Russian Chemical Bulletin, International Edition, Vol. 52, No. 2, pp. 380—384, February, 2003

Rate constants for addition of the $\mathrm{OP^{\bullet}(OPr^{i})_2}$, $\mathrm{Me_3C^{\bullet}}$, and $\mathrm{Me(CH_2)_3{}^{\bullet}CH_2}$ radicals to methano[60]fullerenes $\mathrm{C_{60}CX^1X^2}$ ($\mathrm{X^1 = X^2 = CO_2Et}$; $\mathrm{X^1 = CO_2Me, X^2 = OP(OMe)_2}$; $\mathrm{X^1 = X^2 = OP(OEt)_2}$)

R. G. Gasanov,[a]★ ***V. V. Bashilov,***[a] ***B. L. Tumanskii,***[a] ***V. I. Sokolov,***[a] ***I. A. Nuretdinov,***[b]
V. V. Zverev,[b] ***V. P. Gubskaya,***[b] ***and L. Sh. Berezhnaya***[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: tuman@ineos.ac.ru
[b]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences,*
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: in@iopc.kcn.ru

The rate constants for the addition of the $\mathrm{OP^{\bullet}(OPr^{i})_2}$, $\mathrm{Me_3C^{\bullet}}$, and $\mathrm{Me(CH_2)_3{}^{\bullet}CH_2}$ radicals to the methano[60]fullerenes $\mathrm{C_{60}CX^1X^2}$ ($\mathrm{X^1 = X^2 = CO_2Et}$; $\mathrm{X^1 = CO_2Me}$, $\mathrm{X^2 = OP(OMe)_2}$; $\mathrm{X^1 = X^2 = OP(OEt)_2}$) were determined by ESR spectroscopy. Methanofullerenes are more reactive toward these radicals than $\mathrm{C_{60}}$ fullerene.

Key words: ESR spectroscopy, nitrosodurene, rate constants for addition, methano[60]fullerenes.

Comparison of the reactivity of methano[60]fullerenes and $\mathrm{C_{60}}$ fullerene toward the addition of free radicals appears rather important, especially in view of the fact that the fullerene hemisphere that already contains the methano fragment is attacked predominantly by the radicals.[1] The methano fragment induces deformation of the carbon cage, which changes the curvature of the fullerene surface,[1] introduces steric hindrances, and leads to manifestation of the polar effects near the $\mathrm{X^1X^2C}$ group. These effects may be the reason for changed reactivity of $\mathrm{C_{60}}$ fullerene derivatives.[2] Knowledge of the rate constants for the addition of free radicals to methano[60]fullerenes can be useful for targeted synthesis of fullerene derivatives starting from methano[60]fullerenes.

To this end, we determined by ESR spectroscopy the rate constants for the addition of the $\mathrm{OP^{\bullet}(OPr^{i})_2}$ ($\mathrm{R^1}$), $\mathrm{Me_3C^{\bullet}}$ ($\mathrm{R^2}$), and $\mathrm{Me(CH_2)_3C^{\bullet}H_2}$ ($\mathrm{R^3}$) radicals to the methano[60]fullerenes $\mathrm{C_{60}CX^1X^2}$ ($\mathrm{X^1 = X^2 = CO_2Et}$ (**1**); $\mathrm{X^1 = OP(OMe)_2}$, $\mathrm{X^2 = CO_2Me}$ (**2**); $\mathrm{X^1 = X^2 = OP(OEt)_2}$ (**3**)).

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Degassed reaction mixtures in glass tubes were irradiated using a DRSh-1000 lamp directly in the resonator of the spectrometer at ~20 °C. The bands with $\lambda \approx 366$ nm and $\lambda \geq 620$ nm were cut using glass filters. Before adding the solvent (toluene), the required amount of nitrosodurene (ND) was diluted in a small amount of dichloromethane. The $\mathrm{R^1}$ radicals were generated by decomposition of $\mathrm{Hg[P(O)(OPr^{i})_2]_2}$ (**4**),[3] and the $\mathrm{R^2}$ and $\mathrm{R^3}$ radicals were produced by abstraction of a Br or I atom from the $\mathrm{Me_3CBr}$ or $\mathrm{Me(CH_2)_3CH_2I}$ molecules, respectively, on treatment with $\mathrm{{}^{\bullet}Re(CO)_5}$ radicals resulting from photochemical decomposition of $\mathrm{Re_2(CO)_{10}}$.[4]

Methano[60]fullerenes **1**—**3** were prepared by known procedures.[5]

Results and Discussion

On UV irradiation of toluene solutions containing 10^{-3} mol $\mathrm{L^{-1}}$ of methano[60]fullerenes **1**—**3** and $8.8 \cdot 10^{-3}$ mol $\mathrm{L^{-1}}$ of compound **4**, six doublets are recorded in the ESR spectra (Fig. 1); we assigned these signals to the spin adducts (SA) formed by the $\mathrm{R^1}$ radicals with methano[60]fullerenes **1**—**3**. The constants of HFC with the phosphorus nucleus and the *g*-factors were as follows:

a_P/G	*g*-Factor	a_P/G	*g*-Factor
71.7	2.0029 (**1**, *1*)	67.2	2.0023 (**2**, *4*)
67.7	2.0025 (**1**, *2*)	61.7	2.0023 (**2**, *5*)
65.7	2.0024 (**1**, *3*)	58.7	2.0022 (**2**, *6*)
62.7	2.0023 (**1**, *4*)	72.5	2.0029 (**3**, *1*)
61.2	2.0024 (**1**, *5*)	67.7	2.0026 (**3**, *2*)
58.7	2.0023 (**1**, *6*)	65.7	2.0028 (**3**, *3*)
72.0	2.0028 (**2**, *1*)	64.0	2.0031 (**3**, *4*)
66.7	2.0027 (**2**, *2*)	61.9	2.0027 (**3**, *5*)
66.2	2.0023 (**2**, *3*)	59.0	2.0027 (**3**, *6*)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 364—368, February, 2003.

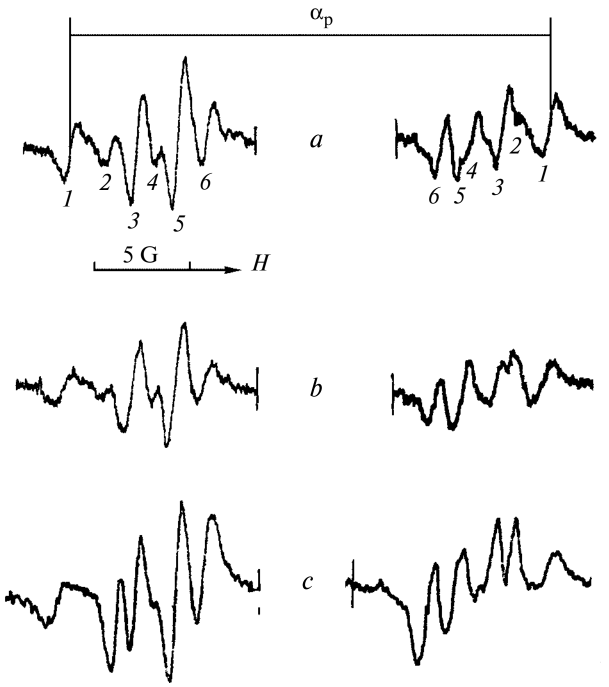

Fig. 1. ESR spectra of spin adducts formed by the $OP^{\bullet}(OPr^i)_2$ radicals (R^1) with methano[60]fullerenes **1** (*a*), **2** (*b*), and **3** (*c*) obtained upon UV irradiation of toluene solutions containing 10^{-3} mol L^{-1} of the corresponding methanofullerene and $8.82 \cdot 10^{-2}$ mol L^{-1} of $Hg[OP(OPr^i)_2]_2$.

Based on the HFC constants, the observed ESR spectra can be assigned to monoaddition products.[1]

Table 1 presents the relative pyramidality values ($\Delta\alpha$) of the carbon atoms of methanofullerenes $C_{60}CH_2$ (**5**) and **2** determined by the HF/6-31G** and DFT/TZ2P calculations with the PBE exchange correlation potential[6] using the GAMESS[7] and PRIRODA[8,9] software. The $\Delta\alpha$ value is defined as the difference between the sum of the bond angles of the atoms in the C_{60} fullerene molecule (348°): $\Delta\alpha = \Sigma\alpha - 348°$. Both computation methods give identical results. In the upper hemisphere of fullerene, the C(3), C(6) and C(9), C(12) atoms (Fig. 2, Table 1) of each of the C(3)—C(4), C(5)—C(6), C(9)—C(10), and C(11)—C(12) bonds are flattened, whereas the pyramidality of the C(4), C(5) and C(10), C(11) atoms (see Table 1) increases. In the lower hemisphere of the methanofullerenes, these changes are less pronounced and inverted, *i.e.*, the pyramidality of the atoms *A* increases, while that of the atoms *B* decreases.

The $C_{60}CH_2$ molecule has C_{2v} symmetry and four equivalent sets of bonds, *cis-1*, *cis-2*, *cis-3*, *trans-2*, *trans-3*, *trans-4*, two *eq-1* bonds, two *eq-2* bonds, and one *trans-1* bond (see Ref. 10) which is common to all four fragments. For example, the C(15), C(21), C(24), and C(30) atoms of the four *cis-2n* bonds are identical and have the same geometric parameters; the SA re-

Table 1. Relative pyramidalities ($\Delta\alpha$/deg) of the carbon atoms of methanofullerenes $C_{60}CH_2$ (**5**) and $C_{60}C(CO_2Me)[P(O)(OMe)_2]$ (**2**) obtained from HF/6-31G** (I) and DFT/TZ2p (II) calculations

Bond	Atom[a]	**5**		**2**
		I	II	II
cis-1[b]	*A*	3.20	3.31	2.48
	B	0.09	0.08	0.44
cis-2[b]	*A*	1.38	1.73	1.71
	B	−0.08	−0.26	−0.29
cis-3[b]	*A*	0.81	0.74	0.66
	B	−0.44	−0.39	−0.39
eq-1[c]	*A*	0.48	0.52	0.59
	B	0.08	0.02	−0.08
eq-2[c]	*A*	−0.13	−0.17	−0.16
	B	−0.13	−0.17	−0.10
trans-4[d]	*A*	−0.06	−0.10	−0.20
	B	−0.03	−0.03	0.01
trans-3[d]	*A*	−0.19	−0.20	−0.17
	B	−0.03	−0.03	0.01
trans-2[d]	*A*	0.06	0.04	0.06
	B	−0.05	−0.01	−0.03
trans-1[d]	*A*	0.04	0.07	0.07
	B	0.04	0.07	0.10

[a] *A* are the C(3), C(6), and C(9) atoms; *B* are the C(4), C(5), C(10), and C(9) atoms.

[b] Three types of bonds in the upper hemisphere.

[c] Two types of bonds in the equatorial plane.

[d] Four types of bonds in the lower hemisphere.

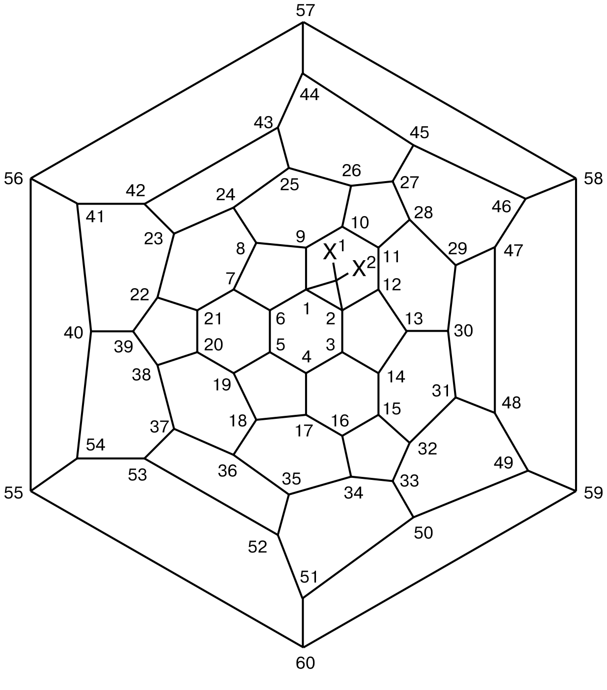

Fig. 2. Schlegel diagram of compounds **1**—**3**.

sulting from the addition of radicals to these atoms should be identical. Asymmetric addends such as $(MeCO_2)C[P(O)(OMe)_2]$ divide the fullerene cage into four nonequivalent fragments, namely, four nonequivalent sets of bonds, *cis-1n*, *cis-2n*, *cis-3n, trans-2n, trans-3n,* and *trans-4n* and two nonequivalent bonds, *eq-1n* and *eq-2n*. Like the bond lengths, the pyramidalities of the atoms forming bonds of the same type in the four fragments of compound **2** differ only slightly from one another. For instance, the degrees of pyramidality ($\Delta\alpha$/deg) of the atoms *B* of the four *cis-2n bonds* (C(15), C(21), C(24), and C(30)) are –0.30, –0.29, –0.22, and –0.23. The isomers formed upon the addition of radicals to the atoms *B* of different *cis-2n* or *cis-3n*, *etc.*, bonds of the same type in compounds $C_{60}CH_2$, **1**, and **3** are equivalent or their characteristics are rather close (in the case of compound **2**). According to calculations, the pyramidality and, hence, the reactivity of six C atoms in compounds **1—3** are higher than in C_{60} fullerene. The six doublets observed in the ESR spectra of the adducts of compounds **1—3** with the R^1 radical indicate the formation of six SA regioisomers in the reaction of R^1 with various double bonds. The addition to the C(4) and C(5) or to the C(10) and C(11) atoms is sterically hindered due to the presence of adjacent substituents. It can be seen from Fig. 1 that, although the intensities of the signals of particular isomers depend on the nature of substituents, signals *5* and *3* are the most intense for all three compounds. We believe that these signals can be assigned to isomers formed upon the addition of radicals to the C(4), C(5) or C(10), C(11) atoms.

In order to determine the reactivity of compounds **1—3** toward the R^1 radicals, we studied the addition of these radicals to molecules **1—3** and to C_{60} fullerene present simultaneously in the reaction mixture. This is exemplified in Fig. 3, which shows the ESR spectrum recorded on UV irradiation of toluene solutions containing compounds **1** (10^{-3} mol L^{-1}), C_{60} (10^{-3} mol L^{-1}), and **4** ($8.82 \cdot 10^{-3}$ mol L^{-1}). Identical spectra were also recorded for compounds **2** and **3**. As can be seen from this spectrum, the signal of the $^{\bullet}C_{60}R^1$ radicals ($a_p = 63.7$ G, $g = 2.0024$) is superimposed on the signals *4* and *5* of two SA regioisomers formed by R^1 radicals with compound **1**. Superposition of signals of the SA formed by R^1 radicals with compounds **1—3** and with C_{60} precluded separate measurements of the rates of their formation or the determination of the rate constants for addition of R^1 to particular C atoms in molecules **1—3** based on the known rate constant for the addition of R^1 to C_{60}.**[11]** However, assuming that the loss of the SA formed from R^1 radicals with compounds **1—3** and with C_{60} occurs at identical rates, the rate constants for the addition of R^1 to particular atoms in molecules **1—3** can be estimated from the intensity of the signals of individual SA. After irradiation has been terminated, the signals of the SA formed by the R^1 radicals with molecules **1—3** and with C_{60} disappear over a period of several seconds, apparently, due to dimerization.**[12]** On repeated exposure to light with $\lambda > 620$ nm, the signals of all SA appear again in the spectra.

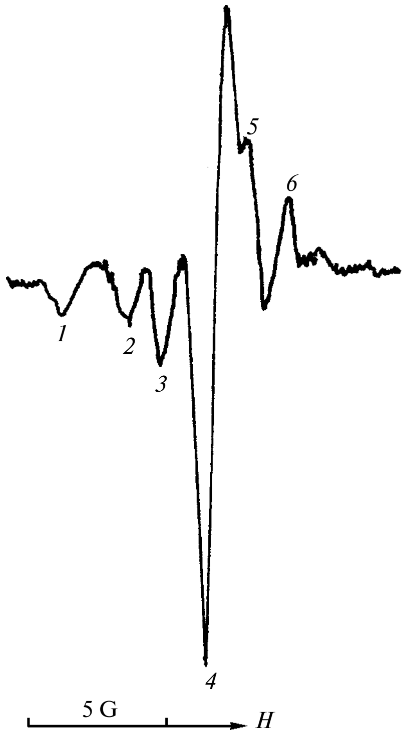

Fig. 3. Low-field part of the ESR spectrum of the spin adducts of $OP^{\bullet}(OPr^i)_2$ radicals with methano[60]fullerene (**1**) (10^{-3} mol L^{-1}) and C_{60} fullerene (10^{-3} mol L^{-1}) (line *4*); $[Hg(OP(Pr^i)_2)_2] = 8.82 \cdot 10^{-2}$ mol L^{-1}.

Analysis of the intensities of the signals of the SA formed by R^1 radicals with molecules **1—3** in the absence (see Fig. 1) and in the presence (see Fig. 3) of C_{60} in the reaction mixture shows that the signal of $^{\bullet}C_{60}R^1$ is approximately 6 times more intense than the signals of individual isomers resulting from the addition of R^1 radicals to compounds **1—3**. However, in view of the fact that the C_{60} molecule contains 60 equivalent carbon atoms and based on the rate constant for the addition of R^1 to C_{60} fullerene ($6 \cdot 10^8$ L mol^{-1} s^{-1}),**[11]** one can assume that the rate constants for the addition of R^1 radicals to each of the six carbon atoms in molecules **1—3** are no lower than 10^9 L mol^{-1} s^{-1}.

The rate constant k_1 for the addition of the R^2 and R^3 radicals to molecules **1—3** was determined using the method of competing reactions.**[13]**

$$R + C_{60}X^1X^2 \xrightarrow{k_1} R^{\bullet}C_{60}X^1X^2, \qquad (1)$$

$R = R^2, R^3$

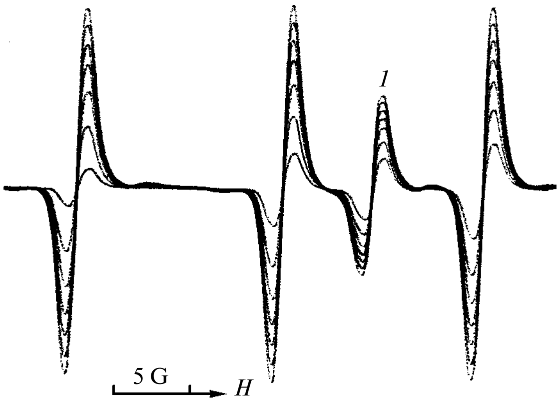

Fig. 4. ESR spectra of spin adducts formed by the $Me_3C^•$ radicals with nitrosodurene ($2.06 \cdot 10^{-3}$ mol L^{-1}) (triplet) and methano[60]fullerene **3** (10^{-3} mol L^{-1}) (singlet, line *1*) (the spectra were recorded at 40 s intervals).

The addition of R to nitrosodurene (ND) was chosen as the reaction competing with reaction (1):

$$\underset{}{R + ND \xrightarrow{k_2} \underset{A}{RN(O^•)Ar},} \qquad (2)$$

where Ar = 2,3,5,6-Me_4C_6H.

The rate constant k_1 was determined from the equation

$$d[A]/d[R^•C_{60}CX^1X^2] = k_2[ND]_0/k_1[C_{60}CX^1X^2]_0, \qquad (3)$$

where $[ND]_0$ and $[C_{60}CX^1X^2]_0$ are the initial concentrations of the spin trap and the methano[60]fullerenes; d[A] and $d[R^•C_{60}CX^1X^2]$ are variations of the intensities of the ESR signals for the iminoxyl radicals A and for the SA formed by R radicals with molecules **1—3** (Fig. 4 and 5). As can be seen from Eq. (3), to determine the rate constant k_1, one should know the rate constants k_2 ($2.0 \cdot 10^8$ and $2.0 \cdot 10^7$ L mol^{-1} s^{-1} for the addition of the R^2 and R^3 radicals, respectively, to ND at room temperature).[14]

On exposure of toluene solutions containing compounds **1—3** (10^{-3} mol L^{-1}), $Re_2(CO)_{10}$, $BrCMe_3$, and ND ($2.06 \cdot 10^{-3}$ mol L^{-1}) to light with $\lambda \approx 366$ nm, the ESR spectra exhibit signals of the SA formed by the R^2 radicals with ND and with compounds **1—3** (Fig. 4). In the case of solutions containing compounds **1—3** ([**1—3**] = 10^{-3} mol L^{-1}), $Re_2(CO)_{10}$, $Me(CH_2)_3CH_2I$, and ND ($[ND]_0 = 3.46 \cdot 10^{-3}$ mol L^{-1}), the spectra contain signals of the SA formed by the R^3 radicals with ND and molecules **1—3** (Fig. 5). The data on variation of the signal intensities of the SA formed by the R^2 and R^3 radicals with ND and with compounds **1—3**, obtained in kinetic experiments, were processed by the least-squares method (correlation coefficient ≥ 0.95). The rate constants for the addition of the R^2 and R^3 radicals to compounds **1—3** found from Eq. (3) are $3.7 \cdot 10^7$, $4.5 \cdot 10^7$, $4.8 \cdot 10^7$, $6.2 \cdot 10^6$, $6.9 \cdot 10^6$, and $1.3 \cdot 10^7$ mol L^{-1}, respectively.

Unlike the spectra of phosphorus-centered radicals R^1, the ESR spectra of the SA formed by carbon-centered radicals R^2 and R^3 with molecules **1—3** exhibited only singlets. Taking account of the above results, one can assume that this singlet is a superposition of the signals corresponding to six regioisomers formed upon the addition of R^2 and R^3 radicals to the C(4), C(5), or C(10), C(11), and C(15), C(21), C(24), C(30) atoms in methano[60]fullerenes **1—3**. The rate constants for the addition of R^2 and R^3 radicals to compounds **1—3** determined in this study do not differ from the values known for C_{60} fullerene (see Ref. 9). Since the number of carbon atoms to which R^2 and R^3 can add is an order of magnitude greater in C_{60} molecule than in molecules **1—3**, each carbon atom in **1—3** is an order of magnitude more reactive than the carbon atoms in C_{60}.

Thus, it was shown that deformation of the carbon cage in methano[60]fullerenes favors substantial enhancement of the reactivity of particular carbon atoms toward the addition of free radicals.

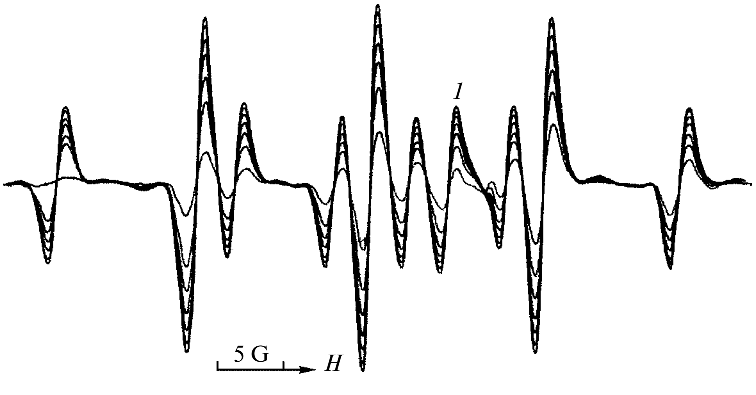

Fig. 5. ESR spectra of spin adducts formed by the R^3 radicals with nitrosodurene ($3.46 \cdot 10^{-3}$ mol L^{-1}) (triplet of triplets) and methano[60]fullerene **1** (10^{-3} mol L^{-1}) (singlet, line *1*) (the spectra were recorded at 40 s intervals).

This work was financially supported by the Russian Foundation for Basic Research (Projects No. 02-03-32900, No. 01-03-33216, No. 96-03-32485, and No. 99-03-32888), The State Science and Engineering Program "Fullerenes and Atomic Clusters" (Project No. 98008, Gemo-2), the Basic Research Programs of the Presidium of the Russian Academy of Sciences "Low-Dimension Quantum Structures," the Ministry of Industry, Science, and Technology of the Russian Federation, and the Tatarstan Academy of Sciences (Project No. 18-05/2000).

References

1. B. L. Tumanskii, E. N. Shaposhnikova, O. G. Kalina, V. V. Bashilov, M. F. Nefedova, S. P. Solodovnikov, N. N. Bubnov, and V. I. Sokolov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 845 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 843].
2. R. C. Haddon, *J. Am. Chem. Soc.*, 1997, **119**, 1797.
3. B. L. Tumanskii, V. V. Bashilov, S. P. Solodovnikov, and V. I. Sokolov. *Izv. Akad. Nauk*, *Ser. Khim.*, 1992, 1457 [*Bull. Russ. Acad. Sci.*, *Div. Chem. Sci.*, 1992, **41**, 1140 (Engl. Transl.)].
4. R. G. Gasanov, E. G. Sadykhov, and R. Kh. Freidlina, *Izv. Akad. Nauk*, *Ser. Khim.*, 1986, 1031 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1986, **35**, 936 (Engl. Transl.)].
5. I. A. Nuretdinov, V. P. Gubskaya, L. Sh. Berezhnaya, A. V. Il´yasov, and N. M. Azancheev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 2083 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 2048].
6. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
7. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
8. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
9. D. N. Laikov, *2nd V. A. Fock All-Russian School (Conference) on Quantum and Computational Chemistry*, Novgorod, 2000, Book of Abstracts, 46.
10. R. Taylor, *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*, Imperial College Press, 1999, 25.
11. R. G. Gasanov, O. G. Kalina, V. V. Bashilov, and B. L. Tumanskii, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1652 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1642].
12. B. L. Tumanskii, V. V. Bashilov, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1992, 1936 [*Bull. Russ. Acad. Sci.*, *Div. Chem. Sci.*, 1992, **41**, 1519 (Engl. Transl.)].
13. R. G. Gasanov and R. Kh. Freidlina, *Usp. Khim.*, 1987, **57**, 447 [*Russ. Chem. Rev.*, 1987, **56**, 264 (Engl. Transl.)].
14. R. G. Gasanov, O. G. Kalina, V. V. Bashilov, and B. L. Tumanskii, *Izv. Akad. Nauk*, *Ser. Khim.*, 1999, 2369 [*Russ. Chem. Bull.*, 1999, **48**, 2344 (Engl. Transl.)].

Received April 12, 2002;
in revised form June 7, 2002