ${}^{3}J = 6.0$) 127.2 (d, ${}^{1}J_{C,H} = 159.7$, d ${}^{4}L = 3.0$ dd ${}^{2}L = 3.3$	127.52		
C _p	${}^{2}J_{C,H} = 3.4$ 125.3 (d, ${}^{1}J_{C,H} = 158.1$,	d, ${}^{3}J_{C,H} = 7.3$) 128.6 (d, ${}^{1}J_{C,H} = 163.5$,	128.61	${}^{2}J_{C,H} = 3.3$) 125.6 (d, ${}^{1}J_{C,H} = 159.7$, d,	, 126.66		
C _{ipso}	t, ${}^{2}J_{C,H} = 6.9$) 126.9 (d, ${}^{2}J_{P,C} = 8.3$, t, ${}^{2}J_{C,H} = 1.3$)	d, ${}^{5}J_{P,C} = 2.9$, t, ${}^{5}J_{C,H} = 7.3$) 132.8 (t, ${}^{3}J_{C,H} = 7.6$, ${}^{2}J_{P,C} = 0$)	136.00	${}^{5}J_{P,C} = 3.8, t, {}^{5}J_{C,H} = 6.0)$ 130.8 (d, ${}^{2}J_{P,C} = 9.1, d,$ ${}^{2}J_{C,H} = 6.2, d, {}^{2}J_{C,H} = 5.7)$	142.41		

Table 5. Parameters of the ¹³C NMR spectra of the phenyl fragments in compounds 2 and 7–9

* Calculated by the GIAO–DFT/PBE/TZ2P method with the exchange-correlation potential.

of the addends is transferred predominantly through the bonds. At the same time, according to the results of calculations, the oxygen atom of the phosphoryl group in the thermodynamically most stable conformation of methanofullerene 7 (Fig. 2) can approach the C(3)-C(4) bond to a distance of 2.99 Å and the hydrogen atom of the phenyl ring at C_o can approach the C(11)-C(12) bond to a distance of 2.89 Å. The distance between the C_{o} atom and the C(11)–C(12) bond is 3.20 Å. As a result, the P=O dipole can shift the electron density from the C(3)-C(4)bond thus shortening it to 1.3877 Å, while the C(11)-C(12) bond is elongated to 1.3897 Å. Therefore, the spectroscopic characteristics and calculated data for adduct 7 demonstrate that the intramolecular interactions between the organic fragments and the fullerene sphere in molecule 7 are quite possible, and it is not inconceivable that these interactions make a contribution to thermal stability of methanofullerenes 7 and 3 and also stabilize the anions generated in the course of electrochemical reduction of these adducts. We did not exclude



Fig. 2. Most thermodynamically stable conformation of methanofullerene 7.

the contributions of other factors as well. The question about stability of the exocyclic cyclopropane fragments in organofullerenes will be discussed for a broader spectrum of methanofullerenes in the future.

To summarize, we prepared new thermally stable phosphorylated methanofullerenes whose electrochemical reduction proceeds reversibly.

Experimental

The IR spectra were measured on a Bruker Vector-22 Fourier spectrometer in KBr pellets for fullerene derivatives and in Nujol mulls for phosphorylated hydrazones and diazo compounds. The ³¹P, ¹H, and ¹³C NMR spectra were recorded on a Bruker WM-250 instrument at v_0 250 MHz (¹H) and 101.2 MHz (³¹P) and on a Bruker MSL-400 instrument at v_0 400.13 MHz (1H), 100.62 MHz (13C), and 161.92 MHz (31P) in $CDCl_3$. The chemical shifts δ were calculated with respect to CDCl₃, Me₄Si, and 85% H₃PO₄. The UV spectra were recorded on a Specord UV-VIS instrument. The mass spectra were obtained on a MALDI TOF MS instrument (Dynamo) with the use of a *p*-nitroaniline matrix. The HPLC analysis was carried out on a Gilson chromatograph (UV detector; normal-phase and C₁₈ reversed-phase columns (Partisil-5 ODS-3); toluene-MeCN, 1 : 1 (v/v) as the eluent, 2 mL min⁻¹; UV-VIS Detector Holochrome detector; λ 328 nm). Elemental analysis for the phosphorus content of the fullerene adducts was carried out by pyrolysis of weighed samples in a quartz tube under a stream of oxygen according to a known procedure.¹⁸

Cyclic voltammetry (CV) studies were carried out with the use of a stationary disk glassy-carbon electrode as a working electrode with a working surface area of 3.14 mm². Cyclic voltammograms (CV curves) were measured with the use of a PI-50-1 potentiostat equipped with a PR-8 programmator and an electrochemical cell according to a three-electrode scheme. The CV curves were recorded with the use of a two-coordinate recorder at a potential scan rate of 50 mV s⁻¹ using a 3 : 1 *o*-DCB-MeCN mixture with Bu₄NBF₄ (0.1 mol L⁻¹) as the background electrolyte. An Ag/0.01 *M* AgNO₃ system in MeCN

served as the reference electrode and a 1-mm diameter platinum wire was used as the auxiliary electrode. The measurements were carried out in a temperature-controlled (25 °C) cell under an argon atmosphere. The concentrations of solutions of fullerene and adducts were $1 \cdot 10^{-3}$ and $2 - 10^{-3}$ mol L⁻¹, respectively. The experimental electron affinities (EA_{exp}) were calculated by the approximation formula $E_p^{red} = 1.0 \cdot EA_{exp} + + \text{const}EA_{exp} = 3.48 + E_p^{red}$ for the Ag/0/01 *M* AgNO₃ system in MeCN.

The theoretical electron affinities were estimated by the PM3 method from the LUMO energies and by the DFT method as the differences between the total energies of the molecules and the corresponding radical anions and were scaled against C₆₀. The chemical shifts of the carbon atoms in the ¹³C NMR spectra and the thermodynamically stable conformation of adduct 7 were calculated by the GIAO method. The wavefunctions and geometric parameters were calculated by the density functional theory (DFT/PBE/TZ2P method) with the exchange-correlation potential¹⁹ and a three-component basis using the PRIRODA 2.10 program.^{20,21} The shielding constants (σ_m) were inverted into the theoretical chemical shifts with respect to Me₄Si (δ_m) according to the equation $\delta_m = \delta(C_{60}) + \sigma(C_{60}) - \sigma_m$.

Anhydrous toluene was prepared by prolonged heating over sodium followed by distillation over LiAlH₄. Anhydrous *o*-dichlorobenzene was prepared by distillation over P_2O_5 . [60]Fullerene was synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhny Novgorod).

The starting phosphonates 1 and 2 were synthesized according to procedures analogous to the methods developed for the synthesis of known diazoorganylphosphonates.^{22,23} Model O,O-diethyl benzylphosphonate 8 was prepared according to a procedure described earlier.²⁴

O,O-Diethyl α -diazoethylphosphonate (1). O,O-diethyl acetylphosphonate (5.3 g, 0.029 mol) was rapidly added to p-toluenesulfonhydrazide (4.82 g, 0.026 mol) dissolved in anhydrous methanol (100 mL). The reaction mixture was stirred for one day, the solvent was removed in vacuo, and the residue was recrystallized from diethyl ether. The crystals were filtered off and washed with diethyl ether. N'-[1-(Diethoxyphosphoryl)ethylidene]-p-toluenesulfonhydrazide was prepared in a vield of 5.19 g (58%), m.p. 100 °C. IR (Nujol mulls), v/cm^{-1} : 2976 (NH), 1228 (P=O). ³¹P NMR (CDCl₃), δ: 7.69, 9.92. The resulting phosphonate was treated with Na_2CO_3 (2.0 g, 0.019 mol) in water (30 mL). The reaction mixture was stirred for 12 h and extracted for 3 days with portions of Et₂O (20 mL). which were separated and changed for new portions every 4 h. To achieve complete decoloration, the aqueous layer was treated with CH₂Cl₂. The combined organic fractions were dried over MgSO₄, the solvent was distilled off, and the residue was distilled in vacuo. Phosphonate 1 was prepared in a yield of 0.9 g (25%), b.p. 49 °C (0.1 Torr). IR (Nujol mulls), v/cm⁻¹: 2082 (N=N), 1254 (P=O). ³¹P NMR (CDCl₃), δ: 22.65. Purification of phosphonate 1 by column chromatography on SiO_2 (hexane $-Et_2O$, 3 : 1, as the eluent) led to partial decomposition of the product due to which satisfactory data of elemental analysis for this compound were not obtained.

O,O-Diethyl α -diazobenzylphosphonate (2). Concentrated HCl (1 mL) and *O,O*-diethyl benzoylphosphonate (5.14 g, 0.02 mol) in THF (5 mL) were added with vigorous stirring to *p*-toluenesulfonhydrazide (3.95 g, 0.02 mol) in THF (20 mL)

at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and then at ~20 °C for 12 h. The solvent was removed in vacuo, the residue was treated with diethyl ether (20 mL), and the precipitate that formed was filtered off. The large crystals, which precipitated from the filtrate upon cooling, were filtered off. 2-[2-(Diethoxyphosphoryl)-1-phenylmethylidene]-1-(p-toluenesulfonyl)hydrazinium hydrochloride was prepared in a yield of 5.34 g (65%), m.p. 94–96 °C. IR (Nujol mulls), v/cm⁻¹: 2776 (NH⁺), 1244 (P=O). ³¹P NMR (THF), δ: 8.62, 7.78. The resulting phosphonate was treated with a solution of Na₂CO₃ (2.5 g, 0.02 mol) in water (50 mL). The reaction mixture was stirred at ~20 °C for 2 days until the precipitate was completely dissolved and an orange oil formed. The reaction mixture was extracted with Et_2O (3×20 mL) until the aqueous layer turned colorless. The combined organic fractions were dried over Na_2SO_4 , the solvent was removed in vacuo, and the residue was cooled to -70 °C. The crystals of compound 2 that formed were rapidly filtered off and washed with cold diethyl ether. Attempts to prepare an analytically pure sample of compound 2 by column chromatography (hexane $-Et_2O$, 6 : 1, as the eluent) failed. The yield was 1.8 g (59%), m.p. 22–24 °C. IR (Nujol mulls), v/cm⁻¹: 2080 (N=N), 1256 (P=O). ³¹P NMR (C₆D₆), δ: 17.98.

O,O-Diethyl α-methyl(methano[1,2][60]fullerenyl)phosphonate (3). A mixture of C₆₀ (0.119 g, 0.16 mmol) and *O,O*-diethyl α-diazoethylphosphonate (1) (0.037 g, 0.19 mmol) was heated in refluxing toluene (50 mL) for 4 h. The conversion of C₆₀ was monitored by HPLC. The solvent was removed *in vacuo* and the residue was chromatographed on a column of silica gel. Unconsumed C₆₀ (toluene as the eluent) was obtained in a yield of 0.009 g and a mixture of adducts 3 (20 : 1 toluene–Et₂O mixture as the eluent; HPLC, normal-phase column, the retention time was 3.7 min), 5 (2.8), and 6 (2.4) was isolated in a yield of 0.047 g. ³¹P NMR, δ, (*J*): 26.00 (0.74), 20.62 (2.45), 20.04 (1.00). ¹H NMR (CDCl₃), δ: CH₃CH₂O – 1.36 (t, ³J_{H,H} = 6.8 Hz), 1.43 (t, ³J_{H,H} = 7.2 Hz), 1.57 (t, ³J_{H,H} = 6.8 Hz); CH₃C – 2.35 (d, ²J_{P,H} = 0.5 Hz), 2.44 (d, ²J_{P,H} = 12.2 Hz), 3.33 (d, ²J_{P,H} = 12.7 Hz); CH₃CH₂O – 4.16 (dq, ³J_{PO,CH} = 6.8 Hz), 4.47 (dq, ³J_{PO,CH} = 6.9 Hz, ³J_{H,H} = 6.8 Hz).

A mixture of adducts **3**, **5**, and **6** was heated in *o*-DCB (5 mL) at 140 °C for 4 h. The solvent was removed *in vacuo*. Adduct **3** was obtained in a yield of 0.053 g (42%). HPLC (normal-phase column); the retention time was 3.7 min. Found (%): C, 88.97; H, 1.43; P, 3.45 C₆₆H₁₃O₃P. Calculated (%): C, 89.59; H, 1.47; P, 3.51. MALDI-TOF MS (*p*-nitroaniline as the matrix), *m/z*: 884 [M]⁺, 907 [M + Na]⁺, 923 [M + K]⁺. UV, λ_{max} /nm: 260, 329, 424, 492, 683. IR (KBr), v/cm⁻¹: 526 (fullerene sphere), 1252 (P=O), 1016, 1044 (P–O–C), 2855, 2925 (C–H). ³¹P NMR (CDCl₃), & 20.00.

O,*O*-Diethyl α-phenyl(methano[1,2][60]fullerenyl)phosphonate (7). A mixture of C_{60} (0.123 g, 0.17 mmol) and phosphonate 2 (0.046 g, 0.18 mmol) was heated in boiling toluene (50 mL) for 3 h. The conversion of C_{60} was monitored by HPLC. The solvent was removed *in vacuo* and the residue was chromatographed on a column of silica gel. Unconsumed C_{60} (toluene as the eluent) was obtained in a yield of 0.0018 g and adduct 7 (a 95 : 5 toluene—MeCN mixture as the eluent) was prepared in a yield of 0.114 g (72%). Found (%): C, 89.42; H, 1.49; P, 3.35. $C_{71}H_{15}O_3P$. Calculated (%): C, 90.06; H, 1.58; P, 3.28. MALDI-TOF MS (*p*-nitroaniline as the matrix), *m/z*: 946 [M]⁺, 969 [M + Na]⁺, 985 [M + K]⁺. UV, λ_{max}/nm : 260, 326, 426, 496, 692. IR (KBr), ν/cm⁻¹: 527, 1187 (P=O), 1399. ³¹P NMR (CDCl₃), δ: 15.42.

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