Spin-adducts of radicals $^{\bullet}P(O)(OPr^i)_2$ and $^{\bullet}CMe_3$ with pyrrolidino[60]fullerenes studied by ESR spectroscopy

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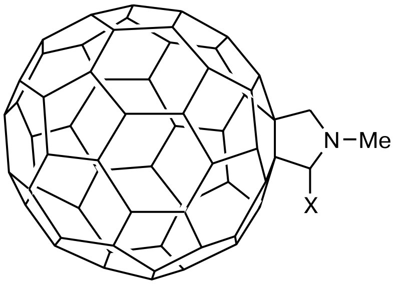
The addition of the $^{\bullet}Bu^t$ (R^1) and $^{\bullet}P(O)(OPr^i)_2$ (R^2) radicals to pyrrolidino[60]fullerenes $C_{60}CH_2NMeCHX$ ($X = C_6H_4N(CH_2CH_2Cl)_2$, 2,6-$(Bu^t)_2C_6H_2OH$, PhC_6H_4, and indol-3-yl) was studied by ESR spectroscopy. The rate constants of R^1 radical addition to these compounds and dimerization of spin-adducts of the R^1 radicals with pyrrolidino[60]fullerenes were determined. Pyrrolidino[60]fullerenes manifest considerably higher reactivity toward the R^1 radicals than fullerene C_{60} and methanofullerenes $C_{60}CX^1X^2$ ($X^1 = X^2 = CO_2Et$; $X^1 = CO_2Me$, $X^2 = OP(OMe)_2$, $X^1 = X^2 = OP(OEt)_2$).

Key words: ESR spectroscopy, pyrrolidino[60]fullerenes, nitrosodurol, addition and dimerization rate constants.

Studies of the reactivity of methano[60]fullerenes toward free radicals showed**1** that the methane fragment produces deformation of the carbon framework, change in the curvature of the fullerene surface, and appearance of the steric hindrances and polar effects near the added group, due to which the reactivity of fullerene C_{60} derivatives changes.

In this work, the addition of the $^{\bullet}P(O)(OPr^i)_2$ and R^1 radicals to pyrrolidinofullerenes (**1—4**) was studied by ESR spectroscopy. The rate constants of addition of the R^1 radicals to these pyrrolidinofullerenes and dimerization of spin-adducts (SA) of the R^1 radicals with compounds **1—4** were determined.



1—4

$X = C_6H_4N(CH_2CH_2Cl)_2$ (**1**), 2,6-$Bu^t_2C_6H_2OH$ (**2**), PhC_6H_4 (**3**), indol-3-yl (**4**)

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Samples in calibrated glass tubes were deaerated in several freezing—evacuation—thawing cycles. Tubes with the reaction mixture were irradiated in a resonator of the spectrometer with the filtered light from a DRSh-1000 lamp at ~20 °C. The band with $\lambda_{max} = 366$ nm was separated using a glass light filter. The kinetic results were processed by the Microsoft Excel program.

For the determination of radical concentrations, TEMPO (Aldrich, solution in toluene, $3 \cdot 10^{-3}$ mol L^{-1}) was used. The concentration of radicals was calculated by a comparison of the amplitude of signals from the SA of the R^1 radicals with pyrrolidinofullerenes with the amplitude of signals from TEMPO, taking into account the difference in linewidths ($\Delta H = 1.60$ G for TEMPO and $\Delta H = 1.65$ G for SA of the R^1 radicals with compounds **1—4**) and multiplicity of the spectra of at the same SHF modulation and power.

Pyrrolidinofullerenes **1—4** were synthesized according to known procedures.**2**

Results and Discussion

UV irradiation of toluene solutions containing compounds **1—4** and $Hg[P(O)(OPr^i)_2]_2$ (**5**), which is a source of the $^{\bullet}P(O)(OPr^i)_2$ (R^2) radicals produces six doublets in the ESR spectra, as in the case of methano[60]fullerenes. These doublets were assigned to the SA of the R^2 radicals

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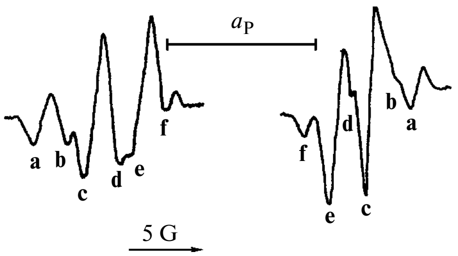

Fig. 1. ESR spectrum of the spin-adduct of the $^{\bullet}P(O)(OPr^i)_2$ radicals with pyrrolidinofullerene **4**.

with compounds **1**—**4** (Fig. 1). The HFC constants with the P nucleus (a_P) are presented below.

Isomer	a_P/G	Isomer	a_P/G
1a	75.1	**3a**	75.0
1b	70.3	**3b**	70.2
1c	68.0	**3c**	68.0
1d	65.0	**3d**	65.0
1e	63.0	**3e**	63.0
1f	60.8	**3f**	60.7
2a	74.8	**4a**	74.5
2b	70.2	**4b**	69.2
2c	67.5	**4c**	67.5
2d	65.0	**4d**	64.0
2e	63.0	**4e**	62.5
2f	60.8	**4f**	59.7

The *g* factors for these radicals are 2.0023—2.0027.

The relative values reflecting the pyramidality (pyramidal angles Δα) of the C atoms of pyrrolidinofullerenes $C_{62}H_4NMe$ (**6**) and **2** calculated by the density functional DFT/PBE/TZ2P method with the Perdew—Burke—Ernzerhof exchange-correlation potential[3] using the PRIRODA program[4,5] and by the semi-empirical PM3 method using the GAMESS program[6] are compared in Table 1. The Δα value was determined as the difference between the sum of bond angles of the C atoms (Σα) in the considered molecule and in fullerene C_{60}. According to the calculations, Σα for fullerene C_{60} is 348°. Therefore, $\Delta\alpha = \Sigma\alpha - 348°$.

The most stable inverse form of molecule **2** is shown in Fig. 2. The flap of the envelope divides the fullerene shell of compound **2** into two nonequivalent fragments, *syn* and *anti*. Comparing the results of calculations of the geometric parameters of compound **6** by the DFT/PBE/TZ2P and PM3 methods, we found that the theoretical values of the sum of bond angles obtained by these methods are close. The greatest difference was observed for the *b* atom of the *cis-2* bond, and the semi-empirical method substantially underestimates the pyramidality of this atom. This should be taken into account in the case of compound **2** when only the semi-empirical PM3 method is applied. In addition, the pyramidality of atoms of the related bonds of different fragments is the same.

Table 1. Relative values of the pyramidality (Δα) and charges (*q*) of the C atoms of pyrrolidinofullerenes (**2** and **6**) and methanofullerenes $C_{61}H_2$ (**7**) and $C_{61}[P(O)(OMe)_2]_2$ (**8**) calculated by the DFT/PBE/TZ2P method

Bond	Atom	Δα/deg				*q* (rel. units)	
		2	**6**	**7**	**8**	**2**	**8**
cis-1	a	5.54	5.53	3.31	2.30	0.0176	0.0074
	b	0.16	0.28	0.08	1.02	−0.0003	0.0103
cis-2	a	1.98	1.63	1.73	1.76	0.0071	0.0048
	b	−0.63	−0.55	−0.26	−0.28	−0.0044	−0.0040
cis-3	a	0.68	0.54	0.74	0.72	0.0002	0.0017
	b	−0.60	−0.53	−0.39	−0.42	−0.0038	−0.0027
eq-1	a	0.86	0.80	0.52	0.49	0.0049	0.0051
	b	−0.22	−0.17	0.02	−0.15	−0.0002	0.0005
eq-2	a	−0.18	−0.11	−0.17	−0.11	−0.0010	−0.0008
	b	−0.07	−0.11	−0.17	−0.08	0.0005	−0.0003
trans-1	a	0.15	0.13	0.07	0.09	0.0004	0.0002
	b	0.10	0.13	0.07	0.09	0.0003	0.0001
trans-2	a	0.10	0.10	0.04	0.06	0.0004	0.0003
	b	−0.06	−0.03	−0.01	0.00	−0.0004	0.0000
trans-3	a	−0.16	−0.20	−0.20	−0.18	0.0002	−0.0005
	b	−0.05	−0.03	−0.03	−0.06	0.0004	0.0004
trans-4	a	−0.19	−0.17	−0.10	−0.23	0.0004	0.0001
	b	0.02	−0.01	−0.03	0.02	−0.0011	−0.0005

As follows from the results of calculations, the *b* atoms of four *cis-2* bonds are maximally pyramidal, *i.e.*, they will primarily be attacked by free radicals. Two other isomers are likely formed due to the attack of atoms of the *cis-3* bonds. In fact, in the ESR spectra of the spin-adducts of the R^2 radicals and compounds **1**—**4**, the lines of four isomers are most intense, and those of two others are less intense. As can be seen from the data in Table 2, the *cis-n* bond lengths of all four fragments of the fullerene shell of pyrrolidinofullerenes (**2** and **6**) and methanofullerenes (**7** and **8**) change consistently.

When irradiation is stopped, the intensities of signals from all six isomers decrease with nearly the same rate, although the kinetics of their decay cannot be measured.

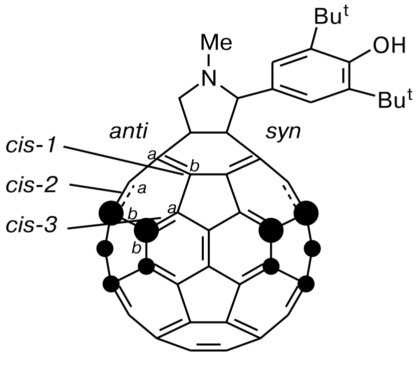

Fig. 2. Distribution of atoms with the greatest pyramidality over the fullerene shell of compound **2** (calculated by the DFT/PBE method).

Table 2. Bond lengths (*d*) of four *cis-n* fragments (*1—4*) of pyrrolidinofullerenes (**2** and **6**) and methanofullerenes (**7** and **8**) calculated by the DFT/PBE method

Compound	*d*/Å				
	1	*2*	*3*	*4*	Average
2	1.3802	1.3811	1.3831	1.3824	1.3817
6	1.3807	1.3807	1.3829	1.3829	1.3818
7	1.3910	1.3910	1.3910	1.3910	1.3910
8	1.3867	1.3881	1.3861	1.3881	1.3872

The rate constants of addition of the R^1 radicals to compounds **1—4** were determined using the competitive kinetic procedure; the reaction

$$R^1 + C_{60}CH_2N(Me)CHX \xrightarrow{k_1} R^1{}^{\bullet}C_{60}CH_2N(Me)CHX \qquad (1)$$

was chosen to be competitive to the addition of the R^1 radicals to nitrosodurol (ND)

$$R^1 + ND \xrightarrow{k_2} \underset{\mathbf{B}}{R^1N(O^{\bullet})Ar}, \qquad (2)$$

$Ar = 2,3,5,6\text{-}Me_4C_6H$.

The k_1 rate constant was calculated by the expression

$$d[\mathbf{B}]/d[\mathbf{A}] = k_2[ND]_0/(k_1[C_{60}CH_2N(Me)CHX]_0), \qquad (3)$$

where $[ND]_0$ and $[C_{60}CH_2N(Me)CHX]_0$ are the initial concentrations of the spin trap and pyrrolidinofullerenes **1—4**, respectively; d[**A**] and d[**B**] are the changes in the intensities of signals of the **A** and **B** radicals. As can be seen from Eq. (3), to determine the k_1 rate constant, one should know the k_2 rate constant. For the addition of the R^1 radicals to ND, $k_2 = 2 \cdot 10^8$ L mol^{-1} s^{-1} at room temperature.[7]

When toluene solutions containing Bu^tBr, $Re_2(CO)_{10}$, and pyrrolidinofullerenes **1—4** are irradiated ($\lambda = 366$ nm), the ESR spectra exhibit a triplet with the HFC constant $a_N = 13.4$ G characteristic of the SA of the R^1 radicals with ND (**B**) and $C_{60}CH_2N(Me)CHX$ (**A**). The formation of the R^1 radicals is described by the scheme

$$Re_2(CO)_{10} \longrightarrow 2\ {}^{\bullet}Re(CO)_5,$$

$${}^{\bullet}Re(CO)_5 + Bu^tBr \longrightarrow BrRe(CO)_5 + \underset{R^1}{{}^{\bullet}Bu^t}.$$

The changes in the concentrations of the **A** and **B** radicals in time calculated by processing of the kinetic curves by the least-squares method are shown in Fig. 3. Based on the experimental results and using the rate constant of radical addition to ND, we determined the rate constants of addition of the R^1 radicals to compounds **1—4** by Eq. (3). For compounds **1**, **3**, and **4** at their initial concentrations $C_0 = 1.12 \cdot 10^{-4}$ mol L^{-1} and the initial concentration of ND of $2.5 \cdot 10^{-4}$ mol L^{-1}, k_1 are equal to $2 \cdot 10^8$, $3 \cdot 10^8$, and 10^8 L mol^{-1} s^{-1}, respectively. For compound **2** at $C_0 = 10^{-3}$ mol L^{-1} and the initial ND concentration of $4 \cdot 10^{-3}$ mol L^{-1}, $k_1 = 3 \cdot 10^8$ L mol^{-1} s^{-1}.

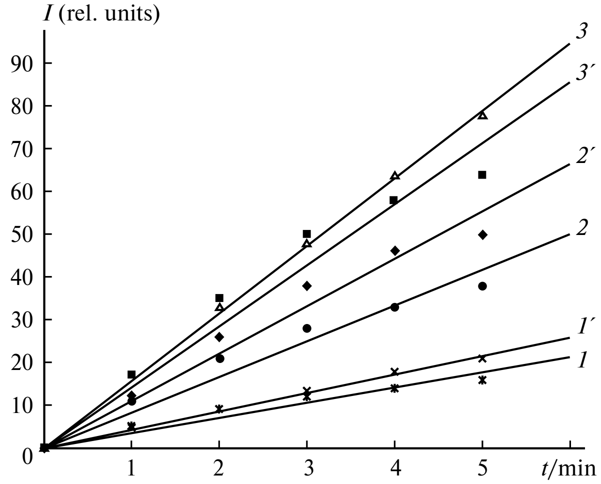

Fig. 3. Plots of the intensity of one line of the triplet of the $R^1N(^{\bullet}O)Ar$ radicals (d[**B**]) (*1—3*) and the singlet of the SA of the R^1 radicals with pyrrolidinofullerenes C_{60} (d[$\mathbf{A}_i$]) (*1´—3´*) *vs.* time: formation of the SA of the R^1 radicals with compounds **1** (*1*, *1´*), **2** (*2*, *2´*), and **4** (*3*, *3´*).

It follows from the comparison of these constants with the rate constants of radical addition to methano[60]fullerenes that an insignificant increase in the pyramidality of the C atoms of the *cis*-bonds results in a noticeable increase in the reactivity of pyrrolidinofullerenes.

In the reaction of Bu^tBr with compounds **1—4**, the ESR spectrum contains a symmetric singlet with

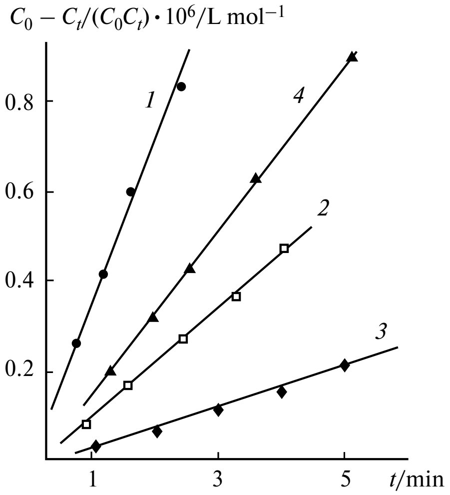

Fig. 4. Plot of the $C_0 - C_t/(C_0C_t)$ value *vs.* time for the spin-adducts of the R^1 radicals with pyrrolidinofullerenes **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*).

$g = 2.0023$, which likely characterizes the superposition of signals from six isomers identified in the addition of the R^2 radicals to compounds **1—4**.

The plots of $C_0 - C_t/(C_0C_t)$ *vs.* time, where C_0 and C_t are the initial and current concentrations of the SA of the R^1 radicals with compounds **1—4**, are shown in Fig. 4. The decay kinetics of these radicals is well described by the second-order equation. Using the data obtained, we determined the rate constants of dimerization (k_3) of the SA of the R^1 radicals with compounds **1—4**, which are equal to $(6.0\pm0.3)\cdot10^3$, $(1.9\pm0.1)\cdot10^3$, $(0.7\pm0.05)\cdot10^3$, and $(2.8\pm0.2)\cdot10^3$ L mol^{-1} s^{-1}.

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